The Preparation and Characterisation of Some Polynitro-Derivatives of 1-Phenylnaphthalene and 1,1'-Binaphthyl

by

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Summary

A study has been made of the nitration of 1,1'-binaphthyl. A total of fourteen nitro derivatives have been observed and of these eleven have been isolated and characterised. The structures of the isolated products have been deduced largely on the basis of spectroscopic data and routes to the formation of the various products discussed. Convenient preparative procedures for the synthesis and isolation of two major nitration products have been developed.

The most highly nitrated derivative which was isolated during the above study is a heptanitrobinaphthyl. It has been found that under very vigorous nitration conditions the extent of nitration of 1,1'-binaphthyl is ultimately limited by oxidation to water soluble products. One of these products has been isolated and characterised. The heptanitrobinaphthyl which has been prepared has proved to be relatively unstable and a decomposition product derived from this compound has also been isolated and characterised.

1-Picrylnaphthalene has been prepared via an Ullmann reaction and the nitration of this compound has been investigated. Convenient procedures for the synthesis and isolation of two polynitroderivatives have been devised. In contrast to the 1,1'-binaphthyl system, tetranitration of the naphthyl moiety in 1-picrylnaphthalene has been found to be relatively facile. Differences between the two systems have been attributed to steric factors.

The infra red, electronic, mass and proton magnetic resonance spectra of 1,1'-binaphthyl, 1-picrylnaphthalene and the various polynitro derivatives obtained from these compounds, have been recorded, where possible, and discussed in terms of steric and electronic factors.

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CHAPTER 1

Introduction

1.1. Purpose of Work

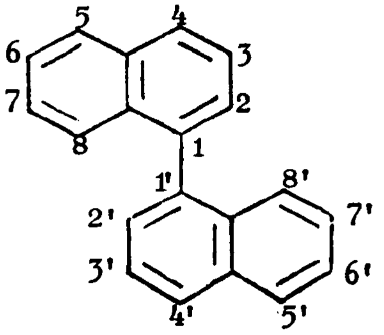
In recent years the development of numerous vehicles for the exploration of interplanatary space has generated interest in the preparation of novel explosives. These explosives are required to meet certain highly specialised requirements which are associated with such spacecraft. Most noteable amongst the special qualities required of an explosive for space application, are the possession of a suitably low vapour pressure and sustained resistance to extremes of temperature. Thus an explosive composition for such application must not sublime appreciably under the high temperature and low pressure conditions which are sometimes encountered in the space environment.[1] Additionally it may have to withstand temperatures of around 150°C, for considerable periods of time, whilst still operating satisfactorily at temperatures, as low as -184°C.[1,2] Such extremes of temperature may result both directly from ambient conditions, and in the case of high temperatures, as a result of such factors as boundarylayer heating in supersonic craft,[1] and preflight sterilisation procedures.[2]

A number of heat resistant explosives are currently available[2,3] and some of these have already found application in space projects. For examples DIPAM (3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl) and HNS (2,2',4,4',6,6'-Hexanitrostilbene) have been used in the "Gemini" and "Apollo" space systems.[1] There is nevertheless a continuing requirement for new thermally stable explosives which will exhibit even more desirable properties than do the existing generation of such compounds. The present work has therefore been directed towards the syntheses of new polynuclear, polynitroaromatic compounds in the hope that the prepared materials will ultimately prove useful as thermally stable explosives.

1.2. Choice of the Systems for Study

The purpose of the present work was to prepare polynitroaromatic compounds of significantly higher molecular weight than the conventional explosives based on a single benzenoid nucleus (eg TNT). Clearly this may be achieved either by coupling a number of benzenoid nuclei together or by employing fused aromatic systems, or both. A considerable amount of work has already been carried out on various polyphenyl systems, though not all of this has been published yet in the open literature. The various polynitro derivatives of naphthalene are also well characterised[4a] as are numerous related series of compounds such as the methylpolynitronaphthalenes,[5] dimethylpolynitronaphthalenes[6] and polynitroacenaphthenes.[7] A survey of the literature revealed however that polynitro derivatives of phenylnaphthalene and binaphthyl had so far received little attention. These systems were therefore chosen for study. As there was no obvious advantage to be gained from the choice of a particular isomer, 1-phenylnaphthalene and 1,1'-binaphthyl were selected on the grounds of availability.

1.3. Previous Work on Nitro Derivatives of 1,1'-Binaphthyl



1,1'-Binaphthyl

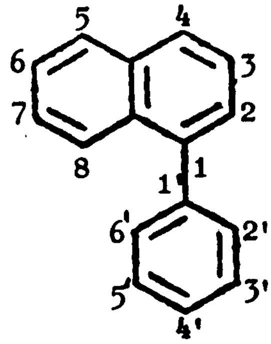
There are few reports in the literature concerning the nitration of 1,1'-binaphthyl. The earliest account is that by Lossen,[8] dated 1867, which reports the preparation of a tetranitro derivative by the action of fuming nitric acid on the hydrocarbon. This author did not however assign a structure to his product. A report, by Julius[9] written at about the same time, relating to the supposed nitration of 1,1'-binaphthyl, has subsequently been proved erroneous by Schoepfle,[10] who showed that the material being nitrated was in fact dinaphthalene oxide and not 1,1'-binaphthyl. In the same paper (1923) Schoepfle describes the nitration of 'true' 1,1'-binaphthyl using nitric acid in acetic acid and identifies both 4-nitro-1,1'-binaphthyl and 4,4'-dinitro-1,1'-binaphthyl. The preparation of 4,4'-dinitro-1,1'-binaphthyl was subsequently repeated.[11] There are no reports of the preparation of any other nitrobinaphthyls by direct nitration, earlier than that by Messers Jones and Joyner[12] published during the current investigation. In their report, Jones and Joyner describe methods for the production of 4,4',5,5'-tetranitro-1,1'-binaphthyl by the direct nitration of 1,1'-binaphthyl using firstly preformed acetyl nitrate, secondly a mixture of nitric and sulphuric acids and thirdly nitronium tetrafluoroborate. They also describe the preparation of this compound by the nitration of 4,4'-dinitro-1,1'-binaphthyl in a mixture of nitric, sulphuric and acetic acids.

A number of polynitrobinaphthyls have been prepared by indirect methods, the most popular method being that employing the Ullmann reaction. Thus the 2,2'-,[13a] 3,3'-[6b] 4,4'-,[10] 5,5'-[14] and 8,8'-[15] dinitro-1,1'-binaphthyls have all been synthesised by the Ullmann reaction as have the 2,2',4,4'-[16] and 4,4',8,8'-[15a] tetranitro-1,1'-binaphthyls. A number of the above dinitro-1,1'-binaphthyls have also been prepared by other methods.[17]

No preparation of a polynitro-1,1'-binaphthyl containing more than four nitro groups has been reported, although at least one unsuccessful attempt has been made at such a preparation. This was an Ullmann reaction intended to prepare 2,2',4,4',5,5'-hexanitro-1,1'-binaphthyl, which was abandoned because purification of the product was too difficult.

1.4. Previous Work on the Nitro Derivatives of 1-Phenylnaphthalene

The literature contains several reports of the direct mononitration of 1-phenylnaphthalene,[18-21] but no reports of its polynitration. The product of direct nitration, in nitric and acetic acids, is generally acknowleged to be 4-nitro-1-phenylnaphthalene, although there is a single early report by Weiss and Woidich which assumes the product to be 8-nitro-1-phenylnaphthalene. This latter assignment is however at variance with the work of other authors[18,20,21] and is considered to be erroneous.[20] The preparation of 4-nitro-1-phenylnaphthalene, via two radical mediated coupling reactions, has also been



1-Phenylnaphthalene

reported.[22]

Three other mononitro-1-phenylnaphthalenes have been prepared using various coupling reactions. Thus 1-(o-nitrophenyl)naphthalene and 1-(p-nitrophenyl)naphthalene have each been prepared via both Ullmann reactions (refs23,24 and 24 respectively) and radical mediated coupling reactions (refs 25,26 and 25-29 respectively). 1-(m-Nitrophenyl)naphthalene however has only been prepared by the arylation of naphthalene using a benzene diazonium salt.[26,29]

Only three dinitro derivatives of 1-phenylnaphthalene have been prepared. Two of these (2-nitro-1-(o-nitrophenyl)naphthalene and 1-(2,6-dinitrophenyl)naphthalene)were prepared via Ullmann reactions, whilst the third (4',7-dinitro-1-phenylnaphthalene) was derived from 4',7-dinitro-1-phenyl-2,3-naphthalene dicarboxylic acid, itself prepared by heating p-nitrophenylpropiolic acid in acetic anhydride.[21]

No higher nitro derivative of 1-phenylnaphthalene had been prepared prior to the current work.

1.5. Preparation of Biaryls

1.5.1. General Methods for the Production of Polynitrobiaryls

The preparation of polynitrobiaryls may be undertaken in a number of ways. The three most direct methods are:-

i) By preparing a hydrocarbon and subsequently nitrating it.
ii) By coupling a prenitrated hydrocarbon.
iii) By various combinations of i) and ii).

Each of these methods is subject to certain limitations. Thus method i) involves the direct nitration of a complex aromatic nucleus, which will inevitably contain many possible sites for substitution. In consequence a mixture of many nitro aromatic products is likely to result and separation of this mixture may be difficult. In addition to this the complexity of the individual products may lead to identification difficulties - particularly with respect to differentiation between isomers.

The above difficulties may, to a large extent, be overcome by employing method ii). Thus the number of isomeric products obtained by this method can frequently be limited by suitable choice of reactants whilst the location of the various nitro groups should be evident from the structure of the reactants. Other problems may however arise when using this technique. Thus the presence of nitro groups in a substrate can effectively preclude the use of certain coupling reactions with that substrate (see section 1.5.2.). Since the number of preparatively useful techniques for coupling biaryls is fairly small, this limitation can in practice become very restrictive. In some instances it can prove impracticable to prepare a specific product by the coupling of two polynitrated species (see for example the restrictions placed upon reactants for a mixed Ullmann reaction - section 1.5.2.5.).

The application of method iii) above will clearly embody some of the advantages and disadvantages associated with each of the methods i) and ii).

1.5.2. Coupling Reactions

The main 'classical' methods of biaryl formation are outlined below together with some indication of their suitability for the present work, bearing in mind the two systems which have been chosen for study.

1.5.2.1. The Scholl Reaction[30]

$$\mathrm{ArH} \xrightarrow[\mathrm{H^+}]{\mathrm{AlCl_3}} \mathrm{Ar\text{-}Ar}$$

(Typically high temperature 100-140°C)

The Scholl reaction involves the elimination of two aryl bound hydrogens with concomitant formation of an aryl-aryl bond under the influence of a Friedel-Crafts catalyst. As such it represents one of the simplest methods for the production of a new aryl-aryl bond. It is most suited to the production of intramolecular bonds since intermolecular Scholl reactions normally give rise to very low yields.[30] The reaction was not therefore a very promising one for the present work. Further, as there are few reports of its use for the preparation of mixed biaryls (that is unsymmetrical intermolecular reactions) its applicability to the preparation of phenylnaphthalene derivatives is questionable. It is also pertinent to note that rearrangements and fissions are possible during the reaction, so the structure of the product is not always certain. This feature would be of particular significance in the preparation of 1,1'-binaphthyl, as this compound is known to readily isomerise to the sterically unhindered 2,2'-isomer under the influence of aluminium chloride.[30] In view of these points the Scholl reaction was not considered suitable for the present work.

1.5.2.2. Radical Mediated Coupling Reactions

There are a number of methods for the preparation of biaryls which involve radical intermediates,[31] but the most commonly used procedures are the Gomberg-Bachmann[32,33] reaction and the decomposition of aroyl peroxides.[32a&b,33] The scopes of these two reactions are essentially similar and both techniques involve the generation of aryl radicals in presence of an aromatic substrate. The two methods differ merely in the nature of the radical source. In both cases the radicals, once generated, couple with the aromatic substrate to produce a biaryl.

Radical mediated coupling reactions suffer from the general problem that, unless the substrate is totally symmetrical, a mixture of isomers is produced because attack of the radical can take place at a number of different sites within the substrate. This problem can be resolved however, by suitable choice of reactants. Thus if totally symmetric compounds such as benzene are used as substrate, only a single product can result. The use of such a technique however, must inevitably place considerable restrictions upon the synthetic utility of the reaction.

The Gomberg-Bachmann Reaction[32,33]

In this case radicals are generated by the decomposition of a diazonium salt under alkaline conditions. The overall reaction may be represented by the equation:-

$$ArN_2^+X^- \quad + \quad Ar' \quad + \quad NaOH \longrightarrow Ar\text{-}Ar' \quad + \quad N_2 \quad + \quad NaX \quad + \quad H_2O$$

The yields obtained from this reaction are not usually high (typically less than 40%), due to the large number of side reactions undergone by diazonium salts. (Whilst alternative procedures may give rise to higher yields (eg the Hey reaction[32,33]: 40-70% where the radicals are generated from an N-nitrosoacetylamine) these generally tend to be less convenient than the Gomberg reaction, whilst still being subject to the same restrictions as to the nature of Ar' - if acceptable yields of biaryls are to be obtained.) The reaction does however function satisfactorily with reactants containing nitro substituents, although there is a paucity of data relating to its use with highly nitrated species. Unfortunately as the reaction generally produces very poor yields in solution, the use of solvents is to be avoided.[32c] In consequence the substrate Ar' needs to be a liquid at 5-10°C. This restriction alone therefore tends to rule out the use of highly nitrated substrates, at least for one component (Ar'). It would also seem to completely preclude the preparation of binaphthyl or any of its nitro derivatives by this method.

Whilst this reaction certainly has some potential for the preparation of 1-phenylnaphthalene and some of its nitro derivatives, the low yields associated with the method, coupled with the restrictions outlined above, made it rather unattractive for the present work. It was therefore not employed.

Aroyl Peroxides[32a&b,33]

In this method radicals are generated from the decomposition of an aroyl peroxide. This is achieved simply be warming the peroxide in an appropriate aromatic solvent which also acts as the substrate. The reaction is represented approximately by the overall but greatly simplified[33] equation:-

$$(ArCO_2)_2 \quad + \quad Ar'H \longrightarrow ArAr' \quad + \quad ArCO_2H \quad + \quad CO_2$$

This procedure is a somewhat cleaner reaction than the Gomberg technique and leads to less tarry by-products. Further the presence of nitro substituents is not merely tolerated in the reaction, but is actually beneficial for the production of biaryls.[34] (Though the situation is a little uncertain regarding the use of highly nitrated species because of a lack of data about the use of such compounds.)

The production of binaphthyl or its derivatives by this method will clearly require the use of naphthoyl peroxides, indeed these would best be employed even for the preparation of phenylnaphthalene (and derivatives), as benzene could then be used as the substrate and so a mixture of isomeric products could be avoided. The utility of this method is however cast in some doubt because difficulties have been experienced in the use of 1-naphthoyl peroxide for this type of reaction.[35] Indeed the only report describing the successful preparation of nitrophenylnaphthalenes by this method describes low product yields.[25]

A further point against the application of this method during the present work, was the fact that the desired naphthoyl peroxides would have required synthesising, prior to actually carrying out the coupling reaction. This was in marked contrast with the Ullmann reaction, which was actually employed, as this utilised commercially available reactants (see later).

In view of the various points discussed above, this method of coupling was not selected for use during the present work.

1.5.2.3. Benzyne Mediated Coupling[36]

In this method a benzyne is generated by the action of an aryl lithium on an aryl halide. Subsequent reaction of this benzyne with further aryl lithium results in the production of a biaryl:-

$$\text{ArX} + \text{Ar'Li} \longrightarrow \text{benzyne (from Ar-X)}$$

$$\text{benzyne} + \text{Ar'Li} \longrightarrow \text{Ar-Ar'}$$

Whilst this procedure can certainly produce good yields of biaryls and is applicable to both benzene and naphthalene substrates,[36] it is not suitable for use with reactants which contain nitro substituents. Thus if there are any nitro groups present in the system, these will react directly with the aryl lithium,[37] so detracting excessively from the desired course of reaction. In consequence, during the present work this method would have been of value only for the preparation of 1,1'-binaphthyl or 1-phenylnaphthalene. In fact as 1,1'-binaphthyl was the only hydrocarbon to be nitrated, and this was available from commercial sources, it proved unnecessary to employ this reaction.

1.5.2.4. Grignard Homo Coupling[38-40] and Aryl Lithium Homo Coupling[40]

The oxidative coupling of Grignard reagents can be achieved by treating them with thallium bromide or a transition metal halide such as $CoBr_2$, $CrCl_3$, or $CuCl_2$:-

$$2\text{ArMgX} \xrightarrow[\text{catalyst}]{} \text{Ar-Ar}$$

Aryl lithium compounds can be dimerised in a similar fashion by treatment with transition metal halides:-

$$2\text{ArLi} \xrightarrow[\text{catalyst}]{} \text{Ar-Ar}$$

Although both reactions are capable of producing biaryls in high yield, neither is particularly suited to the production of unsymmetrical products (such as phenylnaphthalenes). Additionally the coupling of Grignard reagents with thallium bromide is restricted to substrates which do not contain an ortho substituent.[39] In the present context however, the main restriction placed upon the use of these reactions, results from the reactivity of nitro groups towards organometallics. Thus as both Grignard reagents[128] and aryl lithium compounds[37] react directly with nitro groups, it is not feasible to use either of the above reactions for the preparation of polynitro substituted biaryls. The reactions would thus be restricted for present purposes to the preparation of 1,1'-binaphthyl or 1-phenylnaphthalene. As neither of these compounds was actually prepared during the present work, the above coupling techniques were not employed.

1.5.2.5. The Ullmann Reaction[41-44]

The Ullmann reaction involves the coupling of aryl halides using copper:-

$$2\mathrm{ArI} \xrightarrow[\text{Heat}]{\text{Cu}} \mathrm{Ar{-}Ar}$$

The reaction is of broad scope and has been used to prepare many biaryls - both symmetrical and unsymmetrical. Since iodo is the best leaving group the reaction is most often performed with an aryl iodide, although bromides and chlorides have also been used. (But note the optimum choice of reactants for the preparation of unsymmetrical biaryls - below.)

The Ullmann reaction is particularly well suited to the preparation of polynitrobiaryls. Thus a nitro substituent is found to be strongly activating when situated ortho to the site of coupling, whilst in other positions (meta and para), though not significantly activating, it does not inhibit the reaction in any way. The value of this method for the preparation of nitrobiaryls is clearly demonstrated by the numerous reports of such reactions in the literature.[41-44] Indeed it is possible to obtain good yields of both symmetric and unsymmetric polynitrobiaryls from this reaction.

In view of the obvious utility of the Ullmann reaction for the preparation of polynitrobiaryls and also its suitability for the production of unsymmetrical derivatives, this reaction has been employed extensively during the present work. Since the reaction has been utilised for the production of an unsymmetrical phenylnaphthalene derivative it is of interest to examine in greater detail the factors affecting the selection of reactants for a 'mixed' Ullmann reaction.

Normally an unsymmetrical Ullmann reaction will yield significant quantities of three products:-

$$ArX \quad + \quad Ar'X' \xrightarrow[Cu/Heat]{} Ar'Ar' \quad + \quad ArAr' \quad + \quad ArAr$$

However, it is possible by a suitable choice of reactants to obtain predominantly the mixed biaryl ArAr'. This is achieved[42] by employing one 'activated' reagent (say ArX), which contains at least one nitro group ortho to the halogen (in the more general case other electronegative groups may also be employed), and one 'unactivated' compound (Ar'X') without such a group. Additionally the halogen of the activated species (X) should be either Br or Cl, whilst that in the unactivated species should be I (X'). The reason for this is that aryl chlorides and bromides do not undergo self condensation very readily, whilst aryl iodides do. Thus by using a chloride or bromide for the activated species, the yield of the symmetrical product ArAr should be kept to a minimum. On the other hand self condensation of the unactivated species Ar'I is minimised by moderating the reaction temperature. Thus a minimum temperature is employed which although sufficient to promote reaction between the activated ArX and unactivated Ar'X' (X=I), is insufficient to promote self condensation of the unactivated Ar'I. (It is found experimentally[42] that an unactivated aryl halide will undergo reaction with another activated halide at a significantly lower temperature than that required for self condensation of the unactivated species.) Thus, assuming that the above conditions are fullfilled the major product of the reaction should be the mixed biaryl ArAr'. This technique has been used successfully during the present work to produce a high yield of 1-picrylnaphthalene from a mixed Ullmann reaction -see later-. (Picryl = 1,3,5-trinitrophenyl.)

1.6. Preparative Nitrations of Aromatic Compounds

1.6.1. General Considerations

It is possible to carry out preparative nitration reactions under a very wide range of conditions, the method chosen for any particular substrate depending on both the reactivity of that substrate and the nature of the required product. Two problems usually encountered when reacting aromatic compounds are how to effect the appropriate degree of substitution and how to obtain the desired product in good yield. Fortunately as the nitro group strongly deactivates the aromatic nucleus to which it becomes attached (with respect to electrophilic attack), the former problem is not usually severe in nitrations. The most obvious method for controlling the degree of substitution is to limit the quantity of nitrating agent present. Alternatively the reaction temperature can be chosen, in presence of excess nitrating agent, so that further reaction of the desired product occurs only at an insignificant rate. A similar effect can usually be obtained by varying the composition of the nitration medium. On an industrial scale where 'mixed acid' (sulphuric and nitric acids) is invariably used for economic reasons this usually means diluting the mixture with water. However on a laboratory scale, admixture with an organic solvent is often preferable. This may have the additional advantage of creating homogeneous conditions.

The second problem - that of obtaining one isomer in good yield - is a function of the substrate under study. Obviously in many cases such as in the mononitration of symmetrical hydrocarbons (benzene, mesitylene etc), no problem exists since by limiting the extent of nitration a single product is more or less guaranteed. However, as the substrate becomes either unsymmetrical (toluene, o-xylene etc) or more complex (naphthalene, binaphthyl etc) larger numbers of isomeric products become possible. Although the problem is sometimes alleviated when higher degrees of nitration are required, by convergence to a single polynitro compound as the major product, it never completely disappears as there are always quantities of isomeric by-products (eg ortho and para nitrotoluenes converge to form mainly 2,4,6-trinitrotoluene, but some usymmetrical isomers are also formed.)

In practice therefore if a substrate has several sites of similar reactivity a mixture of products will inevitably result. The best that can usually be hoped for is to obtain a uniform degree of nitration so as to simplify the separation problem.

In some cases the isomer distribution of the product can be changed significantly by varying the reaction conditions. This rarely permits a shift to one exclusive product from a mixture of isomers but may nevertheless be preparatively useful. An example of this is the use of acyl nitrates which often produce high ortho to para ratios with certain substrates (phenols, phenolic ethers, aryl amines) relative to either mixed acid or nitric acid alone. Thus for example mono nitration of anisole in a mixture of nitric and sulphuric acids yields mainly paranitroanisole[45] whilst nitration in acetic or benzoic anhydride produces mainly the ortho substituted product.[45-47] Other effects, highly specific to a given type of substrate, are also observed in some cases. With aromatic amines, for example, a change in the acidity of the medium can lead to a change in product distribution due to protonation of the amino group which effectively changes the activating ortho para directing NH_2 substituent into a deactivating meta director (NH_3^+). Normally however a change between the various 'common' nitration media produces very little effect on the isomer distribution of the product. Thus toluene produces substantially the same ortho:para ratio in a large number of nitration media.[48-51] If however a wide enough range of nitration agents are examined, very significant changes of isomer distribution can become apparent. Olah has examined the mononitration of toluene by "all presently known methods"[51] and found in a few cases wide fluctuations in product composition. (This particular study involved the use of over a hundred different nitration media).

Clearly when undertaking direct nitration of a substrate for the first time, it is sensible to conduct the initial experiments in 'common' nitration media utilising readily available reagents. Only if these proved unsatisfactory for any reason would a lengthy examination of the many other possible media(listed by Olah) become necessary.

The production of polynitroaromatic compounds is commonly achieved both in the laboratory and on an industrial scale by the use of stepwise nitration techniques. This approach provides an opportunity for exerting maximum control over the course of a nitration and may also permit isolation of intermediate products. Whilst control of the reaction is clearly important during any nitration process, the latter point assumes particular significance during speculative nitration of a fairly complex nucleus such as 1,1'-binaphthyl. The reason for this is the large number of sites available for substitution in such a molecule, coupled with our inability to identify unambiguously all the possible products, in absence of suitable comparison compounds of known structure. In this situation, the isolation of intermediate products can facilitate the stepwise nitration studies which often become necessary, in order to elucidate the structure(s) of the final product(s).

1.6.2. Nitration Techniques

A number of the more common nitration techniques which are valuable for use with aromatic substrates are outlined below. A more comprehensive account of preparative nitration techniques is given in Methoden der Organischen Chemie.[53] As 1,1'-binaphthyl was thought likely to have a reactivity of similar order to that of benzene, some indication has been given in each of the following sections as to the degree of nitration which can be expected when treating substrates of this reactivity with the various media.

1.6.2.1. Nitration using Nitric Acid in an 'Inert' Organic Solvent

The use of nitric acid diluted with an 'inert' organic solvent is common on a laboratory scale when a fairly mild nitration medium is required. In this context the term 'inert' is used to indicate that there is no chemical reaction between the nitric acid and solvent, although molecular complexes are sometimes formed.[52a] A number of solvents are used for this purpose (ether, nitromethane, chloroform, dioxan, acetic acid etc) but acetic acid is probably the most popular. Acetic acid is a good solvent for many organic compounds and often renders the mixture homogeneous. Reaction in acetic acid solution usually leads to mononitration in compounds where reactivity is similar to that of benzene. For example, mesitylene may be nitrated to mononitromesitylene using this medium,[54a] whilst 1,1'-binaphthyl undergoes mononitration in each of the naphthalenic ring systems to yield 4,4'-dinitro-1,1'-binaphthyl.[10]

1.6.2.2. Nitration using Acyl Nitrates

Acetyl nitrate is a useful nitrating agent which is easy to prepare;[55] it is however highly unstable in the pure state and prone to explode violently even at moderate temperatures.[55] The compound nevertheless remains valuable for aromatic nitrations as its stablility is greatly enhanced by use of a suitable diluent. The addition of a diluent does not appreciably detract from its nitrating action.[56] Nevertheless moderate temperatures must be maintained through-out the reaction so as to prevent decomposition of the reagent.[57]

Acetyl nitrate may be prepared for reaction in situ by the addition of acetyl chloride to a solution of silver nitrate in an inert solvent. However the most convenient technique for the preparation of this reagent in the laboratory is the addition of nitric acid to acetic anhydride, at room temperature. Acetyl nitrate is rapidly formed in the solution[52b] and the resultant mixture is used directly both as solvent and nitrating agent. The temperature at which the addition is carried out, evidently has considerable importance as regards formation of acetyl nitrate in the reaction medium. Thus it has been reported by Bordwell and Garbisch that whilst a vigorous reaction occurs between 70% nitric acid and acetic anhydride at 20-25°C, there is little evidence of any reaction between these reagents at -10°C.[57] Further, as the former solution (containing acetyl nitrate) is a very vigorous nitrating medium whilst the latter 'mixture' is not,[57] the potency of the system must clearly depend considerably upon the temperature profile of a given reaction.

Solutions containing acetyl nitrate are slightly more vigorous nitrating media than solutions of nitric acid in 'inert' organic solvents. Such mixtures typically produce monosubstitution in benzenoid compounds which are not strongly deactivated. Thus toluene may be mononitrated quantitatively to a mixture of ortho and para nitro toluenes.[54b] For fused ring systems a maximum of one nitro group 'per ring' can be introduced using this reagent. Thus acenaphthene may be nitrated to 4-nitroacenaphthene using an equimolar quantity of reagent, whilst 4,5-dinitroacenaphthene is produced in presence of excess acetyl nitrate.[56]

Benzoyl nitrate has broadly similar nitrating properties to acetyl nitrate although in some instances it has proved to be a less satisfactory reagent.[56] It is, however a much more stable compound than acetyl nitrate. Benzoyl nitrate can be readily isolated from the reaction between benzoyl chloride and silver nitrate, but in practice it is more conveniently prepared in situ, by the addition of benzoyl chloride to a solution of silver nitrate and substrate in acetonitrile.[46]

Both acetyl nitrate and benzoyl nitrate can yield unusually high ortho/para product ratios with certain substrates, but this effect, although preparatively useful is not fully understood.[52c]

1.6.2.3. Nitrations Employing Nitric Acid as Both the Solvent and Nitrating Agent

Nitric acid at concentrations ranging from fuming acid to dilute aqueous solution has been widely exploited for aromatic nitrations. In dilute aqueous solution nitric acid is only suited to the nitration of the more reactive compounds such as phenols and amines. There are however narrow limits to the usefulness of this reaction medium as its nitrating action on less reactive species only becomes appreciable at higher temperature where oxidative side reactions can become excessive. With compounds such as the alkyl benzenes hot dilute nitric acid tends to attack the side chain rather than the aromatic ring. Ethyl benzene for example yields α-nitroethylbenzene in 44% yield when treated with dilute nitric acid at 105°C (in a sealed tube).[54c]

The use of fuming nitric acid permits lower temperatures to be used, so reducing the oxidative side reactions. Acetophenone has been nitrated[58] to m-nitroacetophenone in this medium using temperatures down to -20°C. High temperatures may, however, be utilised for compounds which are not particularly susceptible to oxidation. Thus benzene may be nitrated to m-dinitrobenzene by prolonged treatment with boiling nitric acid.[54d] At these high temperature compounds containing methyl groups are likely to be oxidised to the carboxylic acid.

During the course of a nitration in fuming nitric acid, continual dilution of the medium occurs by the water produced in the reaction. It is therefore necessary to use a very large excess of nitric acid in order to obtain satisfactory yields. This problem, which seriously limits the utility of the method, may be overcome by the addition of dehydrating agents. The most commonly used dehydrating agent is sulphuric acid.(See below.)

1.6.2.4. Nitrations Using Mixtures of Concentrated Nitric and Sulphuric Acids

Mixtures of concentrated sulphuric and nitric acids ('mixed acid') are by far the most important and widely used nitrating media both on a laboratory and industrial scale. The effect of the sulphuric acid is to produce a very high degree of ionisation of the nitric acid and hence a high concentration of nitronium ions (the active nitrating species[52d]). A number of other advantages are also associated with the use of concentrated sulphuric acid; it is an excellent solvent, it has a high heat capacity, and it 'binds' any water which is produced during the course of the reaction. A further advantage of 'mixed acid' is that it has diminished oxidation properties relative to nitric acid alone.

'Mixed acid' is a very potent nitration medium being capable of producing tri-nitration in moderately activated benzenoid compounds such as toluene. Its action may however be moderated for use with very reactive substrates or where only a limited degree of nitration is required, by dilution with water or an 'inert' organic solvent coupled with appropriate temperature control. The flexibility of this nitration system with respect to substrates of different reactivity, is well demonstrated by the case of toluene. Mononitrotoluene (a mixture of ortho and para isomers), 2,4-dinitrotoluene and 2,4,6-trinitrotoluene, may each be prepared in high yield[59a] using this medium, the product depending on the choice of reaction conditions. The nitration of benzene in mixed acid can also yield either the mono nitro derivative[60] or the meta dinitro derivative[61] according to the severity of the reaction conditions. Although it is difficult to produce trinitrobenzene by direct nitration, this compound may be prepared (in 71% yield) from meta-dinitrobenzene, by prolonged treatment at high temperature with 100% nitric acid in oleum (60% SO_3).[62] (100% nitric acid may be prepared by vacuum distillation of fuming nitric acid below 0°C.) Nitration mixtures containing oleum whilst being very powerful, can give rise to sulphonation[63] and in some instances compounds have been observed to react more slowly in these media than in those containing only concentrated sulphuric acid.[63] They may therefore be limited in their value as a preparative nitration medium.

1.7. Selection of Routes for the Production of Polynitrobinaphthyls and Phenylnaphthalenes

For the present work, directed at the preparation of polynitrobinaphthyls and phenylnaphthalenes, it was decided to undertake both the direct nitration of a preformed biaryl hydrocarbon and the coupling of prenitrated species. Of the two systems chosen for study, 1,1'-binaphthyl seemed best suited to direct nitration because of its symmetrical structure. Thus it was hoped that the problems of separation and identification of products would be significantly reduced if many of these were of a symmetrical nature. The nitration of 1,1'-binaphthyl was also attractive because the substrate was available from commercial sources. (Contrast the polynitronaphthalene derivatives which would have been required for the alternative approach of coupling prenitrated species; these would have required synthesising.)

In the case of the 1-phenylnaphthalene system the alternative approach - that of coupling a prenitrated hydrocarbon - was adopted. As shown by the above survey the number of coupling reactions suited to the direct preparation of polynitrobiaryls is very small. By far the most promising method of coupling appeared to be the Ullmann reaction and this was confirmed during the course of the current study. In practice it proved most satisfactory to prepare 1-picrylnaphthalene via an Ullmann reaction, then subsequently to nitrate this material. This choice of procedure was made partly due to restrictions inherent in the Ullmann reaction when used to prepare unsymmetrical biaryls (see above) and partly due to the availability of suitable reactants. It was also hoped that subsequent nitration of the naphthyl moiety in picryl naphthalene would be facilitated by the concurrent work on the nitration of 1,1'-binaphthyl. This did in fact prove to be the case.

CHAPTER 2

Discussion of Results - The 1,1'-Binaphthyl System

Abbreviations and Numbering Schemes

For the sake of brevity, the various binaphthyl derivatives discussed in this thesis have been assigned alphabetical labels. These labels, derived from the experimental section, take the form of capital letters and are distinguished by apostrophes thus: 'A'. The contents list for chapter 2, which is contained in the preface, lists both the alphabetical labels and the full chemical names of compounds discussed in the chapter. This list should therefore provide an adequate source of reference for identification of the individual compounds, when they are referred to by label in the text.

Schemes, structures and tables are numbered throughout the thesis as three distinct series. In all cases the first part of the number indicates the chapter in which an item may be found, whilst the second details the individual scheme, structure or table. Roman numerals are used for the numbering of 'schemes' and arabic numerals for that of 'structures' and'tables'. The numbers relating to structures are further distinguished by the use of brackets. Thus for example in chapter two, the first scheme becomes 2:I, the first structure (2-1) and the first table 2-1.

2.1. The Spectra of 1,1'-Binaphthyl (Designated Compound 'A')

The spectra of 1,1'-binaphthyl have so far received little attention in the literature and for this reason they are presented in the appendix. A brief discussion of the spectra is also given (below) in order to highlight those features pertinent to subsequent discussions about the spectra of the various nitrobinaphthyls.

2.1.1. The Infra-red Spectrum

The infra red spectrum of 1,1'-binaphthyl (see appendix) shows a typical (aromatic) C-H stretching frequency at $3030cm^{-1}$ and bands at 1580 and $1500cm^{-1}$ corresponding to C=C stretching vibrations.[64a,65] In the low frequency region there is a very strong band at $800cm^{-1}$ and a doublet at $775/769cm^{-1}$ - presumably due to C-H out of plane deformation vibrations.[64a,65] The nature of the bands in this region can provide information as to the substitution pattern present in a given aromatic nucleus. In the present case the bands are consistent with the presence of α-substituted naphthalene nuclei.[64a,66,67] Structural analysis using this region will be discussed later in some detail.

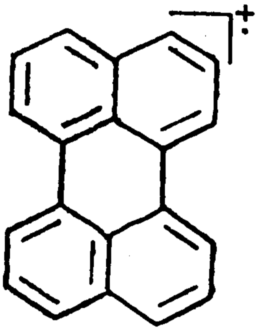
It is interesting to note that there are two crystalline forms of 1,1'-binaphthyl; these have melting points of 144.5-145°C and 157-9°C respectively.[68] Some differencies are noticeable between the infra red spectra of these two forms, the most striking of these being a band at 769cm^{-1} which is evident in the lower melting form but not in the higher.[68] All the 1,1'-binaphthyl used in the present work was predominantly of the lower melting form; the band at 769cm^{-1} is therefore evident in its infra red spectrum.

2.1.2. The Ultra Violet Spectrum

The ultra-violet spectrum of 1,1'-binaphthyl in methanol (see appendix), shows two maxima at λ 210nm, ϵ 7752m^{2}mole^{-1}, (aromatic $\pi \rightarrow \pi^*$ transition) and λ 283nm, ϵ 1323m^{2}mole^{-1}, the fine structure on this band producing a secondary maximum at λ 293nm, ϵ 1244m^{2}mole^{-1}. In fact the spectrum of 1,1'-binaphthyl has been shown to have considerable similarity to that of naphthalene itself[69]; the spectrum thus reflects the steric hindrance (and hence limited conjugation) in the 1,1'-binaphthyl molecule. (Contrast the unhindered 2,2'-binaphthyl which has a spectrum radically different to that of naphthalene[69]).

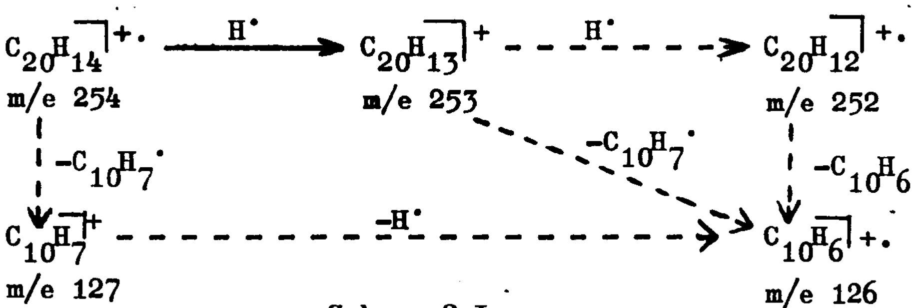
2.1.3. The Mass Spectrum

The mass spectrum of 1,1'-binaphthyl (see appendix) has a molecular ion at m/e 254 which is also the base peak of the spectrum. This ion evidently expels one or two hydrogen radicals to give intense ions at m/e 253 (M - H 93.9%) and m/e 252 (M - 2H 78.8%). The latter



(2-1)

ion possibly has a perylium type structure (2-1). An intense ion at m/e 126 (45.5%) corresponding to $C_{10}H_6^{+\cdot}$ may presumably be derived either via fragmentation of the perylium type ion or by successive loss of $C_{10}H_7^{\cdot}$ and $H^{\cdot}$ from the molecular ion (or vica versa - see scheme 2:I).



Scheme 2:I

A continuous line indicates the presence of a metastable peak for that transition.

2.1.4. The Proton Magnetic Resonance (PMR) Spectrum

The PMR spectrum of 1,1'-binaphthyl in carbon tetrachloride (see appendix) comprises two complex multiplets in the aromatic region at τ2.07-2.40 (4H) and τ2.40-3.12 (10H) (or τ1.80-2.10 (4H) and τ2.10-2.80 (10H) in acetone).

Whilst the spectrum is too complex to interpret by inspection, its division into two multiplets representing integral groups of protons is significant. Thus it has been observed in a number of naphthalene derivatives that α and β protons resonate at significantly different frequencies. This effect tends to produce a division of the spectrum into 'low' and 'high' field regions which are associated with the α and β protons respectively.[72] (This basic division is of course modified by the presence of substituents). A similar effect is evident in the spectrum of naphthalene itself (for which a complete analysis has been performed[70]), in this case a difference of 20.8Hz at 60MHz (0.35ppm) has been reported between the α and β protons (in CS_2). A similar differentiation is maintained in other solvents including carbon tetrachloride and acetone[71]. As the electronic effects within a binaphthyl molecule are likely to bear some resemblance to those in naphthalene itself, a similar separation might be expected between the α and β protons in this compound. A discrepancy is clearly evident however in that 1,1'-binaphthyl contains six α protons and eight β protons, whilst the PMR spectrum shows multiplets (low/high field) in the ratio 4:10. This anomaly could be the result of interaction between the two naphthyl moieties, although as inductive interaction between the systems is likely to be only small and resonance effects are limited by steric hindrance[69] neither of these factors should influence the PMR spectrum very much. Nevertheless, ring currents associated with one naphthalenic system are likely to affect the environment of protons attached to the other. The greatest effect is presumably going to be felt by the 2 and 8 protons (the latter particularly) as these are closest to the second naphthyl moiety. The exact nature of this interaction will probably depend upon the average conformation of the system - which unfortunately is not known with any precision. However, the UV spectrum suggests that the molecule is likely to be well removed from planarity[69] - in this case the 8-proton on one naphthalene system will be located somewhat above the plane of the second aromatic system; in consequence the '8' proton could be subject to shielding by the induced magnetic field which is associated with the second π system. This would of course shift the 8 protons away from the (lower-field) 'α' multiplet and into the higher field 'β' multiplet. In this event the spectrum would contain a low-field region representing four protons (4α) and a high-field region representing 10 protons ($8\beta+2\alpha$). This is exactly the ratio observed in the spectrum of 1,1'-binaphthyl and it is thought that this is the best explanation for the spectrum. However as the precise regions of shielding/deshielding around the binaphthyl molecule are rather uncertain (as indeed is the conformation of the molecule), an alternative possibility exists in that the protons H_2 and H_8 could both be deshielded by the adjacent naphthyl moiety. This situation is most likely to develop if the molecule adopts a cis conformation and it becomes more likely as the angle between the rings decreases (because the induced field around an aromatic system deshields protons in the plane of the aromatic ring). Assuming that H_2 and H_8 are deshielded, the observed spectrum is best explained by proposing a considerable shift of both - sufficient in fact to completely separate them from all the other protons. Thus the low-field multiplet would be assigned exclusively to the protons H_2, H_2', H_8 and H_8'. This explanation however, would require the high-field multiplet to be composed of both α and β protons - which seems unlikely as there is no subdivision of this multiplet (due to the different shifts of α and β protons). In fact the low-field multiplet in binaphthyl does not appear to be significantly shifted (downfield) from the expected value for α protons; thus in naphthalene the α protons resonate at τ 2.15 (CCl_4 [71,72]). This fact is further confirmed by the spectrum of 1-

phenylnaphthalene[73] which produces two distinct multiplets (assignable to α and β protons) at very similar chemical shifts to those observed in 1,1'-binaphthyl:-

1,1'-Binaphthyl: τ2.07-2.40 (4H), τ2.40-3.12 (10H)
1-Phenylnaphthalene: τ2.05-2.45 (3H), τ2.45-2.80 (9H)
(3α protons) (4 β + 5 phenyl protons)

(In this case it is clear from the integration that the low-field multiplet is not due to the protons 2 and 8 alone.) In fact the predominance of a 'cis coplanar' conformation in 1,1'-binaphthyl is thought rather unlikely, as the chemical shifts observed in this compound are fairly close to those of 1,8-diphenylnaphthalene - in which the phenyl rings must be truly perpendicular to the naphthyl moiety:-

1,8-Diphenylnaphthalene: τ2.10-2.28 (2H) τ2.45-2.82 (4H)
(4 β - the phenyl protons)
(resonate at τ3.15 (10H).)

This conclusion therefore ties in with the UV evidence[69] which also suggests that the molecule is well removed from coplanarity. In consequence, substantial deshielding of the protons H_2 and H_8 seems unlikely; thus the best explanation for the spectrum of 1,1'-binaphthyl is that given earlier which assumes shielding of the protons H_8 by the second naphthyl moiety (this explanation is also found to be consistent with the spectra of the various picryl naphthalene derivatives - see chapter 3.)

2.2. Nitration of 1,1'-Binaphthyl

A two stage process comprising initial use of a fairly mild nitration medium followed by treatment with a mixture of concentrated sulphuric and nitric acids was adopted for the nitration of 1,1'-binaphthyl. By this means it was hoped a) to minimise losses due to oxidation and charring and b) to isolate and identify some of the intermediate nitration products. Since Schoepfle had already established[10] that the nitration of 1,1'-binaphthyl in glacial acetic and nitric acids produced 4,4'-dinitro-1,1'-binaphthyl, this technique was employed as one method of mild nitration, when a known pattern of substitution was required. However the use of nitric acid in acetic anhydride was also examined in view of the possibility that a different substitution pattern and/or a higher degree of nitration might be achieved.

2.2.1. The Products of Nitration in Acetic Anhydride/Nitric Acid

The product mixture resulting from the reaction of 1,1'-binaphthyl with nitric acid in acetic anhydride was found to be resolvable by thin layer chromatography (TLC) into eleven distinct species. During subsequent separation and purification of this mixture two further components were detected. Nine of the species were identified as nitro derivatives of 1,1'-binaphthyl and two as oxidation products. A trace of unreacted 1,1'-binaphthyl was also detected but the thirteenth component was not identified. The nine nitrobinaphthyls are listed below.

		Designated as:-
4,4'-Dinitro-1,1'-binaphthyl		'B'
4,8'-Dinitro-1,1'-binaphthyl	(probable structure)	'C-1'
4,4',8-Trinitro-1,1'-binaphthyl	(probable structure)	'C-2'
4,4',5-Trinitro-1,1'-binaphthyl		'D'
A trinitro-1,1'-binaphthyl and A tetranitro-1,1'-binaphthyl	Unknown structures	'E'
4,5,8'-Trinitro-1,1'-binaphthyl	(probable structure)	'F'
4,4',5,5'-Tetranitro-1,1'-binaphthyl		'H'
4,5,x,y-Tetranitro-1,1'-binaphthyl		'I'

The evidence available as to the structure of the various nitrobinaphthyl is presented in the following sections.

2.2.1.1. 4,4'-Dinitro-1,1'-binaphthyl

This material was isolated in small quantities (about 2%) from the nitration of 1,1'-binaphthyl in a mixture of acetic anhydride and nitric acid. However the quantity of this material present in the final product mixture could be reduced to insignificant proportions by modifying the reaction conditions. 4,4'-Dinitro-1,1'-binaphthyl can also be prepared by the nitration of 1,1'-binaphthyl in a mixture of acetic and nitric acids. This method yields around 50% of the dinitrobinaphthyl and was originally reported by Schoepfle,[10] who also established the structure of the compound by synthetic methods.

Although this compound has been previously prepared[10,17] none of its spectra have been reported in the literature; for this reason and also to aid the interpretation of spectra from other nitrobinaphthyls, the ultra violet, infra-red, proton magnetic resonance and mass spectra of the compound have been recorded in the course of the present work and are presented in the appendix. All the data is consistent with the structure assigned by Schoepfle. The salient points of the spectra are summarised below; various aspects will be considered in greater detail elsewhere, by comparison with the spectra of related compounds.

The Infra-red Spectrum

The IR spectrum of 4,4'-dinitro-1,1'-binaphthyl shows a band at 3000cm^{-1} due to aromatic C-H stretching vibrations. It also has two intense bands at 1520 and 1330cm^{-1} which correspond to the nitro (N-O) stretching vibrations; as would be expected there is no indication of any other functional groups.

The Ultra Violet Spectrum

The UV spectrum of 4,4'-dinitro-1,1'-binaphthyl in methanol shows two distinct maxima at λ216nm, ϵ 9260m^{2}mole^{-1} (Ar $\pi \rightarrow \pi^*$) and λ 350nm, ϵ 1520m^{2}mole^{-1}. In addition to these there is a well defined shoulder at λ255nm, ϵ 2230m^{2}mole^{-1} (the 'aromatic nitro band' - see later); this has not been completely resolved from the intense band at λ216nm. Each of the bands therefore shows a slight bathochromic shift relative to α-nitronaphthalene (λ210nm, ϵ 5800m^{2}mole^{-1}; λ340nm, ϵ 300m^{2}mole^{-1} and λ245nm, ϵ 700m^{2}mole^{-1} respectively (methanol)[74].) This is to be expected due to the increased conjugation compared with the naphthalene system - the shift is not large however due to the steric hindrance of the 1,1'-binaphthyl system - this prevents extensive conjugation.[69,75]

The Mass Spectrum

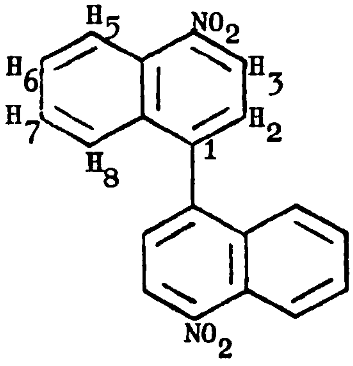
The mass spectrum of 4,4'-dinitro-1,1'-binaphthyl shows a molecular ion at m/e 344 which is also the base peak of the spectrum. The expected fragment ions produced by sequential loss of two nitro radicals are observed at m/e 298 (4.6%) (M - NO_2) and m/e 252 (50%) (M - $2NO_2$). In addition to these there are peaks of low intensity corresponding to the loss of O$^\cdot$, NO$^\cdot$, and (NO$^\cdot$ + CO) from the molecular ion. Such losses are characteristic[76] of nitro aromatic compounds and presumably occur via isomerisation of the nitro group to the nitrite.[77] A scheme showing the major fragmentation pathways for the compound is presented later, along with those of other dinitro-1,1'-binaphthyl.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of 4,4'-dinitro-1,1'-binaphthyl in D_6-benzene (see appendix) comprises the following signals: τ1.5 double doublet (2H) J=8.8Hz, J'=1.0Hz; τ2.32 doublet (2H) J=7.8Hz; τ2.75-3.24

multiplet (6H); $\tau 3.35$ doublet (2H) J=7.8Hz. These signals are in the normal region associated with protons in aromatic nitro compounds. The double doublet at $\tau 1.5$ may be assigned to the protons H_5 which are coupled to H_6,H_7 (and H_8). $J_{H5,6}$= 8.8Hz, $J_{H5,7}$=1.0Hz, $J_{H5,8}$ is too small to be resolved but is evident as line broadening of the double doublet. These coupling constants are fairly typical of those observed in other naphthalenic systems. (eg ortho coupling $\approx$ 8Hz, meta coupling $\approx$ 1Hz para coupling $<$ 1Hz.[70-72,78-83]

The low field at which these protons resonate is due to the combination of two effects - firstly they are α-protons and secondly they are sited 'peri' to a nitro group. The first effect has been previously mentioned with regard to the spectrum of 1,1'-binaphthyl itself; the second is evidently a direct 'proximity' effect and has been observed elsewhere.[70,71,78] Thus for example in the methyl nitro naphthalenes the presence of an α-nitro group is reported to produce a downfield shift of 0.79ppm on the adjacent peri proton[78] (in CCl_4).



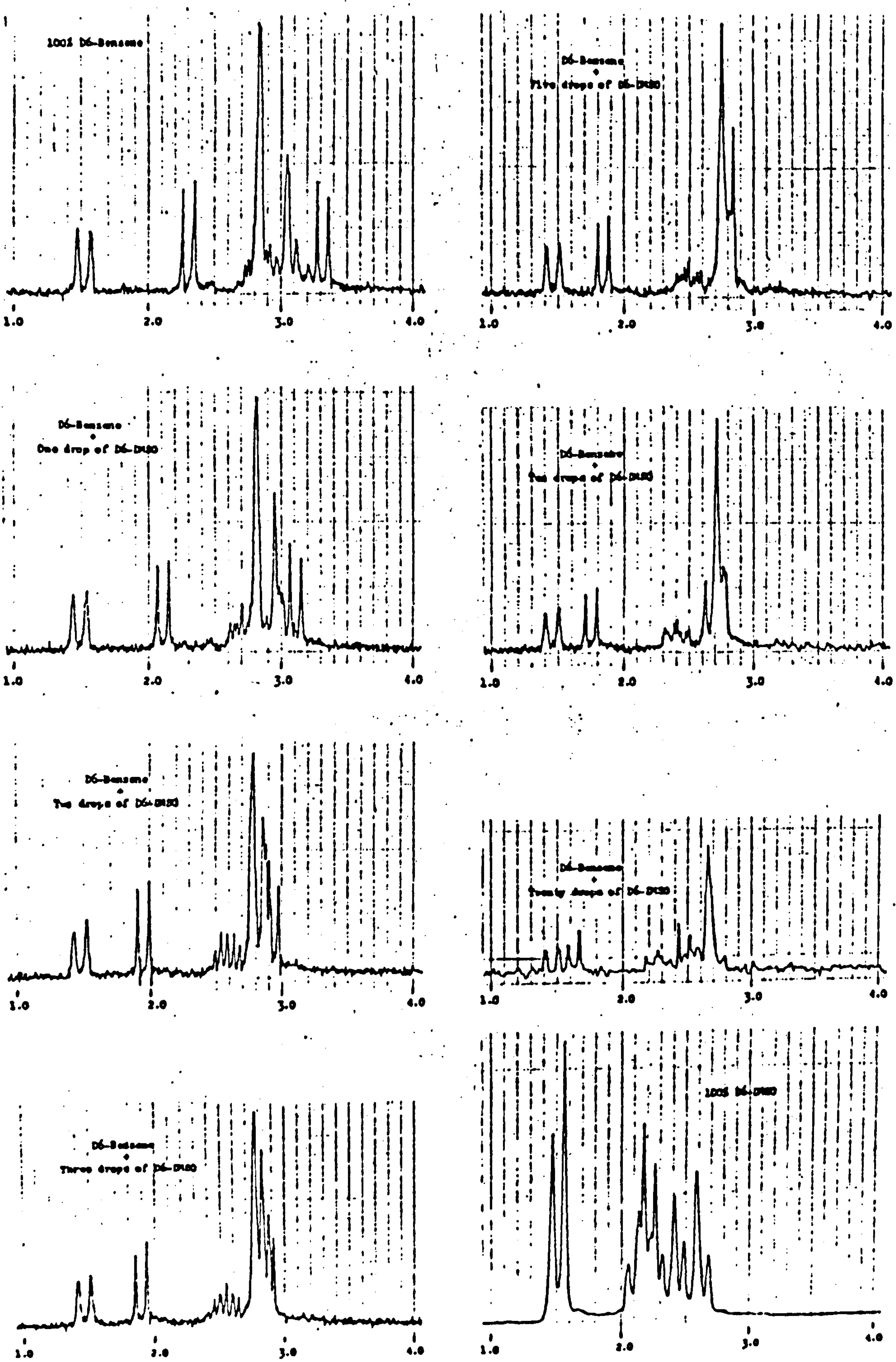
4,4'-Dinitro-1,1'-binaphthyl

The doublets at $\tau 2.32$ and $\tau 3.35$ constitute an AB quartet with J_{AB} = 7.8Hz. These doublets may be attributed to the protons H_3 and H_2; since H_3 will be deshielded by the adjacent ortho nitro group it should resonate at lower field than H_2 and may therefore be assigned to the signal $\tau 2.32$. In consequence H_2 must give rise to the signal at $\tau 3.35$.

It is pertinent to note at this point that the coupling between ortho related protons can vary slightly between different naphthalenic systems,[81] invariably however the numerical value of $J_{\alpha\beta}$ is found to be greater than that of $J_{\beta\beta}$ (usually by something of the order of 1Hz).[70-72,78-83] This observation provides useful confirma-

Figure 1

^{1}H NMR Spectra of 4,4'-Dinitro-1,1'-binaphthyl showing the effect of different solvent mixtures (All Spectra 90MHz)



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tion of the above assignments, thus the larger coupling constant (8.8Hz) is assigned to an $\alpha\beta$ interaction (between H_5 and H_6) whilst the smaller coupling constant (7.8Hz) is attributed to the $\beta\beta$ interaction (between H_2 and H_3).

The remaining protons H_6, H_7 and H_8 must be assigned to the complex multiplet at τ2.75-3.24.

Although the PMR spectra of various nitronaphthalene derivatives have been analysed in considerable detail[71,72,78] it is not possible to make a useful comparison of chemical shifts between these and the nitrobinaphthyls because the various spectra have been recorded in different solvents. The reason for this is that large fluctuations of chemical shift can be produced - by a change of solvent - particularly if a specific solute solvent interaction occurs.[71,72,78,84] (eg one such interaction occurs between acetone and 1,4-dinitronaphthalene.[85]) This type of effect has been clearly demonstrated during the present work using 4,4'-dinitro-1,1'-binaphthyl. Thus substantial differencies are evident between the spectra of this compound in benzene and in DMSO (see appendix). In fact the differencies are so great that it is difficult to relate the DMSO spectrum with the assignments presented above for the spectrum in benzene.

In order to clarify the situation a series of spectra have been recorded in mixed solvent systems containing DMSO/benzene in various ratios. A selection of these spectra are shown in figure 1; they illustrate the changes produced in the PMR spectrum, as DMSO is added dropwise to a solution of 4,4'-dinitro-1,1'-binaphthyl in benzene. It is evident that the addition of DMSO causes a downfield shift on the AB quartet, which is initially sited (100% benzene) at τ2.32/3.25 (H_3/H_2). The two doublets are not equally affected however, the higher signal (H_2) being subject to a greater shift (0.99ppm) than the other (H_3 - 0.76ppm). The addition of DMSO to the benzene solution was continued until all resolution had been lost (due to the precipitation of sample) but throughout this addition the AB quartet continued to move downfield. When however the spectrum was run in 100% DMSO the lower-field doublet (due to H_3) was no longer visible, it is therefore assumed that this doublet becomes coincident with that due to the protons H_5 (in 100% DMSO). Integration of the spectrum (in 100% DMSO) supports this view as the 'doublet' at τ1.56 represents four protons, compared with that at τ1.50 in benzene, which represents only two protons.

The change of solvent evidently has only a minimal effect upon the doublet assigned to H_5 (τ1.50 - benzene); it is interesting to note however that this doublet seems to move upfield very slightly (by about 0.6ppm - benzene→DMSO). On the other hand the multiplet at τ2.75-3.24 (benzene) due to the protons H_6, H_7 and H_8 is seen to move downfield with the change of solvent so that it occurs at τ2.05 -2.72 in 100% DMSO. This multiplet is however too complex to be analysed by inspection.

The precise nature of the interaction between DMSO and 4,4'-dinitro-1,1'-binaphthyl is not fully understood. Presumably one effect of adding this highly polar solvent to a solution of the nitrobinaphthyl in benzene, will be to enhance solvation of the nitro groups; this action should result in an increased charge separation within the nitro groups and consequently greater electron withdrawl from the aromatic ring. Whilst this effect should produce a downfield shift of both H_2 and H_3 , it would be anticipated that the protons ortho to the nitro groups (H_3) would be subject to the greater shift - contrast the effect actually observed in the spectrum - where H_2 seems to be affected more than H_3. In fact it seems likely that in this system some type of specific solvent - solute interaction will also occur. In analagous systems such interaction has been described in terms of the formation of weak 'hydrogen bonds'.[84] Consider for example the spectrum recorded in 100% benzene; in this solvent system some form of weak bonding might be expected between the solute molecules and the benzene, as the latter is a 'π - type' donor.[84] In consequence a prefered molecular orientation between solvent and solute molecules should result, such that those protons in the solute molecule which become 'bonded' to the solvent, are located 'above' the benzene ring and therefore in a shielded environment[84] (see fig2).

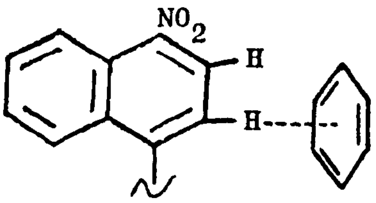

Fig 2

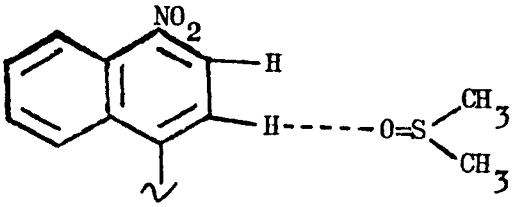

Fig 3

Possibly it is the displacement of benzene as the 'bonding' donor which is responsible for the downfield shift of the spectrum, when DMSO is added to a solution of 4,4'-dinitro-1,1'-binaphthyl in benzene. Thus if a new prefered orientation of solute molecules is adopted relative to DMSO (fig 3), the solute protons should be partially removed from their previous association with benzene. In consequence they will no longer be shielded by the aromatic ring currents and will therefore move to lower field.

2.2.1.2. 4,8'-Dinitro-1,1'-binaphthyl (Probable Structure) Designated Compound 'C-1'

This material was isolated in small quantities (about 2%) when 1,1'-binaphthyl was nitrated with nitric acid in acetic anhydride. It has not been prepared by any other method. The compound analyses correctly for a dinitrobinaphthyl and shows a molecular ion in its mass spectrum at m/e 344.0784 - corresponding to $C_{20}H_{12}N_2O_4$ (calculated m/e 344.0797). The infra-red spectrum has bands consistent with nitro stretching frequencies, and indicates no other functional groups. The compound is clearly therefore a dinitrobinaphthyl, however, its spectra do not facilitate an unambiguous assignment of structure. Thus whilst distinctive features are visible in the spectra to suggest the presence of an 8 nitro group, there are no clear cut indications of a 4 nitro substituent. It is nevertheless most likely that the compound is 4 substituted, because the most reactive sites in 1,1'-binaphthyl, towards nitration, are the 4 positions. This is clearly demonstrated by the high yields of 4-nitro-1,1'-binaphthyl and 4,4'-dinitro-1,1'-binaphthyl which can be obtained under relatively mild nitration conditions[10] and is further supported by the product distribution observed for nitrations in acetic anhydride and nitric acid during the present work. Thus the main bulk (wt%) of products isolated from the nitration of 1,1'-binaphthyl in the latter medium have been found to contain 4,4'- substitution.

Given the reactivity of the 4 position in 1,1'-binaphthyl, nitration of the compound in acetic anhydride and nitric acid seems likely to produce only a very small proportion of products without a 4 nitro substituent. This follows, because even if initial nitration were to take place to a small extent at some other site within the molecule, subsequent attack would still be most likely at the

4 position. This assumes that a) the presence of a nitro group in one naphthalenic system will sufficiently deactivate it to direct subsequent attack to the other, and b) that this nitro group will not significantly modify the substitution pattern obtained in the second naphthalene system. Both of these assumptions seem reasonable since 4-nitro-1,1'-binaphthyl may be nitrated in high yield to 4,4'-dinitro-1,1'-binaphthyl.[10] Thus as two dinitrobinaphthyls have been isolated from the nitration product in acetic anhydride and nitric acid - in approximately equal quantities - and one of these was 4,4'-dinitro-1,1'-binaphthyl, it seems reasonable to propose that the second compound also contains 4 substitution. The spectra certainly appear consistent with this assumption. The various data are discussed below.

The Infra-red Spectrum

The infra-red spectrum of 'C-1' (see appendix) shows a weak band at 3000cm^{-1} due to aromatic C-H stretching vibrations. There are also two very strong bands corresponding to the nitro (N-O) stretching vibrations. The most noteworthy feature of the spectrum however, is a pronounced splitting of these nitro bands, to produce a distinct double maximum in each case. The effect is most noticeable for the symmetric absorption which comprises bands at 1335 and 1365cm^{-1}; the asymmetric frequencies are 1530/1525cm^{-1}. Such variations of frequency reflect the different environments of the two nitro groups and quite wide variations of stretching frequencies are known - between different nitro aromatic compounds - according to the nature of any other ring substituents.[64b,86a] These effects tend to be maximised when a substituent is para to the nitro group unless steric interaction occurs, as in the case of a bulky substituent ortho to the nitro group.

In the present system the only 'substituent' is a nitronaphthalene moiety. If this has a profound effect on the frequency of the nitro stretching vibration it would be expected that a large deviation would occur between the frequencies observed in 4,4'-dinitro-1,1'-binaphthyl (nitro naphthalene moiety para to the nitro group) and 5,5'-dinitro-1,1'-binaphthyl (no substituent para to the nitro group). This does not in fact occur; both systems have asymmetric stretching frequencies close to 1520cm^{-1} and symmetric stretching frequencies close to 1330cm^{-1} (see appendix).

Since there are no other substituents in the compound

'C-1' the explanation of the double nitro stretching frequencies must be a steric one. The only two sites at which a nitro group is likely to experience substantial steric interaction in the binaphthyl nucleus are the 2 and 8 positions. At either of these sites a nitro group will be unable to lie coplanar* with the aromatic ring to which it is attached - due to the close proximity of the adjacent naphthalene system. This twisting of the nitro group away from the plane of the aromatic ring results in reduced conjugation and hence a rise in frequency.[86a] Multiple bands due to this effect have been observed in other systems.[64b,87]

It is difficult to justify the selection of one site - either the 2 or the 8 position - in preference to the other, indeed the location of this substituent is rather uncertain. It is thought however, in view of all the available data, that the 8 position is the most likely - this point will be further discussed later.

Assuming that this dinitrobinaphthyl is in fact 4,8'-substituted, the 4-nitro group would be expected to produce bands in its infra-red spectrum close to 1520 and 1330cm^{-1} ie the frequencies observed in 4,4'-dinitro-1,1'-binaphthyl. On the other hand the 8 nitro substituent being substantially twisted from the plane of the aromatic ring should absorb at rather higher frequency. This is in fact the case, the frequencies being 1530/1525 and 1365/1335cm^{-1} respectively. The rather smaller effect of twisting on the symmetric vibration is consistent with findings in other systems where steric effects do not cause this band to rise above 1530cm^{-1} even in o-nitro-tertiarybutylbenzene.[86a]

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* The crystal structure of 1,5-dinitronaphthalene has been investigated by Trotter[88] who deduced that whilst the naphthalene ring system was planar, an angle of 49° existed between this and the nitro groups. Such an observation clearly suggests that in a nitrobinaphthyl - such as 'C-1' - even a 4-nitro group may be substantially removed from coplanarity with the ring system. This twisting of the nitro group is probably significant even in solution - thus the PMR downfield shift produced by a naphthalenic peri nitro group - on a proton sited ortho to it - is significantly less than that produced by an 'unhindered' nitro group[78] (by about 0.1ppm). In view of this evidence the various references in the present text to the 'coplanar' nitro group must in practice refer to the 'most nearly coplanar' nitro group.

The use of infra-red spectra in assigning substitution patterns to the phenyl nucleus is a well known and widely used technique. As the method is also applicable to a number of polynuclear aromatic systems[65,67,89], including many naphthalene derivatives, it is worthwhile examining it in some detail.

There are three main regions for this type of assigment; the first: 2000-1660cm^{-1} usually gives the most definite assigment of substitution in the phenyl system[64a], but there is little data available on the applicability of these absorptions to the naphthalenic system. Bellamy[64a] concludes that the patterns resulting from the combined effects of two rings differently substituted, will invalidate this region for identification purposes. The second region for study is: 1250-1000cm^{-1} and comprises fairly weak bands; consequently this is used only for confirmation of assignments from other regions. The third region: 1000-650cm^{-1} is widely used and fairly reliable for the benzene nucleus. Absorption bands in this region, assigned on the basis of the number of adjacent hydrogen atoms present in a nucleus are applicable to both benzene[64a] and naphthalene[66,67,90-2,(64a)] nuclei although a somewhat wider tolerance must be used in the latter case when searching for a characteristic band in a specific region. There seems no good reason for discounting these rules in the binaphthyl molecule, although of course, there will be overlapping bands due to each of the four aromatic rings. The results may thus be very complex and the bands rather weak – since more substitution (fewer H's) leads to weaker bands. Even in naphthalene the presence of substituents in both rings can make identification difficult and may sometimes lead to errors.[64a] Cencelj and Hadzi report[90] that generally the number of bands observed in a particular naphthalene derivative considerably exceeds the number predicted by the normal rules – based on the number of adjacent H's (as summarised eg by Bellamy[64a]). They regard this as a serious limitation to the use of these correlation rules in determining substitution patterns. Cannon and Sutherland[65] also regard the spectra of naphthalene derivatives as being too complex for useful interpretation (although their data remains consistent with the usual correlations[64a] for C-H deformation vibrations). Cencelj and Hadzi[90] conclude that whilst the presence of a particular band is not a sufficient proof of the presence of the corresponding group of H atoms, the absence of a band does tend to exclude a particular pattern of substitution. These observations must be highly pertinent to the spectra of the binaphthyl derivatives - which are necessarily more complex than those containing only a single naphthalene nucleus.

The major difficulty of the method, however, when applied to the current work, is the nature of the substituent, since nitro groups can have a profound effect on the spectrum. Thus in general terms they move bands to higher frequency than normal, the extent of shift being roughly related to the degree of substitution. Indeed for highly nitrated materials these effects can be sufficient to move a particular band completely outside the expected region.[64a]

An additional (and serious) complication however, is the normal presence of strong absorptions in the low frequency region near 850 and sometimes 750cm^{-1}, which are a feature of nitroaromatic compounds.[64b] Thus as these bands fall in the same region as those due to the C-H out of plane bending modes, they inevitably complicate interpretation of the substitution patterns. It is unclear however, precisely which vibrational modes give rise to these bands. Thus although it has been suggested[93] that the band at 850cm^{-1} is due to the C-N stretching frequency, there is some doubt about this[94,95] and it may alternatively result from symmetric NO_2 deformation.[96] Nevertheless there remains no doubt that a band exists around 850cm^{-1} in most nitroaromatic compounds and that it is probably associated with the $C-NO_2$ grouping. The origin of the band observed near 750cm^{-1} in some nitroaromatic compounds is similarly uncertain; thus bands in this region have been described both as in plane rocking vibrations of the nitro group[97] and as unidentified ring vibrations.[98] The appearance of a band at this frequency is, however, much less predictable than that at 850cm^{-1} which further complicates analysis of this spectral region. In view of the various points discussed above it seems unlikely that a conclusive and reliable assignment of substitution for 'C-1' (or any other nitrobinaphthyl) could be made on the basis of its infra-red spectrum alone. Nevertheless 'C-1' provides a useful illustration of the problems involved - particularly as the infra-red spectra of two other dinitrobinaphthyls of known substitution (4,4'- and 5,5'-) are available for comparison. The low frequency region in the spectrum of 'C-1' is therefore discussed below.

Since the spectrum shows two very intense doublets at

770/780cm^{-1} and 835/845cm^{-1} the first problem is to establish which of these is due to the presence of the C–NO_2 grouping. As indicated above most nitroaromatic compounds produce a band near 850cm^{-1} so it appears likely that the 835/845cm^{-1} doublet in 'C–1' is at least partly due to the C–NO_2 grouping. Presumably however, the steric factors which cause doubling of the NO_2 (N–O) stretching frequencies in 'C–1' will similarly affect the C–N vibrations. (Although in this case, as conjugation with the π-system tends to increase the C–N bond order, its loss when one of the nitro groups is twisted 'out of plane' should result in a shift of the vibration to lower frequency.) If therefore the "850cm^{-1}" band is due to the C–N stetching vibration,[93] the single band normally observed in nitro aromatic compounds could well become a doublet for 'C–1'. Thus both of the bands at 835/845cm^{-1} could well be due to the C–NO_2 grouping. (It is possible that the "850cm^{-1}" band would double even if it was derived from some other vibrational mode.)

Assignment of the bands at 770/780cm^{-1} are even less certain. Thus if a band is produced in this region due to the rocking vibrations of the nitro groups it might conceivably be doubled by the non planarity of one of the nitro groups. On the other hand the band may be due simply to unidentified ring vibrations.[98] In this context it is pertinent to note that 1,1'-binaphthyl itself has an intense doublet at 765/780cm^{-1} (see appendix) which clearly cannot be due to C–NO_2 vibrations. The possibility also exists that either (or both) of the doublets in 'C–1' arise from partial coincidence of (say) C–NO_2 stretching vibrations, with bands of different origin eg C–H out of plane deformation. An unambiguous assignment of all four bands is clearly impossible.

The bands in the low frequency region of the spectrum of 'C–1' will now be considered with reference to those expected due to C–H out of plane bending vibrations.

In aromatic nuclei containing four adjacent hydrogen atoms, the out of plane C–H deformation vibrations are normally observed in the region 770–735cm^{-1}.[64a] A large number of spectra are available to substantiate this range for the appropriate naphthalene derivatives.[65,66,90–92] (Although the frequency range is inevitably a little wider.)

In the case of 'C–1' there is no band between 770 and

735cm^{-1}, but it probably occurs at a slightly higher frequency - compare for example unsubstituted naphthalene in which the corresponding band occurs at the unexpectedly high frequency[67] of 885cm^{-1}.[99] Additionally the presence of a nitro substituent in the adjacent ring system may tend to increase the frequency of the vibration. Unfortunately in this higher region the vibration may well be partially coincident with the " 750cm^{-1}" band discussed above, this could therefore offer an explanation of the doublet at 770/780cm^{-1}.

The spectrum of 4,4'-dinitro-1,1'-binaphthyl is similar in having no reasonably strong band in the lower part of the range, but a very strong absorbance at higher frequency (765cm^{-1}). In this case the band is not separated into a doublet, this may simply be due to the different siting of the second nitro groups within the molecule. Both dinitrobinaphthyls also have a slight shoulder (750cm^{-1}) on the main band and a very weak band at 730cm^{-1}.

Each of these compounds also contain two adjacent hydrogens in the 4-substituted ring system; consequently they should show the characteristic absorbtion lines due to deformation of these. The frequency range normally quoted for such hydrogens (C-H out of plane deformation) is 860-800cm^{-1}.[64a] Presumably this should be extended to higher frequency in view of the nitro substituent. Therefore in 'C-1' the range should cover not only the bands at 835/845cm^{-1} but also a rather weaker band 870cm^{-1}.

The spectrum of 4,4'-dinitro-1,1'-binaphthyl also has three bands in this region, at 835, 850 and 885cm^{-1}. The first two of these however are much weaker than the third. Since there are two adjacent hydrogens in each half of the molecule the band due to their out of plane deformation should be relatively strong; of the three, the 885cm^{-1} band seems to be the most likely assignment for this vibrational mode. The corresponding band in 'C-1' is presumably that at 870cm^{-1}; once again the differencies in frequencies might be attributed to the change in position of the nitro group in the second naphthalene nucleus.

Although these two spectra are consistent, examination of the spectrum of 5,5'-dinitro-1,1'-binaphthyl reveals a closely similar band at 880cm^{-1}. In this case however the molecule does not contain (only) two adjacent hydrogens, so the band cannot be due to their characteristic C-H out of plane deformation. (The three adjacent hydrogens present in the 5,5'-isomer would be expected to produce a band within the region 810-750cm^{-1}.[64a]) Even if the assignment in 4,4'-dinitro-1,1'-binaphthyl is changed from the 885cm^{-1} band to one of the others in the appropriate region (835/850cm^{-1}) the result would remain ambiguous as the 5,5'- isomer also has a weak band at 840cm^{-1}. (Additional 'inappropriate' bands in the region associated with two adjacent H's have also been observed in 1,8-dimethylnaphthalene and related polynuclear compounds.[67])

Attempts to assign the C-H out of plane bending mode for 'C-1', in the other half of the molecule (three adjacent hydrogens) are even more futile, as the normal range of 810-750cm^{-1} [64a] - suitably broadened for naphthalene derivatives and extended to higher frequency to allow for nitro substitution - could cover all four major bands at 770/780 and 835/845cm^{-1} (partly due to Ar-NO_2?) plus three minor bands. Further the model compound 8,8'-dinitro-1,1'-binaphthyl, ideally required for comparison, is not available. Thus, whilst it is conceivable that two appropriate bands are present in 'C-1' (due to the two differently substituted ring systems), positive assignment is impossible.

As mentioned above, for a complex system such as binaphthyl, even a negative result could be of considerable value, as it would exclude the possibility of a particular substitution pattern. In the present case the absence of C-H deformation bands corresponding to a single isolated hydrogen, could preclude the possibility of 6 or 7 substitution in the system. Unfortunately the uncertain intensity of such a band, and its variable position[66] - even if it existed - prevents it from being of much value. Thus the band is of only medium intensity even in the phenyl system[64a] and in the present case would still be due to only one hydrogen atom despite the much more complex system under consideration. Thus within the appropriate region of about 920-860cm^{-1} (allowing for a nitro substituent) there are two very weak bands which could conceivably be assigned to such a vibration - though it seems that little purpose is served by such speculation. Clearly no firm conclusions can be drawn as to the substitution pattern of 'C-1' on the basis of C-H deformation vibrations.

The Ultra Violet Spectrum

The ultra violet spectrum of 'C-1' in methanol (see appendix) shows two maxima at λ217nm, ϵ 8230m^{2}mole^{-1} (Ar $\pi \rightarrow \pi^*$) and

λ353nm, ϵ 1030m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$ or $\pi — \pi^*$? - see below). In addition there is a rather flat shoulder at λ255nm, ϵ 2000m^{2}mole^{-1}. This compound therefore exhibits a slight bathochromic shift relative to α-nitronaphthalene (λca 210nm, ϵ 5800m^{2}mole^{-1}, λca 245nm, ϵ 700m^2 mole^{-1}, λca 340nm, ϵ 300m^{2}mole^{-1} - methanol[74]); this is to be expected due to the increased conjugation of the binaphthyl molecule. The change should not be large however due to the considerable steric hindrance in the 1,1'-binaphthyl system.[69,75]

According to Gillam and Stern the NO_2 group exhibits two absorbtion bands in the UV region; one is a $\pi \rightarrow \pi^*$ band around 200nm and the other an $n \rightarrow \pi^*$. band close to 270nm.[100] In the present case the former band is completely obscured and the latter partially overlapped by the intense aromatic $\pi \rightarrow \pi^*$ transition. This is normal for aromatic nitro compounds.[101] Nevertheless useful qualitative information relating to the orientation of the nitro group may sometimes be deduced from the UV spectra of aromatic nitro compounds - provided that the 270nm band is not completely obscured -. Thus the presence of a sufficiently bulky substituent ortho to a nitro group can produce a twisting of the nitro group out of the plane of the aromatic ring; this twisting results in a loss of conjugation with the consequence that the aromatic nitro band - around 270nm - is reduced in intensity and shifted to shorter wavelengths; a number of examples are available from the literature.[102-106]

In the case of the compound 'C-1' a sterically hindered 8 nitro group has been proposed. If this nitro group is prevented from lying coplanar with the aromatic ring to which it is attached, there will be a loss of resonance which should cause the band near 270nm to be of lower intensity than the same band in either 4,4'- or 5,5'- dinitro-1,1'-binaphthyl. There may also be a shift to shorter wavelength. The spectra of the three compounds are given in the appendix. In both 4,4'- and 5,5'- dinitro-1,1'-binaphthyls the shoulder at 255nm is distinctly curved although the maxima are not quite resolved due to overlap with the intense aromatic band near 216nm. In the case of 'C-1' a definite flattening of the curve is apparent around 255nm so that the spectrum between 243 and 273nm is practically a straight line. The difference between the curves is consistent with either a reduction of intensity for the band at 255nm in 'C-1' or a shift to shorter wavelength of the same band (or both). Both of these possibilities are consistent with the proposed structure of 'C-1'. To place the comparison on a quantitative basis some values of ϵ for different wavelengths are given in table 2-1.

Table 2-1

Probable Assignment	Aromatic		'Aromatic nitro'					
Isomer	λ_{max} nm	ϵ $m^2 mole^{-1}$	λ^a nm	ϵ $m^2 mole^{-1}$	λ_{max} nm	ϵ $m^2 mole^{-1}$	λ_{max} nm	ϵ $m^2 mole^{-1}$
4,4'-	216	9620	240	2710	255 (sh)	2230	350	1520
5,5'-	218	10600	240	2640	255 (sh)	2150	340	1260
4,8'- ('C-1')	217	8230	240	2730	255 (sh)	2000	353	1030

a= part of the 255nm shoulder

UV Spectral Data for the Dinitro-1,1'-binaphthyls

The changes are not very dramatic but this is to be expected since one of the nitro groups remains substantially coplanar and therefore in extensive conjugation with the aromatic ring. Thus any changes in the spectrum will be partially masked by a residual absorbtion of this coplanar nitro group. The combined effect of a 'static' and a 'shifting' aromatic nitro band offers a reasonable explanation for the flattening of the curve between 243 and 273nm in 'C-1'. Although small the changes shown in the table are in the expected directions. Thus the original shoulder at 255nm reduces in intensity in going from the 4,4'- and 5,5'- isomers to 'C-1', whilst the value of ϵ at slightly shorter wavelength (240nm) increases. This is consistent with a shift of one aromatic nitro band to shorter wavelength.

Quantitative comparisons of extinction coefficients are necessarily difficult, due to the overlapping nature of the bands in this region and it might be argued that the reduction of ϵ at 255nm (in going from the 4,4'- and 5,5'- isomers to 'C-1') might simply be due to the reduction of intensity in the aromatic $\pi \rightarrow \pi^*$ band (at 216nm) which partially overlaps the region of interest. In view of this argument it seems preferable to examine the shape of the shoulder at 255nm rather than its absolute intensity. It should be noted however that if the change in ϵ were solely due to fluctuations of the 216nm band, the intensity of absorbtion at 240nm in 'C-1' should also be lower than in the other isomers - contrast the apparent increase of ϵ which is actually observed.

In addition to the points discussed above some significance may be attached to the actual wavelength of the band at 255nm in the spectrum of 'C-1'. Thus the position of this band provides useful evidence in support of the theory that 'C-1' contains only peri substituted nitro groups. This is because truely unhindered nitro groups, that is 3,6 or 7 substituents, would be expected to absorb at longer wavelength. This point is discussed later in relation to the UV spectrum of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl (section 2.2.2.1.).

At this stage it is pertinent to note an alternative possibility for assignment of the band at 255nm in this compound. Thus Nagakura and coworkers have attributed a band near 260nm in nitrobenzene to intramolecular charge transfer[107], a similar explanation might be postulated for the 255nm band in 'C-1'. Such an assignment does not however affect the qualitative result of having a 'twisted' nitro group, since loss of resonance will still decrease the observed intensity of the band and shift it to shorter wavelength.[107] These workers have also assigned the 340nm band in nitrobenzene to the NO_2 moiety - as an $n \rightarrow \pi^*$ transition - a similar conclusion was reached by Kiss and Horrath[108], although the latter workers consider the 240nm band to be a $\pi \rightarrow \pi^*$ type transition. Clearly in either case a reduction of resonance due to the twisting of a nitro group out of the plane of the aromatic ring should lead to a decrease of intensity in this band. Thus in 'C-1' the rather lower intensity of the (presumably) analogous band near 350nm, as compared with either 4,4'- or 5,5'-dinitrobinaphthyl could be consistent with the presence of an 8 substituted nitro group. There is however a paucity of data in the literature relating to the influence of steric factors on this band. In general it has been rather difficult during the present work to consider wavelength shifts of this band, because it is very broad in the various binaphthyl derivatives studied and this makes accurate determination of its λ_{max} very difficult.

It is interesting to note that the reduced intensity of the aromatic band at 216nm in 'C-1', compared with the 4,4'- and 5,5'-isomers, may itself reflect the presence of an 8 substituent. Thus an 8 nitro group will tend to prevent coplanarity of the two naphthalenic ring systems, so reducing conjugation and hence the intensity of

the band at 216nm (this type of effect has been observed in the biphenyl system[106]).

In summary it may be concluded that the UV spectrum of 'C-1' is consistent with the proposed structure and offers tentative confirmation for the presence of an 8 substituted nitro group.

The Mass Spectrum

i) The Spectra of Compounds related to 'C-1'

In order to analyse the fragmentation pattern of the compound 'C-1' it is useful firstly to examine the mass spectra of some related compounds. The mass spectra of both the mono and dinitro naphthalenes have been described in the literature.[109,110] These are interesting because in addition to the fragmentations normally associated with aromatic nitro compounds it has been observed that a number of the compounds lose neutral CO from their molecular ion.[109] This elimination of CO is peculiar to 1-nitronaphthalene and those dinitronaphthalenes with a 1-nitro substituent, provided that they are also unsubstituted in the 8 position. Thus although of only moderate intensity (less than 20%), the resultant ion is potentially valuable for detecting the presence of a single peri substituted nitro group in related systems.

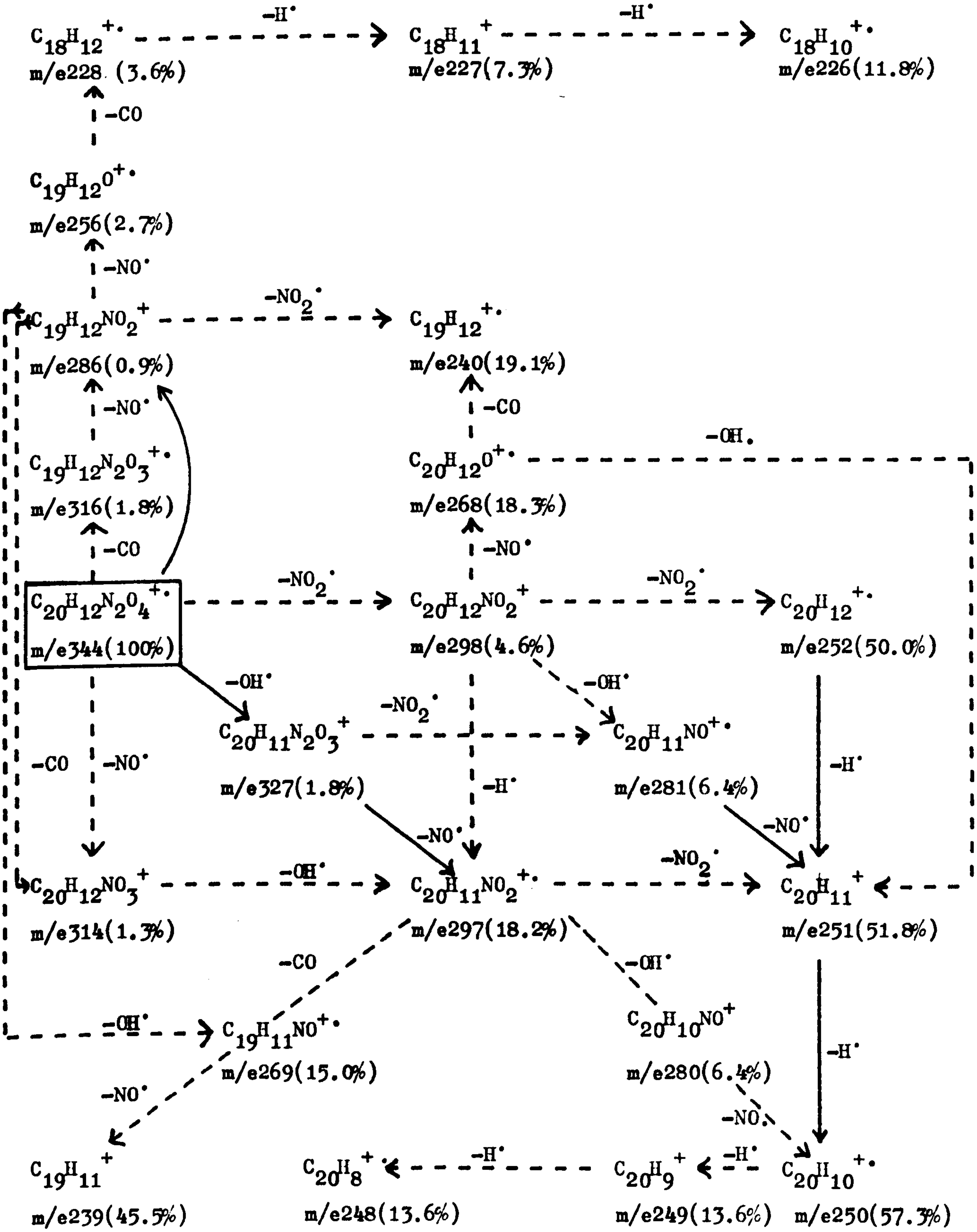
Beynon,Job and Williams have proposed[109] two mechanisms to account for this distinctive loss of CO; these are reproduced in the schemes 2:II and 2:III. The first scheme has also been proposed (independently) by Hartley-Mason, Toube and Williams.[111] Both the mechanisms require initial removal of a hydrogen atom, with a bonding electron, from the 8 carbon atom; it has therefore been suggested[109] that an electron deficiency at this site would hinder the loss of CO. Beynon, Job and Williams have thus related the extent to which the different compounds lose CO from their molecular ions, to the electron density at the 8 position[109] - the most extreme case being that of 1,5-dinitronaphthalene where a high electron deficiency results in a zero loss of CO from the molecular ion. 1,3-Dinitronaphthalene is anomalous in their series as it loses less CO than expected on the basis of electron density calculations. This has been explained[109] through the possible sharing of positive chargebetween the 1 and 3 nitro groups. In the latter case neither of the schemes 2:II or 2:III could be initiated and hence CO could not be lost.

A slightly modified view has been put forward by Brittain, Wells, Paisley and Stickley[110] who consider that the schemes 2:II and 2:III may operate competetively - though one would be expected to predominate in a particular case. The observation that the spectrum of 1,3-dinitronaphthalene shows intense peaks corresponding to the loss of OH˙ and HONO from the molecular ion, leads these authors to conclude that this isomer fragments to an appreciable extent via the analogue of species (2-2) (scheme 2:II). Conversely as the majority of the dinitronaphthalenes do not show such losses to any significant extent, they conclude that the remaining isomers fragment predominantly via the analogue of species (2-3) (scheme 2:III). These authors further suggest that loss of CO from the molecular ion of 1,3-dinitronaphthalene may also occur via the species (2-3) (scheme 2:III), so that its anomalous position - when relating the degree of CO expulsion from the molecular ion, to electron density at the 8 position - may be explained in terms of two competing fragmentation routes. They also observe that the formation of a species such as (2-2) (the dinitro derivative) appears to be more markedly dependent on the electron density at the 8 position than does the formation of a species analogous to (2-3) (the dinitro derivative), hence it is only for the 1,3-dinitronaphthalene that fragmentation via a type (2-2) species becomes important, since this isomer has the highest electron density at the 8 position. Such an observation is of particular significance in the binaphthyl system as the presence of a second naphthalene moiety is likely to result in an increase of electron availability at the '8' position (position 4 according to the binaphthyl numbering system). The views of Brittain et al could therefore lead to the prediction that a binaphthyl nucleus containing a 4 or 5- substituted nitro group would fragment primarily via the analogue of species (2-2) and consequently have an M - CO ion of reduced intensity but enhanced OH loss (as in the case of 1,3-dinitronaphthalene). (This contrasts with the original proposal of Beynon et al where the sole effect of increased electron density at the 8 position (position 4 in the binaphthyl numbering system) would have been to enhance the CO loss.)

There are two dinitro-1,1'-binaphthyls of known structure available for consideration - the 4,4'- and 5,5'- isomers. The fragmentation patterns given below (schemes 2:IV and 2:V summarise the most intense ions of their respective spectra. Bar diagrams and lists of relative intensities are given in the appendix.

Scheme 2:IV

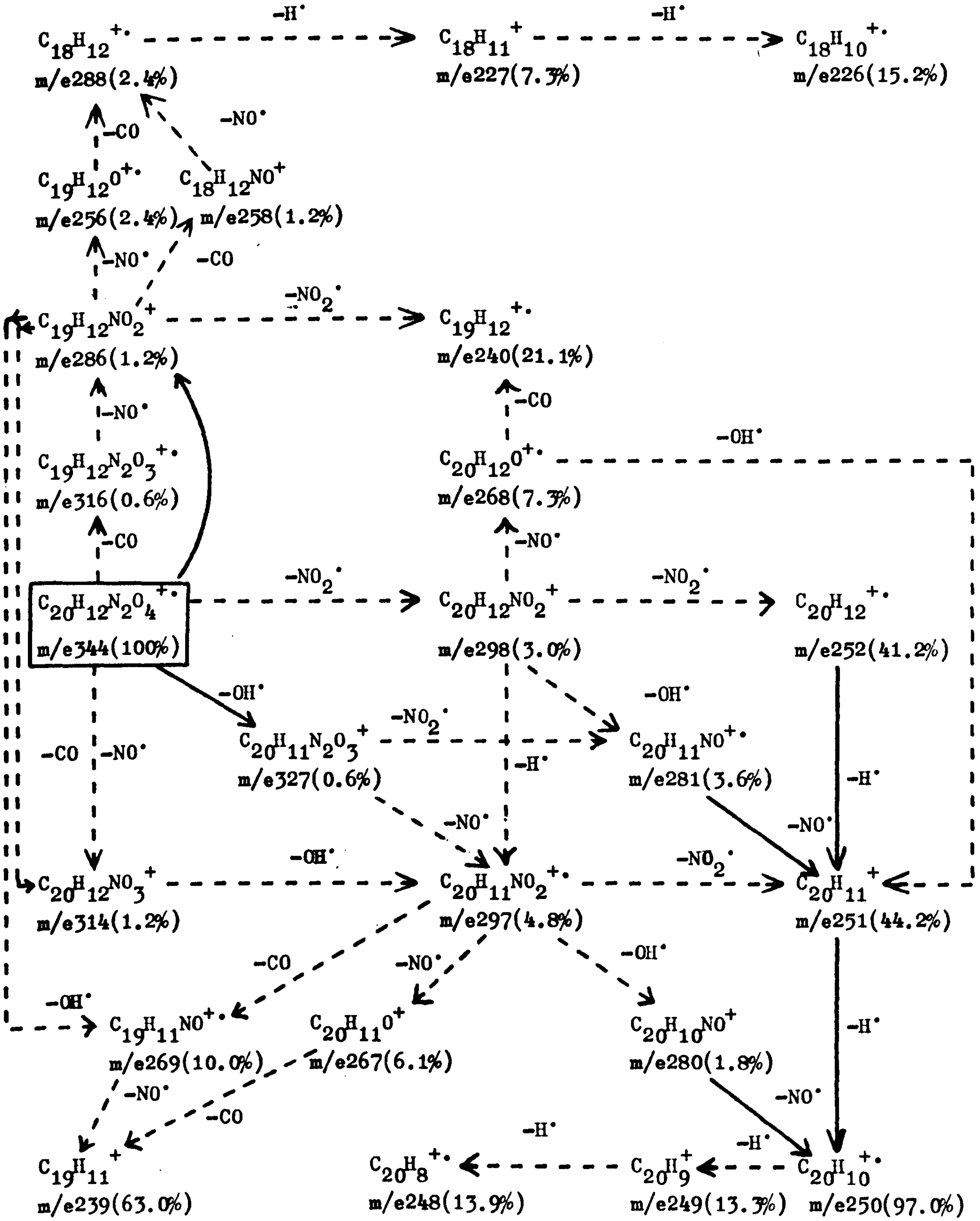
Fragmentation Pattern for the Mass Spectrum of 4,4'-Dinitro-1,1'-binaphthyl



Continuous lines indicate the presence of a metastable to support the proposed transition.

Scheme 2:V

Fragmentation Pattern for the Mass Spectrum of 5,5'-Dinitro-1,1'-binaphthyl



Continuous lines indicate the presence of a metastable to support the proposed transition.

Both 4,4'- and 5,5'-dinitro-1,1'-binaphthyl show very small peaks in their mass spectra due to ions at m/e 316 (1.8% and 0.6% respectively). These are the M - CO ions. Whilst this is to be expected if fragmentation of the molecular ion does occur via the analogue of species (2-2) (scheme 2:II) , in a fashion analagous to that operative for 1,3-dinitronaphthalene, the alternative possibility that the ion at m/e 316 simply fragments more readily than its analogue in the dinitronaphthalenes, must also be considered (see below). The spectra of both the dinitrobinaphthyls differ significantly however, from that of 1,3-dinitronaphthalene, in that the ions corresponding to M - OH occur only with very low probability. (Metastables are evident for each isomer, to substantiate the loss of a hydroxyl radical, from the molecular ion, in a single step.) As the dinitrobinaphthyls can presumably fragment in each of the naphthalenic systems by similar routes, losses of 2OH$^{\bullet}$ and 2HONO should also be considered. The intensity of some relevant ions are summarised in table 2-2.

Table 2-2

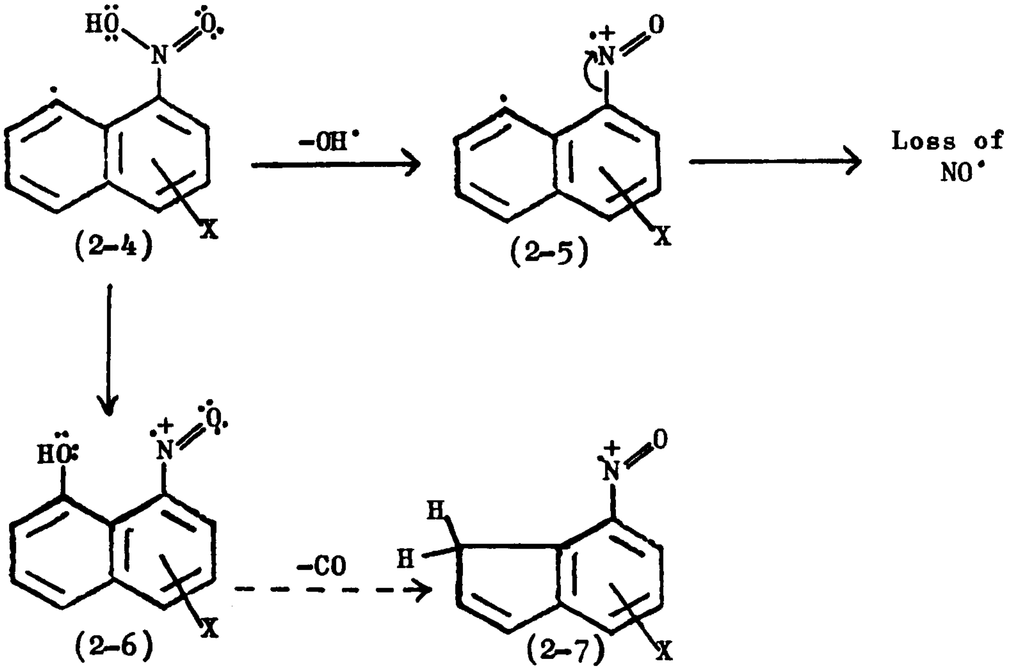
Data from the Mass Spectra of the Dinitrobinaphthyls

	Isomer		
	4,4'-	5,5'-	
	Relative Abundance		Possible Assignment
m/e	%	%	
327	1.8	0.6	M - OH
310	5.5	0.6	M - 2 OH
297	18.2	4.8	M - HONO
280	6.4	1.8	M - HONO - $\dot{O}$H
250	57.3	97.0	M - 2HONO

Although not obviously indicative of fragmentation via an analogue of (2-2) (scheme 2:II), these figures do not preclude such a possibility. Thus it may simply be that the intermediate ions at m/e 327, 310, 297 and 280 are relatively unstable and consequently decay rapidly - presumably to the ion at m/e 250. If this is so the change in stability between the naphthalene and binaphthyl derivatives might be explained in terms of the electron density distributions within the ions (2-4) and (2-5).[109] Thus in changing from

$X = NO_2$ to $X = NO_2C_{10}H_6$ the electron density at the 1-position should increase for both the ions (2-4) and (2-5). As expulsion of NO from the species (2-5) clearly involves loss of the C-N bonding electrons with the neutral molecule, this step should be facilitated by the increase of electron density at the 1-position. It is thus possible that the expulsion of NO from (2-5) occurs much more readily in the dinitrobinaphthyls than the dinitronaphthalenes and in consequence the interim ions occur with much lower probability.

A similar argument to the above may also be applied to the M - 28 ion in each of the dinitrobinaphthyl spectra. Thus the very low intensity of this ion need not preclude significant loss of CO from the respective molecular ions as the M - 28 species may simply be unstable and therefore barely observed. Indeed if the species (2-4), $X = NO_2C_{10}H_6$ does lose CO via (2-6) to (2-7) according to Beynon's mechanism, the enhanced electron density at position 1 in (2-7) due to the presence of a nitronaphthyl moiety (as opposed to $X = NO_2$), should facilitate loss of NO from this species. It appears



in fact that this step is sufficiently favourable for the loss of CO and NO to occur simultaneously, thus a metastable is observed in both spectra for the transition:-

$$C_{20}H_{12}N_2O_4^{+\cdot} \longrightarrow C_{19}H_{12}NO_2^{+} \quad + \quad CNO_2^{\cdot} \qquad M^* = 237.8$$

(Intense)

(Though possibly this metastable is more suggestive of fragmentation via a cyclic '(2-3) type' transition state (scheme 2:III) than it is of a '(2-2) type' species (scheme 2:II) - see below.) This fragmentation taken in conjunction with the losses of ($OH^{\cdot}$ + $NO^{\cdot}$) - via scheme 2:II - in the 'other half' of the binaphthyl system, presumably accounts for the considerable intensity of the ions at m/e 239 (M - HONO - CO - NO) in the spectra of both dinitrobinaphthyls. (The loss of CO and NO may of course occur via the isomerisation of a nitro group to the nitrite,[43] but the intensity of both the metastable at 237.8 and the 'final' ion at m/e 239 seems rather greater than would be expected on the basis of this isomerisation alone.)

By analogy with the case of 1,3-dinitronaphthalene the dinitrobinaphthyls might also be expected to lose CO via the mechanism in scheme 2:III. The effect of substituting $C_{10}H_6NO_2$ in this scheme is analagous to that in the case above (scheme 2:II). Thus electron density should increase at the carbon attached to nitrogen and consequently loss of NO should be facilitated relative to the case of the dinitronaphthalene - in consequence an interim M - CO ion of low intensity would be expected but the 'final' ions should be intense.

In view of the above discussion it seems reasonably likely that fragmentation of the dinitrobinaphthyls could occur, to an appreciable extent by mechanisms similar to those proposed for the nitro and dinitronaphthalenes. Unfortunately however as neither of the known dinitrobinaphthyls produce M - 28 ions of significant intensity, the potential loss of CO from the molecular ion of an unidentified nitrobinaphthyl, does not present a practicable means for detecting the presence of a single peri substituted nitro group.

Finally it is pertinent to note that there is at least one other route by which a stable (M - 2HONO) ion may be formed in the binaphthyl series; thus the molecular ion may simply expel two nitro radicals, followed by two hydrogen radicals. In the present case if two such losses of $H^{\cdot}$ occurred, say from the 8 positions, a ring closed perylium type structure might be formed. Whilst such an ion could well contribute to the considerable intensity of the ion at m/e 250, it could not readily account for ions such as that at m/e 281 (M - NO - OH) etc. Indeed the spectra of both 4,4'- and 5,5'-dinitro-1,1'-binaphthyls show a broad and intense metastable centred at m/e 249.5 which it is difficult to assign to any logical fragmentation observed within the spectrum. One possible explanation of this peak is that both the transitions:-

$$C_{20}H_{12} \longrightarrow C_{20}H_{11} \quad + \quad H^{\cdot} \qquad M^{*} = 250.0$$

and

$$C_{20}H_{11} \longrightarrow C_{20}H_{10} \quad + \quad H^{\cdot} \qquad M^{*} = 249.0$$

are accompanied by intense metastable peaks which, because of their close proximity, overlap to produce a single 'pseudo metastable' midway between the two real values. Unfortunately the spectrum is not sufficiently clear to be unambiguous.

ii) The Mass Spectrum of 'C-1' itself.

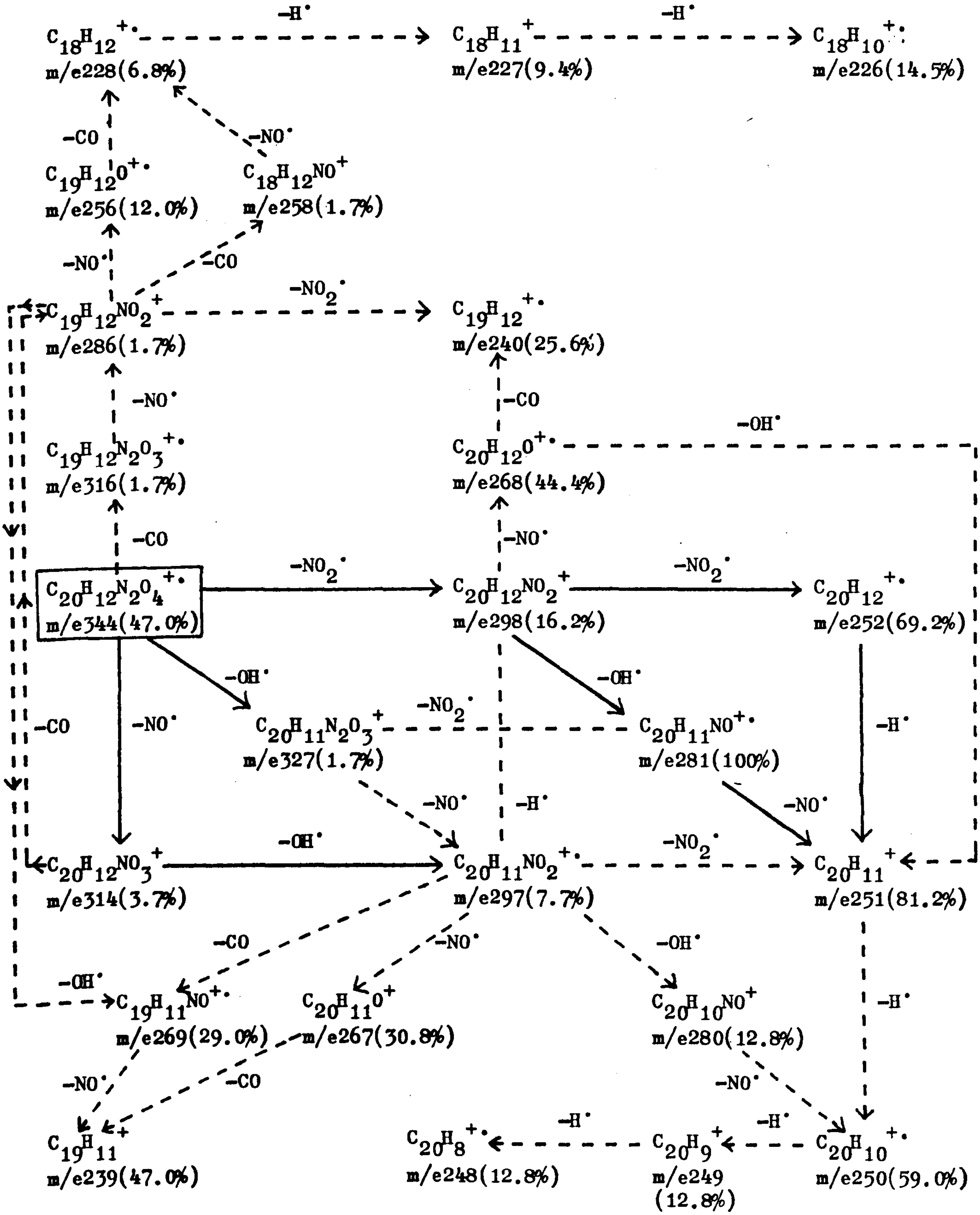
The mass spectrum of 'C-1' is given in the appendix as both a bar diagram and a list of relative intensities. The most intense ions in the spectrum are summarised in the scheme 2:VI. It should be noted that a number of ions of only low intensity, such as M - O, M - NO etc, have been omitted from the scheme for the sake of clarity - although they are included in the list of relative intensities. (Such ions are similarly omitted from all of the fragmentation schemes presented in this thesis.) Whilst these ions have relatively low abundance they are nevertheless of considerable importance because they are typical[76,77] of nitroaromatic compounds; as such however they warrent no further discussion.

In general the spectrum of 'C-1' follows the same overall pattern as those of the 4,4'- and 5,5'- dinitro-1,1'-binaphthyls, but with some interesting variations of intensity. The most striking feature is the reduced intensity of the molecular ion and occurrence of the base peak at m/e 281. Such differences are consistent with the proposed structure and may be explained by the close proximity of the 8 nitro group and adjacent naphthalenic ring system. Thus under the highly energetic conditions of mass spectrometry a rearrangment of the type (2-8)$\rightarrow$(2-9) seems quite likely. Such an isomerisation is rather similar to that proposed both for o-nitrobiphenyl[112] and picryl naphthalene (see chapter 3) to explain the presence of an M - OH ion in their respective spectra. Whilst the spectrum of 'C-1' has a metastable at 310.8 to confirm that a hydroxyl radical is lost in a single step from the molecular ion, such a loss may occur via at least two mechanisms : ie via (2-8)$\rightarrow$(2-9) or through the Beynon type mechanism (scheme 2:II). The former case might reasonably be expected to lead to a ring closed structure (2-11). This species

Scheme 2:VI

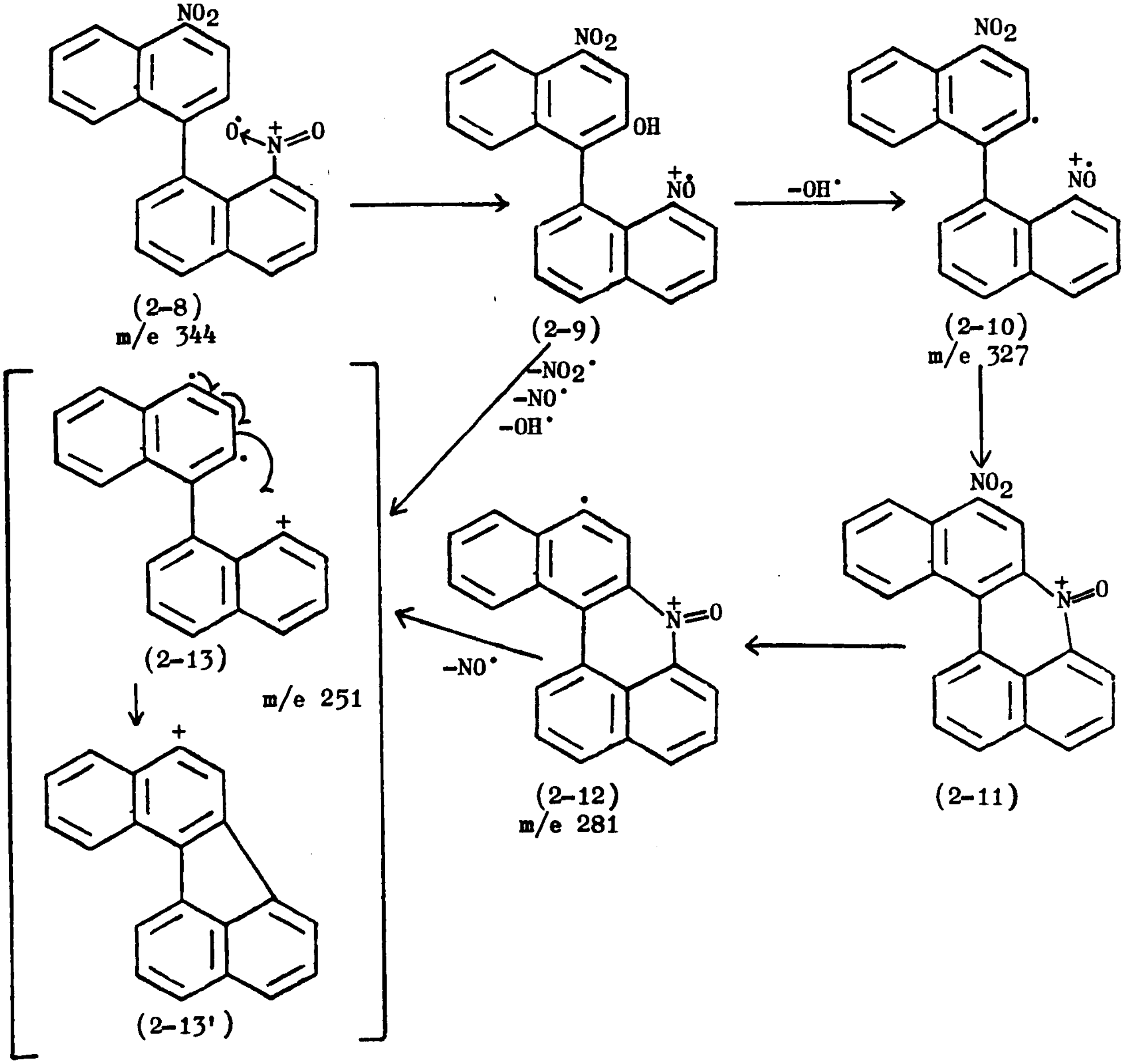
Fragmentation Pattern for the Mass Spectrum of Compound 'C-1'

(4,8'-Dinitro-1,1'-binaphthyl)



Continuous lines indicate the presence of a metastable to support the proposed transition.

Scheme VII



might then lose an NO_2 radical, so generating an ion (2-12) at m/e 281; this transition is supported by the presence of a metastable at m/e 265.0. The ion (2-12) should be relatively stable as further fragmentation would involve the breaking of two bonds, hence it is not unreasonable that it should become the base peak of the spectrum. Loss of the 4- nitro group may of course precede the rearrangement (2-8) → (2-9); indeed there are metastables for the transitions:-

$$\underset{m/e344}{C_{20}H_{12}N_2O_4} \longrightarrow \underset{m/e298}{C_{20}H_{12}NO_2} + NO_2^{\bullet} \qquad M^* = 258.2$$

$$\underset{m/e298}{C_{20}H_{12}NO_2} \longrightarrow \underset{m/e281}{C_{20}H_{11}NO} + OH^{\bullet} \qquad M^* = 265.0$$

An alternative fragmentation is however possible for the species (2-9) in that it may lose $NO_2^{\cdot}$ then $NO^{\cdot}$ (or vica versa). Just such a fragmentation is suggested by the rather greater intensity, in 'C-1', of the ion at m/e 268 ($M - NO_2 - NO$) (44.4%) as compared with either 4,4'- or 5,5'- dinitro-1,1'-binaphthyl. (18.3% and 7.3% respectively). Loss of an hydroxyl radical from the ion at m/e 268 would produce the species (2-13) at m/e 251. (Alternatively loss of CO from the 2 hydroxy substituent would produce the ion at m/e 240 - cf reference 112.) A metastable at m/e 224.2 shows that this ion (m/e 251) may also be produced from that at m/e 281 by loss of neutral NO (2-12) →(2-13). The considerable intensity of the ion (2-13) is consistent with a relatively stable structure possibly of the type (2-13').

If the proposed structure of 4,8'-dinitro-1,1'-binaphthyl is correct the molecular ion might also be expected to lose HONO by a mechanism similar to that proposed for the 4,4'- and 5,5'- dinitro-1,1'-binaphthyls. Such a loss would occur in addition to the fragmentation discussed above and the final 'distinctive' ion resulting would be that at m/e 250 (ie M - 2HONO). The considerable intensity of this ion (59.0%) would tend to support the occurence of such a fragmentation, although the ion may conceivably arise via loss of two nitro radicals and two hydrogen radicals. (cf That discussed above for the isomeric dinitrobinaphthyls.) In the present case such a loss seems considerably less likely since the presence of an 8 nitro group renders it necessary to expel only one hydrogen radical from the ($M - 2NO_2$) ion (at m/e252) in order to obtain a ring closed perylium ion. This latter process may contribute significantly to the intensity of the ion at m/e 251.

In view of the above, one puzzling feature of the spectrum of 'C-1' is a broad metastable peak at m/e 249.5, similar to that observed in the spectra of 4,4'- and 5,5'- dinitro-1,1'-binaphthyl. As explained earlier such a peak might be attributed to the overlap of two metastables at m/e 250.0 and 249.0 respectively. However, in the present case such an explanation would seem to be at variance with the anticipated expulsion of a single hydrogen radical. It may therefore be that the earlier explanation in terms of ring closure, represents an over simplification of the fragmentation.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of 'C-1' in DMSO is given in the appendix. It comprises two complex multiplets at τ1.47-1.90 (4H) and τ1.92-2.72

(8H). Whilst the signals fall in the normal region associated with aromatic protons the spectrum is too complex to be interpreted by inspection. As a full analysis is not possible the following discussion is intended merely to rationalise the spectrum with the proposed 4,8'-substitution.

The different chemical shifts associated with α and β protons have already been discussed with reference to 1,1'-binaphthyl; in view of these differences it would be expected that the protons H_5, H_4' and H_5' in 'C-1' would each resonate at lower field than the β protons, the proton H_8 being once again shielded by the adjacent naphthyl moiety. In fact the situation is modified by the presence of nitro groups, as a β proton sited ortho to a nitro group is normally sufficiently deshielded to make it coincide with the lower-field 'α-multiplet'.[72] Thus the PMR spectrum of 'C-1' might have been expected to yield two multiplets in the ratio (low/high field) 5:7 - the low-field signals corresponding to H_3, H_5, H_4', H_5' and H_7'. The most likely reason that this is not observed is the severe steric hindrance associated with the 8 nitro group. Such hindrance must inevitably reduce the tendency of this substituent to deshield H_7' - because it results both in a loss of resonance and a reduction in the effect of the anisotropic magnetic field which is associated with the nitro group.[78] Presumably in this particular case the deshielding of H_7' is insufficient to remove it from the high-field multiplet. The protons H_3, H_5, H_4' and H_5' are then assignable to the multiplet at τ1.47-1.90 the remainder producing the multiplet at τ1.92-2.72.

The chemical shifts of the two multiplets in 'C-1' are quite close to those observed in 4,4'-dinitro-1,1'-binaphthyl (also in DMSO); thus the protons $H_{2/2'}$ and $H_{5/5'}$ in the 4,4'- isomer resonate at τ1.51, whilst the remaining protons form a multiplet at τ2.01-2.72. This correlation of chemical shifts is to be expected in view of the similarity of structure between these two compounds.

Further Nitration of 4,8'-Dinitro-1,1'-binaphthyl(?) Compound 'C-1'

Whilst all the available spectroscopic data for 'C-1' has been found consistent with this compound being 4,8'-dinitro-1,1'-binaphthyl, it is by no means conclusive. In view of this uncertainty an attempt has been made to obtain additional data from the compound by further nitrating it. Unfortunately as the compound 'C-1' was not isolated in very high yield, it proved necessary to carry out the subsequent nitrations on an extremely small scale. This has lead to difficulties in purifying the products and in consequence the results of the nitrations are not very clear cut.

The product distribution obtained from the nitration of 1,1'-binaphthyl in nitric acid and acetic anhydride, soon established that next to the 4 positions the most reactive sites in the 1,1'-binaphthyl nucleus were the 5 positions (see on). In consequence when only two dinitrobinaphthyl were isolated from the action of acetic anhydride and nitric acid on binaphthyl, and one of these was found to be 4,4'-dinitro-1,1'-binaphthyl, it was initially thought quite likely that 'C-1' would turn out to be 4,5'-dinitro-1,1'-binaphthyl - it was known to be dissimilar to 5,5'-dinitro-1,1'-binaphthyl. The nitration of 'C-1' was therefore undertaken in order to confirm this supposition ie by converting it to 4,4',5,5'-tetranitro-1,1'-binaphthyl (this compound is discussed later). The nitration was duly carried out under conditions suitable for the preparation of a tetranitrobinaphthyl (nitric acid, in excess acetic anhydride with sulphuric acid catalyst) and the resulting product examined by TLC. This product produced (predominantly) two spots on a thin layer chromatogram, both of which had Rf's rather greater than that of the 4,4',5,5'-teta but rather less than that of the 4,4',5-trinitro- 1,1'-binaphthyl. It was therefore concluded that 'C-1' was unlikely to be 4,5'-dinitro-1,1'-binaphthyl. Ideally at this stage the two nitration products of 'C-1' should have been separated and examined in order to facilitate identification of the dinitrobinaphthyl. It was felt however that the isolation of these products would have been of little value as they were almost certainly tri- or unsymmetrical tetranitro- derivatives of 1,1'-binaphthyl and as such were unlikely to be identifiable merely on the basis of their spectra. (At this time no compounds with these Rf's had been identified - so there was no chance of comparing spectra with other materials). Thus the only means of identification was likely to involve stepwise nitration of the different products to higher nitrobinaphthyls which possibly could be identified via their spectra. Regrettably this approach was impossible due to the very small quantity of 'C-1' used for the original reaction, thus there would have been insufficient of the two individual products - after separation - to utilise for further nitration.

Rather than abandon the reaction at this stage (particularly as there was no more of the compound 'C-1' available), it was considered worthwhile to further nitrate the crude mixture in the hope that the two products would converge to a single polynitrobinaphthyl - which would possibly be simpler to identify. The original crude nitration product of 'C-1' was thus further nitrated without purification, in mixed acid. Only one product was finally isolated from the reaction mixture, but there was insufficient of this material for it to be satisfactorily purified. Because of this, only an infra red spectrum of rather poor quality could be obtained from the product and in consequence it has not been positively identified. Nevertheless the spectrum does show some similarity to that of a compound believed to be 2,4,4',5,5',7,8'-heptanitro-1,1'-binaphthyl (compound 'R'), whilst on the other hand it could not reasonably be assigned even to an impure sample of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl (compound 'Q'). Since the nitration of binaphthyl in mixed acid produces predominantly 4,5,7- substitution (see on), the isolation above of a major product which was not 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl, tends to suggest the presence in 'C-1' of a nitro substituent at some site other than the 4,5 or 7 positions. This appears consistent therefore with the proposed structure for 'C-1'. Indeed as 4,8'-dinitro-1,1'-binaphthyl should be a precusor to 2,4,4',5,5',7,8'-heptanitro-1,1'-binaphthyl ('R'), the tentative identification of the nitration product as this compound further supports the structural assignment of compound 'C-1'.

A positive identification of the structure in 'C-1' will ultimately have to be achieved by synthesising the material from appropriate nitronaphthalene derivatives of known structure, via a suitable coupling reaction (eg the Ullmann). This work has not been carried out during the present project however, due to a shortage of time.

2.2.1.3. 4,4',8-Trinitro-1,1'-binaphthyl (Probable Structure) Designated Compound 'C-2'

This material was isolated in extremely small quantities (about 0.2%) from the nitration of 1,1'-binaphthyl in acetic anhydride and nitric acid. It was also prepared in small yield (about 1%), by the nitration of 4,4'-dinitro-1,1'-binaphthyl in the same medium. The compound has not been prepared by any other methods.

The mass spectrum of this compound shows an intense ion at m/e 389 and a fragmentation pattern consistent with that of a trinitrobinaphthyl. The infra-red spectrum shows bands corresponding to nitro stretching frequencies but indicates the presence of no other functional groups. The compound is therefore thought to be a trinitrobinaphthyl. As this material can apparently be prepared by nitration of 4,4'-dinitro-1,1'-binaphthyl, it seems likely that it contains 4,4'- substitution. Whilst this assumption is not indisputable (due to the low yield obtained from the nitration of 4,4'-dinitro-1,1'-binaphthyl), it certainly appears consistent with the known reactivities of the 4 and 4' positions in 1,1'-binaphthyl. However whilst the spectra of the compound are consistent with 4,4'- substitution there are no sufficiently distinctive features to confirm unambiguously the presence of such a structure. Indeed it is difficult even to establish the position of the third nitro group in 'C-2' from the spectroscopic data alone.

Since a nitro group is powerfully deactivating towards electrophilic attack, the 3 nitro substituents in 'C-2' are each likely to occupy different 'rings' within the binaphthyl system. Given that two of the substituents occupy the 4 and 4' positions the third must be 5,6,7 or 8 substituted. Of these the 5 position can be excluded, since an authentic sample of 4,4',5-trinitro-1,1'-binaphthyl has been prepared and shown to be dissimilar to the compound 'C-2' (see below). If however the substituent is in the 8 position the spectra should provide some indication of steric interaction as in the case of 'C-1'. On the other hand to distinguish between a 6 and 7 nitro substituent is likely to be rather more difficult. The spectra of 'C-1' are considered in detail below. On balance it is thought most likely that the third nitro group occupies an 8 position, but such an assignment is by no means certain. Once again the only satisfactory way to unambiguously establish the structure of this compound, will be to prepare it from the appropriate nitronaphthalene derivatives of known structure, via a suitable coupling reaction. This work has not been carried out due to a shortage of time.

The Infra-red Spectrum

The infra-red spectrum of 'C-2' (see appendix) shows a weak band at 3100cm^{-1} corresponding to aromatic C-H stretching vibrations. There are also two very strong bands corresponding to nitro (N-O) stretching vibrations. Although less striking than in the case of 'C-1' both of these nitro bands appear to be split; thus in the case of the asymmetric band there is a shoulder on the side of the main peak, whilst the symmetric stretching frequency is just resolved into two maxima.. The bands occur at 1530/1515cm^{-1} and 1350/1330cm^{-1}. These frequencies appear consistent with the proposed structure (4,4',8-substitution). Thus two bands (at 1515/1330cm^{-1}) occur at frequencies close to those observed in 4,4'-dinitro-1,1'-binaphthyl (1520/1330cm^{-1}) whilst the others (1530/1350cm^{-1}) are at higher frequencies - as would be expected due to twisting of the 8 nitro group out of the aromatic plane. (It is assumed in comparing these frequencies with those observed in the dinitro derivative that the third nitro group in 'C-2' will have a minimal effect upon the frequencies of the other two nitro groups.) A suprising feature of the spectrum however, is that the shoulder occurs in each case on the low frequency side of the band, that is the high frequency band is the stronger of the two. The reverse might have been expected with 4,4',8- substitution as there should be two planar nitro groups but only one twisted out of the aromatic plane. The precise reason for this is unclear, although the intensity of nitro stretching bands tends to be unpredictable.[64b] Possibly the influence of the 8 nitro group upon the stretching frequencies of the 4 nitro substituent is not negligible. Thus if it caused an increase of stretching frequency for the 'planar' 4- nitro group (in the disubstituted naphthalene nucleus) the band due to this substituent might then tend to overlap the higher frequency band resulting from the non coplanar nitro group. The exact magnitude of any such interaction between nitro groups in different rings of the naphthyl moiety is however rather uncertain.

The low frequency region of the IR spectrum is not very helpful, thus there are a large number of bands present and it is difficult to assign even those associated with the aromatic nitro vibrations. There are in fact bands which could be assigned to C-H out of plane bending vibrations for any number of adjacent H's from five to one.

The Ultra Violet Spectrum

The ultra violet spectrum of 'C-2' in methanol (see appendix) shows two resolved maxima at λ214nm, ϵ8210m^{2}mole^{-1} (aromatic $\pi \rightarrow \pi^{*}$) and λ350nm, ϵ 1320m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^{*}$ or $\pi \rightarrow \pi^{*}$ [107,108]). Both of these bands show a slight bathochromic shift relative to the nitronaphthalenes[74] (and 1,5-dinitronaphthalene[113]), once again reflecting the increased conjugation of the binaphthyl system. In addition to the above maxima the spectrum of 'C-2' has a shoulder at λ250nm, ϵ2940m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$). A comparison of this spectrum with that of 4,4'-dinitro-1,1'-binaphthyl shows that the shoulder has moved to shorter wavelength and increased in intensity as would be expected[87] due to the introduction of a third nitro group. As the shoulder is fairly broad and flat it could well represent the envelope of two bands arising from 'planar' and 'non planar' nitro groups (cf 'C-1'). (In the present case however, as there are two 'planar' nitro groups and only one 'non planar' the longer wavelength band should have the greater intensity. The shoulder thus forms an apex at 250nm in contrast to the spectrum of 'C-1', where the two bands (of approximately equal intensity) combine to form practically a straight line. Any conclusions as to the presence or otherwise of an 8 nitro group based on this spectrum must however be highly tentative, as the spectra of other trinitrobinaphthyls in which all the nitro groups are coplanar are not available for a detailed comparison. The only compounds which are available (see below) contain 'non coplanar' nitro groups. The position and intensity of the bands in all the trinitrobinaphthyls isolated, is however very similar, although the main shoulder in 'C-2' is at slightly longer wavelength than in the other compounds. As outlined above this observation is consistent with the presence of two 'planar' nitro groups in 'C-2' which are apparently lacking in the other compounds (see below).

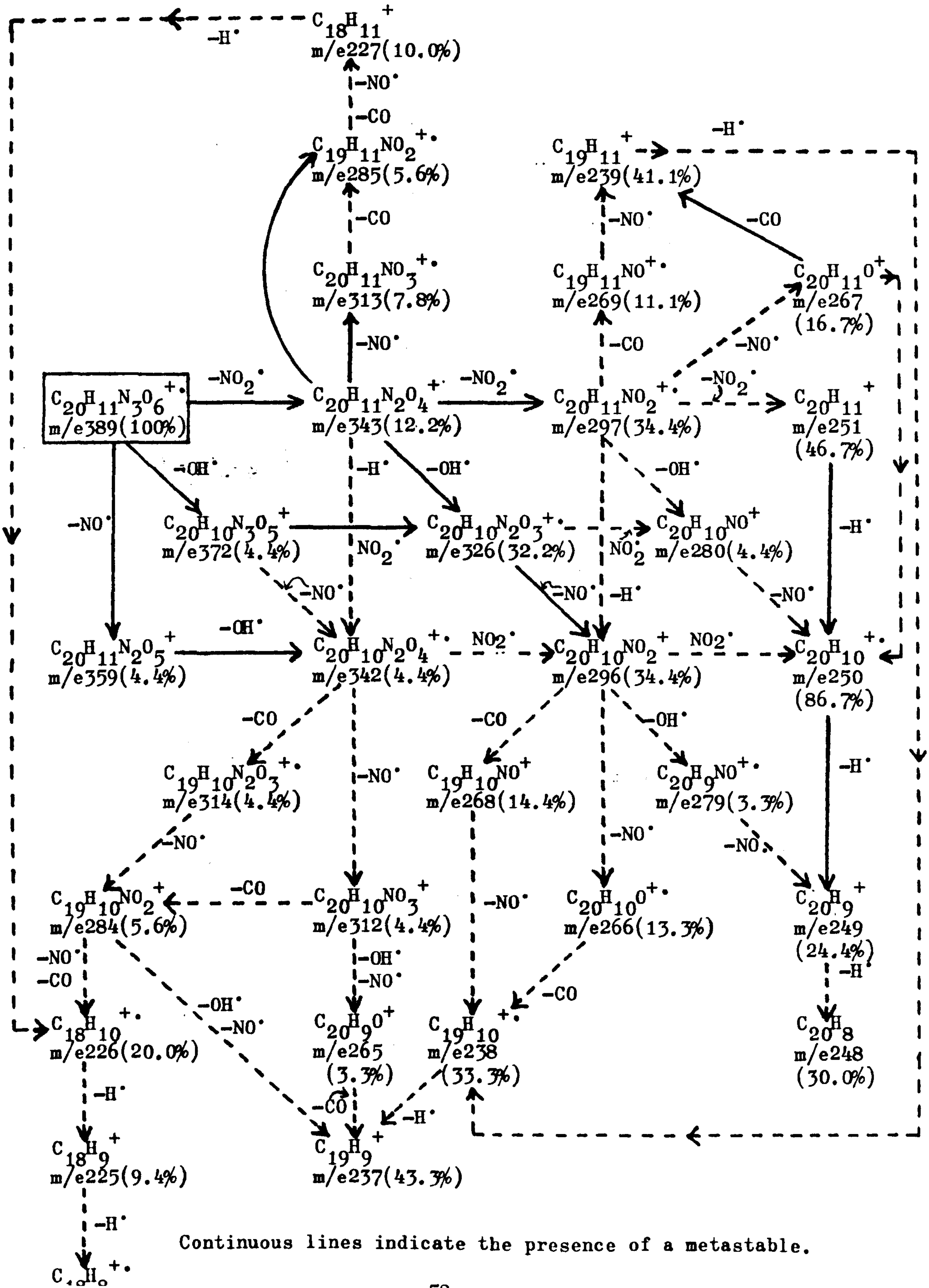
The Mass Spectrum

The mass spectrum of 'C-2' (see appendix) shows a molecular ion at m/e 389 and a breakdown pattern broadly typical of a nitro aromatic compound - see scheme 2:VIII. The loss of three intact nitro groups is thus observed in addition to peaks of low intensity due to typical[76,77] fragmentation of the nitro groups. (eg M - O, M - NO etc.) In addition to the above ions there are many others due to expulsion of NO$^{\cdot}$, CO and OH$^{\cdot}$ in various combinations; these presumably occur through mechanisms similar to those discussed for the dinitrobinaphthyls (but see below).

If the compound 'C-2' is in fact 4,4',8-trinitro-1,1'-binaphthyl, certain similarities would be expected between its mass spectrum and that of 'C-1' - at least in respect of the fragmentations attributable to the 8- nitro group. Assuming that the explanation offered for 'C-1' is correct, regarding the intense ($M - NO_2 - OH$) ion,

Scheme 2:VIII

Fragmentation Pattern for the Mass Spectrum of Compound 'C-2' (4,4',8-Trinitro-1,1'-binaphthyl)



Continuous lines indicate the presence of a metastable.

it follows that a similar ring closed structure could occur for the trinitro derivative and hence a particularly intense $(M - NO_2 - OH)$ ion (or possibly $(M - 2NO_2 - OH)$ ion) might be expected. The spectrum of 'C-2' in fact shows an $(M - NO_2 - OH)$ ion (at m/e 326) which is of much lower intensity than that of its analogue in 'C-1'(m/e281) - 32.2%:100% respectively. It is however of considerably greater intensity than the equivalent ion in either 4,4'- or 5,5'- dinitro-1,1'-binaphthyl. It is clear from the spectrum of 'C-2' that this ion at m/e 326 is formed in a two stage process (just as in 'C-1'), that is, by initial loss of an OH radical followed by loss of a nitro radical (or vica versa); this is shown by the presence of the following metastable peaks:-

$$\underset{m/e\ 389}{C_{20}H_{11}N_3O_6} \longrightarrow \underset{m/e\ 372}{C_{20}H_{10}N_3O_5} + OH^{\cdot} \qquad M^* = 355.7$$

$$\underset{m/e\ 372}{C_{20}H_{10}N_3O_5} \longrightarrow \underset{m/e\ 326}{C_{20}H_{10}N_2O_3} + NO_2^{\cdot} \qquad M^* = 285.7$$

or

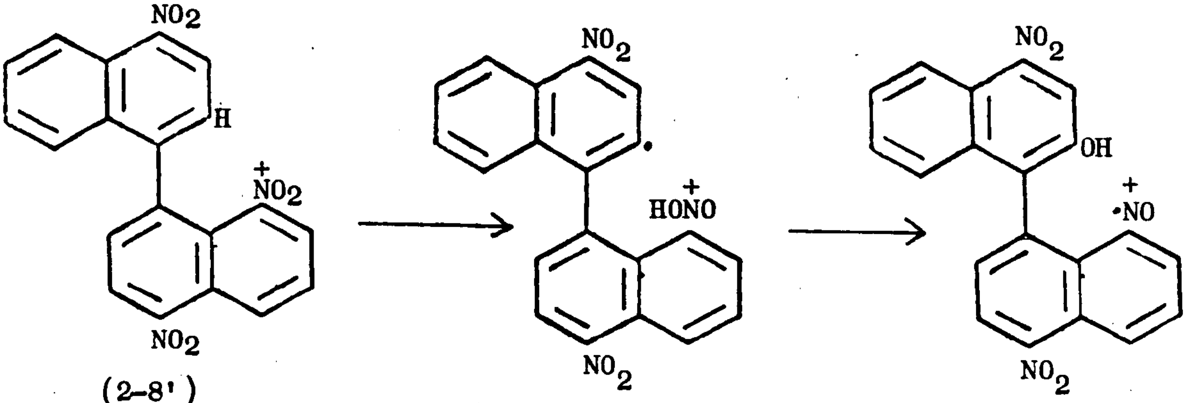
$$\underset{m/e\ 389}{C_{20}H_{11}N_3O_6} \longrightarrow \underset{m/e\ 343}{C_{20}H_{11}N_2O_4} + NO_2^{\cdot} \qquad M^* = 302.4$$

$$C_{20}H_{11}N_2O_4\ {}_{m/e\ 343} \longrightarrow C_{20}H_{10}N_2O_3\ {}_{m/e\ 326} + OH^{\cdot} \qquad M^* = 309.8$$

The variation of intensity observed between 'C-1' and 'C-2' for the $(M - NO_2 - OH)$ ion, must in part be due to the presence of the additional nitro group in the latter, which inevitably creates new fragmentation pathways - some of which must be followed at the expense of the $(M - NO_2 - OH)$ ion. Thus for example, the ion at m/e 343 instead of losing an hydroxyl radical to give the $(M - NO_2 - OH)$ ion, might expel a nitro radical to produce the ion at m/e 297 (34.4%). However if this loss represented a simple expulsion of the 'additional' 4- substituted nitro group, one might argue that the 8- nitro group could still rearrange [(2-8)→(2-9) (scheme VII, pg 50)] leading to loss of OH• and production of a relatively stable ring closed ion at m/e 280 $(M - 2NO_2 - OH)$ - there seems however to be little evidence for this in view of the low intensity of the ion at m/e 280 (4.4%).

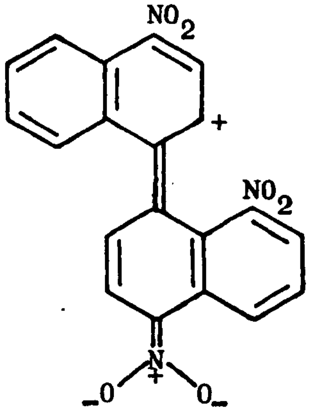
The reduced intensity of the $(M - NO_2 - OH)$ ion in 'C-2', compared with 'C-1', might alternatively be explained by the ability of the former ion to expel a nitro radical - a potentially facile loss which is clearly impossible in the case of the 'C-1' ion. Such a loss should yield an ion at m/e 280, but as has just been pointed out this ion occurs with only low intensity, which is hardly consistent with the stable ring closed structure which it is expected to have.

Evidently if the compound is 4,4',8- substituted, the influence of the 'additional NO_2 group' must extend beyond the simple effects considered above (though doubtless these do lead to reduced intensity of the $(M - NO_2 - OH)$ ion). One point which is worth considering is that of electron withdrawal by the 'additional' nitro group; this effect may well be significant as the rearrangement proposed for 'C-2', that is (2-8')→(2-9'), (as also for 'C-1' ie (2-8)→(2-9)) is rather similar to that proposed by Beynon et al for the nitro/dinitronaphthalenes; thus it could well procede by a similar mechanism:-



(2-8') (2-8'') (2-9')

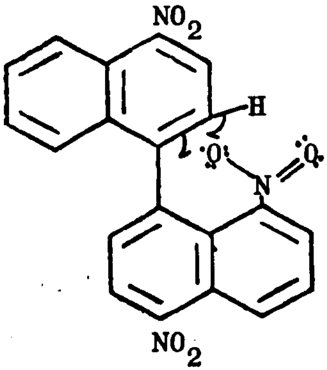
Clearly an electron deficiency at the 2 position should hinder the rearrangment of (2-8')→(2-8'') just as in Beynon's mechanism. Since the 'additional' nitro group in 'C-2' is in fact sited at the 4 position mesomeric electron withdrawal by this group from the 2' position should be possible - structure (2-14).



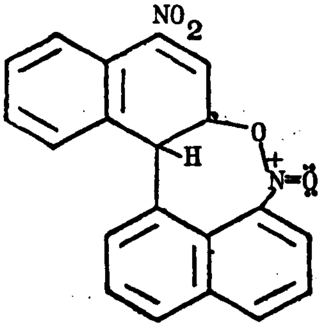
(2-14)

Doubtless such interaction is limited by the relative oscillation of the two ring systems but it could well reduce the tendency of the ion (2-8') to rearrange to (2-9') as compared with (2-8) rearranging to (2-9) for 'C-1'. Further as the 8 nitro group is the most sterically hindered, it might, in absence of a rearrangement, be lost preferentially as a nitro radical; this would of course preclude any subsequent rearrangement of the type (2-8')→(2-9'). If this were so it could explain the low intensity of the ion at m/e280 (above).

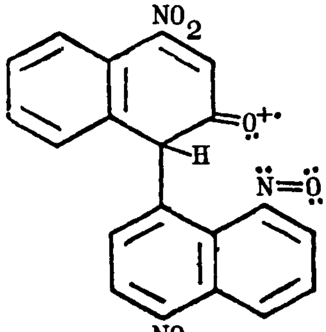
It is interesting to note that isomerisation of the 8 nitro group in this type of compound may be viewed in terms of two competing mechanisms similar in essence to the proposals of Brittain et al[110] for the dinitronaphthalenes. Thus the mechanism (2-8')→(2-9') is analagous to scheme 2:II (pg 40) in the nitro/dinitronaphthalenes, whilst an alternative rearrangement (2-15)→(2-17) is comparable with scheme 2:III (pg 40).



(2-15)



(2-16)



(2-17)

Whilst the former mechanism apparently predominates in 'C-1' (hence the intense ($M - NO_2 - OH$) ion) the lower intensity of the analagous ion in 'C-2' could reflect predominance of the alternative mechanism (2-15)→(2-17). The situation would thus appear comparable with the dinitronaphthalenes in that an electron deficiency at the 2 position could favour fragmentation via a cyclic structure. Participation of the latter mechanism could explain the fairly intense ions at m/e 267, 269 and 239 - if expulsion of CO and NO from a species such as (2-17) did not occur until after loss of the two pendant nitro groups.

Since 'C-2' is 4,4'- substituted it should be possible not only to lose OH and NO radicals via the mechanism (2-8')→(2-9') as outlined above, but also through Beynon's mechanism as discussed for the dinitronaphthalenes. The latter mechanism however cannot alone explain the intensity of the (M - NO_2 -OH) ion, as this intensity considerably exceeds that of the analagous ion in 4,4'-dinitro-1,1'-binaphthyl. (32.2%:6.4% respectively). In fact on the basis of Beynon's mechanism alone the opposite would be expected, as the third nitro group in 'C-2' should reduce the electron density at the 5 position (in one ring at least) and so also reduce the tendency to lose OH•(cf the dinitronaphthalenes). As this is clearly not the case it seems reasonable to propose an alternative rearrangement [(2-8')→(2-9')] which could operate in addition to Beynon's mechanism and so enhance the intensity of the (M - NO_2 - OH) ion. The presence of an 8 nitro group is of course fundamental to the operation of this mechanism.

It would be much more difficult to rationalise the spectrum of 'C-2' if the presence of an 8 nitro group were to be excluded,that is if the alternative structures of 4,4',6 or 4,4',7- trinitrobinaphthyl are considered. The problem is to account for the relatively intense ions (such as m/e 326) which involve loss of OH• (or HONO), as these are not normally expected to be very probable losses for nitro aromatic compounds. Thus as explained above, Beynon's mechanism alone cannot readily explain the intensity of such ions and would in fact predict them as being lower than those observed in 4,4'-dinitro-1,1'-binaphthyl - not higher. With 6 or 7 substitution the problem is that of finding an alternative mechanism whereby OH• (or HONO) can be lost, because neither of the sites is now orientated favourably, relative to a hydrogen atom, so as to promote the loss. Thus the sites are not located 'peri' to a hydrogen atom, neither are they sufficiently close to the second naphthyl moiety that interaction with it could be anticipated. It therefore seems most satisfactory to assume an 8 nitro group in the compound 'C-2', as it is then possible to explain all of the major ions in the spectrum (in terms of 4,4'8- substitution) and also to reconcile the spectrum with that of 'C-1' and the 4,4'-/5,5'- dinitrobinaphthyls. This assignment of structure however, cannot be regarded as conclusive and it would be desirable to have several more closely related model compounds in the 1,1'-binaphthyl series with which to compare the spectrum of 'C-2'.

The Proton Magnetic Resonance Spectrum

There was insufficient of the compound 'C-2' to obtain a satisfactory PMR spectrum.

2.2.1.4. 4,4',5-Trinitro-1,1'-binaphthyl Designated Compound 'D'

This compound was isolated in 24.8% yield from the nitration of 1,1'-binaphthyl in acetic anhydride and nitric acid. It was also prepared from the nitration of 4,4'-dinitro-1,1'-binaphthyl (8%). The material analyses correctly for a trinitrobinaphthyl and shows a molecular ion in its mass spectrum at m/e 389.0647 corresponding to $C_{20}H_{11}N_3O_6$ (calculated 389.0648). The infra red spectrum has bands consistent with nitro stretching frequencies and indicates no other functional groups. The compound is clearly therefore a trinitrobinaphthyl. The structure of this compound has been quite well established. The evidence relating to the assignment of structure is given below. Since the most useful spectroscopic evidence is derived from the mass spectrum this will be considered first.

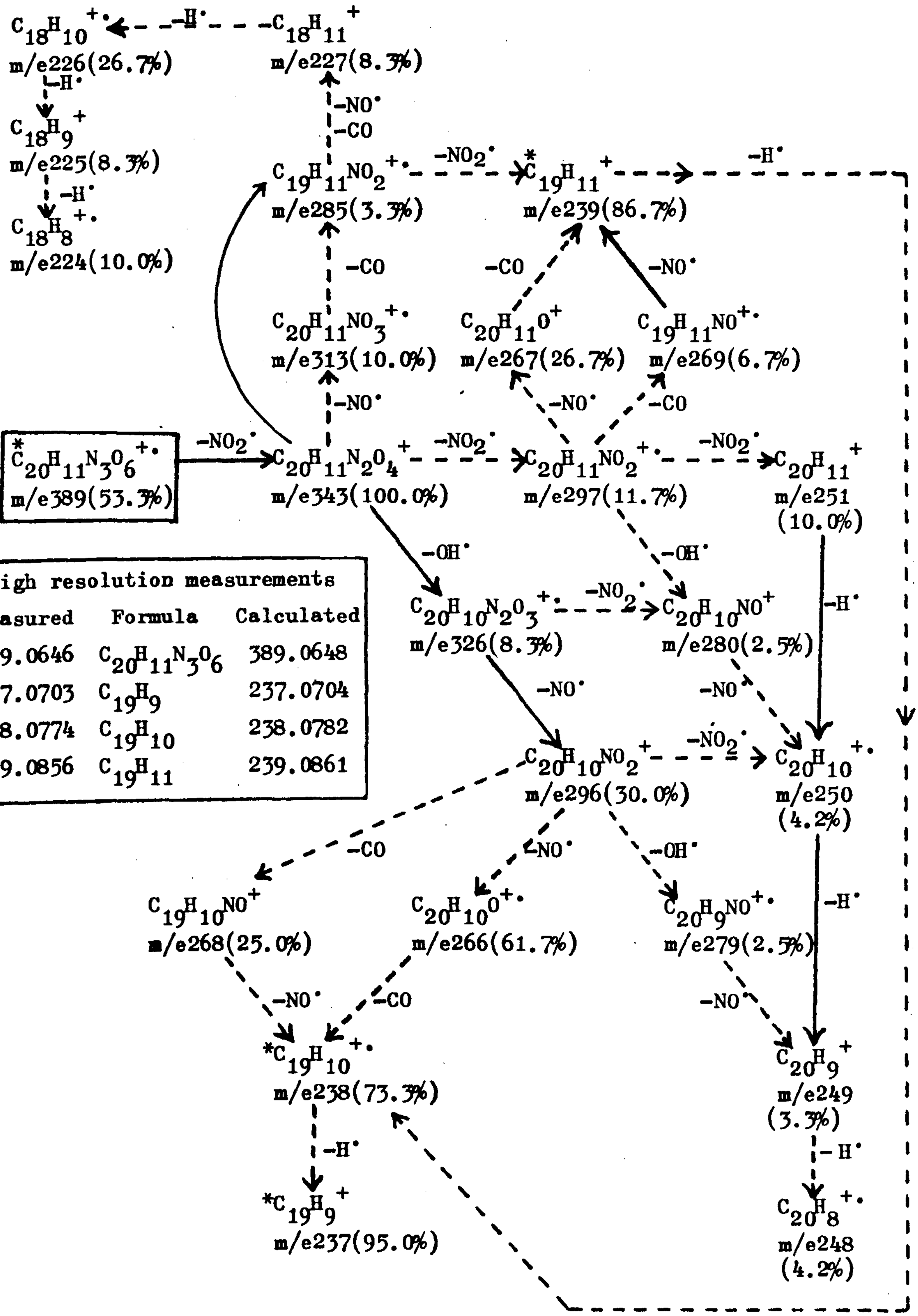
The Mass Spectrum

The major ions in the spectrum of 'D' are indicated in the scheme 2:IX. A full list of relative intensities and a bar diagram are given in the appendix. Whilst the spectrum shows many ions typical of a nitroaromatic compound ($M - NO_2$, $M - 2NO_2$, $M - 3NO_2$ and interim ions of low intensity corresponding to M -O, M - NO etc) there are also a number of unusual and noteworthy features which can be of considerable value in assigning a structure.

Probably the most significant points are the great intensity of the M - 46 ion and the somewhat reduced intensity of the molecular ion. These features can be rationalised by reference to other systems and are most probably indicative of the presence of adjacent peri substituted nitro groups in the compound 'D'. Compare for example the spectra of the dinitronaphthalenes where the 1,8- isomer is unique in possessing a very intense M - 46 ion - coupled with a molecular ion of somewhat reduced intensity.[110] (The spectrum of 1,8-dinitronaphthalene also differs from those of its isomers in having relatively intense ($M - NO_2 - NO$) and ($M - NO_2 - NO - CO$) ions and a relatively weak ($M - 2NO_2$) ion.) The distinctive features in the spectrum of 1,8-dinitronaphthalene are clearly associated with the presence of adjacent peri substituted nitro groups, thus it is apparently interaction between these groups that promotes fragmentation of the molecular ion and so accounts for its somewhat diminished intensity. (A further example of the "adjacent peri" effect has been reported in the 2,3-dimethylnaphthalene system; thus in 1,6,8-trinitro-2,3-dimethylnaphthalene

Scheme 2:IX

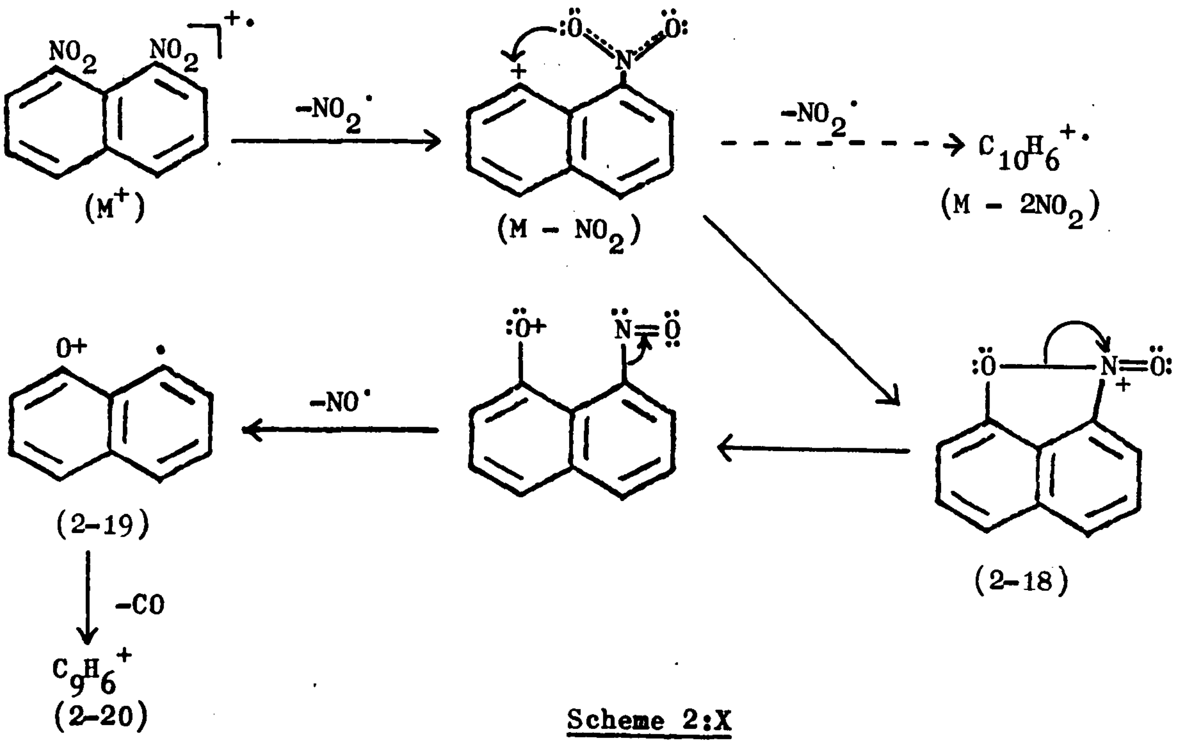
Fragmentation Pattern for the Mass Spectrum of 4,4',5-Trinitro-1,1'-binaphthyl (Compound 'D')



*High resolution measurements

Measured	Formula	Calculated
389.0646	$C_{20}H_{11}N_3O_6$	389.0648
237.0703	$C_{19}H_9$	237.0704
238.0774	$C_{19}H_{10}$	238.0782
239.0856	$C_{19}H_{11}$	239.0861

Continuous lines indicate the presence of a metastable to support the proposed transition the $(M - NO_2)$ ion represents the base peak of the spectrum whilst in 1,5,7-trinitro-2,3-dimethylnaphthalene the molecular ion is the base peak.[114]) Explanation of the intense M - 46 ion may be made either in terms of its easier formation from the molecular ion or by proposing a different fragmentation route for it in the 1,8- compound - as compared with the other isomers. It has been suggested[110] that the low intensity of the $(M - 2NO_2)$ peak in 1,8-dinitronaphthalene is significant in this respect, as metastables in the other isomers show this ion to be derived directly from the $(M - NO_2)$ ion by loss of a nitro radical. Thus it appears that this loss is hindered in the case of 1,8-dinitronaphthalene and that an alternative fragmentation route must operate. Brittain, Paisley, Stickely and Wells[110] have rationalised the situation by proposing that fragmentation of 1,8-dinitronaphthalene takes place predominantly via the scheme 2:X. Thus after facile



Scheme 2:X

loss of a nitro radical from the molecular ion, rearrangement occurs via the species (2-18) such that NO and CO may be readily expelled from the ion. This scheme therefore accounts for each of the anomalies detailed above - including the relatively intense $(M - NO_2 - NO)$ and $(M - NO_2 - NO - CO)$ ions (2-19) and (2-20) . (It should however be noted that these ions occur to a small extent in all the isomers -

being formed presumably via isomerisation of the nitro group to the nitrite.[77])

If the above scheme operates for 1,8-dinitronaphthalene to produce the distinctive features outlined above, it seems reasonable to assume that a similar mechanism could function in a binaphthyl derivative containing two adjacent peri substituted nitro groups. This assumption has been verified during the current investigation (see later). Thus according to the above scheme, if 'D' does contain adjacent peri nitro groups (as the intense M - 46 ion and reduced intensity molecular ion would suggest) its spectrum should also show strong $(M - NO_2 - NO)$ and $(M - NO_2 - NO - CO)$ ions (and a relatively weak $(M - 2NO_2)$ion). Complications are inevitably introduced by the presence of a second naphthyl moiety which is differently substituted, but apart from a simple modification due to this unit the predicted features are observed. The effect of the additional nitro naphthalene nucleus is evidently to 'insert' the loss of HONO into the sequence of events anticipated from the scheme. Thus the ions at m/e 266 $(M - NO_2 - HNO_2 - NO)$ (61.7%) and m/e 238 $(M - NO_2 - HNO_2 - NO - CO)$ (73.3%) are quite intense whilst that at m/e 250 $(M - 2NO_2 - HNO_2)$ is only of low intensity (4.2%). Evidently loss of HONO (as OH˙ and NO˙) occurs immediately after expulsion of the first nitro group, as is indicated by the relatively strong ion at m/e 296 $(M - NO_2 - HONO)$ (30.0%) and metastables for the transitions indicated below:-

$$\underset{m/e\ 389}{C_{20}H_{11}N_3O_6} \longrightarrow \underset{m/e\ 343}{C_{20}H_{11}N_2O_4} + NO_2^{\cdot} \qquad M^* = 302.4$$

$$\underset{m/e\ 343}{C_{20}H_{11}N_2O_4} \longrightarrow \underset{m/e326}{C_{20}H_{10}N_2O_3} + OH^{\cdot} \qquad M^* = 309.8$$

$$\underset{m/e\ 326}{C_{20}H_{10}N_2O_3} \longrightarrow \underset{m/e\ 296}{C_{20}H_{10}NO_2} + NO^{\cdot} \qquad M^* = 268.8$$

The expulsion of OH˙ and NO˙ as indicated above is itself significant in determining the structure of compound 'D' since this type of loss could be consistent with the presence of a single peri substituted nitro group in the 'other' (monosubstituted) naphthyl moiety. That is, loss of HONO could occur via Beynon's mechanism as discussed above for the dinitrobinaphthyls. Indeed as 'D' is a major product of the nitration of 1,1'-binaphthyl, in acetic anhydride/nitric acid, and the 4 and 4' positions are apparently the most reactive sites in this compound towards nitration[10]; 4,4'-substitution might logically be expected in this product. Therefore the structure of 'D' can be tentatively assigned as 4,4'5-trinitro-1,1'-binaphthyl on the basis of the mass spectrum, although of course the spectrum could equally well fit 4,5,5'-trinitro-1,1'-binaphthyl.

The Infra-red Spectrum

The infra red spectrum of 'D' (see appendix) shows a weak band at 3100cm^{-1} corresponding to aromatic C-H stretching and also has two very strong bands at 1355 and 1535cm^{-1} corresponding to the symmetric and asymmetric nitro stretching vibrations. Whilst these bands fall within the expected frequency range it is notable that neither of the bands appears to be split. This is surprising as a doubling of the frequencies might have been anticipated in 4,4',5-trinitro-1,1'-binaphthyl due to steric interaction between the 4 and 5 substitut-ed nitro groups (which must prevent both of them from asuming coplanarity with the naphthalene ring system). Thus it would have been predicted that the isolated (4') nitro group would produce bands close to 1330 and 1520cm^{-1} (ie close to the stretching frequencies of 4,4'-dinitro-1,1'-binaphthyl) whilst the adjacent peri substituted (4 and 5) nitro groups would vibrate at higher frequency due to reduced conjugation with the naphthalenic system. (The anticipated figures for these bands would be 1350 and 1540cm^{-1} ie the frequencies observed in the spectrum of 4,4',5,5'-tetranitro-1,1'-binaphthyl—see below).

Although the absence of multiple bands in the spectrum of 'D' might throw some doubt on the structural assignment given above, stepwise nitration studies have confirmed that 'D' is in fact 4,4',5-trinitro-1,1'-binaphthyl (see below). Evidently therefore, the adjacent 4 and 5 substituted nitro groups in 'D' have stretching frequencies very close to those anticipated (observed: 1355/1535, 'expected': 1350/1540cm^{-1}) whilst the 'isolated' 4'- nitro group is sufficiently above the expected frequencies of 1330/1520cm^{-1} to be unresolved from the 1355/1535cm^{-1} bands. This rise in frequency relative to 4,4'-dinitro-1,1'-binaphthyl is difficult to explain as the 'affected' 4'-nitro group is spacially remote from the 'extra' 5 nitro group. Thus only minimal interaction should occur between the two substituents and it seems quite probable that any such interaction would have to be predominantly indirect, occurring via the steric effect of the additional 5 nitro group. Thus the close proximity of the adjacent peri (4 and 5) nitro groups must distort both from coplanarity with the aromatic ring, so reducing conjugation. Since this conjugation, particularly of the 4- nitro group, must extend to some degree* to the second naphthalenic ring system, a small effect on the frequency of the 4'-nitro group might be expected. It is however the magnitude of the observed shift which is unexpectedly high. Possibly the unsymmetrical nature of the compound necessitates a slight twisting of the 4'-nitro group out of the aromatic plane , in order to minimise the energy of the crystal lattice. (The IR spectrum was recorded as a KBr disc). (A similar effect is observed in other compounds such as 2,4,6-trinitrotoluene and 2,2',4,4',6,6'-hexanitrostilbene. Thus the nitro groups in both of these compounds are twisted out of the aromatic plane, in the crystalline solids, although there is no obvious steric reason for a lack of coplanarity.)

As with the compounds previously discussed the C-H out of plane deformation vibrations for the compound 'D' do not provide an unambiguous indication of structure - the low frequency region of the spectrum is generally rather too complex to be of value.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of compound 'D' in DMSO comprises two complex multiplets at τ1.29-1.76 (4H) and τ1.81-2.92 (7H) (see appendix). Whilst the spectrum is too complex to interpret fully, it is possible to assign protons to either the high- or low-field multiplets according to their 'type' (α or β) and their location relative to the nitro groups. Thus (assuming 4,4'5- substitution) the protons H_3, H_3', H_5' and H_6 can be assigned to the low-field multiplet because H_5' is an α proton (also sited peri to a nitro group) whilst H_3, H_3' and H_6 are all sited ortho to nitro groups. The high-field multiplet then corresponds to the protons H_2, H_2', H_6', H_7, H_7', H_8 and H_8' the first five of these being β protons whilst the last two are α protons each of which are shielded by an adjacent naphthalene system (cf binaphthyl etc).

The above chemical shifts are quite close to those observed in the spectra of both 4,4'-dinitro-1,1'-binaphthyl and 'C-1', which is to be expected in view of the proposed similarity of structure between these compounds.

It has previously been noted that a peri nitro group has

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* As the extent of conjugation between the two naphthalenic systems in 1,1'-binaphthyl is itself relativelysmall due to steric hindrance[69]; it might thus be expected to remain small in the various 1,1'-binaphthyl derivatives.

a substantial proximity effect upon a proton in an adjacent peri position. Thus, provided the nitro group is (substantially) unhindered a considerable downfield shift of the proton results.[71,72,78] If however the nitro group is forced out of the aromatic plane this proximity effect becomes reversed[72,78] and can actually lead to a net shielding of the proton.[72] For example in 2-methyl-1-nitronaphthalene the effect of the nitro group on H_8 has been estimated as +0.27ppm (compared with a naphthalene α proton) whereas in absence of the 2-methyl substituent it is -0.37ppm.[72] In view of this effect it seems unlikely that the 4- nitro group of the compound 'D' is perpendicular to the aromatic system in solution. Thus consider the two cases: i) the 4'-nitro group of 'D' is roughly planar with the aromatic system. In this case H_5' should resonate near to τ1.51 that is the chemical shift observed for H_5 in 4,4'-dinitro-1,1'-binaphthyl (DMSO). ii) The 4'-nitro group of 'D' is roughly perpendicular to the aromatic system. In this event H_5' should resonate at higher field than occurs in case i). The extent of the change may be estimated by reference to the methyl/dimethyl nitronaphthalenes where the difference between having a 'planar' and a 'perpendicular' nitro group is around 0.6-0.7ppm.[72,78] Thus H_5 would be expected to resonate at around τ(1.51 + 0.6/0.76) $\simeq\tau$2.11-2.27. If this occured H_5 would be coincident with the higher field multiplet in 'D' and the integrated ratio of the two multiplets would become 3:8. This is not observed. It thus seems likely that in solution the 4'- nitro group in 4,4',5-trinitro-1,1'-binaphthyl ('D') is roughly coplanar with the aromatic system and that it only becomes substantially distorted in the solid phase possibly due to crystal lattice effects (hence the observed IR spectrum). It must be noted however that the spectra of the methyl/dimethylnitronaphthalenes were recorded in dimethyl acetamide/carbon tetrachloride - not DMSO; the figure of 0.6-0.7ppm quoted above for the shift due to a change in the orientation of the nitro group may therefore be somewhat inaccurate in DMSO. Nevertheless with such a large separation between the multiplets in the spectrum of 'D' it would be necessary to propose a shift of less than 0.15ppm due to twisting of the nitro group, in order to reconcile a 'perpendicular' 4'-nitro group with the spectrum of 'D'. This seems unlikely.

The Ultra Violet Spectrum

The UV spectrum of 'D' in methanol (see appendix) has two resolved maxima at λ 215nm, ϵ 6110m^2mole^{-1} (Ar $\pi \rightarrow \pi^*$) and λ 345nm,

ϵ 900m^{2}mole^{-1} (NO$_2$ $n\rightarrow\pi^*$ or $\pi\rightarrow\pi^*$ [107,108]). In addition there is a single well defined shoulder at λ238nm, ϵ 2790m^{2}mole^{-1} (NO$_2$ $n\rightarrow\pi^*$); these wavelengths are therefore quite close to those observed in 'C-2'. A comparison of the spectrum with that of 4,4'-dinitro-1,1'-binaphthyl however, shows that this $n\rightarrow\pi^*$ band has increased its intensity and shifted to shorter wavelength as would be expected[87] due to the presence of a third nitro group. The wavelength of this shoulder is close to that of a band in 4,4',5,5'-tetranitro-1,1'-binaphthyl (233nm) which must be due to 'out of plane' nitro groups (see below). (Similar shoulders have been noted in 'C-2' (230nm) and a number of other compounds containing 'out of plane' nitro groups - see below.) The spectrum is therefore consistent with the presence of adjacent peri substituted nitro groups which are necessarily rotated well out of the plane of the aromatic nucleus. (The position of the shoulder is presumably determined largely by the non-coplanar nitro groups as there are two of these and only one 'planar' nitro group.)

Stepwise Nitration Studies for Structural Confirmation of the Compound 'D'

As outlined above the spectroscopic evidence clearly suggests that compound 'D' is either 4,4'5- or 4,5,5'- trinitro-1,1'-binaphthyl. Such an interpretation has been confirmed by the further nitration of this material. Thus it has been shown that the compound 'D' can be nitrated to 4,4',5,5'-tetranitro-1,1'-binaphthyl in 65% yield (see experimental).

Although it is difficult to distinguish between 4,4'5- and 4,5,5'- substitution on the basis of the spectroscopic data alone, the considerable yield of compound 'D' which is derived from the nitration of 1,1'-binaphthyl, renders it more likely to be the former isomer, because of the greater reactivity of the 4 and 4' positions. This supposition has in fact been confirmed by synthetic methods, in that it has been shown that compound 'D' can be prepared by the nitration of 4,4'-dinitro-1,1'-binaphthyl, but not by the nitration of 5,5'-dinitro-1,1'-binaphthyl (see experimental section).

2.2.1.5. 4,5,8'-Trinitro-1,1'-binaphthyl (Probable Structure)

Designated Compound 'F'

This material was isolated (16.4%) from the reaction of 1,1'-binaphthyl in acetic anhydride/nitric acid; it has not been prepared by any other method. The compound analyses correctly for a trinitrobinaphthyl and shows a molecular ion in its mass spectrum at 389.0637 which corresponds to $C_{20}H_{11}N_3O_6$ (calculated 389.0647). The infra-red spectrum has bands consistent with nitro stretching frequencies and indicates no other functional groups. The compound is therefore clearly a trinitrobinaphthyl. Although it seems quite likely that the compound is 4,5,8'-trinitro-1,1'-binaphthyl, the evidence is by no means conclusive. Once again an unambiguous determination of structure could best be achieved by synthesising the compound from appropriate nitronaphthalene derivatives of known structure - via a suitable coupling reaction. Such a preparation has not however been completed due to lack of time. The various data available for this compound is considered below.

The Mass Spectrum

The major ions in the spectrum of 'F' are indicated in the scheme 2:XI. A full list of relative intensities and a bar diagram are given in the appendix. The spectrum shows a fragmentation pattern typical of a nitro aromatic compound ($M - NO_2$, $M - 2NO_2$, $M - 3NO_2$, with interim ions of low intensity corresponding to $M - O$, $M - NO$, etc) although some of the ions are of unusually low intensity (see below).

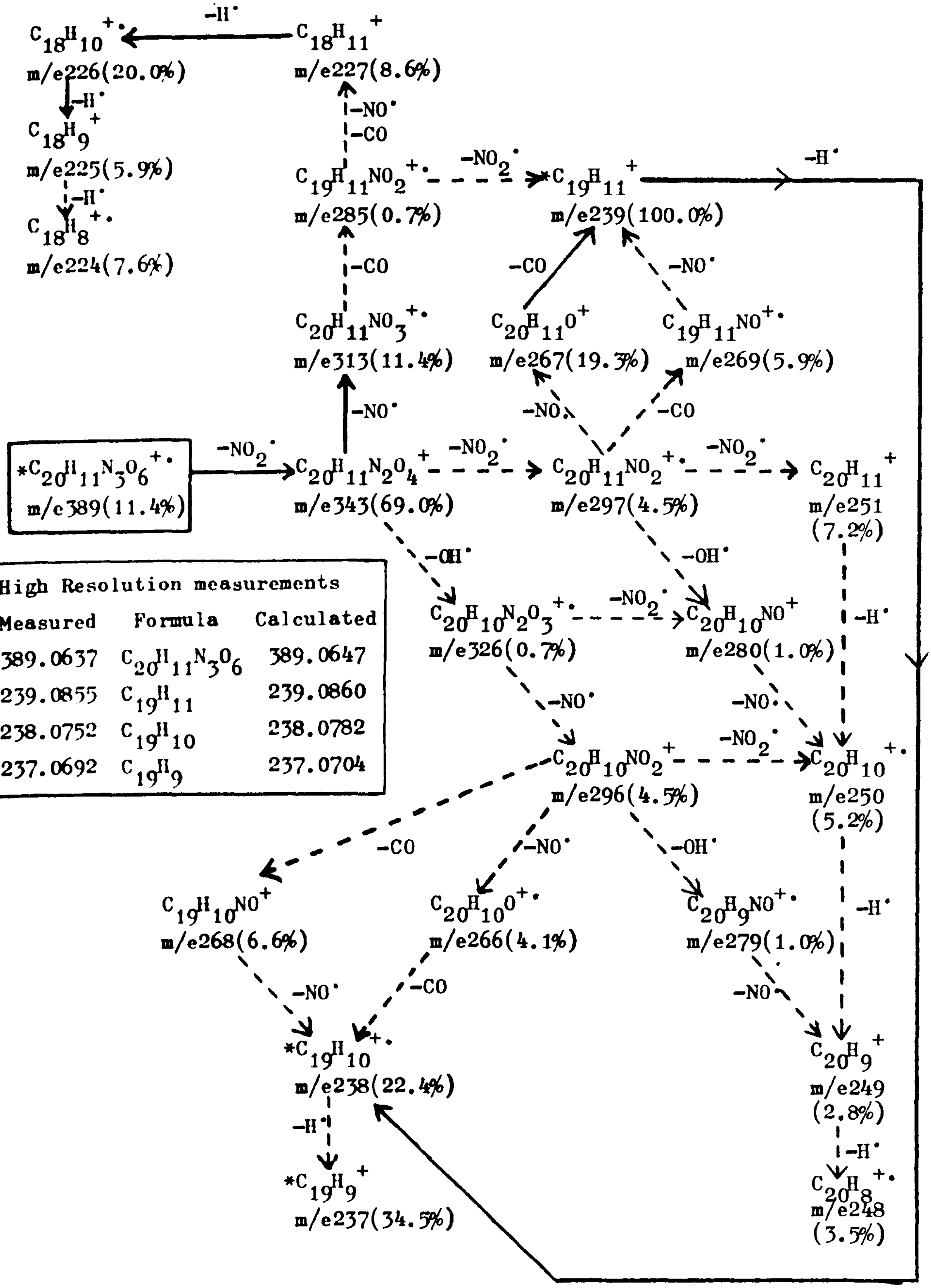
The most informative aspect of the spectrum with respect to structure determination is the relatively low intensity of the molecular ion (11.4%) and the high intensity of the M - 46 ion (69.0%). This feature suggests the presence of adjacent peri substituted nitro groups[110] and has been previously discussed for the compound 'D'. The secondary features associated with such a grouping (ie those analagous to the intense ($M - NO_2 - NO$) & ($M - NO_2 - NO - CO$) ions and the weak ($M - 2NO_2$) ion which are observed in 1,8-dinitronaphthalene) are also evident in the spectrum, although the losses have been modified by the presence of an additional nitronaphthyl moiety, (as in the case of compound 'D'). In the present case however a nitro radical is 'inserted' into the anticipated sequence of losses - in contrast to the spectrum of 'D' where it is HONO that is 'inserted'. Thus the final ions to be observed at relatively high intensity are those at m/e 267 ($M - 2NO_2 - NO$), (19.3%) and m/e 239 ($M - 2NO_2 - NO - CO$) (100%) whilst the ion at m/e 251 ($M - 3NO_2$) is of only low intensity (7.2%).

The expulsion of a nitro radical in the present compound (rather than HONO) is itself of interest in establishing the structure of 'F', because expulsion of HONO has already been associated with the presence of an 'isolated' peri nitro group. Thus if the presence of such a group leads to the loss of HONO via Beynon's mechanism, the

Scheme 2:XI

Fragmentation Pattern for the Mass Spectrum of Compound 'F'

(4,5,8'-Trinitro-1,1'-binaphthyl)



*High Resolution measurements

Measured	Formula	Calculated
389.0637	$C_{20}H_{11}N_3O_6$	389.0647
239.0855	$C_{19}H_{11}$	239.0860
238.0752	$C_{19}H_{10}$	238.0782
237.0692	$C_{19}H_9$	237.0704

Continuous lines indicate the presence of a metastable to support the proposed transition absence of such a loss in 'F' must tend to suggest that the third nitro group in this compound is not situated in the 4'- or 5'- positions. (The former site may be discounted anyway as with adjacent peri substituted nitro groups in the 4 and 5 positions, the presence of a 4' nitro group would render the compound identical with 'D' – which is clearly not the case.)

The main fragmentation pathway in 'F' (as indicated by the most intense ions in the spectrum) thus involves consecutive loss from the molecular ion of the following particles:- $NO_2^{\cdot}$, $NO^{\cdot}$, $NO_2^{\cdot}$, CO, $H^{\cdot}$, and $H^{\cdot}$. Most of these transitions are supported by metastable peaks and between them they account for the most intense ions in the spectrum. As with previous compounds it is uncertain from precisely which sites the hydrogen radicals are lost.

Whilst the mass spectrum clearly indicates the presence of 4,5- substitution, it is not sufficiently distinctive to permit precise identification of the isomer; thus the position of the third nitro group cannot really be ascertained from the spectrum. The best evidence as to the site of the third nitro group comes from the result of further nitrating the compound (see below). In fact it appears most likely that the third nitro group is in the 8 position. The spectra of 'F' are therefore considered hereafter in terms of the (most probable) 4,5,8'- substitution pattern.

Two other compounds believed to contain an 8 nitro group have already been described ('C-1' and 'C-2'). The mass spectra of both these compounds show ($M - NO_2 - OH$) ions of considerable intensity and these have been explained in terms of a rearrangement of the 8 nitro group. The spectrum of the compound 'F' differs from those of 'C-1' and 'C-2' in that the ($M - NO_2 - OH$) ion is vanishingly small. The cause of this anomaly appears to be the presence of adjacent peri substituted nitro groups in 'F', as these apparently provide the molecular ion with a more favourable fragmentation pathway than is available in the compounds 'C-1' and 'C-2'. Thus the 4,5-substituted nitro groups preferentially fragment – via the mechanism discussed above – and so effectively suppress the intensity of ions due to the rearrangement of the 8 nitro group. In fact breakdown of this structural feature is so favourable, that the resulting ions dominate the spectrum of 'F' and also tend to 'drown out' the more 'usual' ions (eg $M - 2NO_2$, $M - 3NO_2$) (A similar effect is observed in other compounds containing adjacent peri substituted nitro groups.)

In summary therefore the mass spectrum of 'F' provides strong evidence in favour of 4,5- substitution, but gives little indication as to the position of the third nitro group, other than confirming that it is neither 4'- nor 5'- substituted.

The Infra-red Spectrum

The infra-red spectrum of 'F' (see appendix) has two very strong bands at $1535cm^{-1}$ and $1355cm^{-1}$ corresponding to the asymmetric and symmetric nitro stretching frequencies. The high frequency band is 'split' and shows a secondary maximum at $1520cm^{-1}$; this is not the case for the low frequency band which comprises a single maximum (at $1355cm^{-1}$). This fact is significant as it has been observed both in the current work and elsewhere,[86a] that the changes in nitro stretching frequencies which accompany a twisting of the nitro group, are more pronounced for the symmetric stretching vibration than for the asymmetric vibration. Thus if the bands at $1520/1535cm^{-1}$ in 'F' resulted from a 'planar' and a 'non planar' nitro group respectively, the symmetric stretching frequency should also be split into two maxima, but with an even greater separation than that observed for the asymmetric band. The absence of such splitting suggests that the double maxima at $1535/1520cm^{-1}$ result from some other cause, for example a simple overlap of the nitro stretching vibration with another, possibly due to aromatic C=C stretching.[64a]

The spectrum of 'F' is thus in accord with the proposed structure of 4,5,8'-trinitro-1,1'-binaphthyl, because in this compound all three of the nitro groups must be twisted out of the aromatic plane due to steric considerations. In consequence all the valence stetching bands should be shifted to 'higher frequency' - where they would presumably coincide. Thus the bands due to the 4,5- substituted nitro groups should lie close to 1535 and $1355cm^{-1}$ (ie the observed values in 4,4',5-trinitro-1,1'-binaphthyl) whilst those due to the 8 nitro group should occur near 1530 and $1365-1350cm^{-1}$ (ie the values observed in 'C-1' and 'C-2'). These figures clearly embrace the bands observed in compound 'F'. It must however be noted that since 'D' produces single 'nitro' bands despite the presence of (presumably) both planar and non planar nitro groups, the lack of splitting in such bands for the compound 'F' does not conclusively signify the existence of an 8-nitro group in this compound.

As with the compounds previously discussed, the low frequency region in the spectrum of 'F' is too complex to provide useful information as to the substitution pattern of this compound.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of 'F' is too complex to interpret fully by inspection and for this reason the following discussion is aimed merely at rationalising it with the proposed structure (ie 4,5,8'-trinitrobinaphthyl).

The spectrum, in DMSO, comprises two complex multiplets at τ1.58–2.03 (4H) and τ2.03–2.68 (7H) (see appendix); this division of the spectrum into 'low' and 'high' field regions, reflects once again the different environments of the various protons. Thus the low-field multiplet (4H) represents the α protons H_4' and H_5' plus the two β protons H_3 and H_6 – which are each sited ortho to a nitro group. The remaining protons must therefore contribute to the high-field multiplet; this suggests both that H_8 is shielded by the second naphthyl moiety (cf 1,1'-binaphthyl), and that H_7' is very little affected by the adjacent 8' nitro group. Presumably the severe steric hindrance of the 8- nitro group is responsible for this effect; a similar absence of deshielding, due to steric hindrance, has already been proposed in the spectrum of 'C-1'.

The observed chemical shifts in 'F' are fairly typical of aromatic nitro compounds and relate quite well to those of both 4,4'-dinitro-1,1'-binaphthyl and 4,4',5-trinitro-1,1'-binaphthyl ('D'). This is only to be expected as the compounds have reasonably similar structures.

The Ultra Violet Spectrum

The UV spectrum of 'F' in methanol (see appendix) shows two resolved maxima at λ220nm, ϵ6320m^{2}mole^{-1} (Ar$\pi \rightarrow \pi^*$) and λ343nm, ϵ 1220m^{2}mole^{-1} (nitro $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ [107,108]). The wavelengths of these maxima are quite similar to those observed in the other trinitrobinaphthyls ('C-2' and 'D'); thus once again the bands exhibit a slight bathochromic shift relative to both α-nitronaphthalene[74] and 1,8-dinitronaphthalene[74]. In addition to the above resolved maxima, the spectrum of 'F' also has a shoulder at λ243nm, ϵ2840m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$). The apex of this shoulder occurs at a slightly shorter wavelength than that in the compound 'C-2'. This is to be expected if 'F' is 4,5,8'- substituted as none of the nitro groups are then coplanar with their respective aromatic rings. In consequence they should all absorb at shorter wavelength than the ('coplanar') 4-nitro groups in 'C-2'. (The position of the band at 250nm in 'C-2' is most likely determined by the 'coplanar' 4-nitro groups as there are two of these as compared with one (potentially) non coplanar group.)

Further Nitration of 4,5,8'-Trinitro-1,1'-binaphthyl(?) (Compound 'F')

Nitration of the compound 'F' under conditions suitable for the preparation of a tetranitrobinaphthyl (nitric acid in excess acetic anhydride with sulphuric acid catalyst), produced as major product a material which is believed to be 4,4',5,8'-tetranitro-1,1'-binaphthyl (compound 'P'). Since the nitration of 1,1'-binaphthyl itself under similar conditions has been shown to lead primarily to 4,5- substitution (see later), it seems likely that the 8'- substituent was already present in the substrate. This result taken in conjunction with the spectroscopic data discussed above, tends to suggest that the compound 'F' is in fact 4,5,8'-trinitro-1,1'-binaphthyl.

2.2.1.6. 4,4',5,5'-Tetranitro-1,1'-binaphthyl Designated Compound 'H'

During the course of the present work this material was first isolated by the action of acetic anhydride and nitric acid on 1,1'-binaphthyl. Product yields using this reaction medium,ranged from 8.3% to 62.1%, depending upon the conditions employed. The compound 'H' has subsequently been prepared by directly nitrating 4,4'-dinitro-1,1'-binaphthyl, 5,5'-dinitro-1,1'-binaphthyl and 4,4',5-trinitro-1,1'-binaphthyl (see experimental); in view of this there can be little doubt of its structure.

The preparation of 4,4',5,5'-tetranitro-1,1'-binaphthyl has also been reported during the course of the present work by Jones and Joyner.[12] These authors have described three methods for its production from binaphthyl using:- i) preformed acetyl nitrate (product yield 50%), ii) a mixture of glacial acetic/nitric and sulphuric acids (product yield 53%) and iii) nitronium tetrafluoroborate (product yield 45%). In general these workers employed much more vigorous nitration conditions for the preparation of this compound than were found necessary during the present work. Indeed when an attempt was made, during the present work, to reproduce method ii) above, complete carbonisation of the substrate resulted. Thus ultimately it proved necessary to reduce both the temperature and duration of this nitration in order to isolate 4,4',5,5'-tetranitro-1,1'-binaphthyl from the reaction. The reason for this discrepancy is unclear although possibly the smaller scale employed during the present work influenced the outcome of the reaction.

Whilst Jones and Joyner assigned their product the structure of 4,4',5,5'-tetranitro-1,1'-binaphthyl and prepared a derivative to confirm this assignment, they did not provide very detailed spectroscopic data for it. Nevertheless the information which is reported appears consistent with the data obtained from compound 'H' during the present investigation. The spectroscopic data obtained from the compound 'H' is discussed below.

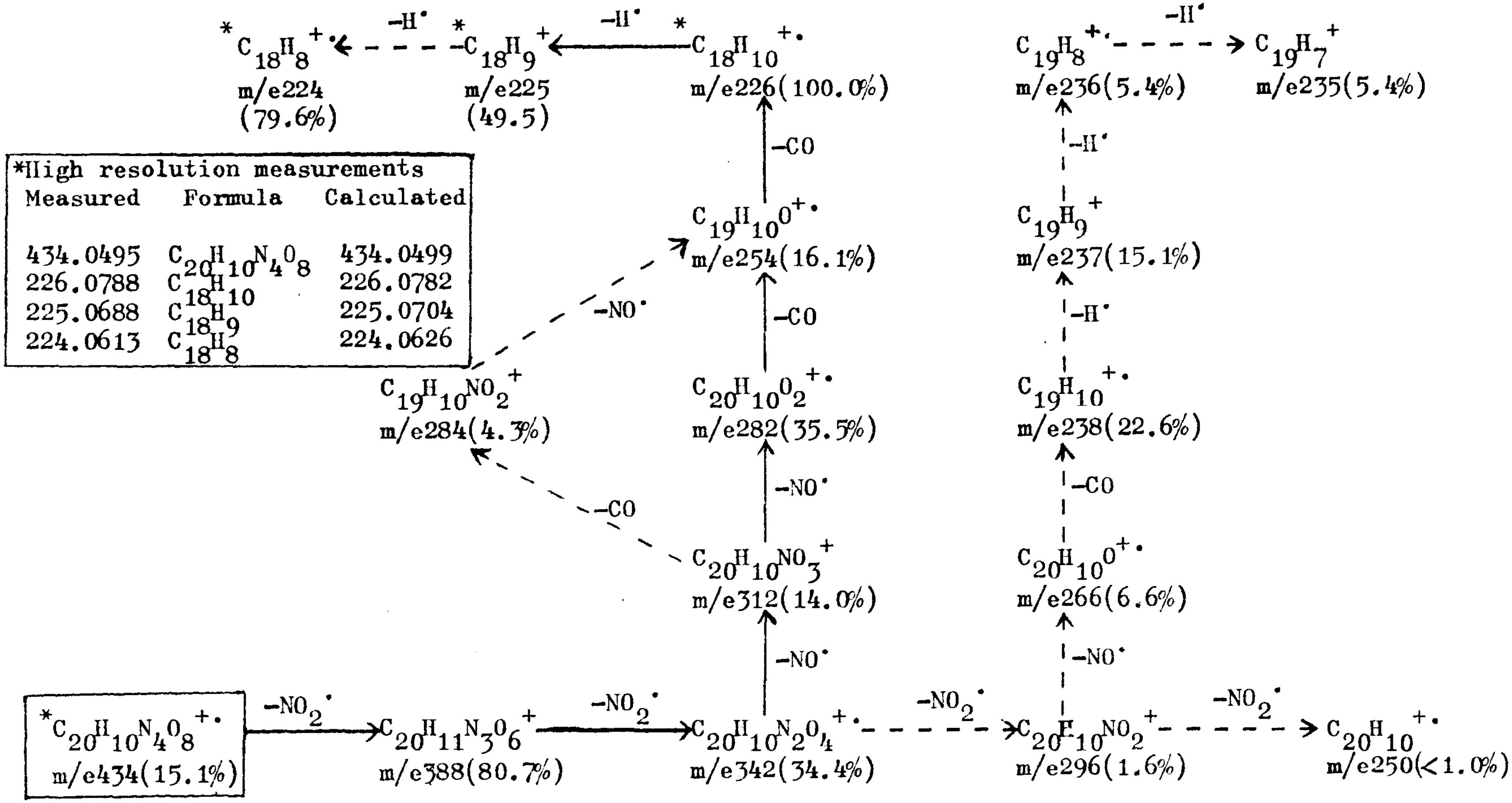
The compound 'H' analyses correctly for a tetranitrobinaphthyl and shows a molecular ion in its mass spectrum at 434.0495 which corresponds to $C_{20}H_{10}N_4O_8$ (theoretical 434.0499). The infra-red spectrum has bands consistent with nitro stretching frequencies and indicates no other functional groups. The compound is thus clearly a tetranitrobinaphthyl. The best evidence as to the structure of 'H' comes from its mass spectrum, this is therefore the first spectrum to be considered.

The Mass Spectrum

A full list of relative intensities and a bar diagram for the mass spectrum of 'H' are given in the appendix; the major peaks in the spectrum are summarised in the scheme 2:XII. Intense ions are evident at m/e 388 (80.7%) and m/e 342 (34.4%) ($M - NO_2$ and $M - 2NO_2$ respectively), however the ions at m/e 296 and m/e 250 (ie $M - 3NO_2$ and $M - 4NO_2$) only occur with low probability (1.6% and less than 1% respectively). As has been previously discussed, a disproportionately intense M - 46 ion can signify the presence of adjacent peri substituted nitro groups in the parent molecule. In the present case the appearance of two relatively intense ions at m/e 388 and m/e 342 might reasonably be interpreted in terms of two sets of adjacent peri substituted nitro groups. Such a hypothesis is supported by the fragmentation pattern observed below m/e 342, as the spectrum is dominated in this region by peaks apparently produced by successive loss of $2NO^{\cdot}$ and 2CO from the m/e 342 ion. This is exactly the type of fragmentation which would be predicted by Brittains'[110] mechanism (scheme 2:X pg 65) if the molecule did contain two independant sets of adjacent peri substituted nitro groups.

Scheme 2:XII

Fragmentation Pattern for the Mass Spectrum of 4,4',5,5'-Tetranitro-1,1'-binaphthyl



*High resolution measurements

Measured	Formula	Calculated
434.0495	$C_{20}H_{10}N_4O_8$	434.0499
226.0788	$C_{18}H_{10}$	226.0782
225.0688	$C_{18}H_9$	225.0704
224.0613	$C_{18}H_8$	224.0626

Continuous lines indicate those transitions which are supported by the presence of a metastable peak.

The main fragmentation pathway of 'H' thus comprises sequential loss of $2NO_2^{\cdot}$, $2NO^{\cdot}$ and 2CO from the molecular ion; each of these transitions being supported by a metastable peak - see scheme 2:XII. The ion at m/e 226 presumably loses one or two hydrogen radicals to give the intense ions at m/e 225 and m/e 224. The first of these transitions is also supported by a metastable peak.

The mass spectrum thus supports the presence of two sets of adjacent peri substituted nitro groups in 'H' and hence also the proposed structure for the compound - 4,4',5,5'-tetranitro-1,1'-binaphthyl.

The Infra-red Spectrum

The infra-red spectrum of 'H' (see appendix) has a weak band at $3010cm^{-1}$ corresponding to aromatic C-H stretching, it also shows two intense bands at 1540 and $1350cm^{-1}$ corresponding to the asymmetric and symmetric stretching frequencies of the nitro group. Both of these bands occur at rather higher frequencies than those observed in 4,4'- (or 5,5'-) dinitrobinaphthyl; this is consistent with the presence of adjacent peri substituted nitro groups - as it is clearly impossible for such groups to remain coplanar with their respective aromatic ring systems. Further as all the nitro groups are likely to form similar angles with their respective aromatic systems there should be no 'splitting' of the NO_2 (N-O) stretching bands, this is in fact the case and none is observed. As with previous compounds the low frequency region of the spectrum is complex and proves to be of little value in confirming the structure of compound 'H'.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of 'H' has been recorded both in acetone and DMSO (see appendix). Whilst the differences between the spectra are relatively small the pattern produced in acetone is marginally better for interpretation; this spectrum is therefore considered below.

The most clearly discernable feature in the spectrum of 'H' is an AB quartet which occurs, in acetone, at τ1.40, doublet, J=7.7Hz (2H), τ1.95, doublet, J=7.7Hz (2H); this is readily assignable to the protons $H_{2/2'}$ and $H_{3/3'}$. Presumably the latter protons will resonate at lower field than the former because they are sited ortho to the nitro groups, thus the signal at τ1.40 may be attributed to the protons $H_{3/3'}$ and that at τ1.95 to $H_{2/2'}$. The observed coupling constant of 7.7Hz is typical of ortho coupled aromatic protons[115] and correlates well with that observed in 4,4'-dinitro-1,1'-binaphthyl (7.8Hz).

In addition to the above quartet it is possible to extract a double doublet (at τ1.57) from the spectrum of 'H' (although there is some overlap of this signal with the doublet at τ1.40). This double doublet (at τ1.57 - 2H) may be assigned to the protons $H_{6/6'}$; thus $J_{H6/7}$ = 7.7Hz, $J_{H6/8}$ = 1.7Hz. The remaining portion of the spectrum comprises a multiplet at τ 1.90-2.50 (4H); whilst this multiplet is difficult to interpret by inspection it is clearly assignable to the protons $H_{7/7'}$ and $H_{8/8'}$. This assumption is confirmed by comparing the spectrum of 'H' with that of 3-nitro ortho-xylene.[116] Thus the pattern of the high-field multiplet in 'H' mirrors that produced in the xylene by the protons H_5 and H_6, although the chemical shifts are rather different. (The similarity between these two is a little less obvious when the spectrum of 'H' is run in DMSO.) The spectrum of 3-nitro ortho-xylene also has a double doublet downfield of the main multiplet which is due to H_4. This signal therefore correlates with the double doublet attributed to $H_{6/6'}$ in the spectrum of 'H'.

The chemical shifts observed in the spectrum of 'H' fall in the normal region for nitroaromatic compounds. However as the spectrum of 4,4'-dinitro-1,1'-binaphthyl has not been recorded in acetone (because of its low solubility), a comparison of chemical shifts between 'H' and the dinitrobinaphthyl is best carried out in DMSO. Using this solvent the observed shifts in 'H' are as follows: AB quartet: τ1.45 ($H_{3/3'}$) / 2.07 ($H_{2/2'}$), double doublet τ1.59 ($H_{6/6'}$) and multiplet: τ2.13-2.53 ($H_{7/7'}$ and $H_{8/8'}$).

A comparison of the spectrum of 'H' with that of 4,4'-dinitro-1,1'-binaphthyl shows that the chemical shift of H_3 is very similar in the two compounds (τ1.45 and τ1.51 respectively - DMSO); this is to be expected in view of their closely related structures. The slightly lower field at which the proton resonates in 'H', is presumably a reflection of the decreased electron density in this compound due to the presence of additional nitro groups.

The chemical shifts for the protons $H_{2/2'}$ are also quite similar in the two compounds; thus in 'H' these resonate at τ2.07, whilst in 4,4'-dinitro-1,1'-binaphthyl they resonate at τ2.22. Once again the signal occurs at lower field in the case of the tetranitrobinaphthyl; whilst this is presumably due to the presence of additional nitro groups, it is unclear why these should have a greater effect on the resonance of H_2 than they do on that of H_3.

It is not possible to make a detailed comparison of chemical shifts for the remaining protons - due to the complexity of the respective multiplets. It is clear however that $H_{7/7'}$ and $H_{8/8'}$ must have approximately similar shifts in the two compounds because the multiplets cover approximately similar regions ('H': τ2.13-2.53, 4,4'-dinitro-1,1'-binaphthyl: τ2.01-2.71). Further it is evident from these figures that the multiplet in 4,4'-dinitro-1,1'-binaphthyl extends to higher field than that in the compound 'H'; this is once again to be expected because the additional nitro groups in 'H' will tend to deshield all the protons which contribute to this multiplet.

The Ultra Violet Spectrum

The ultra violet spectrum of 'H' in methanol (see appendix) shows three resolved maxima at λ 210nm, ϵ 6510m^{2}mole^{-1} (Ar$\pi \rightarrow \pi^*$), λ 233nm, ϵ 5040m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$) and λ 333nm, ϵ 1760m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ cf refs 107,108).

Once again all the bands show a bathochromic shift relative to 1,8-dinitronaphthalene (202nm, ϵ 4660m^{2}mole^{-1}, 231nm, ϵ 2580m^{2}mole^{-1} and 314nm, ϵ 660m^{2}mole^{-1} - methanol[74]) as would be expected due to the increased conjugation of the binaphthyl system. It is interesting to note however that the $n \rightarrow \pi^*$ band in 'H' (at 233nm) is subject to a much smaller shift than is the Ar $\pi \rightarrow \pi^*$ band; this probably results from reduced conjugative interaction between the nitro groups and aromatic system and is presumably due to their mutual non-coplanarity.

The spectrum of 'H' differs from those of the binaphthyl derivatives considered so far, in that the two longer wavelength bands are more clearly defined. This presumably reflects a tendency for all the nitro groups to absorb at similar wavelength, which is to be expected since they are all 'peri' substituted and will most likely have similar angles of inclination to their respective ring systems.

Comparison of the spectrum of 'H' with those of the trinitrobinaphthyls shows that the nitro $n \rightarrow \pi^*$ transition has moved to shorter wavelength and appears with increased intensity. This is to be expected[87] due to the introduction of another nitro group. A similar effect is observed on the long wavelength band (at 333nm); this is consistent with assignment of this band to a nitro transition.[107,108]

In conclusion therefore, it is evident that, all of the spectroscopic data for compound 'H' can be readily explained in terms of the compound being 4,4',5,5'-tetranitro-1,1'-binaphthyl.

page 82 omitted

2.2.1.7. 4,5,x,y-Tetranitro-1,1'-binaphthyl Designated Compound 'I'

Traces of this compound (less than 0.1%) were isolated from the reaction of 1,1'-binaphthyl with nitric acid in acetic anhydride, it has not been prepared by any other method.

Due to the very small quantity of this material which was isolated only a mass spectrum could be recorded. In consequence a full identification of the compound has not been possible. The mass spectrum shows a molecular ion at m/e 434 and a fragmentation pattern consistent with that of a tetranitrobinaphthyl (see appendix). The compound is therefore assumed to be a tetranitrobinaphthyl. The molecular ion in this spectrum was only weak, whilst the base peak occured at m/e 388 (M - 46). As has been previously discussed this combination of weak molecular ion and intense (M - NO_2)ion can indicate the presence of adjacent peri substituted nitro groups. If these are in fact present in the compound 'I' the molecular ion would be expected to fragment via sequential loss of $NO_2^{\cdot}$, $NO^{\cdot}$, $2NO_2^{\cdot}$ and CO to yield an ion at m/e 238. Whilst this ion is undoubtedly intense (62.5%) the lack of any strong peaks in the interim region between m/e 388 and m/e 238 renders it difficult to establish the fragmentation sequence with any certainty. Unfortunately there is also a lack of information regarding metastable peaks due to the presence of impurities in the sample. Thus, as a clear spectrum of the tetranitrobinaphthyl only occured transiently, repeat scans at high multiplier setting, to detect metastables, were not possible. The only metastable peak to be assigned from the low multiplier scan is that at m/e 236.0 which apparently supports the transition: $C_{19}H_{10} \longrightarrow C_{19}H_9 + H^{\cdot}$

Most of the ions in the spectrum may however be assigned in terms of fragmentation pathways previously discussed for other nitrobinaphthyls. The most probable of these are summarised in the scheme 2:XIII.

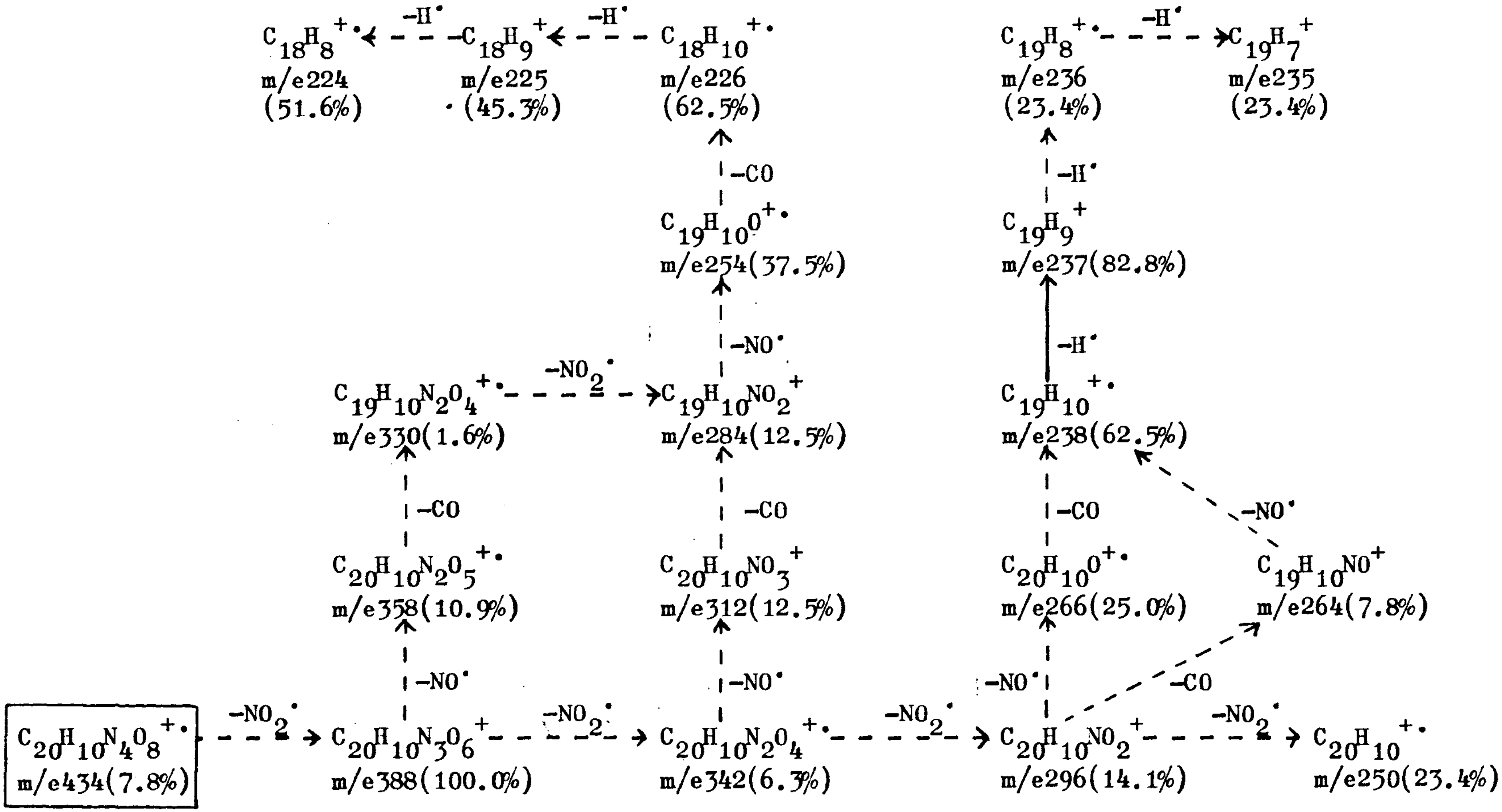
In summary the compound 'I' is probably a tetranitrobinaphthyl and may well be 4,5,x,y- substituted. There is however very little information available about this compound.

2.2.1.8. 4,4',5,8'-Tetranitro-1,1'-binaphthyl (Probable Structure) Designated Compound 'P'

This material was isolated in small yield (1.3%) from the nitration of 1,1'-binaphthyl in nitric acid and acetic anhydride. It was also prepared by the treatment of both 4,4'-dinitro-1,1'-binaphthyl

Scheme 2:XIII

Fragmentation Pattern for the Mass Spectrum of 4,5,x,y-Tetranitro-1,1'-binaphthyl (Compound 'I')



Continuous lines indicate those transitions which are supported by the presence of a metastable peak.

and compound 'F' (4,5,8'-trinitro-1,1'-binaphthyl) in the same reaction medium (product yields 1.1% and 17.9% respectively).

This compound analyses correctly for a tetranitrobinaphthyl and produces a molecular ion in its mass spectrum at m/e 434.0495 corresponding to $C_{20}H_{10}N_4O_8$ (calculated 434.0499). The infra-red spectrum has bands consistent with nitro stretching frequencies and indicates no other functional groups. The compound is therefore clearly a tetranitrobinaphthyl.

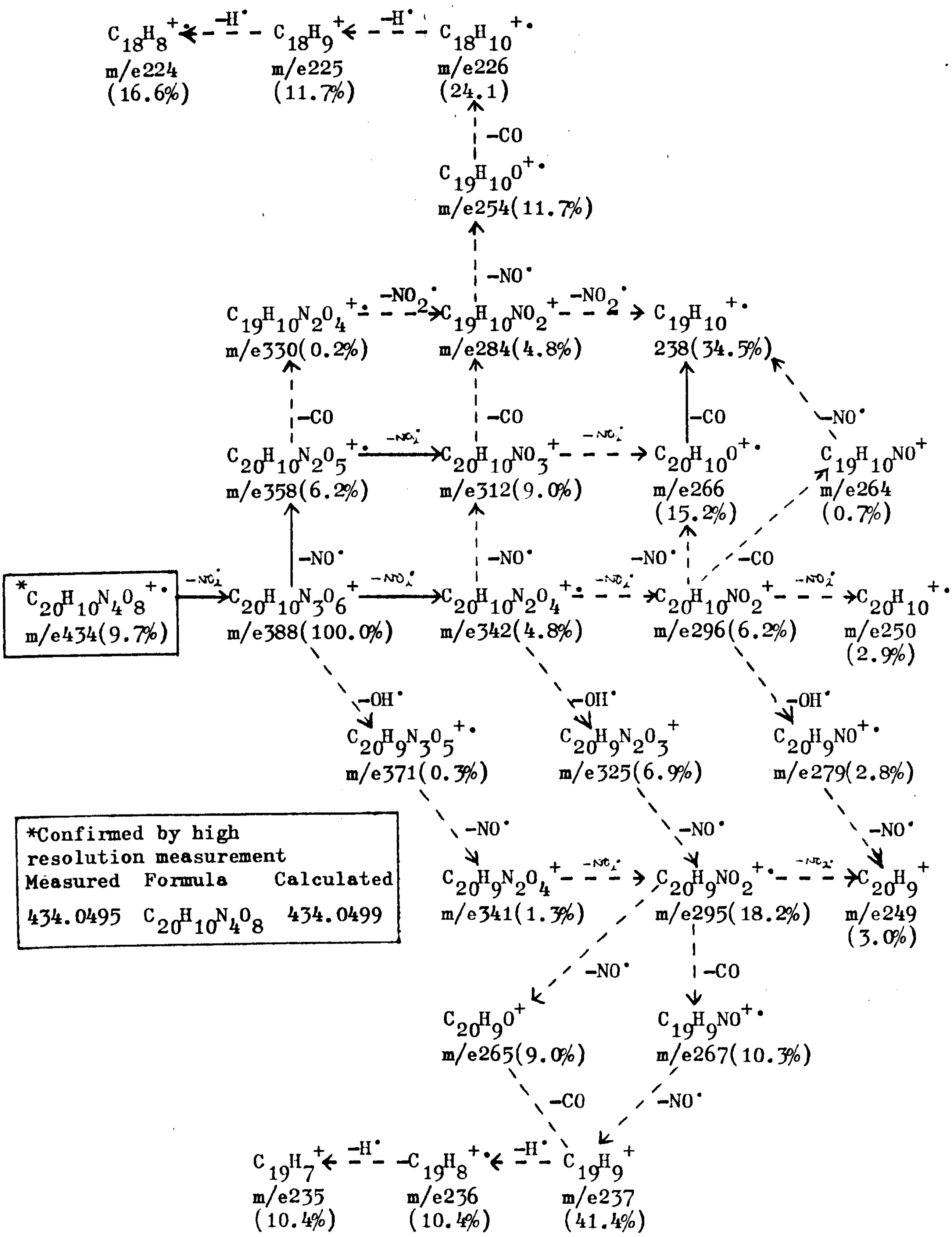
As the compound 'P' can apparently be prepared by the nitration of 4,4'-dinitro-1,1'-binaphthyl, it seems likely that it contains 4,4'-substitution. Although this assumption is not indisputable (due to the low yield obtained from the nitration of 4,4'-dinitro-1,1'-binaphthyl) it is nevertheless quite likely in view of the known reactivity of the 4 and 4' positions in 1,1'-binaphthyl. Whilst the spectra of 'P' are certainly consistent with the presence of 4,4'- substitution, they are not sufficiently distinctive to provide unambiguous confirmation of this structure. The spectroscopic data available for this compound is considered below.

The Mass Spectrum

The major ions in the mass spectrum of 'P' are indicated in the scheme 2:XIV. A full list of relative intensities and a bar diagram are given in the appendix. The spectrum shows a fragmentation pattern fairly typical of a nitro aromatic compound: $(M - NO_2^\bullet)$, $(M - 2NO_2^\bullet)$, $(M - 3NO_2^\bullet)$ and $(M - 4NO_2^\bullet)$ with interim ions of low intensity corresponding to $(M - O^\bullet)$, $(M - NO^\bullet)$ etc. The spectrum also exhibits the distinctive pattern of ion intensities associated with adjacent peri substituted nitro groups: that is, a weak molecular ion but a strong M - 46 ion (in this case the base peak of the spectrum). Subsequent fragmentation of the M - 46 ion, as indicated by the most intense ions in the spectrum, apparently involves sequential loss of $NO^\bullet$, $2NO_2^\bullet$ and CO (see scheme 2:XIV) to form ultimately the ion at m/e 238 (34.3%). (Most of these transitions are supported by the presence of metastable peaks.) In the present case therefore, the fragmentation sequence differs from that observed in 1,8-dinitronaphthalene in that two additional nitro radicals are expelled prior to a molecule of CO. This presumably reflects the presence of an additional dinitronaphthyl moiety and as such appears consistent with the spectrum of 'F' in which just one 'extra' nitro radical is lost. (The difference presumably reflects

Scheme 2:XIV

Fragmentation Pattern for the Mass Spectrum of Compound 'P' (4,4',5,8'-Tetranitro-1,1'-binaphthyl)



*Confirmed by high resolution measurement

Measured	Formula	Calculated
434.0495	$C_{20}H_{10}N_4O_8$	434.0499

Continuous lines indicate those transitions which are supported by the presence of a metastable peak.

the fact that 'F' is a trinitrobinaphthyl whilst 'P' is a tetranitrobinaphthyl.)

Since the presence of 4,4'- substitution has already been assumed (above) the evidence of adjacent peri (4,5-) substitution derived from the mass spectrum, leaves only the position of the fourth nitro group to be established. Unfortunately it is difficult to determine the position of this group from the spectra. In fact the best indication of its location comes from the further nitration of compound 'P' (see below). The results of this nitration suggest that the fourth nitro group is most likely sited at the 8 position. The spectra of 'P' are therefore considered hereafter in terms of the most likely substitution pattern: 4,4',5,8'-tetranitro-1,1'-binaphthyl.

When considering the mass spectra of other compounds the presence of either an 8' nitro group or a 4' nitro group (if sited peri to a hydrogen) has been associated with a distinctive loss of OH radicals. Although both of these structural features are thought to be present in 'P', any such expulsion of OH radicals is likely to become supressed (as with compound 'F'), because the adjacent peri nitro groups provide an alternative and particularly facile fragmentation route - as outlined above. Nevertheless, the M - 46 ion in 'P' appears to fragment to some extent by an alternative route - that is via expulsion of $NO_2^{\cdot}$, $OH^{\cdot}$ and $NO^{\cdot}$ - to give the ion at m/e 295 (18.2%). The first of these transitions is supported by a metastable peak at m/e 301.5:-

$$\underset{m/e388}{C_{20}H_{10}N_3O_6} \xrightarrow{\qquad\qquad} \underset{m/e342}{C_{20}H_{10}N_2O_4} \quad + \quad NO_2^{\cdot} \quad M^* = 301.5$$

Whilst in this pathway expulsion of the hydroxyl radical might conceivably occur by rearrangement of either the 8' nitro group (as in 'C-1'), or the 4' nitro group (as in nitronaphthalene); the latter possibility seems rather unlikely, as the 8' nitro group must greatly reduce electron density at the 5' position and so inhibit operation of the Beynon type mechanism (ie scheme 2:II pg 40). The ultimate fate of the ion at m/e 295 may possibly involve the expulsion of $NO^{\cdot}$ and CO to form the species $C_{19}H_9^+$ (m/e 237); this ion however is also likely to arise by the expulsion of a hydrogen radical from the ion at m/e 238 - a transition which is supported by the presence of a metastable peak at 236.0.

In summary therefore, the mass spectrum of 'P' clearly indicates the presence of adjacent peri substituted nitro groups but is insufficiently distinctive to permit full identification of the isomer. The spectrum is however consistent with the proposed structure of 4,4',5,8'-tetranitro-1,1'-binaphthyl.

The Infra-red Spectrum

The infra red spectrum of 'P' (see appendix) has a weak band at 3040cm^{-1} corresponding to aromatic C-H stretching, it also shows two very strong bands at 1535 and 1360cm^{-1} corresponding to the asymmetric and symmetric NO_2 stretching frequencies. It is however noticeable that neither of the bands appears to be split - a fact which is a little surprising in view of the proposed structure (4,4',-5,8'- substitution). Thus the 4'- nitro group should lie roughly coplanar with the aromatic system to which it is attached, whilst the remaining three nitro groups would be twisted well out of the aromatic plane (due to steric interaction). In consequence the 4'- nitro group would be expected to produce bands at lower frequency than the others, as it is more fully conjugated with the aromatic system. The anticipated values would be: 4'- NO_2 about 1520/1330cm^{-1} (ie at frequencies close to those observed in 4,4'-dinitro-1,1'-binaphthyl), 4-and 5-NO_2's about 1540/1350cm^{-1} (cf 4,4',5,5'-tetranitro-1,1'-binaphthyl) and 8'- NO_2 about 1530/1365-1350cm^{-1} (cf'C-1' and 'C-2'). Evidently in 'P' the 4-, 5- and 8'- nitro groups have stretching frequencies close to the anticipated values whilst the bands due to the 4'- nitro group occur at higher frequencies than expected. In consequence all the bands are coincident. The situation is thus analagous to that observed in 'D' with the 'isolated' 4- nitro group producing bands at an unexpectedly high frequency. Once again, as the spectrum was recorded in the solid phase, it is possible that crystal lattice effects influence the orientation of the nitro groups (cf compound 'D'). As a lack of nitro (N-O) band splitting has already been observed in the compound 'D', for which the structure (4,4',5- substitution) is quite certain, the occurrence of this phenomenon in the spectrum of 'P' cannot really cast doubt on the proposed structure of this compound.

As with the various other compounds which have been discussed, the C-H out of plane vibrations do not provide an unambiguous indication of structure. The low frequency region of the spectrum is in fact too complex to be of value.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of 'P' in DMSO shows two complex multiplets at τ1.22-1.74 (4H) and τ1.74-2.36 (6H). These signals fall in a region typical of nitroaromatic compounds and correlate quite well with the spectrum of 4,4',5,5'-tetranitro-1,1'-binaphthyl (τ 1.45-2.53 in DMSO).

Whilst the spectrum is too complex to interpret by inspection its division into two multiplets in the ratio 4H:6H is consistent with the proposed structure of 4,4',5,8'-tetranitro-1,1'-binaphthyl. Thus the low-field multiplet is attributable to the α-proton H_5' plus the three β-protons $H_{3/3'}$ and H_6 each of which is adjacent to a nitro group. The remaining protons are all attributable to the high-field multiplet; of these only one is an α-proton (H_8) - this must be shielded by the adjacent naphthyl moiety (cf 1,1'-binaphthyl etc) so that it resonates at 'high' field, the rest (H_2, H_2', H_6', H_7 and H_7') are all β-protons. Although H_7 is adjacent to a nitro group it appears once again that the steric hindrance of this group prevents substantial deshielding of the proton. In consequence H_7 remains in the 'high'-field multiplet. This result is consistent with the spectra of both 'C-1' and 'F'.

The Ultra Violet Spectrum

The UV spectrum of 'P' in methanol shows three maxima at λ 212nm, ϵ 5330m^{2}mole^{-1} (Ar $\pi \rightarrow \pi^*$), λ 237nm, ϵ 3220m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$) and λ 347nm, ϵ 1280m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ [107,108]). The aromatic $\pi \rightarrow \pi^*$ band thus occurs at slightly longer wavelength than that in either 1,8-dinitronaphthalene or 1,5-dinitronaphthalene (λ_{max} = 202nm[74] (methanol) and 205nm[113] (ethanol) respectively); this bathochromic shift presumably reflects the increased conjugation of the binaphthyl system. It is also interesting to compare the 212nm band* in 'P', with the analagous absorbtion in 'H' (4,4',5,5'-tetranitro-1,1'-binaphthyl); thus although the bands appear at similar wavelengths, the one in 'P' is rather less intense. This difference probably results from the steric hindrance associated with the 8 nitro group in 'P'. The molecule is thus effectively prevented from adopting anything like a planar configuration and in consequence must lose resonance between the two naphthalenic systems. This loss of resonance presumably accounts for the lower intensity of the band in 'P'.

A comparison of the spectrum of 'P' with those of the trinitrobinaphthyls ('C-2', 'D' and 'F') shows that the nitro $n \rightarrow \pi^*$ band has moved to shorter wavelength and increased in intensity, as would be expected [87] due to the introduction of an additional nitro group. The band at 237nm in 'P' is however less clearly defined than the analagous one in 4,4',5,5'-tetranitro-1,1'-binaphthyl. This difference presumably reflects the less symmetrical nature of 'P', as the various nitro groups will absorb at slightly different wavelengths depending upon the extent of their conjugation with the aromatic system. Thus for example the 4'- nitro group being the least subject to steric hindrance should absorb at longer wavelength than the others - so 'spreading' the absorbtion to longer wavelength. However as this explanation must imply the existance of greater conjugation between the 4'- nitro group and aromatic nucleus than exists for any of the other nitro groups it would seem to be at variance with the infra-red spectrum which shows no splitting of the nitro valence stretching bands. The explanation for this anomaly could simply lie in the fact that the spectra were recorded in different phases - the possible influence of crystal lattice structure on the infra-red spectrum has already been noted.

Further Nitration of 4,4',5,8'-Tetranitro-1,1'-binaphthyl (?) (Compound 'P')

Nitration of the compound 'P' in mixed acid, produced a product (designated as compound 'Y') which is believed to be 2,4,4',5,5',7,8'-heptanitro-1,1'-binaphthyl (ie identical with compound 'R'). However, the small scale of this reaction prevented the material from being fully purified. Thus although the IR spectrum of the product is indistinguishable from that of the compound 'R', the melting point of 'Y' (195-8°C) is significantly lower than that of the heptanitrobinaphthyl 'R' (206.5-8.5°C). The presence of impurities in 'Y' is confirmed by the mass spectrum which although somewhat similar to that of the compound 'R' (see appendix) indicates the presence of some contamination. For example, one peak which is obviously anomalous with respect to the spectrum of 'R' is that at m/e478. As this ion has a moderate intensity in the spectrum of 'Y' but not in that of 'R', it seems reasonable to attribute this ion to the presence of a trace impurity - possibly a hexanitrobinaphthyl (the precursor to 'R'?). If such an impurity is present then the ion at m/e 478 would represent its $(M - NO_2)$ ion. Such an impurity could also account for the greater abundance of fragment ions below m/e 523, which are evident in the spectrum of 'Y' as compared with that of compound 'R'. In spite of these discrepancies it is thought most likely that the compound 'Y' is identical with the compound 'R' and that this is therefore the major nitration product of the compound 'P'.

It is also pertinent to note that when the residues left from the isolation of compound 'Y' were examined by TLC, only a single spot was observed - at the appropriate Rf for the compound 'R'. Thus 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl (compound 'Q') was not detected in the product although the solvent system used to elute the sample should have separated the compounds 'R' and 'Q'. This observation is therefore consistent with the assumption above, that the major nitration product of compound 'P' is the heptanitrobinaphthyl 'R' - not the hexanitrobinaphthyl 'Q'. Thus bearing in mind the fact that nitration of 1,1'-binaphthyl in mixed acid is known to result primarily in 4,5,7-substitution (see later), the above results strongly suggest that the compound 'P' already contains an 8'-nitro substituent. It thus seems most likely that compound 'P' is 4,4',5,8'-tetranitro-1,1'-binaphthyl.

2.2.2. The Products of Nitration of 1,1'-Binaphthyl in Sulphuric and Nitric Acids

2.2.2.1. 4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl (Designated Compound 'Q')

This material was prepared in up to 50% yield by the nitration of 1,1'-binaphthyl in two stages - using i) acetic anhydride and nitric acid and ii) concentrated nitric and sulphuric acids. Although alternative nitration procedures also produced the compound 'Q', they all gave inferior yields to the above method. Thus the use of a mixture of nitric and acetic acids as the preliminary nitration medium led to a 44% yield of the hexanitrobinaphthyl, whilst a two stage reaction employing i) acetic and nitric acids and ii) acetic, nitric and sulphuric acids produced only 32% of the compound 'Q'.

4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl has also been prepared by the nitration of 4,4',5,5'-tetranitro-1,1'-binaphthyl in mixed acid (yields ranged up to 37.3%). Although of little preparative value this procedure was of value in interrelating the structures of the compounds 'H' and 'Q'.

The spectroscopic data available for the compound 'Q' is quite adequate to establish its structure, the data is considered below.

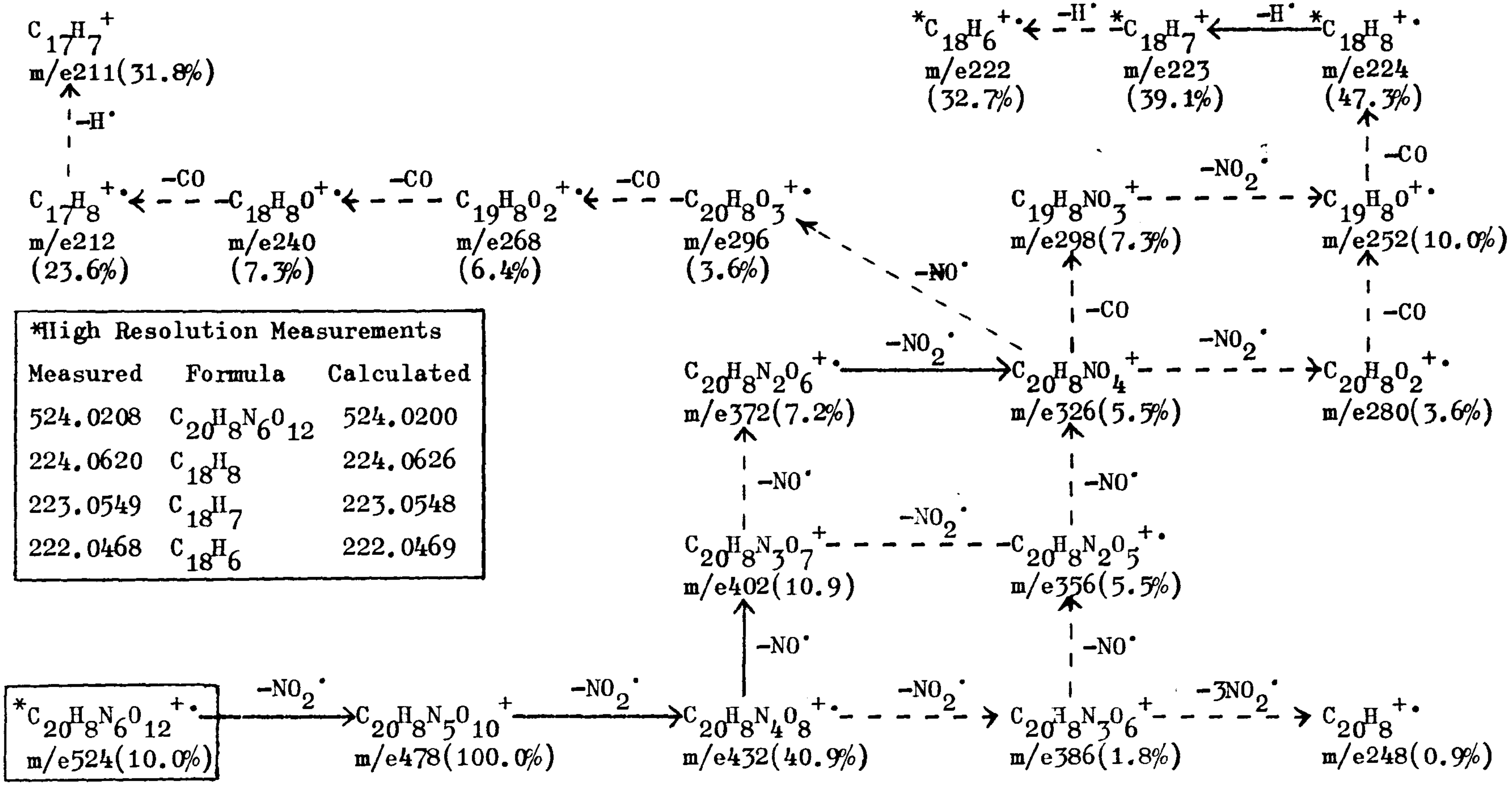
The compound 'Q' analyses correctly for a hexanitrobinaphthyl and shows a molecular ion at m/e 524.0208 in its mass spectrum corresponding to $C_{20}H_8N_6O_{12}$ (calculated 524.0200). The infra-red spectrum shows bands consistent with nitro stretching frequencies but indicates the presence of no other fuctional groups. The compound is therefore clearly a hexanitrobinaphthyl. The best structural evidence comes from the mass and PMR spectra, these are therefore considered first.

The Mass Spectrum

The major ions in the mass spectrum of 'Q' are indicated in the scheme 2:XV. A full list of relative intensities and a bar diagram are given in the appendix. Whilst the spectrum shows many features typical of a nitroaromatic compound ($M - NO_2$, $M - 2NO_2$ etc and interim ions of low intensity corresponding to M - O, M - NO etc) the most significant feature of the spectrum is the weak molecular ion (10.0%) and the particularly intense M - 46 ion (the base peak of the spectrum). As has been previously discussed this feature is indicative of the presence of adjacent peri substituted nitro groups. However in the spectrum of 'Q' not only is the M - 46 ion intense, but so is the M - 92 ion (m/e 432:40.9%). An examination of the spectrum reveals that the fragmentation pattern is consistent with the presence of two sets of adjacent peri substituted nitro groups (ie 4,4',5,5'- substitution). Thus, on the basis of the most intense ions in the spectrum, the molecular ion appears to fragment via sequential loss of $2NO_2^{\bullet}$, $2NO^{\bullet}$, $2NO_2^{\bullet}$ and 2CO to give an intense ion ($C_{18}H_8^{+\bullet}$) at m/e 224 (47.3%). (The identity of this ion has been confirmed by high resolution measurement.) This species may subsequently expell one or two hydrogen radicals to produce ions at m/e 223 ($C_{18}H_7^+$: 39.1%) and m/e 222 ($C_{18}H_6^{+\bullet}$: 32.7%), (see scheme 2:XV for metastable peaks). (Both of these ions have also been confirmed by high resolution measurements.) As would be expected the ions attributable to ($M - 3NO_2$), ($M - 4NO_2$), ($M - 5NO_2$) and ($M - 6NO_2$) occur with very low probability (1.8%, 0.9%, 1.4% and 0.9% respectively). The fragmentation sequence of 'Q' is thus very similar to that observed in 4,4',5,5'-tetranitro-1,1'-binaphthyl, except that in the former compound the two 'additional' nitro groups are lost just prior to expulsion of carbon monoxide. In this respect therefore the spectrum is similar to those of both 'F' and 'P'. All three compounds thus exhibit the

Scheme 2:XV

Fragmentation Pattern for the Mass Spectrum of 4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl (Compound 'Q')



*High Resolution Measurements

Measured	Formula	Calculated
524.0208	$C_{20}H_8N_6O_{12}$	524.0200
224.0620	$C_{18}H_8$	224.0626
223.0549	$C_{18}H_7$	223.0548
222.0468	$C_{18}H_6$	222.0469

Continuous lines indicate those transitions which are supported by the presence of a metastable peak.

basic fragmentation pattern characteristic of adjacent peri nitro groups, (cf 1,8-dinitronaphthalene), but in each case the spectrum is modified by the loss of the additional nitro groups - prior to the expulsion of neutral carbon monoxide.. The spectrum of 'D' is once again essentially similar, but, as discussed earlier it involves expulsion of the 'extra' nitro group as $OH^{\bullet}$ + $NO^{\bullet}$ rather than as $NO_2^{\bullet}$. It thus appears that all the compounds isolated so far - which contain adjacent peri substituted nitro groups - produce rather similar primary fragmentation sequences in their mass spectra.

Based on the forgoing discussion the main inference to be drawn from the mass spectrum of 'Q' is that the compound contains 4,4',5,5'- substitution. This is consistent with the fact that 'Q' can be prepared by the nitration of 4,4',5,5'-tetranitro-1,1'-binaphthyl.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of 'Q' has been recorded in both acetone and DMSO (see appendix), whilst there are significant changes of chemical shift between the two solvents, the coupling pattern remains unchanged and is clearly discernable in both. Thus the spectrum comprises two AB quartets with coupling constants of 2.0 and 7.7Hz respectively:-

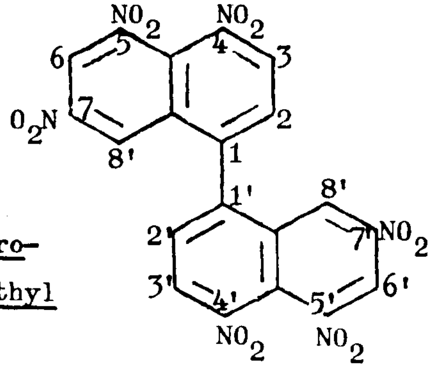
Acetone.

τ 0.95 doublet, J = 2.0Hz (2H); τ 1.07 doublet, J = 2.0Hz (2H); τ 1.13 doublet, J = 7.7Hz (2H); τ 1.63 doublet, J = 7.7Hz (2H).

DMSO

τ 1.01 doublet, J = 2.0Hz (2H); τ 1.21 doublet, J = 7.7Hz (2H); τ 1.44 doublet, J = 2.0Hz (2H); τ 1.90 doublet, J = 7.7Hz (2H).

Assignment of a structure to 'Q' is quite straightforward because the positions of four substituents are already known (ie 4,4',5,5'-). Thus as coupling constants of around 8Hz are normally associated, in aromatic systems, with ortho coupled protons, whilst those of about 2Hz are associated with meta coupled protons[115]; there is only one possible structure for the compound 'Q' - it must be 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl.



4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl

The protons $H_{2/3}$ are thus assigned to the doublets at τ1.13/1.63 (acetone) (J = 7.7Hz) whilst the protons $H_{6/8}$ produce the doublets at τ 0.95/1.07 (J = 2.0Hz). It seems probable that the 3- substituted protons will resonate at lower field than the 2-substituted protons because they are sited ortho to a nitro group. Thus $H_{3/3'}$ should give rise to the doublet at τ 1.13 and $H_{2/2'}$ to that at τ 1.63. Also as the protons $H_{6/6'}$ are each sited 'inbetween' two ortho nitro groups, they are likely to resonate at lower field than $H_{8/8'}$ (which are 'ortho' to just one nitro group and 'para' to another). Thus the doublet at τ 0.95 may be assigned to the protons $H_{6/6'}$ and that at τ1.07 to $H_{8/8'}$. It is pertinent to note here that all the protons which are sited ortho to a nitro substituent, form a group at low field - as would be expected - whilst $H_{2/2'}$ (with no ortho nitro substituents) resonate at significantly higher field.

Comparison of the spectrum of 'Q' with that of 4,4',5,5'-tetranitro-1,1'-binaphthyl ('H') shows that the quartet due to the protons $H_{2/3}$ has moved downfield (by about 0.3ppm), which is reasonable in view of the presence of additional nitro groups. The coupling constant of these protons however, remains essentially unchanged - between the two compounds - as would be expected in view of the similarity of their structures. The protons $H_{6/6'}$ in 'Q' resonate about 0.8ppm downfield of the analagous protons in the tetranitrobinaphthyl; this is consistent with the substitution of a second nitro group 'ortho' to these protons. A shift of similar order is evident for the protons $H_{8/8'}$ and this may also be attributed to the introduction of an 'ortho' nitro group.

The spectrum in DMSO may be assigned using the same considerations as those employed above; in this case the protons $H_{2/2'}$ resonate at τ1.90, $H_{3/3'}$ atτ1.21, $H_{6/6'}$ at τ1.01 and $H_{8/8'}$ atτ1.44. A comparison of this spectrum with that of 4,4',5,5'-tetranitro-1,1'-binaphthyl (in DMSO) shows essentially the same variations that are evident in acetone although the change of solvent has some effect on the magnitude of the shifts observed between the two compounds.

The Infra-red Spectrum

The infra-red spectrum of 'Q' (see appendix) shows a weak band at 3100cm^{-1}, which corresponds to aromatic C-H stretching, it also has very strong bands at 1550 and 1345cm^{-1} due to the asymmetric and symmetric nitro stretching frequencies. The high frequency nitro band shows a secondary maximum at 1530cm^{-1}, but no such splitting is evident in the low frequency band. Since the changes of nitro stretching frequencies, which are associated with a twisting of the nitro group out of the aromatic plane, are more noticeable for the symmetric than for the asymmetric band,[86a] the above data suggests that the 'double' 1550/1530cm^{-1} band is not the result of differently orientated nitro groups. Such a conclusion is surprising in the present case, as the 4 and 5 nitro groups are sterically hindered, whilst the 7 nitro groups are not. (This is clearly supported by the UV spectrum - see below). It appears that the lack of splitting in the symmetric band of 'Q' is anomalous, although it is not without precedent; thus whilst the IR spectrum of o-dinitrobenzene produces two maxima for its symmetric nitro stretching vibration (at 1368/1350cm^{-1}), that of 1,2,4-trinitrobenzene only produces one (at 1348cm^{-1}).[87] Explanation of these anomalies may lie in the fact that the symmetric nitro stretching vibration is subject to coupling effects.[64b,86a] Thus in aromatic compounds, where such coupling probably involves some ring modes,[86a] a change of ring substitution (which modifies the latter) is likely to affect the symmetric nitro stretching frequency - even if there is no change in the force constants or electronic arrangements of the nitro group itself.[86a] Since coupling through resonance effects will be more pronounced for an unhindered nitro group than for a hindered one, the frequency changes produced in each should be different. Whilst the nature of these changes tends to be rather erratic,[86a] in 'Q' they presumably narrow the frequency difference between the 'hindered' and 'unhindered' nitro groups; in consequence the two bands are not resolved. (There is some evidence to suggest that adjacent peri nitro groups form a smaller angle with the aromatic system than do 8- nitro groups (see the PMR spectrum of 'R'). If this is the case the difference of frequency between a 'hindered' and an 'unhindered' nitro group in a compound such as 'Q' might be considerably smaller than that observed in compounds containing an 8- nitro substituent. However since the PMR spectrum of 'R' was recorded in solution whilst all of the IR spectra were recorded in solid phase, this may not be a fair comparison. Thus the nitro stretching frequencies in other compounds eg 'H' suggest that deviation from planarity of adjacent peri substituted nitro groups is considerable - in the crystalline phase.

The low frequency region in the spectrum of 'Q' is fairly complex and proves once again to be of little value for structure determination.

The Ultra Violet Spectrum

The UV spectrum of 'Q' in methanol (see appendix) shows five maxima at λ 210nm, ϵ 6570m^2mole^{-1} (Ar $\pi \rightarrow \pi^*$), λ 230nm (sh), ϵ 5060m^2mole^{-1} (NO_2 $n \rightarrow \pi^*$), λ 266nm, ϵ 3820m^2mole^{-1} (NO_2 $n \rightarrow \pi^*$), λ 326nm, ϵ 1550m^2mole^{-1} and λ 358nm (sh), ϵ 1330m^2mole^{-1} (both NO_2 $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ [107,108]). It is immediately evident that in this spectrum there are two absorption maxima in the region normally associated with the nitro $n \rightarrow \pi^*$ transition. This feature is readily explained however in terms of steric hindrance. Thus whilst the adjacent peri nitro groups are unable to assume coplanarity with the aromatic system - for steric reasons - there is no such restriction upon the 7- nitro groups. In consequence the 4 and 5 nitro substituents (suffering reduced conjugation with the aromatic system) absorb at shorter wavelength than those in the 7 positions. The anticipated wavelength for the adjacent peri nitro groups is about 233nm (ie the measured value in 4,4',5,5'-tetranitro-1,1'-binaphthyl). The observed position of 230nm presumably reflects a slight hypsochromic shift due to the presence of additional nitro groups.[87] Since the 7- nitro groups are expected to absorb at longer wavelength than this, they can reasonably be assigned to the band at 266nm. It is evident however that this band occurs at a longer wavelength than has been observed for any of the nitrobinaphthyls discussed above. The spectrum therefore provides positive evidence that (peri) nitro groups in the binaphthyl system are significantly twisted out of the aromatic plane (as suggested earlier). Consider for example the case of 4,4'-dinitro-1,1'-binaphthyl which produces a band due to the nitro $n \rightarrow \pi^*$ transition at 255nm. Whilst this band is clearly at longer wavelength than that observed for the hindered nitro groups in either 'Q' or 4,4',5,5'-tetranitro-1,1'-binaphthyl (230/233nm respectively), it is clearly at shorter wavelength than the band due to unhindered nitro groups in 'Q' (266nm). This suggests therefore that the nitro groups in 4,4'-dinitro-1,1'-binaphthyl are twisted significantly out of the aromatic plane, but not so drastically as occurs for the compounds with adjacent peri substituted nitro groups.

The various assignments made above correlate well with the spectra of the nitronaphthalenes, thus the unhindered nitro group in β-nitronaphthalene produces a nitro $n \rightarrow \pi^*$ band at about 260nm (methanol)[74] whilst the partially hindered α-nitronaphthalene has the same band at 245nm.[74] In the case of 1,8-dinitronaphthalene the band shifts to 231nm.[74]

The long wavelength maximum in the spectrum of 'Q' is very ill defined (λ_{max} about 326nm) but presumably corresponds to the 333nm band in 4,4',5,5'-tetranitro-1,1'-binaphthyl. That is, it probably arises from the sterically hindered nitro groups (NO_2 $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ [107,108]). If this is correct it is logical to expect the unhindered 7 nitro groups to produce a secondary band at longer wavelength. The spectrum does in fact have a shoulder at 358nm which appears to be too sharply defined to simply represent the decline of the 333nm band (cf the spectra of the other nitrobinaphthyls). If this shoulder is due to a completely unhindered 7- nitro group it should occur at longer wavelength than the bands in any of the nitrobinaphthyls discussed above. This is in fact so (eg 4,4'-dinitro-1,1'-binaphthyl produces a band at 350nm).

Once again the assignments correlate quite well with the spectra of the nitronaphthalenes; thus the 'unhindered' nitro group in β-nitronaphthalene produces a band at 355nm whilst the band in α-nitronaphthalene occurs at 340nm. In the case of 1,8-dinitronaphthalene λ_{max} is even shorter at 314nm.

In view of the foregoing discussion further evidence is now available regarding the structures of the various nitrobinaphthyls detailed above. Thus in several cases where the structure of a compound is uncertain ('C-1', 'C-2', 'F' or 'P') it is now possible on the basis of the UV evidence to rule out the presence of a truly unhindered (ie 3,6 or 7 substituted) nitro group. If such were present they would be clearly evident by the presence of a 'long λ' nitro $n \rightarrow \pi^*$ band in the UV. The absence of any such bands in the various UV spectra, necessarily restricts the possible sites of substitution to peri positions; in each case such an interpretation is consistent with the structures which have already been proposed.

Crystallisation of the Compound 'Q' from Toluene

One interesting fact which was observed during the isolation of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl was that crystallisation of this compound from acetone/toluene (a particularly good method of purification), yielded colourless needles of 'Q', which were apparently contaminated with toluene. (Contrast the dark brown crystals which form from acetic acid.) Thus after drying for about one hour at 90°C these needles were shown (by PMR) to contain about 0.69 moles of toluene per mole of hexanitrobinaphthyl. This toluene was held quite tenaciously, as after an additional 24hrs at 160°C (under reduced pressure) the ratio was only reduced to 0.65 moles of toluene/mole of hexanitrobinaphthyl. The best method for removing the toluene was found to be via recrystallisation of the material from acetone/acetic acid.

The melting point of crystals containing toluene is considerably lower (210-220°C - phase change at 194-198°C) than that of the pure hexanitrobinaphthyl (271.5-275°C) and it is pertinent to note that the former material dissolves only slowly in acetone, which is in marked contrast to the pure material (crystallised from acetic acid) which dissolves instantly in the same solvent.

At the present time it is unclear whether the retention of toluene by 'Q' is due to occlusion of the hydrocarbon within the crystal lattice of the hexanitrobinaphthyl, or whether it results from the formation of an addition compound.

2.2.2.2. 2,4,4',5,5',7,8'-Heptanitro-1,1'-binaphthyl (Probable Structure) (Designated Compound 'R')

This material has been isolated (approx 3%) from the two stage nitration of 1,1'-binaphthyl using i) acetic anhydride and nitric acid and ii) fuming nitric acid and concentrated sulphuric acid boiling under reflux. It has also been isolated in small yield from the treatment of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl in fuming nitric and concentrated sulphuric acids at high temperature. In the later case the compound is thought to be derived from an impurity present in the original substrate (see below). (The main bulk of the hexanitrobinaphthyl is slowly oxidised to water soluble products under these conditions.)

The mass spectrum of 'R' appears to have a molecular ion at m/e 569.0042, corresponding to $C_{20}H_7N_7O_{14}$ (calculated 569.0052). The IR spectrum shows bands consistent with nitro stretching frequencies, but no evidence for the presence of any other functional groups. It therefore seems likely that the compound 'R' is a heptanitrobinaphthyl. The analysis of compound 'R' is however incorrect for a heptanitrobinaphthyl, as the analytical figures fall inbetween those calculted for a heptanitrobinaphthyl and a hexanitrobinaphthyl. Nevertheless, the compound 'R' is thought to be a heptanitrobinaphthyl and the anomalous analytical data is attributed to decomposition of the material prior to analysis and/or the presence of impurities in the sample of 'R'.

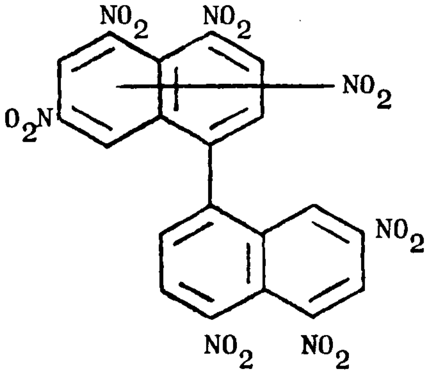
Since the compound 'R' was prepared at one stage from the nitration of 4,4',5,5',7,7'-hexanitrobinaphthyl it was originally assumed that it contained 4,4',5,5',7,7'- substitution and that the seventh nitro group would probably occupy a 2 position. It now appears that this is not the case. As the PMR spectrum of 'R' is particularly significant in establishing this fact, this spectrum is the first to be considered.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of 'R' (see appendix) in acetone comprises one singlet at τ 0.69 (1H) and three sets of AB quartets: τ 0.71 doublet, J = 1.8Hz (1H), τ 0.92 doublet, J = 1.8Hz (1H), τ 1.15 doublet, J = 8.3Hz (1H), τ 1.71 doublet, J = 8.3Hz (1H), τ 1.23 doublet, J = 8.3Hz (1H), τ 1.62 doublet, J = 8.3Hz (1H).

There are considerable changes in the chemical shifts of the various protons when the spectrum is recorded in DMSO, but the splitting pattern remains unaltered. The spectrum is as follows:- τ 0.62 singlet (1H), τ 0.70 doublet, J = 1.8Hz (1H), τ 1.14 doublet, J = 1.8Hz (1H), τ 1.11 doublet, J = 8.3Hz (1H), τ 1.18 doublet, J = 8.3Hz (1H), τ 1.54 doublet, J = 8.3Hz (1H), τ 1.83 doublet, J = 8.3Hz (1H).

Whilst the various signals fall in the anticipated region for a polynitroaromatic compound, the observed splitting patterns do not appear consistent with 4,4',5,5',7,7',x- substitution. Thus if the 'x' substituent was in either the 2- or 3- positions, two dissimilar 'meta' coupled AB quartets should be evident, due to the protons $H_{6/8}$ and $H_{6'/8'}$.

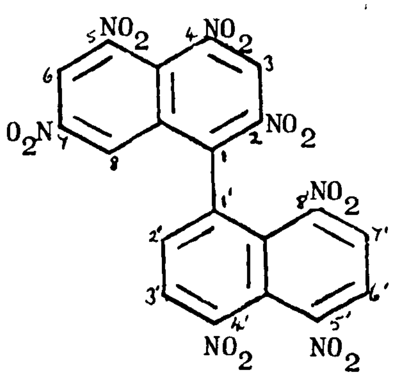


4,4',5,5',7,7',x-heptanitro-1,1'-binaphthyl

In fact this is not observed and only one 'meta coupled' AB quartet is evident. Although it seems unlikely, an exact coincidence between the two sets of signals is conceivable; this event must be ruled out however by the integration, which clearly shows the meta coupled signals to be due to just two hydrogens not four. In any event if x was the 2 or 3 position it would not be possible to explain the two sets of 'ortho' AB quartets which are observed in the spectrum. The possibility of 4,4',5,5',7,7',x- substitution with x = 2 or 3 can therefore be eliminated.

If the compound 'R' is a derivative of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl the only remaining possibilities are that x corresponds to the 6 or 8 positions. Substitution at either of these sites might theoretically account for the observed splitting pattern in the PMR spectrum, but both possibilities appear unlikely on other grounds. Thus the 6 and 8 positions are the most deactivated sites in the molecule - towards electrophilic substitution - and both are subject to severe steric hindrance. Further, the presence of ortho nitro groups in the compound 'R' would be incompatible with the structure of its decomposition product 'S' (see later). It is thus unlikely that the compound 'R' contains 4,4',5,5',7,7'- substitution. The spectrum is therefore consistent with the view expressed above that 'R' is not a nitration product of 'Q', but arises instead from the nitration of an impurity in the original substrate. An alternative possibility is that the heptanitrobinaphthyl 'R' is formed via the rearrangement of compound 'Q'. Whilst such a route seems feasible it is thought less likely, in the light of experimental evidence, than the production of 'R' via nitration of an impurity. Thus the yields of 'R' which were obtained from 'nitration' of 'Q' varied somewhat erratically and showed no apparent correlation with the reaction conditions (see table 4-4 pg193). In contrast it appears significant that the greatest yield of 'R' (7.4%) was obtained when least purification of the substrate was carried out, whilst in a reaction utilising a specially purified sample of 'Q', it proved impossible to positively identify any of the compound 'R' (table 4-4).

Whilst it is possible, by consideration of all the available evidence for 'R', to narrow the various possibilities down to a single 'most likely' structure there is insufficient data available at the present time to provide unambiguous identification of this compound. The various pieces of evidence relating to the structure are presented in the next few sections. Since the PMR spectrum of 'R' could fit several different structures, it is convenient to consider it in the light of some other evidence - which will be discussed more fully at a later stage. The first piece of evidence in this category is derived from the structure of compound 'S' - which is believed to be a decomposition product of 'R'. Thus as the compound 'S' apparently contains two sets of adjacent peri substituted nitro groups (see later), it is likely that its precursor - the compound 'R' - also contains these groupings. The second piece of evidence comes from the mass spectrum of 'R' which has been interpreted as supporting the presence of 2,8'- substitution (see below). It thus seems probable that the compound 'R' contains 2,4,4',5,5',8'- substitution; in this event there is only one possible site for the seventh nitro group, if the compound is to fit the PMR spectrum - that is the 7- position. The proposed structure for 'R' is therefore 2,4,4',5,5',7,8'-heptanitro-1,1'-binaphthyl. This structure seems compatible with the PMR spectrum both in terms of splitting pattern and the observed chemical shifts. Thus the singlet at τ 0.69 (acetone) may be assigned to the uncoupled proton



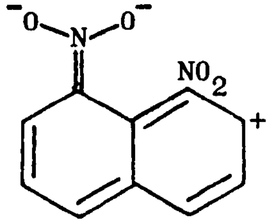
2,4,4',5,5',7,8'-Heptanitro-1,1'-binaphthyl

H_3, which resonates at very low field primarily due to deshielding by the two ortho nitro groups. (Inter-ring coupling is too small to be resolved on the spectrometer used for the present work.) Since electron withdrawl from this site is also possible (mesomerically) by the 5 and 7 nitro groups, these substituents should also contribute to the overall deshielding of the proton.

The AB quartet at τ 0.71/0.92 is readily assigned to the protons $H_{6/8}$ as it has a coupling constant (1.8Hz) of the order associated[115] with meta coupled aromatic protons. The low field at which these protons resonate is consistent with their positioning ortho/ortho and ortho/para to two nitro groups. The shifts for these protons also correlate fairly well with those observed in 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl - for the analagous meta coupled protons $H_{6/8}$ (τ 0.96/1.12, J = 1.8Hz). There is however a small downfield shift (in 'R') as would be expected due to the presence of four nitro groups in the naphthyl moiety of 'R', compared with only three in that of the hexanitrobinaphthyl. Since the deshielding of H_6 is likely to be greater than that of H_8 due to its closer proximity to the 5- nitro group, this proton should produce the signal at τ 0.71 and the 8- proton that at τ 0.92.

The remaining two sets of AB quartets in the spectrum of 'R' (τ 1.15/1.71 and τ 1.23/1.62) may be assigned to the protons $H_{2'}$, $H_{3'}$, $H_{6'}$ and $H_{7'}$. In each case the coupling constants (8.3Hz) are of the order expected for ortho coupled aromatic protons.[115] These values of J are a little greater than those observed in 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl, but this presumably reflects the different substitution of the binaphthyl moiety. (Small changes in the coupling constants of naphthalene have been observed with the introduction of various substituents.[81]) The chemical shifts of these protons however correlate quite well with the shifts observed for H_2 and H_3 in the hexanitrobinaphthyl (τ 1.14/1.63), (small changes are to be expected due to the different patterns of substitution in the two compounds).

A tentative assignment of the various doublets to specific protons in 'R' can be made by correlating the observed chemical shifts with the anticipated electron densities at various sites in the molecule. Thus as the protons H_3' and H_6' are both sited ortho to a nitro group and are also subject to mesomeric electron withdrawl by the second 'peri' nitro group - structure (2-21), it seems likely that these protons will account for the doublets at τ 1.23/1.15. As there



(2-21)

are two nitro groups in the ring containing H_6' but only one in that containing H_3', the resonance at τ 1.15 is most likely attributable to the former proton, whilst that at τ 1.23 probably comes from the latter.

It is pertinent to note that as neither of the peri nitro groups can be completely coplanar with the aromatic system their capacity for mesomeric electron withdrawl must be somewhat reduced. Nevertheless adjacent peri nitro groups can still produce considerable deshielding of a proton sited ortho to one of them. Thus for example in 1,8-dinitronaphthalene the protons H_2 and H_7 resonate at τ 1.70ppm (acetone)[71,72] which represents a downfield shift of 0.79ppm compared with naphthalene itself (H β = τ 2.49, acetone).[71,72]

The remaining doublets in the spectrum of 'R' (τ 1.62 and τ 1.71) must be assigned to the protons H_7' and H_2'. Presumably the signal at lower field is due to H_7', as this proton is sited ortho to a nitro group; the resonance at τ 1.71 must then be due to $H_{2'}$. Since this doublet (at τ 1.71) occurs at higher field than any other signal in the spectrum, its assignment to $H_{2'}$ is entirely logical because this proton is the least subject to deshielding by neighbouring nitro groups. The assignment of the signal at τ 1.62 to H_7' however appears rather less satisfactory, as this is about 0.4-0.5ppm upfield of the protons $H_{3'}/_{6'}$ which are similarly sited 'ortho' to a nitro group. The explanation for this presumably lies in the severe steric hindrance of the 8'-nitro group which must force it to orientate almost perpendicular to the aromatic system. In consequence the group produces less deshielding of H_7' because the effects of both resonance and its anisotropic magnetic field are reduced.[78] It is interesting to note that this assignment suggests the presence of greater steric hindrance for an 8- nitro group than is present for adjacent peri substituted nitro groups. This could indicate that the latter groups form a significantly smaller angle with the aromatic system than do the former. (Such a conclusion would be consistent with other data and could help to explain the absence of splitting for the NO_2 stretching bands in the IR spectrum of compound 'Q'.) Consideration of the steric factors involved - using molecular models - suggests that this is a reasonable conclusion to draw, although it should be noted that a number of other factors (eg specific solvent interaction) can also influence the chemical shifts of individual protons.

The spectrum of 'R' in DMSO may be analysed in an essentially similar fashion to that applied above. This leads to the following assignments: τ 0.62 singlet: H_3, τ 0.7 doublet: H_6, τ 1.11 doublet: H_6', τ 1.14 doublet: H_8, τ 1.18 doublet: H_3', τ 1.54 doublet: H_7', τ 1.83, doublet: H_2'. In general the correlation of chemical shifts noted above between 'R' and 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl are also maintained in DMSO - although there are some small variations in the figures.

The Mass Spectrum

The mass spectrum of compound 'R' (see appendix) is dominated by a single very intense ion at m/e 523 (M - NO_2) (100%). This single peak dwarfs all the remaining ions in the spectrum - none of which exceeds a relative intensity of about 12%. The major ions in the spectrum are summarised in the scheme 2:XVI. The intense M - 46 ion, but weak molecular ion (0.5%), are clearly reminiscent of the pattern resulting from adjacent peri nitro groups. Indeed the various data relating to 'R' makes it difficult to envisage any structure for this compound which does not contain two sets of adjacent peri nitro groups (see particularly the structure of compound 'S' later). The mass spectrum however is not readily compatible with two pairs of such groups, as the ion at m/e 477 (M - $2NO_2$) is of extremely low abundance (0.4%) whilst that at m/e 417 (M - $2NO_2$ - 2NO) has an intensity of only 1.9%. (This contrasts eg with the spectrum of 'H' in which both the corresponding ions have quite high intensities (M - $2NO_2$) : 34.4% and (M - $2NO_2$ - 2NO) : 35.5%.) Nevertheless the 'anticipated' fragmentation pattern (sequential loss of $2NO_2^{\cdot}$, $2NO^{\cdot}$, $3NO_2^{\cdot}$ and 2CO) probably does occur to some extent to yield finally the ion at m/e223 : 8.6% (which presumably expels a hydrogen radical to form the ion at m/e 222 : 11.6%).

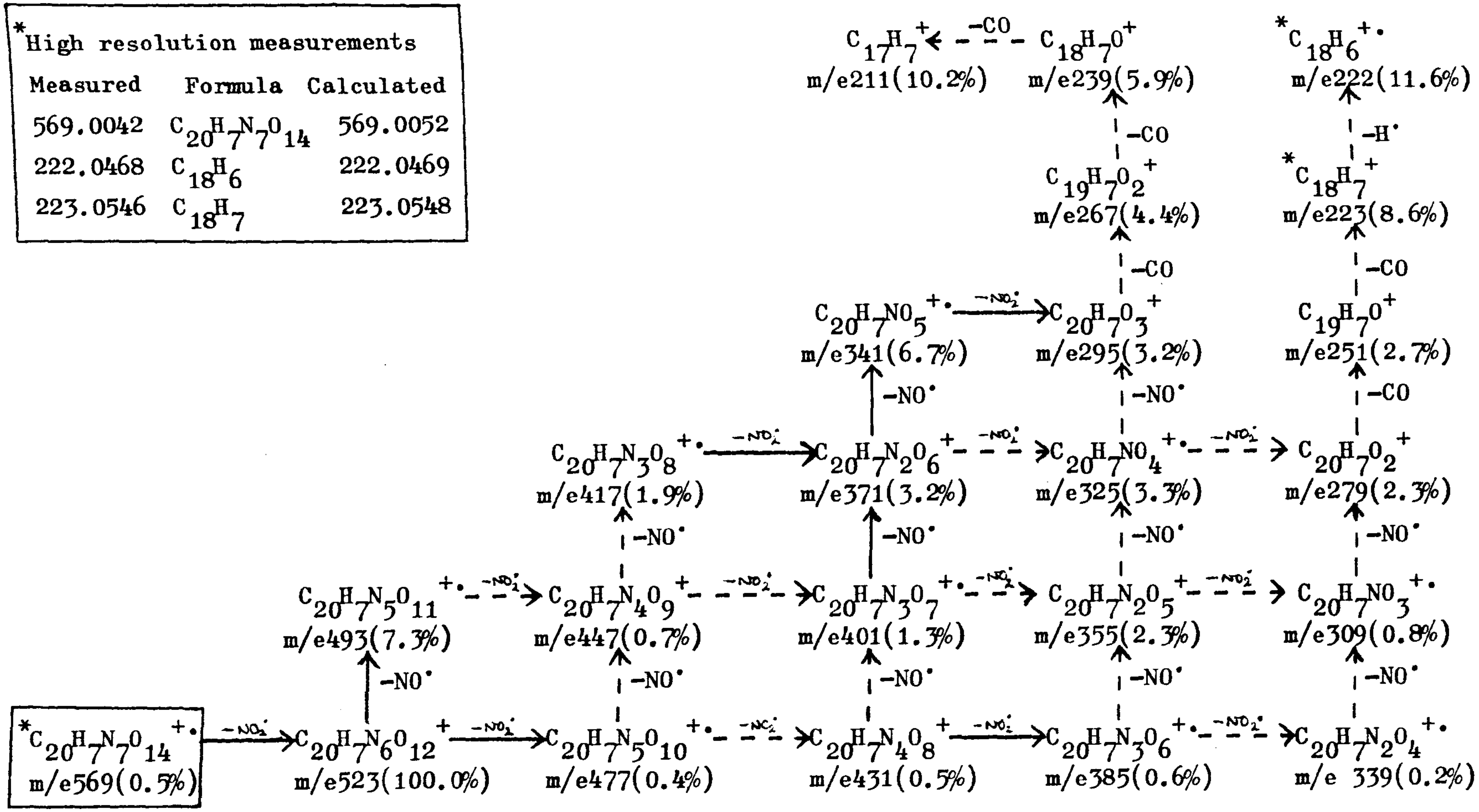
It is possible that the unexpected pattern of intensities which is observed is the result of differences in relative stability between the two sets of adjacent peri nitro groups (with respect to the explulsion of a nitro radical). This could be brought about by the dissimilar patterns of substitution present in the two naphthyl moieties. However an alternative explanation for the spectrum is that another sterically crowded pair of nitro groups is present in 'R' which can expel a nitro radical even more readily than the adjacent peri nitro groups. In fact this explanation is considered the more likely - particularly in view of the formation of compound 'S' from 'R' (see later). Consider for example the presence of both 2 and 8' substituents in a binaphthyl nucleus; clearly extensive interaction must occur between these groups and this interaction would become particularly severe under the energetic conditions of mass spectrometry.

Scheme 2:XVI

Fragmentation Pattern for the Mass Spectrum of 2,4,4'5,5',7,8'-Heptanitro-1,1'-binaphthyl (Compound 'R')

*High resolution measurements

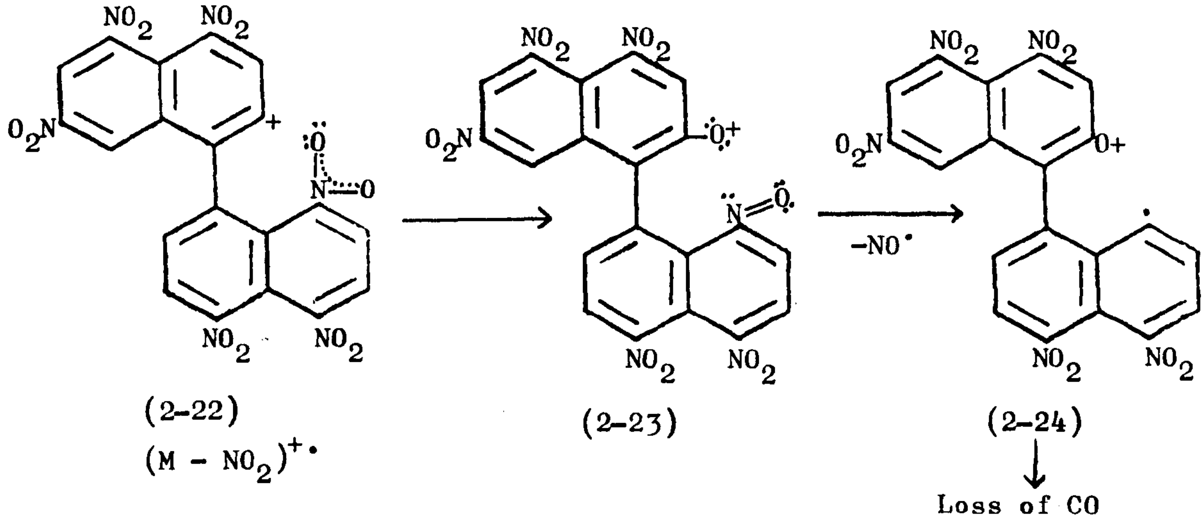
Measured	Formula	Calculated
569.0042	$C_{20}H_7N_7O_{14}$	569.0052
222.0468	$C_{18}H_6$	222.0469
223.0546	$C_{18}H_7$	223.0548



Continuous lines indicate those transitions which are supported by the presence of a metastable peak.

In consequence a molecular ion containing such substitution might well be expected to expel one of these nitro groups very readily - and in preferance to any other. It is thought that 'R' does in fact contain 2,8'- substitution and that it is precisely this effect which leads to the intense M - 46 ion. Whilst it is possible to propose other substitution patterns that might give rise to a similar effect (eg the presence of two 'ortho' nitro groups) the structure of product 'S' (obtained from the decomposition of 'R') suggests that these are unlikely (see later).

In view of the above discussion it seems likely that the M - 46 ion in 'R' will have predominantly a structure of the type (2-22). It is interesting to note that a rearrangement of this structure could occur (2-22)⟶(2-24) leading to the subsequent expulsion of NO˙ and CO, in a fashion reminiscent of that observed in 1,8-dinitronaphthalene (although the rearrangement would be less favourable in the present case as the donor oxygen in (2-22) is not rigidly held in close proximity to the positive charge). In this event there would be three pairs of nitro groups in 'R', each of which could fragment through initial loss of a nitro radical followed by explusion of NO˙ and CO. These fragmentations could thus explain the formation of the ion at m/e211 (10.2%) which presumably forms via the sequential loss from the molecular ion of $3NO_2^{\cdot}$, $3NO^{\cdot}$, $NO_2^{\cdot}$ and 3CO (cf the fragmentation sequence observed for compound 'Q'). Expulsion of NO˙ and CO may also occur via isomerisation of the nitro groups to the nitrite[77]



(2-22)
$(M - NO_2)^{+\cdot}$

(2-23)

(2-24)
↓
Loss of CO

but it seems unlikely that this route could, alone, account for the intensity of the ion at m/e 211. Thus although of low relative abundance this ion is in fact the third most intense ion in the spectrum.

The Infra Red-Spectrum

The infra-red spectrum of 'R' (see appendix) shows a fairly well defined band at 3030cm^{-1} corresponding to the aromatic C-H stretching frequency. The spectrum also shows two very strong absorptions due to NO_2 (N-O) stretching vibrations; of these the higher frequency (asymetric stretching) band is split into two maxima (at 1550/1535cm^{-1}) whilst the symmetric band produces only a single maximum at 1350cm^{-1}. In view of the proposed structure of 'R' this lack of splitting in the symmetric band seems surprising, as the molecule should clearly contain both 'planar' and 'non-planar' nitro groups. The situation seems analagous however to that already discussed for the compound 'Q'; thus if splitting of the assymetric band in 'R' is attributed to differently orientated nitro groups, the absence of splitting in the 'symmetrical' band might once again result from coupling of this vibration with the various ring modes.

The low frequency region of the spectrum shows bands in the anticipated regions for both one and two 'adjacent substituted hydrogens' (900-860 and 860-800cm^{-1} respectively[64a]). There are however no bands of even moderate intensity in the region normally associat-ed with the presence of three adjacent hydrogens (750-810cm^{-1}). Whilst both of these observations correlate well with the proposed structure of the compound, it is uncertain how reliable the evidence is from this region of the spectrum - thus rather erratic variations sometimes occur, as discussed earlier. In fact in the present case it is impossible even to exclude the presence of four adjacent hydrogens (on the basis of the IR spectrum alone) - as there is a strong band at 740cm^{-1}. Nevertheless the absence of a specific band, in the spectrum of a complex molecule, is likely to be more reliable for structural determination than is its presence; in the present case however, the point is of little consequence as it is almost inconceivable that there could be three or four adjacent hydrogens in the compound 'R'.

The Ultra Violet Spectrum

The UV spectrum of 'R' shows five maxima at λ214nm, ϵ 5090 m^{2}mole^{-1} (Ar$\pi \rightarrow \pi^*$); λ 230nm, ϵ 4590m^{2}mole^{-1} (NO_2 n $\rightarrow \pi^*$); λ 265nm (sh), ϵ 3500m^{2}mole^{-1} (NO_2 n $\rightarrow \pi^*$); λ 323nm, ϵ 1550m^{2}mole^{-1} and λ 355nm (sh), ϵ 1240m^2 mole^{-1} (both NO_2 $\pi \rightarrow \pi^*$ or n$\rightarrow \pi^*$ [107,108]). These bands are in very similar positions to those observed in 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl (λ_{max} 210, 230, 266, 326 and 358nm), though they are not so well defined - presumably due to the less symmetrical nature of this compound. The various absorptions are readily assigned in terms of 'hindered' and 'unhindered' nitro groups simply by comparison with the hexanitro derivative. Thus as the 4,4',5,5'- and 8'- nitro groups are all subject to steric hindrance, these are assigned to the 'short wavelength' bands at 230 and 323nm; on the other hand the 7-nitro group is unhindered (as in 'Q') and should therefore contribute to the bands at 265 and 355nm. The position of the 2- nitro group is a little less certain; construction of models suggests that it is much less subject to steric hindrance than is the 8- nitro group and might (depending on the conformation of the system) assume coplanarity with the ring. This fact combined with the intensity of the bands at 265 and 355nm suggests that the 2- nitro group can be regarded as substantially 'unhindered'. Thus although a linear relationship does not necessarily exist between the extinction coefficient of a band and the number of nitro groups contributing to that band; it would seem a little unreasonable to assign the maxima at265/355nm to a single nitro group and those at 230/323nm to six nitro groups, when there is only a relatively small difference in their extinction coefficients. This conclusion would seem to be substantiated by a comparison of the data with that derived from the spectrum of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl (see table 2-3). Thus it is evident from the figures that, for a given type of nitro group (hindered/unhindered) the extinction coefficients are broadly similar between the two compounds. This would only be expected if the number of nitro groups contributing to each band was approximately the same in each compound - a situation which would only occur if the 2- nitro group in 'R' remained substantially unhindered. (In both of the above compounds the lower absorption 'per hindered nitro group' - as compared with the 'unhindered' ones - is readily explained by loss of conjugation between such hindered groups and the aromatic system.)

It is interesting to note that although 'R' contains more nitro groups than the hexanitrobinaphthyl, all its spectral maxima have lower extinction coefficients than the analagous bands in the hexanitro-derivative. This result is surprising but may be attributed to two factors (in addition to any structural differencies). Firstly as a really pure sample of 'R' has never been obtained, inaccuracies are inevitable in preparing a 'standard' spectroscopic solution. Secondly it is possible that 'R' may decompose in solution. Thus when dissolved

Table 2-3

UV Maxima and Extinction Coefficients for the Bands Attributable to the Nitro Groups in the Hexanitrobinaphthyl 'Q' and the Heptanitrobinaphthyl 'R'

4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl			The Heptanitrobinaphthyl 'R'		
i) Hindered Nitro Groups					
λ_{max} (nm)	ϵ ($m^2 mole^{-1}$)	Number of NO_2 groups contributing to the band	λ_{max} (nm)	ϵ ($m^2 mole^{-1}$)	Number of NO_2 groups proposed as contributing to the band
230	5060	4	230	4590	5
326	1550	4	323	1550	5
ii) Unhindered Nitro groups					
266	3820	2	265	3500	2
358	1330	2	355	1240	2

in spectroscopic grade methanol the compound 'R' immediately produced a faint orangy-pink colouration (which is not observed in 'GPR' grade methanol); although the cause of this colouration is uncertain a partial decomposition of 'R' cannot be ruled out. Both of these factors would tend to reduce the 'true' molarity of the standard solution - below that assumed in calculating the extinction coefficients; in consequence the true extinction coefficients may be somewhat greater than those given above.

The various spectra of 'R' thus appear to be consistent with the proposed structure of 2,4,4',5,5',7,8'-heptanitro-1,1'-binaphthyl - although they clearly provide insufficient evidence to assign any structure to this compound unambiguously.

Crystallisation of the Compound 'R' from Toluene

It has been found that when the heptanitrobinaphthyl 'R' is crystallised from toluene the resultant crystals retain some of the hydrocarbon even after prolonged drying. In this respect therefore 'R' is similar to the hexanitrobinaphthyl 'Q' (see earlier). Thus when a sample of 'R' was crystallised from toluene, it was found (by PMR) to retain about 0.24 moles of toluene, per mole of heptanitrobinaphthyl, even after it had been dried for five hours at 110°C under reduced pressure. In the present case however the melting point of the sample seems little affected by the presence of the toluene. Thus the crystals 'with toluene' melt at 206-207°C whilst the 'pure' (?) sample melts at 206.5-208.5°C.

As with the hexanitrobinaphthyl 'Q' it is uncertain whether the toluene is retained by occlusion in the crystal lattice of the hepta-nitrobinaphthyl, or by the formation of an addition complex. (Also in common with the hexanitrobinaphthyl, the toluene is best removed from 'R' by recrystallising it from acetone/acetic acid.)

2.2.3. The Decomposition of 2,4,4',5,5',7,8'-Heptanitro-1,1'-binaphthyl (Compound 'R')

2.2.3.1. Isolation of a Compound of Uncertain Structure Designated Compound 'S'

When a sample of the heptanitrobinaphthyl 'R' was heated in aqueous dimethyl sulphoxide, the bulk of the material decomposed, only a few percent of the heptanitrobinaphthyl being recovered unchanged. Whilst the product apparently comprised a mixture of compounds, only one material was actually isolated - by column chromatography. This compound crystallised from acetone as brilliant orange crystals and was designated as compound 'S1'. When this material was recrystallised (again from acetone), dull orange crystals 'S2' were obtained. It was thought at this stage that the darkening of the crystals might indicate a partial decomposition of the product, the compound 'S2' was therefore characterised without further purification; the spectra of this compound are presented below. An attempt was also made to recover the 'decomposition product' (?) of 'S1', by a fractional crystallisation (acetone/acetic acid) of the residues which remained from the recrystallisation of 'S1'. This process yielded some dark brownish-black crystals 'S3' - which became orange on grinding up.

The infra-red spectra of 'S1', 'S2' and 'S3' are each presented in figure 4; whilst the spectra of 'S2' and 'S3' appear identical, there are small differences between the spectra of 'S1' and 'S2'/'S3'. It is at present uncertain whether these differences result from the presence of impurities in one of the samples, or whether they indicate an actual change of composition between the compounds. Further work will be necessary to clarify the situation.

As the compound 'S1' was only isolated in fairly low yield (16%), there must either be partial decomposition of this product under the reaction conditions, or alternative decomposition routes for the heptanitrobinaphthyl, which do not yield the compound 'S1'. Before considering the possible conversion of 'R' to 'S' it is necessary to discuss the structure of the compound 'S'; the spectra of this product are therefore considered below. In fact, only the spectra of 'S2' are available for consideration because of the decomposition (?) of 'S1' (above).

2.2.3.2. The Spectra of Compound 'S2'

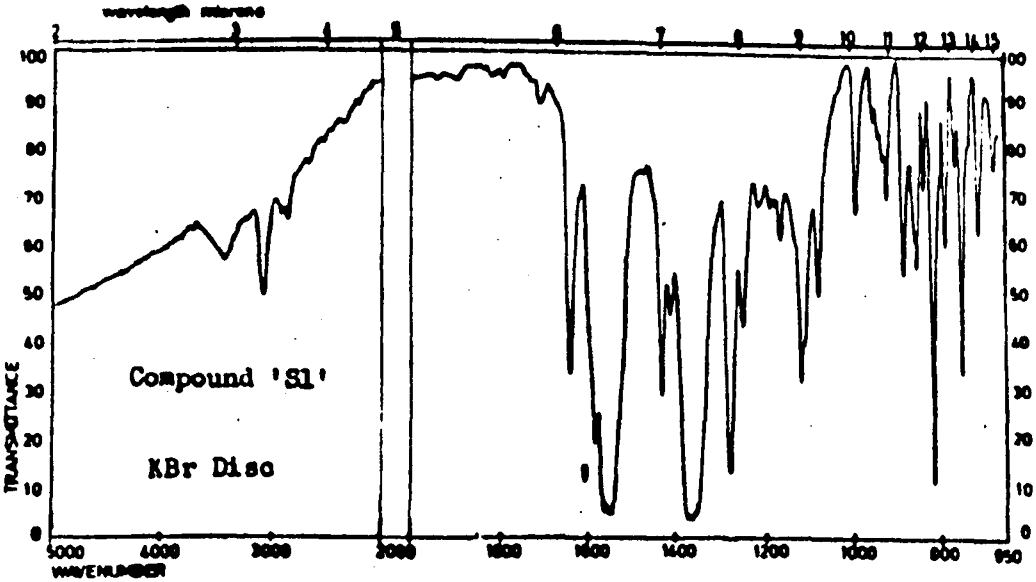
The most useful evidence for establishing the structure of 'S2' is the mass spectrum; this is therefore the first to be examined.

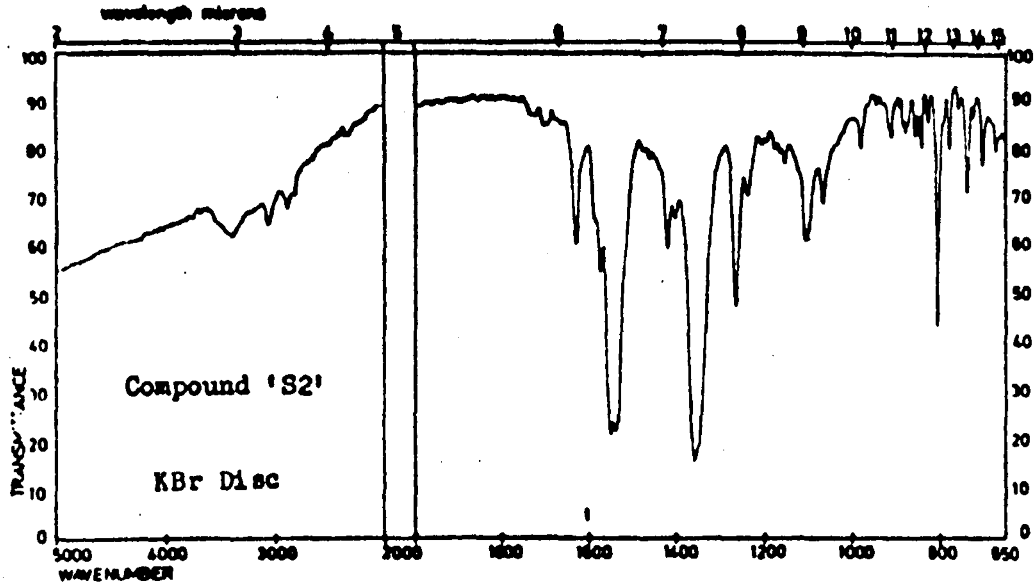
The Mass Spectrum

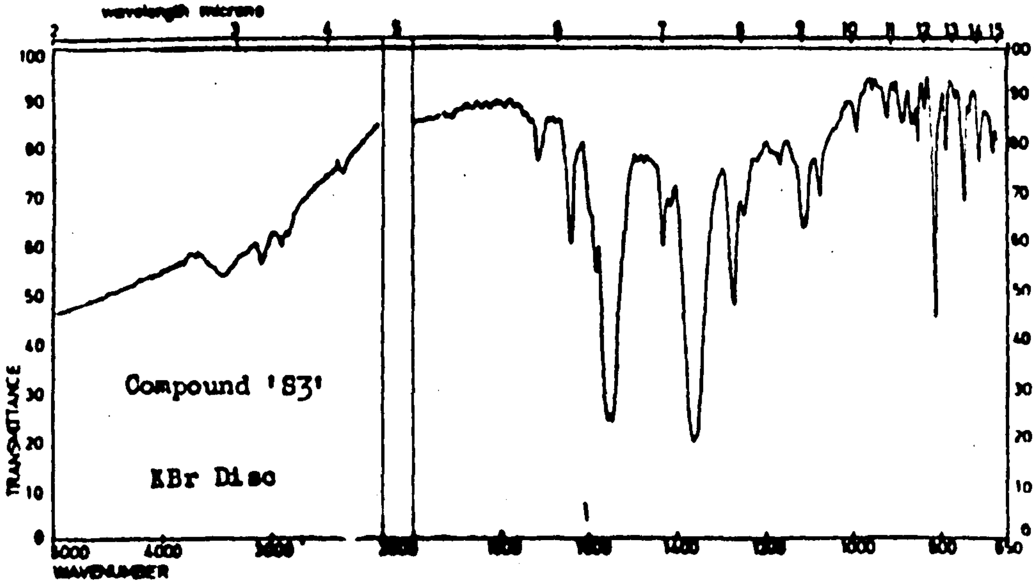
The most abundant ions in the mass spectrum of 'S2' are indicated in scheme 2:XVII. A full list of relative intensities and a bar diagram are given in the appendix.

The spectrum shows a molecular ion at m/e 493 (34.5%)

The Infra-red Spectra of Compound 'S'

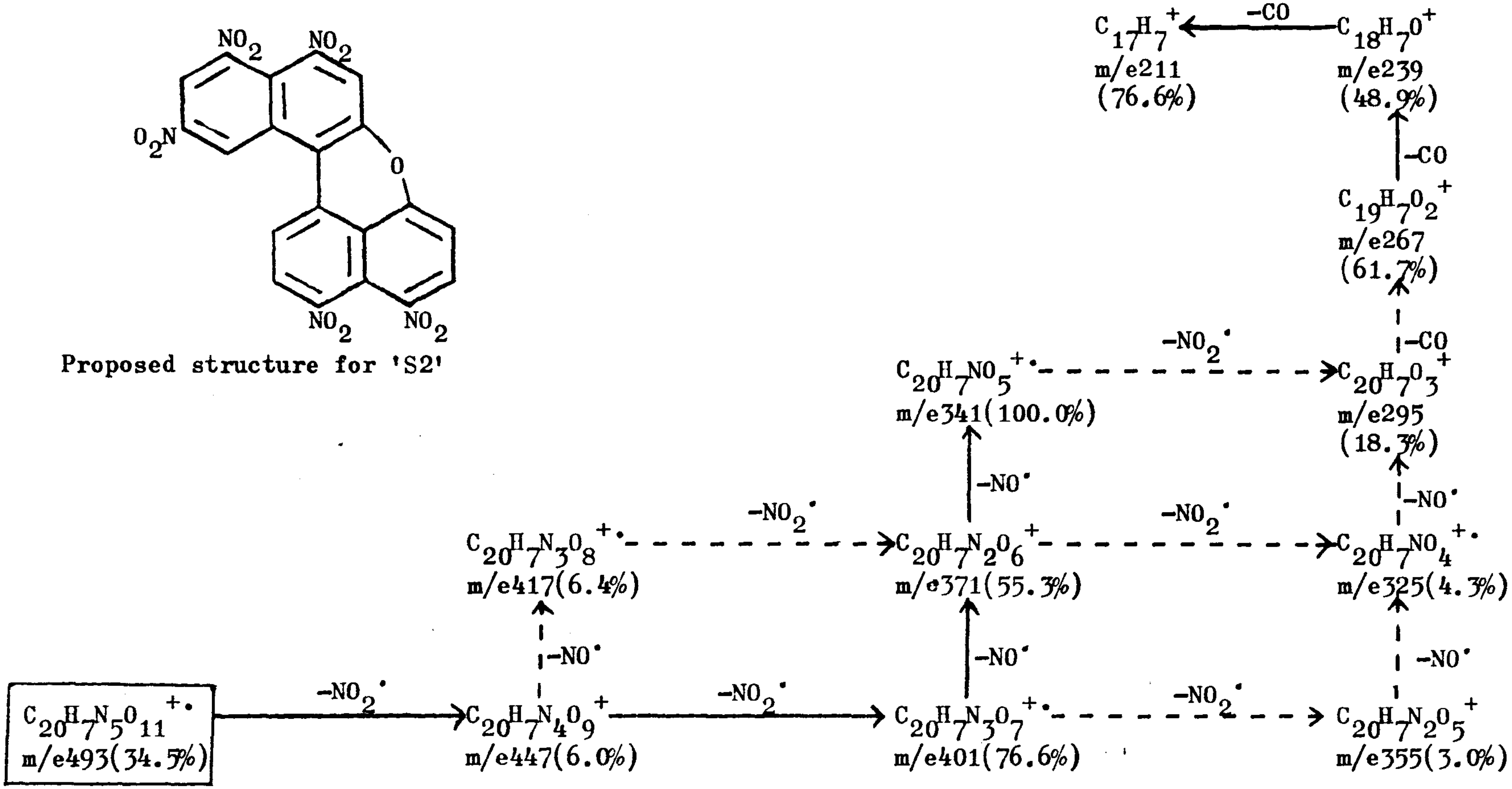






Scheme 2:XVII

Fragmentation Pattern for the Mass Spectrum of Compound 'S2'



Proposed structure for 'S2'

Continuous lines indicate those transitions which are supported by the presence of a metastable peak.

which corresponds to $C_{20}H_7N_5O_{11}$; it thus seems that the binaphthyl nucleus has remained intact in 'S2' and (if the compound is derived from 'R') it means that there has been an effective loss of 'N_2O_3' from the original molecule. Fragmentation of the molecular ion in 'S2', as reflected by the most intense ions in the spectrum, appears to involve the sequential loss of $2NO_2^{\cdot}$, $2NO^{\cdot}$, $NO_2^{\cdot}$ and 3CO . Metastable peaks are evident to support most of the transitions implicit in this sequence of fragmentation - see scheme 2:XVII.

The overall pattern of losses in 'S2' bears considerable similarity to that observed for a nitrobinaphthyl containing two sets of adjacent peri substituted nitro groups (eg 'H' or 'Q'). Thus both show facile loss of two nitro radicals followed by loss of two $NO^{\cdot}$ and ultimately two CO. It is evident however that in addition to these, 'S2' expels a fifth nitro radical and a third molecule of CO. The fragmentation pattern of 'S2' can thus be explained by the presence of five nitro groups in the molecule - of which four are located in peri positions (as two adjacent pairs); there must also be an oxygen function present which is ultimately lost as the 'third' molecule of carbon monoxide. It is pertinent to note that in this scheme the 'fifth' nitro group (ie the one which is not part of an adjacent peri pair) is expelled only after the primary fragmentation of adjacent peri nitro groups has occurred (ie after the loss of $2NO_2^{\cdot}$ and $2NO^{\cdot}$). In this respect the sequence of fragmentation is similar to that observed in the nitrobinaphthyl 'F', 'P' and 'Q' (each of which contain 'extra' nitro group(s) - that is groups in addition to those constituting the adjacent peri pairs).

There is however one significant difference between the spectrum of 'S2' and those of the various nitrobinaphthyls which contain adjacent peri substituted nitro groups. Thus in the case of 'S2' the $(M - NO_2)$ ion occurs with only low intensity, whilst in the nitrobinaphthyls the corresponding ion invariably occurs with very high intensity. Nevertheless the spectrum of 'S2' has a very strong $(M - 2NO_2)$ ion (m/e 401, 76.6%) and in addition there are quite intense metastables for the transitions:-

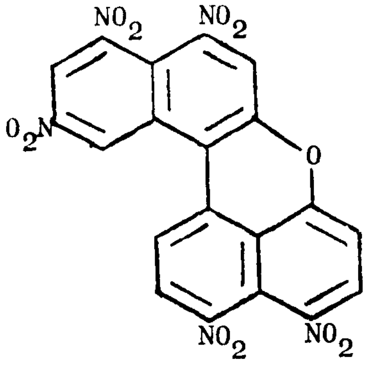
$$\underset{m/e\ 493}{C_{20}H_7N_5O_{11}^{+\cdot}} \longrightarrow \underset{m/e\ 447}{C_{20}H_7N_4O_9^{+}} \quad + \quad NO_2^{\cdot} \qquad M^{*} = 405.3$$

$$\underset{m/e\ 447}{C_{20}H_7N_4O_9^{+}} \longrightarrow \underset{m/e\ 401}{C_{20}H_7N_3O_7^{+\cdot}} \quad + \quad NO_2^{\cdot} \qquad M^{*} = 359.7$$

It thus appears that the low abundance of the $(M - NO_2)$ ion in 'S2' may be the result of a particularly facile fragmentation of this ion -probably via expulsion of a second nitro radical.

Thus on balance it appears most likely that the compound 'S2' does contain two sets of adjacent peri nitro groups - particularly as there is no evidence of alternative fragmentation pathways (eg loss of OH$^\bullet$ or HNO_2). Such fragmentation might be expected, by analogy with the spectra of 4,4'-dinitro-1,1'-binaphthyl, 5,5'-dinitro-1,1'-binaphthyl and 4,4',5-trinitro-1,1'-binaphthyl, if the molecule contained an 'isolated' peri nitro group (ie a nitro group peri to a hydrogen).

Identification of the oxygen function in 'S2' is best made by reference to the infra-red spectrum, which shows no evidence of either a hydroxyl or carbonyl grouping. (The absence of a hydroxyl function is further supported by the mass spectrum which shows no evidence for the loss of OH$^\bullet$). It therefore appears most likely that the oxygen is present in the form of an ether linkage; this explanation is also the most satisfactory for interpretation of the mass spectrum. The proposed structure for 'S2' is that shown below:-



Proposed structure for compound 'S2'

Since expulsion of the 'etherial oxygen' (as CO) involves the breaking of four bonds, this structure explains why the loss occurs only after expulsion of the peripheral nitro groups. The location of four nitro groups in the 4,4',5 and 5' positions has already been discussed; the position of the fifth nitro group cannot however be established with any certainty, on the basis of the mass spectrum alone. At this stage therefore the siting of this nitro group is primarily based upon the assumption that this compound is derived from the heptanitrobinaphthyl 'R'. The possible conversion of 'R' to 'S' is discussed later.

The Infra-red Spectrum

The infra-red spectrum of 'S2' (see appendix and fig 4) shows a weak band at 3100cm^{-1} corresponding to the aromatic C-H stretching frequency. There are also two very strong bands due to the nitro (N-O) stretching vibrations; of these the higher frequency (asymmetric stretching) band is clearly split into a double maximum at 1550/1535cm^{-1}, the symmetric band however produces only a single maximum at 1355cm^{-1} although there is a shoulder at 1345cm^{-1}. (The frequencies of these bands are extremely close to those observed in 'R' itself - 1550/1535 and 1350cm^{-1} respectively.) The bands may be rationalised by essentially similar arguments to those applied to the heptanitrobinaphthyl ('R'). Thus if splitting of the asymmetric band is attributed to the presence of differently orientated nitro groups in 'S2', the absence of such splitting in the symmetric band could once again be due to coupling of this vibration with the various ring modes. Since the change of structure proposed between 'R' and 'S2' , might reasonably be expected to modify the vibrational modes of the ring, it is interesting to note the appearance, in the spectrum of 'S2', of a shoulder at 1345cm^{-1} (on the symmetric NO_2 stretching band). Thus it appears that the two symmetric stretching frequencies may just be visible in 'S2' whereas they are not in the compound 'R'. Presumably in this case the modified ring vibrational modes of 'S2' lead to enhanced frequency separation (as compared with 'R'), between the symmetric stretching vibrations of the differently orientated nitro groups. (The nature of the frequency variations which are produced due to coupling with the ring modes, tends to be rather erratic.[86a])

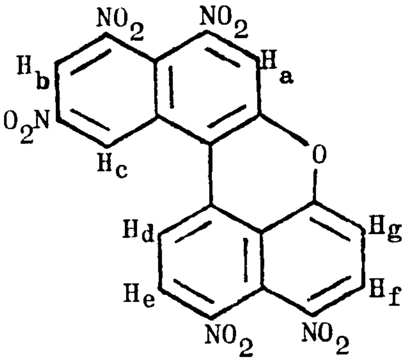
The spectrum of 'S2' also shows a strong band at 1270cm^{-1} which is presumably due to the presence of the ether linkage. The band corresponds to the C-O stretching vibration and the observed frequency is consistent with the carbon atom in this linkage being unsaturated.[64c] The frequency of this band is quite close to that normally found in aryl ethers and is therefore consistent with the location of this linkage in a six membered ring; thus the strain in a ring of this size is not normally sufficient to produce large deviations of frequency from those observed in the acyclic ethers.[64c]

The low frequency region of the spectrum is once again rather too complex to be of value.

The Proton Magnetic Resonance Spectrum

Considerable difficulties were encountered in recording the PMR spectrum of 'S2', due to the extremely small quantity of material which was available (much of the sample was lost in recrystallising 'S1'). In consequence the spectrum is of rather poor quality. Further, it is evident from the spectrum that the sample is contaminated by a relatively large quantity of aliphatic material. Whilst the presence of this material should not interfere with the aromatic region of the PMR spectrum, it is important to note its presence because the UV spectrum of 'S2' was recorded after the PMR spectrum. Thus, as there was insufficient sample to recrystallise, the UV spectrum of 'S2' had to be recorded, using this impure sample; in consequence the UV spectrum must be regarded as being of somewhat doubtful value.

The PMR spectrum of 'S2' (acetone) comprises the following signals: τ -0.12 doublet, J = 1.95Hz, τ 0.89 doublet, J = 1.95Hz, τ 1.10-1.41 multiplet and τ 2.28 doublet, J = 8.79Hz.



'S2'

The doublets at τ -0.12/0.89 constitute an AB quartet with coupling constants of the order normally associated with meta coupled protons;[115] this quartet may therefore be assigned to the protons H_b and H_c. Since the proton H_b is sited ortho to two nitro groups in a 'trinitrated' naphthyl nucleus, it would be expected to resonate at roughly similar field to the protons $H_{6/6'}$ in the hexanitrobinaphthyl 'Q' (ie close to τ 0.95). The signal at τ 0.89 may therefore be assigned to this proton. In consequence the proton H_c must produce the signal at τ -0.12. The extremely low field at which this proton resonates is consistent with the combined effects of two nitro groups (ortho and para to the proton) and the adjacent naphthalene system; thus as the molecule must be almost planar, the proton H_c will be held in close proximity to and in the same plane as, the second naphthyl moiety. In consequence it will be subject to strong deshielding by the induced magnetic field associated with this aromatic system.

Since the doublet at τ 2.28 occurs at rather higher field than the rest of the spectrum it is relatively straightforward to assign. Thus the only protons likely to resonate at (relatively) high field are H_g and H_d - because all the other protons are sited 'ortho' to a nitro group. Further as the proton H_d must be strongly deshielded by the adjacent naphthyl moiety (cf H_c), the signal at τ 2.28 is most likely to arise from the proton H_g. The observed coupling constant for the doublet (8.79Hz) is consistent with the 'ortho' coupling which would be expected for this proton.

The remaining protons must all contribute to the multiplet at τ 1.10-1.41. This assignment seems reasonable because the protons H_a, H_e and H_f would all be expected to resonate in a similar region; thus each of these substituents is a β-proton, sited ortho to a nitro group. (Presumably the deshielding of H_d by the adjacent naphthyl moiety is just sufficient to bring this proton into resonance at similar field.) In fact the region spanned by the multiplet compares quite favourably with the chemical shifts observed in the nitrobinaphthyls; thus for example H_3 in 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl resonates at τ 1.13 whilst in 4,4',5,5'-tetranitro-1,1'-binaphthyl the figure is τ 1.40.

An analysis of the multiplet at τ 1.10-1.41 can be made in the spectrum of 'S2', although a lack of fine resolution in the spectrum causes the assignments to be somewhat tentative. A prime feature of the multiplet which is quite clearly discernable, is a doublet, centered at τ 1.37 with a coupling constant of 8.3Hz. Whilst this value of J seems to differ from that of the doublet at τ 2.28 (by 0.49Hz), this variation is not considered to be significant. Thus when the spectrum was recorded for a second time a coupling constant of 9.3Hz was attributed to the doublet at τ 1.37, (whilst a figure of 8.3Hz was determined for the doublet at τ 2.28). The rather large deviation of coupling constants here - between the two spectra - presumably results from the fairly high level of background noise present in both. It thus appears probable that the signals at τ 1.37 and τ 2.28 constitute an AB quartet (with $J \approx 8.3$Hz). Since the doublet at τ 2.28 has already been assigned to H_g the signal at τ 1.37 must be attributed to H_f.

The remaining lines in this multiplet must be interpreted in terms of an AB quartet (due to $H_{d/e}$) and a singlet (from H_a), if the spectrum is to fit the proposed structure of 'S2'. Although it is difficult to distinguish these features due to overlap (and noise) they are nevertheless thought to be present. Since the multiplet (τ 1.10-1.41 covers only a fairly small range (0.3ppm), H_d and H_e must resonate at quite similar frequencies. This fact explains why the quartet, anticipated for these two protons, is not readily visible; thus as the resonant frequencies of these two protons become more similar, the intensity of the central lines in the quartet will increase at the expense of the outer lines.[117] The limiting case will occur if both protons have identical chemical shifts - in this case the spectrum would collapse to a singlet[117] (an 'A2' spectrum). Two interpretations are therefore possible for the multiplet. Case (i) H_d and H_e happen (coincidentally) to have identical chemical shifts and therefore produce a single line at τ 1.26. In this case the singlet at τ 1.20 would be assigned to H_a. Case (ii) H_d and H_e have quite close (but not identical) chemical shifts. In this case the central lines of the quartet would be large (and close together) whilst the outer lines would be small and could easily be lost in the baseline noise. As the two lines at τ 1.20 and τ 1.26 are of unequal intensity a coincident singlet at τ 1.26 (due to H_a) is implicit in this explanation.

It is possible to calulate for case (ii) the approximate intensities of the four lines (due to $H_{d/e}$) by assuming a value for the coupling constant $J_{Hd/e}$; - a typical value would be about 8.5Hz. The intensity of the various lines in an AB quartet (see fig 5) is given by the following equations:-[117]

Line	Relative Intensity
1	$1 - \sin 2\theta$
2	$1 + \sin 2\theta$
3	$1 + \sin 2\theta$
4	$1 - \sin 2\theta$

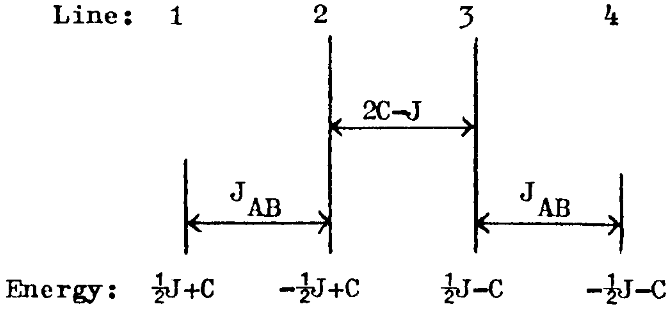


Fig 5

Where C is a positive quantity and θ an angle (between 0 and π) which are together defined by the equations:-[117]

$$C \cos 2\theta = \tfrac{1}{2}\nu_0\delta$$

$$C \sin 2\theta = \tfrac{1}{2}J \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where $\nu_0\delta$ = the difference between the resonant frequencies of the two protons in Hz. Since it is possible to measure the separation of the two centre lines in the proposed quartet in 'S2' (ie between the lines at τ 1.20 and τ 1.26) it is possible to calculate the value of sin 2θ. Thus as the separation of these two lines in 'S2' is 5.3Hz it follows that:-

$$2C - J = 5.3$$

$$\text{Hence} \qquad C = \frac{J + 5.3}{2}$$

Since J has been estimated as 8.5Hz, C becomes equal to 6.9. But from equation (1):-

$$\text{Sin } 2\theta = \frac{\tfrac{1}{2}J}{C}$$

$$\text{Therefore} \qquad \text{Sin } 2\theta = 0.62$$

Hence in 'S2' the lines will have intensities of:-

Line:	1	2	3	4
Intensity:	(1 - 0.62)	(1 + 0.62)	(1 + 0.62)	(1 - 0.62)
ie a ratio of:	1	4.3	4.3	1

Further as it is assumed that J = 8.5Hz the outer lines in 'S2' should be observed at τ 1.12 and τ 1.34. A small peak is in fact visible at τ 1.12 (although it is not sufficiently large to be distinguishable with certainty from the baseline noise). Any signal at τ 1.34 however, must be largely coincident with the doublet at τ 1.37 (J = 8.3Hz). Thus it is interesting to note that in this doublet the line at τ 1.33 is rather more intense than that at τ 1.41 (whereas the opposite would be expected due to the normal 'roofing' effect - if this doublet (τ 1.37) is coupled to that at τ 2.28). This suggests that there could indeed be a coincidence of two signals here. A comparison of intensities is rather difficult due to a drifting baseline, but the ratio of the peaks at τ 1.12/1.20 has been estimated at 1 : 5.1 ; whilst this is reasonably close to the calculated value of 1 : 4.3, the value cannot be regarded as particularly accurate - due to the high noise level in the spectrum. To summarise case (ii) therefore, the protons $H_{d/e}$ would be assigned as an AB quartet τ 1.16 doublet, $J \approx 8.5$Hz, τ 1.31 doublet, $J \gtrsim 8.5$Hz, whilst the proton H_a would give rise to a singlet at τ 1.26. It is not clear from the available data which of the explanations (i) or (ii) is correct, both of the interpretations are however consistent with the proposed structure of 'S2'.

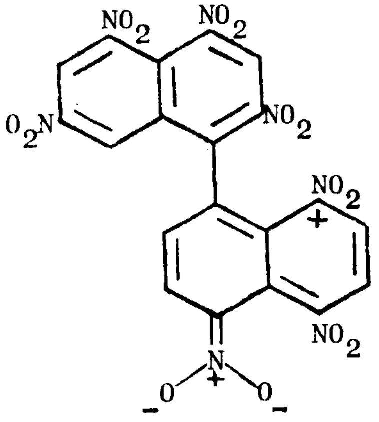
The Ultra Violet Spectrum

The UV spectrum of 'S2' is reproduced in the appendix; there is however no doubt that this spectrum was recorded using an impure sample of the material. Some evidence for this has been noted above from the PMR spectrum and the fact has been confirmed by the very low extinction coefficients observed in the UV spectrum. As there was insufficient material to permit purification of this sample it has not been possible to record an accurate spectrum of the compound. The various maxima visible in the spectrum of the impure 'S2' are given below, it does not however seem worthwhile to discuss this spectrum in detail.
λ 213nm, ϵ 1147m^2mole^{-1}, (Ar$\pi \rightarrow \pi^*$), λ 251nm, ϵ 967m^2mole^{-1}, λ 277nm(sh), ϵ 577m^2mole^{-1}, λ 318nm, ϵ 374m^2mole^{-1}, λ 370nm, ϵ 281m^2mole^{-1}, λ 454nm, ϵ 289m^2mole^{-1}.

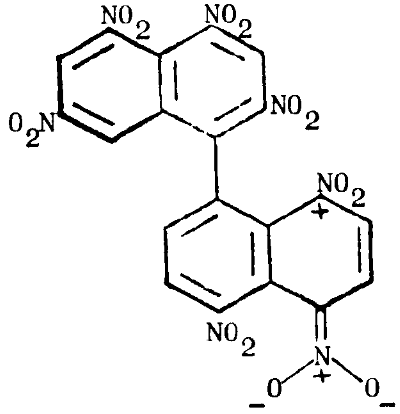
2.2.3.3. The Conversion of 'R' to 'S'

The compound 'R' has been assigned the structure 2,4,4',5,5',7,8'-heptanitro-1,1'-binaphthyl; if this structure is correct the feature most likely to render this compound less stable than the other nitrobinaphthyls, is the presence of two para substituted nitro groups. Thus in general the location of nitro groups either para or ortho to one another, renders a molecule highly susceptible to nucleophilic attack, because each nitro group activates the other towards nucleophilic displacement.[118] In consequence such compounds may be readily hydrolysed. Thus for example 2,3,4,6-tetranitrohydroxybenzene[118] and N,2,3,4,6-pentanitro-N-methyl aniline[119] may be hydrolysed simply by boiling with water (to form 2,4,6-trinitroresorcinol and 3-hydroxy-N,2,4,6-tetranitro-N-methylaniline respectively).

A compound such as 'R', though possibly less sensitive to hydrolysis than the above compounds - due to the presence of fewer nitro groups 'per ring' - is nevertheless likely to undergo hydrolysis under suitable conditions. In fact this reaction is likely to be facilitated by the presence of DMSO. Compare for example the case of 1,2,3,6,8-pentanitrocarbizole. This compound normally requires to be boiled with water, in order to achieve a fairly rapid hydrolysis; however, the same reaction can be achieved at room temperature in only a few minutes if the material is dissolved in (wet) DMSO.[120] In consequence it seems very likely that hydrolysis of the compound 'R' will occur, when it is dispersed in aqueous DMSO - at around 70°C. Of the two para nitro groups in 'R' the 8'- substituent should be the most susceptible to nucleophilic attack because this group is activated by both the 4'- and 5'- nitro groups - structures (2-25) and (2-26).

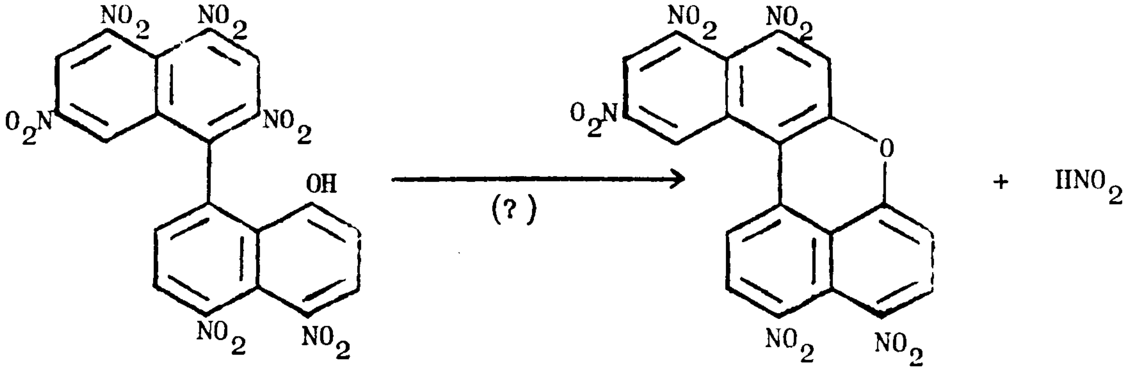


(2-25)



(2-26)

Thus hydrolysis of 'R' would be expected to lead to the compound 'T'.



'T'

'S2'

Since it is actually the compound 'S2' which is isolated after the decomposition of 'R', it seems reasonable to postulate a conversion of the compound 'T' to 'S2' via elimination of a molecule of nitrous acid. Unfortunately the compound 'T' has not been characterised, although in retrospect it seems that there may be some tentative evidence to support its existence. Thus as indicated earlier the analysis of the compound 'R' proved unsatisfactory - the figures falling between the calculated values for a hexa and a hepta nitrobinaphthyl. However, if a comparison is made between the analytical figures obtained for the compound 'R' (C:44.3%; H:1.8%; N:15.6%) and those expected for the compound 'T' (calculated: C:44.4%; H:1.5%; N:15.6%) the two are seen to be very similar. Thus it may be that the attempts to purify the heptanitrobinaphthyl 'R' have simply resulted in its hydrolysis (so that it was the compound 'T' which was analysed and not the compound 'R'). This possibility evidently passed unnoticed at the time of isolation, due to an error - whereby no spectra were recorded from the batch of 'R' ('T'?) which was actually submitted for analysis (see experimental). Thus it is possible that a chance to characterise the compound 'T' was lost. It is worth noting however, that even if this material was the compound 'T', its rather pale yellowish appearance would suggest that it differed (at least superficially) from the compound 'S1' (which was a brilliant fluorescent orange colour). Thus if a chemical difference does exist between the compounds 'S1' and 'S2' its exact nature still remains obscure.

Further work will clearly be necessary in order to clarify the various decomposition products of the heptanitrobinaphthyl 'R'.

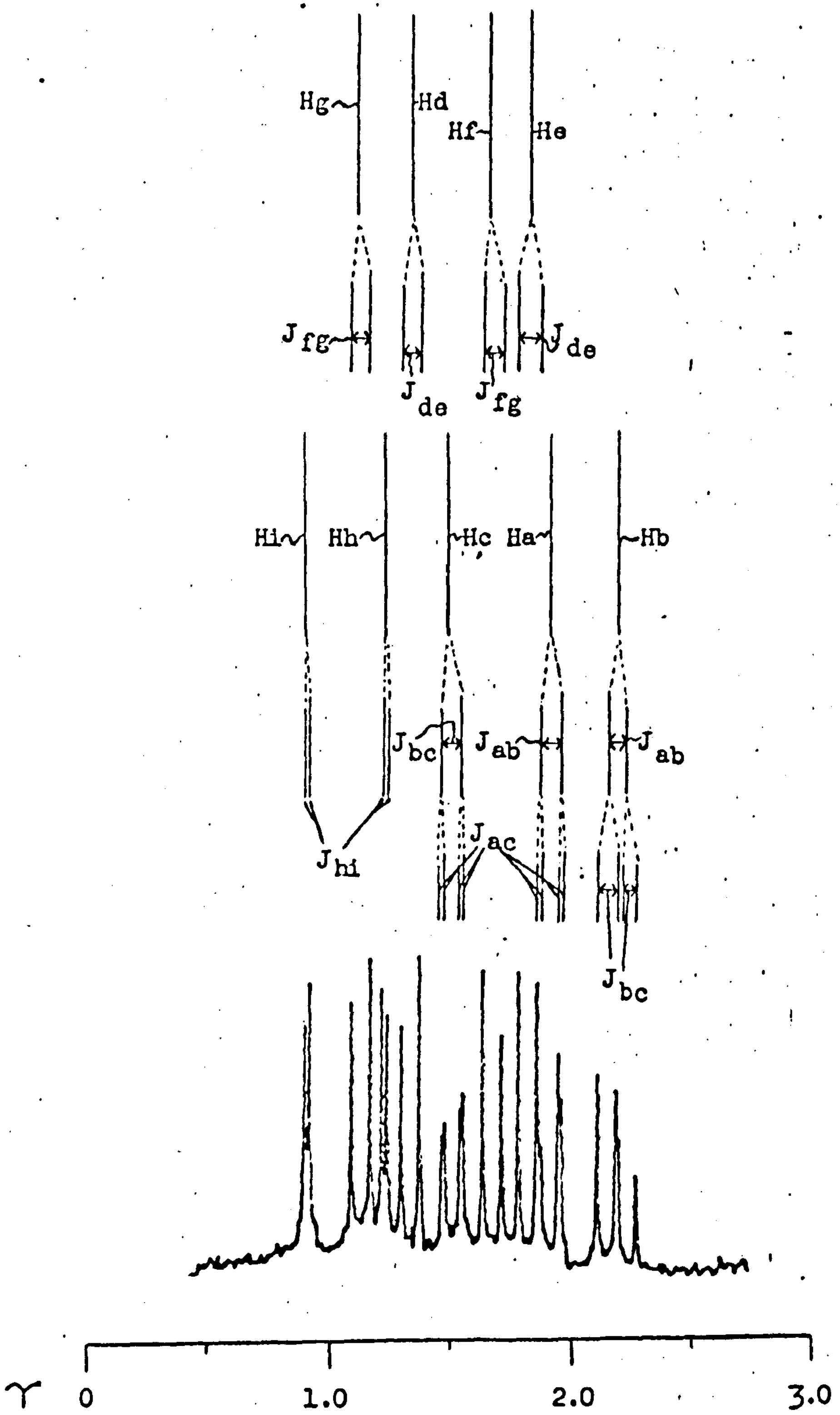
2.3. Preparation of a Pentanitrobinaphthyl of Uncertain Structure Designated Compound 'U'

The nitration of 4,4',5,5'-tetranitro-1,1'-binaphthyl in a mixture of nitric and sulphuric acids to form 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl has already been described. Nitration of the same substrate under similar conditions, but for a shorter period of time, has led to the isolation in 3.6% yield of a pentanitrobinaphthyl, designated compound 'U'. (Some 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl is also formed.) At the time of isolation it was assumed that the compound 'U' was 4,4',5,5',7-pentanitro-1,1'-binaphthyl, subsequent work has however thrown some doubt upon this conclusion; the data is considered below.

The Compound 'U'

The mass spectrum of 'U' shows a molecular ion at m/e 479.03483 corresponding to $C_{20}H_9N_5O_{10}$ (calculated 479.03493). Its infra-red spectrum shows bands consistent with the presence of nitro groups, but shows no evidence of any other functional groups. The compound thus appears to be a pentanitrobinaphthyl. However, an examination of the UV and mass spectra of this compound reveals some unexpected features with respect to the anticipated structure. These features together throw some doubt upon the expected structure of 4,4',5,5',7-pentanitro-1,1'-binaphthyl and will be discussed in some detail below. The anomalies may however be rationalised by assuming that the compound 'U' does not contain 4,4',5,5'- substitution, but instead has just one set of adjacent peri substituted nitro groups and an 8- nitro substituent. Although at first sight this assumption may seem rather unlikely as 'U' was ostensibly prepared from 4,4',5,5'-tetranitro-1,1'-binaphthyl, there is additional evidence in support of it. Thus the further nitration of 'U' does not yield any detectable quantity of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl, despite the fact that this compound is the logical nitration product of 4,4',5,5',7-pentanitro-1,1'-binaphthyl. In fact the product obtained from the nitration of compound 'U' seems likely to be an 8- substituted nitrobinaphthyl - although this assignment is by no means conclusive (see below). It is thus thought that the compound 'U' may be derived from an impurity in the original substrate; this could of course explain the very low yield of the product (3.6%). Such an explanation is thought to be the most satisfactory in view of the overall pattern of results obtained from the nitration of the 1,1'-binaphthyl system. It is however possible that rearrangement of 4,4',5,5'-tetranitro-1,1'-binaphthyl could lead to the production of compound 'U'.

The most likely impurity to be found in 4,4',5,5'-tetranitro-1,1'-binaphthyl is the compound 'P' (4,4',5,8'-tetranitro-1,1'-binaphthyl), because this is a known by-product in the preparation of 'H' and is in fact quite difficult to remove from the compound 'H' by crystallisation. Thus it seems likely that if 'U' is 8- substituted, it could arise from the nitration of the compound 'P'. In this event it must be assumed that the desired product (4,4',5,5',7-pentanitro-1,1'-binaphthyl) - if formed - was never separated from the hexanitrobinaphthyl 'Q' which was also isolated from the reaction. This appears quite reasonable in retrospect, as considerable difficulty was experienced in separating the compound 'U' from 4,4',5,5',7,7'-hexanitrobinaphthyl (either by chromatography or by crystallisation). Thus it might be expected that 4,4',5,5',7-pentanitro-1,1'-binaphthyl - which is more similar in structure to the hexanitrobinaphthyl than is 'U' - would be even more difficult to separate from it. In consequence this pentanitrobinaphthyl could have passed unnoticed in admixture with the hexanitrobinaphthyl (which although identified via its IR and mass spectra



100MHz PMR spectrum of compound 'U' showing coupling pattern.
Figure 6

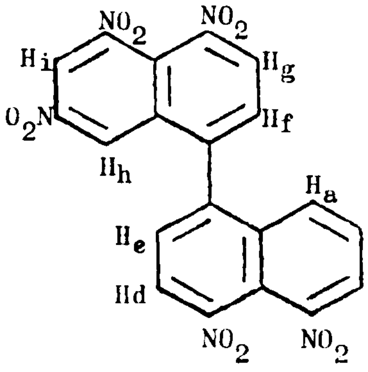
was not further analysed).

The various spectra of the compound 'U' will now be considered in detail in order to establish the most probable structure(s) for this material.

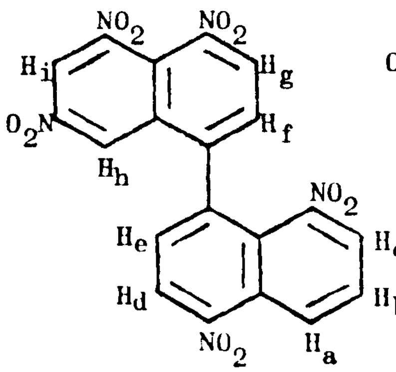
The Proton Magnetic Resonance Spectrum

The PMR spectrum of 'U' (in acetone) is given in the appendix and in figure 6. The spectrum comprises the following signals:-
τ 0.92 doublet, J = 2.0Hz, τ 1.14 doublet, J = 7.8Hz, τ 1.24 doublet, J = 2.0Hz, τ 1.35 doublet, J = 7.8Hz, τ 1.53 double doublet, J = 6.8Hz J' = 1.5Hz, τ 1.70 doublet, J = 7.8Hz, τ 1.85 doublet, J = 7.8Hz, τ 1.94 double doublet, J = 7.7Hz, J' = 1.5Hz τ 2.23 double doublet, J = 7.7Hz, J' = 6.8Hz. Analysis of the spectrum may be readily accomplished in terms of an ABC system and three AB quartets. Evidently two of these quartets (comprising the doublets τ 1.14, 1.35, 1.70 and 1.85) are due to 'ortho coupled' protons (as indicated by the magnitude of their coupling constants [115] - about 8Hz - whilst the third quartet must result from a pair of meta coupled protons (in this case J is only 2Hz).

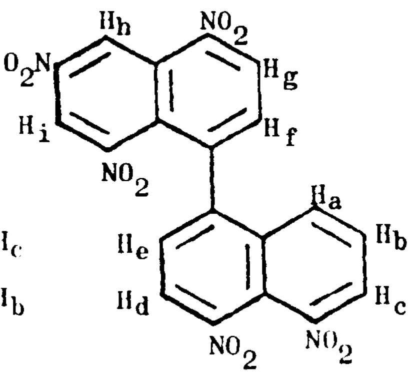
In fitting the spectrum to a specific structure it is pertinent to note that there must be at least one pair of adjacent peri substituted nitro groups in the molecule (see below - the mass spectrum). Allowing for this fact the structures (2-27)→(2-29) provide the best fit for the PMR spectrum. (For the sake of clarity the spectrum is reproduced in fig 6 with the various assignments indicated.) (The only other structures which could fit, would preclude the existance of 4,4'- substitution in 'U' and also require the presence in this compound of nitro groups orientated either ortho or para to one another. Both of these possibilities are discounted because all the likely precursors to 'U' should contain 4,4'- substitution, whilst the compound 'U' it-



(2-27)



(2-28)



(2-29)

self has shown no sign of the instability normally associated with a compound containing 'ortho' or 'para' nitro groups.) Although all three structures (2-27)→(2-29) would be expected to produce the basic pattern observed in the spectrum of 'U' (an ABC multiplet plus three AB quartets), it is necessary, in order to ascertain the most suitable structure for the compound 'U', to estimate the chemical shifts in each. Consider eg the structure (2-27). As part of this structure resembles 'half a molecule' of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl('Q') whilst the remainder is similar to 'half a molecule' of 4,4',5,5'-tetranitro-1,1'-binaphthyl, the chemical shifts in this structure may be estimated by analogy with the spectra of the above compounds. The figures anticipated on this basis are given in table 2-4 together with the shifts actually observed in the spectrum of 'U'. It is quite clear from this table that the two sets of data match up quite well, thus the structure (2-27) is considered to be a 'good fit' for the PMR spectrum of compound 'U'.

Table 2-4

A Summary of PMR Data for Structure (2-27)

Protons	Anticipated Shift τ	Compound from which anticipated shift is derived	Protons	Observed Shift in 'U' τ
f/g	1.63/1.13	'Q'	2/3	1.70/1.14
h/i	1.12/0.96	'Q'	6/8	1.24/0.92
e/d	1.90/1.40	'H'	2/3	1.85/1.35
c	1.57	'H'	6	1.53
b/a	2.5-1.9	'H'	7/8	*2.23/1.94

*This multiplet actually extends over the region τ 2.3-1.89

The spectrum anticipated for structure (2-28) is substantially similar to that predicted for structure (2-27); indeed the only feature which is likely to change significantly between the two spectra is the chemical shift of H_a. Thus although this proton is para to a single nitro group in both structures, it is probably shielded by the adjacent naphthyl moiety in (2-27), but deshielded by the adjacent 'peri' nitro group in structure (2-28). Unfortunately even this differentiation is uncertain because it has been noted[71] that when the spectrum of 1,4-dinitronaphthalene is recorded in acetone, the downfield shift of α-protons due to the adjacent peri nitro groups seems abnormally low. Thus, in acetone, a substantial shift of H_a - between the structures (2-27) and (2-28) - cannot be relied upon. (In any event it is difficult to estimate the chemical shift of H_a, because a full analysis of the ABC multiplet in 4,4',5,5'-tetranitro-1,1'-binaphthyl is lacking.) It therefore seems probable that the structure (2-28) could provide an adequately good fit for the PMR spectrum of 'U'.

A very similar argument applies in comparing the spectra for structures (2-27) and (2-29). Thus the only significant difference expected between these two is in the chemical shift of the proton H_h. Once again shielding of this proton would be expected in structure (2-27), but deshielding in structure (2-29). However, as the extent of this deshielding is uncertain - in acetone - (see above), it is probable that the structure (2-29) could also provide a reasonable 'fit' for the PMR spectrum of 'U'.

It thus appears that all three of the above structures are reasonably consistent with the PMR spectrum of 'U'; in consequence an alternative method will have to be found to distinguish between them.

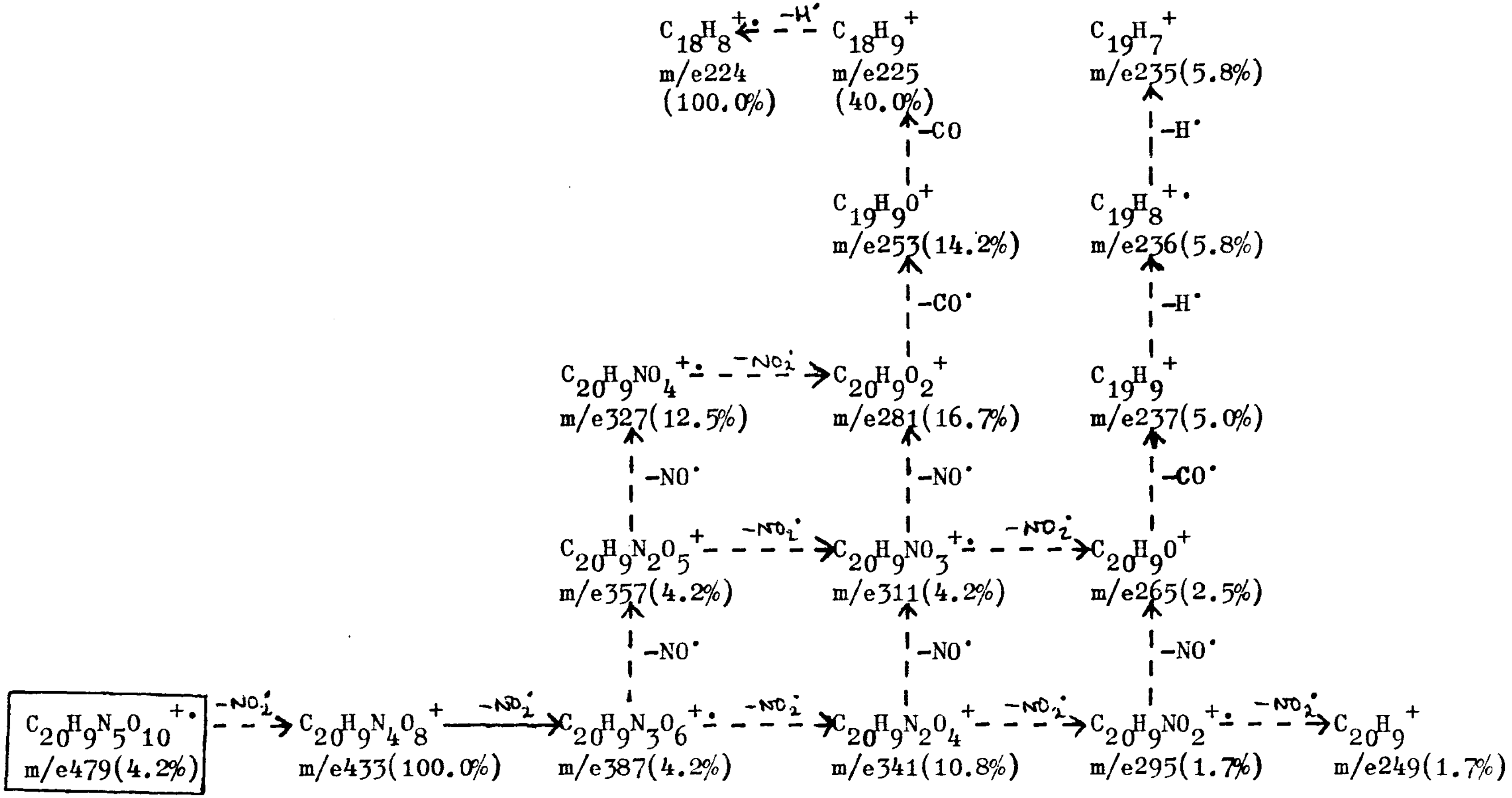
The Mass Spectrum

The most intense ions in the mass spectrum of 'U' are summarised in scheme 2:XVIII; a full list of relative intensities and a bar diagram are given in the appendix. The spectrum is in some respects typical of a nitroaromatic compound, as it shows ions which logically correspond with sequential loss of five nitro radicals from the molecular ion. The intensity of these ions is however very small in some cases - as would be expected due to the presence of adjacent peri substituted nitro groups. It is nevertheless possible to identify the interim ions of low intensity - (M - O), (M - NO) etc - which are characteristic[77] of isomerisation and fragmentation of the individual nitro groups.

It is quite clear from the mass spectrum of 'U' that the compound does in fact contain 4,5- substitution. Thus although the molecular ion is small, the M - 46 ion is the base peak of the spectrum. It is pertinent to note however that the M - $2NO_2$ ion is of only low intensity (4.2%) and it is this feature which seems anomalous with respect to 4,4',5,5'- substitution, that is structure (2-27). Thus the presence of two sets of adjacent peri substituted nitro groups would be expected to result in the facile expulsion of two nitro groups and hence intense ions corresponding to both (M - NO_2) and (M - $2NO_2$) (cf both 4,4',5,5'-tetranitro-1,1'-binaphthyl and 4,4',5,5',7,7'-hexa-

Scheme 2:XVIII

Fragmentation Pattern for the Mass Spectrum of Compound 'U' - a Pentanitro-1,1'-binaphthyl



Continuous lines indicate those transitions which are supported by the presence of a metastable peak.

nitro-1,1'-binaphthyl). It is important to note however that this anomaly does not totally exclude the possibility of 4,4',5,5'- substitution as it may simply be that the $(M - 2NO_2)$ion fragments very readily. Indeed as there is a fairly intense metastable peak at m/e 345.9, it is possible that the expulsion of a nitro radical from the $(M - NO_2)$ ion is a very favourable process:-

$$\underset{m/e433}{C_{20}H_9N_4O_8^{+}} \longrightarrow \underset{m/e\ 387}{C_{20}H_9N_3O_6^{+\cdot}} + NO_2^{\cdot} \qquad M^{*} = 345.9$$

Thus it may simply be the facile nature of this fragmentation which leads to the low observed intensity of the $(M - 2NO_2)$ ion. Indeed the most intense ions in the remaining part of the spectrum are best assigned by assuming subsequent fragmentation of the $(M - 2NO_2)$ ion (see scheme 2:XVIII). The overall breakdown pattern of this compound is in fact quite similar to those of other nitrobinaphthyls which are known to contain 4,4',5,5'- substitution, thus the main fagmentation pathway in 'U', as indicated by the most intense ions, seems to involve the sequential loss from the molecular ion of $2NO_2^{\cdot}$, $2NO^{\cdot}$, $NO_2^{\cdot}$ and 2CO . However whilst the spectrum of 'U' could certainly be consistent with the presence of 4,4',5,5'- substitution - at least with respect to the overall fragmentation pattern - there is no indication why (in the event of such substitution), the $(M - 2NO_2)$ ion should differ from its analogue in compounds such as 'H' and 'Q' by undergoing a particularly facile fragmentation.

It may therefore be concluded that whilst the presence of 4,5- substitution in 'U' seems reasonably certain, the presence of 4,4',5,5'- substitution is not. In consequence it is impossible either to verify or disprove the structure (2-27) on the basis of this spectrum.

The situation is rather different when the alternative structures (2-28) and (2-29) are considered, because each of these contain just one pair of adjacent peri substituted nitro groups; thus neither of these structures would be expected to produce an intense $(M - 2NO_2)$ ion. In absence of 4,4',5,5'- substitution however, an alternative explanation must be found for the main fragmentation pathway (outlined above), because this apparently involves the loss of <u>two</u> $NO^{\cdot}$ and <u>two</u> CO . Thus whilst the presence of 4,5- substitution would be expected to lead to the loss of $NO_2^{\cdot}$, one molecule of $NO^{\cdot}$ and one molecule of CO, the apparent expulsion of a second molecule of both $NO^{\cdot}$ and CO must be attributed to some other cause. (The isomerisation[77] of nitro groups to the nitrite would not be expected to yield particularly abundent fragments and does not therefore provide a satisfactory explanation.) This particular fragmentation can in fact be quite reasonably explained in terms of the 8-. subsituted nitro group. Thus inter-ring rearrangement of an 8- substituted nitro group has already been suggested, whilst considering the mass spectra of other nitrobinaphthyls. Of particular significance here is the possibility (first mentioned with respect to the compound 'C-2') that fragmentation of the 8-nitro substituent might occur via two competing mechanisms, that is, by rearrangements analagous to those depicted in structures (2-8')→(2-9') and (2-15)→(2-17) (pages 60/61). The first of these would result in the expulsion of OH• and NO• whilst the second would produce loss of CO and NO• . In the case of 'C-2' it was suggested that the course of this rearrangement might have been dependant upon the electron density at the 2- position; or specifically that an electron deficiency at this site would favour a cyclic transition state and hence the expulsion of NO• and CO, rather than NO• and OH• . Since there are several nitro groups in the relevent naphthyl ring for both structures (2-28) and (2-29), it seems consistent with earlier reasoning that fragmentation of the 8- nitro group in 'U' should involve expulsion of NO• and CO (via the cyclic transition state). Further as the spectrum of 'C-2' suggests that the expulsion of NO• and CO - due to this rearrangement - occurs only after expulsion of the other nitro groups, it might reasonably be expected that the 8- nitro group in 'U' would also be the last to fragment. Thus fragmentation of the molecular ion via initial loss of $3NO_2^\bullet$ followed by 2NO• and 2CO might in fact be the most favoured sequence; - this could therefore explain why the ion at m/e 341 ($M - 3NO_2$) is reasonably intense (10.8%). (Contrast the situation if 4,4',5,5'- substitution is assumed, as in this case the ($M - 3NO_3$) ion would be much more intense than its analogue in either 'H' or 'Q' - without any apparent explanation).

It is thus assumed that fragmentation of the 8- nitro group in 'U' occurs via the expulsion of NO• and CO - at the expense of the alternative pathway involving expulsion of NO• and OH• - (cf 'C-2'). In consequence the ions such as ($M - NO_2 - OH$) and ($M - 2NO_2 - OH$) are practically non-existent. (It should be noted that the alternative mechanism for the loss of OH• - via the Beynon type mechanism - will also be suppressed, as in both of the structures (2-28) and (2-29) the hydrogen sited peri to a nitro group also has another nitro group located para to it.) In view of this discussion therefore the mass spectrum of 'U' is thought consistent with either of the structures (2-28) or (2-29) - although it is impossible to distinguish between them at the present time.

The overall conclusion to be drawn from above is that the spectrum is probably better explained by the structures (2-28) and (2-29) than by the structure (2-27); such a conclusion however, must be regarded as rather tentative.

The Infra-red Spectrum

The infra-red spectrum of 'U' (see appendix) shows a weak band at $3020cm^{-1}$ corresponding to the aromatic C-H stretching frequency. There are also two very strong bands due to the nitro stretching vibrations; of these the higher frequency (asymmetric stretching) band is clearly split into a double maximum (at $1550/1535cm^{-1}$) whilst the symmetric stretching band produces only a single maximum at $1355cm^{-1}$. These bands may be rationalised by essentially similar arguments to those applied for the hexanitrobinaphthyl 'Q'. Thus if splitting of the asymmetric band is attributed to the presence of differently orientated nitro groups in 'U', the absence of such splitting in the symmetric band could once again be due to coupling of this vibration with the various ring modes.

The actual frequencies of the two 'nitro' bands in 'U' are quite close to those observed in the other nitrobinaphthyls (eg 'H', 'Q' and 'R'); it does not appear possible however, to use these frequencies in distinguishing between the structures (2-27)→(2-29). (At least not without a much more accurate spectrometer.)

The low frequency region of the spectrum is once again of very little value for structural assignment.

The infra-red spectrum of 'U' thus appears consistent with each of the structures (2-27)→(2-29) but does not provide any information as to which of these structures is the correct one.

The Ultra Violet Spectrum

The ultra violet spectrum of 'U' in methanol (see appendix) shows five maxima at λ 210nm, ϵ $5270m^2mole^{-1}$ ($Ar\pi\rightarrow\pi^*$), λ 234nm, ϵ $4430m^2mole^{-1}$ (NO_2 $n\rightarrow\pi^*$), λ 268nm (sh), ϵ $2250m^2mole^{-1}$ (NO_2 $n\rightarrow\pi^*$), λ 326nm, ϵ $1440m^2mole^{-1}$ and λ 355nm (sh), ϵ $1080m^2mole^{-1}$ (both NO_2 $n\rightarrow\pi^*$ or $\pi\rightarrow\pi^*$ [107,108]).

The first point of interest in this spectrum is that the aromatic $\pi\rightarrow\pi^*$ band has a significantly lower extinction coefficient than in either 4,4',5,5'-tetranitro-1,1'-binaphthyl (ϵ 6510m^{2}mole^{-1}) or 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl (ϵ 6570m^{2}mole^{-1}). In fact it is this feature which suggests the presence of an 8- nitro substituent in 'U'. Thus the presence of an 8- nitro group should increase the steric hindrance between the two naphthalene systems and reduce the conjugation between them. In consequence a decrease in the extinction coefficient of the aromatic $\pi \rightarrow \pi^*$ transition would be expected. This effect is demonstrated quite clearly in compounds such as 4,4',5,8'-tetranitro-1,1'-binaphthyl('P') and 2,4,4',5,5',7,8'-heptanitro-1,1'-binaphthyl ('R') which each have extinction coefficients for the aromatic $\pi \rightarrow \pi^*$ band (5330 and 5090m^{2}mole^{-1} respectively) which are significantly smaller than those of either 4,4',5,5'-tetranitro-1,1'-binaphthyl ('H') or 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl('Q') (6510 and 6570m^{2}mole^{-1} respectively). The rather low extinction coefficient for the aromatic band in 'U' would thus tend to favour one of the structures (2-28) or (2-29) for this compound, because the structure (2-27) (which does not contain an 8- nitro substituent) cannot offer any explanation for the relatively weak aromatic band.

Assignment of the remaining bands is quite readily achieved by comparison with the spectrum of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl. Thus the bands at 234/326nm and 268/355nm may be assigned respectively to the 'non planar' and 'planar' nitro groups. (The positions of these maxima are clearly very close to those observed in the hexanitrobinaphthyl.) It is also of interest to compare the extinction coefficients of these bands with the analagous bands in the hexanitrobinaphthyl 'Q'. Thus whilst the short wavelength bands (hindered nitro groups) have quite similar extinction coefficients in both compounds the longer wavelength bands (unhindered nitro groups) do not. In fact the bands at 266nm (hexa) and 268nm (penta) have extinction coefficients in the ratio of 1.7 : 1 (ie roughly 2 : 1). Such a difference might reasonably be expected as there are two unhindered nitro groups in the hexanitrobinaphthyl but only one in the pentanitrobinaphthyl. (Although a linear relationship does not necessarily exist between the extinction coefficient of a band and the number of nitro groups contributing to it, this comparison seems useful as a rough guide). Nevertheless a comparison of the bands at 358nm (hexa) and 355nm (penta) is much less convincing than the above - as the extinction coefficients are in the ratio of 1 : 1.4 (although the band in the hexanitrobinaphthyl is still the most intense).

In conclusion the UV spectrum of 'U' appears consistent with the proposed structures for the compound and specifically favours the presence of an 8- substituent - that is structures (2-28) and (2-29), it does not however provide any positive indication as to which individual structure is the correct one.

Conclusions as to the structure of compound 'U'

On the basis of the spectroscopic evidence it seems reasonable to assume that the compound 'U' has one of the structures (2-27) → (2-29). The evidence overall seems to favour structures (2-28) and (2-29) rather then (2-27), which suggests that the compound is indeed a by-product of the desired nitration - produced by the reaction of an impurity in the original substrate. It is impossible however, on the basis of the spectroscopic evidence, to distinguish reliably between the structures (2-28) and (2-29) - at least at the present time.

2.4. Nitration of Compound 'U' - Preparation of a Hexanitrobinaphthyl of Uncertain Structure - Designated Compound 'V'

It is clear from the above data that the spectra of 'U' are ambiguous and do not provide sufficient information to permit full structural identification of the compound. In view of this the further nitration of 'U' was undertaken (in mixed acid) in order to facilitate its identification. Although only a very small quantity of substrate was available for this nitration (which made purification of the product very difficult), a product 'V' was nevertheless isolated, and some spectra recorded from it. The various spectra of this compound are considered below.

The Compound 'V'

Analysis of the mass spectrum of 'V' is slightly complicated by the presence of a trace impurity (a heptanitrobinaphthyl) but is seems reasonably certain that the molecular ion is at m/e 524 corresponding to $C_{20}H_8N_6O_{12}$. The infra-red spectrum shows bands consistent with nitro stretching frequencies and indicates the presence of no other functional groups. The compound is thus thought to be a hexanitrobinaphthyl; this assumption is confirmed by the PMR spectrum which cannot reasonably be assigned to a heptanitrobinaphthyl (and is certainly not the same as that of the starting material).

The Infra-red Spectrum

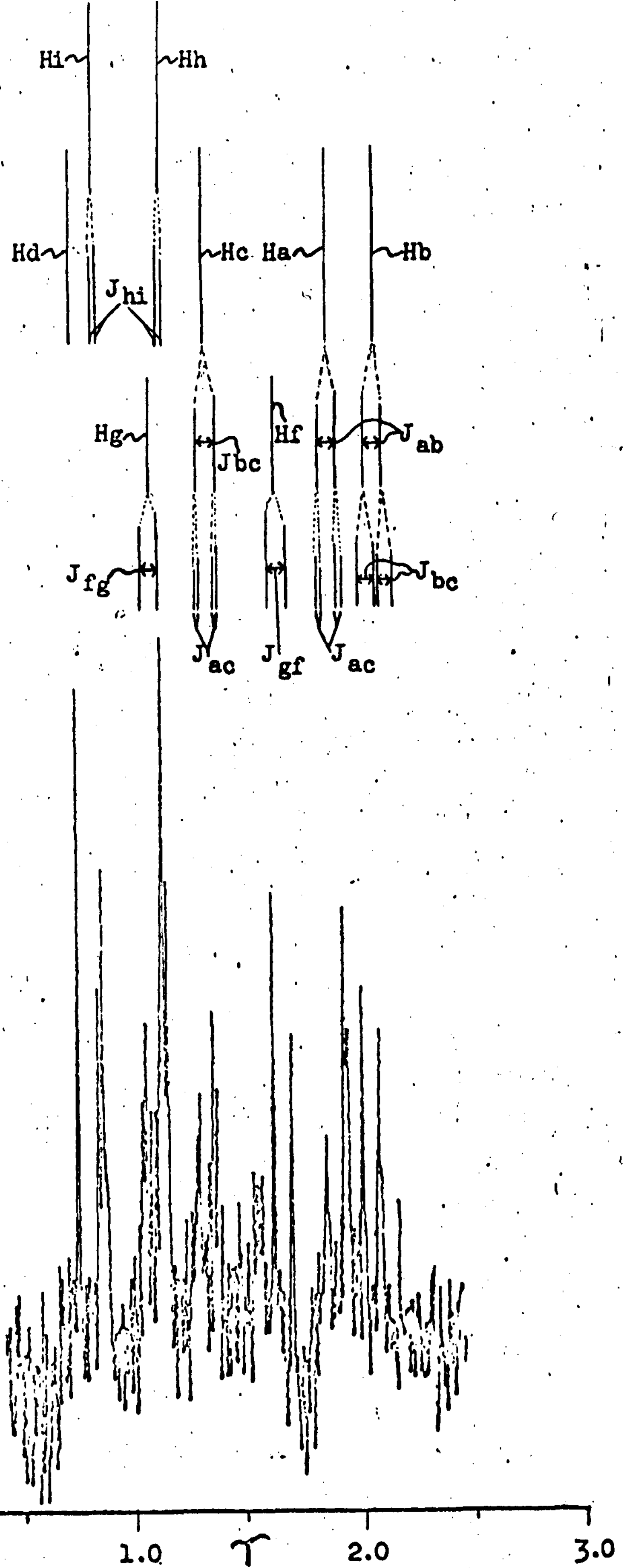
The infra-red spectrum of 'V' (see appendix) shows a weak band at 3050cm^{-1} which corresponds to the aromatic C-H stretching frequency. There are also two very strong bands at 1545cm^{-1} and 1355cm^{-1} corresponding to the nitro (N-O) stretching vibrations.

The overall pattern of the spectrum is extremely similar to that of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl, but there appears to be a small difference between the nitro stretching frequencies in the two compounds. In general however a lack of resolution in the spectrum of 'V' makes it impossible to determine with any certainty whether other subtle differences exist between the two spectra.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of 'V' is reproduced in the appendix and in figure 7; the first point of interest is that the spectrum is not that of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl, indeed no trace of this compound is evident in the spectrum. Since the method used for isolation of 'V' should have detected any of this hexanitrobinaphthyl if it was present, it seems rather unlikely that the compound 'U' is 4,4',5,5',7-pentanitro-1,1'-binaphthyl - that is structure (2-27). An alternative possibility does exist in that the 'expected product' (4,4',5,5',7 - pentanitro-1,1'-binaphthyl) could undergo an 'anomalous' nitration to yield 2,4,4',5,5',7-hexanitro-1,1'-binaphthyl, which may be 'fitted' to the PMR spectrum of 'V'. Such a possibility seems remote however on two counts: i) direct nitration in the 2 position of the binaphthyl nucleus does not seem 'normal' in mixed acid unless there is already an 8- substituent present - possibly for steric reasons (see later), ii) even if an anomalous nitration did occur, there should still be some of the 'normal' product ('Q') produced - which should have been detected.

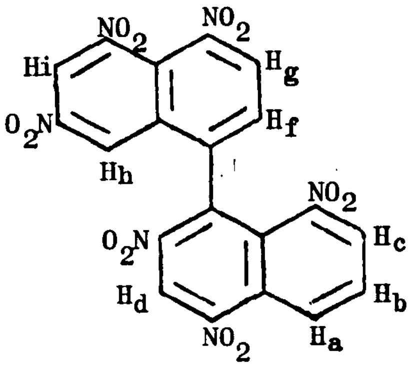
The high noise level which prevails in the spectrum of 'V' (and its overall complexity) makes a full analysis of this spectrum rather difficult; nevertheless an interpretation is given below - although it must be emphasised that the various assignments are not absolutely certain. Thus the spectrum appears to comprise one singlet, two AB quartets (one 'meta' coupled and one 'ortho' coupled) and an ABC multiplet. On this basis the signals may be assigned as follows:- τ 0.75 singlet (H_d), τ 0.85 doublet, J = 1.95Hz (H_i), τ 1.09 doublet J = 8.3Hz (H_g), τ 1.13 doublet, J = 1.95Hz (H_h), τ 1.31 double doublet, J = 7.8Hz, J' = 1.95Hz (H_c), τ 1.65 doublet, J = 8.3Hz (H_f), τ 1.88 double doublet, J = 8.3Hz, J' = 1.5Hz (H_a), τ 2.08 double doublet, J = 8.3Hz J' = 7.8Hz (H_b). The assignments are indicated schematically in figure 7. Since the structure (2-27) has been discounted for compound 'U' (above), the precursor to compound 'V' must have a structure corresponding to either (2-28) or (2-29). Further as nitration of either of these



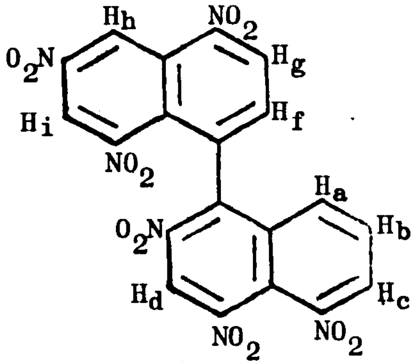
100MHz PMR spectrum of compound 'V' showing the probable coupling pattern.

Figure 7

species is likely to occur in the disubstituted rather than the trisubstituted naphthalene system, there are only two possible structures for the compound 'V' - which will also fit the PMR spectrum. That is the structures (2-30) and (2-31).



(2-30)



(2-31)

Whilst both of these structures will obviously fit the basic pattern of the PMR spectrum (ie one singlet, two AB quartets and an ABC multiplet), it is clearly desirable to compare the 'expected' chemical shifts in each structure with those actually observed. Consider for example the structure (2-30); it is possible to make a fair estimate of the shifts for Hf, Hg, Hi and Hh in this compound, by a comparison with 4,4',5,5'-7,7'-hexanitro-1,1'-binaphthyl as there should be little difference between analagous protons in these two compounds. However, in the case of the protons Ha, Hb, Hc and Hd it is only possible to say that these should resonate at lower field than their analogues in 'U' or 'H' (and in the case of Hd - much lower field). The various figures have been collected together in table 2-5 and it is evident from these that the observed shifts in 'V' correspond well with those anticipated for the structure (2-30). Hence the structure (2-30) seems to provide a satisfactory fit for the PMR spectrum of 'V'. It follows from this that the structure (2-31) will also provide a satisfactory 'fit', as only minor differences are likely between the spectra of (2-30) and (2-31). In fact the only change of any significance expected between these structures is in the chemical shifts of Ha and Hh - as these protons will be deshielded/shielded, depending upon whether they are 'peri' to a nitro group, or a naphthyl moiety. As in the case of 'U' the magnitude of these differences (in acetone) is rather uncertain; however, they may be rather less than would be expected on the basis of work done in other solvents. In consequence it is not possible to distinguish reliably between the structures (2-30) and (2-31) on the basis of the PMR spectrum.

Table 2-5

PMR Data for the Compounds 'U' and 'V'

Protons	Anticipated Shift τ	Derived from	(Protons)	Observed Shift in 'U' τ	Observed Shift in 'V' τ
f/g	1.63/1.13	'Q'	2/3	1.70/1.14	1.65/1.09
h/i	1.12/0.96	'Q'	6/8	1.24/0.92	1.13/0.85
d	well downfield of: 1.40	'H'	2/3	1.85/1.35	0.75
c	downfield of: 1.57	'H'	6	1.53	1.31
b/a	downfield of: 2.5-1.9	'H'	7/8	*2.23/1.94	2.08/1.88

*This multiplet actually extends over the region τ 2.3-1.89

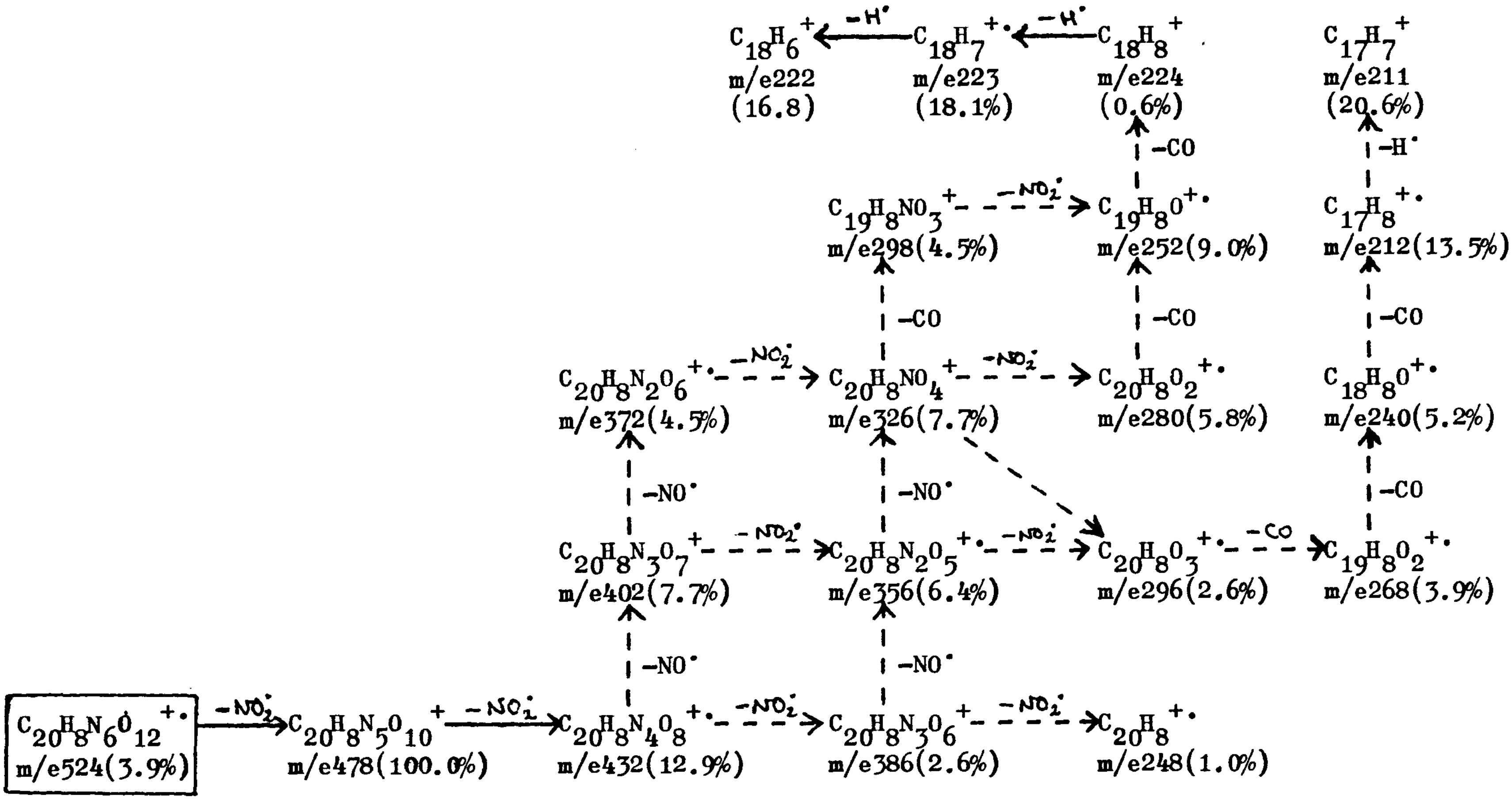
The Mass Spectrum

The mass spectrum of 'V' is given in the appendix as both a bar diagram and a list of relative intensities. The molecular ion in this spectrum is thought to be at m/e 524 - corresponding to a hexanitrobinaphthyl, it appears however that there is a trace impurity present in the compound - probably a heptanitrobinaphthyl. Thus at high multiplier settings it is possible to detect an ion - of extremely low intensity - at m/e 569 (the intensity of this ion is insignificant in comparison with the 'molecular ion' at m/e 524). Nevertheless the presence of such an impurity may well be significant, as the more intense ions from its spectrum are likely to distort the spectrum of compound 'V'. Thus for example an ion is visible at m/e 523 (5.2%) which though unlikely to arise from a hexanitrobinaphthyl, is very likely to arise from a heptanitrobinaphthyl - particularly if it has a pair of adjacent peri substituted nitro groups (the M - NO_2 ion). The intensities of the various ions in the mass spectrum of 'V' must therefore be regarded with some caution, as the identity of the impurity (and hence its breakdown pattern) is not known.

In general the spectrum of 'V' has great similarity to that of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl (although the two are clearly not the same). Indeed a fragmentation scheme has been drawn up for 'V' based primarily upon that of the compound 'Q'. (See scheme 2:XIX which seems to provide a reasonable fit for the most intense ions in the spectrum of 'V'.) The most obvious difference between the spectra of these

Scheme 2:XIX

Fragmentation Pattern for the Mass Spectrum of Compound 'V' - a Hexanitro-1,1'-binaphthyl



Continuous lines indicate those transitions which are supported by the presence of a metastable peak.

two compounds lies in the ratio of intensities observed between their repective (M - NO_2) and (M -$2NO_2$) ions. Thus although the M - 46 ion is the base peak in both spectra, the M - 92 ions have intensities of 40.9% ('Q') and 12.9% ('V'). This feature emphasies the non-equivalence of the two spectra and also seems to indicate either the presence of just one pair of adjacent peri substituted nitro groups in 'V', as in structure (2-30), or the presence of 2,8'- substitution as in structure (2-31) (compare with the fragmentation observed in 'R'). Indeed the main sequence of fragmentation in 'V' (sequential loss of $2NO_2^{\cdot}$, $2NO^{\cdot}$ and 2CO) is compatible with either of the structures (2-30) or (2-31). Thus in both cases the loss of one molecule each of $NO_2^{\cdot}$, $NO^{\cdot}$ and CO would be expected due to the presence of one pair of adjacent peri substituted nitro groups, whilst the loss of a second molecule each of $NO^{\cdot}$ and CO could be attributed to interaction between the 8- nitro group and the adjacent naphthyl ring. In the case of structure (2-30) this rearrangement would be exactly as that in 'U' whilst for structure (2-31) the interaction would be similar to that in compound 'R'. In either event the fragmentation pattern is explained satisfactorily.

Since the precise intensities of the various ions in the spectrum of 'V' is a little doubtful - due to the presence of an impurity, a more detailed discussion of this spectrum does not seem worthwhile.

Conclusions about the Structures of Compounds 'V' and 'U'

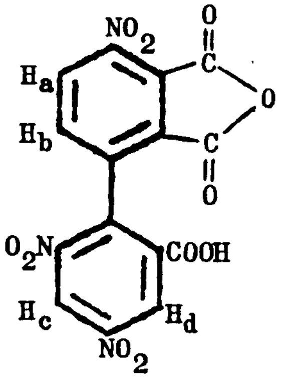
On the basis of the above data it is concluded that the compound 'V' is either 2,4,4',5',7',8- or 2,4,4',5,6',8'- hexanitro-1,1'-binaphthyl. There is however insufficient evidence to distinguish reliably between these two possibilities. It follows from the above conclusion that the compound 'U' is either 4,4',5',7',8- or 4,4',5,6',8'-pentanitro-1,1'-binaphthyl. (ie on the basis of this nitration evidence it seems relatively unlikely that 'U' is 4,4',5,5',7-pentanitro-1,1'-binaphthyl).

It must therefore be assumed that the compound 'U' is derived from an impurity present in the original substrate (4,4',5,5'-tetranitro-1,1'-binaphthyl). Further it seems very likely that this impurity was in fact 4,4',5,8'-tetranitro-1,1'-binaphthyl (compound 'P').

2.5. Isolation of an Oxidation Product of 4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl the Structure of Which is Uncertain - Designated Compound 'Z'

It has been clearly demonstrated during the course of the present work that when 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl is treated for prolonged periods in mixed acid at high temperature the substrate becomes substantially oxidised to water soluble products. As the fate of the hexanitrobinaphthyl under these conditions was of interest, an attempt was made to isolate the main water soluble product from a suitable reaction. Thus a sample of highly purified hexanitrobinaphthyl was treated in a mixture of fuming nitric and concentrated sulphuric acids until most of the substrate (96wt%) had been converted to water soluble products. On work up of the water soluble portion from this reaction, a material 'Z1' was isolated as pale yellow crystals. When dried under reduced pressure (100°C) this material was converted to a white powder 'Z2' (yield 49% on the hexanitrobinaphthyl). Whilst no spectra are available for the compound 'Z1', because of its conversion to 'Z2', several spectra have been recorded for the latter material. These are presented in the appendix.

Unfortunately positive identification of the compound 'Z2' cannot be made at the present time on the basis of the available data. Nevertheless it is suggested that 'Z2' may have the structure (2-32); although not completely satisfactory this explanation is the best available at the present time. The data is considered below.



(2-32)

Proposed Structure for Compound 'Z2'
(Molecular Weight 403)

The Compound 'Z2'

Analysis of the compound 'Z2' gave the following results:- C : 45.6%; H : 2.6%; N : 10.0%. Although these figures deviate significantly from the expected values for structure (2-32) (C : 44.7%;

H : 1.2%, N : 10.4%) it should be noted that the analysis corresponds to an empirical formula of $C_{16}H_{11}N_3(O_{11})$ (= 421). Such a formula seems unreasonable both in view of its high hydrogen content and its inconsistency with the mass spectrum. It is therefore concluded that the analytical figures are inaccurate - possibly due to contamination of the sample.

The Infra-red Spectrum

The infra-red spectrum of 'Z2' (see appendix) shows a band at $3100cm^{-1}$ due to aromatic C-H stretching and two intense bands at 1550 and $1350cm^{-1}$ corresponding to the nitro (asymmetric and symmetric) stretching frequencies. In addition to these absorbtions there are two intense bands at 1810 and $1720cm^{-1}$, the latter also having a shoulder at $1730cm^{-1}$. It is assumed that two of these absorbtions are due to the anhydride carbonyls in structure (2-32), although the frequencies are possibly a little lower than expected in view of the strain which is associated with a five membered ring.[64d] The reason for this is unclear, but the close proximity of the 4-nitro substituent to the anhydride grouping, is likely to influence the carbonyl stretching frequencies.[86b] As the two carbonyl frequencies produced by an anhydride are normally separated by about 60 wavenumbers,[64d] the absorbtions at 1810 and $1730cm^{-1}$ are most likely due to the anhydride function. The band at $1720cm^{-1}$ is therefore assigned to the free carboxylic acid group. Although this band occurs at rather higher frequency than is normally quoted for aryl carboxylic acids (1700-$1680cm^{-1}$ [64e]), such a shift is only to be expected in view of the presence of two nitro groups in the same aromatic ring.

Since the spectrum of 'Z2' was recorded from a pressed disc, it is impossible to identify a band due to the OH grouping. Thus the OH stretching frequencies of carboxylic acids are anomalous in showing no absorbtion when the free acid is examined in the solid state.[64e]

There seems to be little additional evidence to be derived from the spectrum of 'Z2' due to its overall complexity. Thus the various other bands which are normally associated[64d/e] with the anhydride/ carboxylic acid groupings, cannot be identified due to the presence of several overlapping bands. For example the C-O stretching vibration for both classes of compound, normally falls in the range 1320-$1210cm^{-1}$,[64d/e] however, the spectrum of 'Z2' has several overlapping bands in this region which prevents assignment of the individual absorbtions.

The Mass Spectrum

The mass spectrum of 'Z2' is given in the appendix as a bar diagram and a list of relative intensities. The molecular ion in the spectrum is apparently very weak and is therefore difficult to identify with certainty. Nevertheless it is believed to be a peak at m/e 403 (0.3%), this would be consistent with the proposed structure for 'Z2' (2-32) $M^{+} = C_{15}H_{5}N_{3}O_{11}{}^{+\bullet}$. There is a weaker peak at m/e 415 (0.1%) but this is attrubuted to an unidentified impurity. Indeed as the intensity of some peaks varies with repeated scanning of the spectrum, the sample must contain an impurity. Thus a detailed analysis of the spectrum is not worthwhile, although it is pertinent to note that by considering the most intense ions in the spectrum, it is possible to construct two fragmentation pathways each involving the expulsion of $3NO_2$ radicals, 2 molecules of CO_2 and one of CO from the molecular ion (see scheme 2:XX). Such a fragmentation pattern would clearly correlate well with the proposed structure (2-32).

The Proton Magnetic Resonance Spectrum

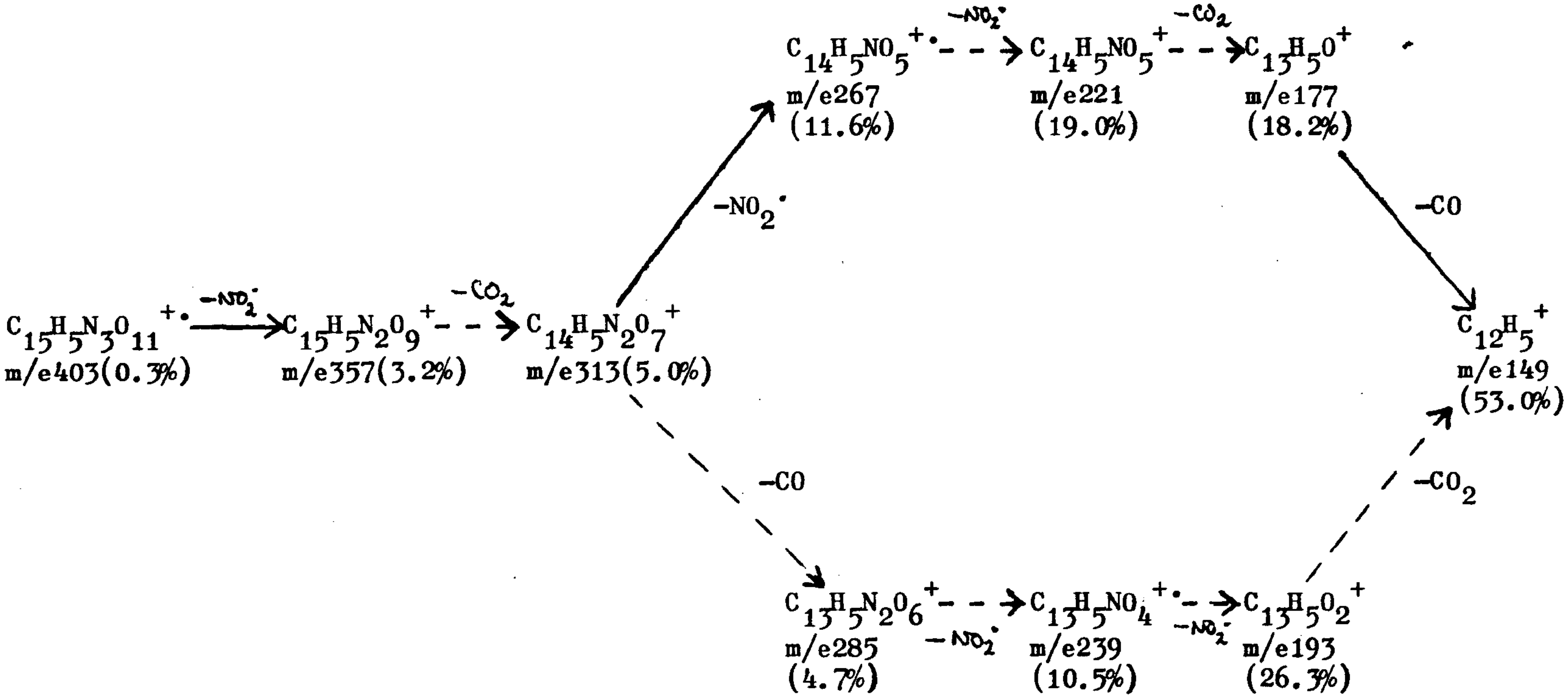
The PMR spectrum of 'Z2' in DMSO (see appendix) comprises two sets of AB quartets as follows:-
τ 0.57 doublet, J = 1.9Hz (1H), τ 0.91 doublet, J = 1.9Hz (1H), τ 1.27 doublet, J = 8.6Hz (1H), τ 1.76 doublet, J = 8.6Hz (1H).
The relatively simple pattern of the spectrum considerably narrows the structural possibilities for the compound 'Z2'. The structure (2-32) however, seems to provide a reasonable fit for the spectrum. Thus the doublets at τ 1.76 and 1.27 are assigned to the 'ortho coupled' protons $H_a/_b$, whilst the doublets at τ 0.91 and 0.57 are assigned to the protons $H_c/_d$. Since H_a is sited ortho to a nitro group it should give rise to the signal at τ 1.27 whilst H_b should produce the doublet at τ 1.76. A comparison of these protons with the 'analagous' ones in say 4,4'-dinitro-1,1'-binaphthyl ($H_{3/2}$: τ 1.56/2.26 respectively) shows that they resonate at much lower field, as would be expected due to the 'replacement' of a benzenoid ring with an electron withdrawing anhydride grouping. In fact a somewhat greater shift is observed for H_b than for H_a and this presumably reflects the influence of the strongly electron withdrawing dinitrobenzoic acid moiety - which is much closer to the former proton than the latter.

In the case of the 'meta coupled' quartet, the doublet at τ 0.57 is assigned to the proton H_c, because a nitro group produces greater deshielding of an adjacent proton than does a carboxylic acid

Scheme 2:XX

Fragmentation Pattern for the Mass Spectrum of Compound 'Z2'

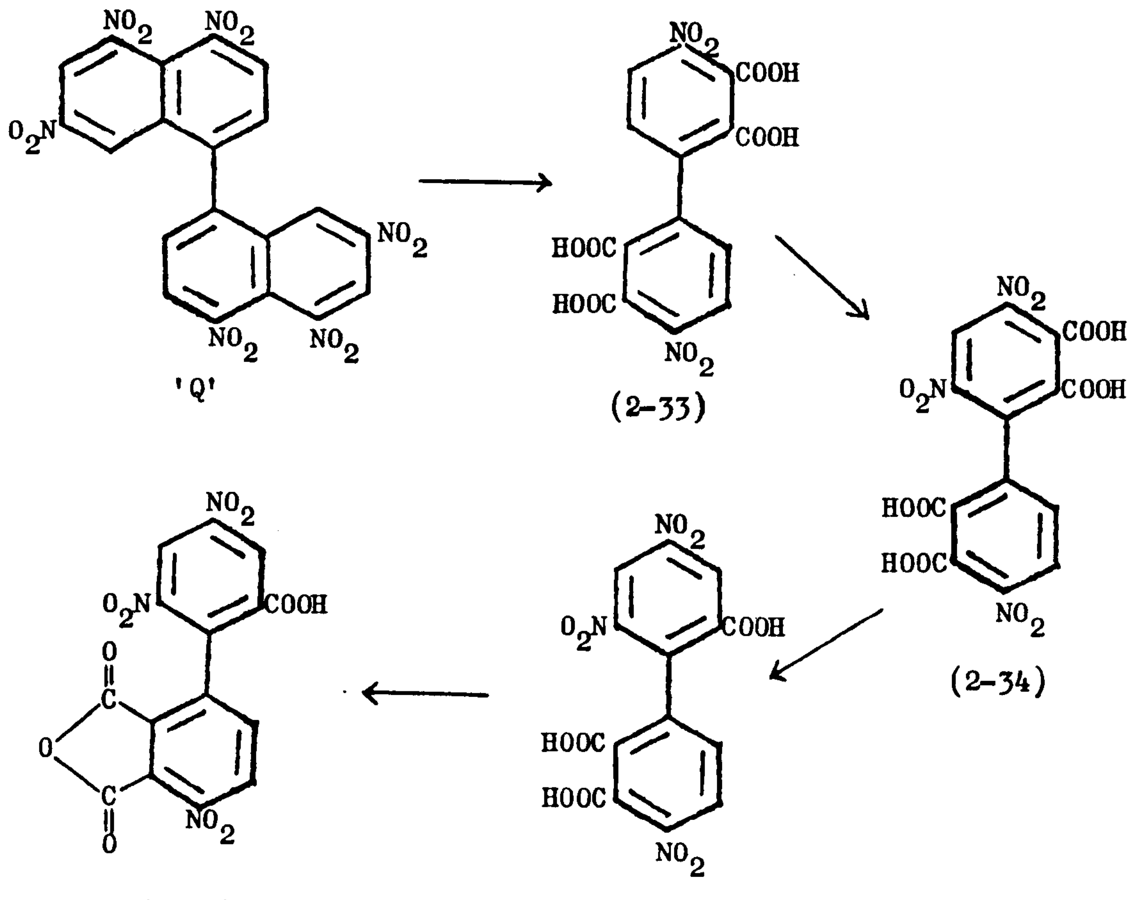
Continuous lines indicate those transitions supported by the presence of a metastable peak.



group.[121] These protons may be compared say with H_6 in compound 'Q' (τ 1.01) as this proton is also flanked by two strongly electron withdrawing groups. In fact both H_c and H_d resonate at lower field than does H_6, but this is explicable because unlike 'Q', 'Z2' contains three strongly electron withdrawing groups in a single benzenoid ring.

The Formation of 'Z2'

Since it is known that nitro (and dinitro) phthalic acids are formed as by-products in the nitration of naphthalene,[4a] it seems reasonable to propose that the binaphthyl system could be oxidised to a dinitro-biphthalic acid such as (2-33). This species could possibly undergo further nitration to yield the compound (2-34). Decarboxylation and dehydration of (2-34) could then yield (2-32), the ortho and para nitro groups producing preferential decarboxylation at the 3- position. Thus if compound 'Z2' is assigned the structure (2-32), then 'Z1' may well have the structure (2-34) or (2-35). It must be assumed in this scheme that deactivation of the species (2-34) is sufficient to prevent the dinitration of both rings under the prevailing reaction conditions.



'Q'

(2-33)

(2-34)

(2-35)

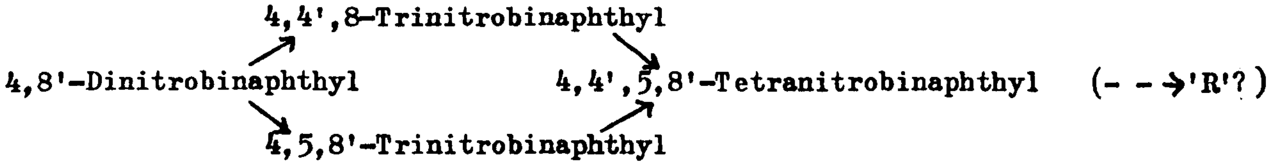
(2-32)

2.6. Conclusions

2.6.1. The Course of Nitration in 1,1'-Binaphthyl

The present work has confirmed the observations of Schoepfle[10] that nitration of 1,1'-binaphthyl under relatively mild conditions (nitric/acetic acids) yields primarily 4,4'-dinitro-1,1'-binaphthyl. Thus all the data available for the products of this reaction is consistent with the proposed structure. It has further been shown that the use of more vigorous reaction conditions (acetic anhydride/nitric acid) produces substitution primarily at the 5- positions - leading ultimately to the preparation of 4,4',5,5'-tetranitro-1,1'-binaphthyl. The latter observation is consistent with recent work by Jones and Joyner,[12] although these authors recommend much harsher conditions for the preparation of this compound than were found necessary during the present work. The main product obtained from the reaction of 1,1'-binaphthyl in mixed acid has been shown to be 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl, however, all attempts to further nitrate this material have resulted merely in oxidation of the substrate to water soluble products.

In addition to the main 4,5- substituted products produced by the nitration of binaphthyl in acetic anhydride/nitric acid, small quantities of other products have been isolated which are thought to contain an 8- nitro substituent. The proposed structures of these compounds: 4,8'-dinitro-1,1'-binaphthyl ('C-1'), 4,4',8-trinitro-1,1'-binaphthyl ('C-2'), 4,5,8'-trinitro-1,1'-binaphthyl ('F'), and 4,4',5,8'-tetranitro-1,1'-binaphthyl ('P') suggest that they constitute a second series of nitration products which are related by the common precursor of 4,8'-dinitro-1,1'-binaphthyl: scheme 2:XXI.



Scheme 2:XXI

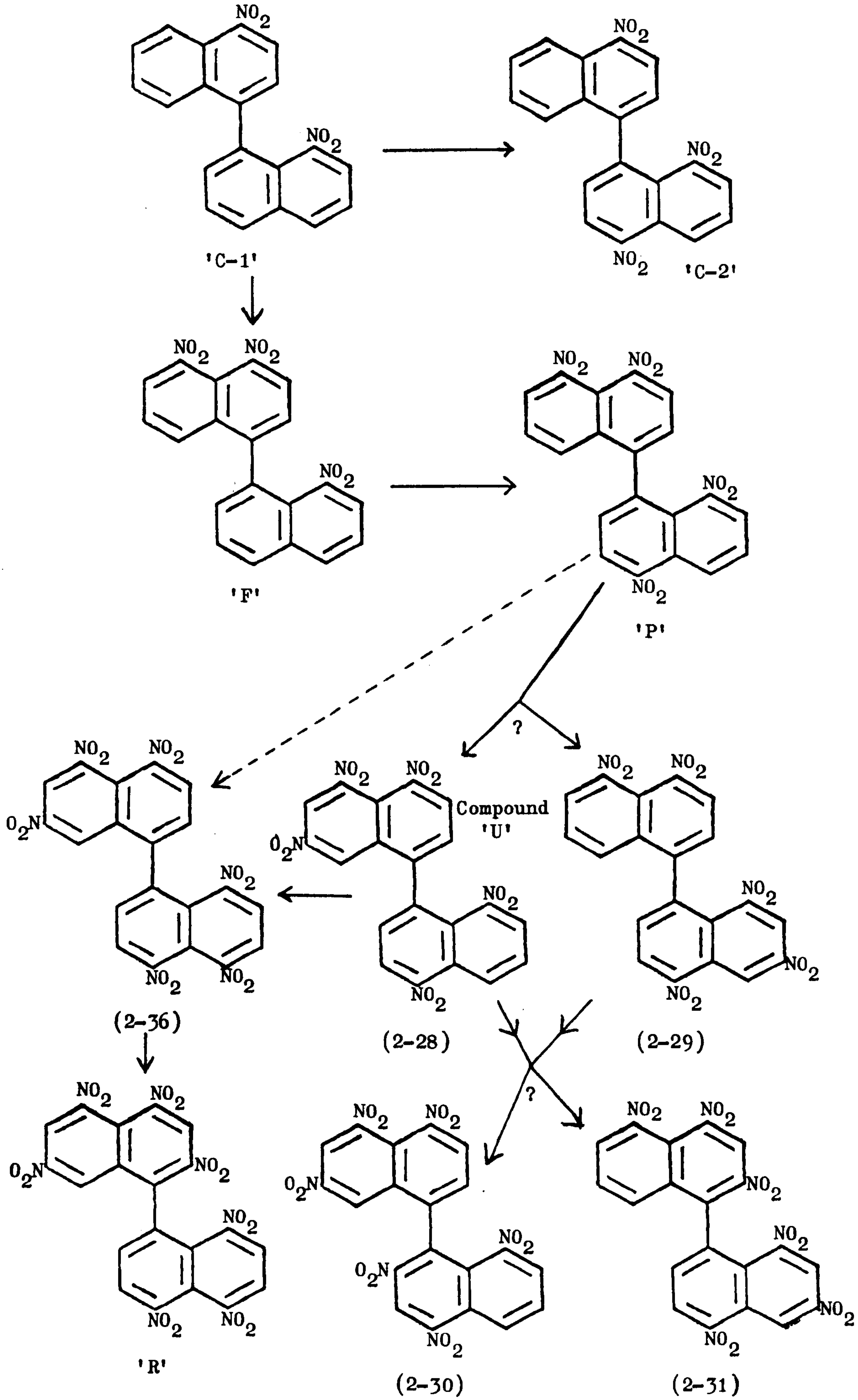
Further, under more vigorous reaction conditions the compound 'P' will become further nitrated and may possibly form the heptanitrobinaphthyl 'R'. This possibility is supported by the fact that a purified sample of 'P' apparently nitrates to the compound 'R' (see experimental). However, only one of the earlier nitration steps (above) has been confirmed in a similar fashion, that is, the conversion of 4,5,8'-trinitro-1,1'-binaphthyl to 4,4',5,8'-tetranitro-1,1'-binaphthyl. Thus a purified sample of compound 'F' has been nitrated to the compound 'P' using nitric acid in acetic anhydride (see experimental).

As it seems likely that the pentanitrobinaphthyl 'U' also contains an 8- nitro substituent, it would appear logical to also include this in the general nitration scheme for the 'minor' products. A possible sequence of nitration for the various 8- substituted nitrobinaphthyls is outlined in scheme 2:XXII. It should be noted that the compounds (2-28) and (2-36) which are shown as possible precursors to 'R', have not been isolated and positively identified, although the structure (2-28) is equivalent to one of those proposed for the pentanitrobinaphthyl 'U'.

Whilst it is possible to assign the structure (2-28) to the pentanitrobinaphthyl 'U' and thereby make it fit neatly into the overall scheme of products, such a conclusion is not necessarily correct. Thus the nitration of 'U' has been shown to produce a compound 'V' which is believed to have either structure (2-30) or (2-31). Both of these structures are obviously dissimilar to (2-36) and further they are incapable of being nitrated to the compound 'R'. The evidence would therefore seem to suggest that 'U' does not nitrate to the compound 'R'. It is however possible that during the preparation of compound 'V' another hexanitrobinaphthyl such as (2-36), or indeed the heptanitrobinaphthyl 'R', was formed but not isolated. Thus the additional products may have been lost during crystallisation of the compound 'V'. This seems a very real possibility because one method of purification for the compound 'R', is to retain it in a solution of toluene/acetone whilst impurities are crystallised out. Thus it is likely that if any of the compound 'R' was produced from the nitration of 'U' it would have remained undetected, in the supernatent liquid, after crystallisation of 'V'. Indeed this was the object of the crystallisation process, as it was originally believed that traces of 'R' were the cause of the impurity peaks in the mass spectrum of 'V'. The hexanitrobinaphthyl (2-36) could presumably have been lost in a similar fashion, if it was formed during the reaction. In consequence it is uncertain whether 'U' can be nitrated to the heptanitrobinaphthyl 'R' and it therefore remains impossible to distinguish between the structures (2-28) and (2-29) for the pentanitrobinaphthyl.

In view of the foregoing discussion it appears likely that the compounds 'C-1', 'C-2', 'F' and 'P' are precursors of the compound

A Possible Nitration Sequence for the 8- Substituted Nitrobinaphthyls



'R' . In this event the isolation of compound 'R' from the nitration of a 'purified' sample of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl seems best explained by the presence of an impurity in the substrate - possibly the compound (2-36). The fact that 'R' was detected at all in such reactions must largely be due to the greater stability of this compound over 'Q' with respect to oxidation in the nitration medium. Thus during prolonged nitration reactions the hexanitrobinaphthyl 'Q' became completely oxidised to water soluble products whilst the compound 'R' survived. Since the only water insoluble product remaining at the end of the reaction was the compound 'R', this product was readily isolated despite its very low yield. The reason for the greater stability of 'R' under these conditions is unclear. Certainly the presence of one 'extra' nitro group in the compound 'R' should tend to deactivate it with respect to oxidation - as compared with 'Q' - but it seems surprising that a single nitro group should have such a great effect.

Possibly any differences between the average molecular conformation prevailing in the two compounds, could influence the relative ease of oxidation of these materials.

Whilst the presence of a severly sterically hindered nitro group has been established from the spectroscopic data for each of the compounds 'C-1', 'C-2', 'F', 'P' and 'R', it is more difficult to make a definative assignment of position for this substituent. Certainly the most reasonable explanation for the observed hinderance is location of the substituent at either the 2- or the 8- position, but there is little evidence to distinguish reliably between these two sites.

On the basis of molecular models it appears very likely that an 8- nitro substituent would be subject to severe steric hinderance whilst a 2- nitro substituent would be much less restricted. The models further suggest that an 8- nitro substituent would be incapable of assuming coplanarity with the aromatic system without gross deformation of bond angles. This contrasts however with the 2- substituent which, subject to the predominance of a favourable molecular conformation, would appear able to closely approach coplanarity with the aromatic system. Such an interpretation is found consistent with the UV spectrum of 'R' which, if it is assumed that the 8- nitro group is hindered, suggest that the 2- nitro substituent lies substantially coplanar with the aromatic system.

It is also pertinent to note that in the case of the compounds 'C-2' and 'P' the presence of a 2- nitro substituent would involve the dinitration of one aromatic ring whilst another remained unsubstituted. As this possibility seems extremely unlikely the presence of a 2- nitro substituent in these compounds can effectively be discounted. Further as the compound 'F' can be nitrated to the compound 'P', a 2- nitro substituent may also be discounted in 'F'. Unfortunately however, this argument cannot be carried back to the compound 'C-1' because no purified sample of this material has ever been nitrated to 'C-2' (or 'F'). In fact selection of the 8- position in binaphthyl as the site of the 'hindered' nitro group, seems a fairly reasonable hypothesis because the peri positions are normally the most reactive sites towards nitration in the naphthalene nucleus. Thus the mono-nitration of naphthalene itself leads primarily to the production of α-nitronaphthalene[4a] whilst dinitration produces a mixture of predominantly the 1,5- and 1,8- isomers in the ratio of 1:2.[4a,122] (This result is little affected by the presence of acetic anhydride,[123] although the conditions used here are somwhat dissimilar to those applied in the present work.) This analogy must be tempered by the fact that the 2- positions of the binaphthyl molecule are activated by mesomeric interaction between the two naphthalenic systems, the extent of such interaction is not likely to be large however, because resonance between the two systems is limited by steric factors.[69,75] (Compare for example the case of biphenyl,[124] where there is evidence to suggest that activation of the 2- and 4- positions is severly limited by non-coplanarity - even though the molecule is not obviously hindered.) In fact it would appear, in view of the reactivity toward nitration of the peri positions in naphthalene, that the yields of 8- substituted nitrobinaphthyls obtained by direct nitration are surprisingly low. It is thought that the reason for this is most likely the steric hinderance prevailing at the 8- position, which must render this site less available to an attacking electrophile than either the 4- or 5- positions. In consequence only minor yields of the 8- substituted products are obtained.

In view of the various points discussed above it is considered most likely that the 'severly hindered' nitro group in each of the compounds 'C-1', 'C-2', 'F', 'P' and 'R', occupies an 8- position. Whilst all the available data is consistent with this conclusion it will be necessary to synthesize the above compounds by unambiguous routes if their structures are to be established conclusively.

It is of ineterest to note that despite several attempts to prepare a higher nitro derivative from 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl, no such product could be isolated. This result is in clear contrast with that obtained from the various 8- substituted nitrobinaphthyls, as these compounds evidently yield the heptanitrobinaphthyl 'R' without undue difficulty. One possible explanation for this anomalie lies in the steric characteristics of the binaphthyl molecule. Thus it is possible that a crucial factor governing the course of reaction,may be the accessibility of the 2- position to an attacking electrophile. Such accessibility will clearly be dependant upon the preferred conformation of the molecule and as the presence of an 8- nitro substituent would be expected to modify this conformation, it might reasonably be expected that this substituent would also influence the 'reactivity' of the 2- position. (The effect of the 8- nitro substituent on molecular conformation is reflected in the UV spectra of the various compouds, by reduced conjugation between the aromatic systems of 8- substituted species. Thus the aromatic $\pi \rightarrow \pi^*$ band in an 8- substituted nitrobinaphthyl, is observed to have a lower extinction coefficient than that of its isomeric analogue without such a substituent. Compare for example 4,4'- (or 5,5'-) dinitro-1,1'-binaphthyl with 'C-1'; 'D' with 'F' and 'H' with 'P'.)

It is thus proposed that once an 8- nitro substituent is present it so modifies the conformation of the binaphthyl molecule that access to the 2- position is facilitated for an attacking electrophile. In fact the presence of an 8- substituent seems likely to result in a roughly perpendicular arrangement of the two naphthyl moieties. It is pertinent to note that it is precisely this conformation which is most likely to permit the 2- nitro group in 'R' to adopt coplanarity with the naphthalene system to which it is attached. That is, in this conformation the 2- nitro group is subject to the least steric hinderance (note discussion of the UV spectrum of 'R').

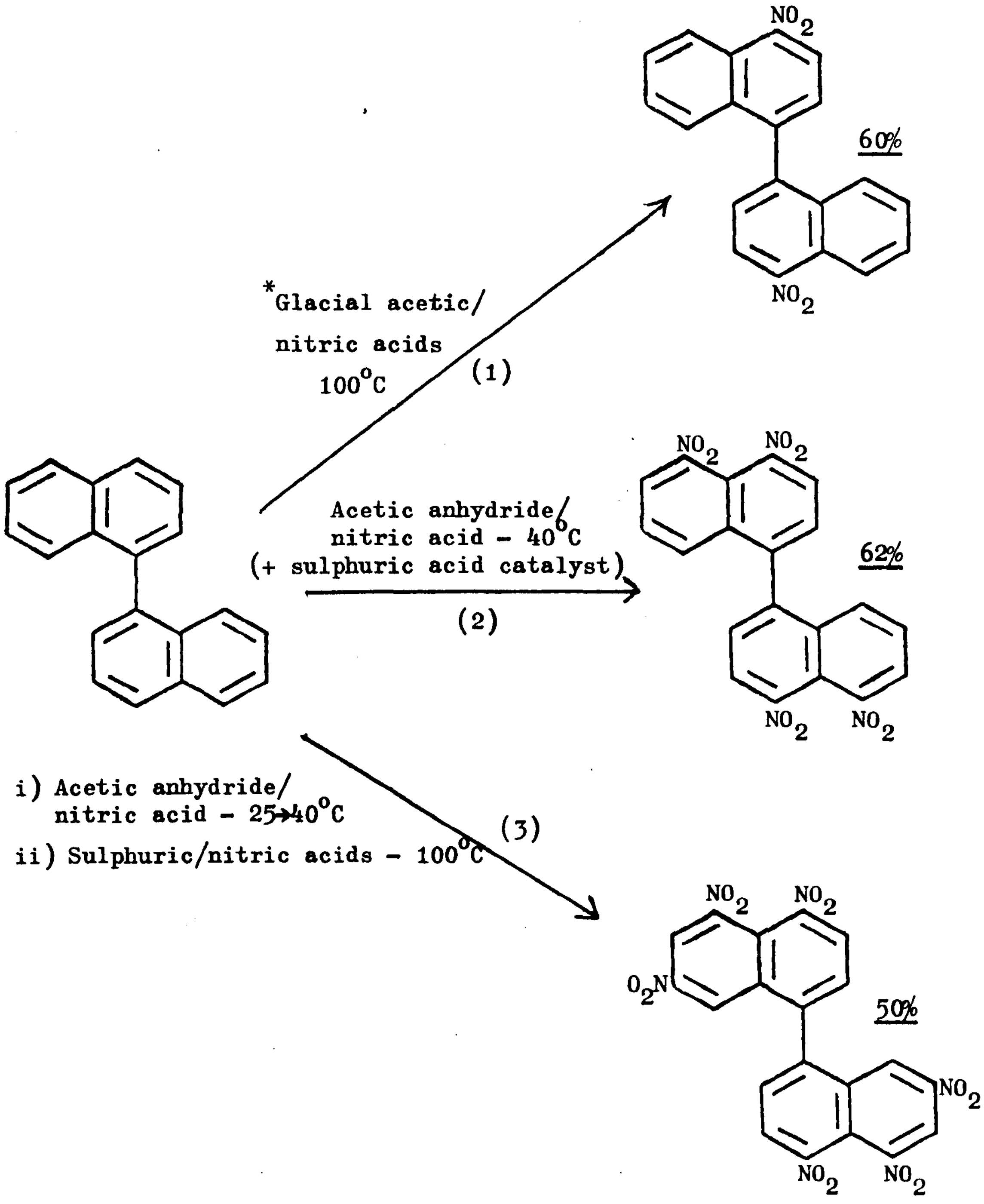
In view of the above conclusions it might be expected that a compound such as 1-picrylnaphthalene would undergo nitration at the 2- position more readily than does 1,1'-binaphthyl because the 2- position in 1-picrylnaphthalene should be less sterically hindered than the analagous site in 1,1'-binaphthyl. This possibility has in fact been verified and it has been shown that a 2- nitro derivative can be prepared from 1-picrylnaphthalene, in mixed acid, without undue oxidation (see chapter 3).

2.6.2. A Summary of Preparative Nitration Methods for 1,1'-Binaphthyl

As a result of the present work it is now possible to identify simple nitration procedures for the preparation of several symmetrical nitrobinaphthyls, these are summarised in scheme 2:XXIII.

Scheme 2:XXIII

A Summary of Preparative Nitration Routes for 1,1'-Binaphthyl



* The minor nitration products produced in this reaction medium have not been identified.

Unsymmetrical (8- substituted) nitrobinaphthyls can only be isolated with some difficulty. Thus whilst a small quantity of the 4,4',5,8'-tetranitro-1,1'-binaphthyl (?) (≈1.3%) can be isolated directly from reaction (2), no unsymmetrical hexanitrobinaphthyls have been isolated from the reaction (3). Nevertheless after prolonged nitration under the conditions of (3) (part ii), it is possible to isolate small quantities of a compound believed to be 2,4,4',5,5',7,8'-heptanitro-1,1'-binaphthyl.

Unsymmetrical di- and trinitrobinaphthyls have only been isolated from nitration reactions carried out in acetic anhydride/nitric acid, in absence of any sulphuric acid as catalyst. In all cases the separation of these products has involved protracted chromatographic techniques.

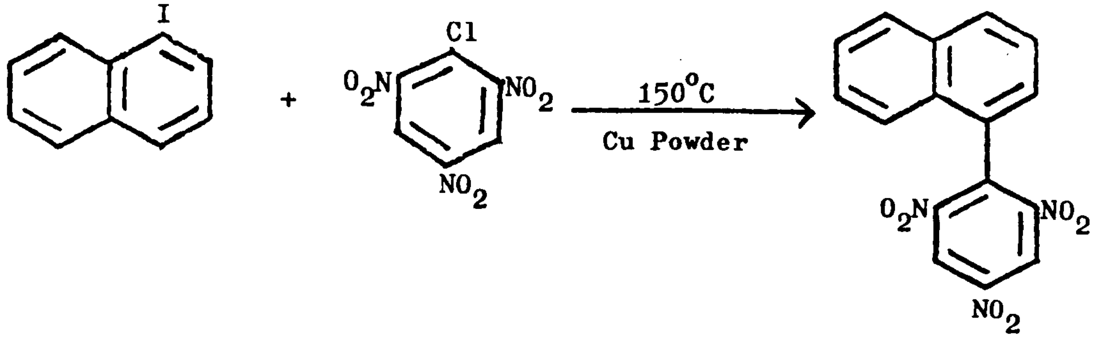
CHAPTER 3

Discussion of Results - The 1-Phenylnaphthalene System

3.1. 1-Picrylnaphthalene

As indicated previously the preparation of 1-phenylnaphthalene derivatives was undertaken via the Ullmann reaction. Since the preparation of this type of compound was clearly going to involve the use of a mixed Ullmann reaction it was necessary, when selecting the reactants, to bear in mind the points outlined in section 1.5.2.5. relating to optimisation of the unsymmetrical products. One major requirement, mentioned in the above section, was that one of the reactants needed to be 'unactivated' - that is lacking a nitro group ortho to the site of coupling. In view of this, the possibility of directly coupling two 'fully nitrated' species via an Ullmann reaction had to be discounted. Thus, inevitably, production of the most highly nitrated derivatives of phenylnaphthalene required a nitration to be carried out, on the coupled biaryl product, once it had been produced. In view of this and the non-availability of polynitrohalonaphthalenes from commercial sources, it proved most convenient to couple an unnitrated naphthyl moiety with a polynitrated phenyl system. The reactants which were actually chosen were 1-iodonaphthalene and 1-chloro-2,4,6-trinitrobenzene (picryl chloride). These compounds not only fulfilled the various requirements for an optimum yield from a mixed Ullmann reaction, but were also readily available from commercial sources. Additionally the low melting point of 1-iodonaphthalene obviated the problem of finding an 'inert' solvent for the reaction.

The preparation of 1-picrylnaphthalene, using these reagents was found to proceed smoothly at about 150°C, the product being isolated either by column chromatography or fractional crystallisation.



1-Picrylnaphthalene

All of the analytical data obtained for the product is consistent with the proposed structure. The spectra of 1-picrylnaphthalene (which had not been prepared previously) are discussed below.

The Infra-red Spectrum

The infra-red spectrum of 1-picrylnaphthalene (see appendix) shows a well defined band at 3020cm^{-1} corresponding to aromatic C-H stretching, it also shows two very strong bands at 1550 and 1350cm^{-1} corresponding to the asymmetric and symmetric NO_2 stretching frequencies. Both of these frequencies lie close to those of the analagous bands in s-trinitrobenzene (1545/1345cm^{-1} - KBr disc[125]) and picryl chloride (1540/1345cm^{-1}- KBr disc[125]) as would be expected due to the structural similarity of the NO_2 containing moieties in each of these compounds. This similarity of frequency coupled with a lack of splitting of the bands in 1-picrylnaphthalene, suggests that all the nitro groups in this compound are similarly orientated and that none of them is subject to very much steric hindrance. This in turn suggests that the two aryl systems are substantially removed from coplanarity so that steric interaction between the 2/6 nitro groups and the adjacent naphthalene moiety is avoided. Such a conclusion is consistent with the evidence which is available for the parent 1-phenylnaphthalene,[69,73] as it appears that this compound is not free to adopt a predominantly coplanar conformation - presumably due to steric factors.

The low frequency region of the spectrum for 1-picrylnaphthalene is too complex to be of value in confirming the structure of the compound.

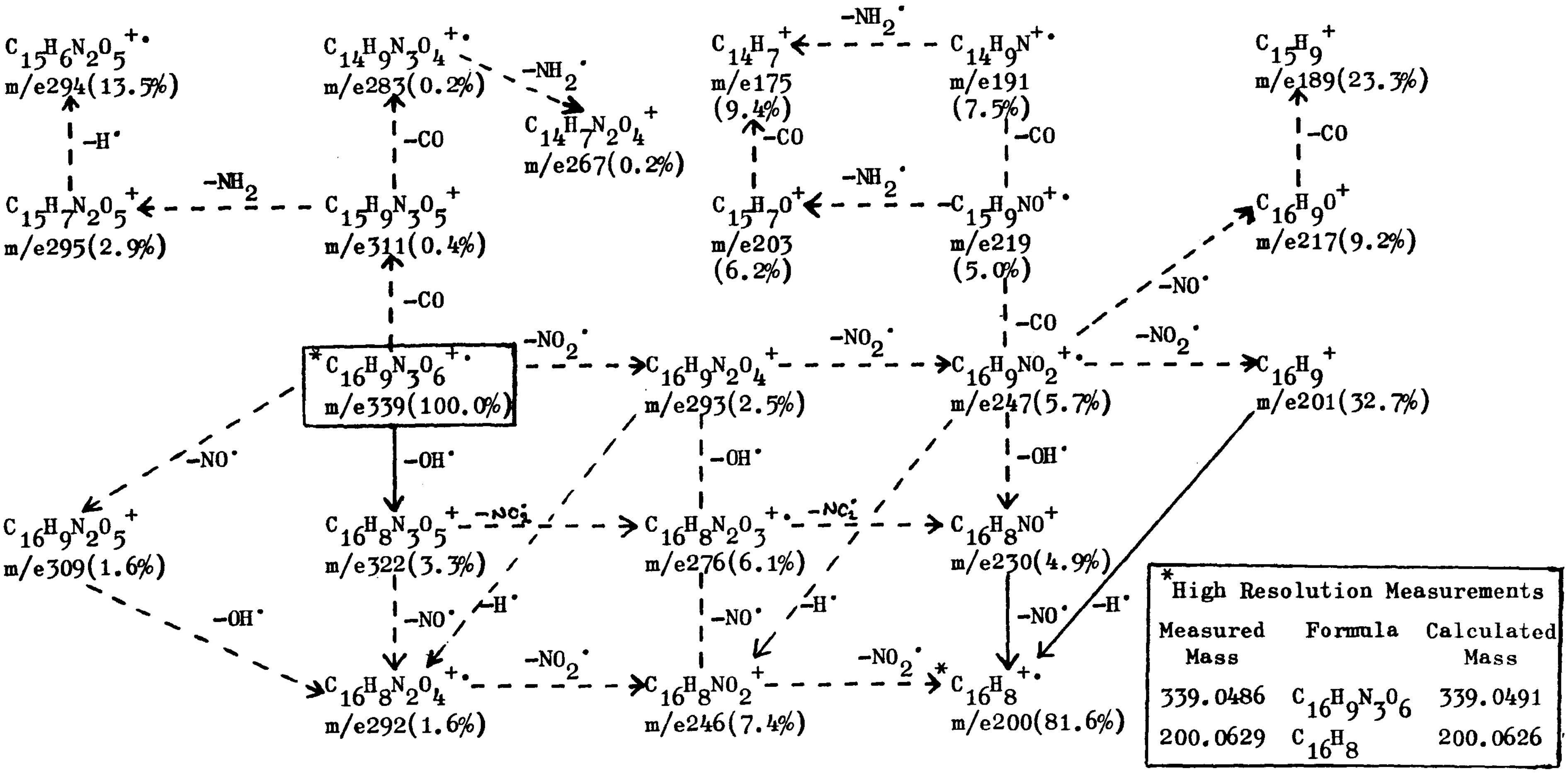
The Mass Spectrum

The major ions in the spectrum of 1-picrylnaphthalene are indicated in the scheme 3:I. A full list of relative intensities and a bar diagram are given in the appendix.

The spectrum shows a molecular ion at m/e 339 which is also the base peak of the spectrum. In fact a relatively intense molecular ion is only to be expected for the compound, as this is normally a characteristicfeature of nitro-aromatic compounds[76] - provided that there are no special structural features (eg adjacent peri substituted nitro groups) to otherwise "distort" the spectrum. In the present case typical fragmentation of the molecular ion is evident, via sequential loss of three nitro radicals (see scheme 3-I), whilst isomerisation of the individual nitro groups gives rise to the usual characteristic

Scheme 3:1

Fragmentation Pattern for the Mass Spectrum of 1-Picrylnaphthalene



*High Resolution Measurements

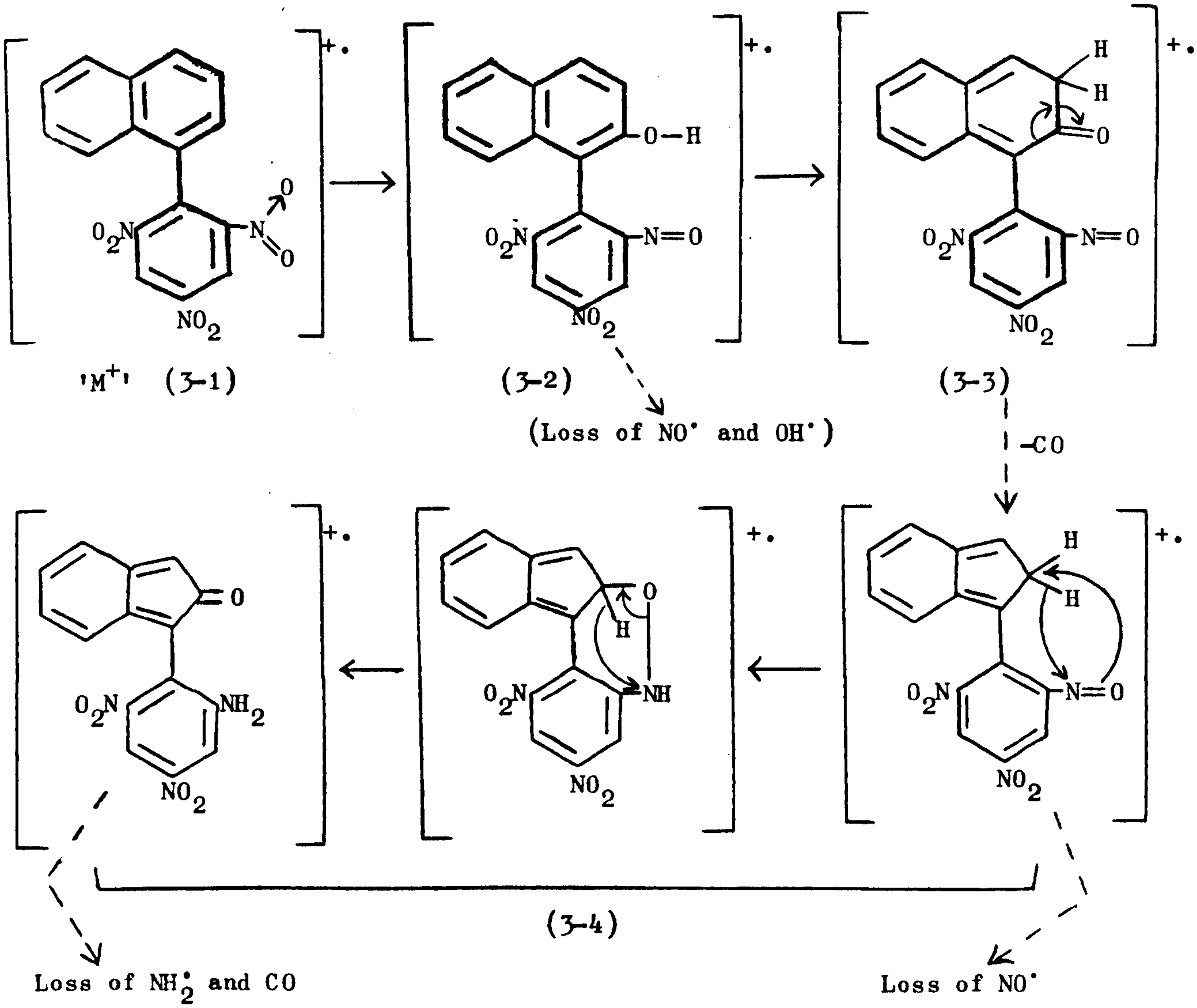
Measured Mass	Formula	Calculated Mass
339.0486	$C_{16}H_9N_3O_6$	339.0491
200.0629	$C_{16}H_8$	200.0626

Continuous lines indicate those transitions which are supported by the presence of a metastable peak.

ions - of relatively low intensity - corresponding to (M - O), (M - NO), etc.

Apparently the molecular ion may also lose $\mathrm{OH}^{\bullet}$ to produce the ion at m/e 322. This transition is supported by a metastable peak at m/e 305.8. Although not particularly abundant (3.3%) the ion at m/e 322 is interesting as it suggests an isomerisation of the parent ion (3-1)→(3-2) (scheme 3:II) in a fashion similar to that proposed for orthonitrobiphenyl[112] (cf s-trinitrobenzene which does not lose $\mathrm{OH}^{\bullet}$). Once formed the nitrosophenylnaphthol (3-2) may lose $\mathrm{OH}^{\bullet}$ and $\mathrm{NO}^{\bullet}$ or it can expel CO via the species (3-3). Subsequent loss of a second molecule of CO via the steps (3-4) though possible, seems to be less important in the nitrophenylnaphthalene system than for o-nitrobiphenyl. Thus in the spectrum of 1-picrylnaphthalene the ion at m/e 283 (M - 2CO) is vanishingly small.

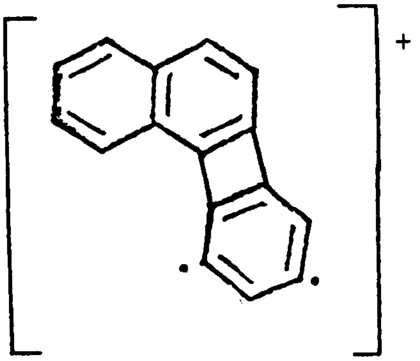
Scheme 3-II



The spectrum of 1-picrylnaphthalene suggests that whilst fragmentation via the scheme 3:II may occur, the loss of one or two nitro radicals is likely to precede it (possibly due to steric considerations). Thus the more abundant ions in the spectrum are 46 or 92 amu lower than the scheme 3:II would suggest (see fragmentation scheme 3:I).

Fragments containing a nitro group may of course lose NO˙ and CO via isomerisation of this group to the nitrite.[77] This mechanism would act quite independantly of the rearrangement described above and it seems likely that both mechanisms would contribute to the overall fragmentation.

In addition to the isomerisation discussed above, formation of the very intense ion at m/e 200 (81.6%) may be due to loss of a hydrogen radical from the species $C_{16}H_9^+$ (m/e 201) (there is a metastable for this transition). A similar loss of H˙ is observed in the spectrum of o-nitrobiphenyl, where it has been suggested that expulsion of $NO_2^{\bullet}$ and H˙ from the molecular ion could lead to the formation of the biphenylene ion. By analogy the ion $C_{16}H_8^+$ may have a ring closed structure such as (3-5). A similar 'cyclic' structure may possibly be attributed to the ion at m/e 294, which is presumably formed by the expulsion of H˙ from the ion at m/e 295.



(3-5)

The PMR Spectrum

The PMR spectrum of 1-picrylnaphthalene in acetone (see appendix) comprises a singlet at τ 0.85 (2H) and two complex multiplets at τ 1.83-2.18 (2H) and τ 2.28-2.68 (5H). The singlet is clearly due to the two equivalent protons of the picryl moiety as these are both strongly deshielded by their siting in between two nitro groups. The chemical shift of this signal correlates well with those of related compounds, as it falls almost exactly midway between the shifts observed for picryl chloride (τ 0.91 - acetone[125]) and s-trinitrobenzene (τ 0.77 - acetone[125]).

The two multiplets may be assigned to the protons of the naphthyl moiety although the coupling patterns are too complex to be analysed by inspection. Nevertheless the division of the multiplets into integral numbers of protons (2H:5H) is significant and probably results from the different chemical shifts which are associated with α and β naphthalenic protons (as discussed earlier). Once again a discrepancy is noted in the spectrum (cf the spectra of 1,1'-binaphthyl and derivatives), in that the implied ratio of α to β protons (2:5) does not correlate with the true ratio (3:4). It thus appears that the 8- substituted proton is again shielded by the adjacent aromatic system so that it resonates at higher field than is normally associated with an α-type proton. Thus the multiplet at τ 1.83-2.18 is assigned to the α-protons H_4 and H_5 whilst that at τ 2.28-2.68 is attributed to the β-protons H_2, H_3, H_6 and H_7, plus the shielded α-proton H_8. The chemical shifts observed for these multiplets are in fact very close to those observed in 1,1'-binaphthyl (τ 1.8-2.1 and τ 2.1-2.8 -acetone- see section 2.1) which suggests that the picryl moiety has very little deshielding effect upon the naphthalenic protons. Such an observation is consistent with the suggestion made above that the two aromatic systems within picrylnaphthalene are prevented from adopting a predominantly coplanar conformation. Indeed the main deshielding effect is evident in the 'β-multiplet' - as a spreading to lower field. This is therefore consistent with electron withdrawal via the inductive rather than the mesomeric effect, that is the deshielding predominantly affects H_2/H_3 and H_8.

The PMR spectrum in DMSO (see appendix) is essentially similar to that above although there are small changes in the observed chemical shifts. Thus the singlet occurs at τ 0.72 and the multiplets at τ 1.75-2.10 and τ 2.20-2.70.

The Ultra Violet Spectrum

The UV spectrum of 1-picrylnaphthalene in methanol (see appendix) shows a single well defined maximum at λ 223nm, ϵ 8900$m^2 mole^{-1}$. The wavelength of this band is therefore very close to that of the analagous band in 1-phenylnaphthalene (λ 227nm, ϵ 5620$m^2 mole^{-1}$ [73,69]). Presumably the slight hypsochromic shift evident in picrylnaphthalene is due to the combined effects of electron withdrawal and increased steric hindrance resulting from the introduction of nitro substituents. It should be noted however that as the nitro groups themselves produce a band at around 200nm ($\pi \rightarrow \pi^*$ transition[100]) the above may not be a fair comparison. Thus the aromatic $\pi\rightarrow\pi^*$ band of 1-picrylnaphthalene will inevitably be distorted by overlap with the nitro transitions.

In addition to the aromatic $\pi\rightarrow\pi^*$ absorption, the spectrum of 1-picrylnaphthalene shows a rather ill defined shoulder at about λ 280nm, ϵ 1270m^{2}mole^{-1}. This is presumably due to the nitro $n\rightarrow\pi^*$ transition. The longer wavelength transition, at about 340nm is even less well defined. Thus although there is some absorbance in the appropriate region, no definite shoulder can be discerned, as the absorbance simply decreases steadily, before reaching zero at around 380nm. The ill defined nature of both these bands renders the spectrum of this compound anomalous with respect to both the nitrobinaphthyls and the other nitrophenylnaphthalenes (see on) which have been prepared during the course of the present work. Thus in all other cases both of the longer wavelength transitions attributable to the nitro moiety, have been clearly discernable. The reasons for the above discrepancies are not readily apparent.

3.2. The Nitration Products of 1-Picrylnaphthalene

3.2.1. The Course of Nitration

Following the successful isolation of 1-picrylnaphthalene, nitration of this compound was undertaken with the intention of achieving maximum polynitration of the naphthalenic system. As some correlation was expected between the reactivity, towards nitration, of the 1-phenylnaphthalene and 1,1'-binaphthyl systems, 1-picrylnaphthalene was initially treated under similar conditions to those employed in the production of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl (mixed acid, 100°C - both with and without preliminary treatment in acetic anhydride/nitric acid). Such treatment yielded 1-picryl-4,5,7-trinitronaphthalene in up to 40% yield, so it is evident that nitration of the naphthyl moiety under these conditions follows an essentially similar course in each of the biaryl systems. This similarity between the two systems - with respect to the pattern of nitration - has recently been shown to extend also to the use of milder nitration media. Thus treatment of 1-picrylnaphthalene in glacial acetic acid/nitric acid (100°C) produces 1-picryl-4-nitronaphthalene,[126] (cf the preparation of 4,4'-dinitro-1,1'-binaphthyl), whilst nitration of the same compound in nitric acid and (excess) acetic anhydride (40°C) in presence of catalytic quantities of sulphuric acid, yields 1-picryl-4,5-dinitronaphthalene[126](cf the preparation of 4,4',5,5'-tetranitro-1,1'-binaphthyl).

The similarity between the two systems does not however extend to the use of more vigorous nitration media. Thus when picrylnaphthalene was treated in a mixture of fuming nitric and concentrated sulphuric acids, boiling under reflux, the substrate was not substantially oxidised to water soluble products, as occurred in the 1,1'-binaphthyl system, instead 1-picryl-2,4,5,7-tetranitronaphthalene was isolated in 43% yield. It is thought that the different behaviour of the two systems under these conditions, may reflect differences in their steric characteristics. Thus the bulk of the 2- and 6- nitro groups in 1-picrylnaphthalene may force this molecule to adopt a conformation in which the two aromatic systems are essentially perpendicular to one another. In contrast 1,1'-binaphthyl, lacking such gross steric hindrance, may adopt a preferred conformation which has a significantly smaller angle between the aromatic ring systems (though these still cannot become coplanar). It is thus postulated that an attacking electrophile would have much better access to the 2- position of a picrylnaphthalene, than the analagous position in a binaphthyl derivative. (Unless the binaphthyl contained an 8- substituent - see chapter 2.) Thus the rate of nitration at the 2- position in 1-picrylnaphthalene is likely to be much greater than that for the analagous binaphthyl derivative.

It is unclear, however, precisely why the picrylnaphthalene derivatives are so much more stable with respect to oxidation than is 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl. As suggested in chapter 2 it may be that differences in the average molecular conformation of the biaryl, have some influence on the susceptibility of the molecule towards oxidation. Thus it appears that it is the species in which the aromatic systems necessarily form a substantial angle to one another (picrylnaphthalene derivatives and the 8- substituted nitrobinaphthyl 'R') that are the least susceptible to oxidation. However in the case of the picrylnaphthalene derivatives a further factor which may be of significance is the low solubility -even at high temperature - of these materials in mixed acid. Thus although 1-picryl-2,4,5,7-tetranitronaphthalene is recovered essentially unchanged from a mixture of fuming nitric and concentrated sulphuric acids which has been boiling under reflux for 40hrs, it is possible that the material simply does not dissolve significantly under these conditions and that it is for this reason that the material is not subject to appreciable oxidation.

The structures of both 1-picryl-4,5,7-trinitronaphthalene and 1-picryl-2,4,5,7-tetranitronaphthalene have been well established by spectroscopic means. (The trinitro derivative has also been nitrated directly to the tetranitro derivative.) The various data available for these two compounds is discussed in the next two sections.

3.2.2. 1-Picryl-4,5,7-trinitronaphthalene

The Mass Spectrum

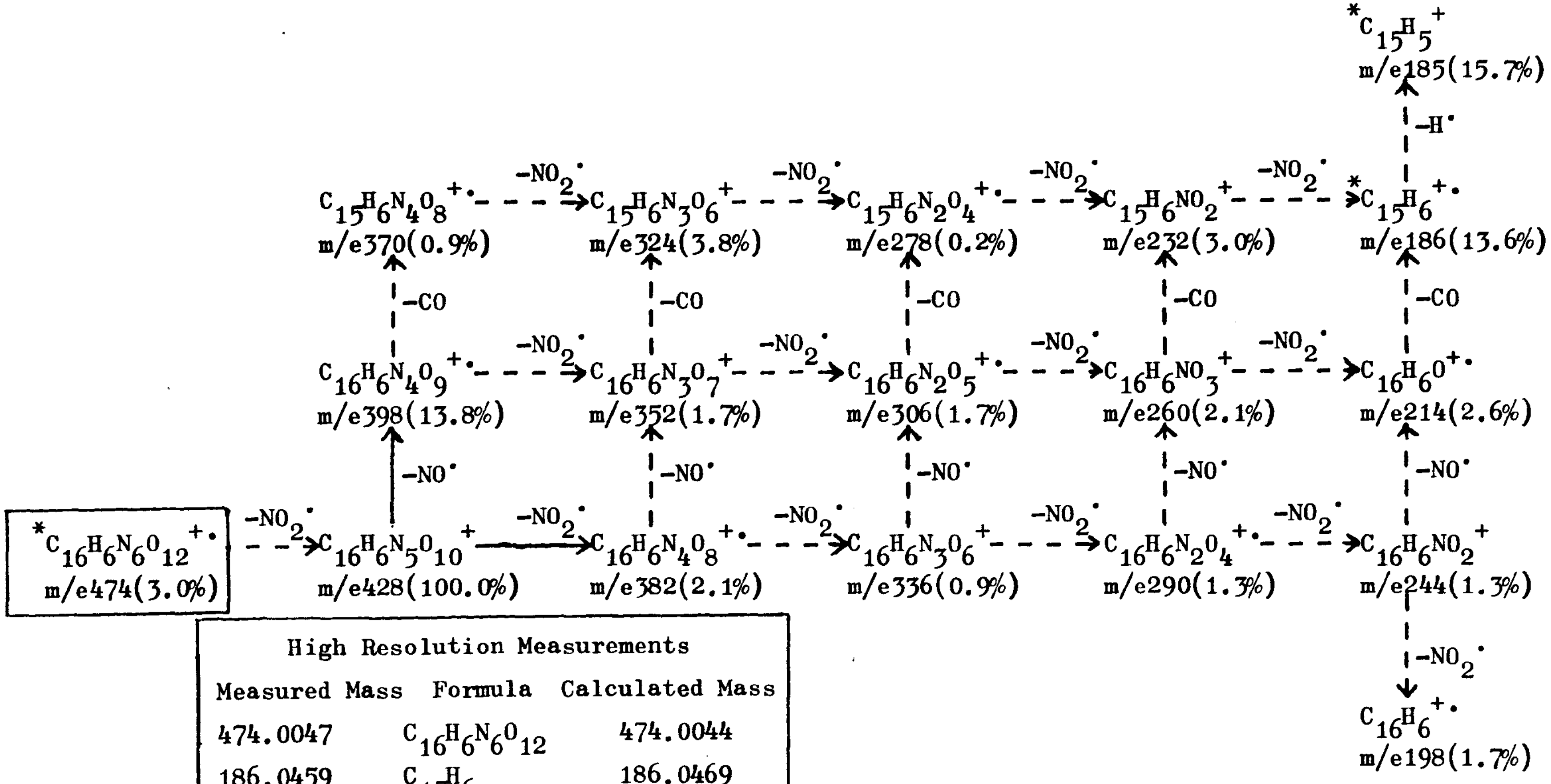
The mass spectrum of 1-picryl-4,5,7-trinitronaphthalene is presented in the appendix in the form of a bar diagram and a list of relative intensities. Whilst the spectrum shows a weak molecular ion at m/e 474 (3.0%), the main feature of the spectrum is a single very intense ion at m/e 428 (M - NO_2) (100%). This peak dwarfs all the remaining ions in the spectrum, none of which exceeds about 14% relative intensity. This feature is clearly indicative of the presence of adjacent peri substituted nitro groups and indeed, the second most intense peak in the spectrum occurs at m/e398 (13.8%) and corresponds to the (M - NO_2 - NO) ion, which itself characterises the breakdown of such a structural feature (see chapter 2). Many of the remaining ions in the spectrum may be rationalised in terms of the normal breakdown of nitroaromatic compounds vis: sequential expulsion of nitro groups (see scheme 3:III) and isomerisation-fragmentation of individual nitro substituents (ie loss of O$^\cdot$, NO$^\cdot$ etc). Indeed the latter isomerisation may also in part account for those ions whose production involves the loss of neutral CO^{77} (see scheme 3:III). The intensity of these particular ions however - relative to that of the great bulk of spectral fragments - is rather too high to be explained by this means alone. Thus these ions are regarded as corroborating evidence for the presence of adjacent peri substituted nitro groups, because the expulsion of neutral CO is characteristic of the fragmentation of this particular structural moiety (see chapter 2). In general however, the large number of fragment ions which are evident in the spectrum and their universally low intensity, must render a detailed analysis of the spectrum of somewhat doubtful value.

The Infra-red Spectrum

The infra red spectrum of 1-picryl-4,5,7-trinitronaphthalene shows a well defined band at 3020cm^{-1} corresponding to aromatic C-H stretching. There are also two very strong bands at 1550 and 1350cm^{-1} corresponding to the asymmetric and symmetric nitro stretching freq-

Scheme 3:III

Fragmentation Pattern for the Mass Spectrum of 1-Picryl-4,5,7-trinitronaphthalene



High Resolution Measurements

Measured Mass	Formula	Calculated Mass
474.0047	$C_{16}H_6N_6O_{12}$	474.0044
186.0459	$C_{15}H_6$	186.0469
185.0387	$C_{15}H_5$	185.0391

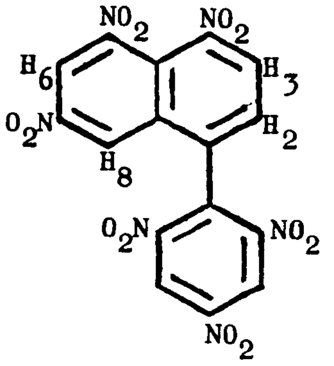
Continuous lines indicate those transitions which are supported by the presence of a metastable peak.

uencies. Although the high frequency band shows a secondary maximum at 1540cm^{-1} the lack of splitting in the symmetric band suggests that this is not directly attributable to the presence of differently orientated nitro groups - that is groups having different angles of twist relative to the aromatic plane. Nevertheless the molecule must contain such groups as the 4,5- substituents must be sterically crowded, whilst the 7- nitro group and those contained in the picryl moiety should be relatively unhindered. It thus appears that a similar situation prevails in this compound to that previously discussed for the hexanitrobinaphthyl 'Q', in that the frequency difference between the hindered and unhindered nitro groups of the naphthyl moiety has been reduced to the point where the two bands are not resolved. Indeed such a situation might reasonably be expected as the two compounds contain rather similarly substituted naphthyl moieties. Thus the nitro stretching frequencies observed in the picrylnaphthalene derivative fall very close to those observed in the hexanitrobinaphthyl (1550/1345cm^{-1}). The frequencies also coincide with those expected for the picryl moiety, thus the two nitro stretching frequencies in 1-picryl-4,5,7-trinitronaphthalene are indistinguishable from those observed for the parent compound 1-picrylnaphthalene.

The low frequency region in the spectrum of 1-picryl-4,5,7-trinitronaphthalene is fairly complex and is of little value for the determination of structure.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of 1-picryl4,5,7-trinitronaphthalene in acetone (see appendix) comprises the following signals:-
τ 0.62 singlet (2H), τ 0.92 doublet, J = 1.8Hz (1H), τ 1.14 doublet, J = 1.8Hz (1H), τ 1.27 doublet, J = 7.8Hz (1H), τ 1.85 doublet J = 7.8Hz (1H).



1-Picryl-4,5,7-trinitronaphthalene

The singlet at τ 0.62 is clearly attributable to the two equivalent protons of the picryl moiety which are expected to resonate at very low field due to their siting in between two nitro groups. The downfield shift of this singlet by 0.23ppm, with respect to that in the parent compound 1-picrylnaphthalene, is presumably due to the introduction of additional electron withdrawing substituents in the naphthyl moiety.

The remaining signals in the spectrum comprise two AB quartets, the doublets with a coupling constant of 7.8Hz being assigned to the ortho coupled protons[115] H_2/H_3, whilst the others (J = 1.8Hz) are attributed to H_6/H_8. Since H_2 is sited 'meta' to a nitro group whilst H_3 is ortho to the same substituent, the latter proton is likely to resonate at lower field than the former and is therefore attributed to the signal at τ 1.27 (therefore H_2 = τ 1.85). Also as H_8 is sited ortho/para to two nitro groups whilst H_6 is situated ortho to two such substituents, H_6 is likely to resonate at lower field than H_8. Thus H_6 is assigned to the signal at τ 0.92 and H_8 to that at τ 1.14.

The spectrum of 1-picryl-4,5,7-trinitronaphthalene in DMSO is essentially similar to that obtained in acetone, except that there are some variations in the observed chemical shifts. The spectrum may thus be assigned in an essentially similar fashion to that described above:- τ 0.55 singlet (2H) - picryl protons; τ 0.85 doublet, J = 1.8Hz (1H) - H_6; τ 1.10 doublet, J = 1.8Hz (1H) - H_8; τ 1.15 doublet, J = 7.8Hz (1H) - H_3; τ 1.81 doublet, J = 7.8Hz (1H) - H_2.

As 1-picryl-4,5,7-trinitronaphthalene contains a naphthalenic nucleus which is substituted in an essentially similar fashion to those in 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl, it is of interest to compare the chemical shifts noted above with those in the hexanitrobinaphthyl. This is done in the table 3-1 both for the spectra in acetone and in DMSO.

Table 3-1

PMR Data for 1-Picryl-4,5,7-trinitronaphthalene and 4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl

1-Picryl-4,5,7-trinitronaphthalene			4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl	
Proton	Acetone τ	DMSO τ	Acetone τ	DMSO τ
H_2	1.85	1.81	1.63	1.90
H_3	1.27	1.15	1.13	1.21
H_6	0.92	0.85	0.95	1.01
H_8	1.14	1.10	1.07	1.44
(Picryl	0.62	0.55)		

It is evident from the table 3-1 that in acetone, with the exception of H_6 which changes little between the compounds, all of the protons resonate at higher field in the picrylnaphthalene derivative than do their analogues in the nitrobinaphthyl. However in DMSO the converse is true, the various protons in the nitrobinaphthyl resonating at higher field than their analogues in the picrylnaphthalene. These figures therefore suggest the presence of specific solvent - solute interactions and it is evident from the above observations that the nature of these interactions varies significantly between the two compounds, for the above solvents. In view of this, any attempts to make a detailed correlation of chemical shifts between the two compounds, seems unlikely to be very meaningful. Nevertheless the supposed similarity in structure of the two compounds would seem to be reasonably substantiated by the fact that the difference of chemical shift observed between the two compounds, for any individual proton in a specific solvent, never exceeds about 0.2ppm despite the solvent effects noted above.

The Ultra Violet Spectrum

The UV spectrum of 1-picryl-4,5,7-trinitronaphthalene in methanol (see appendix) shows five maxima at λ 215nm, ϵ 4820m^{2}mole^{-1} (Ar $\pi \rightarrow \pi^*$); λ 229nm (sh), ϵ 4140m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$); λ 265nm (sh), ϵ 2720m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$); λ 319nm, ϵ 990m^{2}mole^{-1} and λ 353nm (sh), ϵ 620m^{2}mole^{-1} (both NO_2 $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ [107,108]).

The spectrum is clearly reminiscent of that observed for the hexanitrobinaphthyl 'Q' and is interpreted in an essentially similar fashion. The absorbtions are thus assigned in respect of two distinct classes of nitro group - the one being sterically hindered (λ 229/319nm) and the other not (λ265/353nm). The adjacent peri nitro substituents clearly belong to the former category whilst that at the 7- position of the naphthyl moiety belongs to the latter. The three picryl substituents are also presumably unhindered. In both cases the observed frequencies correlate well with those observed in the hexanitrobinaphthyl (hindered: λ 230/326nm; unhindered: λ 266/358nm). A comparison of these figures with those obtained from the spectrum of the parent 1-picrylnaphthalene is complicated by the anomalous nature of the latters spectrum. Nevertheless the band attributed to the nitro $n \rightarrow \pi^*$ transition in 1-picrylnaphthalene (λ 280nm, ϵ 1270m^{2}mole^{-1}) has clearly increased its intensity and moved to shorter wavelength (265nm) in the present compound, as would be expected[87] due to the presence of additional nitro groups. The aromatic $\pi \rightarrow \pi^*$ transition is also affected in the anticipated manner and is seen to have decreased its intensity and moved to shorter wavelength - with respect to that in 1-picrylnaphthalene (λ 223nm, ϵ 8900m^{2}mole^{-1}), due once again to the presence of additional nitro groups.

3.2.3. 1-Picryl-2,4,5,7-tetranitronaphthalene

The Mass Spectrum

The mass spectrum of 1-picryl-2,4,5,7-tetranitronaphthalene is presented in the appendix in the form of a bar diagram and a list of relative intensities. Whilst a very weak molecular ion is visible at m/e 519 (0.2%), the spectrum is dominated by the fragment at m/e 473 (M - NO_2) (100%) which dwarfs all of the remaining ions in the spectrum. This feature is clearly indicative of the presence of adjacent peri substituted nitro groups. Such an interpretation is supported by the intensity of the peak at m/e 443 (M - NO_2 - NO) (21.4%), as this is the second most intense ion in the spectrum, and is itself characteristic of the fragmentation of adjacent peri nitro groups. (See chapter 2.)

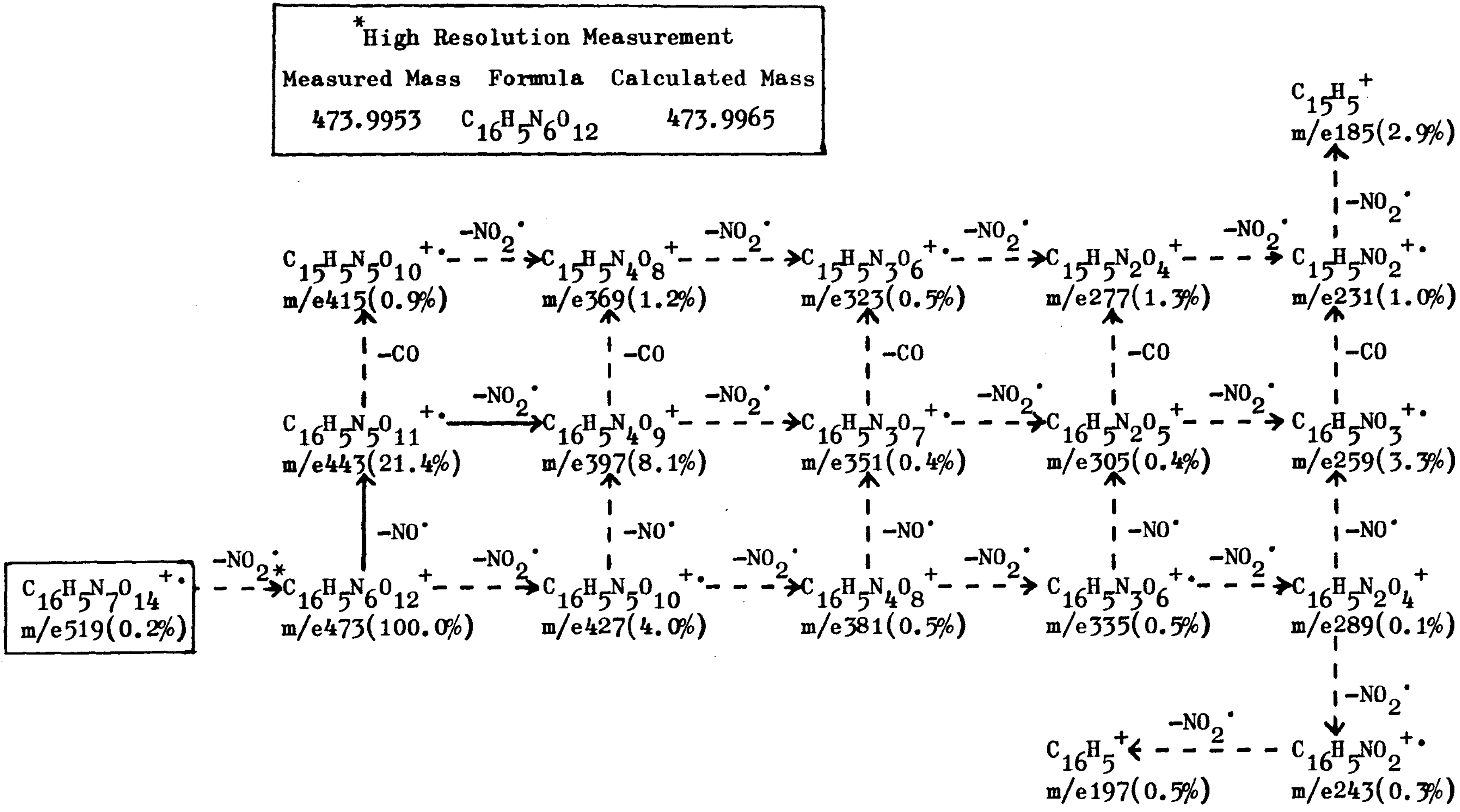
Many of the remaining ions in the spectrum, though of very low intensity, may be rationalised in terms of expulsion of the individual nitro groups (see scheme 3:IV) or isomerisation of the same, leading to loss of O', NO' etc. This represents the normal mode of fragmentation for nitroaromatic compounds. It is pertinent to note however that those ions shown as arising from the loss of neutral CO (scheme 3:IV) may not only be generated via the isomerisation and fragmentation of individual nitro groups,[77] but may also arise as a result of the CO expulsion which occurs as part of the characteristic fragmentation of adjacent peri substituted nitro groups (see chapter 2). In general however, the extremely low intensity of the vast majority of ions in the spectrum precludes a detailed discussion of the various modes of fragmentation.

The Infra-red Spectrum

The infra-red spectrum of 1-picryl-2,4,5,7-tetranitronaphthalene (see appendix) shows a well defined band at 3010cm^{-1} corresponding to aromatic C-H stretching. There are also two very intense bands at 1555 and 1355cm^{-1} which correspond to the asymmetric and symmetric nitro stretching frequencies. Although (in common with the trinitro derivative) the high frequency band shows a secondary maximum (at 1545cm^{-1}), the absence of any such splitting in the symmetric stret-

Scheme 3:IV

Fragmentation Pattern for the Mass Spectrum of 1-Picryl-2,4,5,7-tetranitronaphthalene



*High Resolution Measurement		
Measured Mass	Formula	Calculated Mass
473.9953	$C_{16}H_5N_6O_{12}$	473.9965

Continuous lines indicate those transitions which are supported by the presence of metastable peaks.

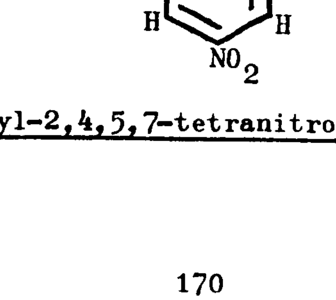
ching band suggests that this feature is not an indication of multiple nitro stretching frequencies. Nevertheless, in common with 1-picryl-4,5,7-trinitronaphthalene this compound must contain nitro substituents which are individually subject to varying degrees of conjugation with the aromatic system. Thus the adjacent peri (4,5-) substituents must be sterically crowded, whilst the 7- nitro group and those contained in the picryl moiety should be relatively unhindered. A similar situation therefore appears to exist in this compound, to that previously discussed for the hexanitrobinaphthyl 'Q' and 1-picryl-4,5,7-trinitronaphthalene, in that the frequency difference between the hindered and unhindered nitro groups of the naphthyl moiety, has been reduced to the point where the two bands are not resolved.

The observed frequencies for the two nitro stretching bands in 1-picryl-2,4,5,7-tetranitronaphthalene fall quite close to those observed in the trinitro derivative (1550/1350cm^{-1}) and thus reflect the rather similar structure of the two compounds. Nevertheless it is pertinent to note that the small shift to higher frequency that is evident in the tetranitro derivative, is in the anticipated direction. Thus the presence of an additional nitro group in this compound would be expected to increase the N-O bond orders, via its effect of reducing conjugation between individual nitro groups and the aromatic ring system.[87]

Once again the low frequency region of the spectrum proves to be of little value for structural determination.

The Proton Magnetic Resonance Spectrum

The PMR spectrum of 1-picryl-2,4,5,7-tetranitronaphthalene in DMSO (see appendix) comprises the following signals:- τ 0.45 singlet (2H), τ 0.55 singlet (1H), τ 0.65 doublet J = 1.9Hz (1H), τ 1.24 doublet J = 1.9Hz (1H).



1-Picryl-2,4,5,7-tetranitronaphthalene

The singlet at τ 0.45 is attributed to the two equivalent protons of the picryl moiety. As these protons alone are sited ortho with respect to two nitro groups, whilst also being located on a benzenoid nucleus containing three nitro substituents, it is only reasonable that they should resonate at lower field than any other protons in the molecule. Such an assignment is confirmed by the integration which shows that this singlet results from two protons. In fact the observed shift for these protons is about 0.1ppm downfield of that noted for the analagous protons in 1-picryl-4,5,7-trinitronaphthalene. This change is consistent with the substitution of a fourth (2- substituted) nitro group in the naphthyl moiety, which must tend to increase electron withdrawal by this grouping,from the picryl moiety. The singlet at τ 0.55 (1H) is assigned to the proton H_3. The low field at which this proton resonates is again due to its siting in between two nitro groups, but,as there are only two nitro substituent in the benzenoid ring to which it is attached, the signal occurs at slightly higher field than is observed for the picryl protons. A substantial downfield shift of 0.6ppm is noted for this proton with respect to the analagous one in 1-picryl-4,5,7-trinitronaphthalene (τ 1.15); such a shift is consistent with the fact that there are now two ortho nitro groups to deshield H_3, as opposed to just one in the trinitro derivative.

The two doublets at τ 0.65 and 1.24 are clearly assigned to the protons H_6 and H_8. As the former proton is sited in between two nitro groups, it presumably gives rise to the lower field signal (τ 0.65), whilst H_8, ortho to just one nitro group is assigned the signal at τ 1.24. A downfield shift of H_6 is thus observed (by 0.2ppm) with respect to the analagous proton in 1-picryl-4,5,7-trinitronaphthalene (τ 0.85). This is to be expected due to the introduction of a fourth nitro substituent into the naphthalenic ring system. However it is interesting to observe that H_8 has been affected in the opposite manner - that is, it has moved to higher field by 0.14ppm as compared with the trinitro derivative - despite the presence of a fourth nitro group. The precise cause of this effect is uncertain, but it probably arises from the steric effect of the additional 2-nitro substituent. Thus steric interaction between the picryl moiety and the 2- nitro substituent of the naphthalene system, seems likely to result in the two aromatic systems adopting near perpendicularity as the preferred conformation - if indeed they do not already have such an orientation. Possibly there is also some distortion of the C1–C1' bond angles such that the phenyl ring is caused to lean towards H_8. In either event a change of the magnetic environment of H_8 will result – due to relocation of the induced fields associated with both the aromatic (phenyl) ring and the 2- and 6- nitro substituents in the picryl moiety. Whilst the precise nature of these changes is open to speculation, the total effect of such changes is presumably to produce a net shielding of the proton H_8.

The Ultra Violet Spectrum

The UV spectrum of 1-picryl-2,4,5,7-tetranitronaphthalene in methanol (see appendix) shows three resolved maxima at: λ 214nm, ϵ 4280m^{2}mole^{-1} (Ar $\pi \rightarrow \pi^*$); λ 258nm (sh), ϵ 3390m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$) and λ 353nm (sh), ϵ 500m^{2}mole^{-1} (NO_2 $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ [107,108]).

The aromatic $\pi \rightarrow \pi^*$ band in this compound thus shows a marginal hypsochromic shift relative to that in the trinitro derivative (λ 215nm, ϵ 4820m^{2}mole^{-1}) and also a slight reduction of intensity. Both of these features probably reflect reduced conjugation between the aromatic systems – due to steric factors.

In view of the similarity of structure between 1-picryl-2,4,5,7-tetranitronaphthalene and 1-picryl-4,5,7-trinitronaphthalene, the spectra of these two compounds might be expected to show considerable similarity, with regard to the various 'NO_2' transitions, although the former compound should show additional absorbtions due to the presence of an 'extra' 2- substituted nitro group. This does in fact appear to be the case although superficially the spectra may appear rather disdimilar. Consider for example the region 225–300nm in the two spectra where the NO_2 $n \rightarrow \pi^*$ transitions are normally observed. The trinitro derivative shows two maxima (at λ 229 and 265nm) in this region, whilst the tetranitro derivative shows just one (at λ 258nm). This difference would be readily resolved if the 'extra' 2- nitro substituent of the tetranitro derivative gave rise to an absorption at around 245nm – that is roughly midway between the two maxima of the trinitro derivative. In this event the three maxima would probably not be resolved and would appear as a single broad hump – as is in fact observed in the spectrum of the tetranitropicrylnaphthalene. In order for the 'extra' nitro group to produce a band at about 245nm, it would presumably have to be subject to a degree of conjugation with the naphthalene system, which fell in between that experienced by an unhindered 7- nitro substituent (λ = 265nm) and that achieved by a 4- or 5- nitro substituent -which formed part of an adjacent peri substituted pair (λ = about 230nm).

Examination of molecular models suggests that such a possibility is quite reasonable in the present case. Thus two extreme situations can be envisaged: in the first an angle of approximately 90° is assumed between the two aromatic systems and in consequence the 2- nitro substituent is free to adopt complete coplanarity with the naphthalenic ring system to which it is attached. In the second the two aromatic ring systems are assumed to approach coplanarity and as a consequence of this the same 2- nitro substituent would be forced well out of the plane of the naphthalenic system. In reality a compromise situation would be envisaged in which neither the two aromatic systems, nor the '2-NO_2'/ naphthalene systems adopted coplanarity, but in which both were twisted so as to minimise the total energy of the system. It is presumed that it is this arrangement which gives rise to rather limited conjugation between the 2- nitro substituent and the naphthalenic system, such that the NO_2 $n \rightarrow \pi^*$ transition occurs at about 245nm.

A similar explanation is applicable to the longer wavelength region of the spectra where the trinitro derivative shows two maxima at λ 319 and 353nm (sh), whilst the tetranitro derivative shows a single shoulder at 353nm. Thus it is assumed that the 'extra' 2- nitro group of the latter material gives rise to an additional band at around 335nm. This absorption would then be expected to prevent resolution of the very ill defined shorter wavelength band which occurs at 319nm in 1-picryl-4,5,7-trinitronaphthalene. The general decrease of ϵ values which is observed for the tetranitro (as compared with the trinitro) derivative, both in this region and the shorter wavelength region (225-300nm), is consistent with a general decrease of conjugation between individual nitro groups and the aromatic system. Such is only to be expected[87] due to the increased number of nitro groups present in the system.

CHAPTER 4

Experimental

4.1. Instruments and Reagents

Proton Magnetic Resonance Spectra

60MHz Spectra were recorded using a Perkin Elmer R10 spectrometer (probe temperature 33.5°C), those at 90MHz on a Perkin Elmer R32 spectrometer (probe temperature 35°C) and those at 100MHz on a Jeol JNM PS 100 spectrometer using the pulsed, Fourier Transform, mode of operation. (Probe at ambient temperature.) Tetramethylsilane was used as internal standard for all except the pulsed spectra; in these the chemical shifts were measured relative to the D_5 solvent peak, the following values being assigned to the solvents:- CD_3SOCD_2H: τ 7.51, CD_3COCD_2H: τ 7.94, C_6D_5H: τ 3.09.

Mass Spectra

These were obtained using an AEI MS9 spectrometer with direct insertion probe. Operating conditions were as follows:-

Ionisation voltage 70ev
Source pressure approx 10^{-6} Torr
Source temperature approx 200-250°C

High resolution measurements were carried out by PCMU Harwell (Resolving power of instrument $M/\Delta M$ approx 10,000).

Infra-red spectra

All samples were recorded in the form of pressed KBr discs using a Unicam SP200 spectrophotometer.

Ultra Violet Spectra

UV spectra were recorded in methanol using a Unicam SP 8000 spectrophotometer. The sole exception to this was the spectrum of 1,1'-binaphthyl which was recorded (in methanol) on a Perkin Elmer 402 spectrophotometer.

Melting Points

These were carried out using a Köfler hot stage microscope.

Analysies

Carbon, hydrogen and nitrogen analyses were carried out either by BMAC Teddington or the MOD, PERME, Waltham Abbey.

Reagents and Purification of Solvents

GP grade reagents were generally found adequate without further purification except for use as solvents - see below. 1,1'-binaphthyl was supplied by Eastman Kodak, picryl chloride by Hopkin and Williams and 1-iodonaphthalene by the Aldrich Chemical Co.

All solvents except acetic acid were flash distilled prior to use in order to remove involatile matter. (This was found essential both for chromatography and small scale crystallisations.) Analar grade acetic acid was used without further purification. In the case of toluene the solvent was eluted from a 450mm silica gel column (Merck Silica gel 60, 70-230 mesh) prior to distillation, the initial 'wet' fraction from this distillation being discarded. Approximately 2.5l of toluene were passed through a single column before the silica gel was replaced.

4.2. Chromatographic Methods and Materials

All column chromatography was carried out using Merck silica gel 60, particle size 0.063-0.200mm (70-230mesh). This material was used without activation. 25mm diameter glass columns were used, of length 150-500mm as appropriate. Each column was fitted with a number 3 glass sinter at the bottom, to support the silica gel; the flow of solvent from the column was controlled by means of a greaseless 'Teflon' tap at the base. Solvent was applied to the top of the column from a dropping funnel which could be detached by means of a greaseless 'clearfit' (B24) joint.

All columns were packed using a slurry of silica gel in the appropriate solvent. They were then washed with approximately 250ml of the same solvent, prior to application of the sample. Elution of the sample would typically take place at the rate of 200ml/min.

Preparative TLC was carried out using Merck silica gel H (type 60). Following preparation, the plates were 'activated' at 80°C for one hour, they were then washed three times with methanol and dried (80°C, 10min) immediately prior to use.

Unless otherwise stated all analytical TLC runs were carried out using Eastman Kodak 6060 chromagram sheet, the developing solvent being run over a distance of 100mm. This technique was widely used for example to check the composition of the various fractions obtained from a column, to establish the purity of crystallised products and to monitor the course of nitration reactions. When monitoring the course of nitration reactions the technique adopted was to withdraw a small aliquot of the reaction medium, quench this in water, filter off the solid and then run this on a TLC plate in the appropriate solvent. Invariably acetone was used to apply the sample to the plate prior to separation.

4.3. General Experimental Techniques

Crystallisation of the various higher nitrobinaphthyl derivatives tends to be very slow. Thus crystallisation was typically carried out by placing the solution in a loosely covered beaker and leaving it overnight under an infra-red lamp (approx 30-40°C). Often when a sample was very pure, crystallisation took place much more rapidly (about 3-4hrs). In the case of mixed solvents, such as acetone/acetic acid, the gradual evaporation of the more volatile component normally caused satisfactory crystallisation of the product. On the other hand more rapid evaporation either caused the formation of tars - particularly on the surface of the liquid - or the precipitation of an amorphous - and impure - sample of the product. (The success of individual crystallisations was monitored by TLC).

All 'final' samples were dried under reduced pressure for about 5hrs at a temperature of about 80°C. However, when acetic acid was used as the recrystallisation solvent, a temperature of about 110°C was normally employed (approx 5hrs) to ensure removal of all traces of solvent. (It was generally found necessary to grind the samples into a fine powder prior to drying, in order to remove all traces of solvent.) As has been noted in chapter 2, if the hexa or heptanitrobinaphthyls 'Q' and 'R' were crystallised from solvent mixtures containing toluene, it was found impossible to remove residual toluene from the sample by merely heating it under reduced pressure. Thus these materials had subsequently to be recrystallised from acetone/acetic acid in order to remove the toluene.

4.4. Nitration of 1,1'-Binaphthyl

4.4.1. General Considerations

1,1'-Binaphthyl was initially treated under an arbitrary set of conditions likely to produce complete reaction to its lower nitro derivatives (ie treatment by an excess of nitric acid in acetic anhydride for two hours at 20°C). The product mixture obtained from this preliminary nitration, was subsequently treated (without purification) with a mixture of concentrated nitric and sulphuric acids. It was intended from the outset to treat the products of the first nitration in mixed acid - without substantial purification of the interim product. Nevertheless a fairly detailed examination of the nitric acid/acetic anhydride product mixture was undertaken, in order to isolate and identify as many products as possible. Once a particular product had been identified, the yield of that product could then be maximised by varying the reaction conditions, whilst monitoring the product distribution by TLC. This technique was utilised repeatedly during the work on the nitration of 1,1'-binaphthyl and proved of particular value for the preparation of the higher nitro derivatives which tended to cocrystallise persistently when in admixture with closely related compounds. Thus purification of the desired product by crystallisation was often dependant upon its being the predominant constituent in the final reaction mixture.

4.4.2. Nitrations in Acetic Anhydride and Nitric Acid.

4.4.2.1. General Nitration Technique

The technique generally adopted for nitration in acetic anhydride was to introduce nitric acid (dropwise) into a slurry of the substrate in acetic anhydride. This method was found the most convenient as it produced rapid dissolution of the substrate in the reaction medium and permitted simple temperature control via the rate of acid addition. Experience had shown that it was difficult to dissolve sufficient substrate in preformed 'acetyl nitrate solution'.

The observations of Bordwell and Garbisch concerning the effect of temperature on the acetyl nitrate reaction[57] (see section 1.6.2.2.) hav been broadly supported by the present work. Thus at 0°C the addition of nitric acid to a slurry of substrate in acetic anhydride gave rise to little reaction, whilst subsequent warming of the mixture to about 15°C resulted in a violent exotherm, with vigorous nitration of the substrate. In view of the apparent lack of reaction at low temperature, the difficulty of controlling the exotherm during subsequent warm up and the potential hazards associated with such an exotherm, this method was abandoned. The addition was instead commenced at room temperature and continued cautiously so as to keep the temperature below 40°C; under these conditions decomposition of the acetyl nitrate should not occur.[57] (If the addition is too rapid an explosive reaction is likely to result.[127])

It is often convenient when carrying out nitrations in acetic anhydride/nitric acid, to maintain anhydrous conditions by the use of excess anhydride. However during the present work, for the preliminary treatment in a two stage nitration, it was found most beneficial to add an excess of nitric acid to the reaction. Thus in several instances a higher yield of the final product was isolated if anhydrous conditions were not maintained during the preliminary nitration. (Possibly this reflects the use of too great an excess of acetic anhydride in the 'anhydrous runs', because an excessive quantity of the anhydride is known to be detrimental to reactions in this medium.[59b])

4.4.2.2. Product Isolation

Most of the products prepared by the action of nitric acid/ acetic anhydride on 1,1'-binaphthyl proved separable by TLC using analytical silica gel plates with toluene as eluent. On a preparative scale however separation of the products was best achieved by column chromatography. The most satisfactory solvent system for this preparative work was found to be a mixture of toluene and acetone. Only a few percent of acetone was necessary, but the addition of this solvent to the toluene greatly accelerated the elution of higher nitrated species. Thus although theoretically toluene alone would have separated most of the polynitrobinaphthyls, in practice the time taken (and the quantity of solvent necessary) to elute the higher nitrated species with this solvent would have been prohibitive.

4.4.2.3. Examples

i) Nitration Using Excess Nitric Acid

Procedure 'A'

Finely powdered 1,1'-binaphthyl (0.5g, 1.97 x 10^{-3} moles) was dispersed in acetic anhydride (12.5ml). Concentrated nitric acid (D1.42, 12.5ml) was added dropwise to this stirred slurry, whilst cooling was maintained on a cold plate. The rate of addition was varied to keep the temperature in the range 35-40°C. (During this addition the substrate dissolved completely.) When all the acid had been added (15-20min), the mixture was stood at ambient temperature for 2hrs.

The reaction was then quenched by pouring it onto water (250ml). The mixture was warmed in order to coagulate the solid, which was subsequently filtered off, washed with water, dried under reduced pressure and dissolved in a minimum of toluene. (The product may alternatively be extracted directly into toluene after quenching the reaction with water. This procedure greatly facilitates dissolution of the product into the toluene.) A sample of this solution was spotted onto Kodak chromagram sheet which was subsequently developed in two dimensions using toluene (Rf=200mm each way). When the chromatogram was examined under UV light (366nm) a total of eleven spots was visible (designated 'A' to 'K', 'A' = highest Rf). One of these spots ('J') became immobile prior to the second development in toluene and was not therefore, completely separated from the spot 'K'. Redevelopment of the chromatogram however, using a mixture of 55% chloroform, 45% industrial methylated spirit and 5% acetic acid, caused migration of the spots 'J' and 'K' to give two well separated species 'L' and 'M'. A rerun of the same solvent system perpendicular to the original development however, caused the spot 'M' to produce two spots 'N' and 'O'. It therefore seems probable that 'M' was decomposing on the silica plate (to 'N' and 'O'). Both of the original highly polar species 'K' and 'J' could be removed from the original reaction mixture by washing with cold aqueous 2M sodium hydroxide; this, combined with their relative instability on silica gel, bright yellow colouration (on TLC plates) and relative abundance, suggests that they were oxidation products. (cf Highly nitrated species which may also react with sodium hydroxide eg the hexanitrobinaphthyl 'Q'. This however is fairly stable on silica gel - for short periods - is colourless (on TLC plates) and would only have been produced in trace quantities, if at all, under these reaction conditions.) During preparative chromatographic separation of the mixture (below), the compounds 'J' and 'K' remained firmly bound to the silica gel of the column - with toluene as eluent - and caused no problems, provided only low percentages of acetone were added to the eluting solvent. They were subsequently removed from the column by washing with methanol and a brief attempt was made to fractionally crystallise the compounds; this was unsuccessful. It seems likely that these residues contained a considerable mixture of compounds, but since they were not of direct interest to the present investigation, their isolation and identification were not pursued.

The main bulk of products from the reaction were separated by column chromatography. Since individual columns (length 450mm) had insufficient resolution to completely separate the applied product mixture, numerous fractions were collected from a column and the composition of each determined on analytical TLC plates. Appropriate fractions were then combined and those containing more than one component were applied to further columns. This process was repeated until separation of all the components had been achieved. Once a fraction had been isolated, which produced essentially a single spot by TLC, the solvent was stripped from it and the product crystallised. In one case (spot 'C') fractional crystallisation was necessary in order to separate two components which had practically identical Rf's in toluene.

The solvents employed for chromatographic separation and subsequent crystallisation of the various products are given in the table 4-1. The analytical data relating to the various products is summarised in table 4-2. The spectra recorded from the products are given in the appendix; these are discussed in chapter 2.

Table 4-1

Solvents Utilised in the Purification of Compounds 'B' - 'I'

Compound Designation	Chromatographic Eluent	Crystallisation Solvents
'B'	100% Toluene	Acetone/Toluene
'C-1'	100% Toluene	Fractional Crystallisation from Acetone/Toluene/Acetic Acid
'C-2'	100% Toluene	
'D'	100% Toluene	Acetone/Toluene/Acetic Acid
'E'	100% Toluene	Washed with Acetic Acid (Insufficient material for crystallisation)
'F'	100% Toluene or 98% Toluene/2% Acetone	Toluene or Acetone/Acetic Acid
'G'	98-95% Toluene/ 2-5% Acetone	—
'H'	98-95% Toluene/ 2-5% Acetone	Toluene/Acetone or Acetone/Acetic Acid
'I'	95% Toluene / 5% Acetone	Acetone/Acetic Acid

When isolated by column chromatography the fraction corresponding to compound 'E' was found to contain such a small quantity of sample that it was impossible to crystallise it. In consequence satisfactory purification of compound 'E' was not achieved, so reliable spectra could not be obtained. Thus during examination of fraction 'E' by mass spectrometry a series of spectra were recorded (by repeated scanning) in which quite wide variations of intensity were observed for individual ions. It was thus concluded that the sample contained a mixture of compounds and therefore no detailed interpretation of the spectrum was possible. It is however pertinent to note that the spectrum contains a moderately strong ion at m/e 434, which probably corresponds

Compound Name	Designation	Total Isolated weight (mg)	gram moles	Yield (mole %)	Melting Point (°C)	Analyses	Molecular Ion	Measured Mass	Calculated Mass
1,1'-Binaphthyl	'A'	Negligible	Negligible	Negligible	-	-	—	—	—
4,4'-Dinitro-1,1'-binaphthyl	'B'	14	4.07×10^{-5}	2.1	248-251	IR and Mass Spectra identical	with those of an authentic sample		
4,8'-Dinitro-1,1'-binaphthyl	'C-1'	19.5	5.67×10^{-5}	2.9	212-216.5	found C:70.3; H:3.6; N:8.3 requires C:69.8; H:3.5; N:8.1	$C_{20}H_{12}N_2O_4$	344.0784	344.0797
4,4',8-Trinitro-1,1'-binaphthyl (?)-impure	'C-2'	<1.8	$<4.63 \times 10^{-6}$	< 0.2	-	-	—	—	—
4,4',5-Trinitro-1,1'-binaphthyl	'D'	190	4.88×10^{-4}	24.8	215-219	found C:62.0; H:2.9; N:11.0 requires C:61.7; H:2.8; N:10.8	$C_{20}H_{11}N_3O_6$	389.0646	389.0647
Unknown	'E'	<0.5	$<1.29 \times 10^{-6}$	< 0.07	-	-	—	—	—
4,5,8'-Trinitro-1,1'-binaphthyl	'F'	125.3	3.22×10^{-4}	16.4	235-236.5	found C:60.9; H:3.0; N:10.8 requires C:61.7; H:2.8; N:10.8	$C_{20}H_{11}N_3O_6$	389.0637	389.0647
Unknown	'G'	-	-	-	-	-	—	—	—
4,4',5,5'-Tetranitro-1,1'-binaphthyl	'H'	71	1.64×10^{-4}	8.3	>345	found C:55.6; H:2.3; N:12.9 C:55.3; H:2.3; N:12.9	$C_{20}H_{10}N_4O_8$	434.0495	434.0499
4,5,x,y-Tetranitro-1,1'-binaphthyl	'I'	< 1	2.30×10^{-6}	<0.1	-	-	—	—	—
Unidentified oxidation products	'J'	-	-	-	-	-	—	—	—
	'K'	-	-	-	-	-	—	—	—

Table 4-2

A Summary of Analytical Data for the Products obtained from the Nitration of 1,1'-Binaphthyl in Acetic Anhydride/Nitric Acid to the molecular ion of a tetranitrobinaphthyl. The absence of an intense ion at m/e 388 however, strongly suggests that this particular compound does not contain any adjacent peri substituted nitro groups. In addition to the above ion there is an intense peak at m/e 389 which seems unlikely to arise from a tetranitrobinaphthyl, this peak therefore suggests the presence of a trinitrobinaphthyl in the mixture (molecular ion = 389). Indeed a close examination of the spectrum suggests that traces of the compound 'F' are present. The ion at m/e 389 is however too intense relative to that at 343, to be explained solely by the presence of the compound 'F', it therefore seems likely that another trinitrobinaphthyl is also present in the mixture.

On the basis of the mass spectrum therefore the fraction 'E' probably contained at least three compounds; one was most likely a tetranitrobinaphthyl (without any adjacent peri substituted nitro groups); one was probably compound 'F' and the third was presumably another (unidentified) trinitrobinaphthyl.

Insufficient of the compound 'G' was isolated to permit its crystallisation, so this material could not be satisfactorily purified either. In fact, no useful spectra could be obtained from this compound and its identity is unknown.

Isolation of the compound 'A', identified as unreacted 1,1'-binaphthyl, was not carried out by column chromatography because the early (colourless) column washings (ie prior to compound 'B') were normally discarded. (A check was however made to ensure that no significant quantities of solid matter left the column in these washings.) This material was instead isolated by TLC during early attempts to separate the products by this technique. (Only a partial separation of the crude mixture was actually achieved by this method. Eluent: chloroform, Rf = 200mm.) The unreacted binaphthyl was recovered from the leading edge of the chromatogram after a two stage separation. It was identified via its mass spectrum.

The above nitration technique was employed mainly as a preliminary treatment for 1,1'-binaphthyl, prior to its nitration in mixed acid. It was of little value as a preparative nitration procedure due to the large number of products produced and the associated separation difficulties. However, since the product mixture contained significant quantities of both 4,4',5,5'-tetranitro-1,1'-binaphthyl ('H') and possible precursors of this compound (4,4'-dinitro-1,1'-binaphthyl and 4,4',5-trinitro-1,1'-binaphthyl), modified reaction conditions were investigated in the hope of making compound 'H' the major product of reaction. A simple extension of the reaction time proved inadequate for this purpose, as even after 68hrs TLC showed the product mixture to contain at least nine components (with 4,4',5-trinitro-1,1'-binaphthyl still a major constituent). The reaction was therefore repeated, but with anhydrous conditions maintained throughout. Sulphuric acid catalyst was also employed:-

ii) Nitration Using Excess Acetic Anhydride and Sulphuric Acid Catalyst

Procedure 'B'

Finely powdered 1,1'-binaphthyl (0.5g, 1.97×10^{-3}moles) was dispersed in acetic anhydride (10ml). Concentrated nitric acid (D1.42, 2.0ml) was added dropwise to this stirred slurry whilst the mixture was cooled on a cold plate. The rate of this addition was varied to keep the temperature in the range 35-40°C. (During this procedure the substrate dissolved completely.) When all the nitric acid had been added, three drops (approx 0.07ml) of concentrated sulphuric acid were added to the mixture (this resulted in a rapid exotherm*). Once the sulphuric acid had been added, the mixture was maintained at 40°C for a total of 2hrs.

(During this time the composition of the supernatant liquid was monitored by TLC - thus after 2hrs no trace of the lower nitro derivatives 4,4'-dinitro or 4,4',5-trinitro-1,1'-binaphthyl could be detected.) Over this 2hr period a precipitate formed (mainly during the first 0.5hrs). The mixture was cooled to 0°C and the precipitate - a white microcrystalline solid - filtered off, washed with water and recrystallised from acetone/acetic acid. The product was dried under reduced pressure to yield 0.1964g of the compound 'H' (IR, PMR spectra and thin layer chromatogram (toluene) identical with those of an authentic sample). The filtrate from above was quenched with excess water and the organic material extracted into chloroform. This extract was washed with saturated sodium bicarbonate solution then water and dried (sodium sulphate). The solvent was stripped from the solution and the solid crystallised twice from acetone/acetic acid. After drying under reduced pressure this yielded a further 0.2031g of compound 'H'. Total yield of 4,4',5,5'-tetranitro-1,1'-binaphthyl ('H') = 0.3995g, 9.21×10^{-4} moles, 46.8%.

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* In this particular reaction the temperature rose briefly to 60°C, the solution was however rapidly cooled back to 40°C (liquid nitrogen).

Whilst the above procedure was very convenient in that much of the product crystallised directly from the reaction medium (repeated crystallisation of the product from acetone/acetic acid -below- tends to be tedious), a superior method for the preparation of the tetranitrobinaphthyl was via a combination of the two sets of conditions outlined above. The procedure, which is described below, also led to the isolation of compound 'P'. It is assumed that this is the ultimate nitration product of compounds such as 'F' which contain an 8- substituted nitro group. (The following method appears to be superior to that described by Jones and Joyner[12] for the preparation of 4,4',5,5'-tetranitro-1,1'-binaphthyl in acetic anhydride/nitric acid. Thus the method below utilises milder conditions than the earlier procedure and also produces a higher yield of 'H'.)

1,1'-Binaphthyl (1g, 3.94 x 10^{-3}moles) was treated with nitric acid (D1.42, 10ml) and acetic anhydride (10ml) according to procedure 'A'. Further acetic anhydride (15ml) was then added slowly with cooling, so as to keep the temperature in the range 35-40°C. Once this had been added, three drops (approx 0.07ml) of concentrated sulphuric acid were cautiously introduced into the solution, whilst keeping the temperature below 40°C. The mixture was then stood for 1hr at 40°C before being poured onto excess water. The suspension was warmed to coagulate the solid which was subsequently filtered off, washed with water, saturated sodium bicarbonate solution and water again. The product was then dried and crystallised three times from acetone/acetic acid. After drying under reduced pressure this yielded 1.037g of compound 'H' (IR, PMR spectra and thin layer chromatogram (toluene) identical with those of an authentic sample.)

The residues from all of the above crystallisations were combined. This material was separated by column chromatography (2-4% acetone, 98-96% toluene) into essentially two fractions, one comprising predominantly the compound 'H' and the other mainly compound 'P'. Crystallisation of the former fraction (twice) from acetone/acetic acid yielded a further 23.3mg of pure 'H'. Repeated crystallisation of the second fraction (acetone/toluene/acetic acid and acetone/acetic acid) yielded ultimately 20.6mg of the compound 'P'. Although there was more of the compound 'P' left in the residues of the above crystallisation it was not thought worthwhile to isolate any further material. Total yield of compound 'P' = 20.6mg, 4.75 x 10^{-5}moles, 1.2%. Total yield of 4,4',5,5'-tetranitro-1,1'-binaphthyl ('H') = 1.06g, 2.44 x 10^{-3}moles,62.1%.

Compound 'P' - 4,4',5,8'-Tetranitro-1,1'-binaphthyl (?)

Mp 269-272.5°C, molecular ion $C_{20}H_{10}N_4O_8$, 434.0495 (measured) 434.0499 (calculated)

Analysis

Found C:55.62; H:2.55; N:12.92

Requires C:55.30; H:2.30; N:12.90

When examined by TLC (Eastman Kodak 6060 chromagram sheet) the compound 'P' was found to have an Rf (one elution with toluene) only marginally less than that of compound 'F'. Thus although the two compounds have discernably different Rf's when they are developed for the full length of a 200mm plate, a mixture of the two compounds would not be fully separated under these conditions.

4.4.3. Nitrations in Mixtures of Glacial Acetic, Nitric and Sulphuric Acids

Since the preparation of 4,4',5,5'-tetranitro-1,1'-binaphthyl was reported during the course of the present work[12] it was of interest to repeat the literature method in order to confirm the identicalness of the product so obtained and the compound 'H'. Thus 1,1'-binaphthyl was nitrated according to the method of Jones and Joyner[12] (24hrs reflux in glacial acetic, nitric and sulphuric acids), but on one fifth of the original scale (ie nitration of 2g of 1,1'-binaphthyl). However under these conditions the entire product carbonised and no significant quantity of any tetranitrobinaphthyl could be isolated. The reason for the carbonisation is unclear though possibly the smaller scale employed during the present work had an adverse influence on the reaction. In view of the failure of the literature method a modified procedure was evolved, using an essentially similar technique but with reduced reaction time and temperature. This proved successful and the compound 'H' was isolated from the reaction:-

To a slurry of 1,1'-binaphthyl (2g, 7.87 x 10^{-3}moles) in glacial acetic acid (10ml) and concentrated sulphuric acid (10ml) was added nitric acid (D1.5, 6ml) in small portions with vigorous stirring whilst keeping the temperature below 30°C. Once the addition was complete the mixture was heated to 100°C for 3hrs. (The reaction was monitored by TLC - this was the reaction period necessary to remove all of the lower nitrated species 'B' - 'F'.) The reaction mixture was cooled and poured onto crushed ice. The precipitate was coagulated by warming, then filtered off, washed with saturated sodium bicarbonate and water. The product was dried and crystallised three times from acetone/acetic acid. This yielded 0.55g, 1.27 x 10^{-3}moles, 16.1% of compound 'H' (IR and PMR spectra and thin layer chromatogram (toluene) identical with those of an authentic sample).

The fairly low yield of 'H' obtained by the above procedure could in part be due to the use of fairly vigorous nitration conditions during the early stages of reaction. A modified procedure was therefore evolved which employed more moderate conditions during the early stages. Since 4,4'-dinitro-1,1'-binaphthyl could be produced in high yield by the nitration of 1,1'-binaphthyl in a mixture of nitric and acetic acids[10], this seemed an ideal method by which to start the reaction, since more vigorous nitration conditions could be created simply be the addition of sulphuric acid. Whilst this approach proved partially successful and a higher yield of compound 'H' was obtained, some difficulty was experienced in carrying out the reaction due to the formation of a large agglomerate of solid matter during the course of the nitration. Repeated attempts to break up this agglomerate meant that the reaction was continued for longer than would normally have been necessary. It seems likely that this extended reaction time could have been at least partially responsible for the only moderate yield of 'H' which was isolated. The modified procedure is as follows:-

Procedure 'C'

1,1'-Binaphthyl (2.5g, 9.84×10^{-3}moles) was dispersed in acetic acid (25ml) and concentrated nitric acid (D1.42, 1ml) added with stirring. The mixture was then heated on a water bath until clear (approx 45min), after which additional nitric acid (2.5ml) was added. The mixture was maintained at 100°C for a further 2.25hrs, then concentrated sulphuric acid (D1.84, 25ml) was added cautiously followed by concentrated nitric acid (15ml). (During addition of the sulphuric acid copious fumes were evolved and the mixture boiled.) The mixture was then returned to the water bath for 1.5hrs. During the above procedure a large insoluble agglomerate formed which could not be dispersed either by agitation with a glass stirring rod or by the addition of more acid. Thus firstly additional nitric acid (5ml) was added, the mixture being heated for 0.5hrs (100°C), then a mixture of sulphuric acid (5ml) and nitric acid (5ml) was added and heating continued on a water bath for another hour. At the end of the above procedure the agglomerate still remained, so the solution was cooled and poured onto crushed ice. The solid was filtered off, washed with water and dried.

The product was crystallised three times from acetone/acetic acid then dried under reduced pressure to yield 0.974g of compound 'H' (IR and PMR spectra and thin layer chromatogram identical with those of an authentic sample). The residues of these crystallisations were combined and subject to column chromatography (2-5% acetone, 98-95% toluene). Appropriate batches of eluent were combined, stripped of solvent and crystallised (twice) from acetone/acetic acid. This led to the isolation of a further 0.104g of compound 'H'. Thus total yield of 4,4',5,5'-tetranitro-1,1'-binaphthyl ('H') = 1.078g, 2.484 x 10^{-3}moles, 25.2%.

The above nitration procedure was carried out three times, but on each occasion an insoluble agglomerate formed similar to that described above. Isolation of the tetranitrobinaphthyl was, however, only carried out once, the nitration being continued in the other instances to prepare the hexanitrobinaphthyl 'Q' (see later - table 4-3).

4.4.4. Nitrations Using Nitric and Sulphuric Acids

4.4.4.1. The Preparation of 4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl

A typical method for the preparation of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl is described below. Although this compound has been prepared by a number of alternative procedures these have generally been found inferior to the method (1) given below. Results from other experiments, showing the effect of employing alternative preliminary nitration media and of varying the ratio of sulphuric to nitric acids, are summarised in table 4-3.

Method (1)

1,1'-Binaphthyl (2g, 7.86 x 10^{-3}moles) was treated with concentrated nitric acid (D1.42, 50ml) and acetic anhydride (50ml) according to the procedure 'A'. The reaction was then quenched by pouring it into excess water. The precipitate was filtered off and dried under reduced pressure to yield 3.77g of crude product. This product was powdered and dispersed in sulphuric acid (D1.84, 125ml). Nitric acid (D1.42, 125ml) was then added, with stirring, whilst keeping the temperature below 65°C. When this addition was complete the mixture was heated on a water bath for a total of 4.25hrs. (Monitoring of the reaction by TLC showed that all the lower nitrobinaphthyls 'B' to 'I' had been consumed after this period of time.) The mixture was then cooled and poured onto crushed ice. The precipitate was filtered off, washed with water, sodium bicarbonate (saturated), water again and dried

Table 4-3

The Preparation of 4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl by the Nitration of 1,1'-Binaphthyl

A Summary of Results

Method no	Quantity of Substrate (g)	Preliminary Nitration					Second Stage Nitration			Yield of Hexanitro-binaphthyl
		Acetic Anhydride (ml)	Acetic Acid (ml)	Nitric Acid (ml)	Sulphuric Acid (ml)	Procedure	Nitric Acid (ml)	Sulphuric Acid (ml)	Notes	
1	2	50	-	50	-	'A'	125	125	method as above	50.1
2	2	50	-	50	-	'A'	25	125	method as above^{a,b}	20.6
3	2	50	-	8	approx 0.07 (3 drops)	'B'	125	125	" (a)	22.2
4	2.5	-	25	28.5	30	'C'	125	125	" (c)	43.7
5	2.5	-	25	28.5	30	'C'^{d}	125^{e}	125	" (f)	32.1

Nitric acid = D1.42 unless otherwise stated. Sulphuric acid = D1.84. The procedures 'A', 'B' and 'C' have already been described.

Notes

a) Entire product was eluted from silica gel columns before isolating any of the compound 'Q'.

b) Reaction maintained at 100°C for 3hrs.

c) Reaction maintained at 100°C for 2.25hrs.

d) Reaction maintained at 100°C for 23.5 hrs.

e) Nitric acid = D1.5.

f) Glacial acetic acid (125ml) was also added. Reaction was for 2.25hrs at 100°C.

under reduced pressure. This crude product was repeatedly crystallised from acetone/acetic acid and acetone/toluene until a pure sample (TLC-20% acetone, 80% toluene) of the compound 'Q' was obtained (0.683g). The residues from all of the above crystallisations were combined, stripped of solvent and applied (in acetone/toluene 1:1) to silica gel columns. Elution with 20% acetone, 80% toluene followed by repeated crystallisation of the appropriate fractions (acetone/toluene), yielded a further 0.580g of 'Q'. The residues of these crystallisations were combined and treated as above. Thus the cycle of crystallisation, elution of residues from silica gel columns, crystallisation, further elution of residues etc, was repeated until no useful quantity of 'Q' could be isolated at the crystallisation stage. A further 0.800g of 'Q' was isolated by this procedure. Total yield of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl = 2.063g, 3.94 x 10^{-3}moles,50.1%.

Mp of 'Q' = 271.5-275.0°C (acetone/acetic acid)
210.0-220.0°C (acetone/toluene)

Analysis		
	Requires	C:45.80; H:1.53; N:16.03
	Found	C:45.82; H:1.68; N:15.78

On Eastman Chromagram plates with an eluting solvent of 20% acetone/80% toluene the compound 'Q' migrated to approximately 0.75Rf.

4.4.4.2. Preparation of 2,4,4',5,5',7,8'-Heptanitro-1,1'-binaphthyl (?) (Compound 'R')

1,1'-Binaphthyl (1g, 3.94 x 10^{-3}moles) was treated with nitric acid (D1.42, 2ml) acetic anhydride (15ml) and sulphuric acid (D1.84, 2 drops = approx 0.05ml) according to procedure 'B'. The crude product from this reaction was dispersed in sulphuric acid (D1.84, 30ml) and fuming nitric acid (D1.5, 30ml) added, the mixture was then boiled under reflux for 12hrs after which time TLC (20% acetone, 80% toluene) suggested that there was no significant quantity of the compound 'Q' remaining in the mixture. (Trace quantities of 'Q' were nevertheless isolated on concentration of the product.) The reaction mixture was cooled and poured onto crushed ice. The product was then filtered off, washed with water, dried and crystallised from acetone/acetic acid. The resultant crystalline material produced two spots on TLC (20% acetone, 80% toluene), one of much greater intensity than the other. Of these the minor component had an Rf appropriate for the compound 'Q', whilst the major one had a slightly greater Rf (compound 'R'). Fractional crystallisation of this material from acetone/toluene yielded ultimately a supernatant liquid which contained exclusively (TLC) the higher Rf component ('R'). The crystalline material thus isolated was then repeatedly crystallised using the same technique to obtain further batches of 'R'. Such crystallisation was continued until contamination of the supernatant liquid by residue (immobile on TLC*), became excessive. The various batches of liquid (each containing predominantly 'R') were then combined, stripped of solvent and crystallised from acetone/toluene to yield the first batch of compound 'R'. Those residues remaining from the above crystallisations, which still contained significant quantities of 'R' (TLC), were combined and applied to silica gel columns (in acetone/toluene 1:1). Elution with 20% acetone/80% toluene followed by fractional crystallisation of appropriate fractions, (as above in acetone/toluene), yielded ultimately supernatant liquid containing predominantly the compound 'R'. Repeated crystallisation of the residual solid, by the same technique, yielded further batches of 'R'. This procedure was repeated until there was insufficient material left to continue. The supernatant liquids from each of the above crystallisations were combined. This material was then subject to repeated fractional crystallisation from acetone/toluene and acetone/acetic acid, until it produced essentially a single spot by TLC (20% acetone, 80% toluene). (During this procedure 1mg of the compound 'Q' was also isolated.) The various batches of 'R' were then combined and the entire product recrystallised from acetone/acetic acid. After drying under reduced pressure this yielded 72.5mg, 1.27×10^{-4} moles, 3.2% of compound 'R'. Mp 206.5-208.5 (acetone/acetic acid), 206.0-207.0 (acetone/toluene).

It was clear from the mass spectrum of this product that it still contained impurities; further 'purification' was therefore undertaken on a small part of the sample before submitting it for analysis. Thus 6mg of the above product 'R' was eluted from a silica column (20% acetone, 80% toluene). The fraction corresponding to the compound 'R' was then stripped of solvent and crystallised twice from acetone/toluene, once from acetone/acetic acid and once from acetone/industrial methylated spirit. It was then dried under reduced pressure to yield 2mg of a compound which analysed as follows:-

Found	C:44.30%;	H:1.83%;	N:15.59%.
A Heptanitrobinaphthyl requires	C:42.18%;	H:1.23%;	N:17.22%.

It is suggested that the product which was actually analysed was not in fact the compound 'R' but some decomposition product derived from

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*20%Acetone/80%toluene

it (see section 2.2.3.3.). Unfortunately however due to an oversight no spectra were recorded from the actual sample which was submitted for analysis, so the exact identity of this sample is uncertain.

Decomposition of the Compound 'R' - Isolation of the Compound 'S'

The final spectrum to be recorded from the compound 'R' was the PMR spectrum - in DMSO. Once this had been obtained an attempt was made to recover the material 'R' from solution. Thus the spectroscopic solution (containing about 50mg of compound 'R' in about 0.4ml of D_6-DMSO) was poured onto water (approx 5ml). A small quantity of distilled acetone (H_6) was then used to wash residual material out of the PMR tube. As a colloidal suspension formed, more water was added to the solution (approx 50ml). The mixture was then stood overnight before being warmed for 4hrs under an IR lamp (approx 50°C) in an attempt to coagulate the solid. This was unsuccessful so the water was stripped off under reduced pressure using a rotovapour (70°C). During this time the colour of the solution changed from brown to red (approx 0.5Hrs). When distillation of solvent had ceased (approx 0.75hrs) an attempt was made to record a PMR spectrum from the solution (now in aqueous DMSO). However no intelligible spectrum could be obtained from the solution, - presumably because the signal from the sample fell below the detection limits of the instrument in use (R10). When the solution was examined by TLC (20% acetone, 80% toluene) the major component appeared as a bright yellow/orange spot at approx 0.75Rf - just ahead of the Rf observed for compound 'R'. (This spot fluoresced under UV radiation of 350nm). In addition to this there was a second faint spot at approximately 0.25Rf, plus an immobile residue on the baseline. The sample was purified by column chromatography (20% acetone, 80% toluene) followed by crystallisation from acetone. After drying under reduced pressure this yielded 7mg of the compound 'S1' as brilliant fluorescent orange crystals. Mp 340°C (change in crystal form at 329°C). To the residues of this crystallisation was added an approximately equal volume of acetic acid. A small quantity of the compound 'R' was then crystallised from this solution. Yield after drying under reduced pressure approx 1mg. (IR spectrum and thin layer chromatogram identical with those of an authentic sample. The mass spectrum was also similar to that of an authentic sample but showed the presence of trace impurities.)

The compound 'S1' was recrystallised from acetone to yield the compound 'S2' (3mg) as dull orange crystals. An attempt was made to fractionally crystallise (acetone/acetic acid) the residues remaining from this crystallisation. However, only one product could be isolated in reasonably pure state, that is the compound 'S3' (0.75mg). This material crystallised as dark brown black crystals but became orange when ground into a fine powder.

4.5. Nitrations of Polynitrobinaphthyls

4.5.1. Nitrations in Mixed Acid

4.5.1.1. The 'Nitration' of 4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl

During attempts to prepare highly nitrated polynitrobinaphthyls 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl was treated with mixed acid under a variety of conditions. A general nitration procedure is described below and the results of individual reactions are summarised in table 4-4. It is evident from this table that at lower temperatures little or no reaction occured, whilst prolonged nitration at high temperatures resulted in almost total oxidation of the substrate to water soluble products.

Nitration of 4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl - General Procedure

4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl (0.3g, 5.72 x 10^{-4}moles) was dispersed in sulphuric acid (D1.84, 10ml) and nitric acid (D1.5, 10ml) added rapidly with stirring. The mixture was then boiled under reflux for 6hrs before being poured onto crushed ice. The product was filtered off, washed with water and dried under reduced pressure. The entire product was applied to several silica gel columns and eluted with 20% acetone/80% toluene. (This removed most of the highly polar oxidation products because these remained bound to the silica gel.) Fractional crystallisation of the eluted product (toluene/acetone) yielded a supernatant liquid which contained exclusively (TLC) the compound 'R'. The crystalline material thus isolated was then repeatedly crystallised using the same technique. At first the supernatant liquid from such crystallisation retained predominantly the compound 'R'. As the procedure was repeated however, later batches of liquid retained mixtures of 'R' and 'Q' until ultimately the crystalline product which was isolated comprised exclusively the compound 'Q'. This product was recrystallised from acetone/acetic acid and dried under reduced pressure to yield 29mg, 5.53 x 10^{-5}moles, 9.7% of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl ('Q'). The various batches of solution which contained predominantly the compound 'R' were combined, stripped of

Table 4-4

A Summary of Results for the 'Nitration' of 4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl

Run Number	Quantity of Substrate (g)	Nitric Acid (D=1.5) (ml)	Sulphuric Acid (D=1.84) (ml)	Reaction Temperature (^{o}C)	Duration of Reaction (hrs)	Isolated Products and Notes
1a	0.5	15	15	35-40	144.0	No reaction. Product to (1b) without isolation.
1b	Product from 1a	+5	-	100	24.0	2mg of water insoluble products - not identified. (a,b)
2	0.25	10	7.5	60	26.0	Substrate recovered unreacted.(a)
3	0.25	10	7.5	60	96.0	Substrate recovered unreacted.
4	0.25	10	7.5	i) 60 ii) 105 iii) Reflux	96.0 3.25 4.0	2.1% of 'R', 14.4% of 'Q'.
5	0.5(c)	15	15	100	24.0	7.4% of 'R', 'Q' not detected.
6	0.25	10	7.5	100	25.0	1mg of water insoluble products - not identified. (a,b)
7	0.3	10	10	Reflux	5.0	1.7% of 'R', 12.0% of 'Q'.
8	0.3	10	10	Reflux	6.0	4.2% of 'R', 9.7% of 'Q'.
9	0.3	7.5	10	Reflux	13.0	3.3% of 'R', 'Q' not detected. (d)
10	1.0	22.5	30	Reflux	49.0	0.5% of 'R'.
11	0.2(f)	4.5	6	Reflux	24.0	8.2mg of water insoluble products isolated - not identified - see below (e,g)

Notes a) Crude product washed with water, saturated sodium bicarbonate solution, then water again. b) Insufficient material to achieve purification. c) Substrate purified less than normal prior to nitration. d) Crude product crystallised from acetone/acetic acid prior to elution from silica gel columns. e) Water soluble product also isolated from this run (compound 'Z' - 48.8%). f) Substrate specially purified - see below. g) Although the water insoluble product was not positively identified due to the small quantity of material isolated, the evidence (see below) suggests that there was only a very small proportion of 'R' present - if indeed there was any at all.

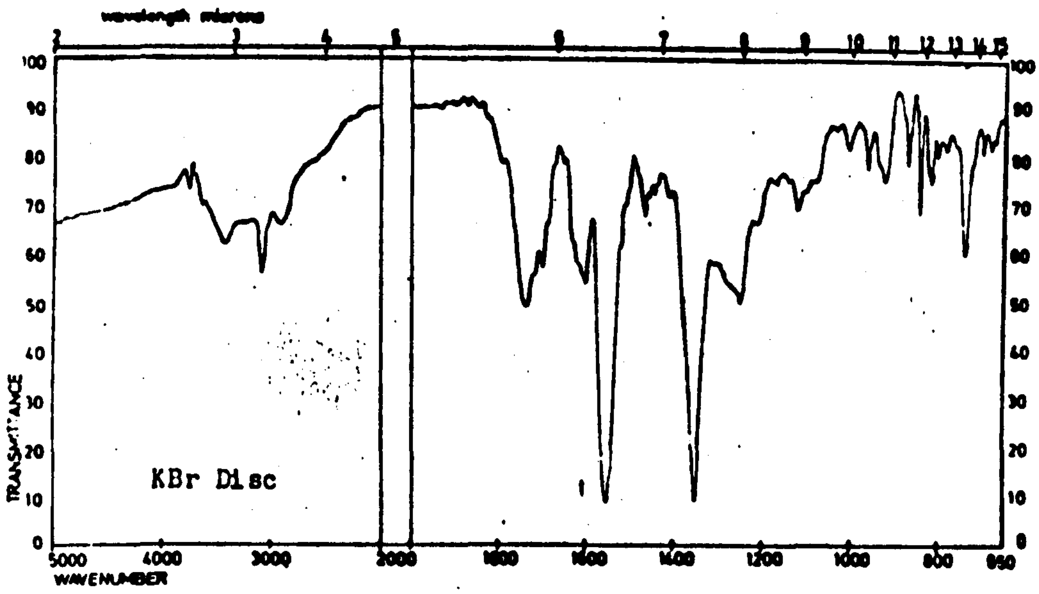
solvent, and fractionally crystallised from toluene/acetone in order to remove the last traces of compound 'Q'. Thus initially a mixture of 'Q' and 'R' crystallised from the solution, then, later, pure 'R'. The latter material was recrystallised from acetone/toluene, then acetone/acetic acid before being dried under reduced pressure to yield 13.6mg, 2.39×10^{-5} moles, 4.2% of the compound 'R'.

The specially purified sample of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl utilised in run 11 was prepared as follows:-

4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl (0.5g) ostensibly pure by TLC and spectroscopic examination, was dissolved in acetone/toluene and eluted from a 450mm silica gel column using a mixture of 20% acetone and 80% toluene. The material eluted in the form of a single fairly broad brown band and this was collected as three fractions. The middle fraction thus obtained, was stripped of solvent and eluted from a second silica column by exactly the same procedure. This time however the middle fraction was stripped of solvent and crystallised three times from acetone/toluene then twice from acetone/acetic acid. After drying under reduced pressure this yielded 0.21g of the purified hexanitrobinaphthyl.

The course of nitration in run 11 was followed, as usual, by TLC. After 24hrs boiling under reflux the reaction mixture produced a single spot on the chromatogram - at about the appropriate Rf for compound 'R' - the reaction was therefore quenched by pouring it onto crushed ice. The water insoluble products were then isolated by filtration and dried under reduced pressure to yield 8.2mg of solid (equivalent to about 4% by weight). Attempts to crystallise this material (methanol/toluene) were unsuccessful, so the solvent was stripped from the sample and an IR spectrum recorded of the crude material. This spectrum (fig 8) shows nitro valence stretching vibrations at 1350/1555cm^{-1} and a band due to C-H stretching at 3100cm^{-1}, however the fingerprint region bears little resemblance to either the heptanitrobinaphthyl 'R' or the hexanitrobinaphthyl 'Q'. Unfortunately the small quantity of this sample which was available and its impure nature prevented any other spectra from being recorded. The melting point of this product was in excess of 340°C although there was a change in the crystalline form at 198-205°C. This compares with a melting point of 206-207°C for the compound 'R' - crystallised from toluene or 206.5-208.5 from glacial acetic acid.

Figure 8



IR Spectrum of the water insoluble product isolated from the nitration of a highly purified sample of 'Q'

The filtrate from run 11, that is the solution containing the water soluble products of reaction, was stripped of the main bulk of water on a rotovapour at ambient temperature. The solution was then left in an open beaker for 5 days (40–50°C) during which time a pale yellow solid crystallised from the solution ('Z1'). This solid was filtered off, washed with water and dried under reduced pressure (100°C, 3hrs) to yield 75mg of compound 'Z2' as a white microcrystalline solid mp>340°C. This material analysed as follows: C:45.60%; H:2.64%; N:9.97%. If the proposed molecular weight of 403 is correct 75mg is equivalent to 1.86 x 10^{-4} moles, 48.8%.

4.5.1.2. The Nitration of 4,4',5,5'-Tetranitro-1,1'-binaphthyl – Preparation of Compound 'Q'

This nitration was originally intended as a preparation of a pentanitrobinaphthyl – hence the 'stepwise' nitration technique. As no significant quantity of a pentanitrobinaphthyl could be detected at the interim stages, the nitration was continued until ultimately the hexanitrobinaphthyl was produced.

4,4',5,5'-Tetranitro-1,1'-binaphthyl (0.25g, 5.76 x 10^{-4} moles) was dispersed in sulphuric acid (D1.84, 7.5ml) and nitric acid

(D1.42, 35μl)added. This mixture was heated on a water bath for 2.5hrs then poured onto ice. The product was filtered off, washed with sodium bicarbonate, water and then dried. This entire product was dispersed in sulphuric acid (D1.84, 7.5ml) and nitric acid (D1.42, 65μl) added. The mixture was then heated on a water bath for 45 minutes. Further nitric acid (D1.42, 0.25ml) was added and the mixture again heated on a water bath for one hour. After cooling it was poured onto ice. The mixture was boiled to coagulate the solid which was filtered off, washed with sodium bicarbonate solution and crystallised from acetone/acetic acid. After drying under reduced pressure this yielded 0.1127g, 2.15 x 10^{-4} moles, 37.3% of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl. (IR and PMR spectra and thin layer chromatogram (20% acetone/80% toluene) identical with those of an authentic sample.)

4.5.1.3. The Nitration of 4,4',5,5'-Tetranitro-1,1'-binaphthyl - Preparation of the Compound 'U'

4,4',5,5'-Tetranitro-1,1'-binaphthyl (0.25g, 5.76 x 10^{-4}moles) was finely ground and dissolved in sulphuric acid (D1.84, 7.5ml) by warming. Nitric acid (D1.42, 0.1ml) was then added and the mixture heated to 100°C for 45minutes. A second aliquot of concentrated nitric acid (0.1ml) was added 10minutes after the first. Once the reaction had been maintained at 100°C for 45minutes the mixture was cooled and poured onto crushed ice. On heating, the solid coagulated and was filtered off then dried under reduced pressure. The product was applied, in acetone, to a 150mm silica gel column and eluted with 20% acetone, 80% toluene until the eluent was colourless. All of this eluent was collected as a single fraction. Fractional crystallisation of the eluent (toluene/acetone) yielded initially 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl then the compound 'U'. The latter material was crystallised twice from acetone/acetic acid/industrial methylated spirit and dried under reduced pressure to yield 9.5mg, 1.983 x 10^{-5}moles, 3.44% of the compound 'U' mp 322-4°C.

All of the hexanitrobinaphthyl recovered from the reaction was recrystallised from glacial acetic acid/acetone to yield 0.104g, 1.985 x 10^{-4}moles, 34.46% of the compound 'Q'.

In a further experiment 0.25g of 4,4',5,5'-tetranitro-1,1'-binaphthyl was treated with sulphuric acid (D1.84, 7.5ml) and nitric acid (D1.42, 90μl) using a similar procedure to that described above. The product of this reaction was isolated by a combination of column chromatography (20% acetone, 80% toluene and 5% industrial methylated spirit (IMS), 95% toluene) and fractional crystallisation (acetone/toluene; acetone/acetic acid/IMS) to yield 10mg 2.09×10^{-5} moles, 3.62% of the compound 'U'. (95% toluene/5% IMS was found to be the best solvent system for the separation of the compounds 'U' and 'Q' by TLC.)

4.5.1.4. Nitration of the Pentanitrobinaphthyl 'U' - Preparation of the Compound 'V'

The pentanitrobinaphthyl 'U' (9.5mg, 1.983×10^{-5}moles) was dispersed in sulphuric acid (D1.84, 1ml) and nitric acid (D1.42, 1ml) added rapidly with stirring. The mixture was heated to 100°C for 30minutes then poured onto crushed ice. The mixture was warmed in order to coagulate the product which was then filtered off and dried under reduced pressure. The product was crystallised once from acetone/acetic acid, three times from acetone/toluene, then once more from acetone/acetic acid. This yielded:1.8mg, 3.43×10^{-6} moles, 17.3% of the compound 'V'.

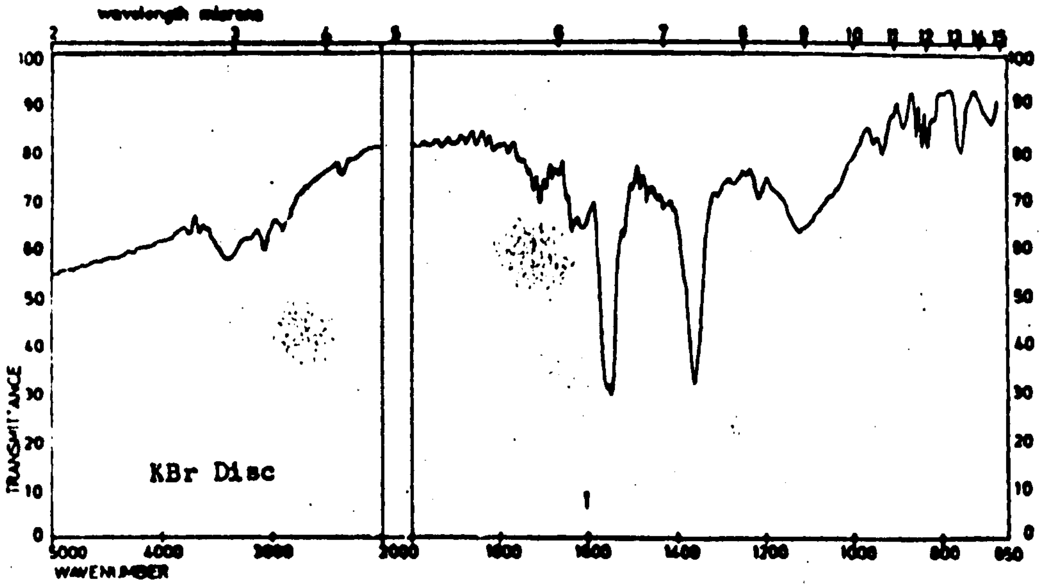
4.5.1.5. The Nitration of 4,4',5,8'-Tetranitro-1,1'-binaphthyl (Compound 'P')

A sample of compound 'P' (14mg, 3.226×10^{-5} moles) was dispersed in sulphuric acid (D1.84, 1ml) then nitric acid (D1.42, 0.1ml) was added rapidly with stirring. The mixture was heated on a water bath for 45min, then cooled and poured onto crushed ice. The product was filtered off, washed with water, sodium bicarbonate, water again then dried. This material was crystallised twice from acetone/acetic acid and dried under reduced pressure to yield: 3mg, 5.272×10^{-6} moles 16.3% of the compound 'Y' mp 195-8°C. None of the compound 'Q' could be detected in the product from this reaction (TLC: 20% acetone, 80% toluene). Thus both the crystalline material 'Y' and the residues of crystallisation produced a single spot by TLC (+ residues). In each case the single spot had an identical Rf to that of the compound 'R'

4.5.1.6. Nitration of the Dinitrobinaphthyl 'C-1'

A sample of the compound 'C-1' (21.6mg, 6.279×10^{-5}moles) was dissolved in acetic anhydride (4ml) by warming. This mixture was cooled to 30°C and nitric acid (D1.42, 0.8ml) added dropwise with stirring at such a rate that the temperature remained between 35-40°C. When all of the nitric acid had been added the mixture was cooled to 20°C and two drops of sulphuric acid (D1.84, approx 0.05ml) added. After a few minutes the mixture was warmed to 40°C and maintained at this temperature for two hours. The mixture was quenched with excess water and the product extracted into chloroform. The extract was washed with water, sodium bicarbonate (saturated), water again then dried over sodium sulphate. TLC (toluene) produced two spots - both with Rf's intermediate between those of 4,4',5,5'-tetranitro-1,1'-binaphthyl and 4,4',5-trinitro-1,1'-binaphthyl. This product was stripped of solvent, dissolved in sulphuric acid (D1.84, 5ml) and nitric acid (D1.42, 0.25ml) added. The mixture was heated on a water bath for 1hr, cooled and poured onto crushed ice. After warming to coagulate it, the product was filtered off, washed with water, sodium bicarbonate (saturated) and water again. The crude product was then partially purified by a combination of column chromatography (toluene and 5% acetone/95% toluene) and crystallisation (acetone/acetic acid, acetone/acetic acid/IMS and acetone/toluene). After drying under reduced pressure 0.6mg of product was isolated. An infra-red spectrum was recorded from this product (see figure 9) but a satisfactory mass spectrum could not be obtained due to the presence of aliphatic impurities.

<u>Figure 9</u>



IR Spectrum of the nitration product of the compound 'C-1'

4.5.2. Nitrations in Acetic Anhydride and Nitric Acid

4.5.2.1. The Preparation of 4,4',5-Trinitro-1,1'-binaphthyl from 4,4'-Dinitro-1,1'-binaphthyl

4,4'-Dinitro-1,1'-binaphthyl (0.25g, 7.267 x 10^{-4}moles) was dispersed in acetic anhydride (7.5ml). Nitric acid (D1.42, 7.5ml) was added to this mixture dropwise, with stirring, at such a rate that the temperature remained between 35-40°C (1.25hrs). The mixture was then stood at ambient temperature for 1.25hrs before being quenched with excess water. The product was filtered off, and separated by a combination of column chromatography and crystallisation, in a manner similar to that described in section 4.4.2.3. for the separation of products from the nitration of 1,1'-binaphthyl. The various products which were isolated from the reaction are summarised in table 4-5.

This experiment was designed to demonstrate that compound 'D' contained 4,4'- substitution. It would therefore have been most satisfactory if 'D' had been the only,or at least the major product of the reaction. This could not however, be achieved. The problem was one of solubility, thus if only the stoichiometric quantity of nitric acid was added to the reaction, the substrate failed to dissolve and was recovered unchanged at the end of the reaction, whilst if sufficient acid was introduced to dissolve the dinitrobinaphthyl the reaction did not stop at the trinitro derivative, but produced a complex mixture of products. The use of alternative nitration media did not readily solve the problem either, as nitric acid in glacial acetic acid did not significantly nitrate the dinitrobinaphthyl, whilst nitric acid in sulphuric acid proved less controllable than nitric acid in acetic anhydride. It therefore proved necessary to employ a nitration technique basically similar to that originally used for the preparation of 'D' (section 4.4.2.3.), which produced a complex mixture of products. The multiple products were then separated by appropriate techniques. The product mixture actually obtained by the above method appeared, at least superficially (TLC), to be very similar to that produced by the nitration of binaphthyl under similar conditions. Indeed the major products of the reaction (see table 4-5) had all been previously identified from the nitration of 1,1'-binaphthyl. However two additional compounds were also isolated - compounds 'W' and 'X'. As only very small quantities of these compounds were separated it was not possible to fully identify them. The significant data is noted below, the

Table 4-5

A Summary of the Products Obtained by the Nitration of 4,4'-Dinitro-1,1'-binaphthyl in Acetic Anhydride/Nitric Acid

Compound Name	Designation	Total Isolated Product		Yield
		(g)	(Moles)	(%)
4,4'-Dinitro-1,1'-binaphthyl (Unreacted)	'B'	0.0440	1.279×10^{-4}	17.6
				Yield based on reacted substrate (%)
4,4',5-Trinitro-1,1'-binaphthyl	'D'	0.0185	4.756×10^{-5}	7.9
4,4',8-Trinitro-1,1'-binaphthyl	'C-2'	0.0030	7.712×10^{-6}	1.3
4,4',5,5'-Tetranitro-1,1'-binaphthyl	'H'	0.0280	6.452×10^{-5}	10.8
4,4',5,8'-Tetranitro-1,1'-binaphthyl	'P'	0.0028	6.452×10^{-6}	1.1
A Tetranitrobinaphthyl	'W'	0.0003	6.912×10^{-7}	0.1
A Pentanitrobinaphthyl	'X'	0.0050	1.044×10^{-5}	1.7

spectra are given in the appendix.

Compound 'W' (Melting point 266–270°C)

Only a mass spectrum could be recorded from this material. This spectrum (see appendix) shows that the sample was not very pure, because a number of intense peaks at low m/e values changed their relative intensities with time. Nevertheless, as the impurity peaks do not extend above about m/e 150, some useful data can be extracted from the spectrum. Thus a weak ion at m/e 434 (3.0%) is believed to be the molecular ion of the spectrum, whilst two fragment ions at m/e388 (4.0%) and m/e 342 (20.5%) are most likely attributable to (M - NO_2) and (M - $2NO_2$) ions. (Since the ions at low m/e have been discounted as resulting from impurities, the ion at m/e 200 has been taken as the base peak of the spectrum.) These assignments are confirmed by the presence of interim ions of low intensity (M - O), (M - NO) etc which are characteristic of the fragmentation of individual nitro groups.[77] The remaining ions in the spectrum - down to m/e 200 - are however of very low intensity so that it is impossible to assign any fragmentation sequence to the spectrum. The structure of the compound 'W' is thus essentially 'unknown', although it seems likely that the compound is a tetranitrobinaphthyl. (The spectrum is clearly dissimilar to that of any other nitrobinaphthyl which has been isolated.)

Compound 'X'

The mass spectrum of this compound shows a molecular ion at m/e 479 and a breakdown pattern consistent with that of a pentanitrobinaphthyl. The dominant feature of the spectrum is the very intense ion at m/e 433 (M - NO_2) which may indicate the presence of 4,5- substitution. This spectrum is extremely similar to that of the compound 'U' - although a number of minor variations occur in the intensities of individual ions. It is doubtful whether these fluctuations are sufficiently large to be of significance.

The IR spectrum of 'X' shows two bands which are consistent with the presence of nitro valence stretching vibrations. Of these the higher frequency (asymmetric stretching) band is split into two maxima at 1550/1535cm^{-1}, whilst the lower frequency (symmetric stretching) band produces a single maximum at about 1355cm^{-1}. There is no evidence for the presence of any other functional groups in 'X'. Whilst there is considerable similarity between the IR spectrum of 'X' and that of the compound 'U' some discrepancies are clearly evident (see appendix). It is unclear however whether these arise due to the presence of an impurity in 'X' or whether the two compounds are in fact dissimilar.

Whilst the above evidence certainly suggests that the compound 'X' is a pentanitrobinaphthyl, its structure is somewhat uncertain. Thus whilst it is conceivable that this material is identical with the compound 'U' there is insufficient evidence to establish this fact conclusively.

Although the overall yield of pure nitroaromatic products obtained from the above reaction was very low (approx 23%) the two major products to be isolated were 4,4',5-trinitro-1,1'-binaphthyl (7.9%) and 4,4',5,5'-tetranitro-1,1'-binaphthyl (10.8%). This result is thought strongly indicative of 4,4'-substitution in the compound 'D', although in view of the low yields it cannot be regarded as conclusive evidence. It is pertinent to note in this context that whilst the above nitration of 4,4'-dinitro-1,1'-binaphthyl producès compound 'D' albeit in small yield, a similar nitration of 5,5'-dinitro-1,1'-binaphthyl did not produce any detectable trace (by TLC) of the compound 'D'.

4.5.2.2. The Preparation of 4,4',5,5'-Tetranitro-1,1'-binaphthyl from 4,4'-Dinitro-1,1'-binaphthyl*

4,4'-Dinitro-1,1'-binaphthyl (0.5g, 1.453 x 10^{-3}moles), prepared by the method of Schoepfle,[10] was dispersed in sulphuric acid (D1.84, 2.5ml). To this stirred solution was added firstly glacial acetic acid (2.5ml), then nitric acid (D1.42, 1.5ml). The mixture was heated on a water bath for 2.5hrs then cooled to ambient temperature and the precipitate filtered off. This precipitate was crystallised twice from acetone/acetic acid to yield 0.1929g of 4,4',5,5'-tetranitro-1,1'-binaphthyl (IR and PMR spectra and thin layer chromatogram identical with those of an authentic sample). The acidic residues from above (in nitric/sulphuric/acetic acids) were poured onto ice. The precipitate was filtered off, washed with water, dried, then crystallised twice from acetone/acetic acid. This yielded a further 0.0793g of the compound 'H'. Total yield of compound 'H' = 0.2722g, 6.272 x 10^{-4} moles 43.2%.

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* The preparation of 4,4',5,5'-tetranitro-1,1'-binaphthyl by the nitration of 4,4'-dinitro-1,1'-binaphthyl has also been reported by Jones and Joyner.[12] These authors employed a mixture of nitric, sulphuric and acetic acids boiling under reflux for 28hrs. (Yield = 50%)

4.5.2.3. The Preparation of 4,4',5,5'-Tetranitro-1,1'-binaphthyl from 5,5'-Dinitro-1,1'-binaphthyl

5,5'-Dinitro-1,1'-binaphthyl (15mg, 4.360 x 10^{-5} moles), prepared by the method of Scholl,[14,*] was finely ground and dispersed in acetic anhydride (1ml). Nitric acid (D1.42, 0.2ml) was added dropwise to this stirred solution whilst cooling was maintained on a cold plate. The rate of addition was maintained such that the temperature of the solution remained in the range 35-40°C. When all the nitric acid had been added, one small drop of sulphuric acid (D1.84, approx 0.01ml) was added to the solution. The mixture was then stood under an IR lamp; initially the temperature rose to 65°C, but this was brought down fairly rapidly to 40°C. After 1.25hrs a material had crystallised from the solution. This was filtered off, washed with water and crystallised from acetone/acetic acid to yield 8.5mg, 1.958 x 10^{-5} moles, 44.9% of 4,4',5,5'-tetranitro-1,1'-binaphthyl. (IR and mass spectra and thin layer chromatogram (toluene) identical with those of an authentic sample.)

4.5.2.4. The Preparation of 4,4',5,5'-Tetranitro-1,1'-binaphthyl from 4,4',5-Trinitro-1,1'-binaphthyl

4,4',5-Trinitro-1,1'-binaphthyl (0.2g, 5.14 x 10^{-4} moles) was dispersed in acetic anhydride (4ml). Nitric acid (D1.42, 0.8ml) was added dropwise to this stirred solution whilst cooling was maintained on a coldplate. The rate of this addition was varied such that the temperature of the solution remained in the range 35-40°C. Following addition of the nitric acid, two drops of sulphuric acid (D1.84, approx 0.05ml) were added to the solution. The mixture was maintained at about 40°C for 2hrs, then cooled to ambient temperature and the solid filtered off. This was washed with water, recrystallised from acetone/acetic acid and dried under reduced pressure to yield 0.145g, 3.341 x 10^{-4} moles, 65.0% of 4,4',5,5'-tetranitro-1,1'-binaphthyl. (IR and PMR spectra and thin layer chromatogram (toluene) identical with those of an authentic sample.)

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* The 1-Iodo-5-nitronaphthalene required for this method was prepared from 1-amino-5-nitronaphthalene by a standard diazotisation procedure followed by treatment with potassium iodide solution. The product was purified by crystallisation consecutively from acetone/IMS, acetic acid and benzene.

4.5.2.5. The Preparation of 4,4',5,8'-Tetranitro-1,1'-binaphthyl (Compound 'P') from 4,5,8'-Trinitro-1,1'-binaphthyl (Compound 'F')

A sample of compound 'F' (20mg, 5.141×10^{-5} moles) was dissolved in acetic anhydride (4ml) and nitric acid (D1.42, 0.8ml) added to the stirred solution, whilst cooling was maintained on a cold plate. The rate of addition was controlled such that the temperature remained in the range 35-40°C. When all the nitric acid had been added, the mixture was cooled to 25°C and two drops of sulphuric acid (D1.84, approx 0.05ml) were added. On warming, an exotherm caused the temperature to rise briefly to 60°C, however the mixture was rapidly cooled to 40°C and this temperature was then maintained for two hours. At the end of this period.the reaction was quenched by pouring it into excess water and the product extracted into chloroform. The solution was washed with sodium bicarbonate (saturated) and water, then stripped of solvent. This crude product was purified by a combination of column chromatography (2% acetone/98% toluene) and crystallisation (acetone/acetic acid). After drying under reduced pressure 4mg, 9.22×10^{-6} moles, 17.9% of the compound 'P' was isolated. (IR and mass spectrum and thin layer chromatogram (toluene) identical to those of an authentic sample).

4.6. The Preparation of 1-Picrylnaphthalene

Picryl chloride (5g, 0.020 moles) and 1-iodonaphthalene (10g, 0.039 moles) were heated in an open beaker to 145°C (during which time the picryl chloride dissolved). Copper powder (3.8g, 0.069 moles) was added to this mixture with frequent stirring so as to maintain the reaction at 150-160°C (approx 45min). Once all of the copper had been added, the mixture was heated for a further 30 minutes at 150-160°C with occasional stirring. (Extended reaction times are detrimental to the reaction and can lead to the production of by-products which are difficult to remove from the 1-picrylnaphthalene.) After cooling the product was extracted with boiling toluene and applied directly to a 450mm column of silica gel. The column was eluted with toluene until no further coloured matter was removed (approx 500ml). Picryl naphthalene was crystallised directly from the toluene eluent. This crystallisation was facilitated by the addition of a little hexane fraction or (better) IMS, as these tended to keep residual iodonaphthalene in solution. When the solution had finally been reduced to small bulk and cooled, the iodonaphthalene separated as a red oily tar which was decanted off. The product was recrystallised from toluene/IMS then toluene to yield large golden yellow crystals of 1-picrylnaphthalene (brilliant fluorescent yellow crystals from IMS). The product was dried under reduced pressure to yield 3.82g, 0.011 moles, 55.8% .

Mp 178.5-180°C.	Requires	C:56.6%; H:2.7%; N:12.4%
	Found	C:56.3%; H:2.7%; N:12.1%

Fractional crystallisation of the residual liquor yielded (immediately after picryl naphthalene) faintly yellow needles of impure trinitrobenzene. When recrystallised from carbon tetrachloride (twice) colourless needles of pure 1,3,5-trinitrobenzene were obtained (IR and mass spectra identical to those of an authentic sample). However, trinitrobenzene and 1-iodonaphthalene appear to cocrystallise from toluene /IMS. The resulting mixture has an IR spectrum which is very similar to that of picrylnaphthalene itself and care must be taken to distinguish between impure picrylnaphthalene and this mixture. The simplest method of identifying a particular batch of crystals (and assessing purity of picryl naphthalene) is by PMR spectroscopy. Thus the presence of 1-iodonaphthalene is readily ascertained by the presence of three distinct peaks upfield from the normal 1-picrylnaphthalene spectrum (at about τ3.2-3.6), whilst trinitrobenzene produces a second singlet close to that of picrylnaphthalene (eg at $\sim\tau$ 0.7 in acetone).

4.7. The Nitration of 1-Picrylnaphthalene

4.7.1. The Preparation of 1-Picryl-4,5,7-trinitronaphthalene using i) Nitric Acid/Acetic Anhydride and ii) Nitric/Sulphuric Acid

1-Picrylnaphthalene (0.21g, 6.20 x 10^{-4} moles) was dispersed in acetic anhydride (5ml). Concentrated nitric acid (D1.42, 5ml) was added dropwise to this stirred slurry at such a rate that the temperature did not exceed 40°C. Once the addition was complete the mixture was maintained at 35°C for 2hrs then poured onto excess water. The solid was filtered off, dried under reduced pressure and dispersed in concentrated sulphuric acid (D1.84, 5ml). Concentrated nitric acid (D1.42, 5ml) was added slowly to this stirred slurry, then the mixture was heated on a water bath for 3hrs. (During this period product crystallised from the solution.) After cooling, the product was filtered off, washed with water and crystallised twice from acetone/acetic acid. After drying under reduced pressure this yielded 0.032g of 1-picryl-4,5,7-trinitronaphthalene. The mixed acid filtrate from above was poured onto crushed ice and the solid product filtered off and dried. This material was added to the remnants of the above crystallisations and the combined material crystallised repeatedly from acetone/acetic acid until additional pure 1-picryl-4,5,7-trinitronaphthalene was isolated (0.0847g). Total isolated product (1-picryl-4,5,7-trinitronaphthalene) = 0.1167g, 2.462 x 10^{-4} moles, 39.7%. Mp = 307-311.5°C.

Analysis		
	Requires	C:40.51%; H:1.27%; N:17.72%
	Found	C:40.79%; H:1.42%; N:17.60%

4.7.2. The Preparation of 1-Picryl-4,5,7-trinitronaphthalene using Nitric/Sulphuric AcidsDirectly

1-Picrylnaphthalene (0.5g, 2.65 x 10^{-3}moles) was finely ground and dispersed in sulphuric acid (D1.84,10ml). Nitric acid (D1.42, 10ml) was added rapidly with stirring. The mixture was heated to 100°C for 3.5hrs during which time cream coloured needles separated from the solution. These were filtered off, and washed with water. The residual nitration mixture was poured onto crushed ice and the solid filtered off. This portion of the product was washed with water, saturated sodium bicarbonate solution (twice), water again then crystallised from acetone/acetic acid to yield 45mg of crude product. This material was combined with the product crystallised directly from the mixed acid and the entire product recrystallised slowly from acetone/acetic acid (approx 14hrs). After drying under reduced pressure (approx 100°C), this yielded 1-picryl-4,5,7-trinitronaphthalene - 0.465g, 9.81 x 10^{-4} moles, 36.5%. (IR and PMR spectra identical with those of an authentic sample.)

Since the yield of 1-picryl-4,5,7-trinitronaphthalene obtained by this method is only 3% less than that described in section 4.7.1., this is regarded as the best method of preparation for the material. Thus the above procedure is substantially quicker and easier to carry out than that described in section 4.7.1..

4.7.3. The Preparation of 1-Picryl-2,4,5,7-tetranitronaphthalene

1-Picrylnaphthalene (1g, 2.95 x 10^{-3}moles) was dispersed in sulphuric acid (D1.84, 25ml) and fuming nitric acid (D1.50, 25ml) added rapidly with stirring. The mixture was then boiled under reflux for 7hrs during which time some product crystallised from the solution. The mixture was cooled and this solid filtered off and washed with water. The mixed acid filtrate was poured onto ice, then warmed to coagulate the solid, which was filtered off and washed with water. This material was crystallised from acetone and combined with the material which had crystallised directly from the mixed acid. The total product was recrystallised twice from acetone to yield 0.5228g, 1.07 x 10^{-3}moles, 36.3% of 1-picryl-2,4,5,7-tetranitronaphthalene mp 285-287.5°C.

Analysis Requires C:36.99%; H:0.96%; N:18.88%
Found C:37.56%; H:1.10%; N:18.35%

A further reaction was carried out using a similar procedure to the above, but with 0.5g, 1.47 x 10^{-3}moles of 1-picrylnaphthalene, 10ml of sulphuric acid and 10ml of nitric acid. This yielded 0.329g, 6.3 x 10^{-4}moles, 42.8% of pure 1-picryl-2,4,5,7-tetranitronaphthalene without isolating any material from the mixed acid filtrate. That is, only the material which crystallised directly from the mixed acid was purified.

4.8. The Nitration of 1-Picryl-4,5,7-trinitronaphthalene to 1-Picryl-2,4,5,7-tetranitronaphthalene

1-Picryl-4,5,7-trinitronaphthalene (0.2g, 4.22 x 10^{-4} moles) was dispersed in concentrated sulphuric (D1.84, 10ml). Nitric acid (D1.50, 10ml) was added rapidly to the mixture which was then boiled under reflux for 5hrs. The mixture was cooled to ambient temperature and the crystalline product filtered off and washed with water. The mixed acid filtrate was poured onto ice and the solid matter filtered off. This solid material was crystallised from acetone, then combined with the material above which had crystallised directly from the mixed acid. The total product was recrystallised twice from acetone to yield 0.0634g, 1.22 x 10^{-4}moles, 29.0% of 1-picryl-2,4,5,7-tetranitronaphthalene.

4.9. The Prolonged treatment of 1-Picryl-2,4,5,7-tetranitronaphthalene in Mixed Acid - 40hrs Boiling Under Reflux

Finely powdered 1-picryl-2,4,5,7-tetranitronaphthalene (0.13g) was dispersed in concentrated sulphuric acid (D1.84, 15ml) and nitric acid (D1.50, 10.75ml) added rapidly.. The mixture was boiled under reflux for 40hrs then cooled to 10°C and the solid, in the form of long needles, was filtered off. The product was washed in water and dried under reduced pressure to give 0.15g of solid material. This product produced infra-red and PMR spectra identical to those of the starting material.

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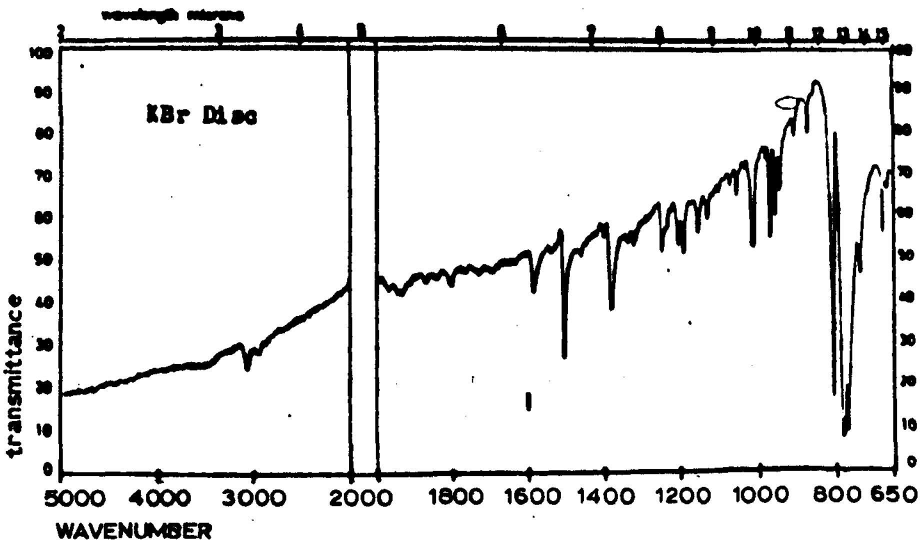
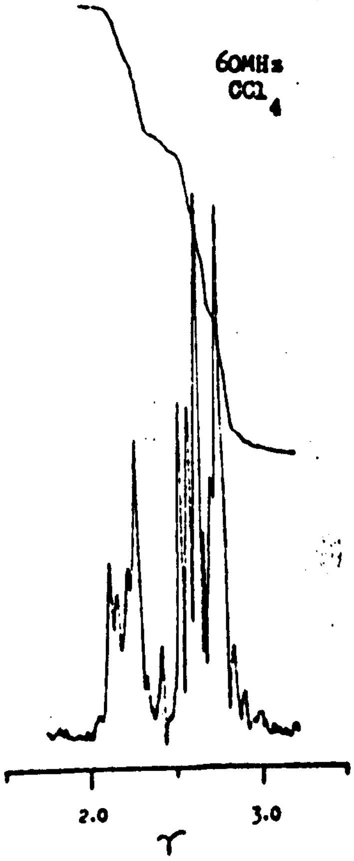
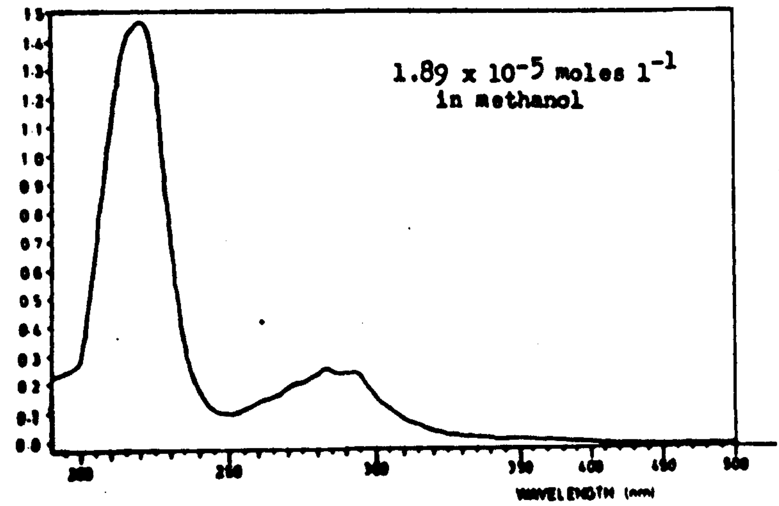
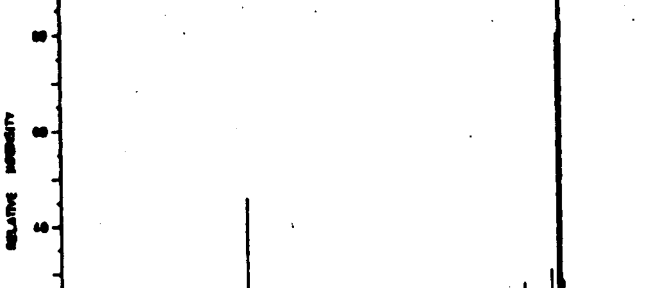
APPENDIX

Spectra of 1,1'-Binaphthyl



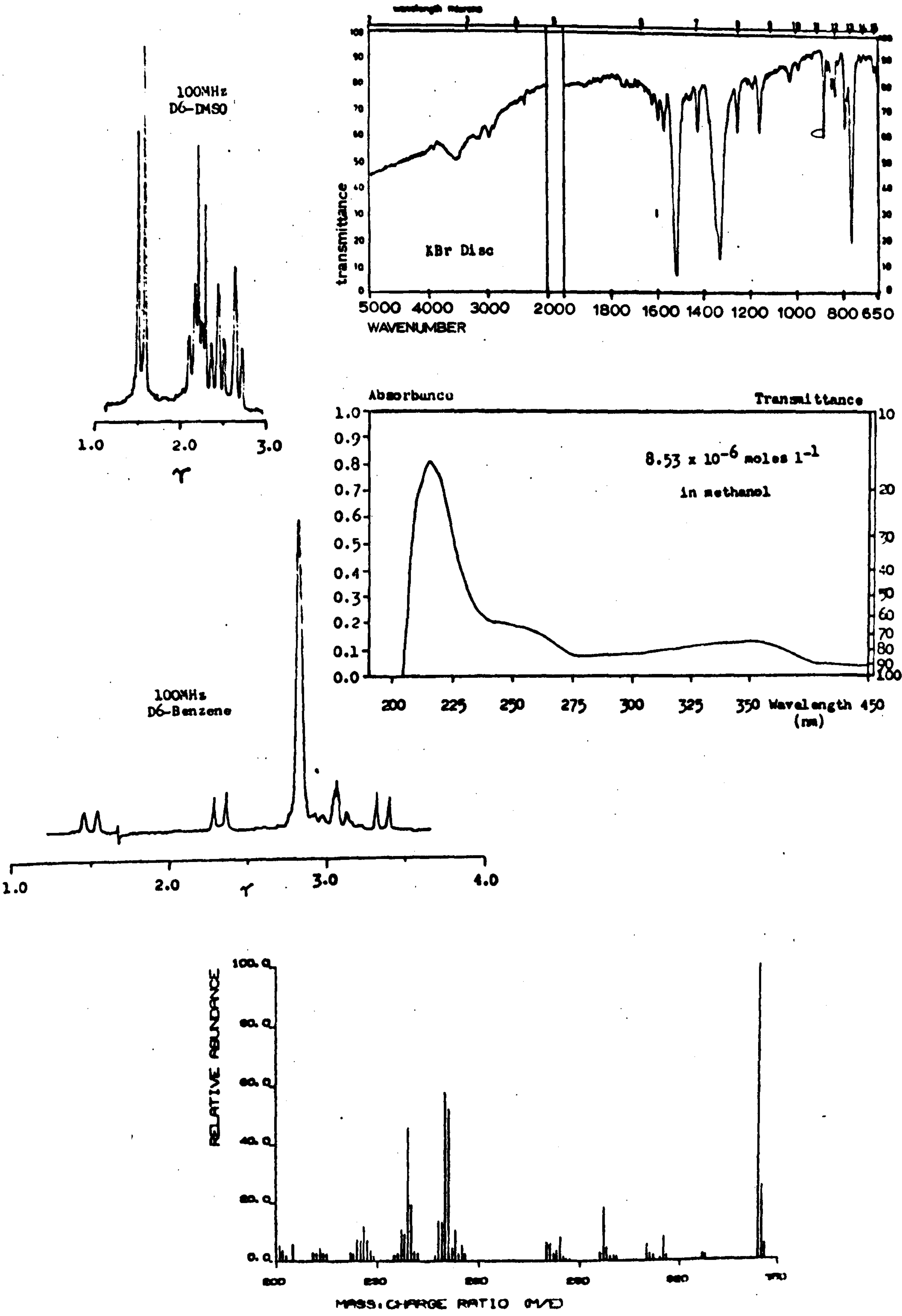




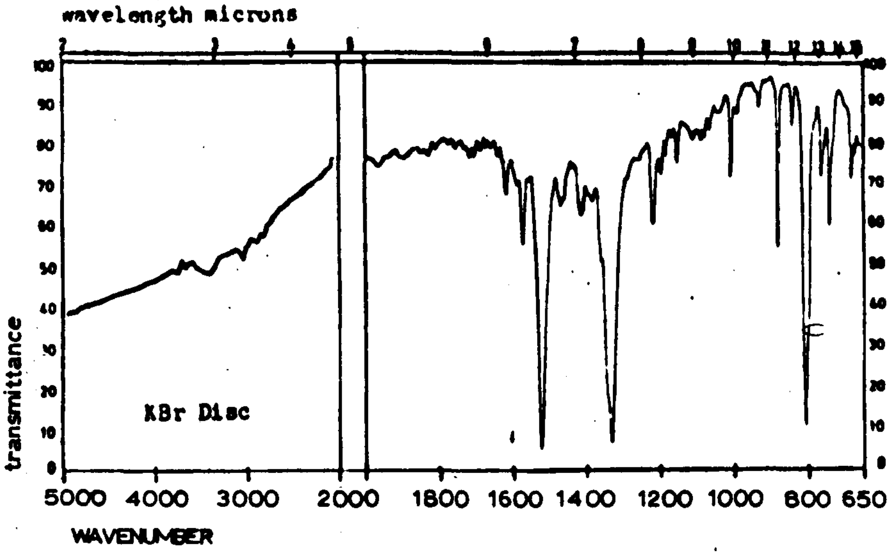


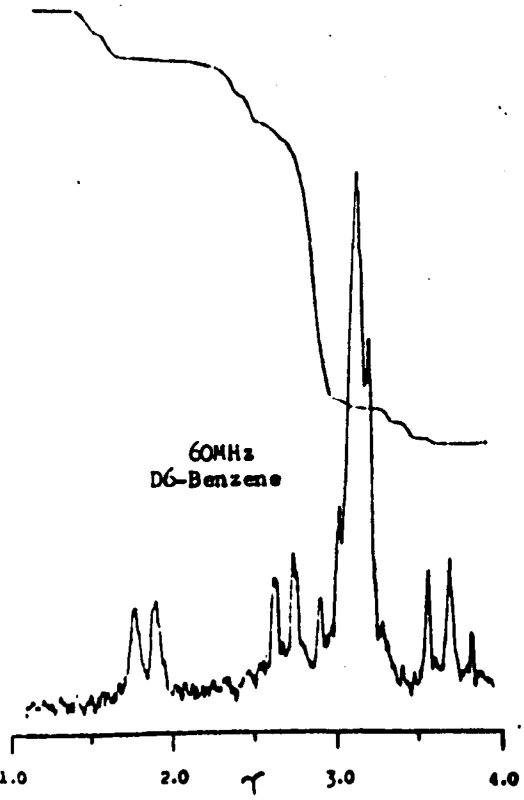
I

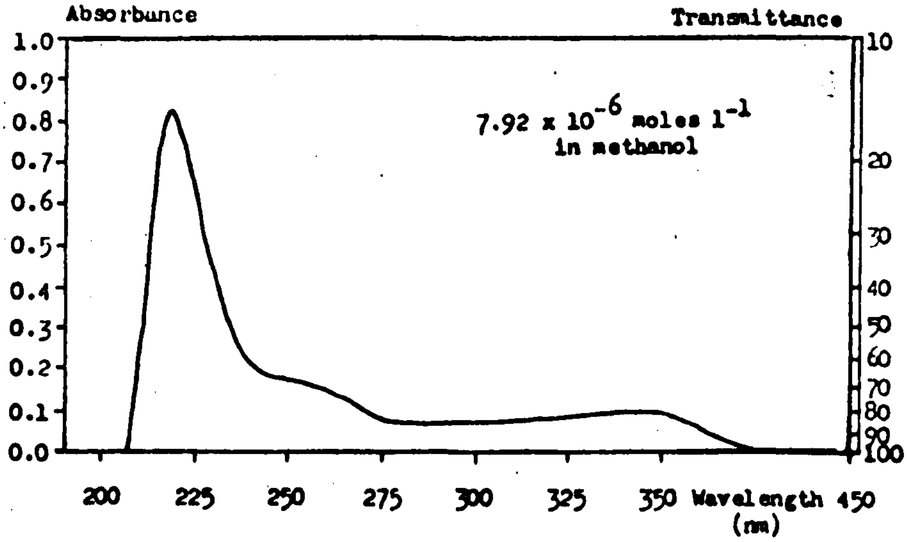
Spectra of 4,4'-Dinitro-1,1'-binaphthyl

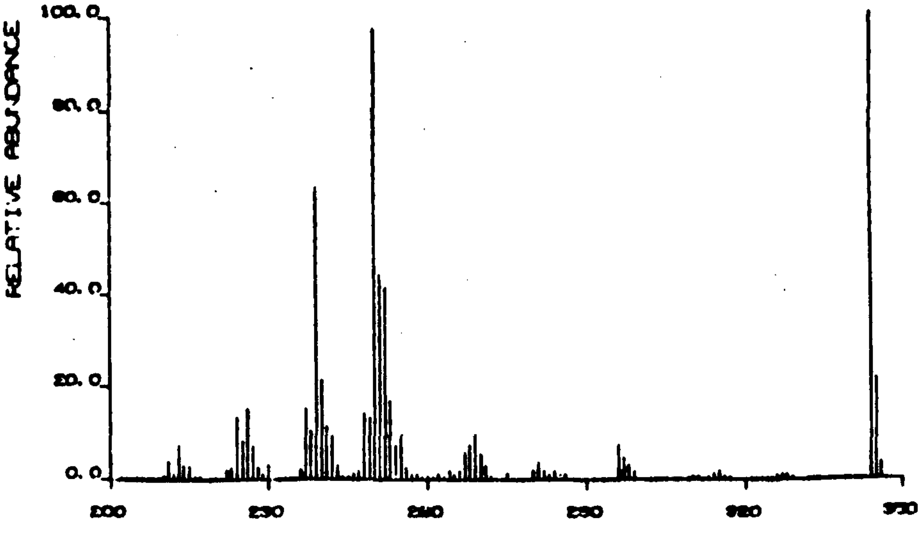


Spectra of 5,5'-Dinitro-1,1'-binaphthyl





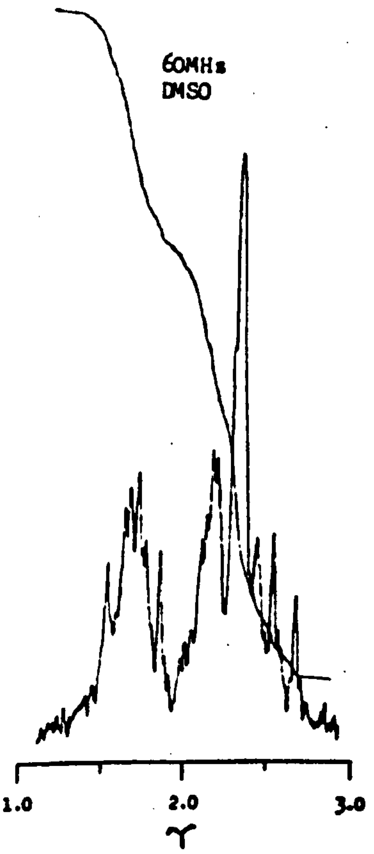


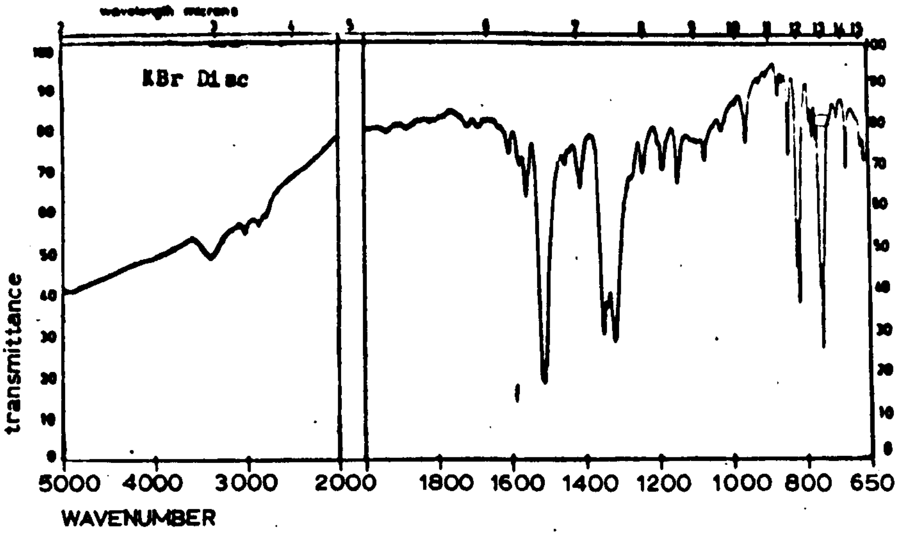


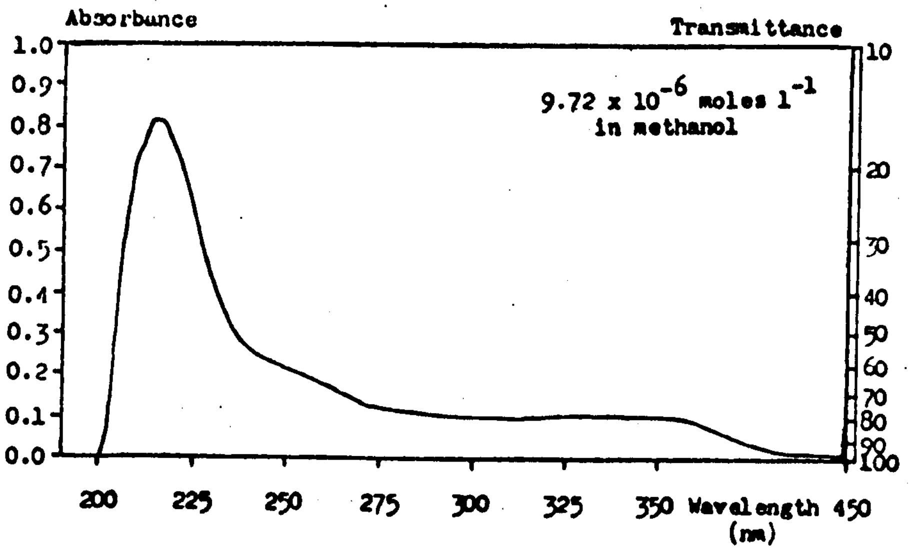
III

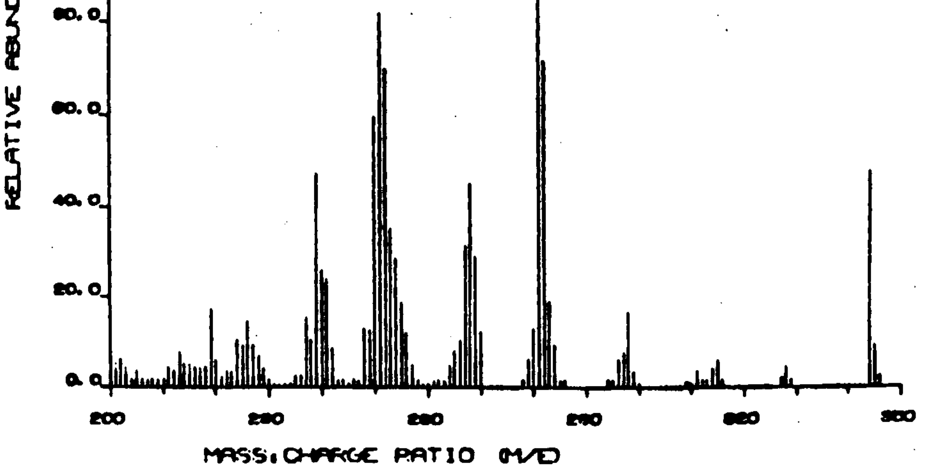
Spectra of the Compound 'C-1'

4,8'-Dinitro-1,1'-binaphthyl (?)



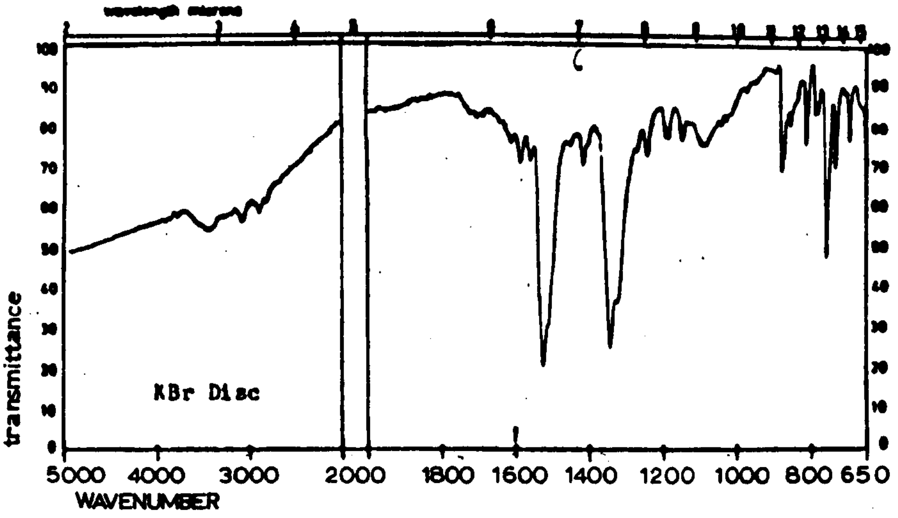


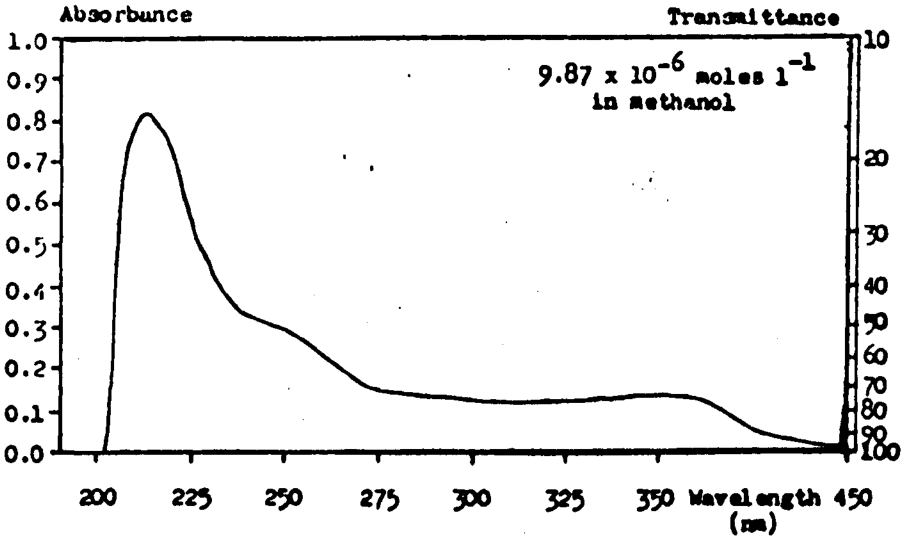


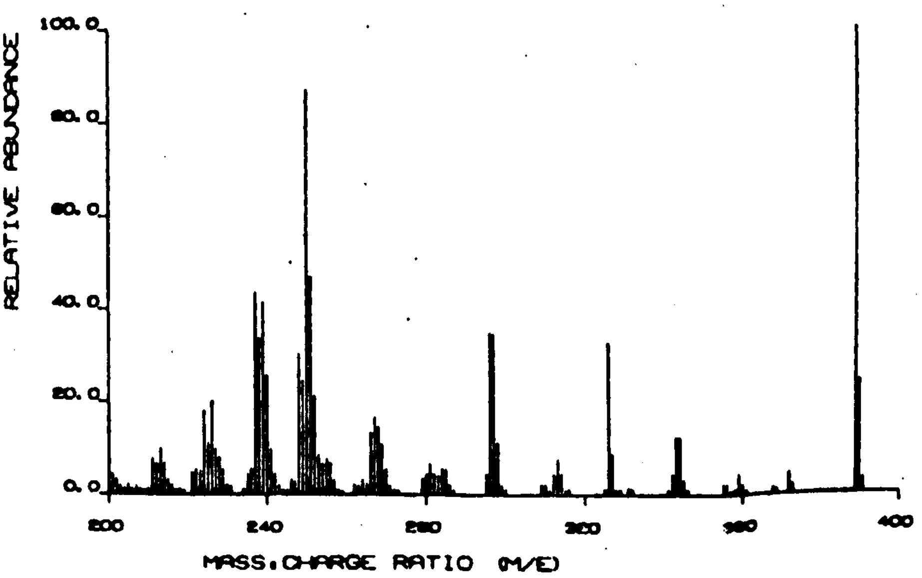


Spectra of the Compound 'C-2'

4,4',8-Trinitro-1,1'-binaphthyl (?)

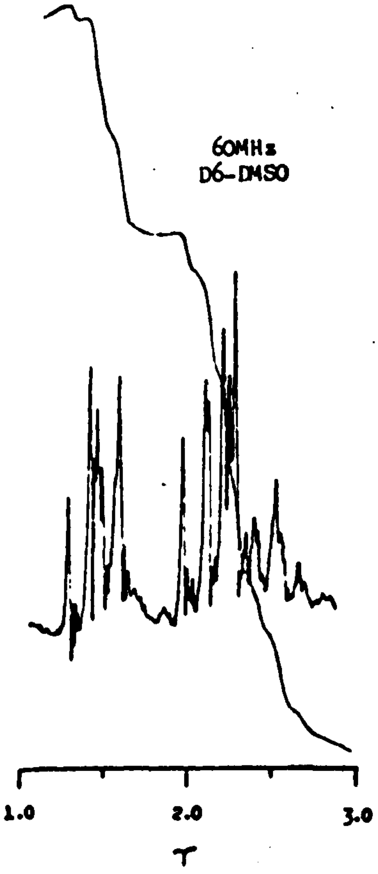


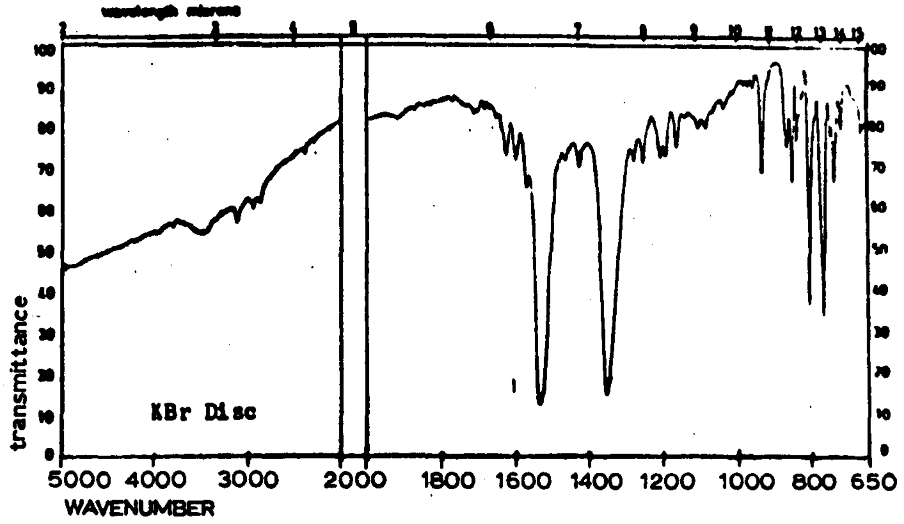


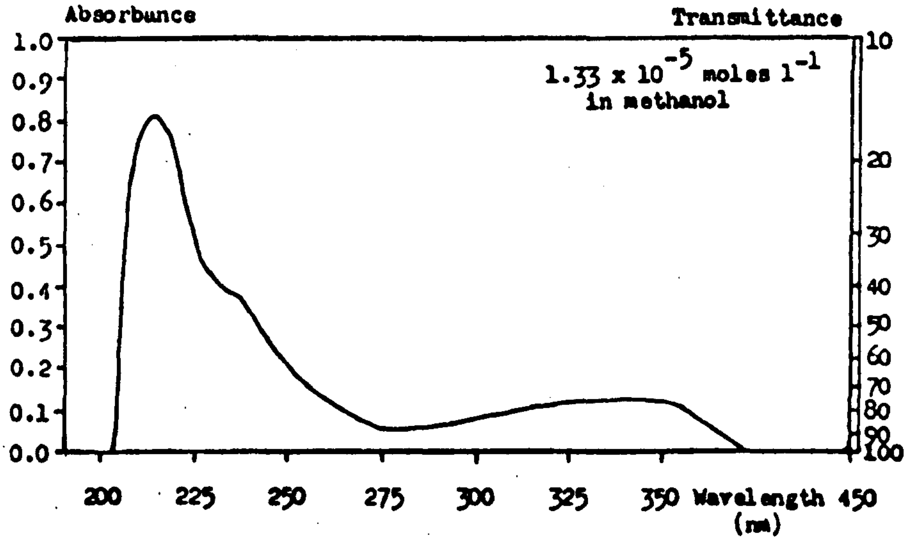


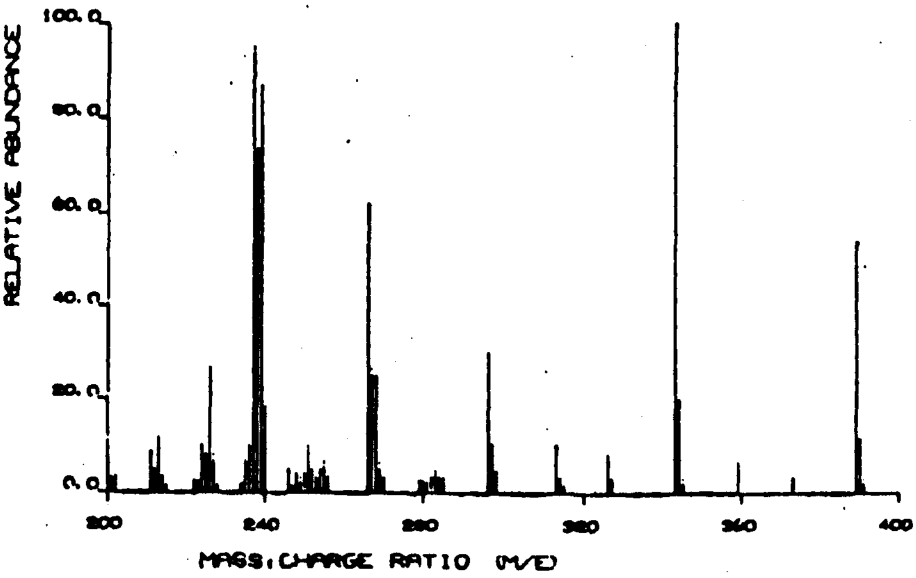
Spectra of the Compound 'D'

4,4',5-Trinitro-1,1'-binaphthyl





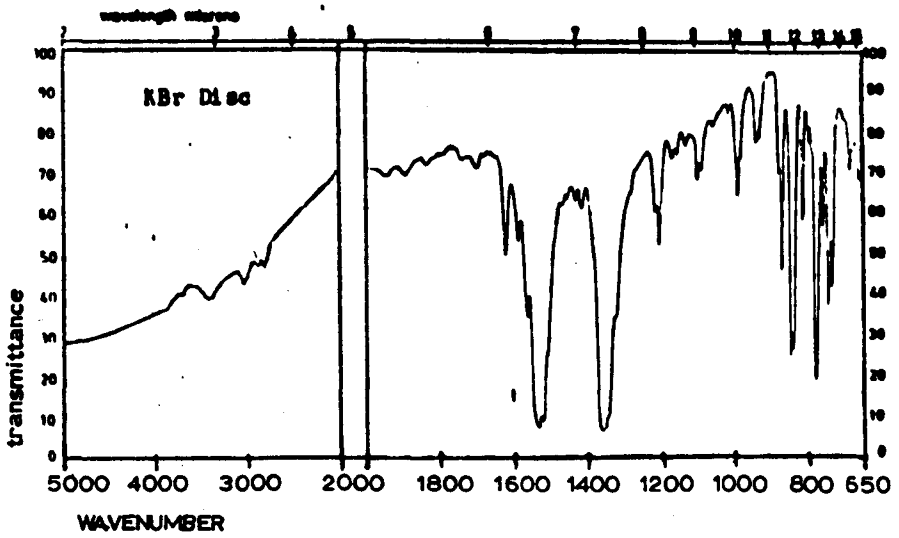


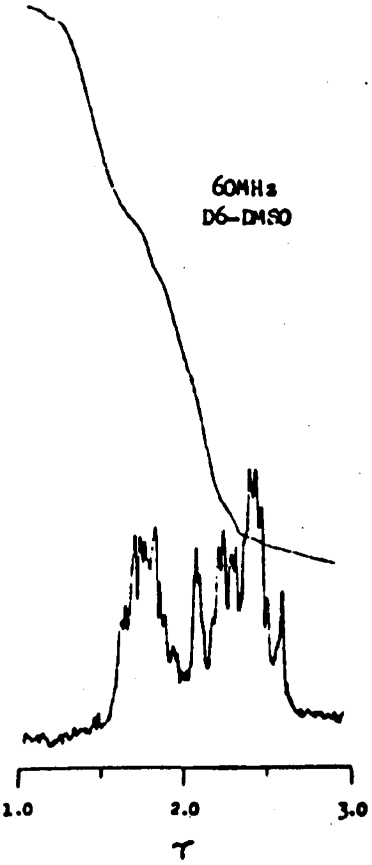


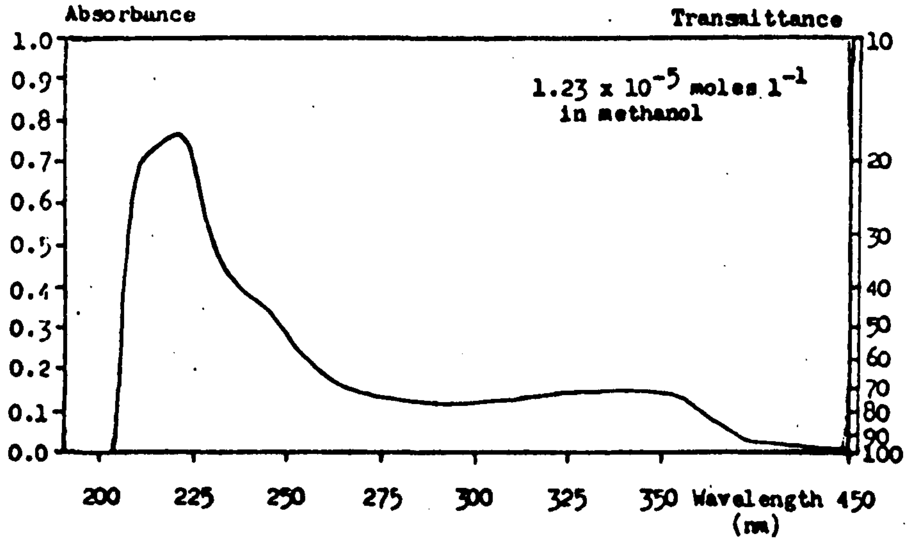
VI

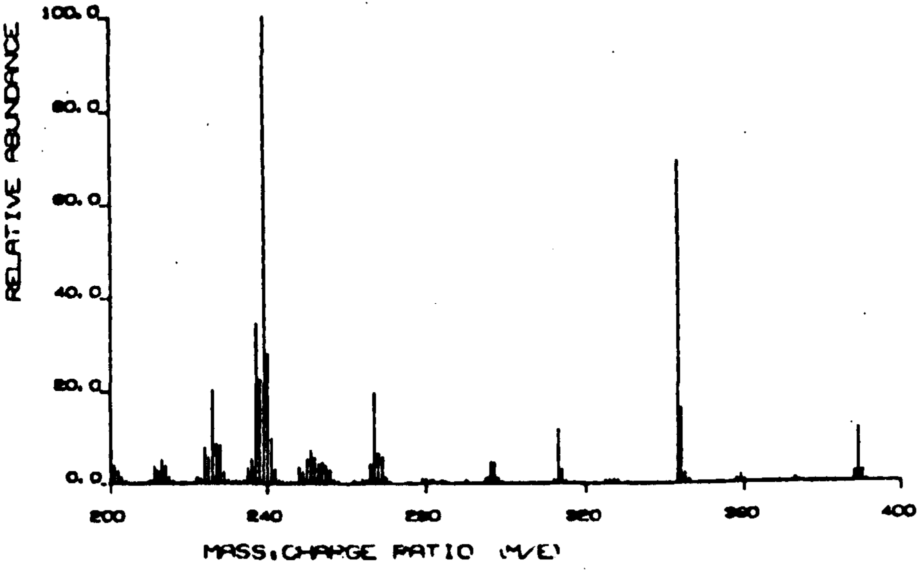
Spectra of Compound 'F'

4,5,8'-Trinitro-1,1'-binaphthyl (?)





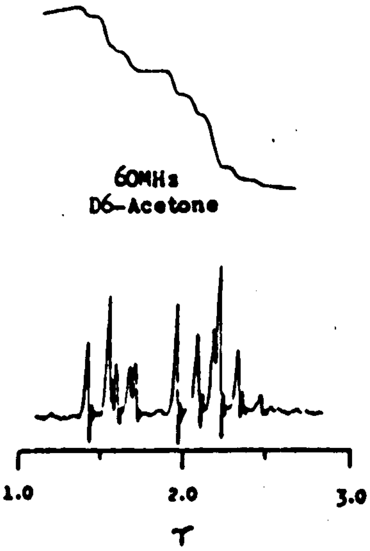


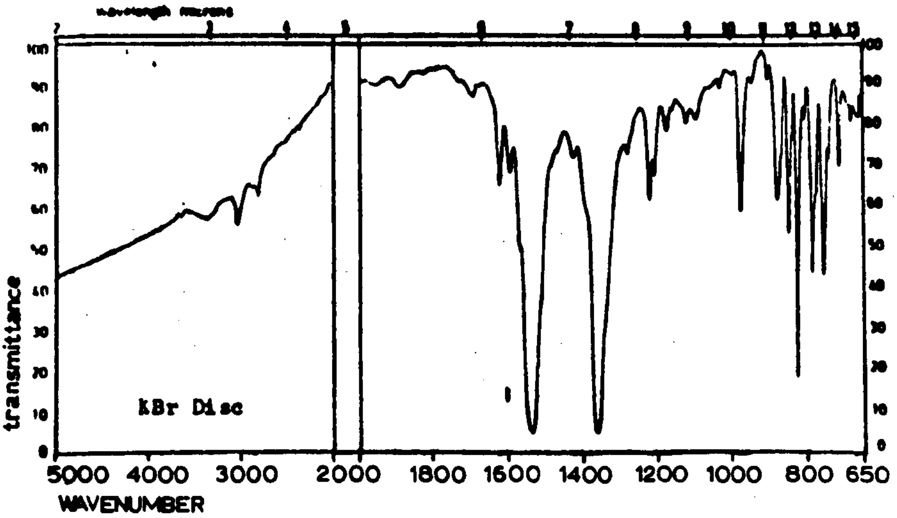


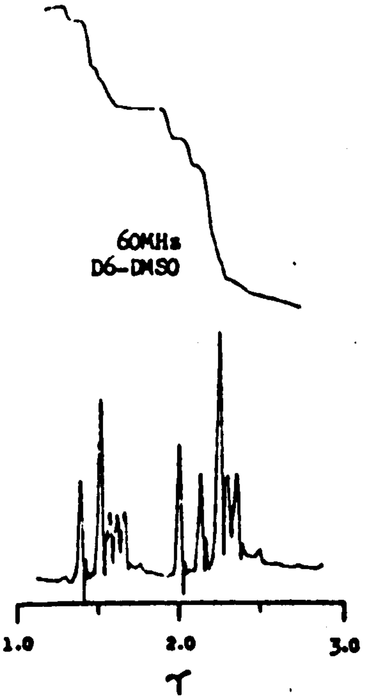
VII

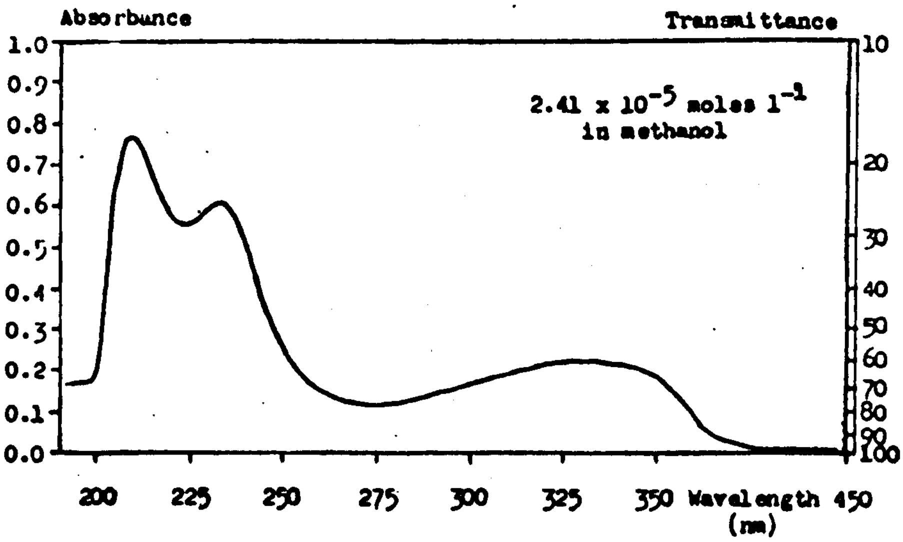
Spectra of Compound 'H'

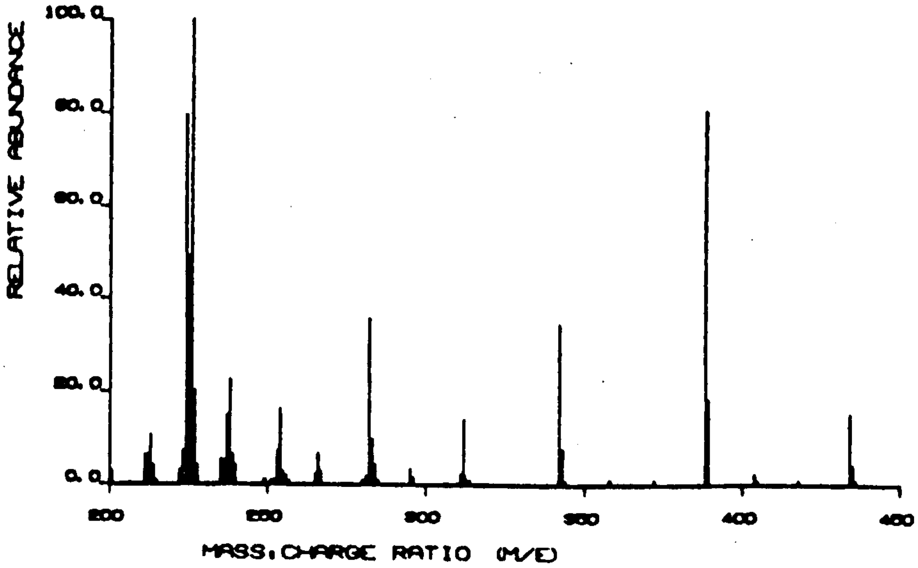
4,4',5,5'-Tetranitro-1,1'-binaphthyl





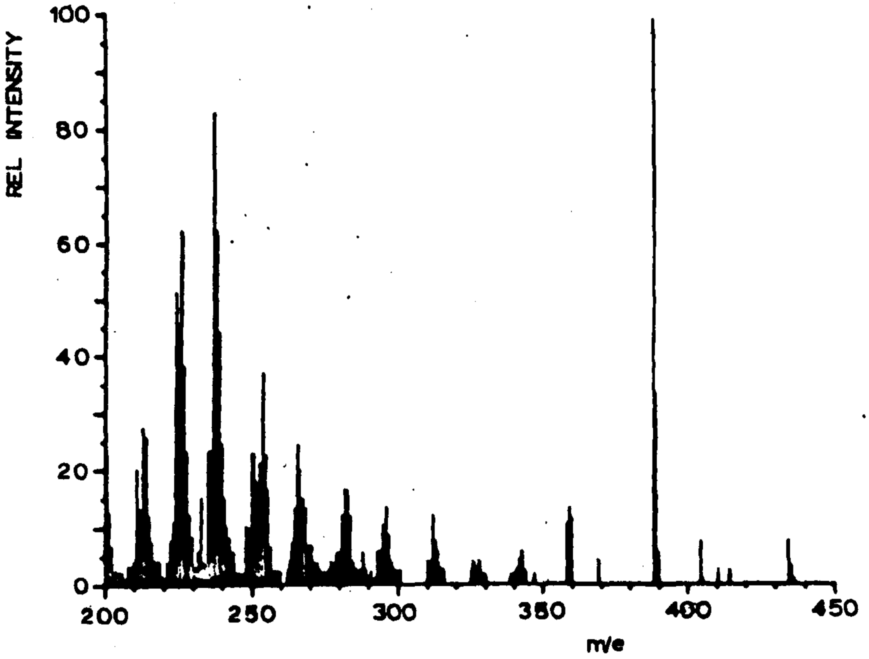






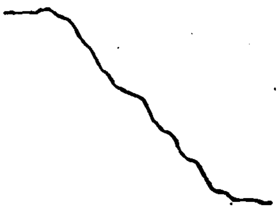
VIII

Mass Spectrum of Compound 'I'

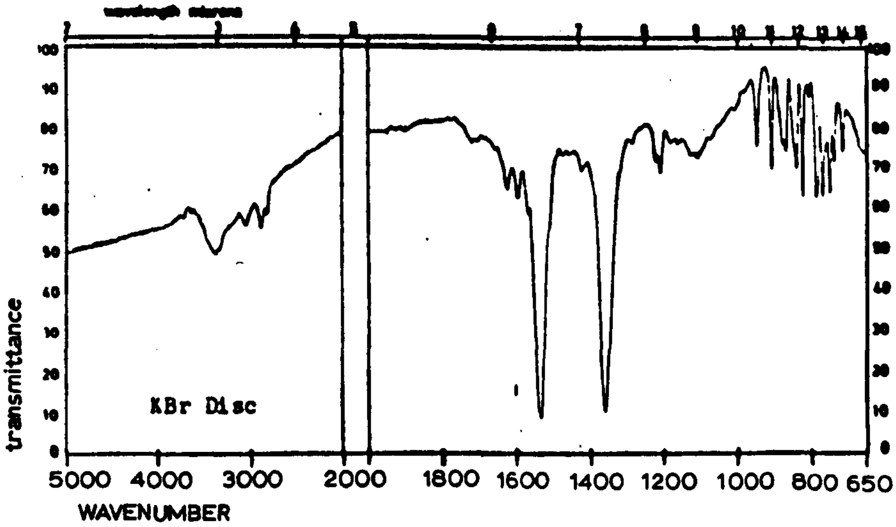


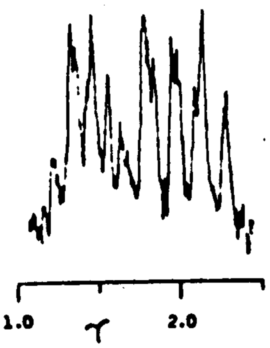
Spectra of Compound 'P'

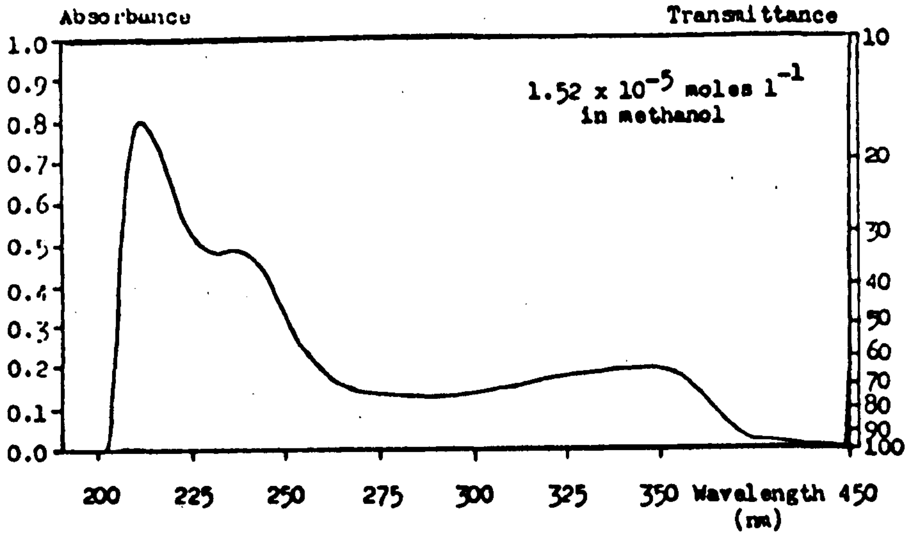
4,4',5,8'-Tetranitro-1,1'-binaphthyl (?)



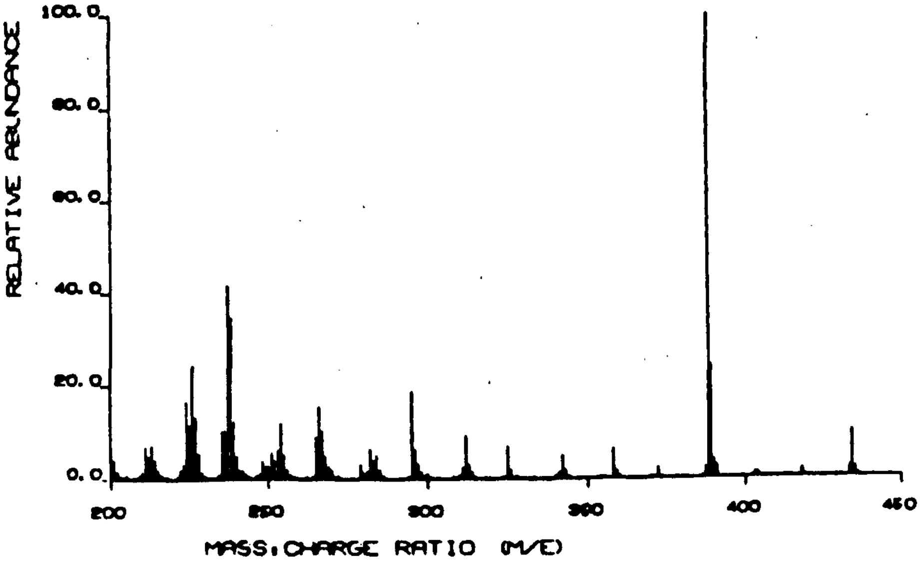
60MHz
D6-DMSO







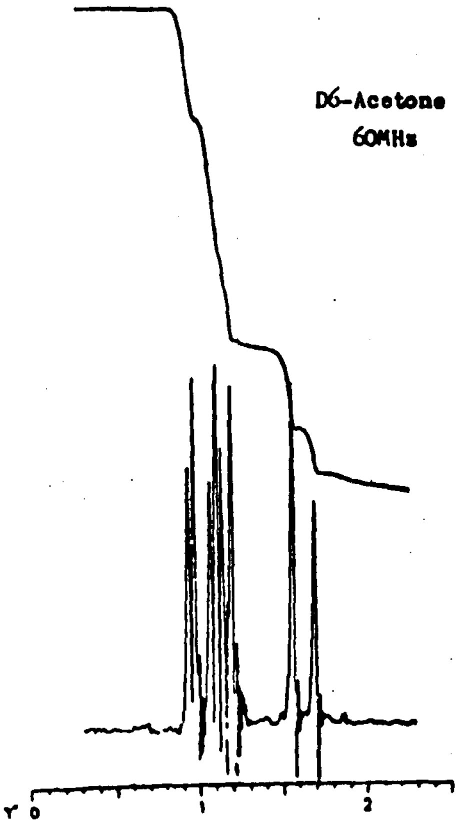
1.52×10^{-5} moles l^{-1}
in methanol

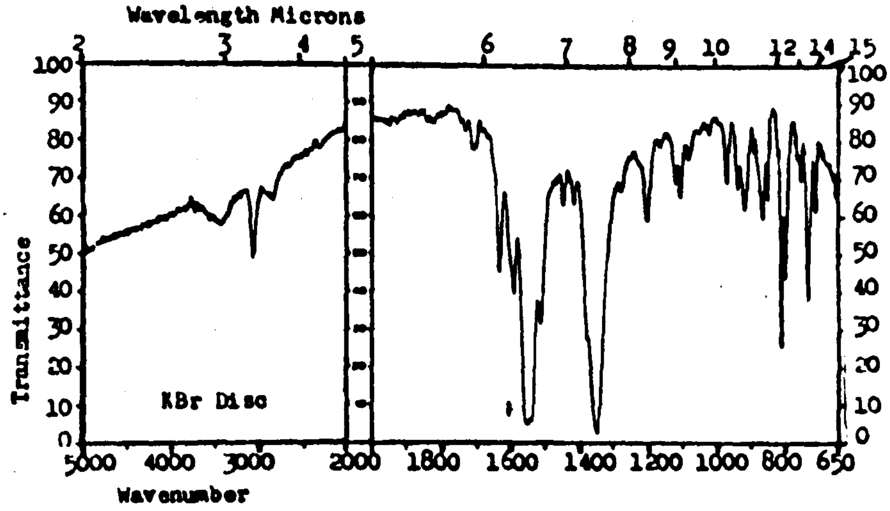


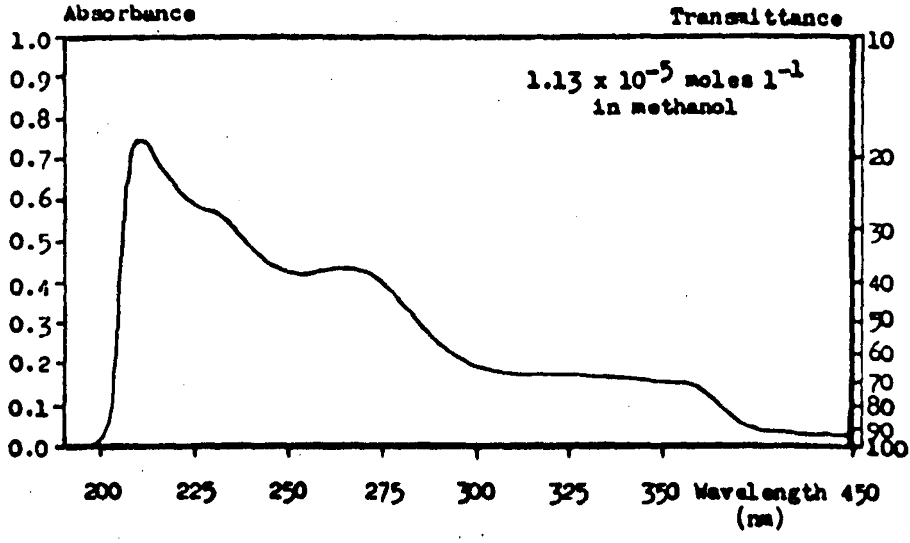
X

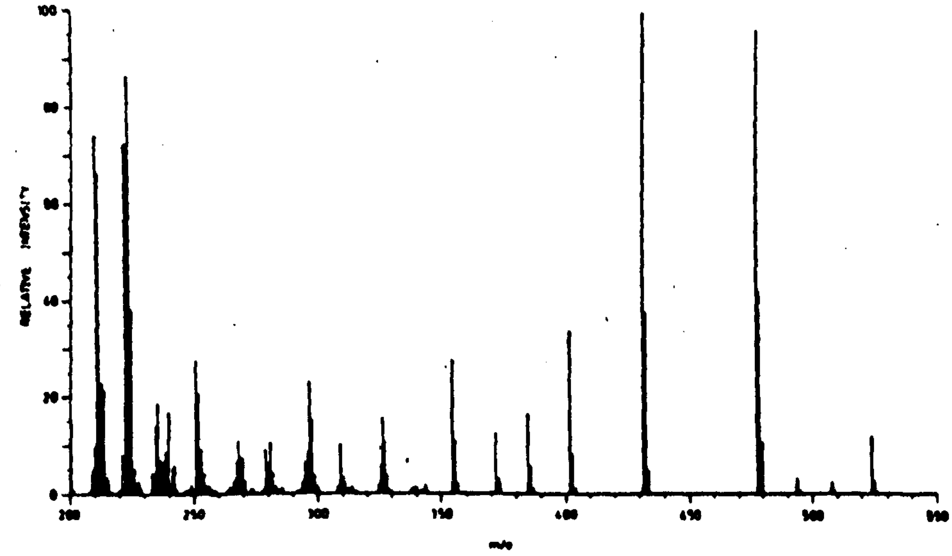
Spectra of the Compound 'Q'

4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl







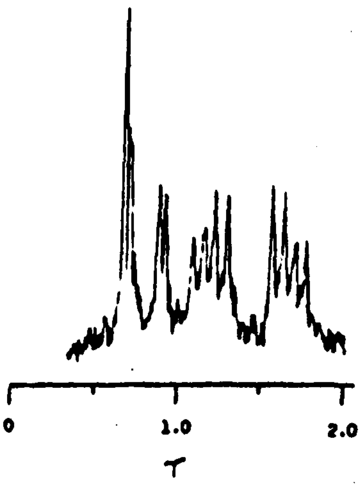


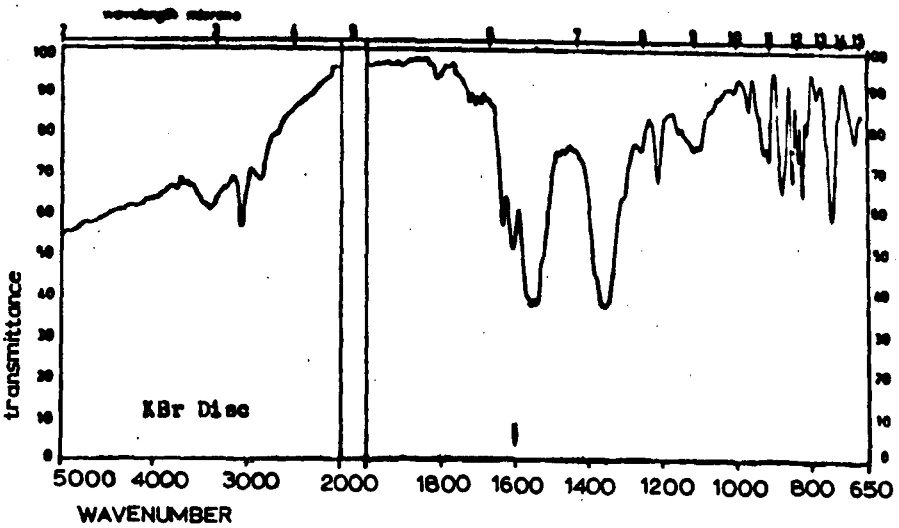
Spectra of Compound 'R'

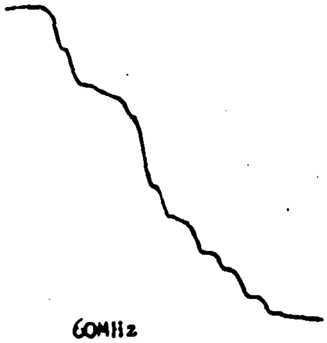
2,4,4',5,5',7,8'-Heptanitro-1,1'-binaphthyl (?)

c

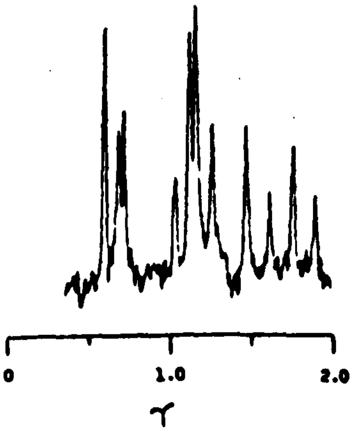
60MHz
D6-Acetone

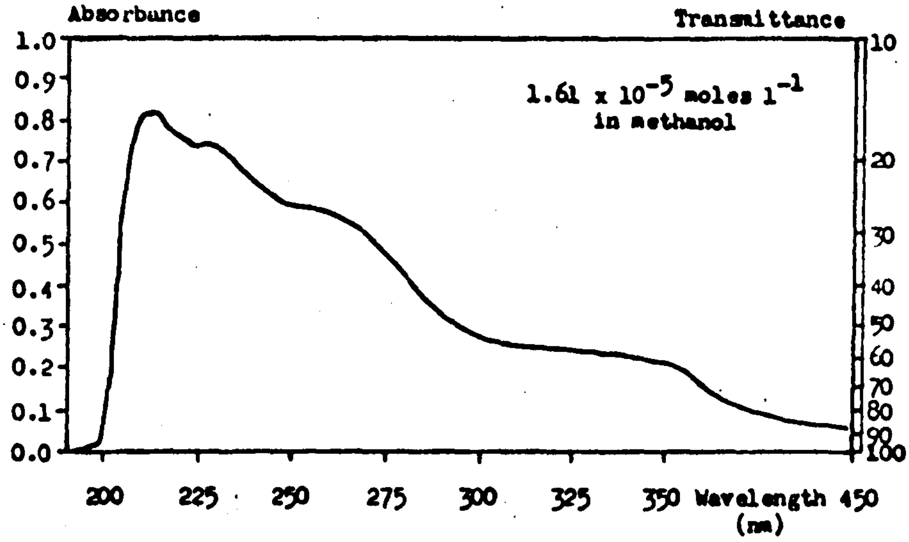


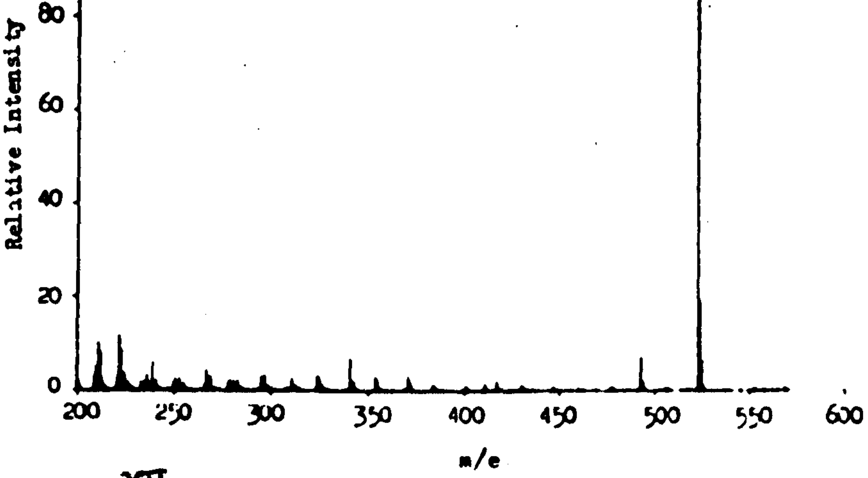




60MHz
D6-DMSO

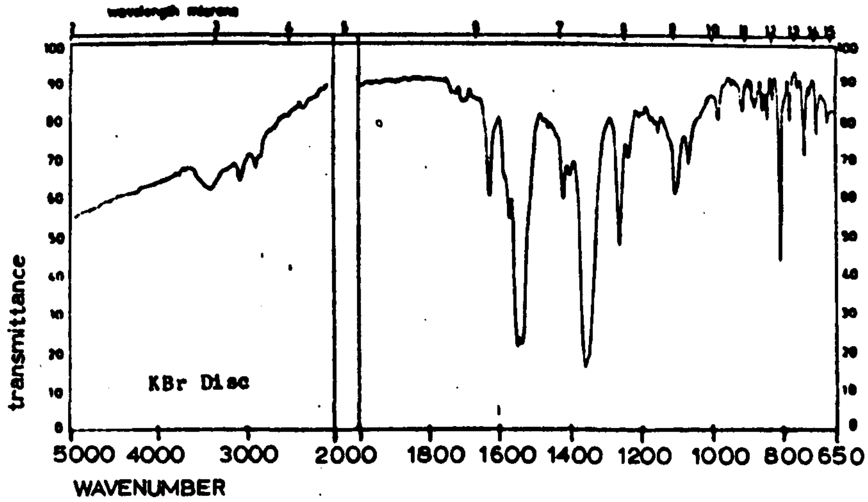


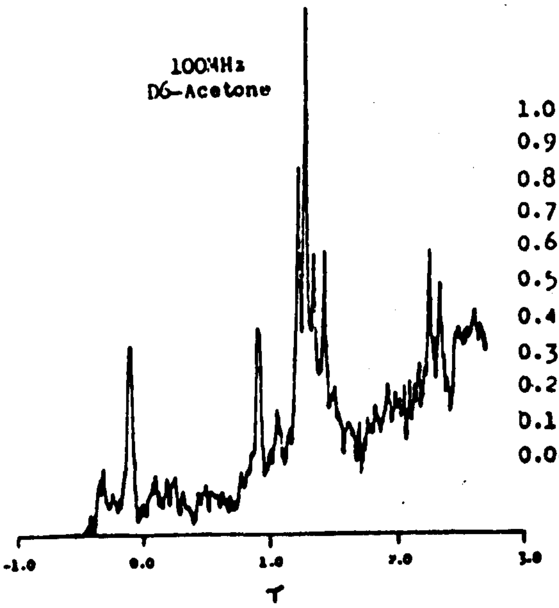


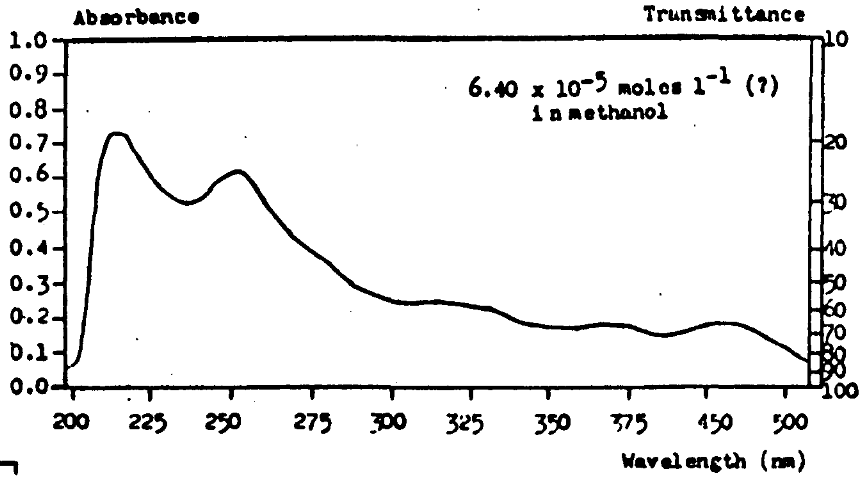


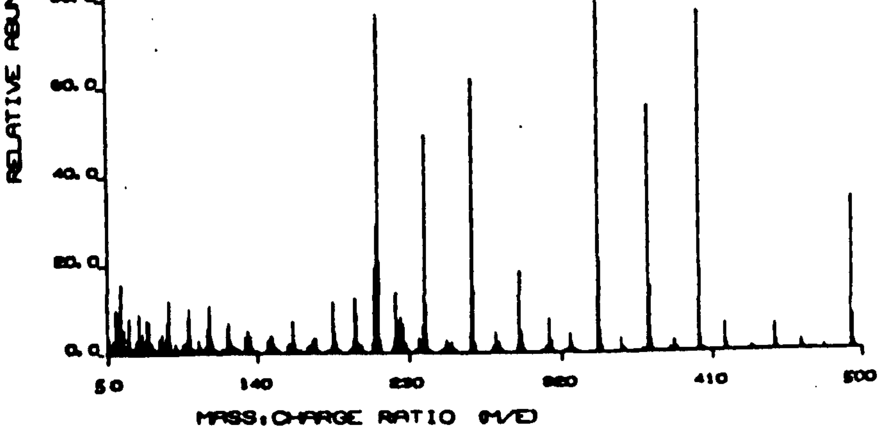
XII

Spectra of Compound 'S-2'



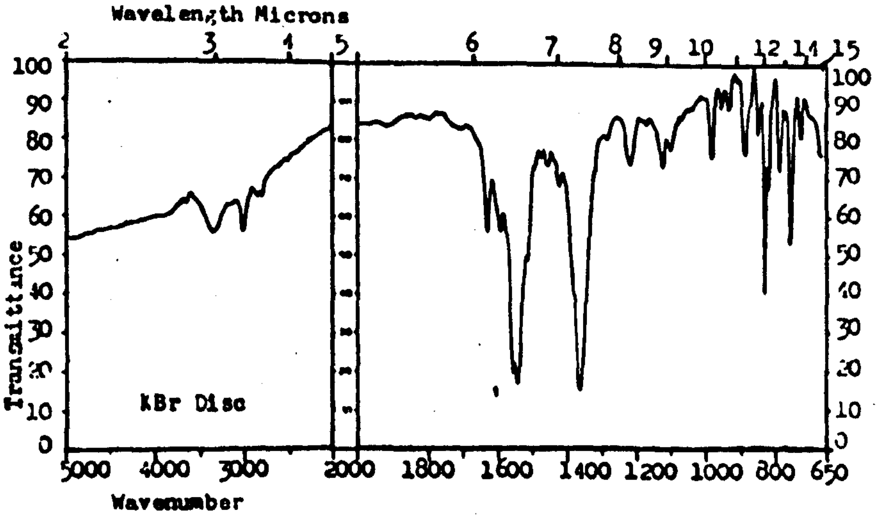






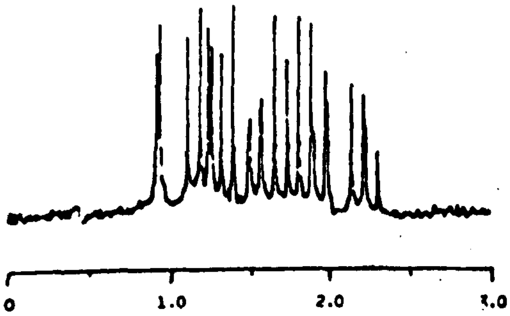
Spectra of the Compound 'U'

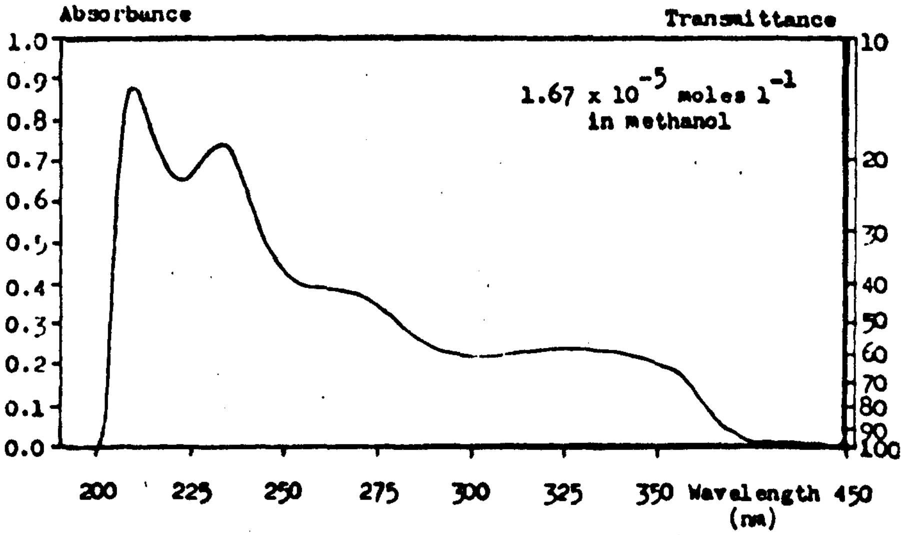
A Pentanitro-1,1'-binaphthyl

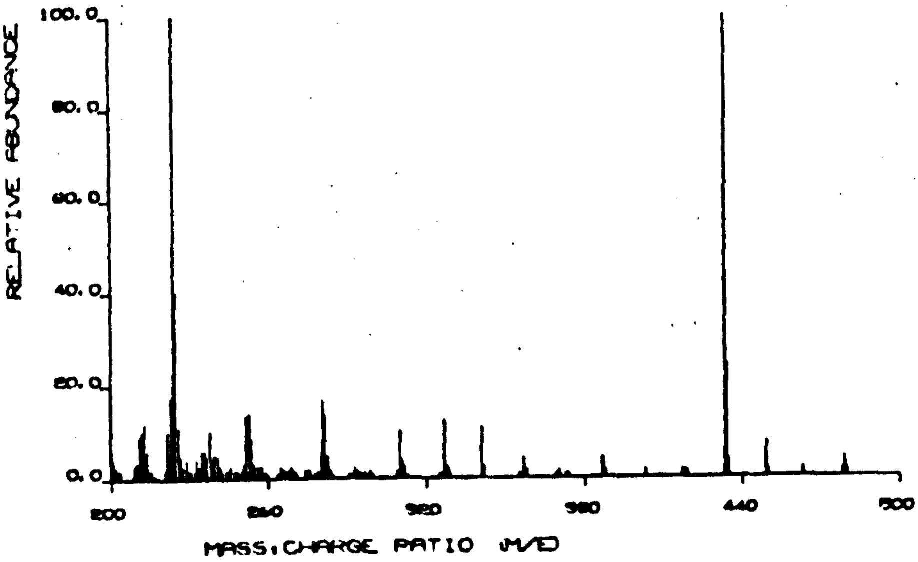


100MHz

D6-Acetone

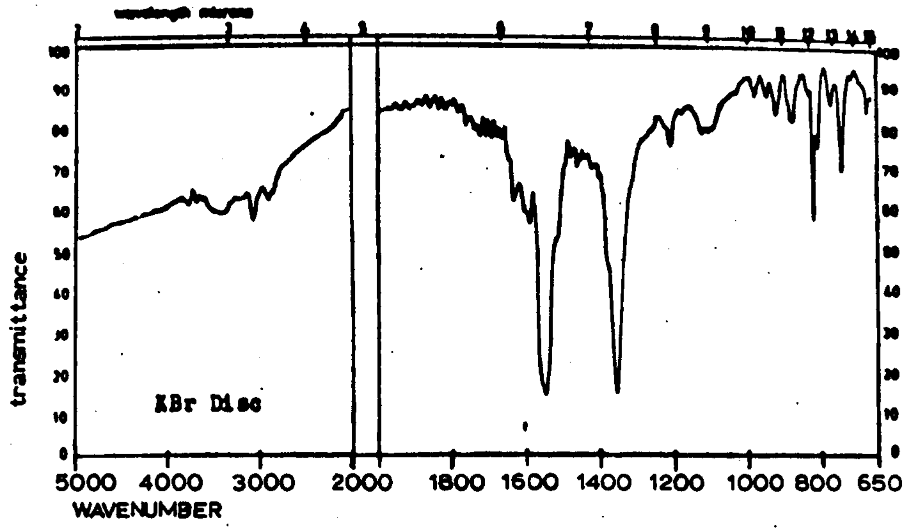


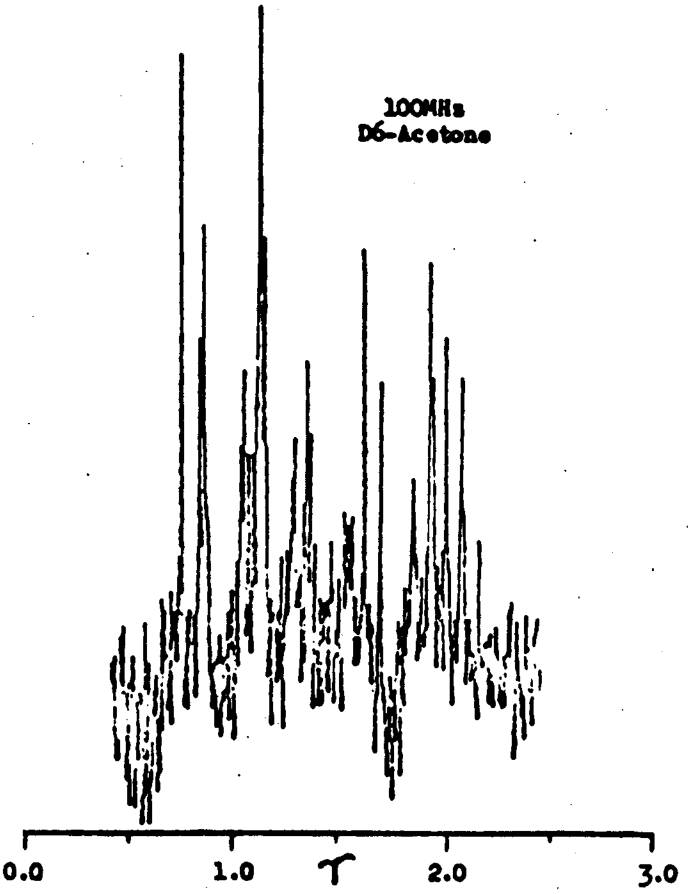


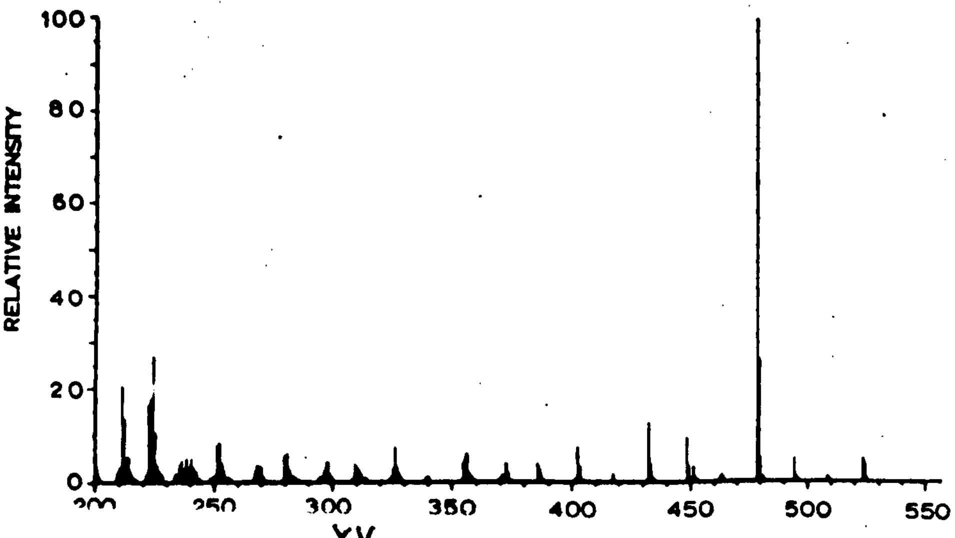


Spectra of Compound 'V'

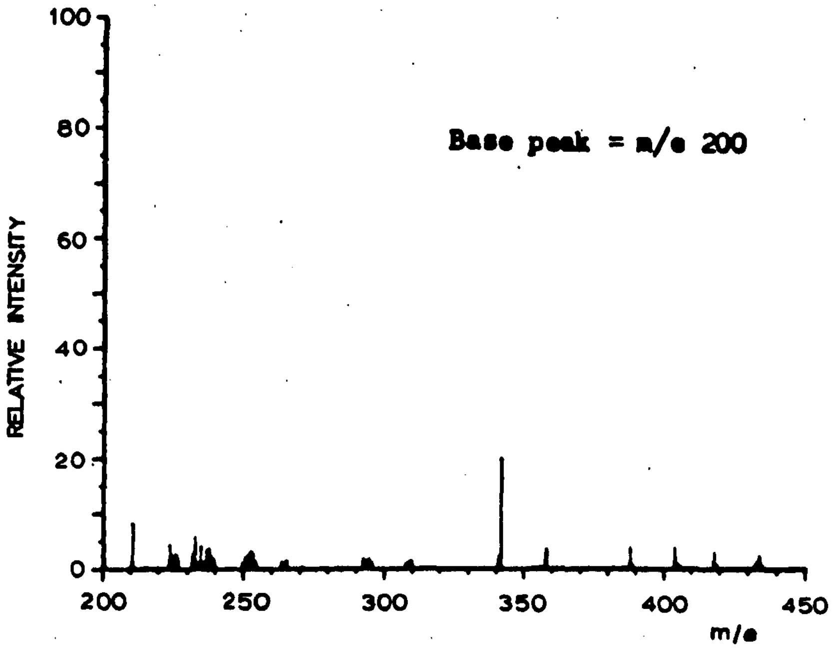
(The Nitration Product of Compound 'U')



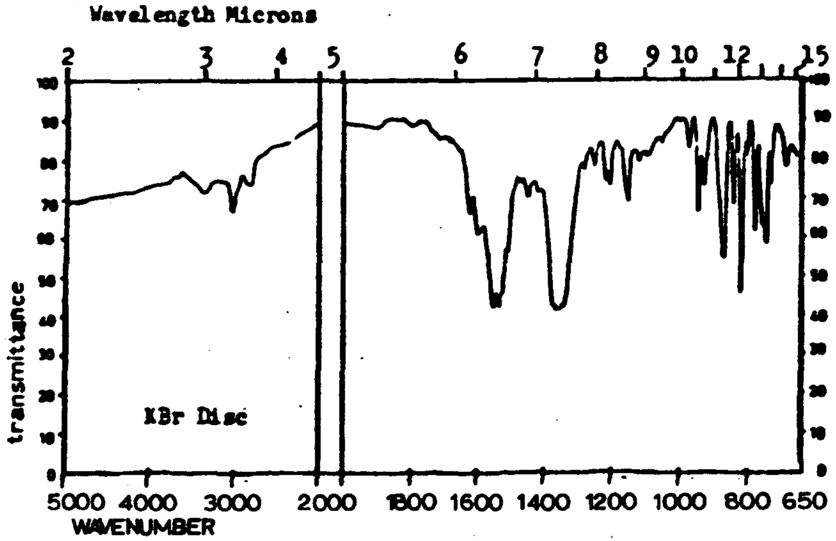


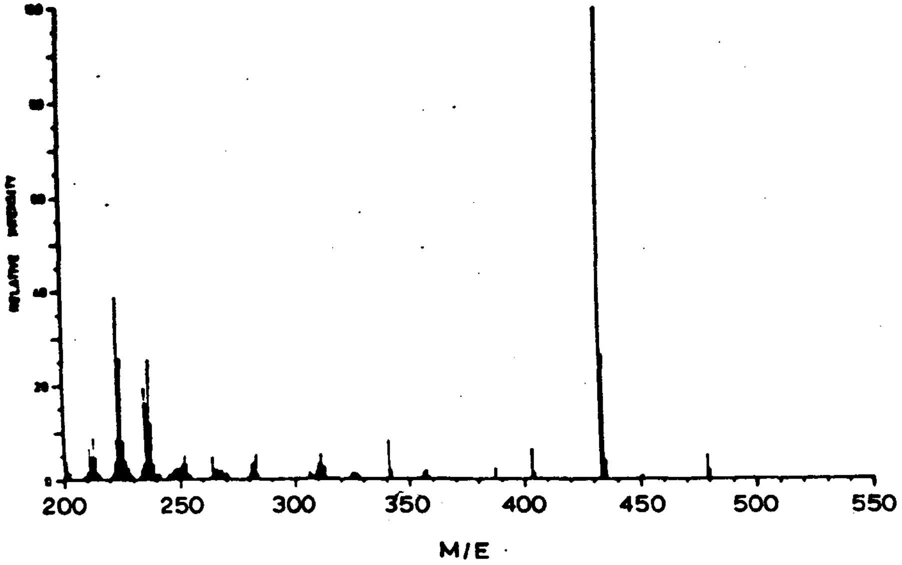


Mass Spectrum of Compound 'W'

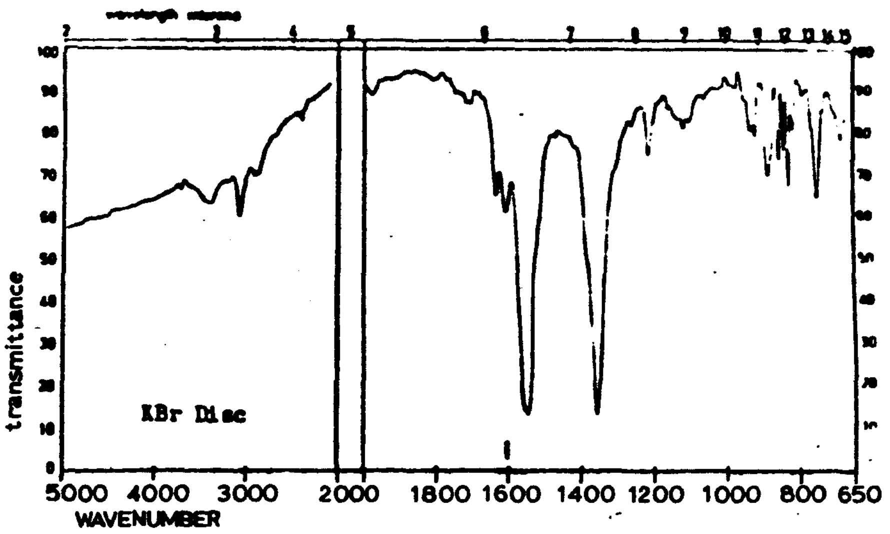


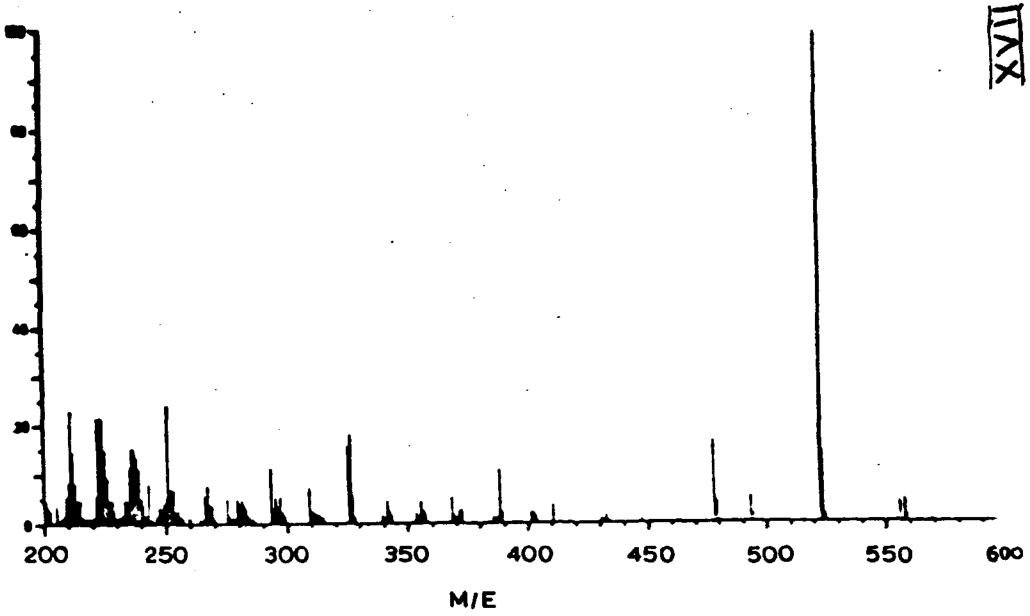
Spectra of Compound 'X'





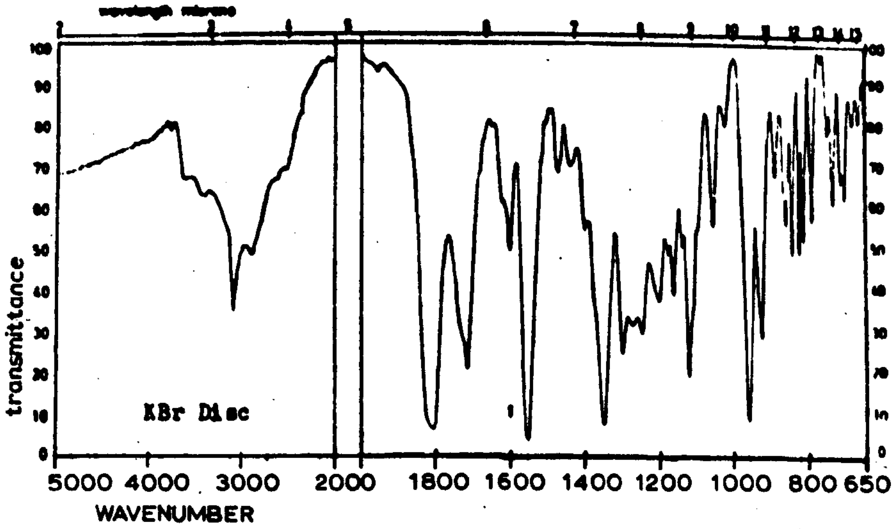
Spectra of Compound 'Y'

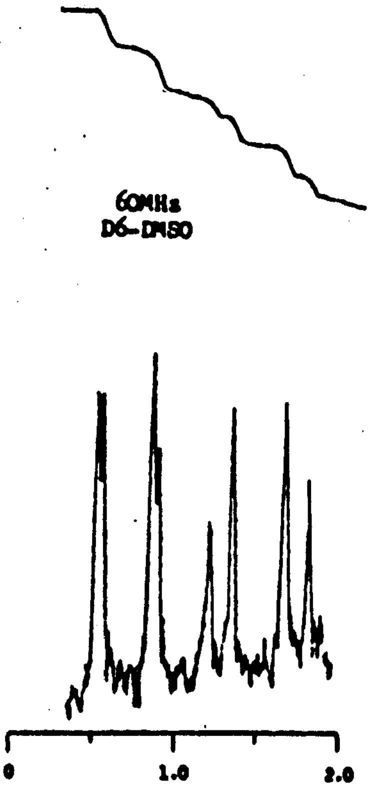


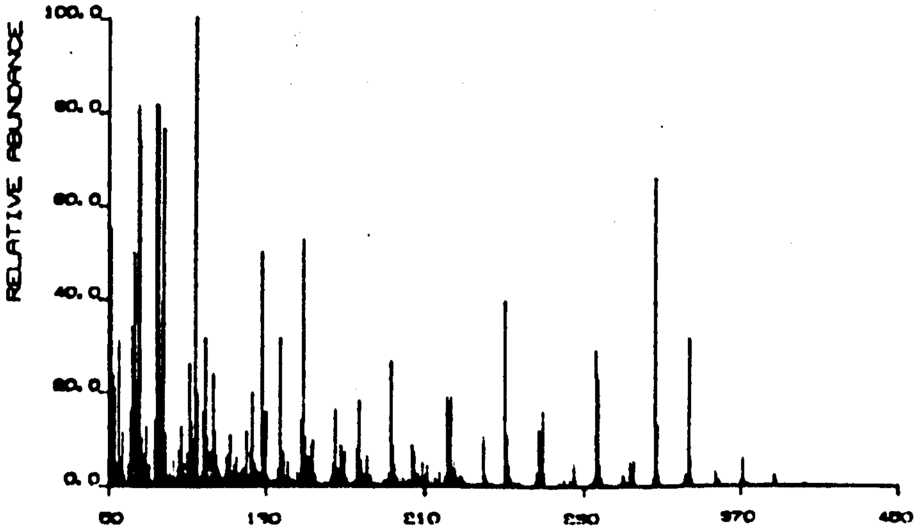


XIV

Spectra of Compound 'Z2'

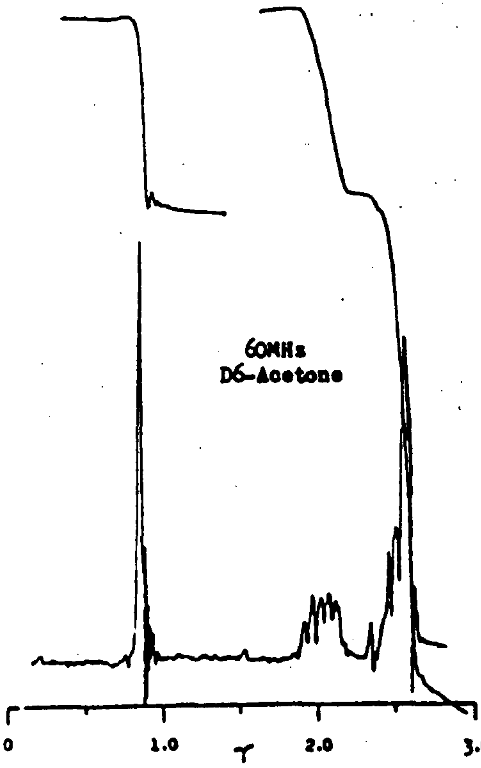


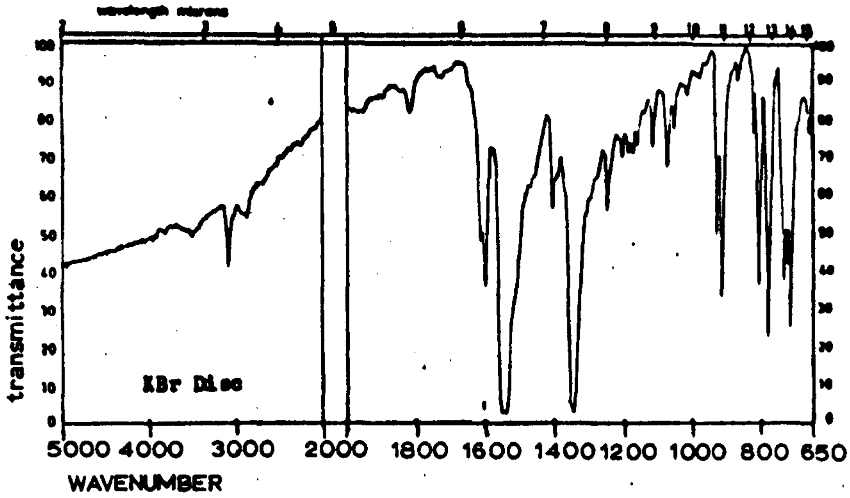


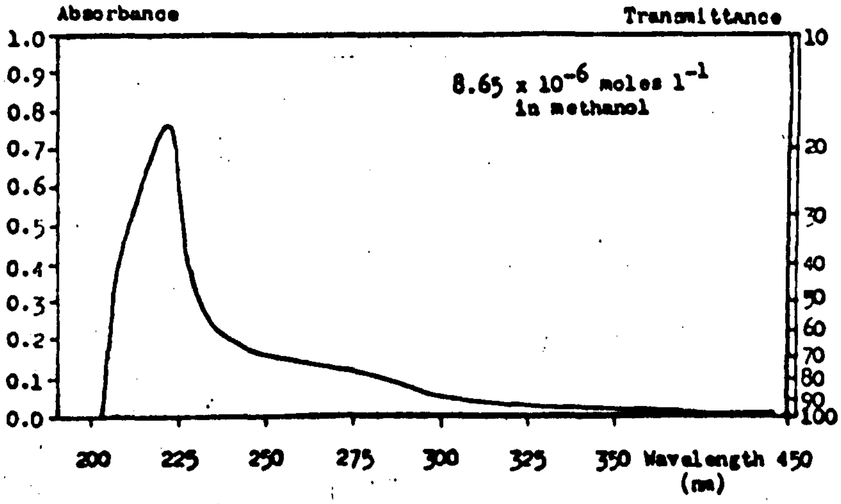


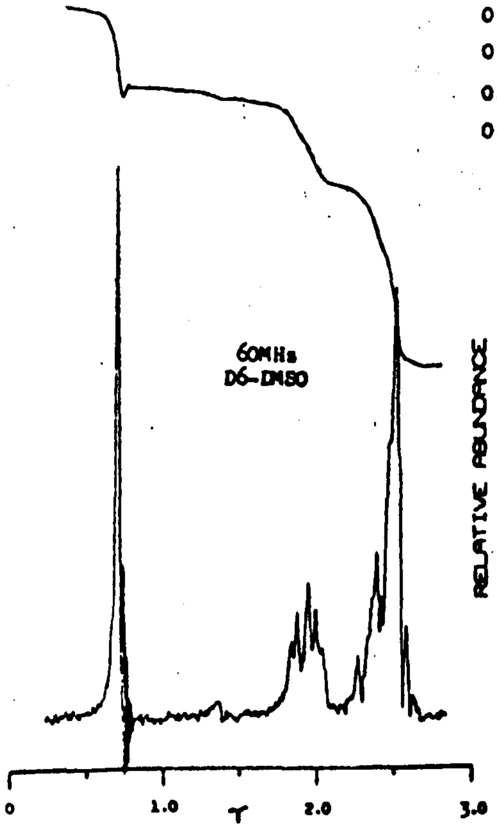
XVIII

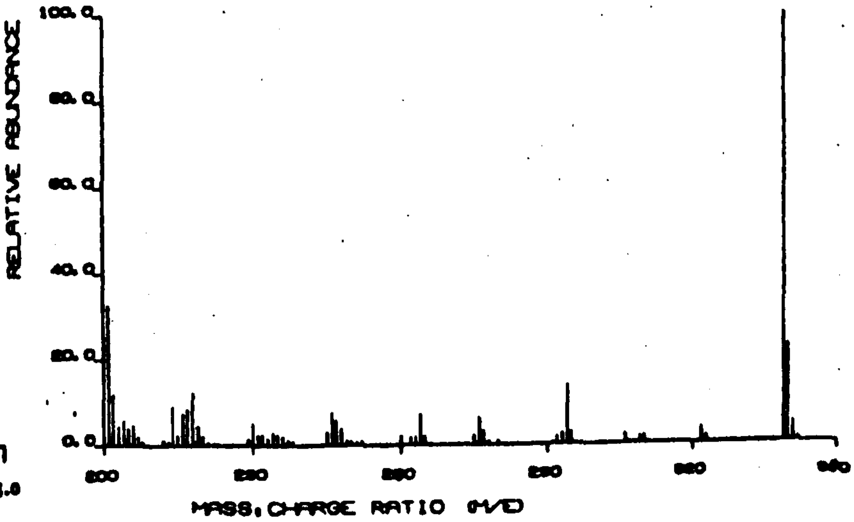
Spectra of 1-Picrylnaphthalene



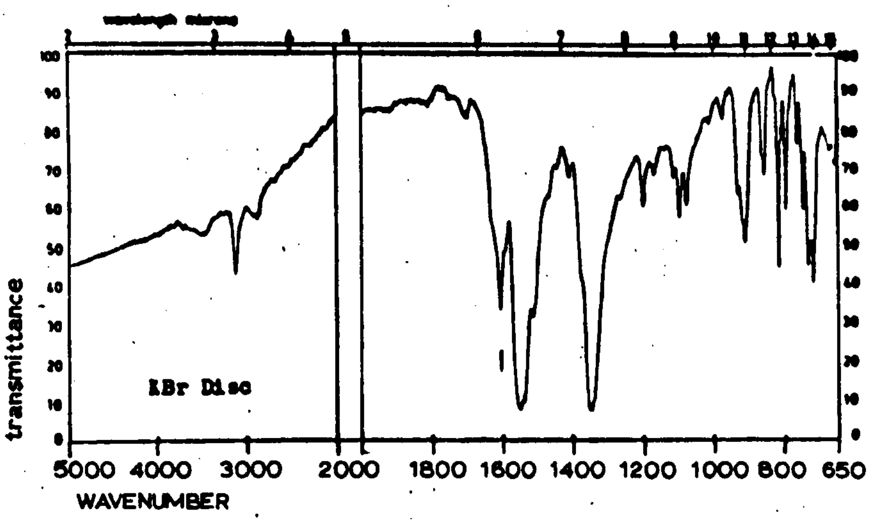


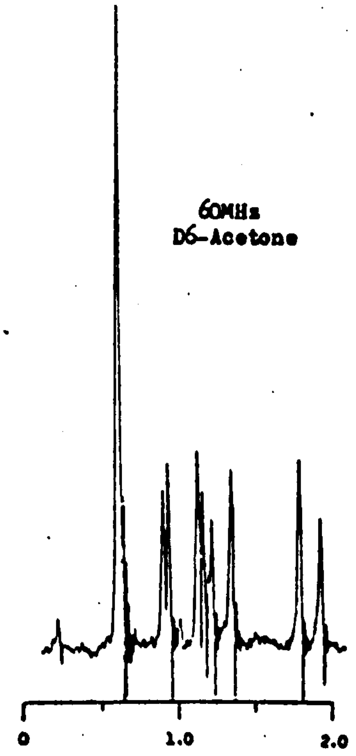


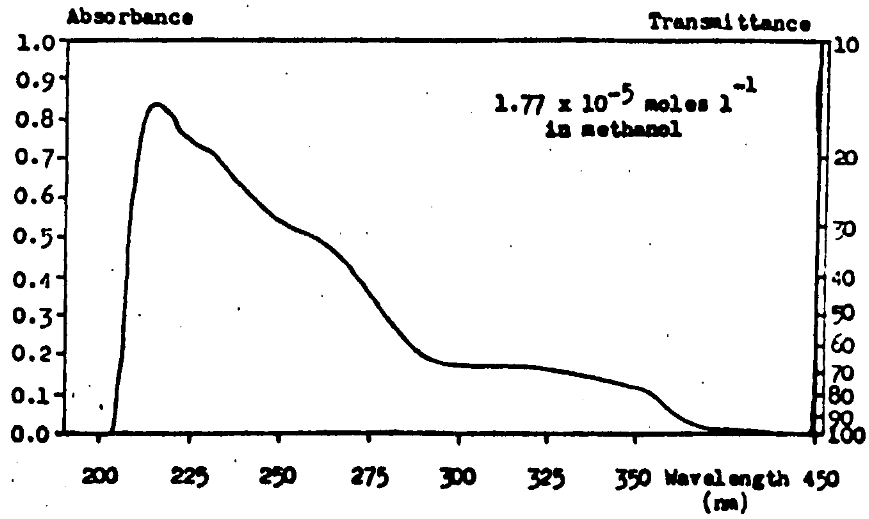


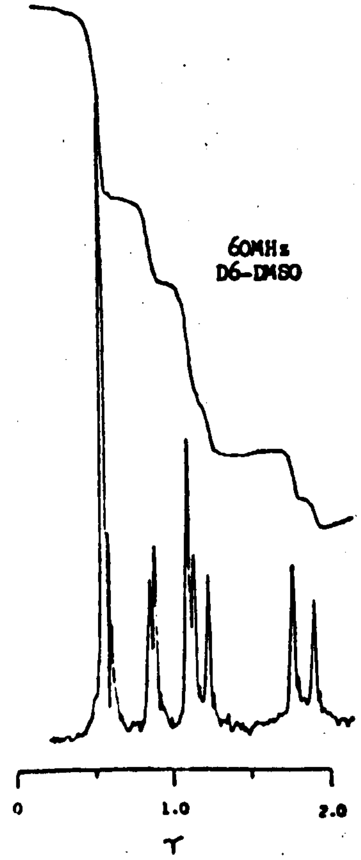


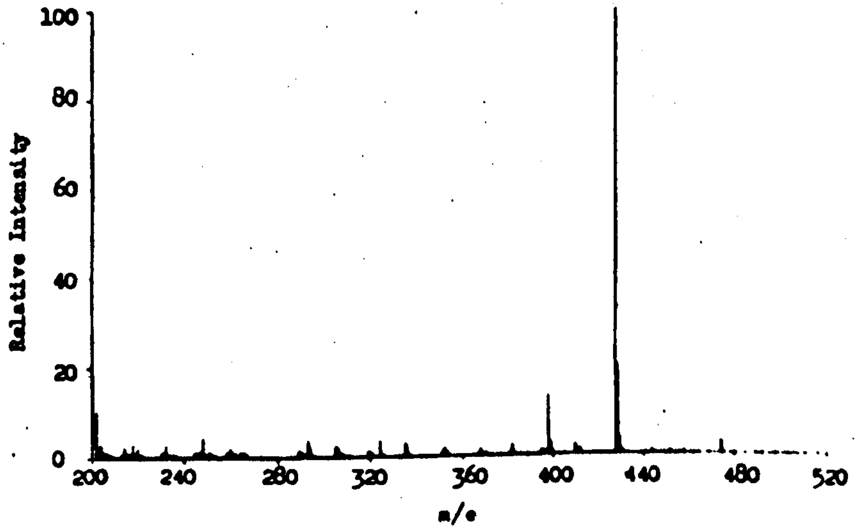
Spectra of 4,5,7-Trinitro-1-picrylnaphthalene



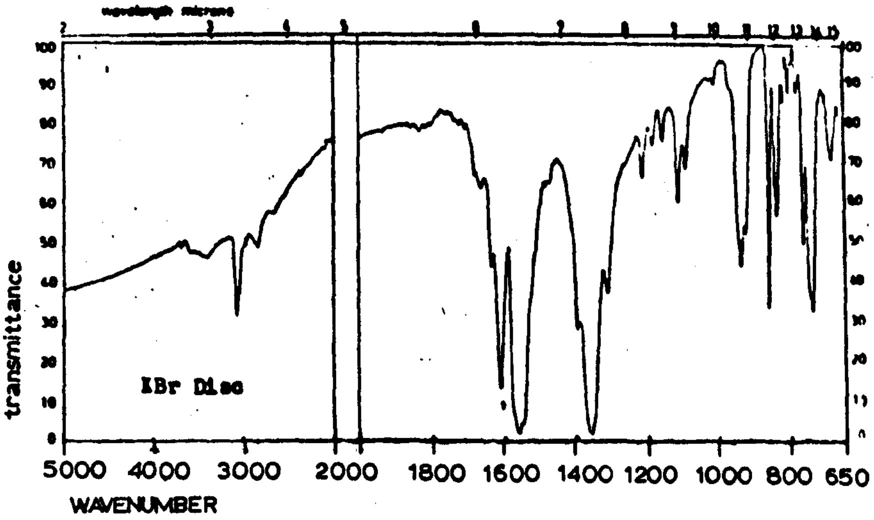


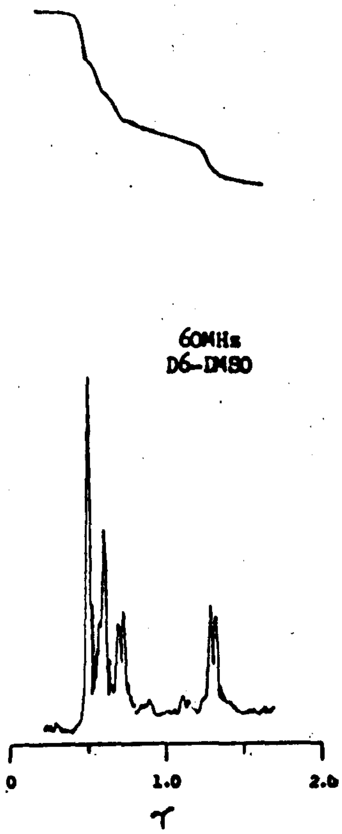


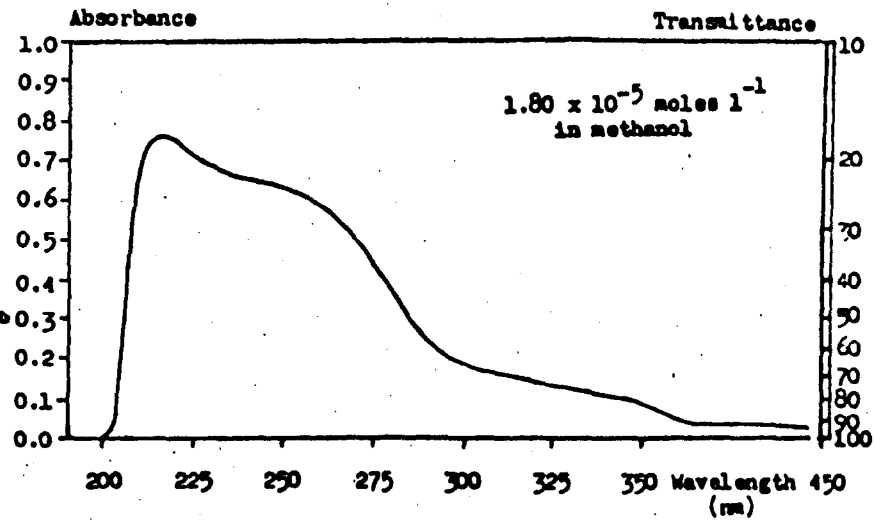


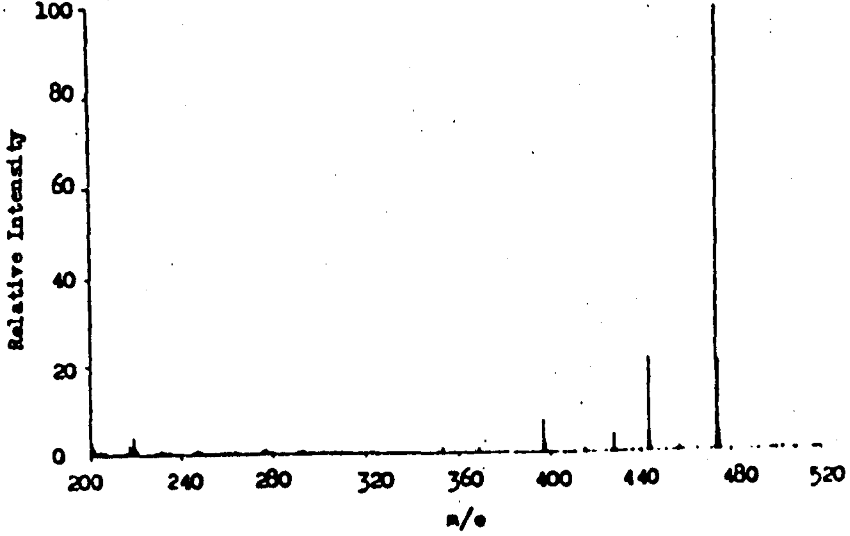


Spectra of 2,4,5,7-Tetranitro-1-picrylnaphthalene









Mass Spectrum of 5,5'-Dinitro-1,1'-binaphthyl

M/E	REL INT	M/E	REL INT
200.00	4.85	259.00	0.61
210.00	0.61	260.00	0.61
211.00	3.64	261.00	0.61
212.00	1.21	262.00	1.21
213.00	7.27	263.00	0.61
214.00	3.03	264.00	1.82
215.00	3.03	265.00	1.21
216.00	0.61	266.00	1.82
217.00	0.61	267.00	6.06
222.00	1.82	268.00	7.27
223.00	2.42	269.00	9.70
224.00	13.33	270.00	5.45
225.00	8.48	271.00	3.03
226.00	15.15	272.00	0.61
227.00	7.27	275.00	1.21
228.00	2.42	280.00	1.82
229.00	1.21	281.00	3.64
230.00	3.03	282.00	1.82
236.00	1.82	283.00	1.21
237.00	15.15	284.00	1.82
238.00	10.30	285.00	1.21
239.00	63.03	286.00	1.21
240.00	21.21	296.00	7.27
241.00	11.52	297.00	4.85
242.00	9.09	298.00	3.03
243.00	3.03	299.00	1.82
244.00	0.61	310.00	0.61
245.00	0.61	311.00	0.61
246.00	1.21	312.00	0.61
247.00	1.82	313.00	0.61
248.00	13.94	314.00	1.21
249.00	13.33	315.00	1.82
250.00	96.97	316.00	0.61
251.00	44.24	317.00	0.61
252.00	41.21	326.00	0.61
253.00	16.97	327.00	1.21
254.00	7.27	328.00	1.21
255.00	9.70	329.00	0.61
256.00	2.42	344.00	100.00
257.00	1.21	345.00	21.82
258.00	1.21	346.00	3.64

Mass Spectrum of 4,4'-Dinitro-1,1'-binaphthyl

m/e	RI	m/e	RI
200.00	4.55	254.00	2.73
201.00	5.45	255.00	5.45
202.00	3.64	256.00	2.73
203.00	1.82	258.00	0.60
205.00	5.45	267.00	2.2
211.00	2.73	268.00	18.30
212.00	2.73	269.00	15.00
213.00	4.55	280.00	6.36
214.00	2.73	281.00	6.36
215.00	2.73	282.00	2.73
222.00	2.73	283.00	3.64
223.00	2.73	284.00	8.18
224.00	7.27	285.00	1.82
225.00	7.27	286.00	0.91
226.00	11.82	287.00	0.91
227.00	7.27	296.00	2.73
228.00	3.64	297.00	18.18
229.00	1.82	298.00	4.55
235.00	1.82	299.00	1.82
236.00	2.73	300.00	1.82
237.00	10.91	301.00	1.82
238.00	9.09	310.00	5.45
239.00	45.45	311.00	2.73
240.00	19.09	312.00	1.82
241.00	3.64	314.00	1.36
242.00	2.73	315.00	8.18
247.00	1.82	316.00	1.82
248.00	13.64	327.00	1.82
249.00	13.64	328.00	1.82
250.00	57.27	344.00	100.00
251.00	51.82	345.00	25.45
252.00	50.00	346.00	5.45
253.00	10.91		

Mass Spectrum of Compound 'D'
4,4',5-Trinitro-1,1'-binaphthyl

M/E	REL INT
200.00	6.67
201.00	3.33
202.00	3.33
211.00	8.33
212.00	5.00
213.00	11.67
214.00	3.33
215.00	1.67
222.00	2.50
223.00	2.50
224.00	10.00
225.00	8.33
226.00	26.67
227.00	8.33
228.00	1.67
234.00	1.67
235.00	6.67
236.00	10.00
237.00	95.00
238.00	73.33
239.00	86.67
240.00	18.33
246.00	5.00
247.00	1.67
248.00	4.17
249.00	3.33
250.00	4.17
251.00	10.00
252.00	5.00
253.00	3.33
254.00	5.00
255.00	6.67
256.00	3.33
266.00	61.67
267.00	26.67
268.00	25.00
269.00	6.67
270.00	3.33
279.00	2.50
280.00	2.50
281.00	2.50
282.00	3.33
283.00	5.00
284.00	3.33
285.00	3.33
296.00	30.00
297.00	11.67
298.00	5.00
313.00	10.00
314.00	3.33
315.00	1.67
326.00	8.33
327.00	3.33
343.00	100.00
344.00	20.00
345.00	3.33
359.00	6.67
373.00	3.33
389.00	93.33
390.00	11.67
391.00	3.33

Mass Spectrum of Compound 'C-1'
4,8'-Dinitro-1,1'-binaphthyl (?)

M/E	REL INT	M/E	REL INT
200.00	5.98	251.00	61.20
201.00	5.13	252.00	69.23
202.00	5.98	253.00	35.04
203.00	4.27	254.00	28.21
204.00	1.71	255.00	18.80
205.00	3.42	256.00	11.97
206.00	1.71	257.00	5.13
207.00	1.71	258.00	1.71
208.00	1.71	259.00	0.85
209.00	1.71	260.00	0.85
210.00	1.71	261.00	1.71
211.00	4.27	262.00	1.71
212.00	3.42	263.00	1.71
213.00	7.69	264.00	5.13
214.00	5.13	265.00	8.55
215.00	5.13	266.00	10.26
216.00	4.27	267.00	30.77
217.00	4.27	268.00	44.44
218.00	4.27	269.00	29.06
219.00	17.09	270.00	11.97
220.00	5.98	278.00	1.71
221.00	2.56	279.00	5.98
222.00	3.42	280.00	12.82
223.00	3.42	281.00	100.00
224.00	10.26	282.00	70.94
225.00	9.40	283.00	18.80
226.00	14.53	284.00	9.40
227.00	9.40	285.00	1.71
228.00	6.84	286.00	1.71
229.00	4.27	294.00	1.71
230.00	1.71	295.00	1.71
231.00	0.85	296.00	5.98
232.00	0.85	297.00	7.69
233.00	0.85	298.00	16.24
234.00	0.85	299.00	3.42
235.00	2.56	300.00	0.85
236.00	2.56	309.00	0.85
237.00	15.38	310.00	0.85
238.00	10.26	311.00	3.42
239.00	47.01	312.00	1.71
240.00	21.64	313.00	1.71
241.00	23.93	314.00	3.70
242.00	8.55	315.00	5.98
243.00	1.71	316.00	1.71
244.00	1.71	327.00	1.71
245.00	0.85	328.00	4.27
246.00	1.71	329.00	1.71
247.00	1.71	344.00	47.01
248.00	13.92	345.00	9.40
249.00	13.92	346.00	2.56
250.00	58.97		

Mass Spectrum of Compound 'C-2'
4,4',8-Trinitro-1,1'-binaphthyl (?)

M/E	REL INT	M/E	REL INT
200.00	7.78	263.00	2.22
201.00	4.44	264.00	3.33
202.00	3.33	265.00	3.33
203.00	2.22	266.00	13.33
204.00	1.11	267.00	16.67
205.00	2.22	268.00	14.44
206.00	1.11	269.00	11.11
207.00	2.22	270.00	5.56
208.00	1.11	271.00	2.22
209.00	1.11	272.00	1.11
210.00	1.11	273.00	1.11
211.00	7.78	279.00	3.33
212.00	6.67	280.00	4.44
213.00	10.00	281.00	6.67
214.00	6.67	282.00	4.44
215.00	3.33	283.00	4.44
216.00	2.22	284.00	5.56
217.00	1.11	285.00	5.56
218.00	1.11	286.00	2.22
219.00	1.11	287.00	1.11
221.00	4.44	295.00	4.44
222.00	5.56	296.00	34.44
223.00	5.56	297.00	34.44
224.00	17.78	298.00	11.11
225.00	11.11	299.00	2.22
226.00	20.00	300.00	1.11
227.00	10.00	309.00	2.22
228.00	7.78	310.00	2.22
229.00	5.56	311.00	1.11
230.00	2.22	312.00	4.44
231.00	2.22	313.00	7.78
234.00	1.11	314.00	4.44
235.00	4.44	315.00	1.11
236.00	5.56	316.00	1.11
237.00	43.33	325.00	1.11
238.00	33.33	326.00	32.22
239.00	41.11	327.00	8.89
240.00	25.56	328.00	1.11
241.00	10.00	329.00	1.11
242.00	4.44	331.00	1.11
243.00	2.22	332.00	1.11
244.00	1.11	341.00	1.11
245.00	1.11	342.00	4.44
246.00	3.33	343.00	12.22
247.00	3.33	344.00	12.22
248.00	30.00	345.00	3.33
249.00	24.44	346.00	1.11
250.00	66.67	353.00	2.22
251.00	46.67	356.00	2.22
252.00	21.11	357.00	1.11
253.00	8.89	358.00	1.11
254.00	6.67	359.00	4.44
255.00	7.78	360.00	2.22
256.00	6.67	361.00	1.11
257.00	3.33	365.00	1.11
[illegible]	1.11	369.00	1.11
[illegible]	1.11	372.00	4.44
262.00	2.22	373.00	2.22
		389.00	100.00
		390.00	24.44
		391.00	3.33

Mass Spectrum of

1,1'-Binaphthyl

M/E	REL INT
50	4.8
51	6.1
52	1.2
55	3.6
56	1.2
57	2.4
62	2.4
63	6.1
74	5.4
75	6.1
76	2.4
77	3.6
78	1.2
81	1.8
82	4.2
83	1.8
84	1.2
97	1.2
98	1.2
99	1.8
100	3.6
101	3.6
102	1.8
111	1.8
112	6.7
113	13.9
114	4.8
115	1.2
119	1.8
120	2.4
125	18.2
126	45.4
127	13.3
128	1.8
149	1.8
150	3.6
151	2.4
152	1.8
153	0.6
161	0.6
162	0.6
163	3.0
164	0.6
165	0.6
174	1.8
175	1.2
176	1.8
186	0.6
187	3.0
188	1.2
189	1.8
197	0.6
198	1.2
199	1.8
200	4.2
201	1.8
202	1.8
211	1.8
212	1.2
213	3.6
214	0.6
215	1.8
222	1.8
223	1.8
224	7.3
225	4.8
226	8.5
227	1.8
237	1.8
238	1.2
239	27.3
240	4.8
248	4.8
249	4.8
250	29.7
251	13.9
252	78.8
253	93.9
254	100.0
255	27.3

Mass Spectrum of Compound 'F'
4,5,8'-Trinitro-1,1'-binaphthyl (?)

M/E	REL INT	M/E	REL INT
200.00	6.21	255.00	4.14
201.00	4.14	256.00	2.76
202.00	2.76	257.00	1.03
203.00	1.72	258.00	0.69
204.00	0.69	262.00	0.69
210.00	0.69	263.00	0.69
211.00	3.79	264.00	1.03
212.00	2.76	265.00	1.03
213.00	5.17	266.00	4.14
214.00	3.79	267.00	19.31
215.00	1.72	268.00	6.55
216.00	0.69	269.00	5.86
222.00	1.38	270.00	1.38
223.00	1.38	271.00	0.69
224.00	7.59	279.00	1.03
225.00	5.86	280.00	1.03
226.00	20.00	281.00	1.03
227.00	8.62	282.00	0.69
228.00	8.28	283.00	0.69
229.00	2.76	284.00	0.69
230.00	1.03	285.00	0.69
231.00	0.69	290.00	0.69
232.00	0.69	295.00	1.03
233.00	0.69	296.00	4.48
234.00	0.69	297.00	4.48
235.00	3.45	298.00	1.38
236.00	5.17	299.00	0.69
237.00	34.48	312.00	0.69
238.00	22.41	313.00	11.38
239.00	100.00	314.00	2.76
240.00	27.59	315.00	0.69
241.00	10.00	325.00	0.69
242.00	3.10	326.00	0.69
243.00	1.03	327.00	1.03
244.00	0.69	328.00	0.69
245.00	0.69	343.00	68.97
246.00	0.69	344.00	16.21
247.00	0.69	345.00	2.41
248.00	3.45	346.00	0.69
249.00	2.76	358.00	0.69
250.00	5.17	359.00	1.72
251.00	7.24	360.00	0.69
252.00	5.52	373.00	0.69
253.00	4.48	374.00	0.34
254.00	4.48	388.00	2.07
		389.00	11.38
		390.00	2.41
		391.00	0.69

Mass Spectrum of Compound 'H'
4,4',5,5'-Tetranitro-1,1'-binaphthyl

M/E	REL INT
200.00	11.83
201.00	3.23
211.00	6.45
212.00	6.45
213.00	10.75
214.00	4.30
215.00	1.08
222.00	3.23
223.00	7.53
224.00	79.57
225.00	49.46
226.00	100.00
227.00	20.43
228.00	4.30
235.00	5.38
236.00	5.38
237.00	15.05
238.00	22.58
239.00	6.45
240.00	4.30
242.00	1.08
251.00	1.08
252.00	1.08
253.00	7.53
254.00	16.13
255.00	3.23
256.00	2.15
257.00	1.08
265.00	2.15
266.00	6.45
267.00	3.23
280.00	1.08
281.00	2.15
282.00	35.48
283.00	9.68
284.00	4.30
285.00	1.08
295.00	3.23
296.00	1.61
311.00	2.15
312.00	13.98
313.00	2.15
314.00	1.08
342.00	34.41
343.00	7.53
344.00	1.08
358.00	1.08
372.00	1.08
388.00	80.65
389.00	18.28
404.00	2.15
405.00	1.08
418.00	1.08
434.00	15.05
435.00	4.30
435.00	1.08

Mass Spectrum of Compound 'I'

4,5,x,y-Tetranitro-1,1'-binaphthyl

M/E	REL INT	M/E	REL INT
200	26.6	260	3.1
201	23.4	262	3.1
202	12.5	263	4.7
203	7.8	264	7.8
204	3.1	265	14.1
205	3.1	266	25.0
206	3.1	267	20.3
207	1.6	268	15.6
208	3.1	269	14.1
209	3.1	270	7.8
210	4.7	271	7.8
211	21.9	272	4.7
212	14.1	273	4.7
213	28.1	274	3.1
214	26.6	275	3.1
215	12.5	276	3.1
216	7.8	277	4.7
217	4.7	278	4.7
218	4.7	279	6.3
219	4.7	280	6.3
220	1.6	281	12.5
221	4.7	282	17.2
222	7.8	283	17.2
223	10.9	284	12.5
224	51.6	285	4.7
225	45.3	286	3.1
226	62.5	287	3.1
227	39.1	288	6.3
228	23.4	289	3.1
229	12.5	290	1.6
230	7.8	291	3.1
231	3.1	292	1.6
232	6.3	293	6.3
233	15.6	294	6.3
234	4.7	295	10.9
235	23.4	296	14.1
236	23.4	297	9.4
237	82.8	298	4.7
238	62.5	299	3.1
239	43.8	300	3.1
240	25.0	301	3.1
241	15.6	310	4.7
242	10.9	311	4.7
243	9.4	312	12.5
244	6.3	313	7.8
245	3.1	314	6.3
246	3.1	315	3.1
247	3.1	316	3.1
248	10.9	325	3.1
249	10.9	326	4.7
250	23.4	327	3.1
251	23.4	328	4.7
252	18.7	329	1.7
253	21.9	330	1.6
254	37.5	338	1.6
255	23.4	339	1.6
256	17.2	340	3.1
257	7.8	341	4.7
258	3.1	342	6.3
259	3.1	343	6.3
		344	3.1
		347	1.6
		358	10.7
		359	14.0
		360	12.5
		369	4.7
		388	100.0
		389	34.4
		390	6.3
		404	7.8
		405	10.9
		410	3.1
		414	3.1
		434	7.8
		435	4.7
		436	1.6

Mass Spectrum of Compound 'P'

4,4',5,8'-Tetranitro-1,1'-binaphthyl

M/E	REL INT	M/E	REL INT
200.00	5.52	277.00	0.21
201.00	4.14	278.00	0.21
202.00	1.72	279.00	2.76
203.00	0.83	280.00	1.17
204.00	0.69	281.00	1.86
205.00	0.97	282.00	6.21
206.00	0.41	283.00	3.79
207.00	0.41	284.00	4.83
208.00	0.41	285.00	2.00
209.00	0.97	286.00	0.62
210.00	1.66	287.00	0.34
211.00	6.90	288.00	0.21
212.00	4.83	292.00	0.14
213.00	7.24	293.00	0.21
214.00	4.14	294.00	0.48
215.00	2.07	295.00	18.28
216.00	1.03	296.00	6.21
217.00	0.48	297.00	3.10
218.00	0.48	298.00	1.45
219.00	0.41	299.00	0.90
220.00	0.14	300.00	0.97
221.00	0.69	301.00	0.48
222.00	2.07	302.00	0.71
223.00	3.31	303.00	0.14
224.00	16.55	304.00	0.14
225.00	11.72	308.00	0.28
226.00	24.14	309.00	0.34
227.00	13.10	310.00	0.62
228.00	5.52	311.00	2.78
229.00	1.72	312.00	8.97
230.00	0.83	313.00	2.97
231.00	0.41	314.00	1.52
232.00	0.48	315.00	0.55
233.00	0.55	316.00	0.14
234.00	1.03	323.00	0.14
235.00	10.34	324.00	0.28
236.00	10.34	325.00	6.90
237.00	41.38	326.00	1.86
238.00	34.48	327.00	0.48
239.00	12.41	328.00	0.48
240.00	4.83	329.00	0.21
241.00	2.07	330.00	0.71
242.00	1.86	340.00	0.69
243.00	1.10	341.00	1.31
244.00	0.69	342.00	4.83
245.00	0.34	343.00	1.86
246.00	0.90	344.00	0.48
247.00	1.17	354.00	0.14
248.00	3.59	355.00	0.14
249.00	2.97	356.00	0.14
250.00	2.90	357.00	0.21
251.00	5.52	358.00	6.21
252.00	3.79	359.00	1.52
253.00	6.21	360.00	0.48
254.00	11.72	370.00	0.41
255.00	5.17	371.00	0.28
256.00	2.21	372.00	1.93
257.00	1.24	373.00	0.34
258.00	0.55	374.00	0.14
259.00	0.41	386.00	0.34
260.00	0.41	387.00	2.21
261.00	0.41	388.00	100.00
262.00	0.48	389.00	24.14
263.00	0.41	390.00	3.79
264.00	0.69	391.00	2.62
265.00	8.97	403.00	0.83
266.00	15.17	404.00	0.83
267.00	10.34	405.00	0.21
268.00	4.83	418.00	1.52
269.00	2.83	419.00	0.55
270.00	1.93	433.00	2.21
271.00	0.69	434.00	9.66
272.00	0.62	435.00	2.21
273.00	0.21	436.00	0.48
274.00	0.21		

Mass Spectrum of Compound 'Q'

4,4',5,5',7,7'-Hexanitro-1,1'-binaphthyl

M/E	REL INT	M/E	REL INT
200	5.5	270	2.7
201	2.7	271	1.8
202	0.9	279	4.5
203	0.9	280	3.6
207	4.5	281	5.5
208	1.8	282	3.6
209	3.6	283	1.8
210	5.5	284	0.9
211	31.8	285	0.9
212	23.6	293	1.4
213	7.3	294	1.4
214	8.2	295	0.9
215	1.8	296	3.6
216	1.8	297	9.1
220	0.9	298	7.3
221	4.5	299	1.8
222	32.7	309	5.5
223	39.1	310	1.8
224	47.3	324	0.9
225	20.0	325	2.7
226	6.4	326	5.5
227	1.8	327	5.0
228	1.8	328	2.7
229	0.9	329	0.9
233	2.7	336	0.4
234	2.7	337	0.9
235	9.0	338	0.9
236	11.8	339	0.9
237	5.5	340	0.9
238	5.5	341	1.4
239	5.5	342	1.4
240	7.3	355	14.5
241	3.6	356	5.5
242	3.6	357	0.9
247	0.9	372	7.2
248	0.9	373	1.8
249	1.8	374	1.8
250	1.8	385	6.4
251	10.9	386	1.8
252	10.0	402	10.9
253	4.5	403	3.6
254	2.7	404	0.9
255	1.4	416	0.9
256	1.4	432	40.9
257	0.9	433	9.1
264	1.4	434	2.7
265	1.4	448	0.9
266	1.8	462	0.5
267	5.0	478	100.0
268	6.4	479	24.5
269	3.6	480	5.4
		493	0.9
		494	4.1
		495	1.4
		508	1.4
		509	0.5
		523	6.8
		524	10.0
		525	2.3
		526	0.9

Mass Spectrum of Compound 'R'

2,4,4',5,5',7,8'-Heptanitro-1,1'-binaphthyl

M/E	REL INT	M/E	REL INT
200.00	1.88	300.00	0.34
201.00	1.91	301.00	0.44
202.00	0.75	302.00	0.25
203.00	0.38	303.00	0.44
204.00	0.22	304.00	0.13
205.00	0.13	306.00	0.19
207.00	0.22	307.00	0.16
208.00	0.47	308.00	0.81
209.00	3.44	309.00	0.84
210.00	5.31	310.00	0.41
211.00	10.16	311.00	2.59
212.00	8.13	312.00	0.88
213.00	3.13	313.00	1.31
214.00	1.31	314.00	0.47
215.00	0.88	315.00	0.94
216.00	0.44	316.00	0.22
217.00	0.31	317.00	0.13
218.00	0.19	324.00	3.03
219.00	0.25	325.00	3.34
220.00	0.72	326.00	1.41
221.00	2.66	327.00	1.19
222.00	11.56	328.00	0.38
223.00	8.59	329.00	0.69
224.00	3.59	330.00	0.22
225.00	3.91	331.00	0.72
226.00	1.69	333.00	0.13
227.00	1.72	338.00	0.22
228.00	0.91	339.00	0.19
229.00	0.91	340.00	0.22
230.00	0.31	341.00	6.72
231.00	0.25	342.00	1.69
232.00	0.24	343.00	2.06
233.00	2.09	344.00	0.53
234.00	1.66	345.00	0.25
235.00	2.13	354.00	3.00
236.00	3.44	355.00	2.28
237.00	1.78	356.00	0.75
238.00	1.47	357.00	0.41
239.00	5.94	358.00	0.16
240.00	2.13	359.00	0.16
241.00	2.50	360.00	0.16
242.00	0.81	364.00	0.13
243.00	0.63	369.00	0.19
244.00	0.41	370.00	0.28
245.00	0.31	371.00	3.19
246.00	0.34	372.00	1.66
247.00	0.57	373.00	0.66
248.00	0.31	374.00	0.19
249.00	0.31	381.00	0.13
250.00	1.69	384.00	1.19
251.00	2.72	385.00	0.63
252.00	1.81	386.00	0.25
253.00	2.88	387.00	0.25
254.00	0.94	388.00	0.13
255.00	1.94	393.00	0.13
256.00	0.78	400.00	0.38
257.00	0.94	401.00	1.31
258.00	0.31	402.00	0.41
259.00	0.41	403.00	0.16
260.00	0.22	404.00	0.16
261.00	0.16	407.00	0.28
263.00	0.16	411.00	1.53
264.00	0.31	412.00	0.25
265.00	0.41	414.00	0.13
266.00	1.09	415.00	0.25
267.00	4.38	416.00	0.13
268.00	2.41	417.00	1.94
269.00	3.16	418.00	0.47
270.00	0.84	419.00	0.16
271.00	0.69	425.00	0.22
272.00	0.31	430.00	1.03
273.00	0.34	431.00	0.53
274.00	0.19	432.00	0.41
275.00	0.16	433.00	0.16
278.00	2.00	447.00	0.72
279.00	2.28	448.00	0.25
280.00	1.34	449.00	0.25
281.00	2.41	461.00	0.13
282.00	1.06	476.00	0.13
283.00	2.41	477.00	0.41
284.00	0.84	478.00	0.69
285.00	0.84	479.00	0.22
286.00	0.25	492.00	0.16
287.00	0.47	493.00	7.34
288.00	0.16	494.00	1.78
289.00	0.13	495.00	0.34
292.00	0.16	507.00	0.72
293.00	0.16	522.00	0.16
294.00	0.28	523.00	100.00
295.00	3.19	524.00	18.75
296.00	1.97	525.00	6.75
297.00	3.44	526.00	1.00
298.00	1.03	527.00	0.13
299.00	1.06	539.00	0.13
		545.00	0.13
		553.00	0.34
		568.00	0.34
		569.00	0.50
		570.00	0.13

Mass Spectrum of Compound 'S-2'

M/E	REL INT	M/E	REL INT	M/E	REL. INT	M/E	REL. INT
50.00	3.40	108.00	0.43	186.00	4.68	283.00	2.55
51.00	3.40	109.00	1.28	187.00	2.55	284.00	0.85
52.00	1.70	110.00	5.53	188.00	0.85	285.00	0.85
53.00	2.98	111.00	10.64	189.00	0.43	294.00	1.70
54.00	2.55	112.00	3.40	195.00	0.43	295.00	18.30
55.00	9.79	113.00	2.13	196.00	0.85	296.00	4.68
56.00	4.26	114.00	0.85	197.00	2.98	297.00	2.13
57.00	9.36	115.00	0.85	198.00	12.34	298.00	0.85
58.00	15.74	116.00	0.43	199.00	8.51	309.00	0.43
59.00	1.28	119.00	0.85	200.00	2.13	310.00	0.43
60.00	5.53	120.00	0.85	201.00	1.70	311.00	1.28
61.00	1.28	121.00	0.85	202.00	1.70	312.00	0.85
62.00	3.40	122.00	5.53	203.00	0.43	313.00	7.66
63.00	8.09	123.00	6.81	208.00	2.13	314.00	2.55
64.00	1.28	124.00	2.98	209.00	19.15	315.00	0.85
65.00	1.28	125.00	1.70	210.00	28.51	322.00	0.43
66.00	1.28	126.00	1.28	211.00	76.60	323.00	0.43
67.00	2.98	127.00	0.85	212.00	20.43	324.00	0.85
68.00	2.13	128.00	0.85	213.00	3.40	325.00	4.26
69.00	8.94	129.00	0.85	214.00	1.28	326.00	1.70
70.00	3.40	133.00	3.40	220.00	0.85	327.00	0.85
71.00	4.68	134.00	5.11	221.00	3.40	328.00	0.43
72.00	0.85	135.00	2.55	222.00	13.62	329.00	0.43
73.00	2.98	136.00	3.83	223.00	7.66	341.00	100.00
74.00	7.66	137.00	1.28	224.00	5.11	342.00	20.85
75.00	7.23	138.00	0.43	225.00	8.09	343.00	5.11
76.00	2.13	139.00	0.43	226.00	2.98	344.00	1.28
77.00	2.55	140.00	0.43	227.00	6.81	355.00	2.98
78.00	0.85	145.00	0.43	228.00	2.13	356.00	0.85
79.00	1.28	146.00	2.98	229.00	0.85	357.00	0.85
80.00	0.85	147.00	2.55	230.00	0.85	358.00	0.43
81.00	3.40	148.00	3.83	233.00	0.85	368.00	0.43
82.00	2.13	149.00	3.83	234.00	0.85	369.00	0.43
83.00	4.26	150.00	2.13	235.00	0.85	370.00	0.43
84.00	2.13	151.00	1.28	236.00	3.40	371.00	55.32
85.00	3.40	152.00	0.85	237.00	1.70	372.00	14.89
86.00	6.81	153.00	0.43	238.00	6.38	373.00	2.98
87.00	11.91	158.00	1.70	239.00	48.94	374.00	0.43
88.00	2.98	159.00	2.13	240.00	11.06	385.00	0.85
89.00	0.85	160.00	1.28	241.00	2.98	386.00	0.43
90.00	0.43	161.00	7.23	242.00	0.85	387.00	2.55
91.00	2.13	162.00	2.13	243.00	0.43	388.00	0.85
92.00	0.85	163.00	0.85	249.00	0.43	389.00	0.85
93.00	0.85	164.00	0.43	250.00	0.85	401.00	76.60
94.00	0.85	165.00	0.43	251.00	1.70	402.00	17.87
95.00	2.13	166.00	0.43	252.00	2.98	403.00	3.40
96.00	1.70	170.00	1.28	253.00	1.70	404.00	0.43
97.00	2.55	171.00	1.70	254.00	1.70	405.00	0.43
98.00	7.66	172.00	1.28	255.00	2.55	417.00	6.38
99.00	10.21	173.00	2.55	256.00	0.85	418.00	1.70
100.00	3.40	174.00	3.40	257.00	0.85	419.00	0.43
101.00	1.28	175.00	2.98	258.00	0.43	433.00	0.85
102.00	0.85	176.00	0.43	266.00	4.26	434.00	0.43
103.00	0.85	177.00	0.43	267.00	61.70	447.00	5.96
104.00	0.85	182.00	0.43	268.00	14.04	448.00	2.13
105.00	2.98	183.00	0.43	269.00	2.13	449.00	0.43
106.00	1.28	184.00	1.28	279.00	1.28	463.00	2.55
107.00	0.85	185.00	11.49	280.00	1.28	464.00	0.43
				281.00	4.68	477.00	0.85
				282.00	1.70	493.00	34.47
						494.00	7.66
						495.00	1.70
						496.00	0.43

Mass Spectrum of Compound 'U'

M/E	REL INT	M/E	REL INT
200.00	5.83	268.00	1.67
201.00	4.17	269.00	2.50
202.00	2.50	270.00	1.67
203.00	1.67	271.00	1.67
204.00	1.67	274.00	1.67
209.00	2.50	275.00	1.67
210.00	3.33	276.00	1.67
211.00	9.17	277.00	0.83
212.00	10.00	278.00	0.83
213.00	11.67	279.00	1.67
214.00	5.83	280.00	5.00
215.00	1.67	281.00	16.67
216.00	1.67	282.00	13.33
217.00	0.83	283.00	5.00
221.00	1.67	284.00	1.67
222.00	10.00	285.00	0.83
223.00	17.50	291.00	0.83
224.00	100.00	292.00	0.83
225.00	40.00	293.00	2.50
226.00	10.83	294.00	1.67
227.00	5.00	295.00	1.67
228.00	2.50	296.00	0.83
229.00	4.17	297.00	1.67
230.00	1.67	298.00	0.83
231.00	1.67	299.00	1.67
232.00	1.67	300.00	0.83
233.00	4.17	309.00	1.67
234.00	2.50	310.00	10.00
235.00	5.83	311.00	4.17
236.00	5.83	312.00	2.50
237.00	5.00	313.00	0.83
238.00	10.00	325.00	0.83
239.00	4.17	326.00	0.83
240.00	5.00	327.00	12.50
241.00	5.00	328.00	2.50
242.00	2.50	329.00	1.67
243.00	1.67	341.00	10.83
244.00	1.67	342.00	2.50
245.00	1.67	355.00	0.83
246.00	2.50	356.00	0.83
247.00	1.67	357.00	4.17
248.00	1.67	358.00	1.67
249.00	1.67	369.00	0.83
250.00	1.67	370.00	1.67
251.00	3.33	371.00	0.83
252.00	13.33	373.00	0.83
253.00	14.17	374.00	0.83
254.00	8.33	387.00	4.17
255.00	3.33	388.00	1.67
256.00	2.50	403.00	1.67
257.00	2.50	417.00	1.67
258.00	2.50	418.00	1.67
259.00	1.67	419.00	1.67
260.00	0.83	433.00	100.00
264.00	0.83	434.00	24.17
265.00	2.50	435.00	4.17
266.00	1.67	449.00	7.50
267.00	1.67	450.00	1.67
		463.00	1.67
		478.00	1.67
		479.00	4.17
		480.00	1.67

Mass Spectrum of Compound 'V'

M/E	REL INT	M/E	REL INT
200	5.2	300	1.3
201	2.6	308	0.6
202	1.3	309	3.9
209	2.6	310	3.2
210	3.2	311	2.6
211	20.6	312	1.9
212	13.5	313	0.6
213	5.2	314	1.3
214	5.2	324	1.3
215	2.6	325	3.2
216	1.3	326	7.7
217	0.6	327	3.2
221	1.9	328	1.9
222	16.8	329	0.6
223	18.1	339	1.3
224	27.7	340	1.3
225	11.6	355	4.2
226	3.9	356	6.4
227	2.6	357	1.9
228	1.9	358	1.3
233	1.9	369	0.6
234	1.9	370	1.3
235	3.9	371	1.3
236	5.8	372	4.5
237	3.2	373	1.7
238	5.2	374	0.6
239	3.2	375	0.6
240	5.2	385	3.2
241	3.2	386	2.6
242	2.6	387	1.3
243	1.3	401	1.3
244	0.6	402	7.7
248	1.0	403	3.2
249	1.3	404	0.6
250	1.9	418	1.9
251	8.4	432	12.9
252	9.0	433	4.5
253	4.5	434	1.3
254	2.6	448	9.7
255	1.3	449	3.2
256	1.3	450	0.6
257	0.6	451	3.9
267	2.6	452	1.3
268	3.9	453	0.6
269	3.2	462	0.6
270	3.2	463	1.3
271	1.3	464	0.6
279	5.8	478	100.0
280	5.8	479	26.5
281	6.5	480	5.2
282	2.6	481	1.3
283	1.3	494	5.2
284	1.4	495	1.3
285	0.5	496	0.6
286	0.6	508	1.3
294	1.3	509	0.6
295	1.3	523	5.2
296	2.6	524	3.9
297	4.5	525	0.6
298	4.5		
299	1.9		

Mass Spectrum of Compound 'W'

M/E	REL INT
200	100.0
201	3.5
211	8.5
224	4.5
225	2.5
226	3.0
227	2.5
232	3.0
233	6.0
234	1.5
235	4.0
236	2.0
237	3.5
238	4.0
239	2.5
240	2.0
250	1.5
251	2.5
252	3.0
253	3.5
254	3.0
255	1.5
264	1.5
265	1.5
266	2.0
293	2.0
294	1.5
295	2.0
296	1.5
308	1.5
309	1.5
310	2.0
341	2.3
342	20.5
358	3.5
388	4.0
389	1.0
404	4.0
405	1.5
406	0.5
418	4.0
419	1.5
433	1.5
434	3.0
435	1.5

Mass Spectrum of Compound 'X'

M/E	REL INT	M/E	REL INT
200	6.7	300	1.5
201	3.7	301	0.7
202	1.5	309	1.5
203	0.7	310	3.7
209	1.5	311	5.9
210	2.2	312	3.0
211	7.4	313	3.0
212	5.2	325	1.5
213	9.6	326	1.5
214	5.2	327	1.5
215	1.5	328	0.7
216	0.7	341	8.9
221	0.6	342	2.2
222	4.4	356	1.5
223	8.9	357	2.2
224	39.5	358	0.7
225	25.2	371	0.7
226	7.4	387	2.2
227	4.4	403	6.7
228	3.0	404	1.5
229	1.5	417	0.7
230	0.7	433	100.0
233	2.2	434	26.7
234	3.7	435	4.4
235	20.0	449	1.5
236	16.3	450	0.7
237	25.9	451	0.7
238	12.6	479	5.2
239	3.7	480	2.2
240	1.5		
241	2.2		
242	1.5		
245	1.5		
246	1.5		
247	2.2		
248	3.0		
249	2.2		
250	2.2		
251	3.7		
252	5.9		
253	3.7		
254	1.5		
255	0.7		
264	5.2		
265	2.2		
266	2.2		
267	1.5		
268	2.2		
269	1.5		
270	1.5		
280	1.5		
281	3.0		
282	3.7		
283	5.9		
284	1.5		
296	2.2		
297	1.5		
298	0.7		
299	2.2		

Mass Spectrum of Compound 'Z2'

M/E	REL INT
50.00	50.00
51.00	55.26
52.00	23.68
53.00	21.05
54.00	4.47
55.00	31.58
56.00	5.79
57.00	11.58
58.00	2.11
59.00	1.05
60.00	4.47
61.00	15.79
62.00	34.21
63.00	50.00
64.00	21.58
65.00	81.58
66.00	73.68
67.00	10.53
68.00	6.32
69.00	12.63
70.00	4.47
71.00	5.79
72.00	1.05
73.00	13.95
74.00	61.58
75.00	81.58
76.00	21.05
77.00	39.47
78.00	76.32
79.00	11.32
80.00	2.11
81.00	3.42
82.00	2.11
83.00	5.53
84.00	1.84
85.00	3.68
86.00	7.37
87.00	12.63
88.00	4.74
89.00	4.47
90.00	6.84
91.00	26.32
92.00	13.42
93.00	9.74
94.00	100.00
95.00	19.74
96.00	1.84
97.00	2.89
98.00	15.79
99.00	31.58
100.00	10.26
101.00	6.84
102.00	7.11
103.00	23.95
104.00	11.32
105.00	6.58
106.00	3.42
107.00	2.89
108.00	1.84
109.00	2.63
110.00	6.05
111.00	6.84
112.00	10.79
113.00	3.16
114.00	4.47
115.00	6.32
116.00	2.63
117.00	3.16
118.00	3.68
119.00	3.95
120.00	11.58
121.00	2.37
122.00	7.11
123.00	20.00
124.00	5.00
125.00	4.74
126.00	3.16
127.00	2.89
128.00	50.00
129.00	5.53
130.00	15.79
131.00	2.37
132.00	1.32
133.00	1.05
134.00	1.58
135.00	1.58
136.00	3.68
137.00	31.58
138.00	7.37
139.00	7.11
140.00	2.11
141.00	5.26
142.00	1.84
143.00	1.58
144.00	1.32
145.00	1.05
146.00	2.89
147.00	2.37
148.00	13.95
149.00	52.63
150.00	10.26
151.00	6.32
152.00	6.05
153.00	3.68
154.00	9.74
155.00	2.89
156.00	0.79
157.00	0.79
158.00	0.53
159.00	0.26
160.00	0.79
161.00	0.53
162.00	0.79
163.00	1.84
164.00	4.74
165.00	16.58
166.00	3.42
167.00	3.42
168.00	8.68
169.00	5.00
170.00	7.11
171.00	1.84
172.00	0.53
173.00	0.53
174.00	0.79
175.00	1.05
176.00	7.63
177.00	18.16
178.00	5.26
179.00	3.68
180.00	2.11
181.00	6.32
182.00	2.11
183.00	2.63
184.00	0.79
185.00	0.79
186.00	0.53
187.00	0.53
188.00	0.53
189.00	0.53
190.00	1.32
191.00	1.05
192.00	2.63
193.00	26.32
194.00	8.42
195.00	4.74
196.00	1.84
197.00	1.05
198.00	0.53
199.00	1.84
200.00	0.79
250.00	39.47
251.00	10.79
252.00	4.47
253.00	1.84
254.00	0.53
255.00	0.79
256.00	0.53
257.00	0.79
258.00	0.26
265.00	0.53
266.00	2.89
267.00	11.58
268.00	5.26
269.00	15.79
270.00	2.89
277.00	0.53
278.00	0.53
279.00	0.26
280.00	1.32
281.00	0.53
282.00	0.26
283.00	1.32
284.00	0.53
285.00	4.74
286.00	1.05
293.00	0.26
294.00	0.53
295.00	1.58
296.00	28.95
297.00	22.89
298.00	4.47
299.00	1.84
300.00	0.26
301.00	0.26
302.00	0.26
308.00	0.53
309.00	0.79
310.00	2.11
311.00	0.79
312.00	0.79
313.00	5.00
314.00	2.37
315.00	5.26
316.00	0.53
325.00	1.32
326.00	65.79
327.00	12.63
328.00	2.11
329.00	0.53
340.00	0.53
341.00	2.11
342.00	2.37
343.00	31.58
344.00	5.53
345.00	1.32
357.00	3.16
358.00	1.05
359.00	1.05
370.00	0.79
371.00	6.05
372.00	0.79
373.00	0.53
374.00	0.53
387.00	2.11
388.00	1.05
402.00	0.26
403.00	0.26
415.00	0.13
201.00	0.79
202.00	1.32
203.00	0.79
204.00	8.68
205.00	7.37
206.00	2.63
207.00	2.89
208.00	1.58
209.00	5.00
210.00	1.84
211.00	4.47
212.00	1.05
213.00	0.53
214.00	0.53
215.00	1.84
216.00	0.79
217.00	3.16
218.00	0.53
219.00	0.53
220.00	1.84
221.00	18.95
222.00	11.05
223.00	18.95
224.00	3.42
225.00	5.53
226.00	1.84
227.00	1.05
228.00	2.37
229.00	1.84
230.00	1.05
231.00	0.53
232.00	0.53
233.00	0.53
234.00	0.53
235.00	0.53
236.00	0.53
237.00	0.53
238.00	0.53
239.00	10.53
240.00	2.11
241.00	1.58
242.00	0.53
243.00	0.53
244.00	0.79
245.00	0.26
246.00	0.26
247.00	0.26
248.00	0.26
249.00	0.53

Mass Spectrum of Compound 'Y'

M/E	REL. INT
200	7.5
201	4.6
202	3.7
203	2.5
204	0.5
205	3.7
206	0.8
207	1.3
208	1.7
209	5.8
210	8.7
211	22.9
212	15.0
213	8.7
214	4.6
215	4.6
216	1.3
217	1.7
218	1.3
219	1.3
220	1.3
221	6.2
222	22.0
223	22.5
224	21.7
225	15.4
226	10.0
227	5.0
228	5.0
229	2.9
230	1.3
231	1.3
232	2.1
233	5.0
234	4.6
235	11.3
236	15.4
237	15.4
238	13.8
239	11.7
240	5.4
241	3.7
242	2.1
243	8.3
244	1.3
245	1.3
246	1.7
247	3.3
248	2.9
249	4.2
250	5.4
251	23.8
252	6.7
253	6.7
254	2.9
255	3.3
256	2.1
257	2.1
259	2.1
260	2.1
264	2.1
265	2.1
266	5.8
267	7.9
268	4.2
269	3.7
270	1.3
275	5.4
276	2.1
277	1.3
278	2.1
279	5.8
280	4.2
281	5.4
282	3.7
283	3.3
284	2.1
285	1.7
286	1.3
293	11.7
294	3.3
295	5.8
296	3.3
297	5.8
298	2.9
299	2.1
309	7.5
310	2.9
311	2.9
312	2.1
313	1.7
314	1.3
315	1.3
325	15.8
326	18.8
327	6.2
328	1.7
339	2.1
340	1.3
341	5.0
342	2.9
343	2.1
353	2.5
354	1.7
355	5.0
356	3.3
357	1.7
368	5.4
369	1.7
370	1.3
371	3.3
372	3.3
385	1.3
386	1.3
387	1.3
388	11.3
389	2.5
401	2.5
402	2.5
403	2.1
410	4.2
430	1.3
431	1.3
432	1.7
433	1.3
447	2.1
478	17.0
479	4.6
480	0.8
493	5.4
494	1.3
523	100.0
524	15.0
525	1.7
556	4.2
558	4.6
559	1.3
569	0.8

Mass Spectrum of
1-Picrylnaphthalene

M/E	REL INT
200.00	81.63
201.00	32.65
202.00	11.84
203.00	4.49
204.00	5.71
205.00	4.08
206.00	4.49
207.00	2.04
208.00	0.82
209.00	0.41
212.00	1.22
213.00	1.22
214.00	8.98
215.00	2.45
216.00	7.35
217.00	8.57
218.00	12.24
219.00	4.49
220.00	2.04
221.00	0.82
222.00	0.41
223.00	0.41
229.00	1.22
230.00	4.90
231.00	2.45
232.00	2.45
233.00	1.63
234.00	2.86
235.00	2.45
236.00	2.04
237.00	1.22
238.00	0.82
245.00	2.86
246.00	7.35
247.00	5.71
248.00	3.67
249.00	1.22
250.00	0.82
251.00	0.82
252.00	0.82
260.00	2.04
261.00	0.41
262.00	1.63
263.00	2.04
264.00	6.94
265.00	2.04
266.00	0.41
275.00	2.04
276.00	6.12
277.00	3.27
278.00	0.82
280.00	0.82
281.00	0.41
291.00	0.41
292.00	1.63
293.00	2.45
294.00	13.47
295.00	2.86
296.00	0.41
297.00	0.41
306.00	2.04
307.00	0.41
308.00	0.41
309.00	1.63
310.00	1.63
311.00	0.41
322.00	3.27
323.00	1.63
339.00	100.00
340.00	22.45
341.00	4.49
342.00	0.82

Mass Spectrum of
1-Picryl-4,5,7-trinitronaphthalene

M/E	REL INT
200.00	1.25
202.00	10.21
203.00	2.98
204.00	2.98
205.00	1.70
206.00	1.28
207.00	1.28
208.00	0.85
209.00	0.85
210.00	0.43
211.00	0.43
212.00	0.43
213.00	1.70
214.00	2.55
215.00	1.28
216.00	0.85
217.00	1.28
218.00	2.98
219.00	1.28
220.00	2.13
221.00	0.85
222.00	0.85
223.00	0.43
224.00	0.43
225.00	0.43
226.00	0.43
227.00	0.43
228.00	0.43
229.00	0.43
230.00	1.28
231.00	2.13
232.00	2.98
233.00	1.28
234.00	0.85
235.00	0.85
236.00	0.85
237.00	0.85
238.00	0.43
239.00	0.43
240.00	0.43
241.00	0.43
242.00	0.43
243.00	0.43
244.00	1.28
245.00	1.28
246.00	1.28
247.00	1.70
248.00	4.26
249.00	0.85
250.00	0.85
251.00	1.70
252.00	0.85
253.00	0.85
254.00	0.43
255.00	0.43
256.00	0.43
257.00	0.43
258.00	1.28
259.00	1.70
260.00	2.13
261.00	1.28
262.00	1.28
263.00	0.85
264.00	1.28
265.00	1.28
266.00	1.28
267.00	0.85
289.00	1.28
290.00	1.28
291.00	0.85
292.00	0.85
293.00	4.26
294.00	2.13
295.00	0.85
296.00	0.43
297.00	0.43
305.00	2.13
306.00	1.70
307.00	0.85
308.00	0.85
309.00	0.43
310.00	0.43
311.00	0.43
319.00	0.85
320.00	0.85
321.00	0.85
322.00	0.43
323.00	0.43
324.00	3.83
325.00	0.85
326.00	0.43
335.00	2.55
336.00	0.85
337.00	0.43
351.00	0.85
352.00	1.70
353.00	1.28
354.00	0.85
367.00	0.43
368.00	1.28
369.00	0.43
370.00	0.85
371.00	0.43
381.00	0.43
382.00	2.13
383.00	0.43
395.00	0.85
396.00	0.85
397.00	0.85
398.00	13.19
399.00	2.55
400.00	0.85
410.00	2.13
411.00	0.85
412.00	1.28
428.00	100.00
429.00	20.00
430.00	3.83
431.00	0.85
444.00	0.85
452.00	0.64
456.00	0.64
474.00	2.98
475.00	0.43

Mass Spectrum of
1-Picryl-2,4,5,7-tetranitronaphthalene

M/E	REL INT
200.00	0.70
201.00	2.79
202.00	1.52
203.00	1.40
204.00	0.73
205.00	0.98
206.00	0.59
207.00	0.82
215.00	0.34
216.00	0.49
217.00	2.55
218.00	1.10
219.00	4.40
220.00	1.08
221.00	0.66
229.00	0.66
230.00	0.57
231.00	0.98
232.00	0.56
233.00	0.69
234.00	0.38
235.00	0.63
245.00	0.51
246.00	0.73
247.00	1.65
248.00	0.68
249.00	0.56
259.00	1.33
261.00	0.37
263.00	0.89
264.00	0.48
265.00	0.92
275.00	0.37
276.00	0.91
277.00	1.31
278.00	0.36
279.00	0.71
283.00	0.36
291.00	0.40
293.00	0.68
305.00	0.38
307.00	0.61
310.00	0.34
323.00	0.50
351.00	0.39
353.00	1.22
369.00	1.16
397.00	8.08
398.00	1.93
399.00	0.34
415.00	0.89
427.00	0.55
428.00	4.24
429.00	0.74
443.00	21.42
444.00	4.22
445.00	0.77
457.00	1.53
473.00	100.00
474.00	20.17
475.00	4.39
476.00	0.56
489.00	0.25
503.00	0.48
519.00	0.18

Courses attended during the period October 1973 - November 1976 in fulfilment of CNAA regulations:-

1973 - 1974

Basic Algol Programming (18 lecture/practical sessions)
Symposium: Patents in the Chemical Industry (1 day)
Electronics for Chemists (15 lecture/practical sessions)

1974 - 1975

Symposium: Energy the Uncertain Future (2 days)
NMR Spectroscopy (40 lectures)
Mass Spectrometry (28 lectures)
Symposium: Recent Developments in Mechanistic Organic Chemistry ($\frac{1}{2}$ day)

1975 - 1976

Symposium: Recent Advances in Photographic Chemicals (1 day)
Symposium: Applications of Woodward-Hoffmann Rules to Synthetic Organic Chemistry (1 day)

Approximately 30 research colloquia, on topics of general chemical interest, were attended during the period 1973 - 1976.

Two colloquia were presented at Kingston Polytechnic during the course of the present study. These colloquia dealt with the subject matter of this thesis.