Studies on

Nitro-1,5-Dimethylnaphthalenes

and

Nitro-2,3-Dimethylnaphthalenes

by

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Summary

The synthesis of nitro-2,3-dimethylnaphthalenes has been undertaken,and fourteen previously unreported dinitro,trinitro,tetranitro and pentanitro derivatives of 2,3-dimethylnaphthalene have been prepared. The synthesis of nitro-1,5-dimethylnaphthalenes has also been undertaken, and seven previously unreported mononitro,dinitro,trinitro and tetranitro derivatives of 1,5-dimethylnaphthalene have been prepared. The positive and negative ion mass spectra,electronic spectra and nuclear magnetic resonance spectra of these compounds have been recorded and discussed in terms of the structures of the compounds. The electron spin resonance spectra of the radical anions of two of the symmetrically substituted compounds have been recorded.

The reactions of polynitro-2,3-dimethylnaphthalenes with methoxide ion and sulphite ion have been investigated,and the Meisenheimer complexes so formed characterised by NMR spectroscopy. In a number of cases solid Meisenheimer complexes have been isolated. The reaction of 4-nitro-1,5-dimethylnaphthalene with hydroxide ion was found to produce dinitro derivatives of naphthastilbene and naphthabibenzyl,resulting from coupling via the 1-methyl group. The reactions of polynitro-1,5-dimethylnaphthalenes with methoxide ion, sulphite ion,diethylamine and triethylamine in dimethylsulphoxide solvent have been investigated *in situ* by NMR spectroscopy,and benzyl-type ions resulting from

abstraction of methyl hydrogen atoms were found to have been produced. The reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with methoxide ion in tetrahydrofuran solvent was investigated,and a solid Meisenheimer complex was isolated.

The association constants for the formation of charge-transfer complexes between benzene and the polynitro-1,5-dimethylnaphthalenes and polynitro-2,3-dimethylnaphthalenes have been determined by nuclear magnetic resonance spectroscopy,and it has been shown that polynitro-1,5-dimethylnaphthalenes are stronger electron-acceptors than polynitro-2,3-dimethylnaphthalenes.

The rates of nitration of a number of mononitro, dinitro and trinitro derivatives of 1,5-dimethylnaphthalene and 2,3-dimethylnaphthalene have been investigated and the rates correlated with theoretical reactivity indices derived from Hückel Molecular Orbital calculations.

Chapter One. The Synthesis of Nitro-1,5-Dimethylnaphthalenes and Nitro-2,3-Dimethylnaphthalenes

1.1 Introductory Survey.

1.2 The Synthesis of Nitro-2,3-Dimethylnaphthalenes.

1.3 The Synthesis of Nitro-1,5-Dimethylnaphthalenes.

1.1 Introductory Survey

1.1.1 Introduction

Nitroaromatic compounds are of great importance both in industry and in the laboratory[1]. Nitrobenzene is the simplest of the nitroaromatic compounds but at the same time it is the most important from an industrial point of view[2]. Nitrobenzene is used as an intermediate in a wide range of processes, including the manufacture of azo dyes, rubber, photographic chemicals and drugs. Polynitroaromatic compounds are used commercially as non-initiating high explosives, the most important being 2,4,6-trinitrotoluene (α-TNT)[3] which has replaced picric acid as the major military explosive. An interesting aspect of explosives technology in recent years has been the development of explosives which are thermally stable and of low volatility. Such explosives are required for space applications where materials are frequently subjected to conditions of high temperature and low pressure. The most commonly used explosive for space research to date has been 2,2',4,4',6,6'-hexanitrostilbene (HNS)[4,5,6]. This compound may be prepared from α-TNT by treatment with base[4].

1.1.2 The Synthesis of Nitroaromatic Compounds

(A) Methods of Nitration

Nitroaromatic compounds do not exist in nature, and must therefore be prepared by synthetic methods. The first nuclear substituted nitroaromatic compound to be recorded was nitrobenzene, prepared by Mitscherlich in 1834 by the action of fuming nitric acid on benzene[7]. Shortly

afterwards,this preparation was repeated using a mixture of nitric and sulphuric acids[8],and this latter method has since become the single most important method of effecting aromatic nitration on an industrial scale.

The various means of carrying out the synthesis of nitroaromatic compounds may be broadly classified into direct and indirect methods. A direct method of synthesis may be defined as one in which the precursor is reacted directly with the nitrating agent,and the products obtained in a single step. The vast majority of industrial syntheses of nitroaromatic compounds involve direct nitration methods. Some compounds cannot be synthesised in appreciable yields by direct methods,e.g.the yield of m-dinitrotoluene from the nitration of toluene is only 4%[9]. Indirect methods,involving more than one step,must therefore be used in such cases. Thus the synthesis of m-dinitrotoluene may be achieved in good yield via the intermediacy of the readily obtained p-nitrotoluene[10]:-

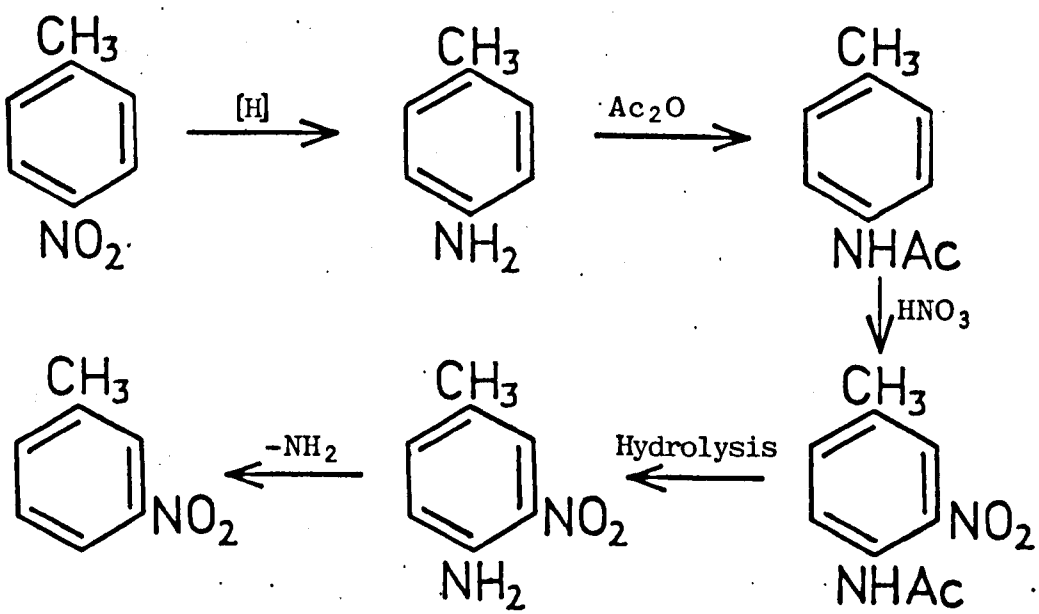


Fig.1.1.1

Indirect methods have also been used for the synthesis of compounds which can be prepared by direct methods, but only with difficulty. For example 1,3,5-trinitrobenzene has been prepared by the nitration of m-dinitrobenzene[11], but because the latter compound is deactivated towards electrophilic substitution, fuming mixed acid was required for the synthesis. The most commonly used method for the synthesis of 1,3,5-trinitrobenzene is the oxidation of the more readily obtained 2,4,6-trinitrotoluene followed by decarboxylation to give the required product[12].

(B) Nitration Media

(a) Anhydrous Nitric Acid

Anhydrous nitric acid acts as a fairly powerful nitration agent, and may be used, for example, for the conversion of nitrobenzene to 1,3-dinitrobenzene[13]. The kinetics of this reaction have been thoroughly investigated and the rate found to be dependent only upon the concentration of the substrate, a result which is consistent with reaction via molecular nitric acid[14]. However, Ingold and his co-workers have demonstrated that it is the nitronium ion that is the active species in the nitration of aromatic compounds in anhydrous nitric acid[15]. These workers showed that self-dehydration occurred in nitric acid thus :-

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

Raman studies[16] have confirmed a 1:1 ratio of nitrate and nitronium ions in anhydrous nitric acid, and this tends to rule out auto-protolysis as an alternative dissociation, as this would produce nitrate ions only:-

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$

Anhydrous nitric acid is not as powerful a nitrating agent as nitric acid in sulphuric acid because at room temperature only 3% dissociation to the nitronium ion actually takes place[17]. Studies of the infrared spectra of nitric acid in the liquid[18] and vapour[19] phases suggest that this small dissociation is due to the formation of hydrogen-bonded dimers :-

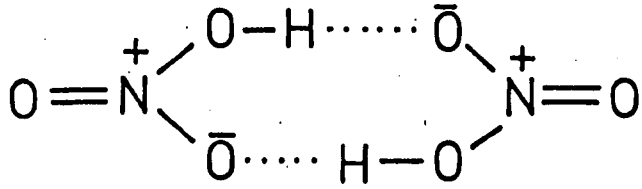


Fig.1.1.2

(b) Aqueous Nitric Acid

The presence of water in nitric acid causes a reduction in the rate of nitration as compared to anhydrous conditions, the reduction in rate being considerably greater than would be expected from a simple dilution of the active nitrating species. For example, the rate of nitration of nitrobenzene using anhydrous nitric acid is reduced to one-sixth on addition of 5% water[14]. Raman spectroscopy has indicated that the concentration of nitronium ions in nitric acid falls below the level of spectroscopic detection when more than 5% water has been added[20]. It has been shown from the freezing-point curve of the H_2O-HNO_3 system[21] and from Raman studies[22] that a monohydrate is formed which is in equilibrium with hydroxonium and nitrate ions :-

$$O_2N\text{-}O\text{-}H\cdots\cdots OH_2 \rightleftharpoons NO_3^- + H_3O^+$$

The formation of the hydrate suppresses self-dehydration

and thus leads to a decrease in the nitronium ion concentration. Considerable doubts existed about the actual nitrating species present in aqueous nitric acid, as the formation of the nitronium ion had been shown to be slight[20]. Ingold and his co-workers studied the nitration of sodium benzylsulphonate using aqueous nitric acid, and concluded that the nitracidium ion ($H_2NO_3^+$) was the active nitrating agent, though they could not exclude reaction via a small concentration of nitronium ions present in the system[23,24]. Banton and his co-workers[25,26] later demonstrated that the nitronium ion was the active nitrating species by studies on the nitration of the 2-phenylethanesulphonate anion. They observed initial zeroth-order rate constants which were similar to the zeroth-order rate constant of the ^{18}O exchange between labelled water and nitric acid .

$$HNO_3 + H^+ \rightleftharpoons NO_2^+ + H_2O$$

$$H_2{}^{18}O + NO_2^+ \rightleftharpoons H\,{}^{18}O.NO_2 + H^+$$

The rate of incorporation of ^{18}O into nitric acid must be dependent upon the rate of production of the nitronium ion, and as this rate was the same as the rate of nitration of the aromatic substrate (under zeroth-order conditions), the nitronium ion must be the active nitrating species. Had the effective nitrating species been the nitracidium ion, there would have been no connection between the two rates of reaction.

(c) Nitric Acid in Inert Organic Solvents

With regard to nitration, an "inert solvent system" may be defined as one in which no chemical reaction occurs between the solvent and nitric acid. Examples of such

solvents are acetic acid,chloroform,nitromethane and diethyl ether. The infrared and Raman spectra of systems composed of nitric acid and either chloroform or carbon tetrachloride were found to consist of a simple superimposition of the spectra of the two components, with no evidence for the presence of nitronium or nitrate ions[27,28]. Similar results were obtained from studies of solutions of nitric acid in acetic acid[29]. Such nitration media may be regarded simply as diluted anhydrous nitric acid. Kinetic studies of nitrations in inert organic solvents such as nitromethane[30],nitrobenzene[31] and acetic acid[32] have been made. The result of these studies was that kinetic order is dependent upon the reactivity of the substrate. For example,reactive compounds such as toluene, nitrated in nitromethane,gave zeroth-order kinetics with respect to the concentration of the aromatic compound,the rate-controlling step being the formation of the nitronium ion[30]. First order-kinetics were observed when less reactive compounds,e.g.1,2,4-trichlorobenzene,were nitrated in either nitromethane or acetic acid,the rate-controlling step being the attack of the nitronium ion upon the aromatic compound[33]. For a single aromatic compound,the rate of nitration decreases as the basicity of the solvent increases, e.g.the zeroth-order rate constant for the nitration of toluene in nitromethane at 20° is thirty times that for the nitration of toluene in acetic acid at 20°. This effect must be due to the more basic solvents forming addition complexes with nitric acid,thereby reducing the concentration of nitric acid available for reaction.

(d) Nitric Acid in Acetic Anhydride

Unlike"inert"organic solvents,acetic anhydride reacts with nitric acid with the resultant formation of acetyl nitrate. However,other species are found to be present,dependent upon the relative concentrations of nitric acid and acetic anhydride in the solution[34]. Thus when acetic anhydride is the major constituent,only acetic acid and acetyl nitrate are found to be present,but when nitric acid is the major constituent,acetic acid,acetyl nitrate and dinitrogen pentoxide are present. At nitric acid concentrations greater than 90%,dinitrogen pentoxide is the principal species present,with only minute amounts of acetyl nitrate. Acetyl nitrate has also been synthesised from acetic anhydride and dinitrogen pentoxide[35]. These observations have led to the postulate that the following equilibria are present in nitric acid/acetic anhydride systems :-

$$Ac_2O + 2HNO_3 \rightleftharpoons N_2O_5 + 2AcOH$$

$$N_2O_5 + Ac_2O \rightleftharpoons 2AcONO_2$$

It is because of these equilibria that doubt has always existed as to the nature of the electrophilic species responsible for nitration in this medium. The first systematic study of nitration by acyl nitrates was made by Ingold and his co-workers,who proposed that dinitrogen pentoxide was the species that effected substitution[36]. More recently,however,Paul[37] found that the kinetics of nitration of benzene by nitric acid in acetic anhydride were inconsistent with attack by dinitrogen pentoxide,and obtained evidence for the nitronium ion being the species

responsible for nitration. It has also been suggested, from the observation of the stereoselective reaction of acetyl nitrate with butenes, that protonated acetyl nitrate is the active electrophile present in acetic anhydride/nitric acid mixtures[38]. Kuhn and Olah[39] have reported that acetyl nitrate can be obtained from the reaction of acetic acid with nitronium salts. This evidence suggests that the nitronium ion, as a solvated species, does play a part in acetyl nitrate nitrations.

Nitrations in acetic anhydride have long been associated with the formation from some aromatic compounds of higher proportions of *ortho*-nitro products than are formed under other conditions. For example, the nitration of acetanilide using acetic anhydride as the solvent yields *ortho*-nitroacetanilide as the major product, whereas when acetic acid is used as the solvent the major product is *para*-nitroacetanilide[40]. Although various theories have been put forward to explain this phenomenon, there appears to be no single postulate that can be applied to all the compounds exhibiting this effect. This subject has been discussed in detail[41].

(e) Nitric Acid in Sulphuric Acid

The nitric acid/sulphuric acid system, referred to as "mixed acid", has been the subject of a considerable number of investigations. It was established at an early stage that the function of sulphuric acid in the mixtures could not simply be that of removing water formed during the nitration of an aromatic compound, and thereby preventing the reverse reaction, since nitration is irreversible anyway[42].

$$ArH + HNO_3 \rightarrow ArNO_2 + H_2O$$

Hantzsch[43] studied the effect of added nitric acid upon the freezing point of sulphuric acid, and obtained a van't Hoff factor *(i)* of 3 for the system, indicating the presence of three ions. He therefore suggested that because sulphuric acid is stronger than nitric acid, a di-protonated nitric acid species is formed, according to the following equilibrium:-

$$HNO_3 + 2H_2SO_4 \rightleftharpoons H_3NO_3^{++} + 2HSO_4^-$$

This conclusion was supported by ultraviolet absorption spectra[44] and electrical conductance values[45] of nitric acid/sulphuric acid mixtures. Later, Ingold and his co-workers[46] repeated Hantzsch's cryoscopic work on mixed acid systems, and obtained an i value of 4.4. They concluded that the nitronium ion is formed in accordance with the following equilibrium :-

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

The discrepancy between the experimental value of i of 4.4 and the theoretical value of i of 4.0 was attributed to the association of nitric acid with water formed as a result of the de-protonation of the hydroxonium ions. Thus the function of sulphuric acid in "mixed acid" is to provide a strongly acidic medium towards which nitric acid acts as a base forming the nitronium ion. The concentration of nitronium ions in nitric acid may be estimated readily by Raman spectroscopy[47]. In this way it was found that the addition of sulphuric acid to nitric acid markedly increased the concentration of nitronium ions. In mixtures containing more than 90% sulphuric acid (by weight) the conversion of nitric acid to nitronium ions has been shown

to be complete[48].

1.1.3 Nitro Derivatives of Benzene and Toluene

Nitrobenzene was first prepared in 1834[7] by the nitration of benzene using anhydrous nitric acid, and was first manufactured commercially in 1856[49]. The three dinitrobenzenes were obtained from the nitration of nitrobenzene using mixed acids[50]. The principal product was m-dinitrobenzene with much smaller yields of o- and p-dinitrobenzenes. The latter two compounds have been obtained in better yields by indirect methods[51,52]. 1,3,5-trinitrobenzene was obtained by the nitration of m-dinitrobenzene using nitric acid in oleum[11]. 1,2,3- and 1,2,4-trinitrobenzenes were prepared from 2,6- and 2,4-dinitroanilines respectively by indirect methods[53,54]. Two tetranitrobenzenes have been synthesised; 1,2,3,5-tetranitrobenzene was prepared by the oxidation of picryl hydroxylamine[55], and 1,2,4,5-tetranitrobenzene was prepared by the oxidation of 1,3-dinitro-4,6-dihydroxylaminobenzene[56]. There are no polynitrobenzenes recorded in the literature containing more than four nitro groups.

Nitrotoluenes are obtained from the nitration of toluene using mixed acids to yield mixtures of o- and p-nitrotoluenes, with only a minute yield of m-nitrotoluene[9]. The *meta* isomer has been obtained in better yield by an indirect route[10]. Many of the dinitrotoluenes can be prepared by the direct nitration of the mononitrotoluenes. The nitration of p-nitrotoluene yields 2,4-dinitrotoluene[9]; the nitration of o-nitrotoluene yields 2,4- and 2,6-dinitrotoluenes[57]; the nitration of m-nitrotoluene yields 2,3-[9],

2,5- and 3,4-dinitrotoluenes[58]. 3,5-dinitrotoluene has been prepared indirectly from 3,5-dinitro-p-toluidine[59]. The most important trinitrotoluene is 2,4,6-trinitrotoluene (α-TNT),used as an explosive for military purposes. The synthesis of α-TNT has been achieved on a commercial scale by the direct nitration of toluene[60]. From the crude product,2,3,4-[61],2,3,6-[62] and 2,4,5-trinitrotoluenes[63] have also been obtained. 2,3,5-trinitrotoluene may be prepared by the direct nitration of 2,3-dinitrotoluene[64]. 3,4,5-trinitrotoluene may be obtained from 3,5-dinitro-p-toluidine by an indirect method[65]. Only one tetranitro derivative of toluene,2,3,4,6-tetranitrotoluene, has been recorded in the literature[66]. This compound may be prepared via the oxidation of 2,4,6-trinitro-m-toluidine. There is no recorded pentanitro derivative of toluene.

1.1.4 Nitro Derivatives of Naphthalene and Alkylnaphthalenes

The nitration of naphthalene to 1-nitronaphthalene using anhydrous nitric acid was first described by Laurent in 1835[67],shortly after the nitration of benzene was reported. This synthesis has been carried out on an industrial scale using mixed acid,which gives a product comprising 95% 1-nitronaphthalene[68]. As 2-nitronaphthalene is formed in such low yield by this method (less than 5%), an indirect method has been devised for the synthesis of this compound[69]. All of the ten isomeric dinitronaphthalenes have been synthesised. Nitration of 1-nitronaphthalene yields 1,5- and 1,8-dinitronaphthalenes[70,71]; nitration of 2-nitronaphthalene yields 1,6- and 1,7-dinitro-

naphthalenes [72]. 1,2-,1,3-,1,4- and 2,3-dinitronaphthalenes have been synthesised from the corresponding dinitro derivatives of tetrahydronaphthalene[72,73]. 2,6-dinitronaphthalene has been prepared from 2,6-dinitro-1-naphthylamine[74]. 2,7-dinitronaphthalene may be obtained from 3,6-dinitronaphthalic acid [75]. Seven trinitronaphthalenes have been recorded in the literature. Nitration of 1,5-dinitronaphthalene yields 1,3,5- and 1,4,5-trinitronaphthalenes [76]; nitration of 1,8-dinitronaphthalene yields 1,3,8-trinitronaphthalene[78]; nitration of 2,7-dinitronaphthalene yields 1,3,6-trinitronaphthalene[78]. 1,2,3-[79], 1,2,4-[80] and 1,2,5-trinitronaphthalenes [81] have been synthesised via the oxidation of the corresponding dinitronaphthylamines. Five tetranitronaphthalenes have been reported. 1,3,5,8- and 1,4,5,8-tetranitronaphthalenes have been obtained from the nitration of 1,5-dinitronaphthalene [82]; 1,2,5,8-tetranitronaphthalene has been obtained from the nitration of 1,2,5-trinitronaphthalene [82]; 1,3,6,8-tetranitronaphthalene has been obtained from the nitration of 2,7-dinitronaphthalene [83]; 1,3,5,7-tetranitronaphthalene may be prepared via the nitration of 2,6-dinitronaphthalene[84]. No polynitronaphthalenes containing more than four nitro groups have been recorded to date in the literature.

The nitration of 1-methylnaphthalene[85] and 2-methylnaphthalene[86] to the mononitro stage has been reported in some detail[87]. Three dinitro derivatives of 1-methylnaphthalene have been reported, *viz* 2,4-,4,5- and 4,8-dinitro-1-methylnaphthalenes[88]. The most highly nitrated 1-methylnaphthalene so far reported is 2,4,5-trinitro-1-methyl-

naphthalene[89,90].

Of the dialkyl substituted naphthalenes, acenaphthene and the dimethylnaphthalenes have received the most attention with respect to nitration studies. All three mononitroacenaphthenes have been reported; 3-nitro- and 5-nitroacenaphthene may be prepared by the direct nitration of acenaphthene[91], but 4-nitroacenaphthene must be prepared by an indirect method[92]. A number of dinitro, trinitro, tetranitro and pentanitro derivatives of acenaphthene have been prepared by the direct nitration of the three mononitroacenaphthenes[93]. All of the ten isomeric dimethylnapthalenes have been nitrated as far as the mononitro stage[94]. Dinitro derivatives of 1,4-, 1,6-, 1,7-, 2,3-, 2,6- and 2,7-dimethylnaphthalenes have been prepared by the direct nitration of the respective parent hydrocarbons[95,96,97]. Only 2,6-dimethylnaphthalene has been nitrated as far as the tetranitro stage[98].

The synthesis of new nitro derivatives of 1,5- and 2,3-dimethylnaphthalenes is reported below. Prior to this work, the only nitro derivatives of these hydrocarbons reported in the literature were 2-nitro-1,5-dimethylnaphthalene[94], 4-nitro-1,5-dimethylnaphthalene[94], 1-nitro-2,3-dimethylnaphthalene[94], 5-nitro-2,3-dimethylnaphthalene[94], 6-nitro-2,3-dimethylnaphthalene[94] and 1,8-dinitro-2,3-dimethylnaphthalene[95].

1.2 The Synthesis of Nitro-2,3-Dimethylnaphthalenes

(A) Nitro-2,3-Dimethylnaphthalenes Prepared by Direct Methods

1.2.1 1,4-Dinitro-2,3-Dimethylnaphthalene;1,5-Dinitro-2,3-Dimethylnaphthalene;and 1,8-Dinitro-2,3-Dimethylnaphthalene

Treatment of 2,3-dimethylnaphthalene(1) with a solution of nitric acid in acetic anhydride using the calculated amount of nitric acid for mononitration yielded a mixture of 1-nitro-2,3-dimethylnaphthalene(2) and 5-nitro-2,3-dimethylnaphthalene(3). Nitration of 5-nitro-2,3-dimethylnaphthalene yielded two dinitro isomers,1,5-dinitro-2,3-dimethylnaphthalene(4) and 1,8-dinitro-2,3-dimethyl-naphthalene(5). The products were separated by a combination of fractional crystallisation and column chromatography. 1,8-dinitro-2,3-dimethylnaphthalene was identified by comparison with an authentic sample prepared by a literature method [95]. 1,5-dinitro-2,3-dimethyl-naphthalene was identified by NMR spectroscopy. The ratio of 1,5-dinitro-2,3-dimethylnaphthalene to 1,8-dinitro-2,3-dimethylnaphthalene in the product mixture was found to be approximately 40:60,showing that nitration of 5-nitro-2,3-dimethylnaphthalene had occurred preferentially at the 4-position rather than the 1-position. On steric grounds, the product ratio would have been expected to be the reverse of that observed,due to the hindrance at the 4-position by the nitro group at the 5-position. The explanation is probably that the 4-position is *"meta"* to the nitro group at the 5-position,and as such is a favoured site for nitration. A further discussion of this point is given in Chapter 3.

Nitration of 1-nitro-2,3-dimethylnaphthalene using nitric acid in acetic anhydride yielded 1,5-dinitro-2,3-dimethylnaphthalene, 1,8-dinitro-2,3-dimethylnaphthalene and 1,4-dinitro-2,3-dimethylnaphthalene(6). The products were separated by column chromatography,and the product ratio found to be *ca* 1:1:1. This product ratio implies that the deactivating effect of the nitro group in the methyl-substituted ring of 1-nitro-2,3-dimethylnaphthalene counterbalanced the activating influence of the methyl groups to some extent,with the overall result that the rate of nitration in the methylated ring was similar to that for the non-methylated ring. A further discussion of this product ratio is given in Chapter 3.

The synthesis of 1,5-dinitro-2,3-dimethylnaphthalene, 1,8-dinitro-2,3-dimethylnaphthalene and 1,4-dinitro-2,3-dimethylnaphthalene was also achieved by the nitration of 2,3-dimethylnaphthalene using the calculated amount of nitric acid in acetic anhydride for conversion to the dinitro stage. The process undoubtedly proceeds via the intermediacy of 1-nitro-2,3-dimethylnaphthalene and 5-nitro-2,3-dimethylnaphthalene (see fig.1.2.1).

1.2.2 <u>1,4,5-Trinitro-2,3-Dimethylnaphthalene</u>

Nitration of 1,5-dinitro-2,3-dimethylnaphthalene, 1,8-dinitro-2,3-dimethylnaphthalene and 1,4-dinitro-2,3-dimethylnaphthalene using the stoichiometric amount of nitric acid in sulphuric acid for conversion to the trinitro stage yielded in each case 1,4,5-trinitro-2,3-dimethylnaphthalene(7) as the sole trinitro derivative (fig.1.2.1).

There was no evidence for the formation of any other trinitro derivative in any case,e.g.1,5-dinitro-2,3-dimethylnaphthalene might have been expected to yield 1,5,7-trinitro-2,3-dimethylnaphthalene,but no trace was found of this compound in the product. The absence of alternative trinitro products is discussed in Chapter 3.

1.2.3 1,4,5,7-Tetranitro-2,3-Dimethylnaphthalene

The synthesis of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene(8) was achieved by the nitration of 1,4,5-trinitro-2,3-dimethylnaphthalene using a mixture of nitric acid and sulphuric acid. There are two sites which are activated towards nitration in 1,4,5-trinitro-2,3-dimethylnaphthalene,and hence two products are to be expected upon nitration (see fig.1.2.1). The 7-position is strongly activated towards nitration by the nitro group at the 5-position,to which it is *meta*,and it is at the 7-position that 95% of the substitution takes place. The 8-position,although *para* to the 5-position,and therefore not activated towards nitration by the 5-nitro group,is however *"meta"* to the 1-position. Substitution at the 8-position to give 1,4,5,8-tetranitro-2,3-dimethylnaphthalene (9) did occur,but only to the extent of 5% of the total yield. A further discussion of the product ratio is given in Chapter 3.

1,4,5,7-tetranitro-2,3-dimethylnaphthalene, being the major product,was easily isolated from the product mixture by fractional crystallisation,but it was not possible to isolate 1,4,5,8-tetranitro-2,3-dimethylnaphthalene in this way. Column chromatography was not

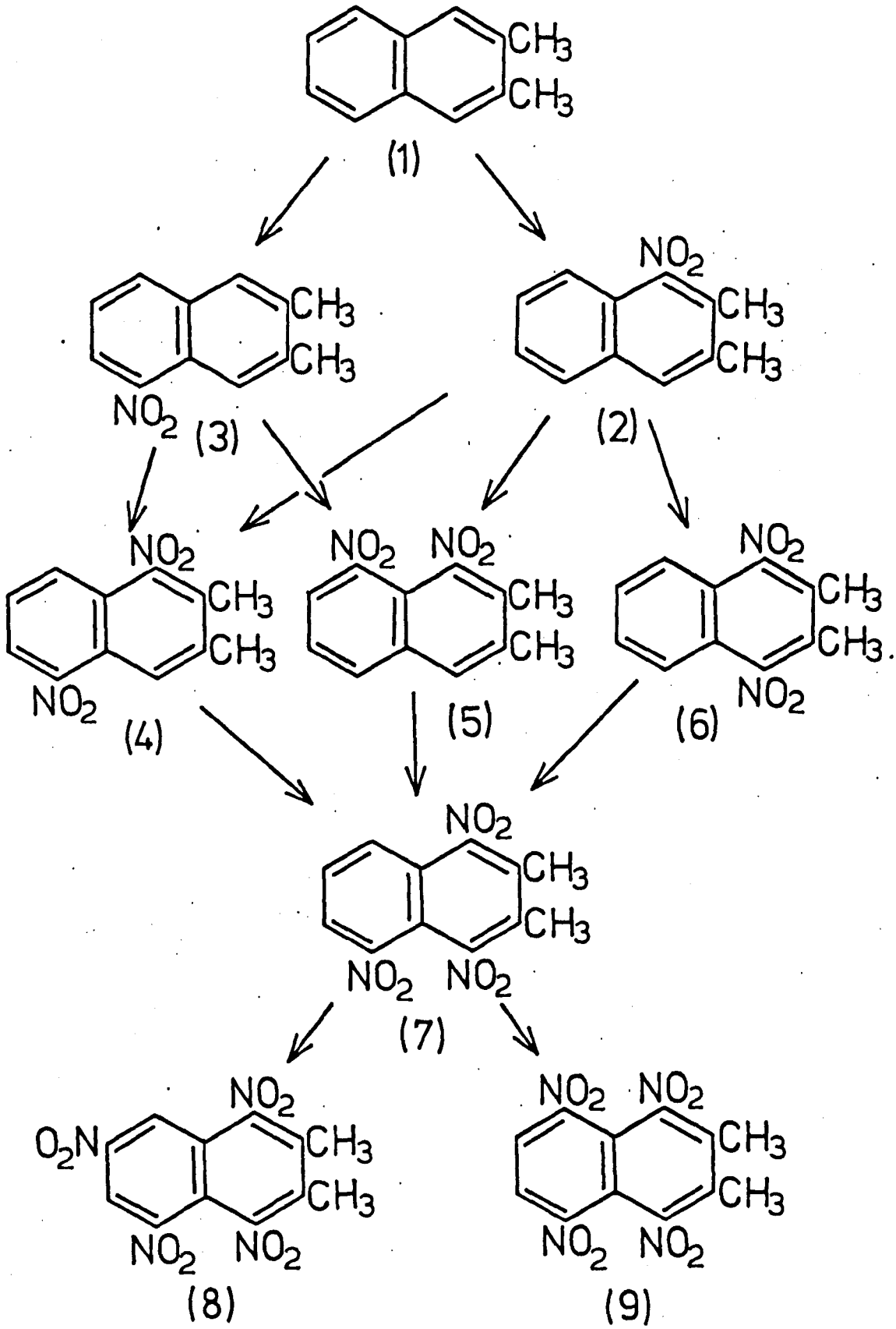


Fig.1.2.1 Direct synthetic route for the preparation of 1,4,5,7-and 1,4,5,8-tetranitro-2,3-dimethylnaphthalene.

possible as rapid decomposition of the product mixture occurred on all the stationary phases used. 1,4,5,8-tetranitro-2,3-dimethylnaphthalene(9) was confirmed as being present in the product mixture by comparing the NMR spectrum of the mixture with the NMR spectrum of a pure sample of compound 9 obtained by an indirect method (see section 1.2.6).

1,4,5,7-tetranitro-2,3-dimethylnaphthalene was also obtained by the nitration of 1-nitro-2,3-dimethylnaphthalene using an excess of nitric acid in sulphuric acid. It is fair to conclude that the synthetic route involved the intermediacy of 1,4-,1,5-and 1,8-dinitro-2,3-dimethylnaphthalene,and 1,4,5-trinitro-2,3-dimethylnaphthalene,as shown in fig.1.2.1.

Attempts were made to obtain pentanitro derivatives of 2,3-dimethylnaphthalene by the nitration of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene in forcing conditions. However,it was found that only oxidation occurred under these conditions.

(B) Nitro-2,3-Dimethylnaphthalenes Prepared by Indirect Methods

1.2.4 5,8-Dinitro-2,3-Dimethylnaphthalene

The synthesis of 5,8-dinitro-2,3-dimethylnaphthalene(11) could not be carried out by direct nitration methods,since this compound has a greater number of nitro groups in the non-methylated ring than in the methylated ring. Two synthetic routes were employed for this synthesis,both involving the intermediacy of 5-nitro-2,3-dimethylnaphthalene. The first method

(fig.1.2.2 - Route A) involved the treatment of 5-nitro-2,3-dimethylnaphthalene(3) with alkaline hydroxylamine to give 5-amino-8-nitro-2,3-dimethylnaphthalene(10). Diazotisation of this latter compound,followed by treatment with sodium nitrite resulted in the replacement of the amino group with a nitro group to give 5,8-dinitro-2,3-dimethylnaphthalene(11). The second method (fig.1.2.2 - Route B) involved the reduction of 5-nitro-2,3-dimethyl-naphthalene to 5-amino-2,3-dimethylnaphthalene(12). This compound was then acetylated by treatment with acetic acid/acetic anhydride to give 5-acetamido-2,3-dimethyl-naphthalene(13). Nitration of compound 13,using sufficient nitric acid in acetic anhydride for mononitration only, yielded a mixture of 5-acetamido-8-nitro-2,3-dimethyl-naphthalene(14) and 5-acetamido-6-nitro-2,3-dimethyl-naphthalene(15),the function of the acetamido group in compound 13 having been not only to "protect" the 5-amino group,but also to provide *ortho/para* direction in the nitration. The yield of the *ortho*-substituted product (15) was found to be less than 5%,and was not isolated. The *para*-substituted product (14) was obtained in a pure state by fractional crystallisation. Compound 14 was then hydrolysed to 5-amino-8-nitro-2,3-dimethylnaphthalene(10), and converted to 5,8-dinitro-2,3-dimethylnaphthalene by the method indicated above.

1.2.5 <u>1,5,8-Trinitro-2,3-Dimethylnaphthalene</u>

5,8-dinitro-2,3-dimethylnaphthalene has two sites which are highly activated towards nitration,*viz* the 1- and 4-positions. Consequently,nitration of 5,8-dinitro-

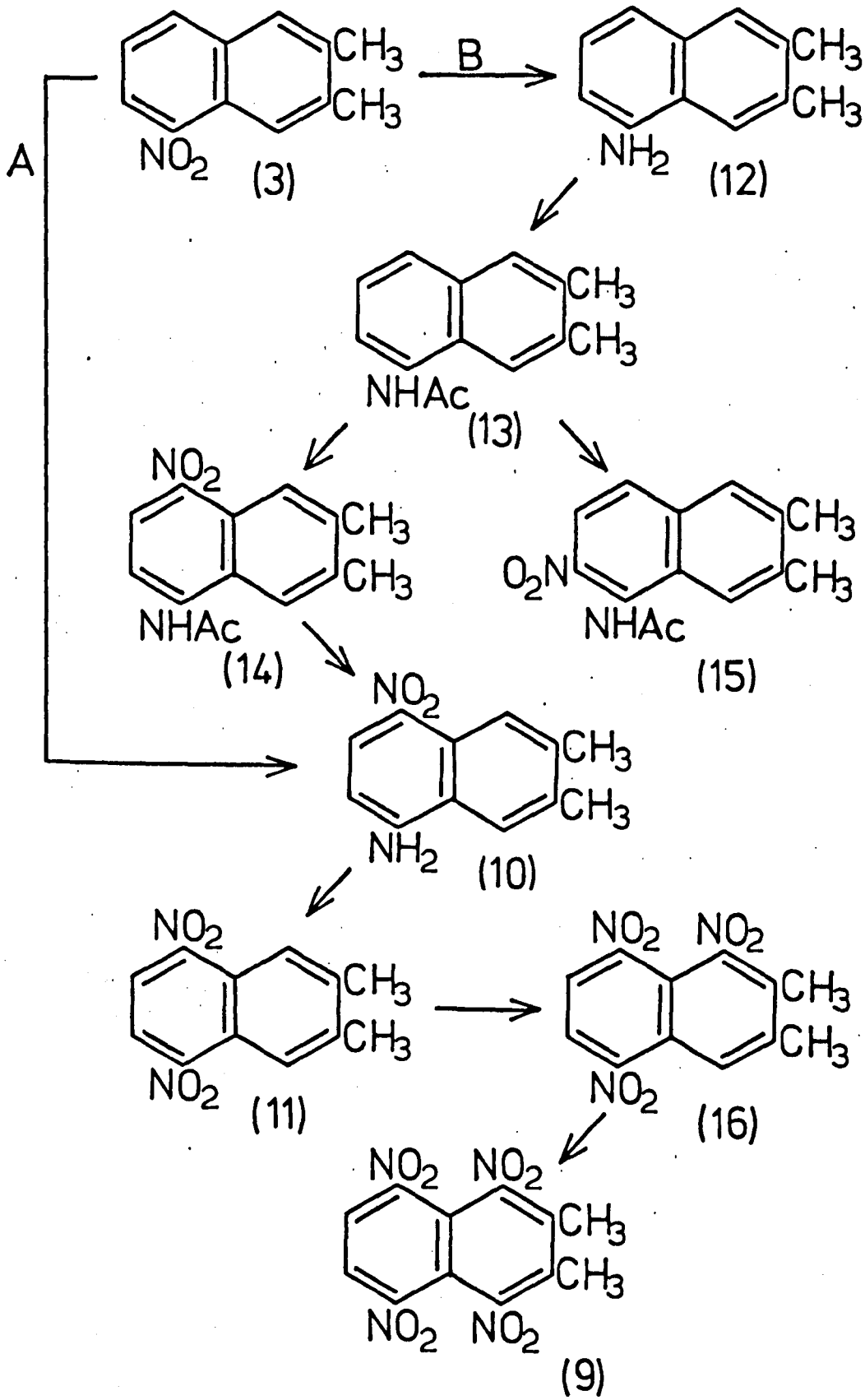


Fig.1.2.2 Indirect synthetic route for the preparation of 1,4,5,8-tetranitro-2,3-dimethylnaphthalene.

2,3-dimethylnaphthalene,using the calculated amount of nitric acid in sulphuric acid for nitration to the trinitro stage,resulted in substitution in the methylated ring only to give 1,5,8-trinitro-2,3-dimethylnaphthalene (16). Only one trinitro product was possible,as the 1- and 4-positions of 5,8-dinitro-2,3-dimethylnaphthalene are equivalent.

1.2.6 1,4,5,8-Tetranitro-2,3-Dimethylnaphthalene

1,4,5,8-tetranitro-2,3-dimethylnaphthalene(9) was prepared as a minor product (less than 5%) when 1,4,5-trinitro-2,3-dimethylnaphthalene was nitrated using mixed acid (see section 1.2.3). The former compound was synthesised and isolated in a pure state by the nitration of 1,5,8-trinitro-2,3-dimethylnaphthalene using mixed acid,and by the nitration of 5,8-dinitro-2,3-dimethyl-naphthalene using an excess of nitric acid in sulphuric acid. It may be concluded that 1,5,8-trinitro-2,3-dimethyl-naphthalene was an intermediate in the latter process (see fig.1.2.2).

Nitration of 1,4,5,8-tetranitro-2,3-dimethyl-naphthalene in forcing conditions did not produce any detectable amounts of pentanitro or hexanitro products.

1.2.7 5,7-Dinitro-2,3-Dimethylnaphthalene

5,7-dinitro-2,3-dimethylnaphthalene(19),like 5,8-dinitro-2,3-dimethylnaphthalene,contains a greater number of nitro groups in the non-methylated ring than in the methylated ring,and could not be synthesised by direct nitration methods. The method employed (fig.1.2.3) for the synthesis involved the conversion of 5-nitro-2,3-

dimethylnaphthalene(3) to 5-amino-2,3-dimethylnaphthalene (12),which was then acetylated to 5-acetamido-2,3-dimethyl naphthalene(13). Nitration of the latter compound using nitric acid in acetic anhydride resulted in substitution in the non-methylated ring only,to give 5-acetamido-6,8-dinitro-2,3-dimethylnaphthalene(17) as the sole product. Hydrolysis of compound 17 yielded 5-amino-6,8-dinitro-2,3-dimethylnaphthalene(18);the amino group of which was removed via diazotisation to give 5,7-dinitro-2,3-dimethyl-naphthalene(19).

1.2.8 <u>1,5,7-Trinitro-2,3-Dimethylnaphthalene and 1,6,8-Trinitro-2,3-Dimethylnaphthalene</u>

Nitration of 5,7-dinitro-2,3-dimethylnaphthalene using the calculated amount of nitric acid in sulphuric acid for conversion to the trinitro stage gave 1,5,7-trinitro-2,3-dimethylnaphthalene(20) and 1,6,8-trinitro-2,3-dimethylnaphthalene(21)(fig.1.2.3). In this particular case,the structures of the products could not be assigned from their NMR spectra because each spectrum exhibited the same number of resonances and the same splitting pattern. The two isomers were distinguished,however,by consideration of their respective mass spectra. It is known that polynitronaphthalenes having nitro groups on adjacent *peri*-positions,e.g.1,8-dinitronaphthalene,undergo fragmentation on electron impact to yield a stable $(M-NO_2)^+$ ion which gives rise to the base peak in the spectrum [99]. Where only one of an adjacent pair of *peri*-positions is occupied,e.g.1,5-dinitronaphthalene,the parent (M^+) ion gives rise to the base peak in the mass spectrum. These

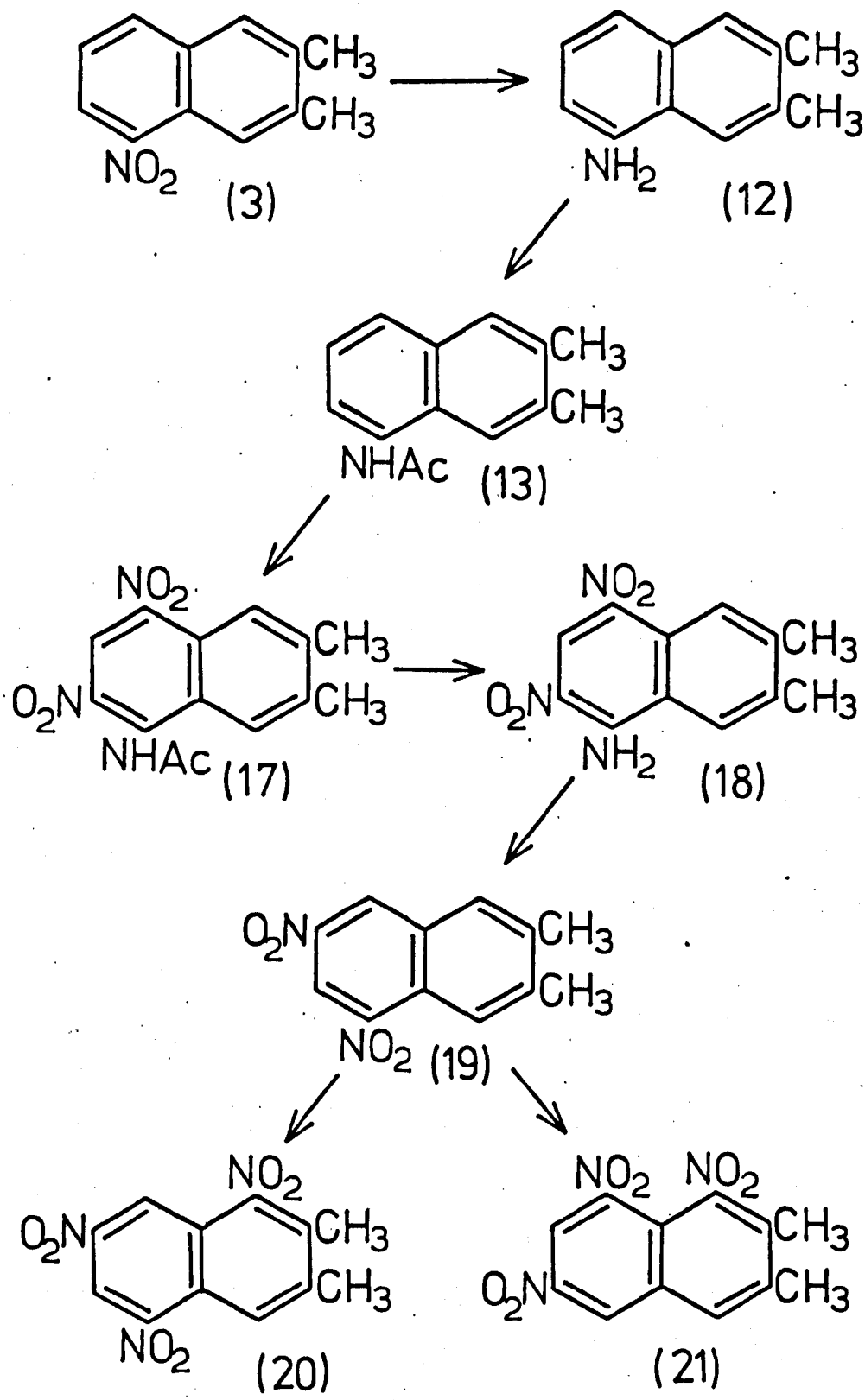


Fig.1.2.3 Synthetic route for the preparation of 1,5,7-and 1,6,8-trinitro-2,3-dimethylnaphthalene.

effects were clearly demonstrated in the positive ion mass spectra of 1,6,8-trinitro-2,3-dimethylnaphthalene and 1,5,7-trinitro-2,3-dimethylnaphthalene respectively (see Chapter 4).

The product ration of 1,5,7-trinitro-2,3-dimethylnaphthalene and 1,6,8-trinitro-2,3-dimethylnaphthalene was found to be *ca* 30:70,showing that nitration of 5,7-dinitro-2,3-dimethylnaphthalene occurred preferentially at the 4-position rather than at the sterically less hindered 1-position. This is probably because the 4-position is a *"meta"* position in relation to the nitro groups at the 5- and 7-positions,and as such is favoured for nitration over the 1-position,which is an *"ortho/para"* position with respect to the nitro groups.

1.2.9 5,6,8-Trinitro-2,3-Dimethylnaphthalene

Of the trinitro-2,3-dimethylnaphthalenes prepared in this work,5,6,8-trinitro-2,3-dimethylnaphthalene(22) is unique in that all three nitro groups are substituted in the non-methylated ring,and therefore this compound could not be synthesised by any direct nitration method. The synthesis was achieved via the intermediacy of 5-amino-6,8-dinitro-2,3-dimethylnaphthalene(18),which was prepared by the method outlined in section 1.2.7 and then converted to 5,6,8-trinitro-2,3-dimethylnaphthalene via diazotisation and treatment with sodium nitrite.

1.2.10 1,5,6,8-Tetranitro-2,3-Dimethylnaphthalene and 1,5,7,8-Tetranitro-2,3-Dimethylnaphthalene

Nitration of 5,6,8-trinitro-2,3-dimethylnaphthalene using the calculated amount of nitric acid in sulphuric

acid for conversion to the tetranitro stage gave a mixture of 1,5,6,8-tetranitro-2,3-dimethylnaphthalene(23) and 1,5,7,8-tetranitro-2,3-dimethylnaphthalene(24) in a ratio of *ca* 30:70. This indicated that the 4-position in 5,6,8-trinitro-2,3-dimethylnaphthalene is favoured over the 1-position with respect to nitration in mixed acid.

1.2.11 1,4,5,6,8-Pentanitro-2,3-Dimethylnaphthalene

Nitration of 5,6,8-trinitro-2,3-dimethylnaphthalene using an excess of nitric acid in sulphuric acid gave 1,4,5,6,8-pentanitro-2,3-dimethylnaphthalene(25) as the sole product. This is the most highly nitrated dimethylnaphthalene produced in this work,and it is worthwhile to observe that the synthesis was achieved using fairly mild nitration conditions,*viz* concentrated nitric acid and sulphuric acid. In contrast,the attempted forced nitration of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene using fuming mixed acids failed to introduce any extra nitro groups into the nucleus. This illustrates the importance of indirect synthetic methods in the production of nitroaromatic compounds.

1.2.12 Experimental Section

Unless otherwise stated,column chromatography was carried out with Merck silica gel(0.05-0.2mm) using 400 x 20mm columns,and eluting with 1:1 benzene-petroleum spirit(b.p.60-80^{o}). Mass spectral molecular weights were determined with an AEI MS9 mass spectrometer. NMR spectra were recorded on a Perkin-Elmer R10 spectrometer (tetramethylsilane as internal reference). The structures of the nitration products were assigned from NMR and mass

spectra.

(i) Synthesis of 1,4-dinitro-2,3-dimethylnaphthalene 1,5-dinitro-2,3-dimethylnaphthalene and 1,8-dinitro-2,3-dimethylnaphthalene

(a) Nitration of 5-nitro-2,3-dimethylnaphthalene - Nitric acid (*d* 1.42;0.5ml) was added dropwise during 0.5h to a solution of 5-nitro-2,3-dimethylnaphthalene(3)(1g) in acetic anhydride (10ml),the temperature being maintained below 10° in an ice-bath. After standing at 20° for 1h, the solution was poured into water (50ml). The precipitate was filtered off,washed with water,and dried *in vacuo* to give a pale yellow solid (1.06g). The first crop from recrystallisation of this solid from petroleum spirit (b.p.60-80°) gave *1,8-dinitro-2,3-dimethylnaphthalene*(5) (0.45g) m.p.243-5°(lit[95] 245°). (Found: C,58.2; H,4.5; N,11.3. $C_{12}H_{10}N_2O_4$ requires C,58.5; H,4.1; N,11.4%); τ($CDCl_3$) 2.0-2.5(4H,m),7.54(3H,s) and 7.61(3H,s); *m/e* 246 (M^+). The remaining crops were combined and column chromatographed to give two fractions. Evaporation of the first fraction to dryness gave *1,5-dinitro-2,3-dimethylnaphthalene*(4)(0.39g,32%),m.p.160°(Found: C,58.5; H,4.6; N,11.3. $C_{12}H_{10}N_2O_4$ requires C,58.5; H,4.1; N,11.4%); τ($CDCl_3$) 1.5-2.5(4H,m),7.49(3H,s) and 7.65(3H,s,broadened); *m/e* 246 (M^+). Evaporation of the second fraction to dryness gave (5)(0.14g;total 0.59g,48%).

(b) Nitration of 1-nitro-2,3-dimethylnaphthalene - Nitric acid (*d* 1.42;0.5ml) was added dropwise during 0.5h to a solution of 1-nitro-2,3-dimethylnaphthalene(2)(1g) in acetic anhydride (10ml),the temperature being maintained

below 10°. After standing at 20° for 1h, the solution was poured into cold water (50ml). The precipitate was filtered off, washed with water, and dried *in vacuo* to give a pale yellow solid (0.97g). The first crop from recrystallisation of the solid from petroleum spirit (b.p.60-80°) gave (5)(0.21g), m.p.245°. The remaining crops were combined and column chromatographed to give three fractions. Evaporation of the first fraction to dryness gave *1,4-dinitro-2,3-dimethylnaphthalene*(6)(0.28g,23%), m.p.197°. (Found: C,58.4; H,4.2; N,11.1. $C_{12}H_{10}N_2O_4$ requires C,58.5; H,4.1; N,11.4%); τ($CDCl_3$) 2.31(4H,s) and 7.58(6H,s); *m/e* 246 (M^+). Evaporation of the second fraction to dryness gave (4)(0.30g,25%), m.p.160°. Evaporation of the third fraction to dryness gave (5)(0.08g; total 0.29g,24%).

(c) Nitration of 2,3-dimethylnaphthalene - Nitric acid (*d* 1.42; 1ml) was added dropwise during 0.5h to a solution of 2,3-dimethylnaphthalene(1)(1g) in acetic anhydride (10ml) maintained in an ice-bath at below 10°. The mixture was then allowed to stand at 20° for 2h, and poured into water (50ml). The precipitated product was filtered off, washed with water, and dried *in vacuo* to give a pale yellow solid. The first crop from recrystallisation of the product from petroleum spirit (b.p.60-80°) and benzene (10:1) gave (5) (0.3g), m.p.243-5°. The residual solution was evaporated to small bulk, and column chromatographed to give three fractions. Evaporation of the first fraction to dryness gave (6)(0.26g,17%), m.p.197°. Evaporation of the second fraction to dryness gave (4)(0.35g,22%), m.p.160°. The

final fraction,upon evaporation to dryness,gave a further quantity of (5)(0.08g;total 0.38,24%).

(ii) *Synthesis of 1,4,5-trinitro-2,3-dimethylnaphthalene*

(a) *Nitration of 1,5-dinitro-2,3-dimethylnaphthalene* - A solution of 1,5-dinitro-2,3-dimethylnaphthalene (2g) in sulphuric acid (*d* 1.84;30ml) was prepared,and nitric acid (*d* 1.42;0.5ml) added dropwise during 10 min,with stirring. The mixture was allowed to stand at 20° for 2h,and poured onto crushed ice (50g). The precipitate was filtered off, washed with water,and dried *in vacuo* to give a white solid (2.1g). Recrystallisation from glacial acetic acid gave *1,4,5-trinitro-2,3-dimethylnaphthalene*(7)(2.0g,88%),m.p.175°. (Found: C,49.3; H,3.3; N,14.4. $C_{12}H_9N_3O_6$ requires C,49.5; H,3.1; N,14.4%); τ($CDCl_3$) 1.75-2.30(3H,m),7.50(3H,s) and 7.55(3H,s); *m/e* 291 (M^+).

(b) *Nitration of 1,8-dinitro-2,3-dimethylnaphthalene* - To a solution of 1,8-dinitro-2,3-dimethylnaphthalene (2g) in sulphuric acid (*d* 1.84;25ml) was added during 15 min nitric acid (*d* 1.42;0.5ml),with stirring. The mixture was stirred for a further 2h,and poured onto crushed ice (50g). The precipitate was filtered off,washed with water, and dried *in vacuo* to give a white solid (1.9g,81%). The NMR spectrum was found to consist only of that of (7); there was no evidence for the presence of any other compound.

(c) *Nitration of 1,4-dinitro-2,3-dimethylnaphthalene* - To a solution of 1,4-dinitro-2,3-dimethylnaphthalene in sulphuric acid (*d* 1.84;30ml) was added nitric acid (*d* 1.42; 0.5ml) dropwise,with stirring. The stirring was continued for 1h,and then the mixture was poured onto crushed ice (50g).

The precipitate was filtered off,washed with water,and dried *in vacuo* to give a white solid (1.6g,68%). As far as could be seen from the NMR spectrum of the product,the only compound present was (7),with no evidence for the presence of any other compound.

(iii) *Synthesis of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene*

(a) *Nitration of 1,4,5-trinitro-2,3-dimethylnaphthalene* - Nitric acid (*d* 1.42;1.5ml) was added to a solution of 1,4,5-trinitro-2,3-dimethylnaphthalene (1g) in sulphuric acid (*d* 1.84;30ml). The mixture was stirred for 1h,and then poured onto crushed ice (50g). The precipitate was filtered off,washed with water,and dried *in vacuo* to give a white solid (1.05g). The NMR spectrum of the product showed that it was a *ca* 95:5 mixture of *1,4,5,7-tetranitro-2,3-dimethylnaphthalene*(8) and *1,4,5,8-tetranitro-2,3-dimethylnaphthalene*(9). Recrystallisation of the product mixture from glacial acetic acid gave pure (8)(0.97g,84%), m.p.279°. (Found: C,42.9; H,2.5; N,16.2. $C_{12}H_8N_4O_8$ requires C,42.9; H,2.4; N,16.7%); τ($CDCl_3$) 1.07 and 1.22(2H,ABq,J_{AB} 2Hz), 7.37(3H,s) and 7.44(3H,s); *m/e* 336 (M^+). Evaporation of the mother liquor to dryness gave a residue from which it was not possible to obtain (9),since all attempts at column chromatography failed due to heavy decomposition on the stationary phases employed.

(b) *Nitration of 1-nitro-2,3-dimethylnaphthalene* - Nitric acid (*d* 1.42;2ml) was added dropwise,with stirring to a solution of 1-nitro-2,3-dimethylnaphthalene (1g) in sulphuric acid (*d* 1.84;25ml). Stirring was continued for 1h,and the mixture was then poured onto crushed ice (50g).

The precipitate was filtered off,washed with water,and dried *in vacuo* to give a white solid (1.3g). The NMR spectrum of a sample of the solid indicated that the ratio of (8) to (9) was similar to that obtained by the nitration of 1,4,5-trinitro-2,3-dimethylnaphthalene. Recrystallisation of the product mixture from glacial acetic acid yielded (8)(1.15g,69%),m.p.279°.

Attempted further nitration of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene - 1,4,5,7-tetranitro-2,3-dimethylnaphthalene (0.1g) was dissolved in sulphuric acid (*d* 1.90; 5ml),and nitric acid (*d* 1.50;2ml) added. The mixture was stirred at 35° for 1 month,and then poured onto crushed ice (100g). No solid product was obtained; ether extraction of the aqueous solution yielded an oil of molecular weight *ca* 280,the IR spectrum of which suggested that oxidation to an acid had occurred. There was no evidence for the formation of any pentanitro- or hexanitro-2,3-dimethylnaphthalenes.

(iv) *Preparation of 5,8-dinitro-2,3-dimethylnaphthalene*

(a) A solution of 5-nitro-2,3-dimethylnaphthalene (1.1g) in 95% ethanol (10ml) was added to a solution of hydroxylamine hydrochloride (3g) in 95% ethanol (50ml), and the mixture maintained at 60° whilst a solution of potassium hydroxide (10g) in methanol (30ml) was added dropwise,with stirring,during 1h. Heavy deposition of potassium chloride was observed during the reaction. After stirring for 2h,the mixture was poured into water (300ml). The precipitate was filtered off,washed with water,and dried. Recrystallisation from 95% ethanol gave *5-amino-8-nitro-*

2,3-dimethylnaphthalene(10)(0.7g,54%),m.p.188°. (Found: C,66.4; H,5.5; N,13.0. $C_{12}H_{12}N_2O$ requires C,66.7; H,5.6; N,13.0%). Diazotisation of (10) was carried out by adding the solid (1g) to a mixture of sulphuric acid (*d* 1.84;4ml) and glacial acetic acid (25ml),and cooling to 5° in an ice-bath. The cooled mixture was added slowly to a solution of sodium nitrite (5g) in sulphuric acid (*d* 1.84;5ml). After standing for 0.5h,the red diazonium mixture was poured into a mixture of sodium nitrite (10g),sodium bicarbonate (20g) and water (200ml). The brown precipitate (0.7g) was filtered off,dried,and chromatographed to give *5,8-dinitro-2,3-dimethylnaphthalene*(11)(0.06g,5%),m.p.177°. (Found: C,58.2; H,4.4; N,11.3. $C_{12}H_{10}N_2O_4$ requires C,58.5; H,4.1; N,11.4%); τ($CDCl_3$) 1.82(2H,s),2.01(2H,s) and 7.48 (6H,s); *m/e* 246 (M^+).

(b) A solution of 5-nitro-2,3-dimethylnaphthalene (8.5g) in 95% ethanol (150ml) was refluxed with hydrazine hydrate (15ml) in the presence of 10% palladium on charcoal (0.1g) for 10h. Hot filtration,followed by cooling,gave *5-amino-2,3-dimethylnaphthalene*(12)(7.0g,96%),m.p.65°. (Found: C,84.3; H,7.5; N,8.1. $C_{12}H_{13}N$ requires C,84.2; H,7.6; N,8.2%). (12)(7g) was added to a mixture of glacial acetic acid (25ml) and acetic anhydride (25ml). Cooling resulted in the separation of *5-acetamido-2,3-dimethylnaphthalene*(13),which was filtered off,washed with water,and dried (8.0g,92%), m.p.162°. (Found: C,77.7; H,6.8; N,6.5. $C_{14}H_{15}NO$ requires C,77.8; H,7.0; N,6.6%). (13)(7g) was dissolved in acetic anhydride (70ml),and nitric acid (*d* 1.42;1.85ml) added dropwise whilst cooling in ice. The mixture was poured

into water (200ml),and the product filtered off and dried (4.5g). Recrystallisation from 95% ethanol gave *5-acetamido-8-nitro-2,3-dimethylnaphthalene*(14)(4.0g,53%),m.p.182°. (Found: C,65.0; H,5.4; N,11.0. $C_{14}H_{14}N_2O_3$ requires C,65.1; H,5.4; N,10.9%). 5-acetamido-6-nitro-2,3-dimethylnaphthalene (15) could not be obtained from the mother liquor,as no suitable stationary phase could be found for column chromatography. (14)(6.25g) was refluxed with 95% ethanol (100ml) and 70% sulphuric acid (10ml) for 3h. On cooling and pouring into N sodium hydroxide (300ml),5-amino-8-nitro-2,3-dimethylnaphthalene(10) was precipitated,and filtered off and dried (4.14,79%). (10)(1g) was added to a mixture of sulphuric acid (*d* 1.84;5ml) and glacial acetic acid (25ml),and cooled to 5°in an ice-bath. The cooled mixture was added to a solution of sodium nitrite (15g),sodium bicarbonate (25g) and water (200ml). The precipitate (0.6g) was filtered off,dried and column chromatographed to give 5,8-dinitro-2,3-dimethylnaphthalene(11)(0.05g,4%),m.p.177°.

(v) *Synthesis of 1,5,8-trinitro-2,3-dimethylnaphthalene*

A solution of nitric acid (*d* 1.42;0.25ml) in sulphuric acid (*d* 1.84;25ml) was prepared,and a portion (0.75ml) added to a solution of (11)(0.03g) in sulphuric acid (*d* 1.84;3ml). The mixture was stirred for 2h,and poured onto crushed ice (20g). The precipitate was filtered off,washed with water,and dried *in vacuo* to give *1,5,8-trinitro-2,3-dimethylnaphthalene*(16)(0.025g,70%),m.p.170°. (Found: C,42.9; H,3.5; N,14.1. $C_{12}H_9N_3O_6$ requires C,49.5; H,3.1; N,14.4%); τ($CDCl_3$) 1.67(1H,s),1.88(2H,s),7.38(3H,s) and 7.48(3H,s); *m/e* 291 (M^+).

(vi) *Synthesis of 1,4,5,8-tetranitro-2,3-dimethylnaphthalene*

(a) Nitration of 1,5,8-trinitro-2,3-dimethylnaphthalene - Nitric acid (*d* 1.42;0.05ml) was added to a solution of (16)(0.02g) in sulphuric acid (*d* 1.84;5ml). The mixture was stirred for 1h,and poured onto crushed ice (20g). The precipitate was filtered off,washed with water,and dried *in vacuo* to give 1,4,5,8-tetranitro-2,3-dimethylnaphthalene (9)(0.02g,87%),m.p.160° (dec.). (Found: C,42.3; H,2.1; N,16.1. $C_{12}H_8N_4O_8$ requires C,42.9; H,2.4; N,16.7%); τ($CDCl_3$) 1.80 (2H,s) and 7.42(6H,s); *m/e* 336 (M^+).

(b) Nitration of 5,8-dinitro-2,3-dimethylnaphthalene - Nitric acid (*d* 1.42;0.1ml) was added to a solution of (11) ((0.03g) in sulphuric acid (*d* 1.84;5ml). After stirring for 1h at 20°,the mixture was poured onto crushed ice (30g). The precipitate was filtered off,washed with water,and dried *in vacuo* to give (9)(0.035g,85%),m.p.160°(dec.).

Attempted further nitration of 1,4,5,8-tetranitro-2,3-dimethylnaphthalene -

A solution of (9)(0.01g) in a mixture of nitric acid (*d* 1.50;1ml) and sulphuric acid (*d* 1.90;5ml) was prepared, and was maintained at 50° for 1 day. The mixture was poured onto crushed ice (30g) and the solid precipitate removed as crop 1. The filtrate was neutralised with excess sodium bicarbonate (20g),and extracted with ether (2 x 50ml). The extract was dried with anhydrous magnesium sulphate (20g),and the solution evaporated to dryness to yield crop 2. The NMR spectrum of each crop indicated that only (9) was present.

(vii) <u>*Preparation of 5,7-dinitro-2,3-dimethylnaphthalene*</u>

5-acetamido-2,3-dimethylnaphthalene(13)(8g) was dissolved

in acetic anhydride (100ml),and nitric acid (*d* 1.50;4ml) added dropwise,with stirring,over a period of 15 min, the temperature being maintained below 10° in an ice-bath. The mixture was poured into water (500ml) and the product filtered off and dried. Recrystallisation from 95% ethanol gave *5-acetamido-6,8-dinitro-2,3-dimethylnaphthalene*(17) (4.6g,41%),m.p.190°. (Found: C,55.0; H,4.2; N,13.7. $C_{14}H_{13}N_3O_5$ requires C,55.5; H,4.3; N,13.9%). (17)(4.6g) was refluxed for 16h in 95% ethanol containing 70% sulphuric acid (15ml). Cooling and neutralising the reaction mixture with N sodium hydroxide (300ml) resulted in the precipitation of *5-amino-6,8-dinitro-2,3-dimethylnaphthalene*(18),which was filtered off and dried (3.0g,76%),m.p.150°. (Found: C,55.0; H,4.2; N,16.0. $C_{12}H_{11}N_3O_4$ requires C,55.2; H,4.2; N,16.1%). Diazotisation of (18) was effected by adding the solid (0.6g) to a mixture of sulphuric acid (*d* 1.84;2ml) and glacial acetic acid (15ml),the resulting mixture being cooled to 5° in an ice-bath,and then added to a solution of sodium nitrite (1g) in sulphuric acid (*d* 1.84;5ml). After standing for 0.5h,the red diazonium solution was poured into a solution of ferrous sulphate (10g) and ethylene glycol (20ml) in water (30ml). The brown precipitate was filtered off,dried,and column chromatographed to give *5,7-dinitro-2,3-dimethylnaphthalene*(19)(0.08g,14%),m.p.156°. (Found: C,58.2; H,4.4; N,11.3. $C_{12}H_{10}N_2O_4$ requires C,58.5; H,4.1; N,11.4%); τ($CDCl_3$) 1.10(2H,s),1.60(1H,s),2.08(1H,s), 7.43(3H,s) and 7.47(3H,s).(the singlet at τ1.10 was found to split into an AB quartet on addition of C_6D_6); *m/e* 246(M^+).

(viii) *Nitration of 5,7-dinitro-2,3-dimethylnaphthalene*

Nitric acid (*d* 1.42;0.12ml) was added to a solution of (19)(0.5g) in sulphuric acid (*d* 1.84;20ml). The mixture was stirred at 20° for 2h,and then poured onto crushed ice (50g). The precipitate was filtered off,washed with water, and dried *in vacuo* to give a pale yellow solid (0.4g). Column chromatography of the solid yielded two fractions. Evaporation of the first fraction to dryness gave *1,5,7-trinitro-2,3-dimethylnaphthalene*(20)(0.095g,16%),m.p.169° (yellow needles). (Found: C,49.3; H,3.5; N,14.6. $C_{12}H_9N_3O_6$ requires C,49.5; H,3.1; N,14.4%); τ($CDCl_3$) 1.05 and 1.21 (2H,ABq, J_{AB} 2Hz),1.46(1H,s),7.35(3H,s) and 7.54(3H,s); *m/e* 291 (M^+). Evaporation of the second fraction to dryness gave *1,6,8-trinitro-2,3-dimethylnaphthalene*(21)(0.232g,39%), m.p.178°(white needles). (Found: C,49.6; H,3.1; N,14.7. $C_{12}H_9N_3O_6$ requires C,49.5; H,3.1; N,14.4%); τ($CDCl_3$) 1.05 and 1.21(2H,ABq,J_{AB} 2Hz),1.84(1H,s),7.35(3H,s) and 7.46(3H,s); *m/e* 291 (M^+).

Preparation of 5,6,8-trinitro-2,3-dimethylnaphthalene

5-amino-6,8-dinitro-2,3-dimethylnaphthalene(18)(0.9g) was added to a mixture of sulphuric acid (*d* 1.84;1.5ml) and glacial acetic acid (15ml),and cooled to 5° in an ice-bath. The mixture was added to a solution of sodium nitrite (1g) in sulphuric acid (*d* 1.84;4ml),and allowed to stand for 0.5h. The red diazonium solution was poured into a mixture of sodium nitrite (7g),sodium bicarbonate (15g) and water (150ml) to give a buff-coloured precipitate,which was filtered off and dried. The product (0.3g) was chromatographed on a column of silica gel (350 x 20mm) using pure benzene as eluent to give *5,6,8-trinitro-2,3-dimethylnaphthalene*(22)

(0.15g,18%),m.p.152°. (Found: C,50.2; H,3.6; N,13.9. $C_{12}H_9N_3O_6$ requires C,49.5; H,3.1; N,14.4%); τ($CDCl_3$) 1.22 (1H,s),1.61(1H,s),2.35(1H,s),7.40(3H,s) and 7.45(3H,s); *m/e* 291 (M^+).

(ix) Nitration of 5,6,8-trinitro-2,3-dimethylnaphthalene

A solution of nitric acid (*d* 1.42;2.5ml) in sulphuric acid (*d* 1.84;25ml) was prepared,and a portion (0.4ml) added to a solution of (22)(0.2g) in sulphuric acid (*d* 1.84;6ml). The mixture was maintained at 35°for 1h,and then poured onto crushed ice (10g). The resulting precipitate was filtered off,washed with water,and dried *in vacuo* to give a white solid (0.2g). Elemental analysis showed that the product was a mixture of tetranitro-2,3-dimethylnaphthalenes. (Found: C,42.9; H,2.3; N,16.3. $C_{12}H_8N_4O_8$ requires C,42.9; H,2.4; N,16.7%). The NMR spectrum of a sample of the product in $CDCl_3$ showed that it was a *ca* 70:30 mixture of *1,5,6,8-tetranitro-2,3-dimethylnaphthalene*(23) and *1,5,7,8-tetranitro-2,3-dimethylnaphthalene*(24); τ(23) 1.40(1H,s), 1.60(1H,s),7.43(3H,s) and 7.54(3H,s); τ(24) 1.23(1H,s), 2.18(1H,s),7.35(3H,s) and 7.43(3H,s). Attempts were made to separate the mixture by column chromatography. However, the products proved inseparable due to decomposition on the various stationary phases used.

(x) Synthesis of 1,4,5,6,8-pentanitro-2,3-dimethylnaphthalene

Nitric acid (*d* 1.42;1ml) was added to a solution of (22)(0.13g) in sulphuric acid (*d* 1.84;10ml). The mixture was stirred at 50°for 2h,and then poured onto crushed ice (50g). The resulting precipitate was filtered off,washed with water, and dried *in vacuo* to give *1,4,5,6,8-pentanitro-2,3-dimethyl-*

naphthalene(25)(0.05g,34%),m.p.175°. (Found: C,37.2; H,2.4; N,17.8. $C_{12}H_7N_5O_{10}$ requires C,37.8; H,1.8; N,18.4%); τ($CDCl_3$) 0.81(1H,s),7.29(3H,s) and 7.36(3H,s); *m/e* 381 (M^+).

1.3 The Synthesis of Nitro-1,5-Dimethylnaphthalenes

(A) Nitro-1,5-Dimethylnaphthalenes Prepared by Direct Methods

1.3.1 4,8-Dinitro-1,5-Dimethylnaphthalene

Nitration of 1,5-dimethylnaphthalene(26) using fuming nitric acid/1,2-dichloroethane gave 4-nitro-1,5-dimethylnaphthalene(27) in greater than 98% yield. Nitration of the latter compound using an excess of fuming nitric acid in 1,2-dichloroethane resulted in the substitution of a second nitro group into the aromatic nucleus and,as far as could be determined by NMR spectroscopy,4,8-dinitro-1,5-dimethylnaphthalene(28) was the sole product.

1.3.2 4,6-Dinitro-1,5-Dimethylnaphthalene

4,6-dinitro-1,5-dimethylnaphthalene(29) has one nitro group *para* to the 1-methyl group,and one nitro group *ortho* to the 5-methyl group. The synthesis of this compound was therefore achieved by the nitration of 4-nitro-1,5-dimethylnaphthalene using nitric acid in acetic anhydride, a reagent which has the characteristic of inserting nitro groups *ortho* as well as *para* to a methyl group in an aromatic ring. A mixture of 4,8-dinitro-1,5-dimethylnaphthalene and 4,6-dinitro-1,5-dimethylnaphthalene was obtained in a ratio of *ca* 3:1. A discussion of the isomer proportions obtained in this reaction is given in Chapter 3.

1.3.3 2,4,8-Trinitro-1,5-Dimethylnaphthalene

Nitration of either 4,6-dinitro-1,5-dimethylnaphthalene or 4,8-dinitro-1,5-dimethylnaphthalene using the calculated amount of nitric acid in sulphuric acid for conversion to the trinitro stage produced 2,4,8-trinitro-1,5-dimethylnaphthalene(30). Only one trinitro product

is possible from the nitration of 4,8-dinitro-1,5-dimethylnaphthalene,but in the case of 4,6-dinitro-1,5-dimethylnaphthalene it might be expected that 2,4,6-trinitro-1,5-dimethylnaphthalene would be formed in addition to 2,4,8-trinitro-1,5-dimethylnaphthalene. However,the NMR spectrum of the product indicated that only the latter compound was present. Obviously nitration at the position *ortho* to the

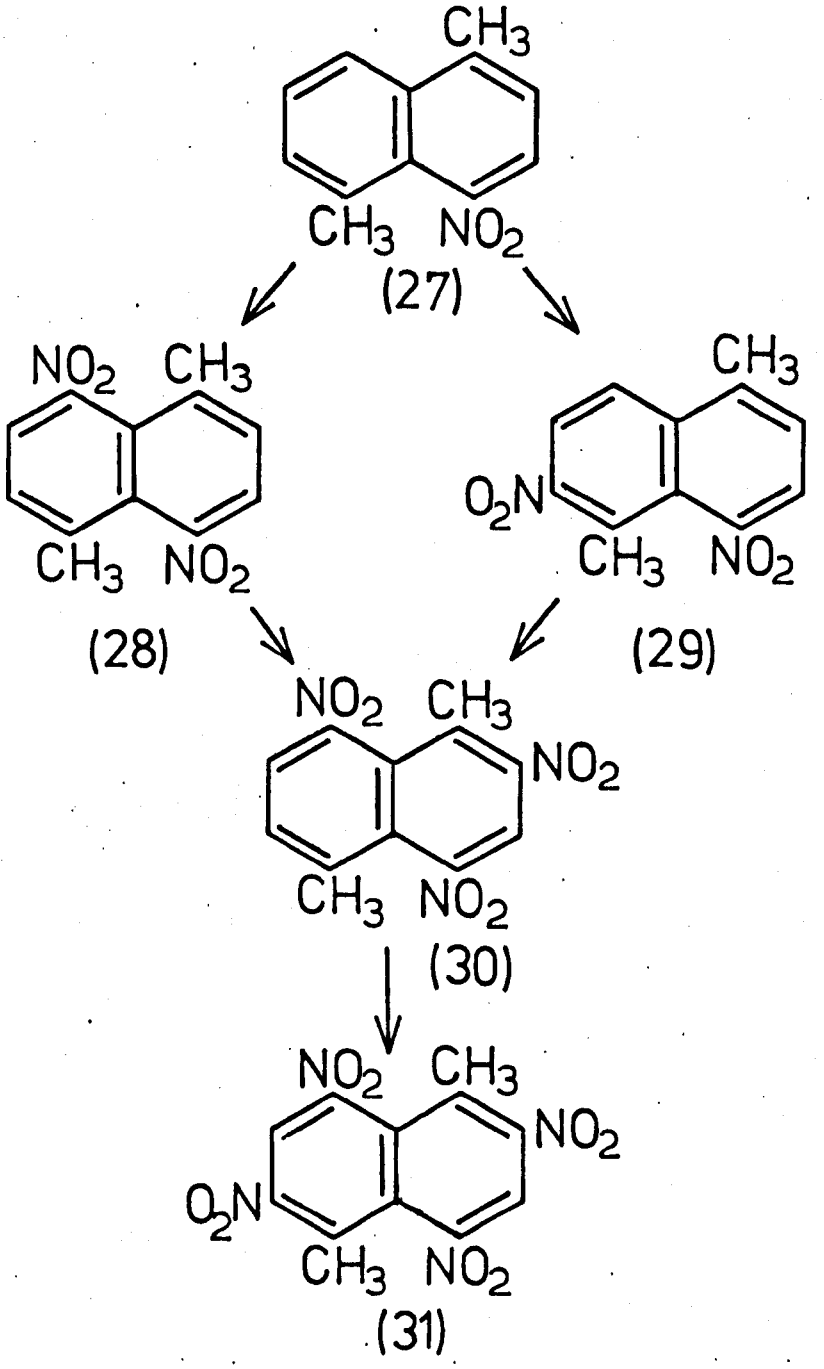


Fig.1.3.1 Synthetic route for the preparation of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene.

1-methyl group in 4,6-dinitro-1,5-dimethylnaphthalene is much slower than nitration at the position *peri* to the 1-methyl group,probably partly due to steric effects.

1.3.4 2,4,6,8-Tetranitro-1,5-Dimethylnaphthalene

2,4,6,8-tetranitro-1,5-dimethylnaphthalene(31) was prepared by the nitration of 2,4,8-trinitro-1,5-dimethylnaphthalene using nitric acid in sulphuric acid,and by the nitration of 4-nitro-1,5-dimethylnaphthalene using an excess of nitric acid in sulphuric acid. The steps postulated for the latter reaction are shown in fig.1.3.1.

(B) Nitro-1,5-Dimethylnaphthalenes Prepared by Indirect Methods

1.3.5 3-Nitro-1,5-Dimethylnaphthalene

Nitro derivatives of 1,5-dimethylnaphthalene containing a nitro group substituted *meta* to a methyl group cannot be synthesised by direct nitration methods. To date only *ortho* and *para* nitro derivatives of 1,5-dimethylnaphthalene have been reported in the literature[94]. The synthesis of 3-nitro-1,5-dimethylnaphthalene(36) was achieved by first reducing 4-nitro-1,5-dimethylnaphthalene to 4-amino-1,5-dimethylnaphthalene(32). This latter compound was formylated to give 4-formamido-1,5-dimethylnaphthalene(33). The formamido group directs nitro groups *ortho* to itself when nitric acid in acetic anhydride is used as the nitration medium,and this effect is stronger than the *ortho/para* directing effect of the methyl group in the same ring. Thus nitration of 4-formamido-1,5-dimethylnaphthalene yielded 4-formamido-3-nitro-1,5-dimethylnaphthalene(34),hydrolysis of which gave 4-amino-3-nitro-1,5-dimethylnaphthalene(35). Removal of the amino group of the latter compound via

diazotisation yielded 3-nitro-1,5-dimethylnaphthalene.

1.3.6 2,4,7-Trinitro-1,5-Dimethylnaphthalene

The synthesis of 2,4,7-trinitro-1,5-dimethylnaphthalene(38) was achieved by the nitration of 3-nitro-1,5-dimethylnaphthalene using the calculated amount of nitric acid in sulphuric acid for conversion to the trinitro stage. A small quantity of a dinitro product, identified as 4,7-dinitro-1,5-dimethylnaphthalene(37) was also obtained,and was separated from the main product by column chromatography. There was no trace of the *ortho* substituted product,3,6-dinitro-1,5-dimethylnaphthalene, and it must be concluded that nitration under these conditions occurs preferentially at the position *para* to the 5-methyl group in 3-nitro-1,5-dimethylnaphthalene.

An attempt was made to nitrate 2,4,7-trinitro-1,5-dimethylnaphthalene in forcing conditions using fuming mixed acids,in order to obtain tetranitro- and pentanitro-1,5-dimethylnaphthalenes. However,this was found to result in the oxidation of the methyl groups.

1.3.7 Experimental Section

(i) Synthesis of 4,8-dinitro-1,5-dimethylnaphthalene

1,5-dimethylnaphthalene(26)(1g) was dissolved in 1,2-dichloroethane (50ml),and nitric acid (*d* 1.50;0.8ml) added dropwise, with stirring,over a period of 15 min,the reaction being cooled in an ice-bath. After standing at 20° for 1h,the reaction mixture was washed with water (2 x 50ml),dried with magnesium sulphate,and the solvent removed to yield *4-nitro-1,5-dimethylnaphthalene*(27)(1.2g,93%),m.p.62° (lit.m.p.62-3°[94]). (27)(0.5g) was dissolved in 1,2-dichloro-

ethane (50ml),and nitric acid (*d* 1.50;1ml) added dropwise, with stirring,over a period of 10 min,the reaction being cooled in an ice-bath. The mixture was allowed to stand at 20° for 1h,and then washed with water (2 x 100ml),dried with magnesium sulphate,and the solvent removed to yield a yellow solid (0.6g). Recrystallisation from benzene afforded *4,8-dinitro-1,5-dimethylnaphthalene*(28)(0.55g,89%), m.p.171°(long needles). (Found: C,58.2; H,4.3; N,11.3. $C_{12}H_{10}N_2O_4$ requires C,58.5; H,4.3; N,11.4%); τ($CDCl_3$) 2.1 and 2.5(4H,ABq,J_{AB} 8Hz),7.4(6H,s); *m/e* 246 (M^+).

(ii) *Synthesis of 4,6-dinitro-1,5-dimethylnaphthalene*

4-nitro-1,5-dimethylnaphthalene (1g) was dissolved in acetic anhydride(50ml),and nitric acid (*d*1.50;2ml) added dropwise,with stirring,over a period of 0.5h,the reaction mixture being cooled in a ice-bath. After standing at 20° for 2h,the acetic anhydride solution was hydrolysed by pouring into water (200ml),and the solid product (0.6g) collected. Column chromatography gave two yellow bands, which were removed as individual fractions. Evaporation of the first fraction to dryness gave (28)(0.26g,21%). Evaporation of the second fraction to dryness gave *4,6-dinitro-1,5-dimethylnaphthalene*(29)(0.08g,7%),m.p.165°. (Found: C,58.6; H,4.0; N,11.1. $C_{12}H_{10}N_2O_4$ requires C,58.5; H,4.1; N,11.4%); τ($CDCl_3$) 1.9 and 2.15(2H,ABq,J_{AB} 9Hz),2.1 and 2.25(2H,ABq,J_{AB} 7Hz),7.20(3H,s),and 7.50(3H,s); *m/e* 246 (M^+).

(iii) *Synthesis of 2,4,8-trinitro-1,5-dimethylnaphthalene*

(a) *Nitration of 4,8-dinitro-1,5-dimethylnaphthalene* - (28)(0.4g) was dissolved in sulphuric acid (*d* 1.84;10ml), and nitric acid (*d* 1.42;0.1ml) added. The mixture was

stirred at 20° for 0.5h, and then poured onto crushed ice (20g). A white solid was obtained which upon recrystallisation from glacial acetic acid yielded *2,4,8-trinitro-1,5-dimethylnaphthalene*(30)(0.32g,67%), m.p.220°. (Found: C,49.6; H,3.1; N,14.7%. $C_{12}H_9N_3O_6$ requires C,49.5; H,3.1; N,14.4%); τ($CDCl_3$) 1.8(1H,s), 1.9 and 2.3(2H,ABq, J_{AB} 7Hz), and 7.35(6H,s); *m/e* 291(M^+).

(b) Nitration of 4,6-dinitro-1,5-dimethylnaphthalene - (29)(0.1g) was dissolved in sulphuric acid (*d* 1.84;10ml), and nitric acid (*d* 1.42;0.025ml) added. After stirring at 20° for 0.5h, the mixture was poured onto crushed ice (20g), and the product collected (0.09g,76%). The NMR spectrum of the product indicated that only 2,4,8-trinitro-1,5-dimethylnaphthalene was present; there was no evidence for the formation of 2,4,6-trinitro-1,5-dimethylnaphthalene.

(iv) <u>*Synthesis of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene*</u>.

(a) Nitration of 2,4,8-trinitro-1,5-dimethylnaphthalene - (30)(0.3g) was dissolved in sulphuric acid (*d* 1.84;5ml), and nitric acid (*d* 1.42;0.4ml) added dropwise. After stirring at 20° for 1h, the reaction mixture was poured onto ice (20g), and the solid product collected. Recrystallisation from glacial acetic acid gave *2,4,6,8-tetranitro-1,5-dimethylnaphthalene*(31)(0.31g,90%), m.p.239° (rhomboidal crystals). (Found: C,42.9; H,2.5; N,16.2. $C_{12}H_8N_4O_8$ requires C,42.9; H,2.4; N,16.7%); τ(CD_3COCD_3) 0.8(2H,s) and 7.50(6H,s); *m/e* 336 (M^+).

(b) Nitration of 4-nitro-1,5-dimethylnaphthalene - (27)(0.2g) was dissolved in sulphuric acid (*d* 1.84;5ml), and nitric acid (*d* 1.42;0.5ml) added dropwise. After stirring for 3h at 20°, the mixture was poured onto crushed ice (20g), and the

solid product collected. Recrystallisation from glacial acetic acid gave (31)(0.21g,88%),m.p.239°.

(v) Synthesis of 3-nitro-1,5-dimethylnaphthalene

4-nitro-1,5-dimethylnaphthalene (6.2g) was dissolved in 95% ethanol (100ml),and refluxed with hydrazine hydrate (20ml) in the presence of 10% palladium on charcoal (0.1g) for 5h. Hot filtration,followed by cooling,yielded *4-amino-1,5-dimethylnaphthalene*(32)(5.1g,90%),m.p.55°. (Found: C,83.7; H,7.6; N,8.2. $C_{12}H_{13}N$ requires C,84.2; H,7.6; N,8.2%). (32)(5.1g) was dissolved in 90% formic acid (10ml), and refluxed for 1h. On cooling,*4-formamido-1,5-dimethylnaphthalene*(33) precipitated,and was filtered off,washed with water,and dried,(5.3g,89%)m.p.140°. (Found: C,77.8; H,6.1; N,7.4. $C_{13}H_{13}NO$ requires C,78.4; H,6.5; N,7.0%). (33)(5.3g) was dissolved in acetic anhydride (25ml) and acetic acid (25ml). To this solution was added nitric acid (*d* 1.42;1.7ml) with stirring and cooling in an ice-bath. After standing for 1h,the solution was hydrolysed in water, and the fawn-coloured product collected. Recrystallisation from 95% ethanol gave *4-formamido-3-nitro-1,5-dimethylnaphthalene*(34)(3g,46%),m.p.156°. (Found: C,63.5; H,4.8; N,11.3. $C_{13}H_{12}N_2O_3$ requires C,63.9; H,4.9: N,11.4%). (34) (3g) was refluxed in a mixture of methanol (30ml) and hydrochloric acid (*d* 1.18;3ml) for 2h. On cooling and neutralising with N sodium hydroxide (300ml),*4-amino-3-nitro-1,5-dimethylnaphthalene*(35) was obtained (2.2g;83%),m.p.129°. (Found: C,66.4; H,5.5; N,13.0. $C_{12}H_{12}N_2O_2$ requires C,66.7; H,5.6; N,13.0%). (35)(2.2g) was dissolved in acetic acid (50ml) to which was added a solution of sodium nitrite (3g)

in sulphuric acid (*d* 1.84;10ml). After standing for 0.5h, the red diazonium solution was poured into a mixture of ferrous sulphate (15g),water (200ml) and ethylene glycol (50ml). A brown solid (0.9g) was obtained which was column chromatographed to give *3-nitro-1,5-dimethylnaphthalene* (36)(0.38g,19%),m.p.92°. (Found: C,72.0; H,5.9; N,6.7. $C_{12}H_{11}NO_2$ requires C,71.6; H,5.5; N,7.0%); τ(CCl_4) 1.30-2.60 (5H,m) and 7.20(6H,s); *m/e* 201 (M^+).

(vi) *Synthesis of 2,4,7-trinitro-1,5-dimethylnaphthalene* (36)(0.28g) was dissolved in sulphuric acid (*d* 1.84;10ml), and nitric acid (*d* 1.42;0.18ml) added,with stirring. The reaction mixture was allowed to stand at 20°for 1h,and then poured onto crushed ice (20g). The product was filtered off,washed with water,and dried (0.22g). Column chromatography of the product gave two yellow bands,one strong and one weak,which were removed as individual fractions. Evaporation of the first fraction to dryness gave *2,4,7-trinitro-1,5-dimethylnaphthalene*(38)(0.17g,42%),m.p.169°. (Found: C,49.3; H,3.5; N,14.6. $C_{12}H_9N_3O_6$ requires C,49.5; H,3.1; N,14.4%); τ($CDCl_3$) 0.8 and 1.55(2H,ABq,J_{AB} 2Hz),1.70(1H,s),6.98(3H,s) and 7.30(3H,s); *m/e* 291 (M^+). Evaporation of the second fraction to dryness gave *4,7-dinitro-1,5-dimethylnaphthalene* (37)(0.008g),m.p.146°. (Found: C,58.0; H,4.2; N,11.3. $C_{12}H_{10}N_2O_4$ requires C,58.5; H,4.1; N,11.4%); τ($CDCl_3$) 1.55 and 2.30(2H,ABq,J_{AB} 2Hz),2.00 and 2.81(2H,ABq,J_{AB} 7Hz),7.18 (3H,s),and 7.40(3H,s); *m/e* 246 (M^+).

Attempted further nitration of 2,4,7-trinitro-1,5-dimethylnaphthalene - (38)(0.1g) was dissolved in sulphuric acid (*d* 1.90;5ml),and nitric acid (*d* 1.50;2ml) added. The mixture

was maintained at 50°for 1 month,and then poured onto crushed ice. A small quantity of solid product was obtained, the infrared spectrum of which suggested that oxidation to acids or hydroxy-compounds had taken place.

Chapter Two. Reactions of Base with Nitro-1,5-Dimethylnaphthalenes and Nitro-2,3-Dimethylnaphthalenes

2.1 Introductory Survey.

2.2 Reactions of Base with Nitro-2,3-Dimethylnaphthalenes.

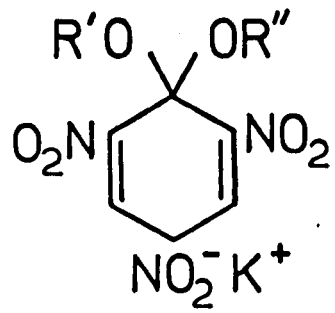
2.3 Reactions of Base with Nitro-1,5-Dimethylnaphthalenes.

2.4 Interactions of Weak Lewis Bases with Nitro-1,5-Dimethylnaphthalenes and Nitro-2,3-Dimethylnaphthalenes.

2.1 Introductory Survey

2.1.1 Meisenheimer Complexes

It is well known that nitroaromatic compounds will react with bases to yield highly coloured solutions, and indeed investigations into these reactions have been in progress since the late nineteenth century[100,101]. In 1900, Jackson [102] isolated solid products from the reactions of alkoxides with alkyl picrates, and proposed that the products possessed "quinoidal" structures resulting from addition at the 1-position, as in I (fig.2.1.1).

I 

R', R" = alkyl

Fig.2.1.1

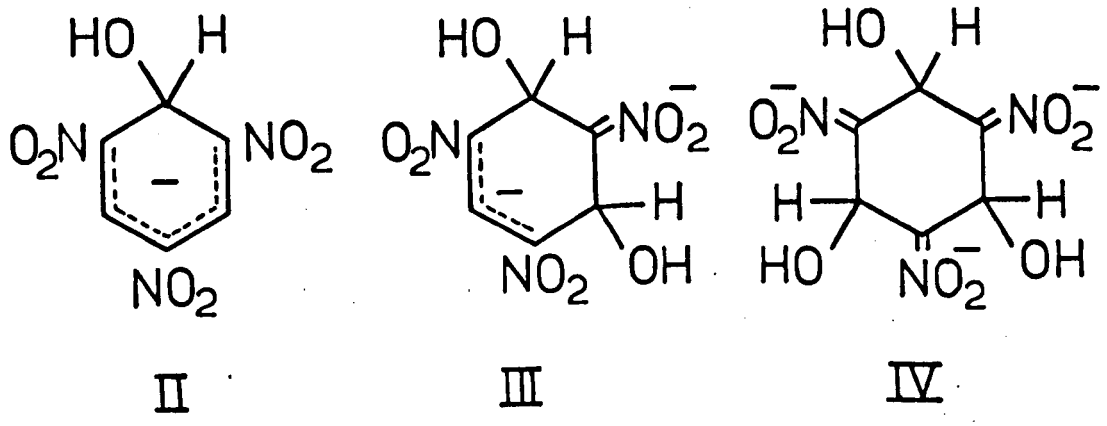
Such structures were preferred to those resulting from addition of an alkoxy group at a nuclear site occupied by a nitro group[103], or from the abstraction of a nuclear hydrogen atom [104]. Confirmation of Jackson's structure was obtained in 1902 by Meisenheimer[105], who obtained the same product from the reaction of ethoxide with methyl picrate as from the reaction of methoxide with ethyl picrate. This class of complex, in which two alkoxy groups are substituted at a single site in a cyclohexadienate ring, subsequently became known as "Meisenheimer complexes", though this name is now used to describe all anionic sigma-

complexes. These complexes are of great significance as they are formally analagous to the "Wheland intermediates" involved in nucleophilic aromatic substitution.

2.1.2 Methods of Investigating Meisenheimer Complexes

(a) Ultraviolet-Visible Spectroscopy

It is a characteristic of Meisenheimer complexes that their solutions absorb light strongly in the visible region. The reactions of 1,3,5-trinitrobenzene and some 1-substituted 2,4,6-trinitrobenzenes with bases have been investigated,and the ultraviolet-visible spectra of the resulting systems compared[106-114]. The transitions which result in the absorption of light in the visible region have been attributed to charge-transfer between the ring and the nitro groups[115],and consequently the forms of the spectra are dependent upon the extent of delocalisation in the ring systems. For example,the spectrum of the 1:1 complex of 1,3,5-trinitrobenzene with hydroxide ion (II) consists of two peaks at λ_{max} 445 and 485nm [116]. On increasing the concentration of base to yield a 2:1 complex (III), the spectrum changes to one containing a single peak at λ_{max} 500nm [116]. Finally,on increasing the base concentration to yield a 3:1 complex (IV),no visible absorption can be observed [117]. The stages in the addition of hydroxide ion are shown in fig.2.1.2. The observations with regard to peak maxima have been shown to be consistent with H.M.O. calculations [118]. Thus in II,there is extensive delocalisation, and two visible maxima would be predicted. In III,only one peak would be expected,the delocalisation being less than in II. In IV there is no delocalisation in the ring,and



II III IV

Fig.2.1.2

no visible maxima would be expected as the $C=NO_2^-$ chromophore only gives rise to absorption in the ultraviolet region.

Visible spectroscopy provides a ready means of indicating that a Meisenheimer complex is present in a solution because the spectra of most 1:1 complexes are very similar,consisting of two distinct maxima in the visible region,the molar extinction coefficient of the longer wavelength band being about half that of the shorter wavelength band[119]. However,the positions of the maxima,and their molar extinction coefficients,are dependent upon the solvent systems used. Thus the spectrum of the Meisenheimer complex resulting from attack of methoxide ion at the 1-position in anisole consists of two peaks at λ_{max} 414 and 487nm,with molar extinction coefficients in a ratio of 1.44:1,when recorded in methanol solution[120]. On changing the solvent to tetrahydrofuran,the peaks appear at 407 and 504nm,with molar extinction coefficients in a ratio of 1.19:1[120]. There does not seem to be any simple way of correlating these effects with any single physical property of the solvent.

(b) Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectroscopy has proved to be of considerable importance in the investigation of Meisenheimer complexes. It is fair to say that since 1964,when NMR spectroscopy was first applied to the study of Meisenheimer complexes, more work has been done on the subject than had been accomplished in the previous 80 years. This is because proton NMR spectroscopy gives information about the environment of hydrogen atoms in a complex,and thus provides structural information directly,unlike visible spectroscopy, which can only indicate the class of complex present,e.g. 1:1,1:2,1:3,and cannot distinguish complexes of the same type. Thus attack of a nucleophile at a ring position occupied by a hydrogen atom or a substituent containing hydrogen atoms,e.g.methoxy,will result in an upfield shift in the position of resonance of the hydrogen atom or atoms concerned. For example,the position of resonance of the methoxy protons in 2,4,6-trinitroanisole (DMSO solvent) moves from τ5.93 to τ6.97 on addition of methoxide ion at the 1-position[121]. This upfield shift is due firstly to a change in hybridisation of the ring carbon atom from sp^2 to sp^3,and secondly to an increase in electron density resulting from the addition of an electron-donating species at that carbon atom.

Investigations of Meisenheimer complexes by NMR spectroscopy are experimentally simple,the reactants being mixed directly in the NMR sample tube. However,the concentrations required for NMR measurements are considerably higher than those required for visible spectroscopy,which

could result in different types of products being formed in each case,e.g.π-complexes where the concentrations of the reactants are low,and σ-complexes where the concentrations of the reactants are high. This was not found to be the case,however,when the NMR and visible spectra of 1,3,5-trinitrobenzene/aliphatic amine systems were recorded simultaneously over a range of concentrations[122,123]. It was deduced from the results that the species giving rise to the spectra were the same in each case.

(c) Infrared Spectroscopy

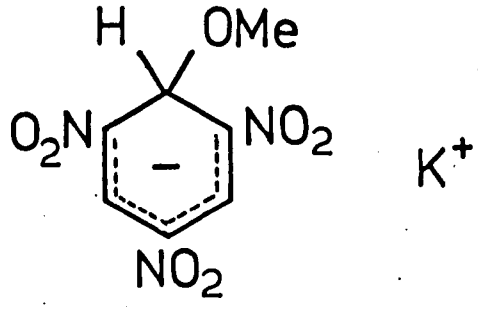
Unlike NMR spectroscopy,infrared spectroscopy does not readily yield structural information about a complex. Infrared spectroscopy is of more use as a means of characterising a complex,as in the case of visible spectroscopy. The spectrum of the product of the reaction of 2,4,6-trinitroanisole with methoxide ion features strong bands characteristic of a ketal-type compound [124], i.e. one in which two alkoxy groups are substituted at the same saturated carbon atom. This clearly indicates that a Meisenheimer complex is obtained rather than a charge-transfer complex,for which no such bands would be observed. Further evidence for the formation of a Meisenheimer complex may be obtained from the characteristic absorptions of the nitro group. The addition of a nucleophile to the nucleus of a nitroaromatic compound results in a partial transfer of a negative charge to the nitro groups,which increases the bond order of the C-N bonds and decreases the bond order of the N-O bonds [125]. Therefore it would be expected that the frequencies of the symmetric and asymmetric stretch

modes of the nitro groups would be decreased on formation of a Meisenheimer complex. This is found to be the case. Thus for 2,4,6-trinitroanisole,the N-O symmetric stretching frequency decreased from 1343 to 1291 cm^{-1},and the N-O asymmetric stretching frequency decreased from 1552 to 1492 cm^{-1} on reaction with methoxide ion[126].

2.1.3 Reactions of Base with 1,3,5-Trinitrobenzene and 1-Substituted 2,4,6-Trinitrobenzenes

(a) Alkoxides

The isolation of a solid product by the action of methanolic potassium hydroxide on 1,3,5-trinitrobenzene was first described in 1895[127]. The visible spectrum of this product suggested that a 1:1 anionic sigma-complex had been produced,and a structure (V) was proposed for the product (fig.2.1.3).

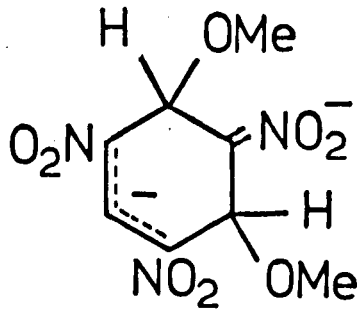


V

Fig.2.1.3

The reaction between 1,3,5-trinitrobenzene and methoxide ion has also been investigated by NMR spectroscopy[121,128]. When DMSO is used as the solvent,the spectrum of an equimolar mixture of the two reactants corresponds exactly with structure V above [121]. When an excess of methoxide is

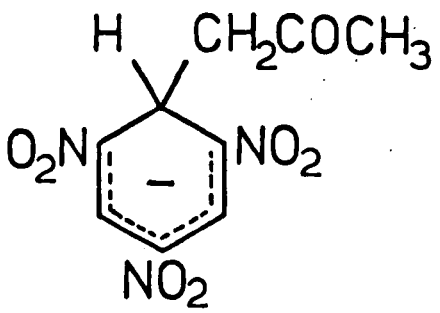
present,the spectrum is found to be consistent with the formation of a di-methoxide adduct[128](VI - fig.2.1.4).



VI

Fig.2.1.4

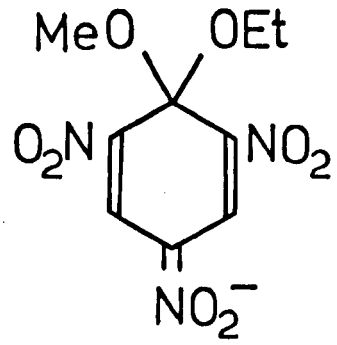
When acetone is used as the solvent,the 1:1 adduct formed initially (V) undergoes solvolysis to yield an acetonate adduct[128] (VII - fig.2.1.5).



VII

Fig.2.1.5

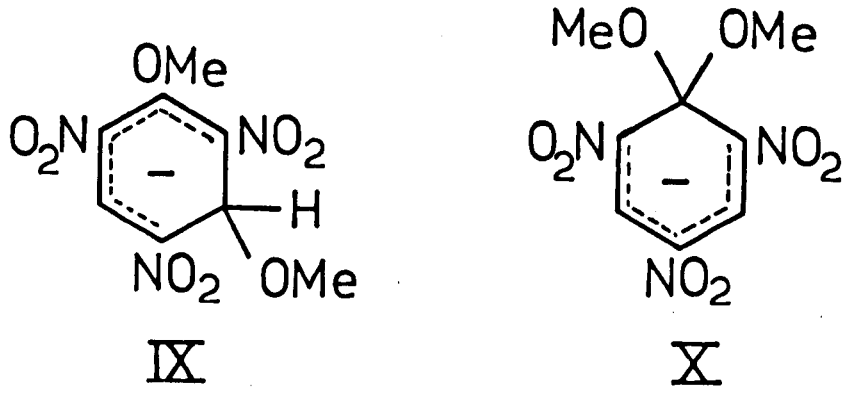
The reaction of alkoxides with 2,4,6-trinitroanisole has received considerable attention since Meisenheimer's pioneering work in the early 1900's. Meisenheimer proposed that the reaction of ethoxide ion with 2,4,6-trinitroanisole produced a C-1 adduct[125](VIII - fig.2.1.6). Proof of this structure was provided by the production of a compound having the same visible spectrum as VIII from the reaction of methoxide ion with trinitro-



VIII

Fig.2.1.6

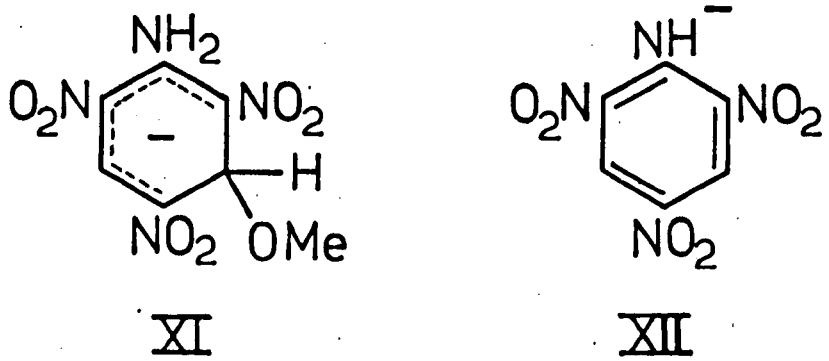
phenetole[105]. However,it was pointed out that products having either two methoxy groups or two ethoxy groups located at the 1-position,which might have been formed by disproportionation,have almost identical spectra to Meisenheimer's product,and hence the use of visible spectra as proof of structure is meaningless here [129]. Although infrared spectra have tended to confirm the Meisenheimer structure[130,131],it was not until 1964 that really conclusive evidence was obtained by the introduction of NMR spectroscopy. The spectrum of the product of the reaction of methoxide with 2,4,6-trinitroanisole was found to consist of only two peaks,in an integral ratio of 1:3, corresponding to structure X[121](fig.2.1.7). Had attack of methoxide ion taken place at a ring site occupied by a hydrogen atom,then the two ring hydrogen atoms would have become non-equivalent and would have coupled. This latter species (IX) was later shown to be present as a short-lived transient species,which rearranged to the thermodynamically more stable form (X)[132]. At higher methoxide concentrations,further attack appears to take place to give a 2:1 adduct where methoxy groups have added at the 1- and 3-positions [133].



IX X

Fig.2.1.7

The reactions of alkoxides with 1-amino-2,4,6-trinitrobenzene (picramide) have been shown to be different to the corresponding reactions with trinitroanisole. Rather than attack taking place at the 1-position,which had been suggested [134],attack of methoxide takes place at the 3-position to give XI [133] (fig.2.1.8). This is clearly indicated by the NMR spectrum,which shows a doublet of doublets for the ring protons [133]. In addition,proton abstraction of an amino group proton takes place to give the conjugate base of picramide [135] (XII).



XI XII

Fig.2.1.8

The proportions of adduct (XI) and conjugate base (XII) in the product mixture were found to be 80% and 20% respectively, in DMSO solvent [135]. When ethoxide was used,the proportion of adduct was less than for methoxide,and when *tert*-butoxide

was used,only the conjugate base was formed,suggesting that the bulkiness of the attacking species governs the proportion of adduct formed [118].

(b) Aliphatic Amines

It is important to distinguish between the reactions of trinitrobenzene and its derivatives with aliphatic amines and the reactions with aromatic amines. The former give rise to direct chemical reactions,whereas the latter usually give rise to weakly bonded charge-transfer complexes [136,137].

The actual form of the interaction between 1,3,5,-trinitrobenzene and aliphatic amines has always been in doubt. The higher electrical conductivity of these systems was taken to indicate that a single electron-transfer reaction had taken place to yield a trinitrobenzene radical anion[137],and was supported by the detection of weak electron spin resonance signals [138]. It was also suggested that abstraction of a ring proton could take place in certain circumstances,e.g.the reaction of 2-amino-ethanol with 1,3,5-trinitrobenzene [139]. From kinetic and calorimetric measurements of the reaction of diethylamine with 1,3,5-trinitrobenzene,it was established that a stoichiometric ratio of 2 equivalents of amine to 1 equivalent of nitro-aromatic was involved [140]. It was shown that the visible spectrum of the system,in either polar or non-polar solvents, was similar to the spectra of 1:1 alkoxide/1,3,5-trinitro-benzene systems[141,142]. This indicated that a Meisenheimer complex had been formed via attack at the 1-position to give a zwitterion (XIII) followed by proton abstraction

to give species XIV (fig.2.1.9).

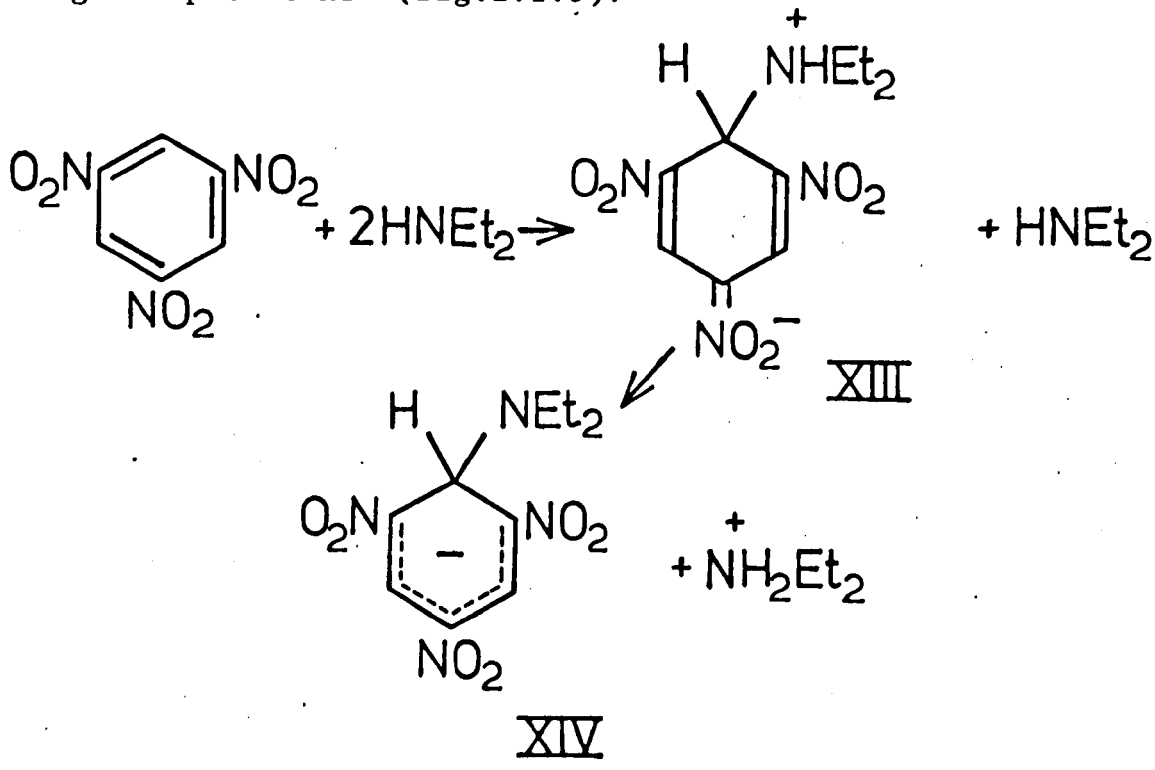


Fig.2.1.9

This conclusion is supported by NMR evidence[143]. In protic solvents such as ethanol the stoichiometry of the 1,3,5-trinitrobenzene/amine systems has been found to be 1:1, but this has been attributed to attack of ethoxide on the nitroaromatic to give 1:1 ethoxide complexes[108,137]. In chloroform,3:1 nitroaromatic/amine stoichiometries have been observed,and have been attributed to solvation of the complex formed from a 2:1 interaction by an extra molecule of amine[108,144]. When acetone is used as solvent,the formation of the Meisenheimer complex takes place as above, but it is then subject to solvolysis,the amine group being replaced by an acetonate group[132]. However,further reactions also take place. For example,the trinitrobenzene/diethylamine system produces N,N-diethyl-4-nitroaniline as one of many final products[145].

2,4,6-trinitroanisole appears to react with diethylamine in DMSO to give an adduct resulting from attack at the 1-position [133]. However, these conclusions are open to doubt, and it has been suggested that a diethylmethylammonium picrate may be formed instead [118]. Picramide does not appear to react with aliphatic amines in DMSO to give amine adducts [133,146].

(c) Sulphite Ion

Although sulphite ion is a weak nucleophile, it will form Meisenheimer complexes with 1,3,5-trinitrobenzene and its derivatives. It was discovered at an early stage that 1,3,5-trinitrobenzene would dissolve in dilute aqueous solutions of sulphite ion to give red-coloured solutions from which the nitroaromatic could be recovered by acidification, provided the solution was reasonably fresh [147]. It was later found that solid crystalline products could be isolated having a stoichiometry of two equivalents of sulphite to one equivalent of 1,3,5-trinitrobenzene [148]. If aqueous solutions of these solids were allowed to stand for long periods, phenols were obtained. The visible spectra of solutions of the complexes were found to be consistent with 1:1 Meisenheimer complexes [149,150], which changed to spectra consistent with 2:1 complexes on addition of further amounts of sulphite ion [151]. Similar conclusions were obtained from NMR studies [151]. It was suggested that a range of adducts is formed in aqueous solution as the concentration of sulphite ion is increased, i.e. 1:1, 1:2 and 1:3 [148]. This may be compared to the reaction of hydroxide ion with 1,3,5-trinitrobenzene (see above).

Sulphite ion reacts with 2,4,6-trinitroanisole to give a product resulting from addition at the 3-position[151]. At higher sulphite concentrations,addition of sulphite also takes place at the 5-position. These results have been confirmed by NMR and visible spectroscopy[151]. Similarly, sulphite ion reacts with picramide to give adducts of 1:1 and 2:1 stoichiometry[151].

2.1.4 Reactions of Base with Nitro and Polynitrotoluenes

(a) Nitro and Dinitrotoluenes

The treatment of o- and p-nitrotoluenes with a variety of strong bases has been found to produce coupled products together with other products resulting from oxidation of the methyl group. As long ago as 1880[152],the reaction of p-nitrotoluene with methanolic alkali was observed to produce insoluble products similar to those obtained from the attempted reduction of p-nitrotoluene using sodium in methanol[153]. Eventually,p,p'-dinitrobibenzyl and p,p'-dinitrostilbene were isolated from the product mixture and identified[154]. Green and his co-workers reacted a number of *ortho*-substituted p-nitrotoluenes, including 2,4-dinitrotoluene,with methanolic potassium hydroxide,and obtained the corresponding substituted p,p'-dinitrobibenzyls and p,p'-dinitrostilbenes [155,156,157]. The synthesis of p,p'-dinitrostilbene and p,p'-dinitrobibenzyl from p-nitrotoluene in methanolic alkali has been well studied,and it has been found that the most efficient process involves the passage of oxygen through the reaction mixture [158]. The mechanism for this reaction is believed to be an oxidative coupling,similar to Glazer coupling of

alkynes,in which abstraction of a proton from the methyl group takes place to form an ion stabilised by the *para*-nitro group,which can then form a free radical. The following scheme has been proposed by Tsuruta *et al*[159] :-

$$(NO_2)RCH_3 + KOH \rightarrow (NO_3)RCH_2^-K^+ + OH^\cdot$$

$$(NO_2)RCH_2^-K^+ \rightarrow (NO)RCH_2^\cdot + OK^\cdot$$

$$(NO)RCH_2^\cdot + O_2 \rightarrow (NO_2)RCH_2^\cdot + O$$

$$(NO_2)RCH_2^-K^+ + O_2 \rightarrow (NO_2)RCH_2^\cdot + O_2K$$

$$(NO_2)RCH_2^\cdot \rightarrow \text{Coupled products}$$

where R represents the (C_6H_4) species.

Sodamide in piperidine has been used to obtain p,p'-dinitrobibenzyl from p-nitrotoluene,and o,o'-dinitrobibenzyl from o-nitrotoluene[160]. The latter synthesis has also been accomplished using diphenylamide in liquid ammonia[161]. Russell and Janzen have studied the reaction of p-nitrotoluene with a solution of potassium *tert*-butoxide in *tert*-butanol in the absence of oxygen,a process which gave good yields of p,p'-dinitrobibenzyl rather than p,p'-dinitrostilbene[162]. They found that paramagnetic species were generated,and obtained evidence from the ESR spectra of the species that the reaction proceeds via the disproportionation of the p-nitrotoluene radical :-

$$4CH_3C_6H_4NO_2 \rightarrow 2CH_3C_6H_4NO_2^{\doteq} +$$

p,p'-dinitrobibenzyl

This mechanism suggests that it should be possible to increase the yield of p,p'-dinitrobibenzyl by the addition of an electron acceptor,e.g.nitrobenzene,and this was indeed found to be the case[163].

(b) 2,4,6-Trinitrotoluene

The reaction of 2,4,6-trinitrotoluene with strong bases,e.g.hydroxide and methoxide,differs from the reactions of other 1-substituted 2,4,6-trinitrobenzenes with bases. Early workers in the field reported the preparation of a solid product from the reaction of potassium methoxide with 2,4,6-trinitrotoluene which upon acidification yielded stilbene derivatives[164]. This was taken to indicate the formation of a C-1 Meisenheimer complex,but this claim has not been confirmed due to the synthesis being apparently unreproduceable. Later workers suggested that the 2,4,6-trinitrobenzyl ion is formed in strong base conditions[165], and pointed to the visible spectra of such systems,which are not entirely consistent with 1:1 Meisenheimer complexes[166]. Unfortunately,conclusive spectroscopic evidence from NMR has not been forthcoming because addition of methoxide to a solution of 2,4,6-trinitrotoluene in DMSO results in the immediate loss of the spectrum; this has been attributed to the presence of radical anions[133]. The formation of the 2,4,6-trinitrobenzyl anion has been strongly disputed by Servis[133],who interpreted the available evidence as indicating that attack at the 3-position had taken place. The formation of a benzyl-type anion has been confirmed by NMR in the case of 4-nitrobenzyl cyanide,in which reaction with base yields an anion which is stabilised by the powerfully electron withdrawing cyanide group[167]. It is reasonable therefore to assume that a 2,4,6-trinitrobenzyl anion could be formed in which the negative charge is stabilised by the picryl group. The reaction of 2,4,6-

trinitrotoluene with sodium hypochlorite has been investigated on a preparative basis,and found to produce 2,2',4,4',6,6'-hexanitrostilbene (HNS)[168]. Evidence for the involvement of the 2,4,6-trinitrobenzyl anion was obtained by trapping the intermediate 2,4,6-trinitrobenzyl chloride,from which it was known HNS could be obtained by reaction with base[168]. Further evidence was obtained by quenching the reaction immediately after commencement using deuterated acid (DCl),from which it was observed that one deuterium atom was incorporated in the methyl group of 2,4,6-trinitrotoluene[169]. Further research demonstrated that the 2,4,6-trinitrobenzyl anion would function as a nucleophile,in the reaction of nitroaryl halides with trinitrotoluene in alkali solution [169].

The reaction of 2,4,6-trinitrotoluene with weak bases appears to result in the formation of Meisenheimer complexes due to attack at the 3-position. The visible spectrum of the 2,4,6-trinitrotoluene/sulphite complex, having maxima at 465 and 485nm,is entirely consistent with formation of a 1:1 Meisenheimer complex[147,150]. The reaction with cyanide has been studied by NMR spectroscopy, and attack of the nucleophile at the 3-position confirmed, although the complex is very short-lived[170]. The 2,4,6-trinitrotoluene/alkali/acetone system has been studied by visible spectroscopy,and the maxima at 462 and 532nm have suggested the formation of a Meisenheimer complex resulting from addition of acetonate ion at the 3-position [171].

2.1.5 Reactions of Base with Polynitronaphthalenes and Substituted Polynitronaphthalenes

The reactions of polynitronaphthalenes with base have not received as much attention as the reactions of polynitrobenzenes with base. The reaction of 1,3-dinitronaphthalene with either methoxide ion,acetonate ion,or nitromethyl ion results in addition at the 4-position, which may clearly be observed by NMR spectroscopy[172,173]. The visible spectra of these systems differ from the spectra of comparable 1:1 polynitrobenzene/base adducts in that they feature only one visible maximum rather than two[174]. There appears to be no evidence for attack of base at the 2-position in 1,3-dinitronaphthalene.

The reactions of 1-alkoxy-2,4-dinitronaphthalene with base results in addition at the 1-position,e.g. 1-methoxy-2,4-dinitronaphthalene reacts with methoxide ion to give a C-1 adduct,as confirmed by NMR spectroscopy[175]. The visible spectrum of this system features two widely separated maxima,similar to the spectra of Meisenheimer complexes derived from polynitroanisoles[175]. However, the molar extinction coefficient of the lower energy band is greater than that of the higher energy band,unlike in the case of polynitroanisoles. Addition of methoxide at the 3-position in 1-methoxy-2,4-dinitronaphthalene has been postulated in certain circumstances,but not confirmed by NMR spectroscopy[176]. Addition at the 1-position has also been observed for the reactions of either methoxide or ethoxide with 1-ethoxy-2,4-dinitronaphthalene[175].

Few investigations into the reactions of base

with methyl substituted polynitronaphthalenes appear to have been made. The reaction of base with 2,4,5-trinitro-1-methylnaphthalene has been investigated only on a qualitative basis,i.e.the colours of solutions obtained from various bases were noted[89]. No further research appears to have been undertaken on this type of system.

2.1.6 Charge-Transfer Complexes

(a) Introduction

Charge-transfer complexes result from the weak interaction of electron donors and electron acceptors,in which a partial transfer of electronic charge from the donor to the acceptor takes place. Electron donors take the form of either n-donors,which can donate non-bonding electrons from lone pairs,e.g.amines,or π-donors,which can donate electrons from their delocalised π-systems, e.g.aromatic hydrocarbons. Electron acceptors are invariably electron deficient species. The most common organic acceptors are the π-acceptors,which include aromatic systems containing electron withdrawing substituents such as nitro and cyano groups. Many theories have been put forward to explain the bonding in charge-transfer complexes,the most generally accepted theory being the valence-bond description of Mulliken[177]. This subject has been extensively reviewed[178,179,180].

The subject of charge-transfer complexes is fairly wide-ranging,and for the purposes of this work, reference will be restricted to the π-complexes formed from π-donors and polynitroaromatic compounds.

(b) Methods For Investigating Charge-Transfer Complexes

The strength of the interaction between electron donors and acceptors may by determined in a number of ways. The interactions are weak, the enthalpy of formation being of the order of a few Kcals/mole. It is, therefore, customary to express the strength of the interaction in terms of the association constant Kc^{AD} for the equilibrium :-

$$D + A = DA$$

where D represents the donor, A the acceptor, and DA the complex. Kc^{AD} is therefore expressed as

$$\frac{[AD]}{[A][D]}$$

where [AD], [A] and [D] represent the concentrations of the reacting species at equilibrium.

Electronic Spectroscopy

Generally, a charge-transfer complex gives an electronic absorption spectrum which still retains the absorptions of the components, modified to some extent, together with absorption bands characteristic of the complex itself. These latter bands are the result of intermolecular charge-transfer transitions involving electron transfer from the donor to the acceptor. The intensity of the charge-transfer bands can be used as a measure of the concentration of the complex in a given solution. By combining the expression for the association constant Kc^{AD} with the expression for Beer's law, i.e.

$$\frac{Abs}{l} = \varepsilon_{\lambda}^{AD}.[AD]$$

where Abs is the absorption of the charge-transfer band, l the path length, and ε_λ^{AD} the molar extinction coefficient at wavelength λ, the following expression, known as the Benesi-Hildebrand equation, was formulated[181,182] :-

$$\frac{[A]_o}{Abs/l} = \frac{1}{Kc^{AD}.\varepsilon_\lambda^{AD}} \cdot \frac{}{[D]_o} + \frac{1}{\varepsilon_\lambda^{AD}}$$

assuming $[D]_o$ and $[A]_o$ are small, and $[D]_o \gg [A]_o$. Under these conditions, a plot of $[A]_o/(Abs/l)$ *vs* $[D]_o^{-1}$ should be linear with slope $(Kc^{AD}.\varepsilon_\lambda^{AD})^{-1}$ and intercept $(\varepsilon_\lambda^{AD})^{-1}$, from which Kc^{AD} may be readily determined.

NMR Spectroscopy

The rates of formation and decomposition of charge-transfer complexes are rapid compared to the NMR time scale, and thus any particular proton will resonate at a frequency which is the time-averaged resultant of the frequencies at which it would resonate in the complexed and uncomplexed forms. The NMR spectrum of an acceptor in solution is shifted upfield on addition of a donor. If a resonance shifts by ΔHz for a concentration of donor of $[D]_o$, then it can be shown that the following expression holds for the formation of a 1:1 complex :-

$$\frac{1}{\Delta} = \frac{1}{Kc^{AD}} \cdot \frac{1}{\Delta_o^{AD}} \cdot \frac{1}{[D]_o} + \frac{1}{\Delta_o^{AD}}$$

where Δ_o^{AD} is the chemical shift of the proton in the fully complexed form. The value of Δ_o^{AD} for individual protons will be different, and this provides valuable structural information about the complex, as the higher the value of Δ_o^{AD}, the nearer that proton must be to the centre of the complex. The above equation was derived by Hanna and

Ashbaugh [183], and is formally analagous to the Benesi-Hildebrand equation, seen above. However, in practice this equation is often used in a rearranged form [184]:-

$$\frac{\Delta}{[D]_o} = -\Delta K_c^{AD} + \Delta_o^{AD}.K_c^{AD}$$

Provided $[D]_o \gg [A]_o$, a plot of $\Delta/[D]_o$ *vs* Δ should be linear with slope $-K_c^{AD}$ and intercept $\Delta_o^{AD}.K_c^{AD}$.

(c) Charge-Transfer Complexes Derived from Polynitroaromatic Compounds and Aromatic Donors

The complexes formed from the interaction of 1,3,5-trinitrobenzene and a number of aromatic hydrocarbons, e.g. benzene, toluene, p-xylene, have been studied in detail by NMR spectroscopy, and the values of Δ_o for the acceptor protons compared [185]. These values decreased as the size of the donor molecule increased, suggesting that steric effects govern the strength of the interaction between the donor and acceptor. This conclusion has been supported by the determination of the association constants of the complexes formed from hexamethylbenzene and the three isomeric trinitrobenzenes, which have complexing abilities in the order 1,3,5->1,2,4->1,2,3-trinitrobenzene [186]. This order correlates with the increase in steric hindrance of the nitro groups. Complexes formed from the interaction of benzene with the six isomeric trinitrotoluenes have been investigated, and evidence for the orientations of the two components in each system obtained from the values of Δ_o for each proton [187]. In each case the benzene molecule has been shown to be sited preferentially over the least sterically crowded part of the molecule.

Polynitronaphthalenes have not received as much attention with regard to charge-transfer complex formation as have the nitrobenzenoid compounds. The interactions of the ten isomeric dinitronaphthalenes with N,N,N',N'-tetramethyl-p-phenylene diamine have been investigated, and the strongest acceptors found to be those having the greatest number of β-nitro groups, *viz* 2,7- and 2,6-dinitronaphthalenes, as β-nitro groups apparently have higher electronegativities[188]. The weakest acceptors were found to be those having sterically hindered nitro groups or not having any β-nitro groups, i.e. 1,8-, 1,5- and 1,2-dinitronaphthalenes.

2.2 Results and Discussions of Reactions of Base with Nitro-2,3-Dimethylnaphthalenes

2.2.1 Reactions of 1,6,8-Trinitro-2,3-Dimethylnaphthalene with Methoxide Ion

The reaction of 1,6,8-trinitro-2,3-dimethylnaphthalene with methoxide ion was performed by dissolving the nitroaromatic in DMSO-d_6, and adding the calculated equivalent quantity of sodium methoxide-d_3 in methanol-d_4. This provided a deuterated system which allowed the reaction to be followed by NMR spectroscopy. The NMR spectrum of 1,6,8-trinitro-2,3-dimethylnaphthalene consists of two singlets in the τ7-8 region (methyl resonances), and one singlet and a doublet of doublets in the τ1-3 region (aromatic resonances), as shown in fig.2.2.2a. On addition of one equivalent of methoxide-d_3, one of the low-field doublets was observed to shift to the mid-field region, as shown in fig.2.2.2b. This would appear to be conclusive evidence for the formation of a Meisenheimer complex, with a methoxy-d_3 group attacking the nucleus probably at the 5-position, to give compound 39 (fig.2.2.1), rather than at the more sterically crowded 7-position.

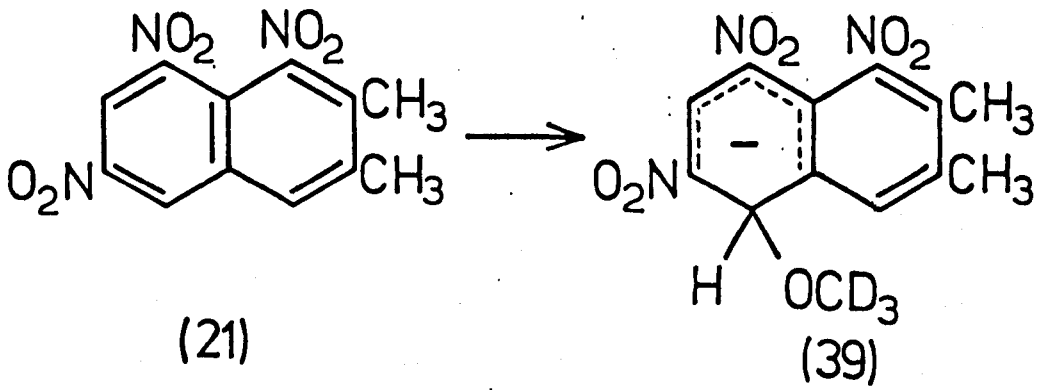


Fig.2.2.1

On addition of a further equivalent of methoxide-d_3, the peaks disappeared slowly, presumably due to the precipitation of solid materials.

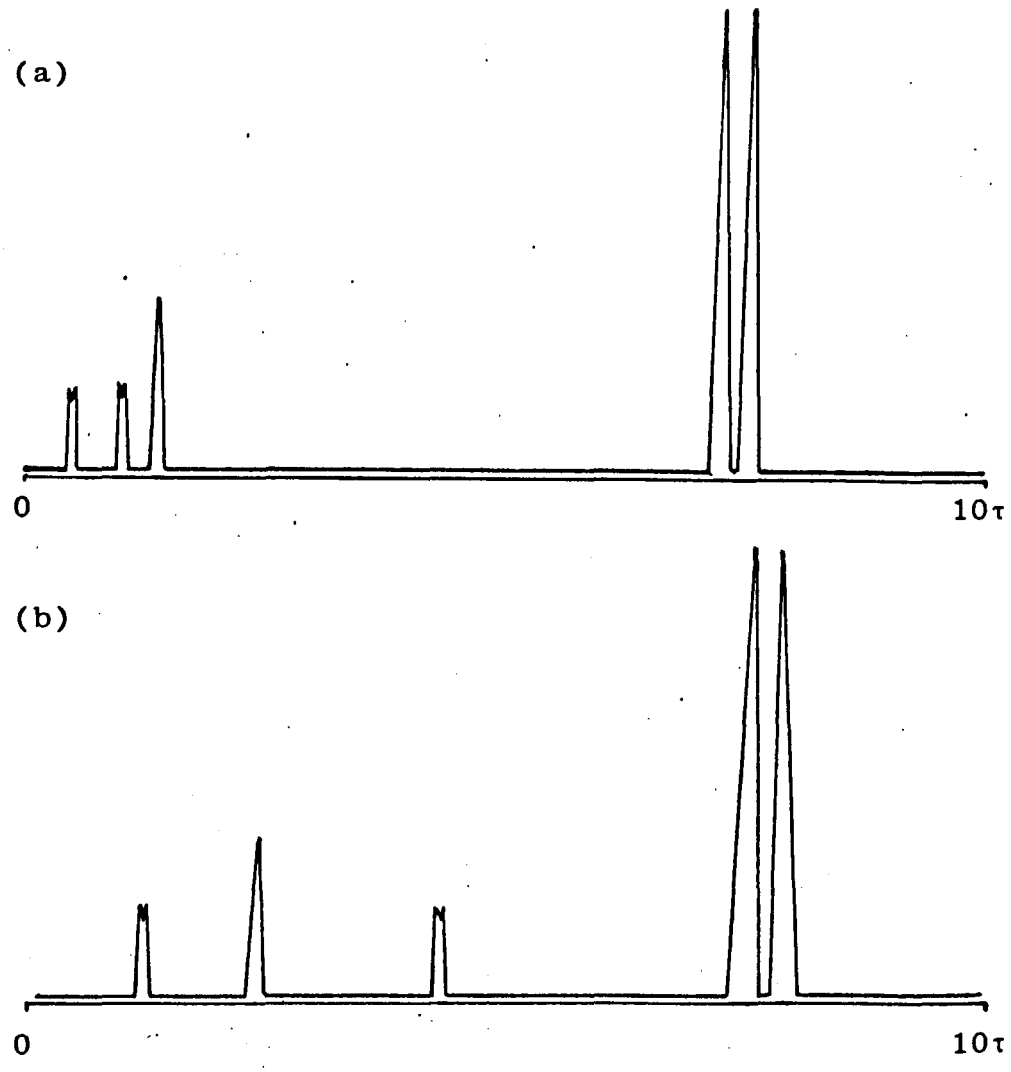


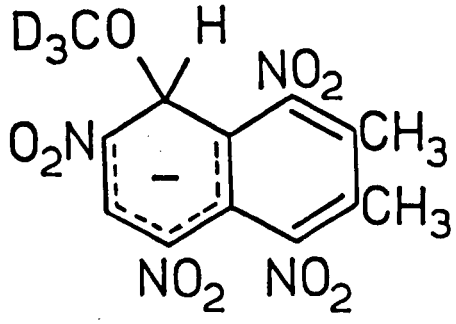
Fig.2.2.2 (a) Normal spectrum of 1,6,8-trinitro-2,3-dimethylnaphthalene in DMSO-d_6. (b) Spectrum after the addition of one equivalent of sodium methoxide-d_3 in methanol-d_4.

The reaction of 1,6,8-trinitro-2,3-dimethylnaphthalene with methoxide ion was studied on a preparative basis by mixing the reactants in equimolar proportions in

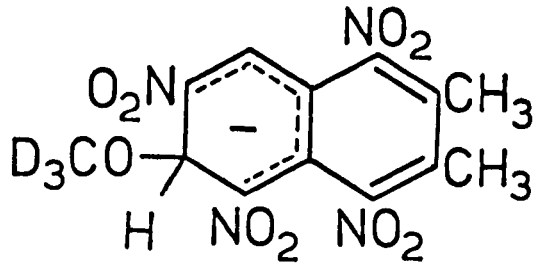
an inert solvent (dichloromethane) under an atmosphere of dried nitrogen,care being taken to exclude all traces of moisture. In this way,a dark red solid was obtained, the elemental analysis of which showed that a 1:1 complex had been formed. That this compound was a Meisenheimer complex and not a charge-transfer complex was demonstrated by its properties of (a) being water soluble,hydrolysing to give the starting material,(b) being explosive when subjected to rapid heating,and (c) not giving a mass spectrum,indicative of an ionic species. Attempts to obtain an NMR spectrum failed because of the insolubility of the compound in "inert" solvents,e.g.carbon tetrachloride, and because of decomposition of the compound (accompanied by evolution of gas) in polar solvents such as DMSO.

2.2.2 Reaction of 1,4,5,7-Tetranitro-2,3-Dimethylnaphthalene with Methoxide Ion

The NMR spectrum of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene in DMSO-d_6 is shown in fig.2.2.5a. Upon addition of one equivalent of sodium methoxide-d_3 in methanol-d_4 the spectrum changed to that shown in fig.2.2.5b, where one of the low-field doublets had shifted to the mid-field region. This is consistent with the formation of the anionic sigma-complex 40a,where the methoxy-d_3 group has attacked the 8-position rather than the 6-position (to give 40b) for steric reasons (fig.2.2.3). The NMR spectrum of the reaction system also showed a set of low intensity peaks analagous to,and adjacent to,each of the main peaks, indicating that the complex 40b was also formed,but only to a very small extent.



(40a)



(40b)

Fig.2.2.3

On addition of a further equivalent of methoxide-d_3 ion, the NMR spectrum changed to that shown in fig.2.2.5c. The spectrum suggested that two species were present, one giving rise to the mid-field resonances and the other giving rise to the low-field resonances. The species giving rise to the mid-field resonances was probably the di-methoxy-d_3 adduct 41a, which can exist in *cis* and *trans* forms. The *trans* form, in which the methoxy-d_3 groups are on opposite sides of the plane of the ring, probably gave rise to the mid-field doublets; the *cis* form, in which the methoxy-d_3 groups are on the same side of the plane of the ring, and may therefore experience similar environments, probably gave rise to the mid-field singlet. *Cis-trans* isomerism in 1,2 sigma-complex adducts has been reported recently[194,195]. The low-field resonances could have resulted from the formation of a neutral compound, e.g. one in which a nitro group had been replaced by a methoxy-d_3 group. One such compound is 41b (fig.2.2.4). However, the spectrum (fig.2.2.5c) could have resulted from species other than 41a and 41b.

The visible spectrum of the 1:1 complex formed between 1,4,5,7-tetranitro-2,3-dimethylnaphthalene and methoxide ion in DMSO is shown in fig.2.2.6a. The spectrum

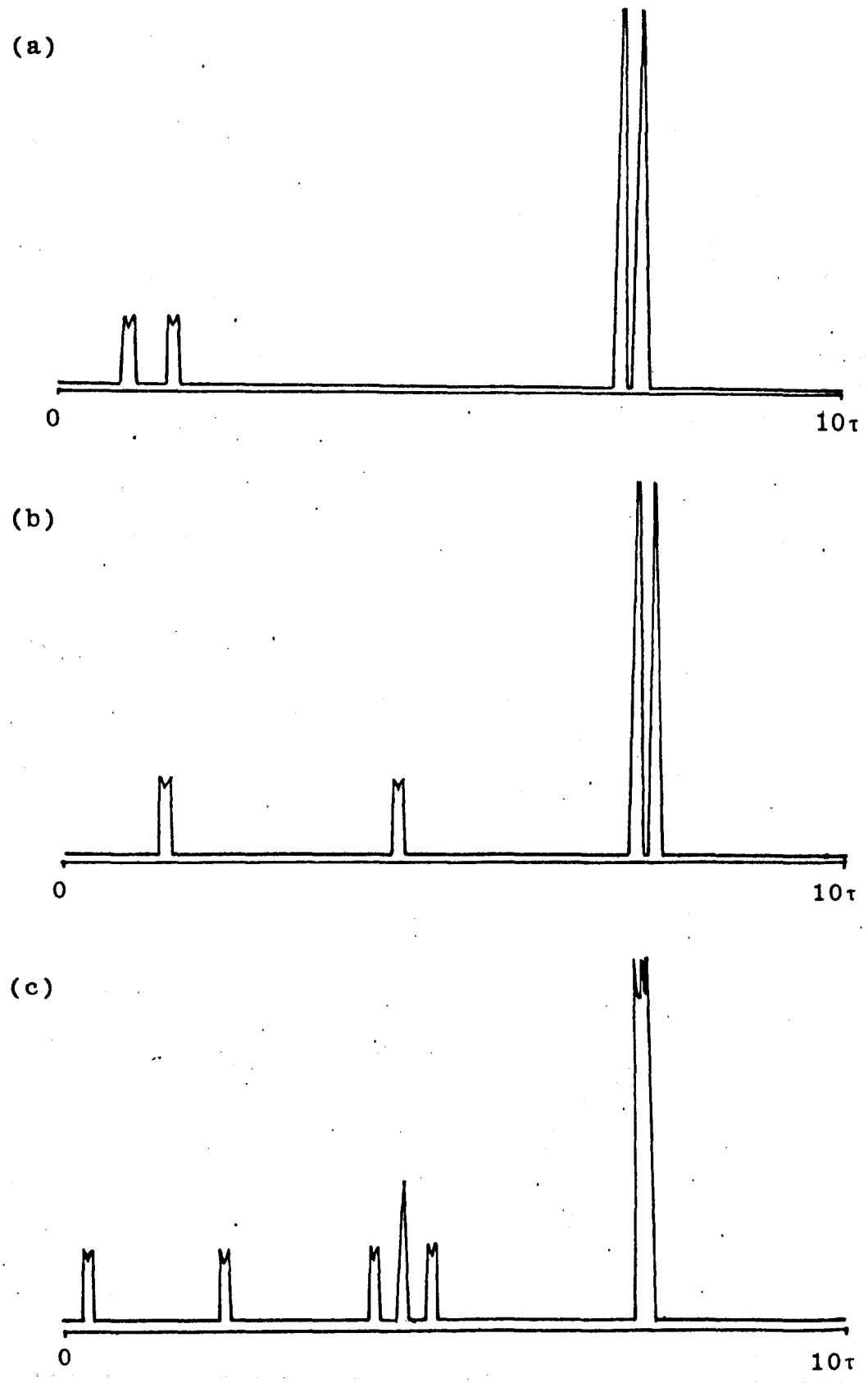


Fig.2.2.5 (a) Normal NMR spectrum of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene in DMSO-d_6. (b) Spectrum after the addition of one equivalent of methoxide-d_3. (c) Spectrum after the addition of two equivalents of methoxide-d_3.

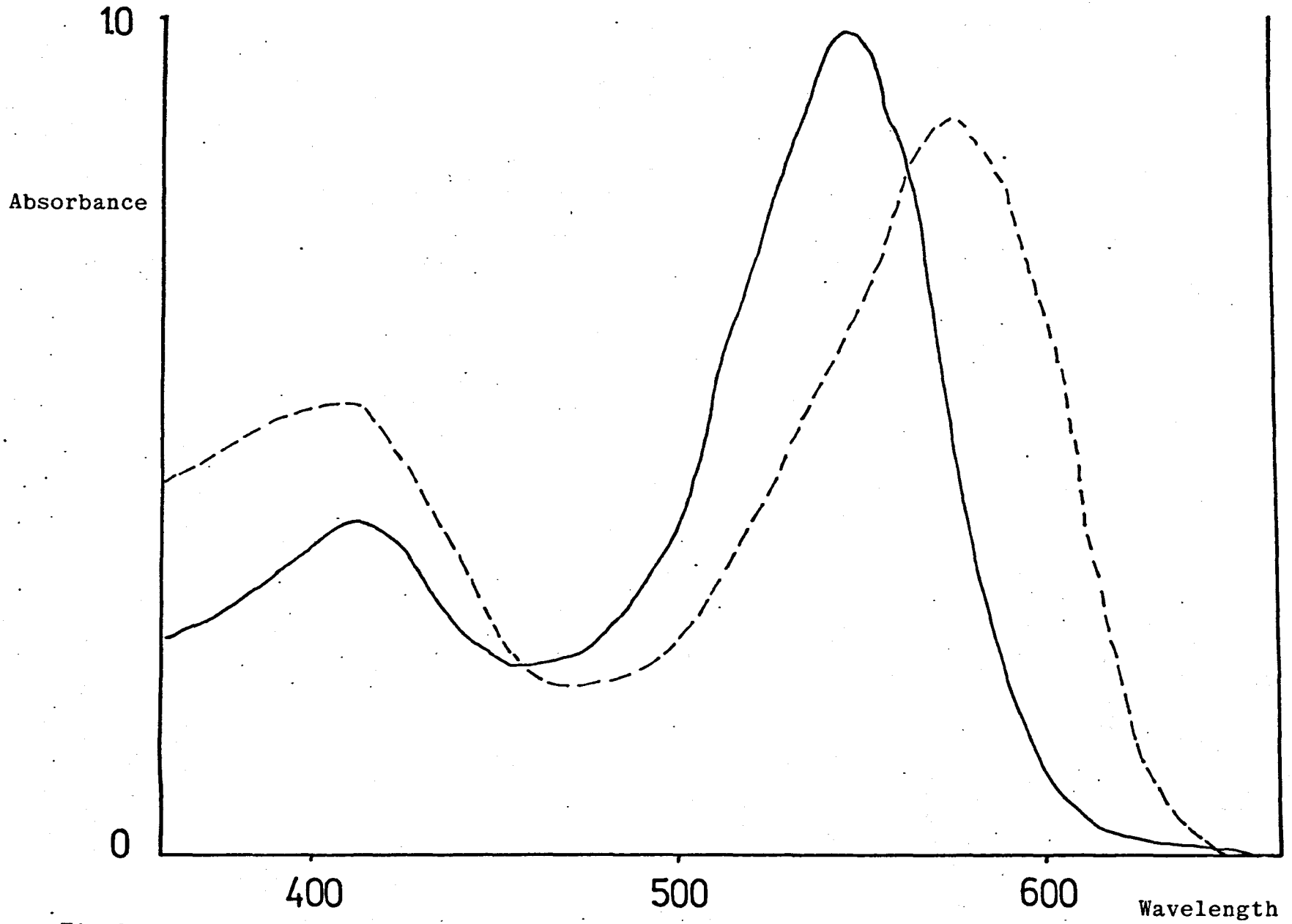
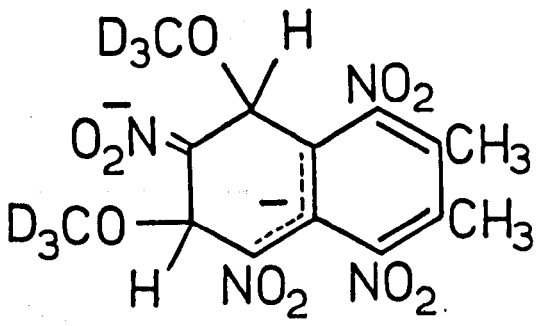
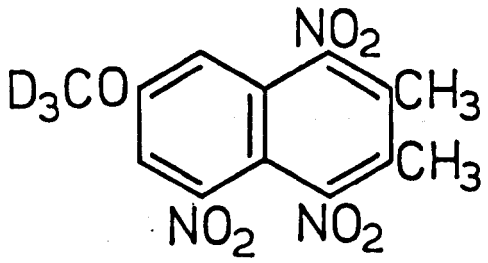


Fig.2.2.6 Visible spectra of the reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene with (a) methoxide ion (—) (b) sulphite ion (---).



(41a)



(41b)

Fig.2.2.4

features two peaks,at 414 and 549nm,the molar extinction coefficients of which are in a ratio of *ca* 1:2. This is a feature common to the spectra of other Meisenheimer complexes based on the naphthalene nucleus [118].

The reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene with methoxide ion in a 1:2 molar ratio in tetrahydrofuran solvent gave a red precipitate which had the properties of an anionic sigma complex,*viz* it was water soluble,hydrolysed to give the starting material, exploded on heating,and did not give a mass spectrum. The elemental analysis of the product suggested that a 2:1 sodium methoxide/1,4,5,7-tetranitro-2,3-dimethylnaphthalene complex had been formed. However,the compound decomposed on dissolving in DMSO-d_6,and no satisfactory NMR spectrum could be obtained. Consequently the structrure of the compound could not be assigned.

2.2.3 Reaction of 1,4,5,7-Tetranitro-2,3-Dimethylnaphthalene with Sulphite Ion

Dissolution of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene in a 1M aqueous solution of sodium sulphite gave a strong red coloration. The coloration intensified on warming,suggesting that it was not due to a charge-

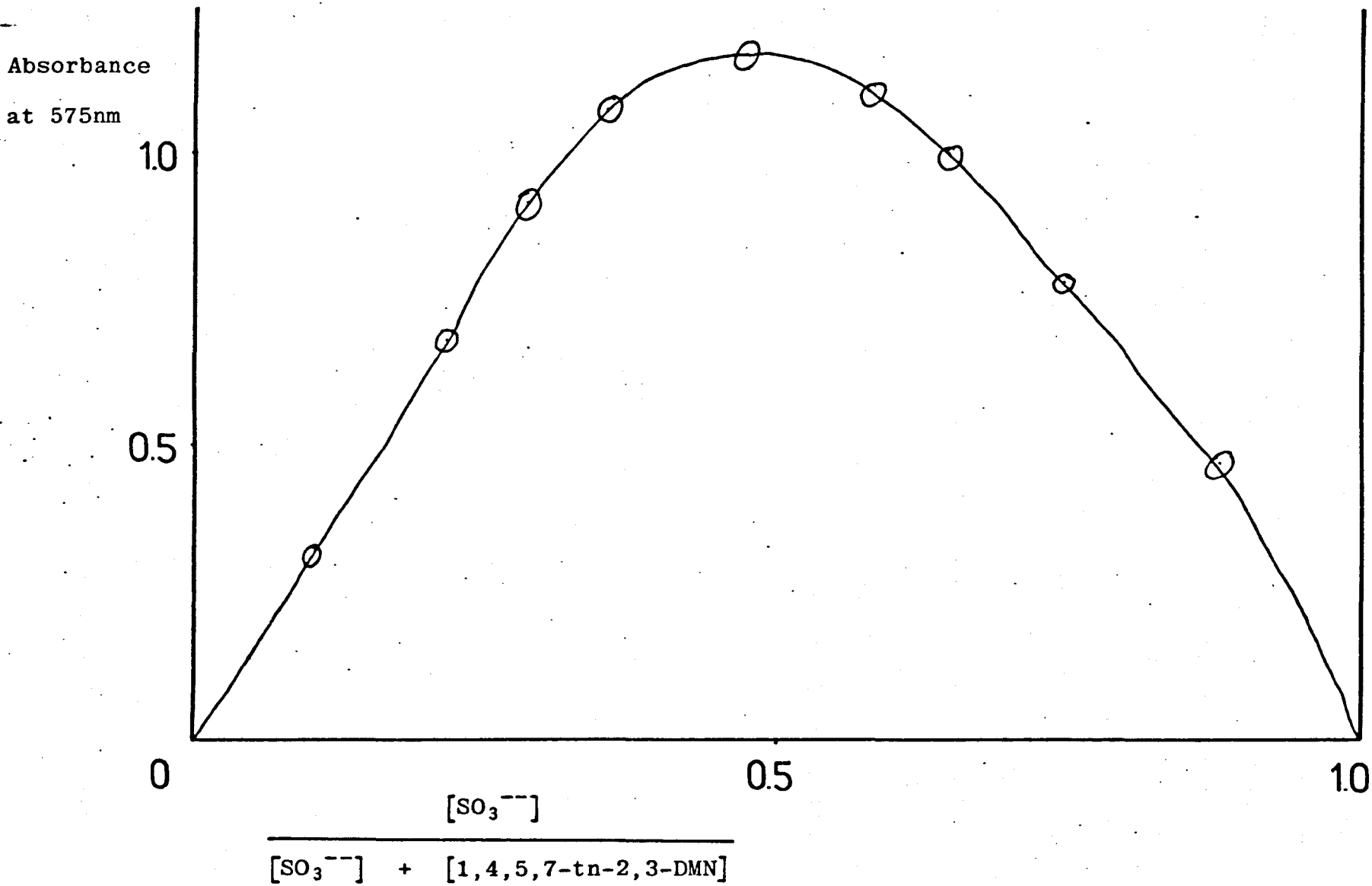
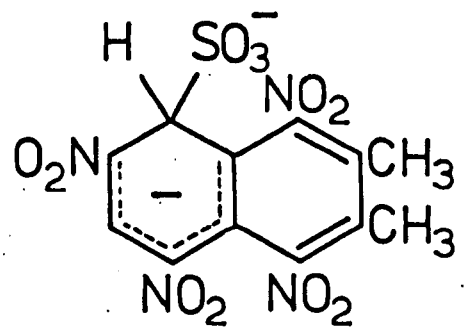


Fig.2.2.7 Job plot of the reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene with sulphite ion.

transfer complex. On acidification, sulphur dioxide was evolved, and the starting material was precipitated. This indicated that an anionic sigma complex had been formed, and this was supported by the visible absorption spectrum which exhibited two bands at λ_{max} 410 and 575nm (fig.2.2.6b), characteristic of anionic sigma complexes formed from the reaction of sulphite ion with naphthalene derivatives. The stoichiometry of the complex was found to be 1:1 by Job's method of continuous variation (fig.2.2.7).

The NMR spectrum of the complex formed between sulphite ion and 1,4,5,7-tetranitro-2,3-dimethylnaphthalene is shown in fig.2.2.9b. The change in the spectrum of the nitroaromatic on addition of sulphite ion is analagous to that for the addition of methoxide ion, indicating that the complex probably had the structure (42) shown in fig.2.2.8.



(42)

Fig.2.2.8

However, in contrast to the comparable reaction with methoxide-d_3 (sec.2.2.2), no further change in the NMR spectrum was observed on the addition of a further equivalent of sulphite ion. This probably reflects the

lower basicity of sulphite ion compared to methoxide-d_3 ion.

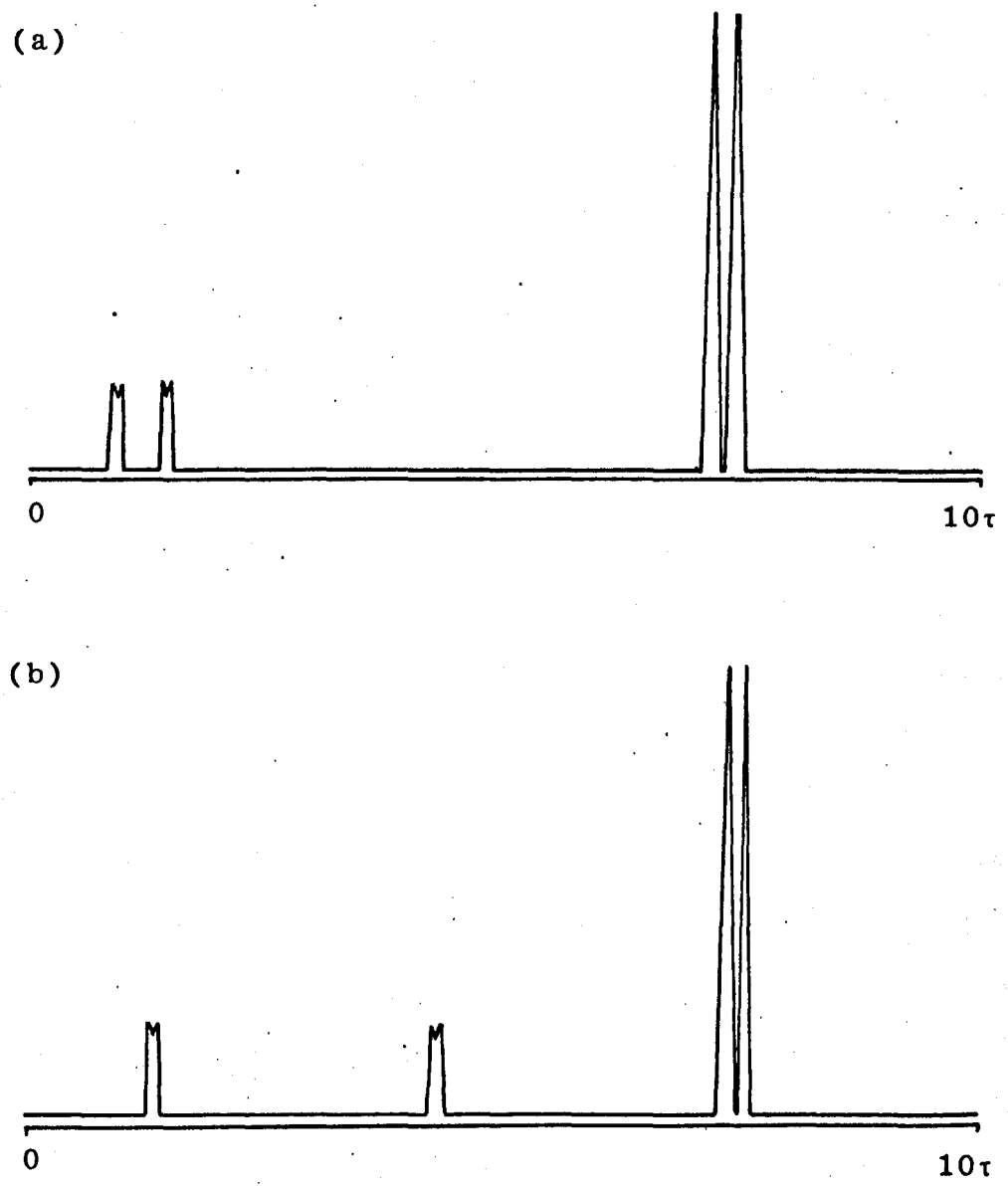


Fig.2.2.9 (a) Normal spectrum of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene in DMSO-d_6. (b) Spectrum after the addition of one equivalent of 1M sodium sulphite in deuterium oxide.

2.2.4 Experimental Section

(i) Reaction of 1,6,8-trinitro-2,3-dimethylnaphthalene with methoxide ion

NMR Spectrum - 1,6,8-trinitro-2,3-dimethylnaphthalene (0.0291g) was dissolved in DMSO-d_6 (0.4ml),and the NMR spectrum recorded (fig.2.2.2a); the aromatic resonances were at τ0.58 and 1.05(2H,ABq,J_{AB} 2Hz),and 1.35(1H,s). 2M sodium methoxide-d_3 in methanol-d_4 (50μl) was added,and the NMR spectrum recorded (fig.2.2.2b); the new positions of the aromatic resonances were τ1.20 and 4.25(2H,ABq,J_{AB} 2Hz),and 2.38(1H,s). Addition of a further quantity of methoxide-d_3 ion resulted in the loss of the spectrum.

Preparative Reaction - 1,6,8-trinitro-2,3-dimethylnaphthalene (0.062g) was dissolved in freshly distilled dichloromethane (50ml) contained in a flask flushed with dried nitrogen. 1M sodium methoxide in dried methanol (0.5ml) was added,and the mixture stirred for 0.5h. Evaporation of the solvent to half-volume precipitated a dark red solid (0.035g), which was filtered off under an atmosphere of nitrogen. M.p.160° (dec.). Elemental analysis: Found: C,45.0; H,11.8; N,6.1; Na,6.1. $C_{12}H_9N_3O_6.NaOCH_3$ requires C,45.2; H,3.5; N,12.2; Na,6.7%. No mass spectrum could be obtained.
A portion of the product (0.01g) was dissolved in water, producing a red coloured solution. After standing for 24h, a white solid precipitated,which was filtered off,dried, and the mass spectrum recorded. This showed that the precipitate was 1,6,8-trinitro-2,3-dimethylnaphthalene.

(ii) Reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene with methoxide ion

NMR Spectrum - 1,4,5,7-tetranitro-2,3-dimethylnaphthalene (0.021g) was dissolved in DMSO-d_6 (0.4ml),and the NMR spectrum recorded (fig.2.2.5a); the aromatic resonances were at τ0.90 and 1.35(2H,ABq,J_{AB} 2Hz). An equivalent quantity of 2M sodium methoxide-d_3 in methanol-d_4 (30μl) was added,and the spectrum re-recorded (fig.2.2.5b); the new positions of the aromatic resonances were τ1.26 and 4.16. A further quantity of methoxide-d_3 ion was added (30μl),and the spectrum recorded; the positions of the resonances (low to mid-field) were τ0.25,2.0,3.95,4.43 and 4.70 (fig.2.2.5c). The further addition of methoxide-d_3 ion did not change the spectrum.

Visible Spectrum - A 10^{-4}M solution of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene in DMSO was prepared by dissolving 0.00336g of the compound in 100ml of freshly distilled DMSO. To a portion (10ml) of this solution was added 0.2M sodium methoxide in methanol (5μl),and the visible spectrum recorded (fig.2.2.6a).

Preparative Reaction - 1,4,5,7-tetranitro-2,3-dimethylnaphthalene (0.336g) was dissolved in dried tetrahydrofuran (200ml) contained in a flask flushed with dried nitrogen. 2M sodium methoxide in methanol (1ml) was added,producing initially a red coloration,followed by a red precipitate. After stirring for 4h,the precipitate was filtered off under an atmosphere of nitrogen,and collected (0.11g).

Elemental analysis - Found: C,37.6; H,3.3; N,12.2; Na,10.0. $C_{12}H_8N_4O_8.(NaOCH_3)_2$ requires C,37.8; H,3.2; N,12.6; Na,10.3%.

A quantity of the solid (0.05g) was dissolved in water, producing a red coloured solution. After 24h,a white material was precipitated,and this was filtered off. The mass spectrum of this material showed that it was 1,4,5,7-tetranitro-2,3-dimethylnaphthalene.

(iii) *Reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene with sulphite ion*

Qualitative Reaction - 1,4,5,7-tetranitro-2,3-dimethylnaphthalene (0.5g) was added to a 1M aqueous solution of sodium sulphite (200ml). On stirring,the nitroaromatic dissolved to give a red coloured solution. Upon warming to 60^{o} ,the colour of the solution intensified,but weakened again on cooling. Acidification of the solution with 2N hydrochloric acid (50ml) resulted in the precipitation of a white solid,accompanied by the evolution of sulphur dioxide gas. The solid was collected,and the mass spectrum recorded. This showed that the precipitate was 1,4,5,7-tetranitro-2,3-dimethylnaphthalene.

Visible Spectrum - 1,4,5,7-tetranitro-2,3-dimethylnaphthalene (0.00336g) was dissolved in freshly distilled DMSO (1ml) and 1M aqueous sodium sulphite solution (10µl) added. The volume was made up to 100ml with DMSO,and the visible spectrum recorded (fig.2.2.6b).

Job Plot - A series of solutions of constant molar concentration was prepared by mixing stock solutions of (a) aqueous sodium sulphite (0.1M) and (b) 1,4,5,7-tetranitro-2,3-dimethylnaphthalene in DMSO (0.1M),and making up the volumes with DMSO to produce solutions of concentration 2×10^{-4} . The absorbances of each solution at 575nm were

recorded using an SP600 spectrophotometer,and the results plotted as shown in fig.2.2.7.

NMR Spectrum - 1,4,5,7-tetranitro-2,3-dimethylnaphthalene (0.0336g) was dissolved in DMSO-d_6 (0.4ml). The NMR spectrum was recorded (fig.2.2.9a),and then 1M sodium sulphite in deuterium oxide (100µl) added. The spectrum was again recorded (fig.2.2.9b); the new aromatic resonances were at τ1.40 and 4.32. The addition of further amounts of sulphite ion did not change the spectrum.

2.3 Results and Discussions of Reactions of Base with Nitro-1,5-Dimethylnaphthalenes

2.3.1 Reaction of 4-Nitro-1,5-Dimethylnaphthalene with Potassium Hydroxide in Methanol

Reaction of 4-nitro-1,5-dimethylnaphthalene (27) with methanolic potassium hydroxide led to the precipitation of *trans*-5,5'-dimethyl-4,4'-dinitro-*bis*-1,2(1-naphthyl) ethene (43) in good yield (>55%) and a low yield (*ca* 1%) of 5,5'-dimethyl-4,4'-dinitro-*bis*-1,2(1-naphthyl)ethane (44).

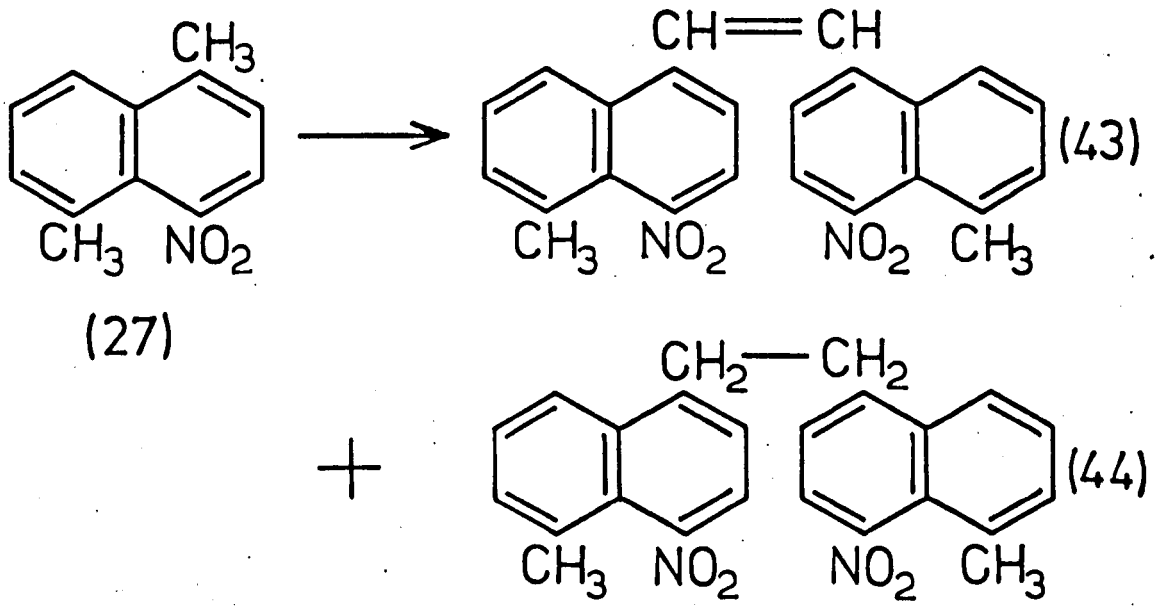
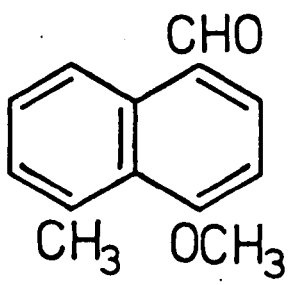


Fig.2.3.1

In reporting the reaction of p-nitrotoluene under the same conditions as used above,Green[156] observed that initially only the saturated product,dinitrobibenzyl,(corresponding to the saturated compound 44) was produced,but by allowing the reaction to proceed for longer periods the unsaturated product,dinitrostilbene,(corresponding to the unsaturated compound 43) was produced,and that the final product ratio

approached 1:1. He therefore concluded that the unsaturated product was derived from the oxidation of the saturated product. In order to determine if this was true for the 4-nitro-1,5-dimethylnaphthalene reaction,the experiment was repeated,but samples were withdrawn at regular intervals, and analysed by NMR spectroscopy. This indicated that one hour after the commencement of the reaction,a small amount of compound 44 was present,together with compounds 27 and 43. After longer times,the samples contained only compounds 27 and 43,the latter being in the majority. If compound 44 had been present in all the samples,the amounts increasing with time,it would have been reasonable to conclude that compounds 43 and 44 were formed competitively. The results therefore suggest that the reaction sequence is probably 27→44→43. Samples taken more than 24 hours after the commencement of the reaction were found to contain only 4-methoxy-5-methyl-1-naphthaldehyde (45),a product which must have been formed by the oxidation of the ethylene bridge of compund 43,together with replacement of the nitro group by a methoxy group.



(45)

Fig.2.3.2

2.3.2 Reaction of 4-Nitro-1,5-Dimethylnaphthalene with Potassium *Tert*-Butoxide in *Tert*-Butanol

The reaction of 4-nitro-1,5-dimethylnaphthalene with potassium *tert*-butoxide in *tert*-butanol was performed in a similar manner to Russell and Janzen's reaction of p-nitrotoluene with this base[162]. Care was taken to exclude oxygen by degassing all the solvents used in the reaction. The product was found to consist almost entirely of the saturated dimer (44). The reaction probably proceeded via the disproportionation of the 4-nitro-1,5-dimethylnaphthalene radical, in an analogous manner to the comparable reaction of p-nitrotoluene (sec.2.1.4a).

The reaction was repeated with the reaction vessel open to the atmosphere. After 24 hours, the yield of the unsaturated dimer (43) had risen significantly compared to the reaction performed in the absence of oxygen, though not to the same extent as in the reaction of 4-nitro-1,5-dimethylnaphthalene with methanolic potassium hydroxide. It is fair to assume that the production of compound 43 occurred via the oxidation of compound 44, as in sec.2.3.1.

2.3.3 Reaction of 2,4,8-Trinitro-1,5-Dimethylnaphthalene with Methoxide Ion

The NMR spectrum of 2,4,8-trinitro-1,5-dimethylnaphthalene in DMSO-d_6 is shown in fig.2.3.3a. Addition of one equivalent of methoxide ion caused the spectrum to change to that shown in fig.2.3.3b where, as compared to the original spectrum, one of the methyl resonances (τ7-8) had disappeared, two mid-field peaks had appeared, and the aromatic resonances had remained unchanged, although shifted

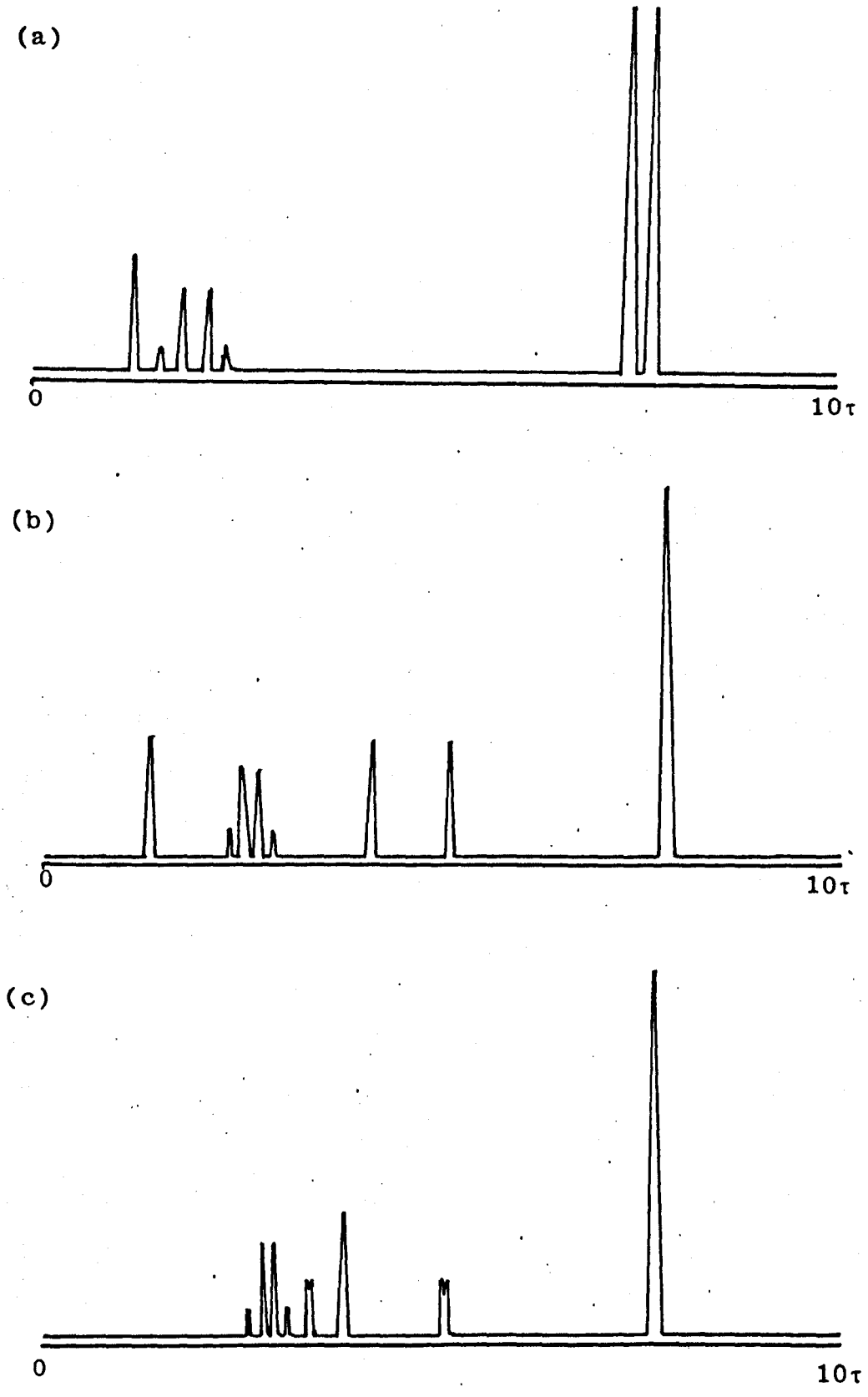


Fig.2.3.3 (a) Normal spectrum of 2,4,8-trinitro-1,5-dimethylnaphthalene in DMSO-d_6. (b) Spectrum after the addition of one equivalent of methoxide-d_3. (c) Spectrum after the addition of three equivalents of methoxide-d_3.

to slightly higher field. The integral ratio of the peaks (from low to high field) was 1:2(quartet):1:1:3,which implies a structure in which there is one uncoupled aromatic proton, two coupled aromatic protons,two uncoupled "olefinic" or "sigma" type protons,and one methyl group. This accounts for eight protons,and as there are nine protons in 2,4,8-trinitro-1,5-dimethylnaphthalene it must be concluded that abstraction of a proton from one of the two methyl groups took place on reaction with base,the resultant group giving rise to the two mid-field resonances. In order to confirm that abstraction of a proton had taken place,the contents of the NMR sample tube were poured out into an excess of hydrochloric acid-*d* in deuterium oxide immediately after the spectrum corresponding to fig.2.3.3b had been recorded. This resulted in the precipitation of a solid product,the mass spectrum of which showed that the major component was 2,4,8-trinitro-1,5-dimethylnaphthalene-*d*. The NMR spectrum of the solid was recorded in deutero-chloroform,and the ratio of the integrals of the methyl and aromatic resonances found to be approximately 5:3,as compared to 6:3 for 2,4,8-trinitro-1,5-dimethylnaphthalene, indicating that incorporation of deuterium had taken place at a methyl group position. This is clear evidence that the species obtained on reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with methoxide-d_3 ion contains a "benzyl-type" $-CH_2^-$ group. However,the NMR spectrum of the reaction product (fig.2.3.3b) contains two single-proton peaks attributable to this group,and not one two-proton peak which might be expected for a $-CH_2^-$ group.

It is postulated therefore that there exists in solution an equilibrium between a "quinoidal" form (46a) and an "aromatic" form (46b) of the ion formed on reaction with methoxide-d_3, in which almost 100% of the species present is of the "quinoidal" form. However, on addition of D^+ ions reaction must take place only via the "aromatic" form (to give compound 47), and thus the "quinoidal" form is converted to the "aromatic" form as the latter species is removed by reaction.

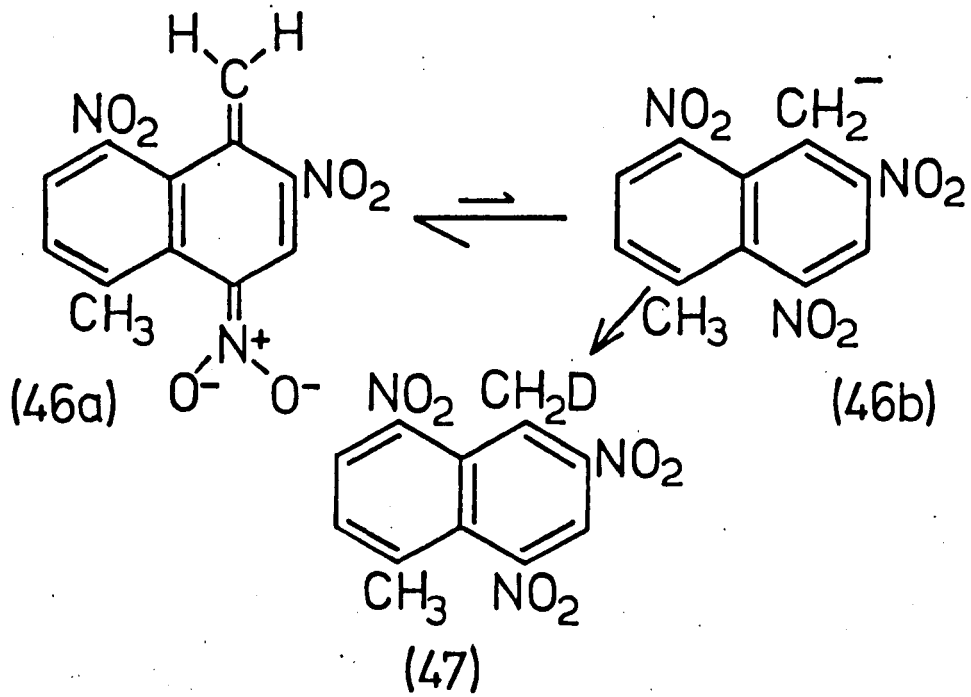


Fig.2.3.4

The "olefinic" protons of species 46a have different environments, and therefore have different chemical shifts (fig.2.3.3b). It might be expected that these protons would couple to give a doublet of doublets, but this was not found to be the case. This is consistent with the NMR spectra of compounds containing exocyclic $C=CH_2$ groups where there is 1,3 conjugation between the olefinic group and another π-bonded group, e.g. itaconic anhydride (fig.2.3.5)

for which the geminal coupling constant of the olefinic protons is negligible[190] .

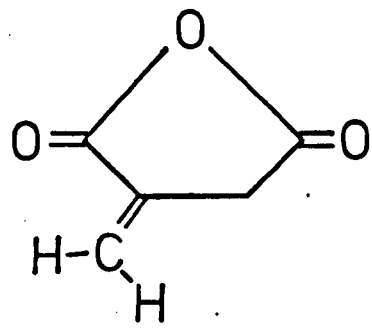
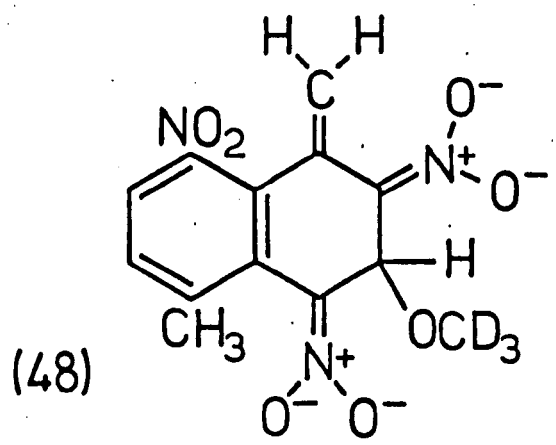


Fig.2.3.5

When the reaction between 2,4,8-trinitro-1,5-dimethylnaphthalene and methoxide-d_3 ion was repeated using a molar ratio of greater than 1:1,the spectrum shown fig.2.3.3c was obtained,in which the resonance having the lowest chemical shift,corresponding to the 3-proton,had shifted to mid-field,and the mid-field resonances which appeared in fig.2.3.3b as singlets were present as a doublet of doublets. The shift of the resonance position of the 3-proton indicates that addition of a methoxy-d_3 group had occurred to give a complex with the following structure (48) :-



(48)

Fig.2.3.6

It would appear that the reduction of conjugation between

the $C=CH_2$ group and the ring compared to species 46a was such that the geminal coupling constant of the olefinic protons was markedly increased.

2.3.4 Reaction of 2,4,8-Trinitro-1,5-Dimethylnaphthalene with Diethylamine

Addition of one equivalent of diethylamine to a solution of 2,4,8-trinitro-1,5-dimethylnaphthalene in DMSO-d_6 gave the same NMR spectrum as obtained for the addition of one equivalent of methoxide-d_3 ion (fig.2.3.3b). Thus it may be concluded that the same anionic species (46a) was formed in both cases. Further addition of diethylamine did not result in a change in the initial spectrum, in contrast to the reaction with methoxide-d_3 ion where sigma bond formation at the 3-position occurred. This probably did not occur for diethylamine because of the lower basicity of this species, and because of the steric effects of the nitro groups at the 2- and 4-positions.

2.3.5 Reaction of 2,4,6,8-Tetranitro-1,5-Dimethylnaphthalene with Methoxide Ion

The NMR spectrum of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene in DMSO-d_6 is shown in fig.2.3.7a. Addition of one equivalent of methoxide-d_3 ion caused the spectrum to change to that shown in fig.2.3.7b, where the single aromatic proton peak was split into two peaks, both at higher field than the original peak, the single methyl proton peak was halved in intensity, and two new peaks had appeared in the mid-field region. The integral ratio of the peaks (from low to high field) was 1:1:1:1:3, suggesting that, as for 2,4,8-trinitro-1,5-dimethylnaphthalene, proton

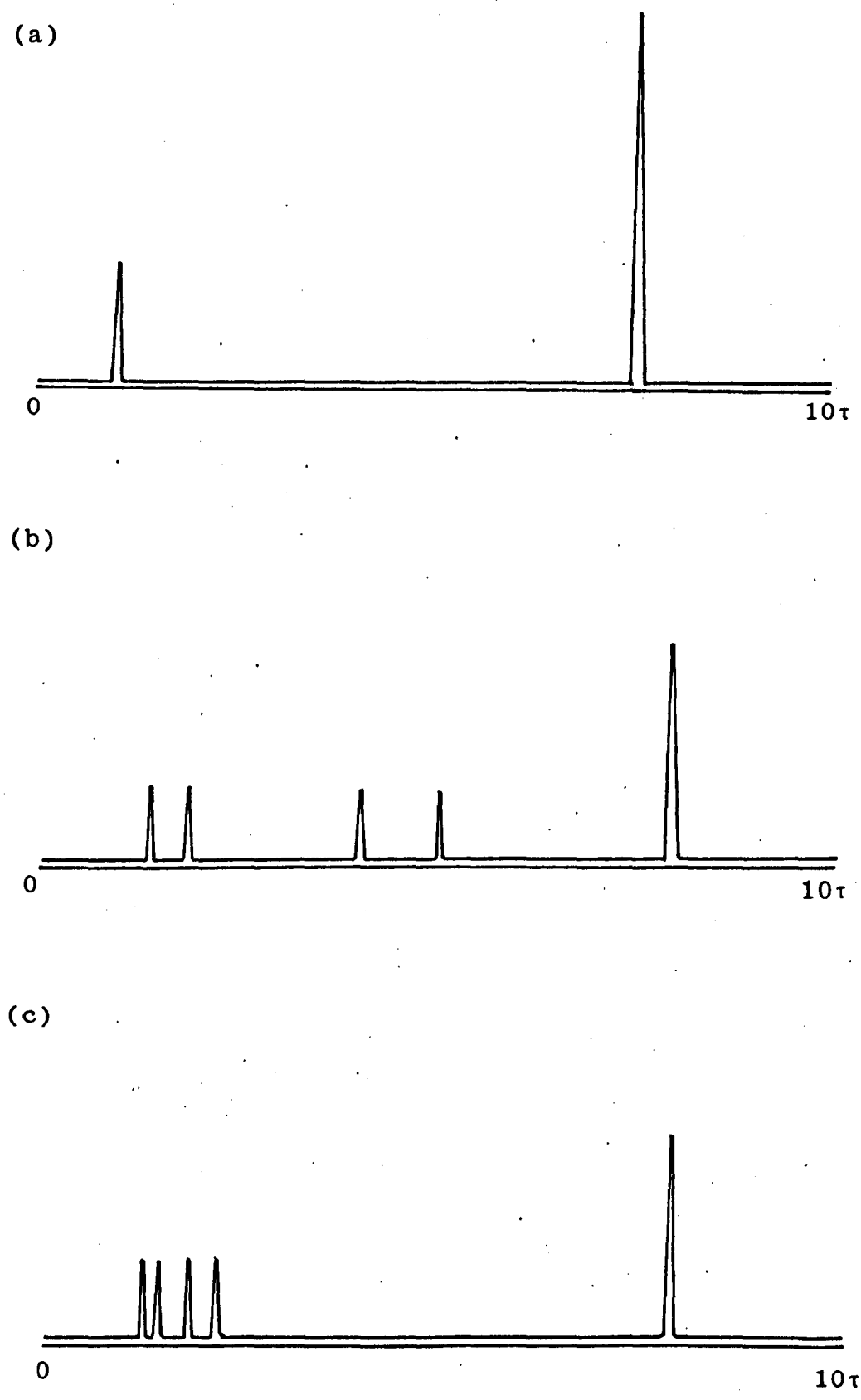


Fig.2.3.7 (a) Normal spectrum of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene in DMSO-d_6. (b) Spectrum recorded immediately after the addition of one equivalent of methoxide-d_3. (c) Spectrum *(b)* after 0.5h.

abstraction from the 1-methyl group had occurred to give a "benzyl" type ion,existing as an equilibrium between an "aromatic" form (49a) and a "quinoidal" form. However, the NMR spectrum shown in fig.2.3.7b was observed to diminish in intensity slowly,and was replaced by the spectrum shown in fig.2.3.7c,consisting of four single-proton peaks in the low-field region,and one three-proton peak in the high-field region. In the case of the reaction of methoxide ion with 2,4,5,7-tetranitro-1,8-dimethyl-naphthalene,an NMR spectrum similar to that shown in fig.2.3.7b was obtained which did not change with time[191]. This latter compound has a methyl group substituted at the adjacent *peri*-position to the 1-methyl group,i.e.the 8-position,whereas 2,4,6,8-tetranitro-1,5-dimethylnaphthalene has a nitro group substituted at this position. This could imply that a modification of the initially formed ion,which gives rise to the spectrum shown in fig.2.3.7b, takes place due to the proximity of the nitro group at the 8-position to the olefinic group at the 1-position. A possible modified form is species 49c,fig.2.3.8,in which the nitro groups at the 2- and 8-positions participate in intramolecular hydrogen-bonding with the hydrogen atoms of the olefinic group. Due to the intramolecular hydrogen-bonding,the positions of resonance of the olefinic protons would be expected to shift to lower field. Thus species 49c should give rise to an NMR spectrum consisting of one methyl peak in the high-field region,two aromatic single-proton peaks in the low-field region,and two single-proton peaks corresponding to the olefinic protons,also in

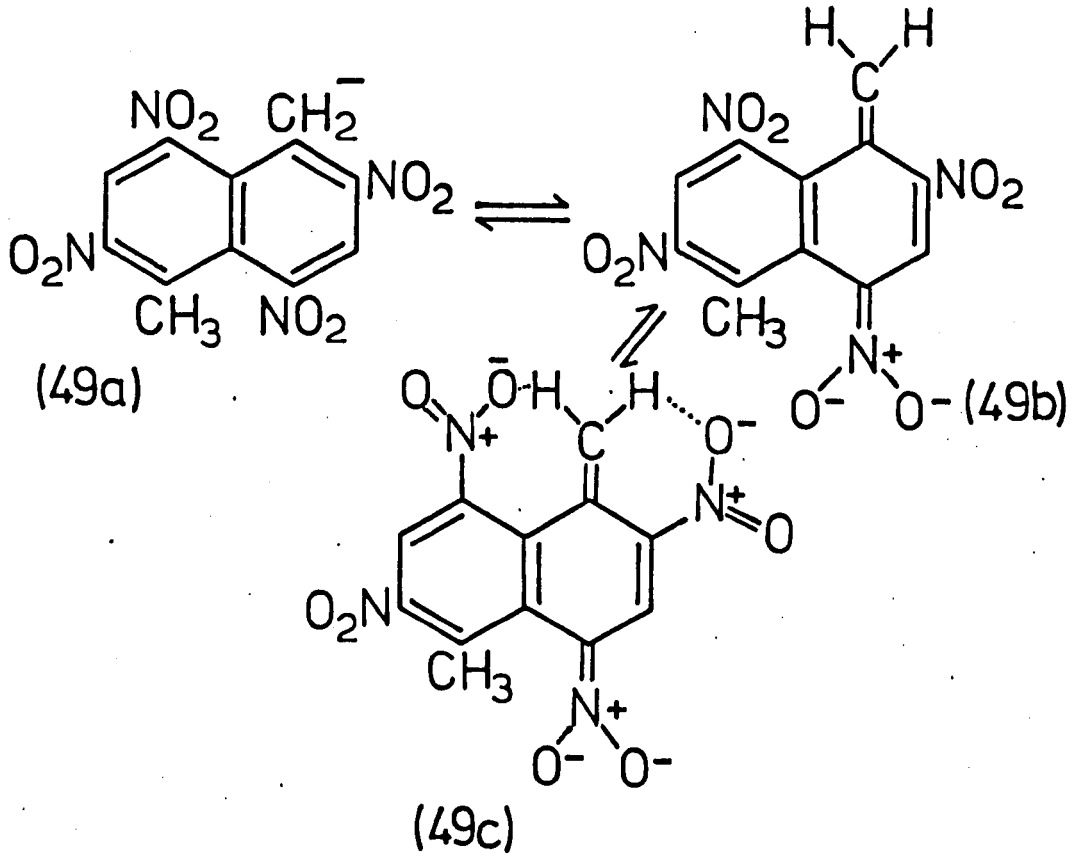


Fig.2.3.8

the low-field region; this is consistent with the observed spectrum (fig.2.3.7c).

Immediately after the spectrum corresponding to fig.2.3.7c was recorded,the contents of the NMR sample tube were treated with hydrochloric acid-*d* in deuterium oxide,and a solid obtained,the mass spectrum of which showed it to be 2,4,6,8-tetranitro-1,5-dimethylnaphthalene-*d*. It seems probable,therefore,that as in the case of 2,4,8-trinitro-1,5-dimethylnaphthalene,reaction with D^+ ions took place only via the "aromatic" form (49a),and that species 49c was converted to species 49a as the latter was removed by reaction.

The reaction between 2,4,6,8-tetranitro-1,5-dimethylnaphthalene and methoxide-d_3 ion was repeated using an excess of methoxide-d_3 ion. The same spectra as

those described above were obtained in this way.

The UV-visible spectrum of the 1:1 2,4,6,8-tetranitro-1,5-dimethylnaphthalene/methoxide ion system shown in fig.2.3.10a features two peaks at λ_{max}385 and 590nm. This may be compared to the UV-visible spectrum of the postulated 2,4,6-trinitrobenzyl anion,which exhibits peaks at λ_{max}370 and 510nm [166].

The reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with methoxide ion was studied on a preparative basis by adding an excess of sodium methoxide to a solution of the nitroaromatic in dried tetrahydrofuran. An orange solid was obtained which possessed similar properties to the Meisenheimer compound synthesised from the reaction of sodium methoxide with 3,5,6,8-tetranitroacenaphthene [192], in that it was soluble in water,hydrolysed to give the starting material,and detonated violently on touch. No mass spectrum could be obtained for the product,consistent with an ionic compound. The NMR spectrum of a saturated solution of the product in DMSO-d_6 was too weak in intensity to be used in the assignment of the structure of the product. However,elemental analysis of the product showed that a 2:1 adduct of sodium methoxide and 2,4,6,8-tetranitro-1,5-dimethylnaphthalene had been formed. Thus the reaction in tetrahydrofuran differed from that in DMSO-d_6 where there was no indication from the NMR spectrum of 2:1 adduct formation in the presence of excess methoxide ion. Clearly abstraction of a methyl proton in the tetrahydrofuran reaction could not have taken place to give species such as 49a,49b or 49c,as the elemental analysis of the product

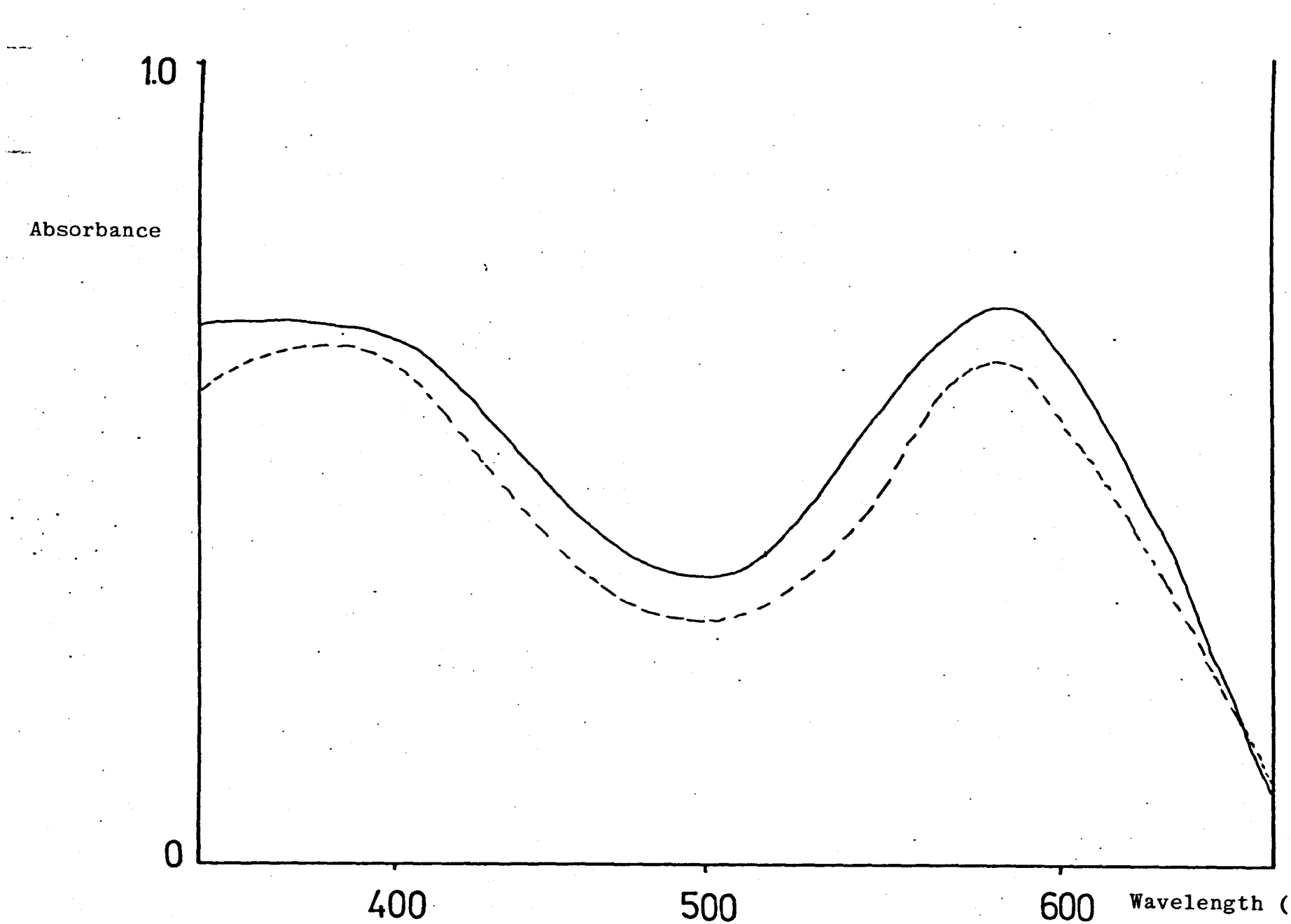
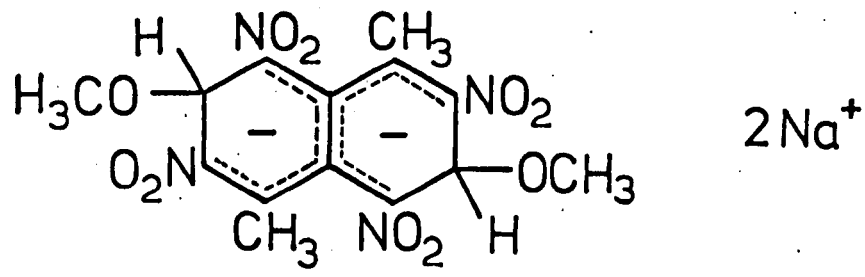


Fig.2.3.10 UV-Visible spectra of the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with (a) methoxide ion (—) (b) diethylamine (---).

would have corresponded to that of the sodium salts of these species. Based on the foregoing,and on a knowledge of the properties of Meisenheimer complexes,it is likely that the product isolated from the reaction in tetrahydrofuran had the structure (50) shown in fig.2.3.9.



(50)

Fig.2.3.9

2.3.6 Reactions of 2,4,6,8-Tetranitro-1,5-Dimethylnaphthalene with Diethylamine and Triethylamine

The NMR spectrum obtained immediately after the addition of one mole equivalent of diethylamine to a solution of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene in DMSO-d_6 is shown in fig.2.3.11b. This spectrum is almost identical to the spectrum obtained from the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with methoxide-d_3 ion (fig.2.3.7b). The spectrum (fig.2.3.11b) changed with time to the spectrum shown in fig.2.3.11c,which is almost identical to the spectrum obtained with methoxide-d_3 ion shown in fig.2.3.7c. It may be assumed,therefore,that the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with diethylamine in a 1:1 molar ratio produced the same species as the reaction with methoxide-d_3 ion (fig.2.3.8).

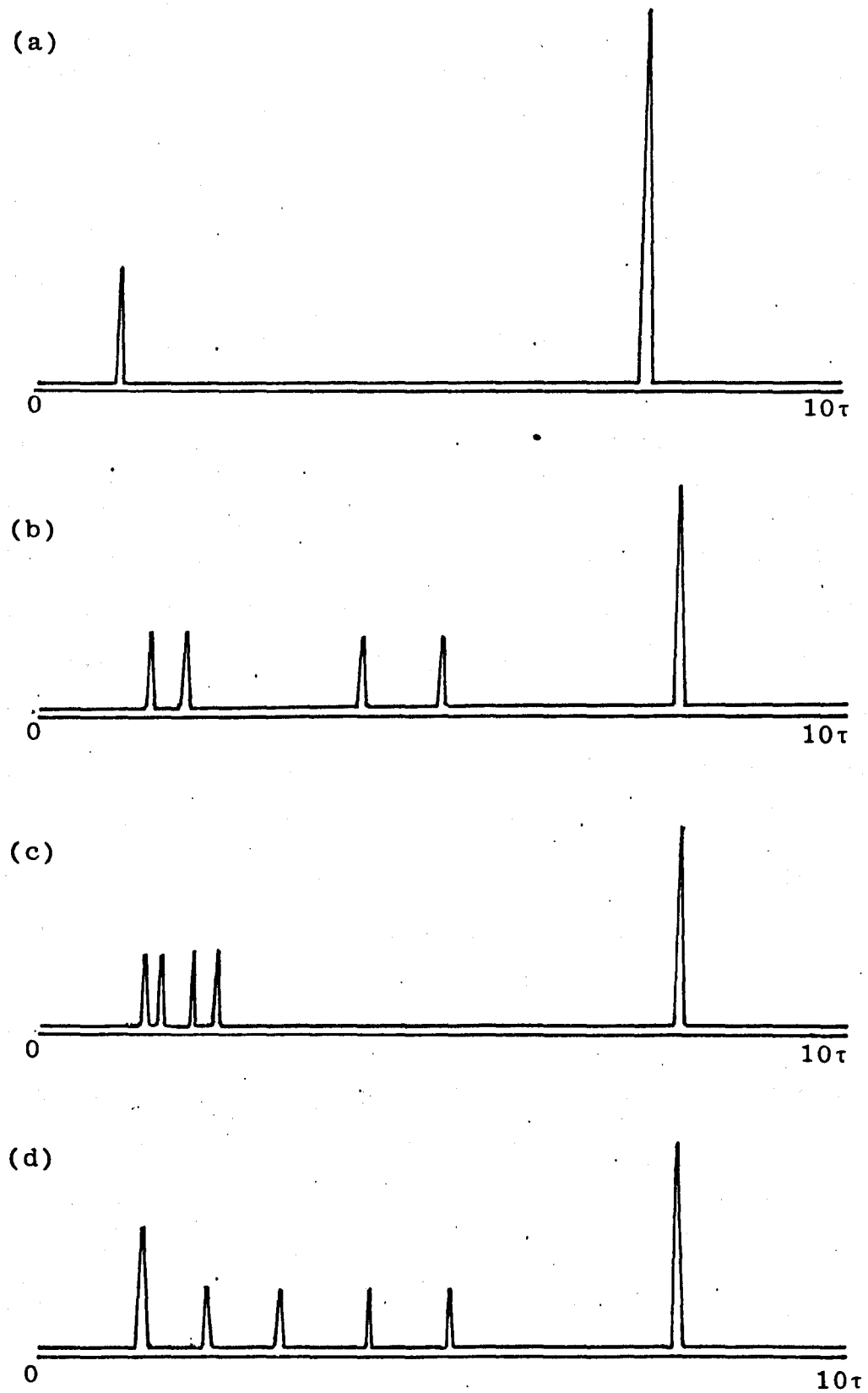


Fig.2.3.11 (a) Normal spectrum of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene in DMSO-d_6 (b) Spectrum recorded immediately after the addition of one equivalent of diethylamine. (c) Spectrum *(b)* after 1h. (d) Spectrum after the addition of two equivalents of diethylamine.

Addition of an excess of diethylamine,to give an amine/ nitroaromatic ratio of greater than 1:1,resulted in the loss of the NMR spectrum shown in fig.2.3.11c,and the formation of the spectrum shown in fig.2.3.11d,which consists of six individual peaks in an integral ratio of 2:1:1:1:1:3 (from low to high field). This spectrum did not change with time,nor did it change on addition of further amounts of diethylamine. The identical spectra (figs.2.3.11b,c and d) were obtained by the treatment of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with triethylamine, although the conversion of spectrum 2.3.11b to 2.3.11c,and of spectrum 2.3.11c to 2.3.11d,was considerably slower than for diethylamine. As the spectra obtained for the reaction with both diethylamine and triethylamine were identical,the species responsible for the spectra could not have been the result of sigma addition of amine molecules,as this would have given rise to different spectra in each case. This was further confirmed by the observation that the spectra of the amines in the respective systems (omitted from the reproduced spectra for reasons of clarity) consisted of only one set of resonances in each case. Had addition of amine molecules taken place,then two sets of resonances,corresponding to the amines in the free and complexed forms,would have been observed in each case. An interesting feature of the spectrum shown in fig.2.3.11d (excess amine) is that it arises from nine protons,whereas the spectrum shown in fig.2.3.11c (1:1 amine/ nitroaromatic ratio) arises from seven protons. A possible, though highly speculative,explanation of this phenomenon is

that addition of excess amine results in abstraction of H^+ ions from water molecules present in the solvent to give OH^- ions,which then attack the species giving rise to the spectrum shown in fig.2.3.11c (49c) to yield species such as 51a or 51b,as shown in fig.2.3.12.

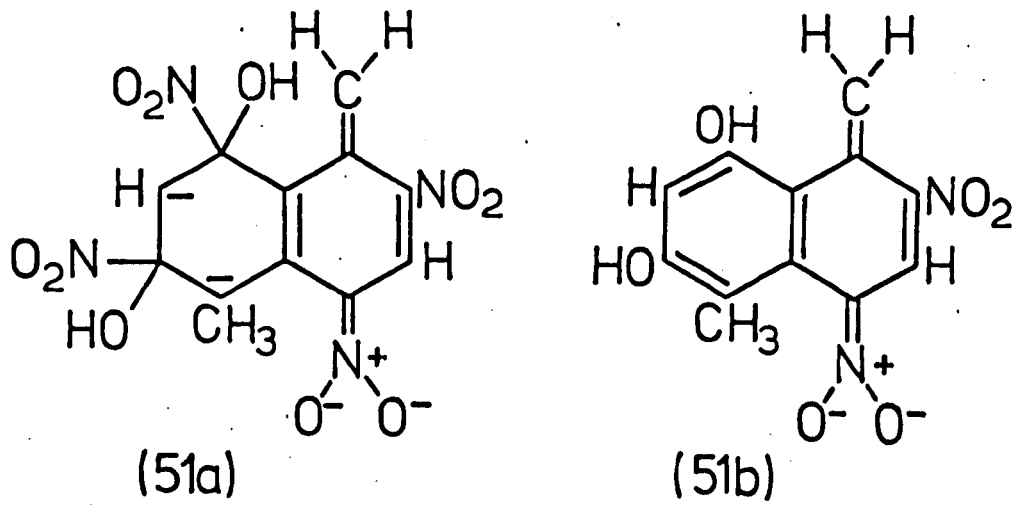


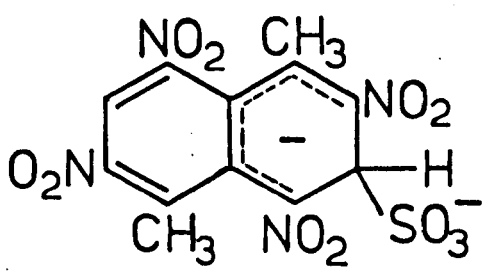
Fig.2.3.12

In species 51a,hydroxyl groups are added at two ring positions occupied by nitro groups; in species 51b,the hydroxyl groups have displaced the nitro groups completely. Attack of an electrophile at a ring position occupied by a nitro group is known to occur,*cf* trinitrobenzene[189],and can result in the complete displacement of a nitro group. Species 51a and 51b both contain nine protons,as required by the species giving rise to the spectrum shown in fig.2.3.11d. Both species contain one methyl group,which would give a resonance at high field,an exocyclic olefinic group,which would give two resonances at mid-field,and two ring protons which would give two resonances at low field. In the case of species 51a,the hydroxyl protons might be expected to have the same chemical shifts,and could resonate at low field due to the de-shielding effect

of the nitro groups. In the case of 51b,the hydroxyl protons are of a phenolic type,which would resonate at low field,and again might be expected to have the same chemical shifts. Therefore,either of the two species (51a and 51b) could give an NMR spectrum consistent with the spectrum shown in fig.2.3.11d.

2.3.7 Reaction of 2,4,6,8-Tetranitro-1,5-Dimethylnaphthalene with Sulphite Ion

Reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene in DMSO-d_6 with sulphite ion in a 1:1 molar ratio initially gave the NMR spectrum shown in fig.2.3.14b. This spectrum is consistent with the formation of a Meisenheimer complex having the structure (52) shown in fig.2.3.13.



(52)

Fig.2.3.13

The initial spectrum (fig.2.3.14b) gradually diminished in intensity as a new spectrum (fig.2.3.14c) appeared, which was the same as the final spectrum obtained from the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with one equivalent of either methoxide ion,diethylamine or triethylamine (fig.2.3.7c and 2.3.11c). This suggests that initially sigma addition of sulphite takes place at

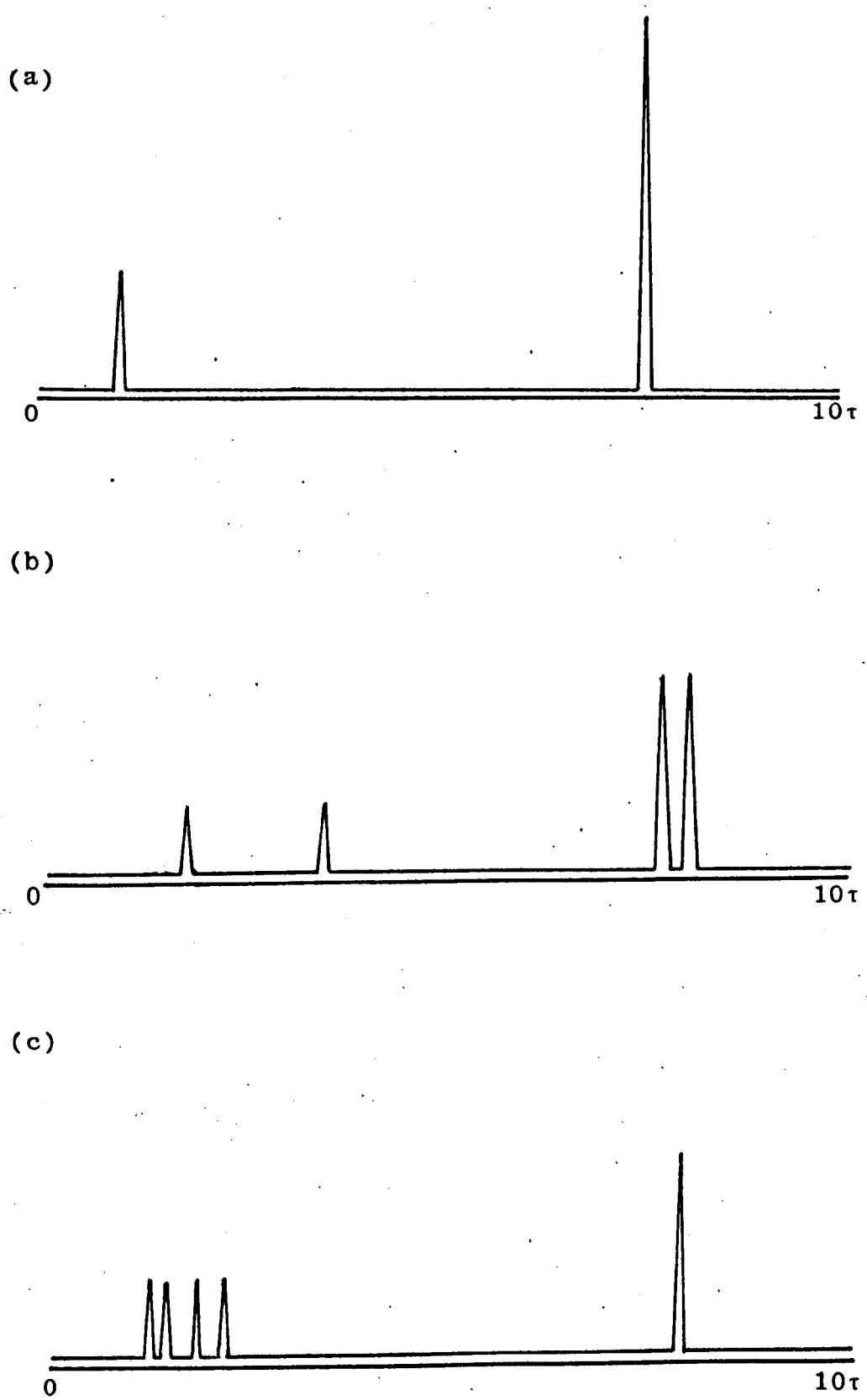


Fig.2.3.13 (a) Normal spectrum of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene. (b) Spectrum recorded immediately after the addition of one equivalent of sulphite ion. (c) Spectrum *(b)* after 5h.

the 3-position,but this sulphite adduct reacts to give a species having a structure corresponding to species 49c (fig.2.3.8). The addition of further amounts of sulphite ion to the system did not result in a change in the final spectrum (fig.2.3.14c).

2.3.8 Experimental Section

(i) Reaction of 4-nitro-1,5-dimethylnaphthalene with potassium hydroxide in methanol

Preparative Run - 4-nitro-1,5-dimethylnaphthalene (27)(1g) was dissolved in methanol (50ml),and 30% potassium hydroxide in methanol (30ml) added. An immediate red coloration was observed. After stirring for 12h,a yellow solid was obtained (0.6g). Recrystallisation from nitrobenzene gave yellow crystals of *trans*-5,5'-dimethyl-4,4'-dinitro-*bis*-1,2(1-naphthyl)ethene (43)(0.55g,55%), m.p.282°. (Found: C,66.1; H,4.4; N,7.1. $C_{24}H_{18}N_2O_4$ requires C,66.3; H,4.5; N,7.0%); τ($CDCl_3$) 2.2-2.6(6H,m) and 7.45 (3H,s); *m/e* 398 (M^+),high resolution mass spectrometry gave the molecular formula as $C_{24}H_{18}N_2O_4$. The mother liquor was evaporated to dryness,and the residue extracted with benzene. The extract was run on a silica gel TLC plate (0.3mm;200 x 200mm) using 1:1 benzene/petroleum spirit (b.p.60-80°) as eluent. The band at R_f 0.95 was removed, and the material extracted from the silica gel with methanol; this was found to be the starting material (27). The band at R_f 0.89 was removed,extracted with methanol, and found to be 5,5'-dimethyl-4,4'-dinitro-*bis*-1,2(1-naphthyl) ethane (44)(0.01g,1%),m.p.220°. (Found: C,65.9; H,5.1; N,6.9. $C_{24}H_{20}N_2O_4$ requires C,66.0; H,5.0; N,7.0%); τ($CDCl_3$) 2.3-2.6

(5H,m),6.55(2H,s) and 7.65(3H,s); *m/e* 400 (M^+),high resolution mass spectrometry gave the molecular formula as $C_{24}H_{20}N_2O_4$.

Semi-Kinetic Run - 4-nitro-1,5-dimethylnaphthalene (27)(1g) was dissolved in methanol (50ml),and 30% potassium hydroxide in methanol (30ml) added. The mixture was stirred in an open flask at 20°,and samples (5ml) withdrawn at hourly intervals,each being drowned out in dilute hydrochloric acid (2N;25ml). The solid products were collected,and the NMR spectra recorded in $CDCl_3$. The first sample was found to contain compounds 27,43 and 44. The second and subsequent samples contained only compounds 27 and 43. The final sample,taken 24h after the commencement of the run,contained only 4-methoxy-5-methyl-1-naphthaldehyde (45),m.p.73°. (Found: C,77.6; H,6.2. $C_{13}H_{12}O_2$ requires C,78.0; H,6.0%); $\tau(CDCl_3)$ -0.1(1H,s),0.7 (1H,s),2.3-2.6(2H,m),2.10 and 3.10(2H,ABq,J_{AB} 9Hz),6.0(3H,s) and 7.15(3H,s); *m/e* 200 (M^+),high resolution mass spectrometry gave molecular formula as $C_{13}H_{12}O_2$.

(ii) *Reaction of 4-nitro-1,5-dimethylnaphthalene with potassium tert-butoxide in tert-butanol*

A solution of potassium *tert*-butoxide in *tert*-butanol was prepared by adding clean potassium metal (1.9g) to dried *tert*-butanol (50ml). This solution was degassed, and added to a solution of 4-nitro-1,5-dimethylnaphthalene (1g) in degassed *tert*-butanol (25ml) in a flask flushed with nitrogen. A deep red coloration was observed. After stirring at 20° for 8h,the mixture was poured into water (400ml),and the product collected (0.46g). The NMR spectrum

of the product indicated that compounds 44 and 43 had been produced in a ratio of *ca* 95:5. Column chromatography of the product on silica gel (400 x 20mm) using 1:1 benzene/petroleum spirit(b.p.60-80°) afforded compound 44 (0.40g,40%),m.p.220°,in a pure state. The reaction was repeated in an identical manner,but with the flask open to the atmosphere. After 24h,the solution was drowned out in water (400ml),and the product collected (0.50g). The NMR spectrum of the product indicated that the ratio of compound 44 to compound 43 was *ca* 80:20.

(iii) *Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with methoxide ion*

2,4,8-trinitro-1,5-dimethylnaphthalene (0.019g) was dissolved in DMSO-d_6 (0.4ml) and the NMR spectrum recorded (fig.2.3.3a); τ1.24(1H,s),1.70 and 2.16(2H,ABq, J_{AB} 8Hz),7.46(3H,s) and 7.52(3H,s). 2M sodium methoxide-d_3 in methanol-d_4 (30μl) was added,and the spectrum recorded (fig.2.3.3b); τ1.37(1H,s),2.57 and 2.79(2H,ABq, J_{AB} 8Hz), 4.12(1H,s),5.13(1H,s) and 7.85(3H,s). The solution was poured into deuterium oxide (5ml) containing 20% hydrochloric acid-*d* in deuterium oxide (0.2ml),and the solid product (0.011g) collected. The NMR spectrum of the solid was recorded in $CDCl_3$; the integral ratio of the aromatic peaks to the methyl peaks (including a small multiplet attributed to CH_2D) was 1:1.75 (*cf* 1:2 for the starting material). This indicated that 75% of the starting material had been monodeuterated. The mass spectrum of the product gave the parent peak at *m/e* 292, corresponding to 2,4,8-trinitro-1,5-dimethylnaphthalene-*d*,

with a smaller peak at *m/e* 291,corresponding to 2,4,8-trinitro-1,5-dimethylnaphthalene (fig.2.3.15a).

2,4,8-trinitro-1,5-dimethylnaphthalene (0.019g) was dissolved in DMSO-d_6 (0.4ml) and 2M sodium methoxide-d_3 in methanol-d_4 (90µl) added. The spectrum was recorded (fig.2.3.3c); τ 2.64 and 2.87(2H,ABq,J_{AB} 8Hz),3.68(1H,s), 3.27 and 5.00(2H,ABq,J_{AB} 2Hz),and 7.60(3H,s). Addition of further quantities of methoxide-d_3 ion did not change the spectrum.

(iv) Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine

2,4,8-trinitro-1,5-dimethylnaphthalene (0.029g) was dissolved in DMSO-d_6 (0.4ml),and diethylamine (10µl) added. The NMR spectrum exhibited the following peaks :- τ1.29(1H,s),2.45 and 2.70(2H,ABq,J_{AB} 8Hz),4.07(1H,s),5.10 (1H,s),and 7.82(3H,s)(*cf* fig.2.3.3b). There was no change in the spectrum on the addition of further amounts of diethylamine.

(v) Reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with methoxide ion

NMR Spectrum - 2,4,6,8-tetranitro-1,5-dimethylnaphthalene (0.021g) was dissolved in DMSO-d_6 (0.4ml),and the spectrum recorded (fig.2.3.7a); τ1.00(1H,s) and 7.50(3H,s). 2M sodium methoxide-d_3 in methanol-d_4 (30µl) was added, and the spectrum recorded immediately (fig.2.3.7b); τ1.30 (1H,s),1.79(1H,s),4.05(1H,s),4.98(1H,s) and 7.88(3H,s). After 0.5h,a new spectrum (fig.2.3.7c) was found to have completely replaced the previous spectrum; τ1.20(1H,s), 1.36(1H,s),1.79(1H,s),2.16(1H,s) and 7.83(3H,s). The

solution was poured into a mixture of deuterium oxide (5ml) and 20% hydrochloric acid-*d* in deuterium oxide (0.2ml), and the solid product collected (0.010g). The mass spectrum of the product indicated that only 2,4,6,8-tetranitro-1,5-dimethylnaphthalene-*d* was present (fig.2.3.15b).

2,4,6,8-tetranitro-1,5-dimethylnaphthalene (0.021g) was dissolved in DMSO-d_6 (0.4ml) and 2M sodium methoxide-d_3 in methanol-d_4 (90µl) added. The NMR spectrum was recorded immediately,and was found to be identical with fig.2.3.7b. After 0.5h,the spectrum had changed to that shown in fig.2.3.7c,and did not change further with time.

UV-Visible Spectrum - 0.2M sodium methoxide in methanol (5µl) was added to a 10^{-4}M solution of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene (10ml),and the UV-visible spectrum recorded using a 10mm path-length cell (fig.2.3.10a); peaks were observed at λ_{max} 385 and 590nm.

Preparative Reaction - 2,4,6,8-tetranitro-1,5-dimethylnaphthalene (0.336g) was dissolved in freshly distilled and dried tetrahydrofuran (200ml) contained in a reaction vessel flushed with dried nitrogen. On addition of 2M sodium methoxide in methanol (1ml) a red coloration immediately formed. After stirring for 2h,an orange solid was precipitated,and was filtered off under an atmosphere of nitrogen. The product (0.12g,m.p.130^{o}dec.) became brown on exposure to light. This compound was found to detonate violently if either heated rapidly or scraped on a glass sinter disc. Elemental analysis :- Found: C,37.1; H,3.1; N,12.9; Na,10.5. $C_{12}H_8N_4O_8.(2NaOCH_3)_2$ requires C,37.8; H,3.2; N,12.6; Na,10.3%. No mass spectrum could be obtained

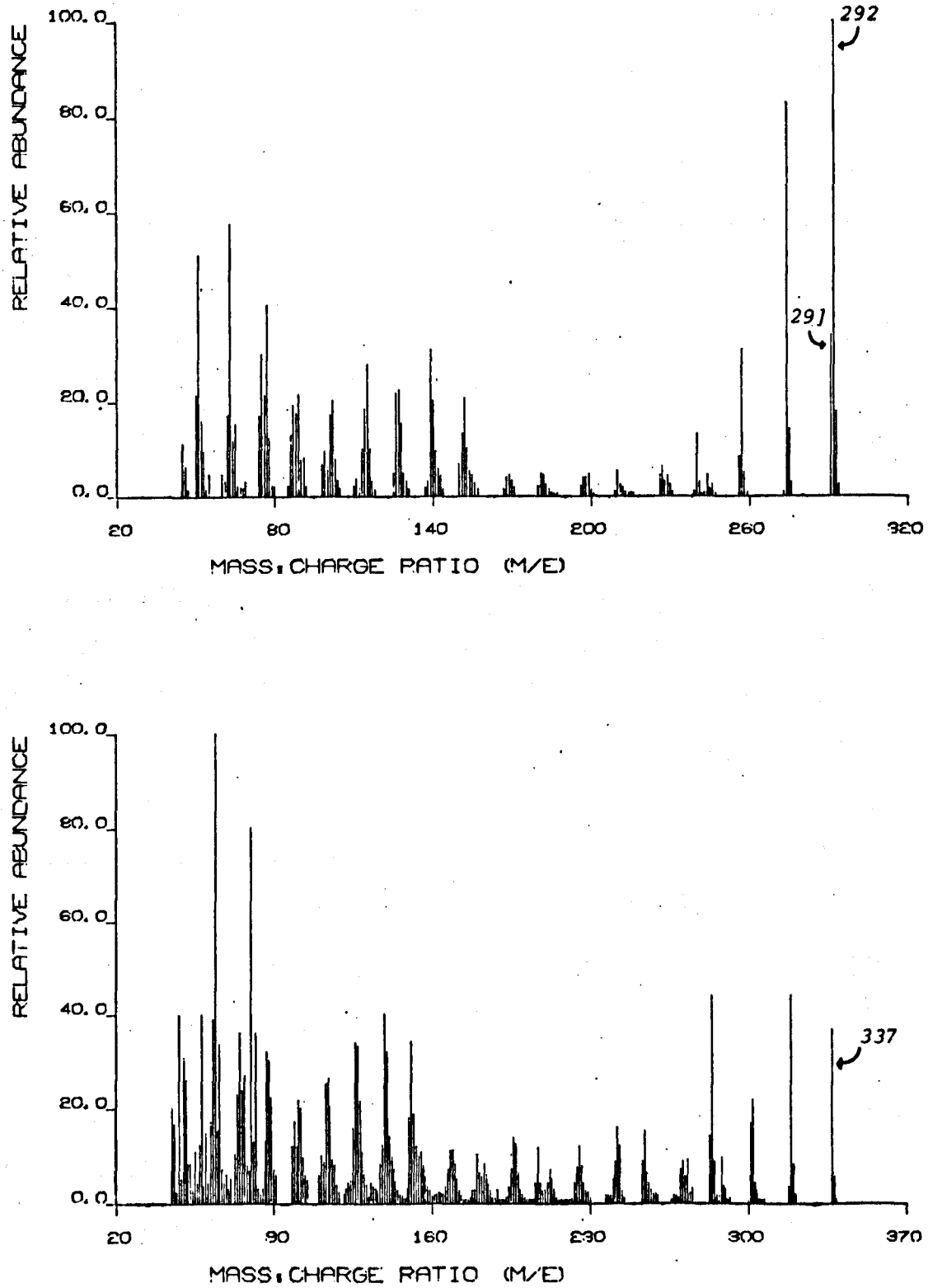


Fig.2.3.15 Mass spectra of deuterated products obtained from (a) 2,4,8-trinitro-1,5-dimethylnaphthalene and (b) 2,4,6,8-tetranitro-1,5-dimethylnaphthalene.

for the product. The NMR spectrum of the solid in DMSO-d_6 was weak,apparently due to reaction on dissolution,and peaks could not be accurately detected. On hydrolysis of the solid in water a white product was obtained,the mass spectrum of which showed that it was 2,4,6,8-tetranitro-1,5-dimethylnaphthalene.

(v) Reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with diethylamine

NMR Spectrum - 2,4,6,8-tetranitro-1,5-dimethylnaphthalene (0.034g) was dissolved in DMSO-d_6 (0.4ml),and diethylamine (10µl) added. The spectrum was recorded immediately (fig.2.3.11b); τ1.17(1H,s),1.66(1H,s),3.96(1H,s),4.92(1H,s) and 7.83(3H,s). This spectrum diminished in intensity slowly,and after 1h had been completely replaced by a new spectrum (fig.2.3.11c); τ1.00(1H,s),1.20(1H,s),1.66(1H,s), 2.00(1H,s) and 7.80(3H,s). A further quantity of diethylamine (10µl) was added,and the spectrum recorded (fig.2.3.11d); τ1.29(2H,s),2.07(1H,s),2.92(1H,s),4.03(1H,s),5.14(1H,s) and 7.81(3H,s). This spectrum did not change on the addition of further quantities of diethylamine.

UV-Visible Spectrum - Diethylamine (1µl) was added to a 10^{-4}M solution of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene in DMSO (100ml),and the UV-visible spectrum recorded (fig.2.3.10b); λ_{max} values were 385 and 590nm.

(vii) Reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with triethylamine

2,4,6,8-tetranitro-1,5-dimethylnaphthalene (0.034g) was dissolved in DMSO-d_6 (0.4ml),and triethylamine (10µl) added. The spectrum was recorded; τ1.17(1H,s),1.66(1H,s),

3.95(1H,s),4.92(1H,s) and 7.83(3H,s) (*cf* fig.2.3.11b). The spectrum was recorded again after 1h,and was observed to be gradually changing to one having the following peaks:- τ1.01(1H,s),1.18(1H,s),1.66(1H,s),2.01(1H,s) and 7.81(3H,s) (*cf* fig.2.3.11c). Conversion was found to be complete in 3h. A further quantity of triethylamine (10μl) was added, and the spectrum was found to change to one having the following peaks:- τ1.27(2H,s),2.07(1H,s),2.93(1H,s),4.03(1H,s), 5.14(1H,s) and 7.81(3H,s) (*cf* fig.2.3.11d),conversion being complete in 2h. The addition of further quantities of triethylamine did not change this latter spectrum.

(viii) *Reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with sulphite ion*

2,4,6,8-tetranitro-1,5-dimethylnaphthalene (0.034g) was dissolved in DMSO-d_6 (0.4ml),and a solution of sodium sulphite in deuterium oxide (1M;0.1ml) added. The NMR spectrum was recorded (fig.2.3.13b); τ1.76(1H,s),3.44(1H,s),7.61(3H,s) and 7.99(3H,s). The spectrum was re-recorded at hourly intervals,and after 5h the spectrum was found to have changed to that shown in fig.2.3.13c; τ1.01(1H,s),1.18(1H,s),1.66 (1H,s),1.99(1H,s) and 7.86(3H,s). This spectrum did not change upon the addition of further quantities of sulphite ion.

2.4 Interactions of Weak Lewis Bases with Nitro-1,5-Dimethylnaphthalenes and Nitro-2,3-Dimethylnaphthalenes

2.4.1 Introduction

The electron donor-electron acceptor interactions between benzene-d_6 as Lewis base and the polynitroaromatic compounds 1,4,5,7-tetranitro-2,3-dimethylnaphthalene, 2,4,8-trinitro-1,5-dimethylnaphthalene and 2,4,6,8-tetranitro-1,5-dimethylnaphthalene as Lewis acids were investigated by NMR spectroscopy using the method described in section 2.1.6(b). Application of this method to the systems studied gave the plots shown in figs.2.4.4,2.4.5 and 2.4.6. The values derived from these plots for the equilibrium constants (K*c*) of the interactions and for the chemical shifts (Δ_o) of the protons in the 1:1 donor-acceptor complexes are summarised in table 2.4.1. It can be seen from the table that the values of K*c* derived from measurements made on the aliphatic and aromatic proton resonances are within experimental error.

2.4.2 1,4,5,7-Tetranitro-2,3-Dimethylnaphthalene

It can be seen from table 2.4.1 that the average value of K*c* for the interaction between 1,4,5,7-tetranitro-2,3-dimethylnaphthalene and benzene-d_6 is lower than for the corresponding interactions of the polynitro-1,5-dimethyl-naphthalenes,indicating that the former compound is a weaker electron acceptor than the latter compounds. The value of Δ_o for a particular proton reflects the proximity of the proton in the acceptor moiety to the donor molecule and to the centre of the donor-acceptor complex. It is noteworthy that for the 1,4,5,7-tetranitro-2,3-dimethyl-

Table 2.4.1 Equilibrium constants (Kc) and chemical shifts (Δ_o) observed in the interactions between benzene-d_6 and some polynitrodimethylnaphthalenes[a] at 33.5°.

Acceptor	Aromatic Protons			Aliphatic Protons		
		Kc kg.mol^{-1}	Δ_o Hz		Kc kg.mol^{-1}	Δ_o Hz
1,4,5,7-tetranitro-2,3-dimethylnaphthalene	(H-6)	0.123±0.008	80.4±5.5	(CH_3-2)	0.131±0.010	40.3±2.5
	(H-8)	0.117±0.009	85.1±6.8	(CH_3-3)	0.129±0.009	42.4±3.0
2,4,8-trinitro-1,5-dimethylnaphthalene	(H-3)	0.151±0.008	56.7±3.8	(CH_3-1)	0.145±0.020	59.3±4.6
	(H-6)	0.142±0.011	75.2±4.5	(CH_3-5)	0.141±0.012	69.2±5.7
	(H-7)	0.155±0.025	81.5±5.3			
2,4,6,8-tetranitro-1,5-dimethylnaphthalene	(H-3), (H-7)	0.112±0.015	78.5±5.1	(CH_3-1), (CH_3-5)	0.171±0.011	60.5±4.3

a Dichloromethane solvent.

naphthalene/benzene-d_6 complex, the Δ_o values for the aromatic protons are approximately double those for the aliphatic protons, indicating that the structure of the complex must approximate to that shown in fig.2.4.1, where the shape of the benzene-d_6 molecule is represented by broken lines.

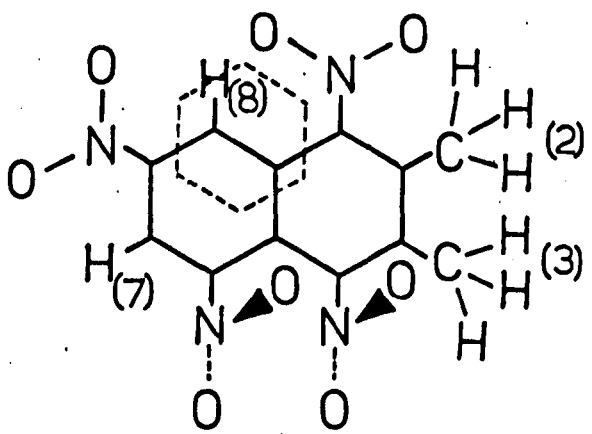


Fig.2.4.1

The orientation of the benzene-d_6 donor molecule over the non-methylated ring as shown above undoubtedly arises because steric hindrance between the donor molecule and the sterically crowded non-planar groups in the methylated ring prevents the donor from being sited over this ring or over the central point of the acceptor molecule.

2.4.3 <u>2,4,8-Trinitro-1,5-Dimethylnaphthalene</u>

The average value of Kc recorded for the 2,4,8-trinitro-1,5-dimethylnaphthalene/benzene-d_6 complex is similar to that reported for the 2,4,6-trinitrotoluene/benzene complex recorded in a polar solvent [187], which would be expected due to the structural similarities of the two acceptor compounds. From table.2.4.1 it can be seen that the values of Δ_o for either the aliphatic or aromatic protons appears to be highest for protons nearest

the 7-position,and it may be assumed that the centre of the complex is near that position. One possible structure is shown in fig.2.4.2.

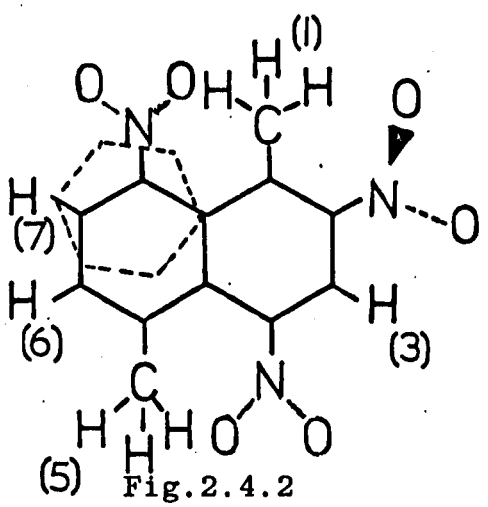


Fig.2.4.2

This would appear to be reasonable from consideration of the steric crowding in the molecule. Of the three nitro groups in the acceptor molecule,the 2-nitro group is the most hindered,due to the 1-methyl group,and it may be twisted out of the plane of the ring by as much as 40°, whereas the nitro groups at the 4- and 8-positions are relatively less hindered and may be almost coplanar with the ring. Consequently,the disubstituted ring is the less sterically crowded of the two rings and it would be expected that the centre of the donor-acceptor complex would be nearest this part of the acceptor molecule.

2.4.4 2,4,6,8-Tetranitro-1,5-Dimethylnaphthalene

The average value of Kc for the 2,4,6,8-tetranitro-1,5-dimethylnaphthalene/benzene-d_6 complex is higher than for the corresponding complex with 2,4,8-trinitro-1,5-dimethylnaphthalene (table 2.4.1). This would be expected as the former compound has four nitro groups and should therefore be a stronger acceptor than the latter compound,

which has only three nitro groups. The Δ_o values for the aliphatic and aromatic protons of the 2,4,6,8-tetranitro-1,5-dimethylnaphthalene/benzene-d_6 complex suggest that a possible structure of the complex is that shown in fig.2.4.3.

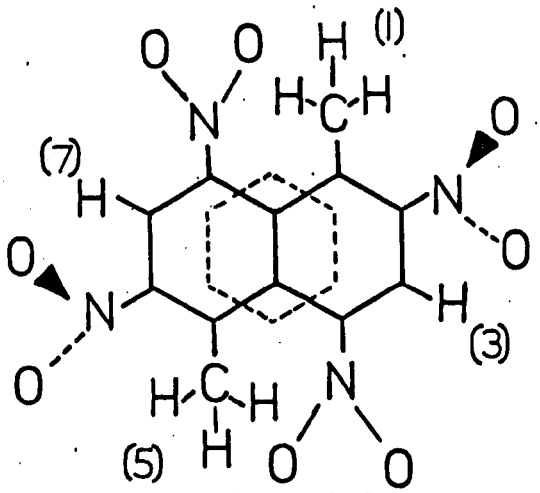


Fig.2.4.3

Due to the symmetry of the acceptor, the donor molecule must lie over the centre of the acceptor. This would be expected from steric considerations as the nitro groups at the 2- and 6-positions are twisted out of the plane of the ring to a great extent, thus making those regions of the acceptor molecule the most sterically crowded.

2.4.5 Experimental Section

Saturated solutions of each polynitroaromatic compound in freshly distilled dichloromethane were prepared. A series of mixtures of these solutions and benzene-d_6 (99.5%) was prepared by accurately weighing out the liquids into NMR sample tubes. Chemical shift measurements of the acceptor compound resonances were made on a Perkin-Elmer R10 NMR spectrometer operating at 60.004MHz, at a temperature of 33.5°. Each measurement, relative to TMS as internal standard, was made in triplicate and the results averaged.

The results were analysed by the computer programme "ROVERS" [193] on an Elliot 4120 computer using the Foster and Fyfe equation [184]. The values of K_C and Δ_o (see table 2.4.1) were evaluated from a least-squares plot drawn by the computer. These plots are reproduced below in figs.2.4.4, 2.4.5 and 2.4.6.

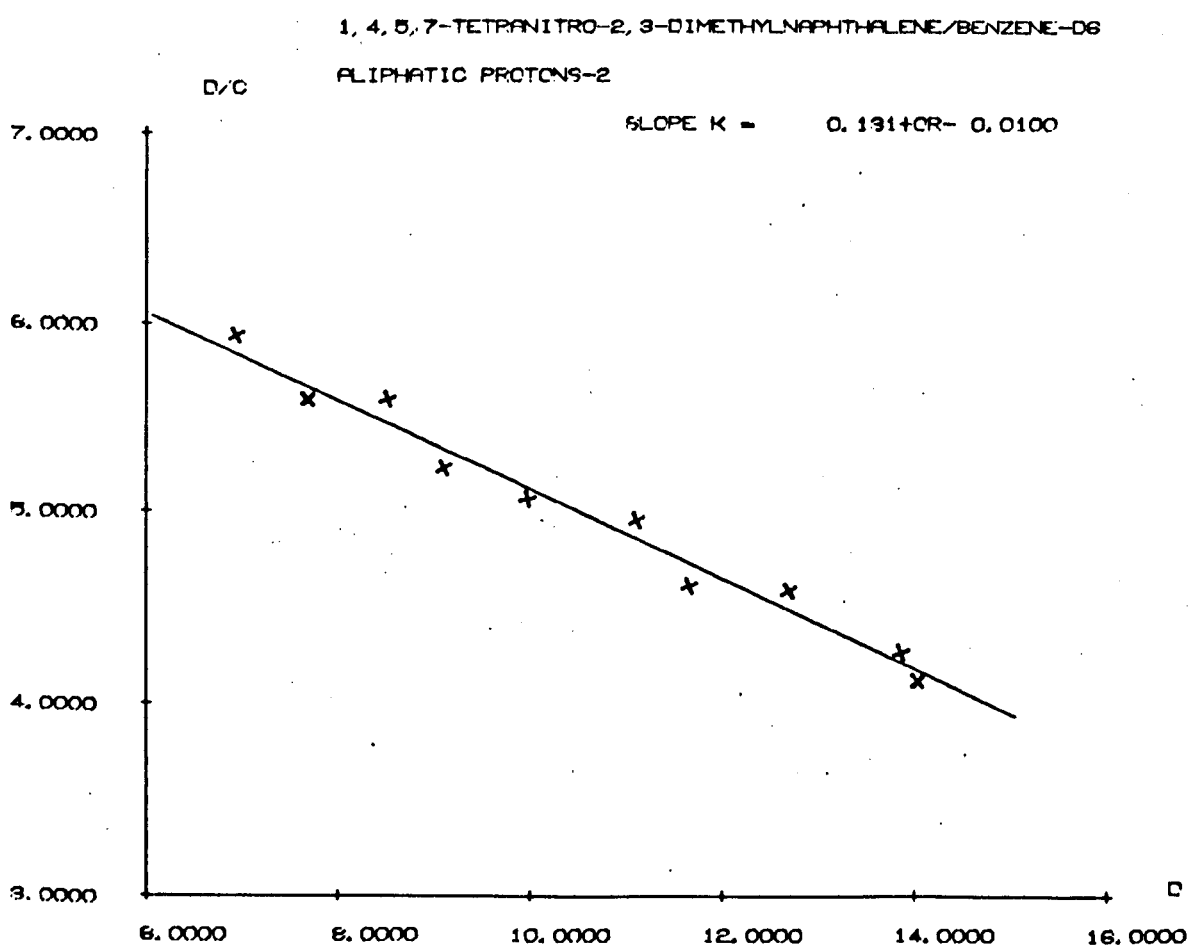


Fig.2.4.4 (a)

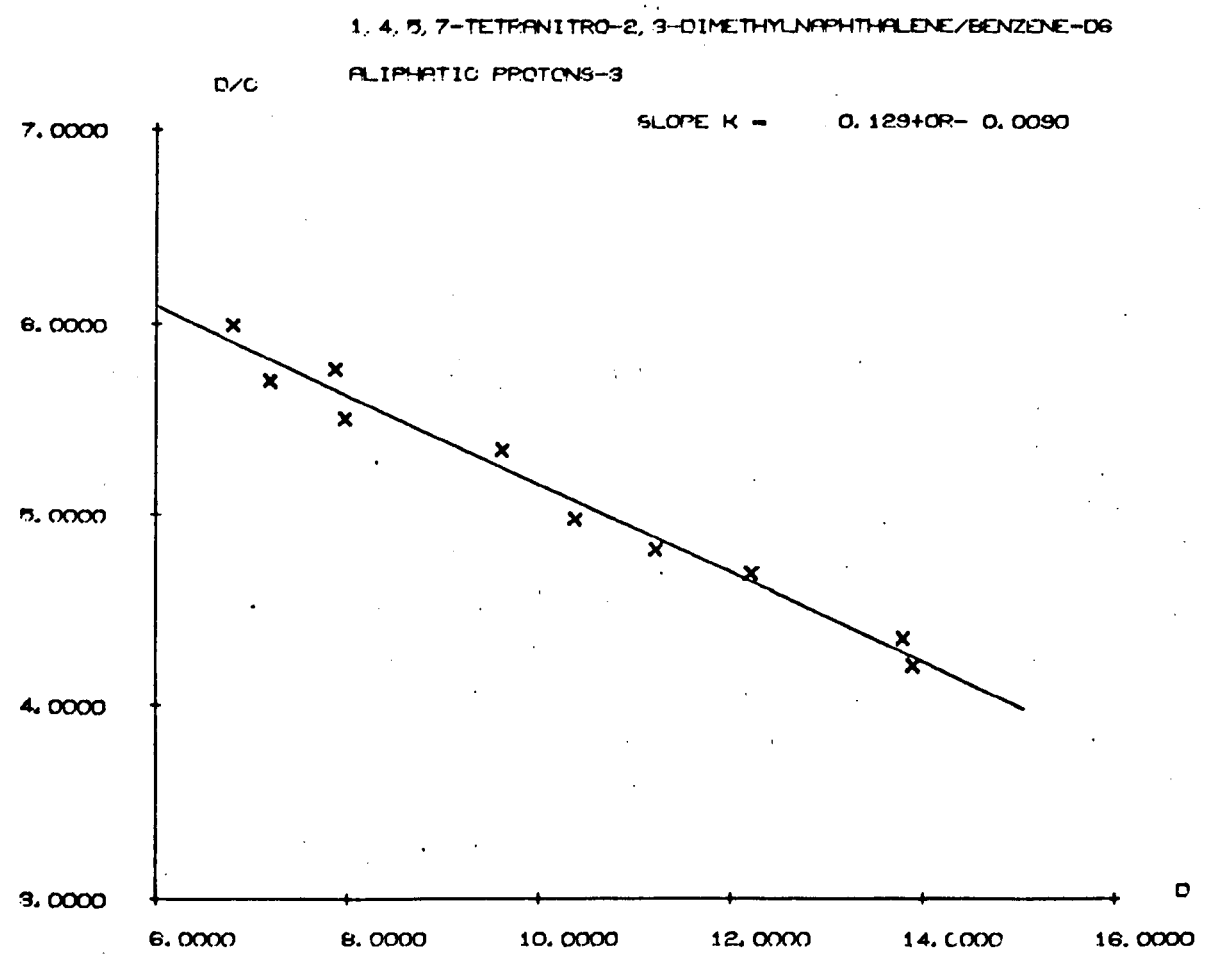


Fig.2.4.4(b)

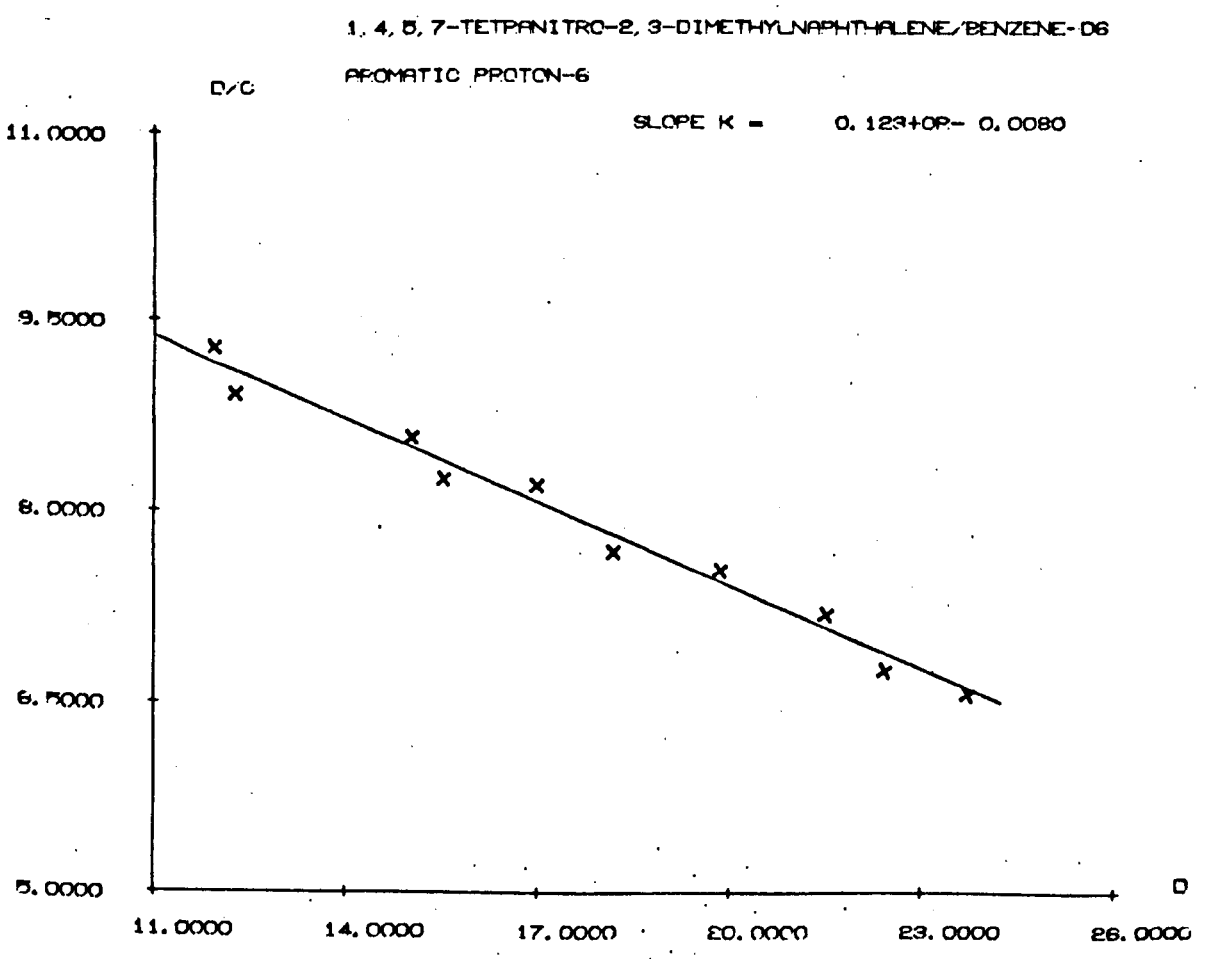


Fig.2.4.4(c)

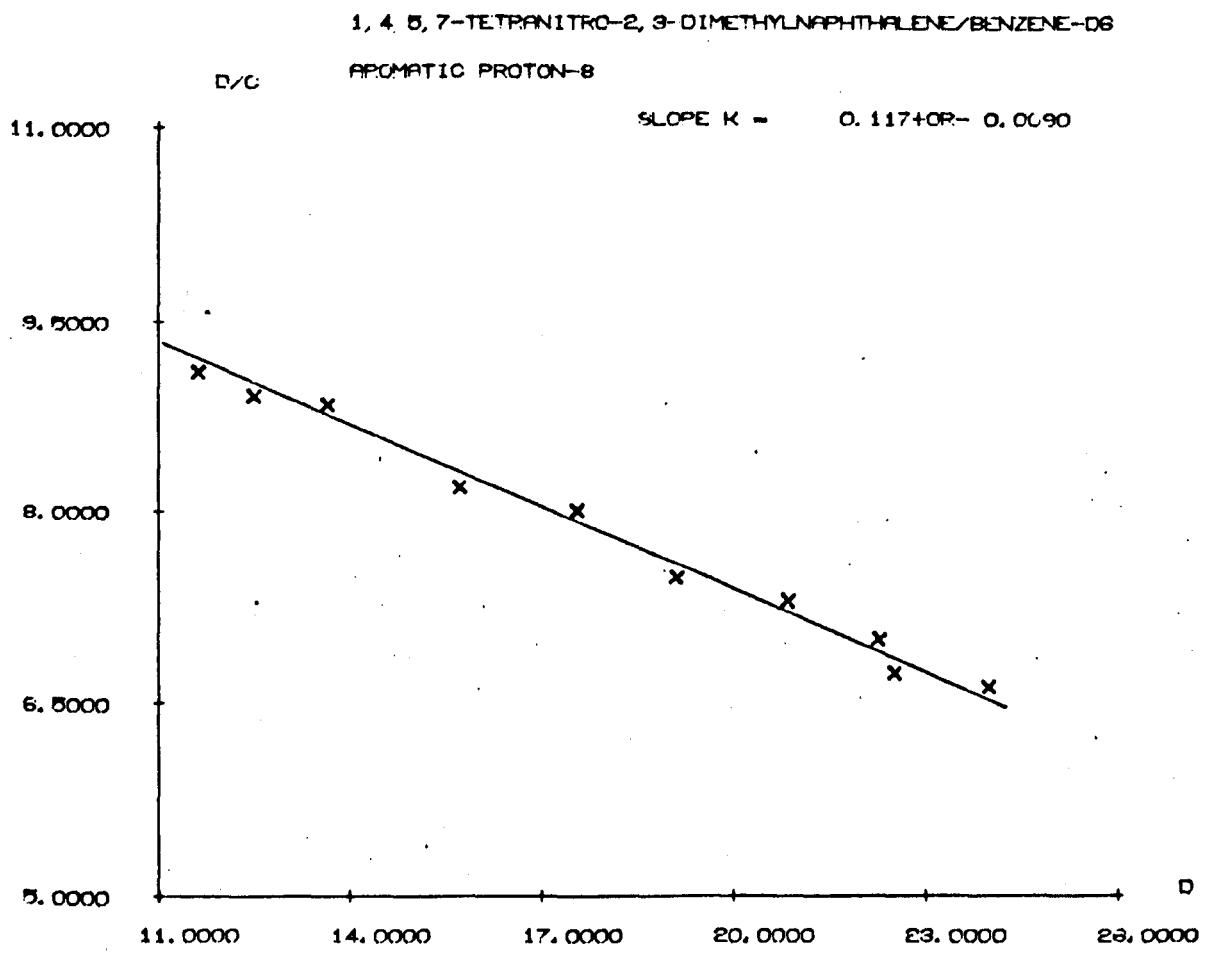


Fig.2.4.4(d)

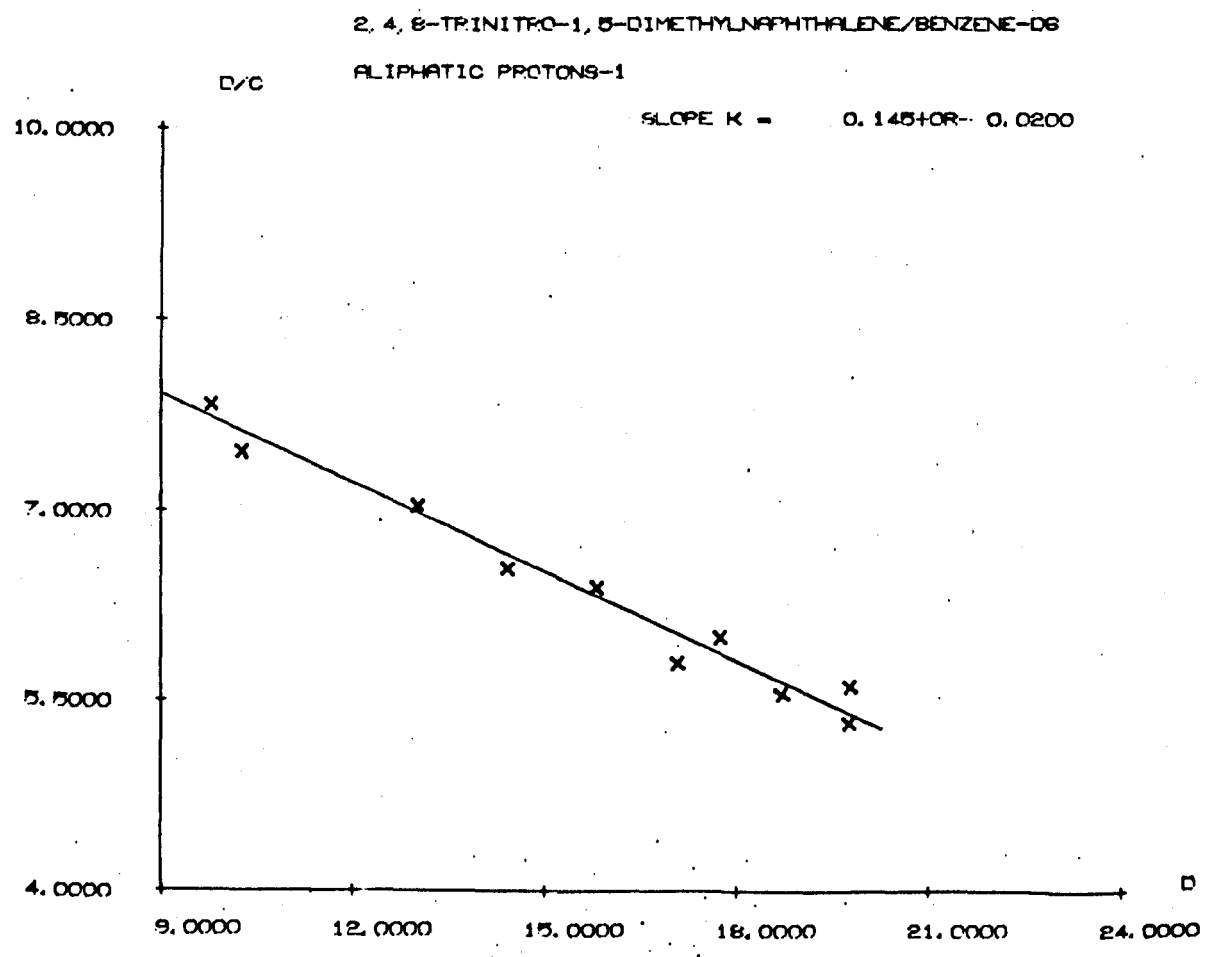


Fig.2.4.5(a)

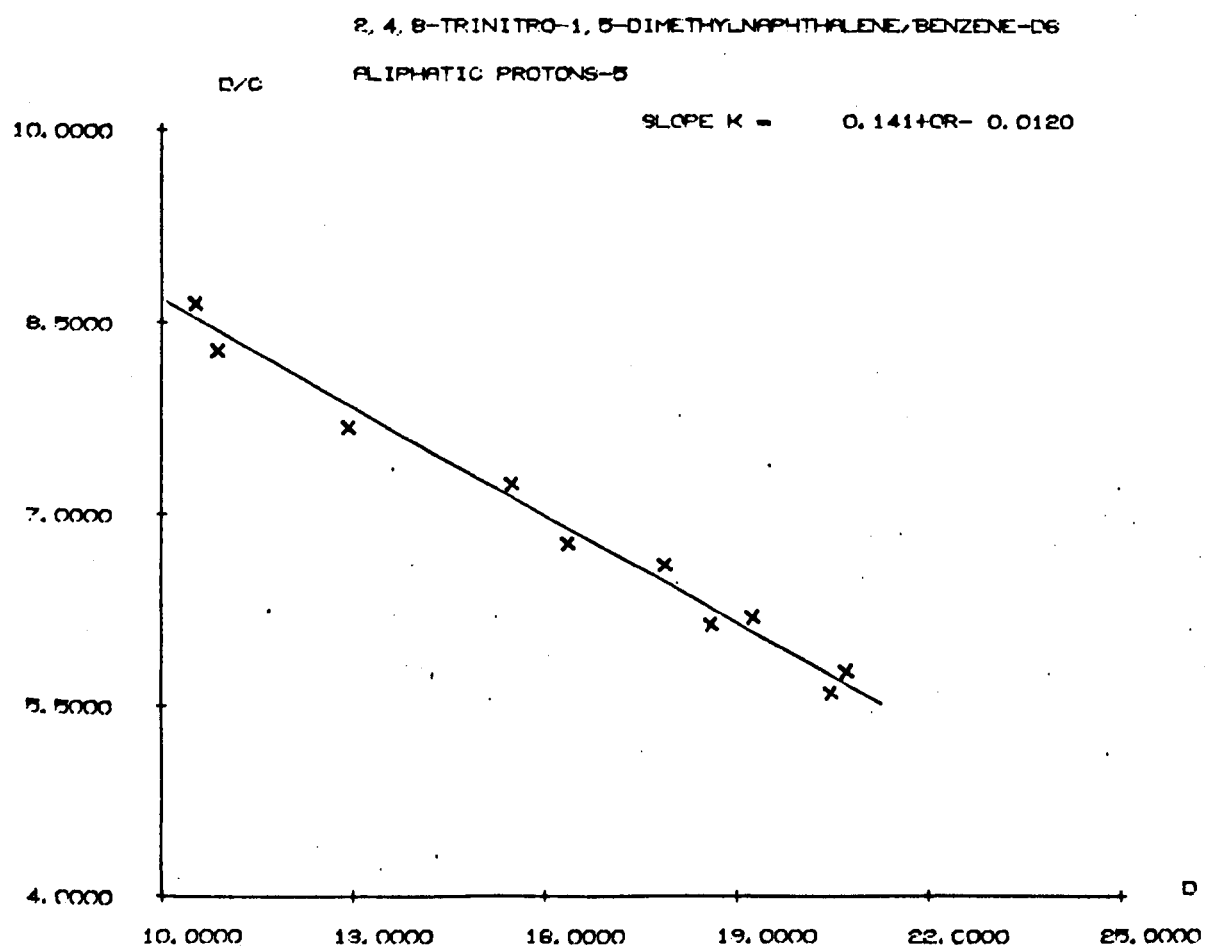


Fig.2.4.5(b)

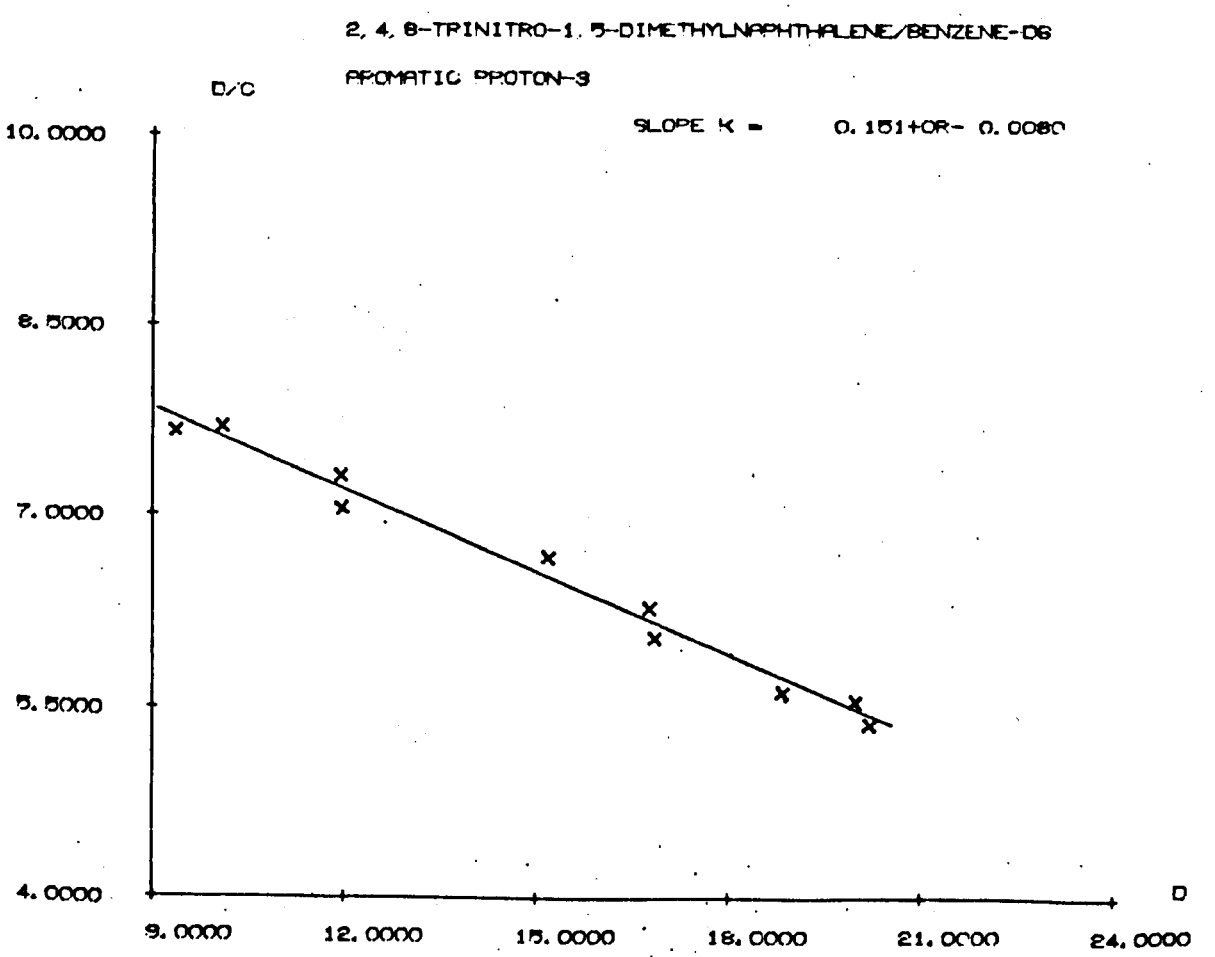


Fig.2.4.5(c)

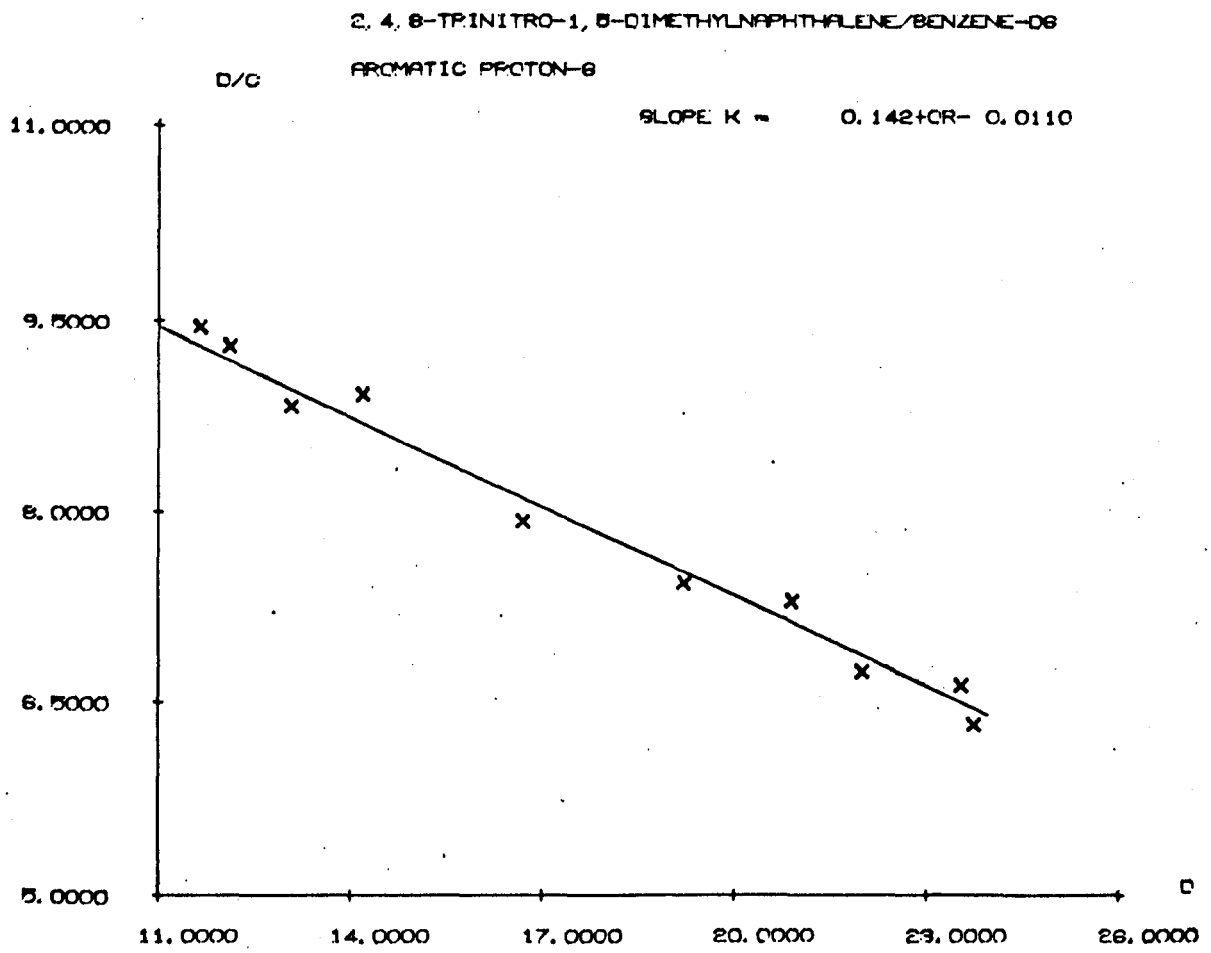


Fig.2.4.5(d)

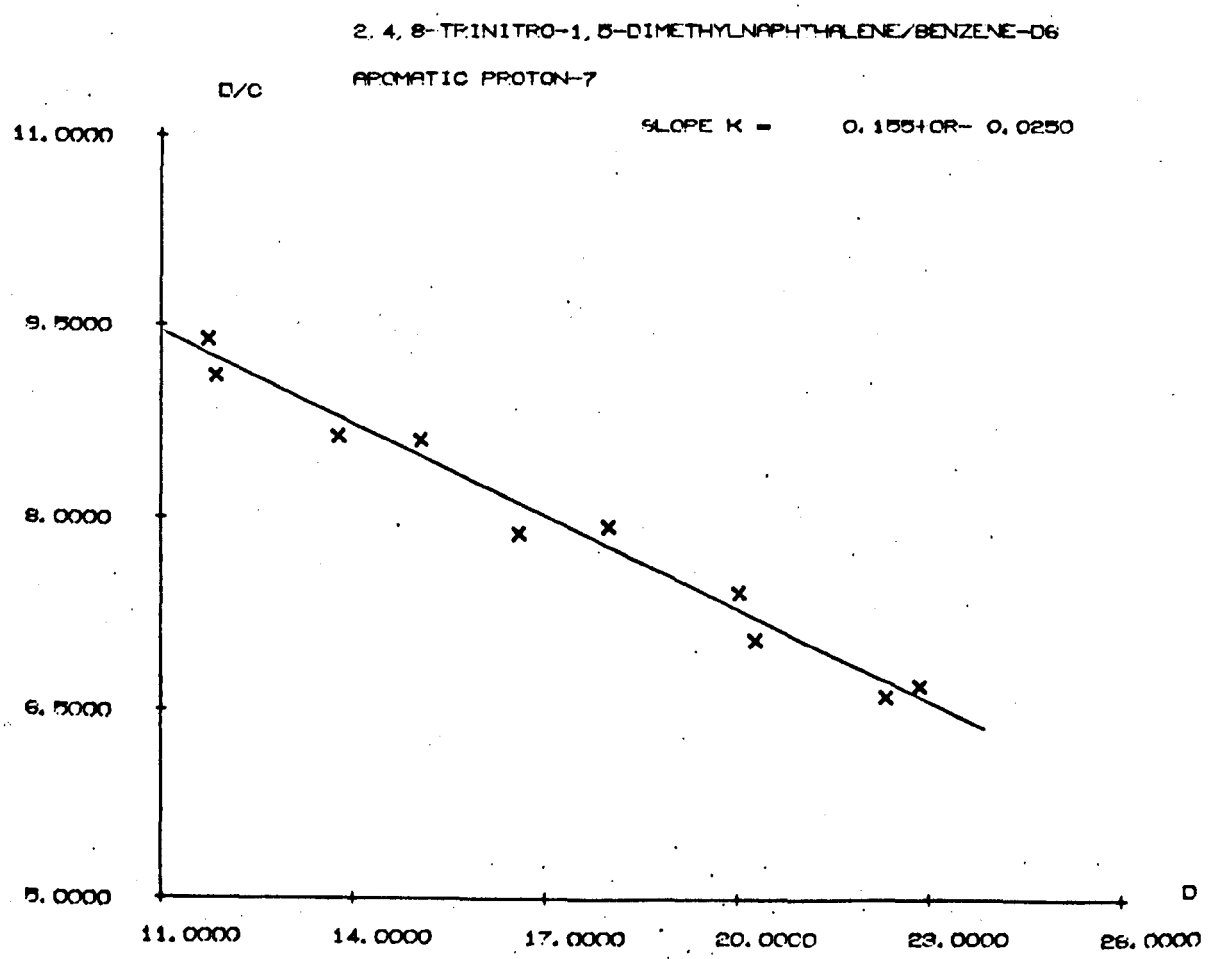


Fig.2.4.5(e)

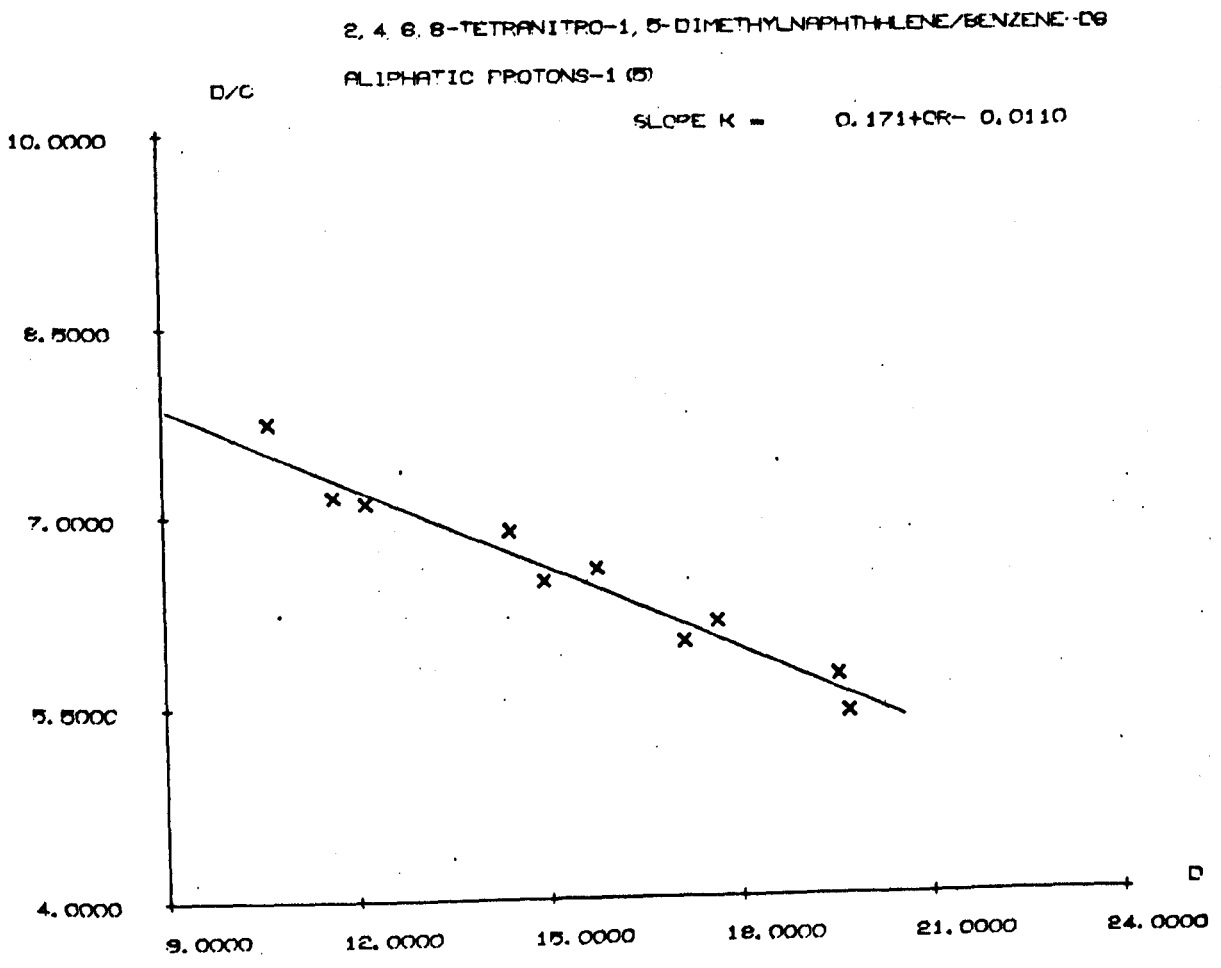


Fig.2.4.6(a)

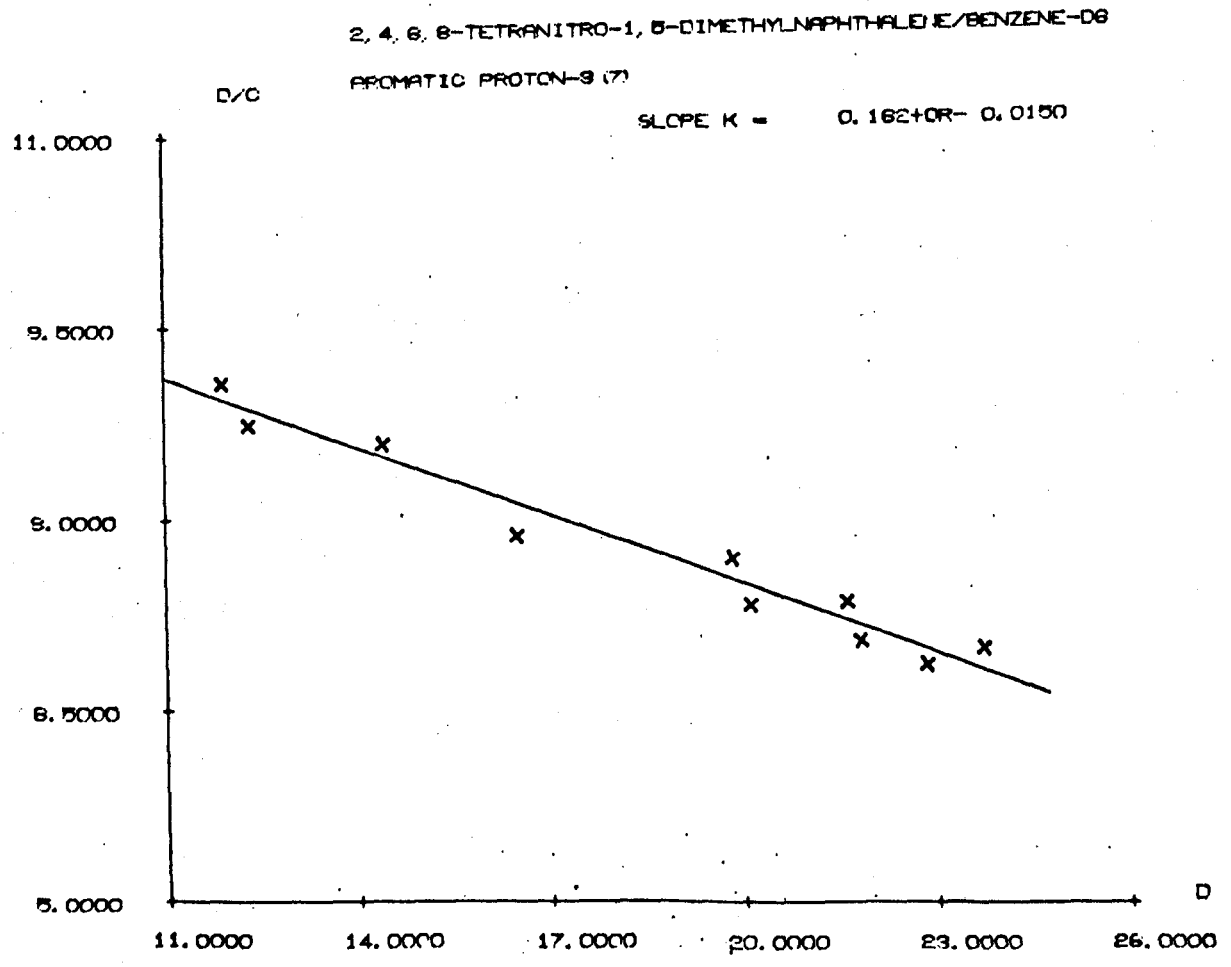


Fig.2.4.6(b)

Chapter Three. Rates of Nitration of Nitro-1,5-Dimethylnaphthalenes and Nitro-2,3-Dimethylnaphthalenes

3.1 Introductory Survey.

3.2 Partial Rate Factors and Reactivity Indices for the Nitration of Mononitro-1,5-Dimethylnaphthalenes and Mononitro-2,3-Dimethylnaphthalenes.

3.3 Partial Rate Factors and Reactivity Indices for the Nitration of Dinitro-1,5-Dimethylnaphthalenes and Dinitro-2,3-Dimethylnaphthalenes.

3.4 Partial Rate Factors and Reactivity Indices for the Nitration of 2,4,8-Trinitro-1,5-Dimethylnaphthalene and 1,4,5-Trinitro-2,3-Dimethylnaphthalene.

3.5 Experimental Section

3.1 Introductory Survey

3.1.1 Introduction

The effects of substituents in a benzene ring upon the reactivity of the ring,and upon the position of further substitution in the ring,have frequently been investigated by nitration studies. Early work by Holleman [196] led to the classification of substituent groups as either *ortho/para* or *meta* directing,and to the determination of the relative directing powers of different groups. He recognised the connection between orientation and activation, i.e.*ortho/para* directing substituents generally activate the nucleus towards electrophilic substitution,whereas *meta* orientating substituents generally deactivate the nucleus towards electrophilic substitution. These conclusions were later confirmed by Ingold and his co-workers [197,198]. Nitration studies have also been used for investigating correlations of theoretical reactivities,as calculated from Molecular Orbital theory,with experimentally determined reaction rates and partial rate factors [199,200].

3.1.2 Kinetics of Nitration

(a) Nitric Acid/Acetic Anhydride

The kinetics of nitration of aromatic compounds by nitric acid in acetic anhydride has been the subject of a number of investigations,although the early workers obtained misleading results. For example,Wibaut [201] studied the nitration of benzene in nitric acid/acetic anhydride and obtained evidence for second order (overall) kinetics, but this was later disproved by Cohen [202] who proposed fourth order (overall) kinetics,first order in the concentration

of benzene and third order in the concentration of acetyl nitrate [203]. More recently, Paul[204] investigated this system and obtained rates obeying a third order kinetic law, first order in the concentration of benzene and second order in the concentration of acetyl nitrate. Confusion undoubtedly arose because the early workers had failed to take into account certain factors affecting the reaction rates. For example, the kinetic order of nitration can vary between zero and one with respect to the concentration of the aromatic. Consider the following system :-

$$HNO_3 + Ac_2O \underset{b}{\overset{a}{\rightleftharpoons}} \underset{+\ AcOH}{AcONO_2} \xrightarrow[ArH]{c} ArNO_2 + 2AcOH$$

If the concentration of the aromatic compound ArH were high, or if the compound was highly reactive, then the acetyl nitrate would be removed by reaction as soon as it was formed, i.e. process *c* would be the most important process. In this case the kinetic order of nitration would be zero, as the rate would not be dependent upon the concentration of the aromatic compound, but would be dependent upon the rate of production of acetyl nitrate (process *a*). If the concentration of the aromatic compound was low, or its reactivity was low, then process *b*, i.e. the rate of decomposition of acetyl nitrate, would predominate over process *c*, and in this case the kinetic order would be one, as the rate would be entirely dependent upon the concentration of the aromatic compound. Therefore, unless precautions were to be taken, the observed kinetic order for the nitration of a particular compound could change from zero, at the start of the reaction, to one towards the end of the reaction as

the concentration of the compound decreased. In the case of zero order reactions, the dependence of the rate constants upon the concentration of acetyl nitrate varies according to the concentration of acetic acid present. It will be seen from the scheme above that the addition of acetic acid to the system should repress the formation of acetyl nitrate, and thereby reduce the rate of the reaction. This is found to be the case[205,206]. Thus for the nitration of anisole or mesitylene (conc.>0.1 mol.l^{-1}) using acetyl nitrate in acetic anhydride (conc.0.006-0.22 mol.l^{-1}) the rate of reaction in the absence of added acetic acid was found to vary according to the third power of the concentration of acetyl nitrate, whereas in the presence of added acetic acid the rate was found to depend upon the second power of the concentration of acetyl nitrate[207].

(b) Nitric Acid/Sulphuric Acid

The kinetic study of nitration of aromatic compounds by nitric acid in sulphuric acid was first successfully undertaken by Martinsen in 1904[208]. He showed that the nitration of nitrobenzene and of several other compounds is second order, the rate being proportional to the concentration of the aromatic compound and to that of the nitric acid. In his investigations, Martinsen showed that as the concentration of sulphuric acid in an aqueous sulphuric acid solvent increases, the rate of nitration first increases to a maximum at about 90% sulphuric acid, and then decreases[209]. It is clear that the increase in the acidity of the solvent as the proportion of sulphuric acid is increased gives rise to two opposing effects.

Firstly,at concentrations of sulphuric acid over 80%,the increase of acidity causes a rapid increase in the nitronium ion concentration[210,211],as shown in the following scheme :-

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

Hence a rapid increase in the rate of nitration will result. Secondly,the increased acidity causes conversion of the aromatic compound into a hydrogen-bonded complex with sulphuric acid,and then into a cation. Thus the first effect is predominant in governing the rate of nitration in solvents containing up to 90% sulphuric acid,at which point the concentration of nitronium ions has become almost constant. At higher concentrations of sulphuric acid,the second effect becomes kinetically important and gives rise to an overall decrease in the rate of nitration as the acidity is further increased,due to the formation of positive ions from the aromatic substrate which tends to resist the attack of electrophiles[212].

3.1.3 Partial Rate Factors

Partial rate factors,originally called "coefficients of activation" by Ingold[213],have been introduced as a means of expressing the reactivity of a particular reaction site in a molecule in terms of the reactivity of a reaction site in a standard molecule, commonly one position in the benzene nucleus. Thus if a reagent reacts with a carbon atom at position r in a molecule with a rate constant k_r,and with any position in benzene with a rate constant k_B,then the ratio k_r/k_B is termed the "partial rate factor". In order to calculate the

partial rate factors for various reaction sites in a compound, three quantities must be known :-

(1) The overall rate of reaction of the compound with respect to the standard.

(2) The percentage of total substitution at each site.

(3) A statistical factor relating to the number of equivalent sites in the compound under investigation.

A suitable example may be provided by the nitration of toluene using nitric acid/acetic anhydride. The particular factor for substitution at the *ortho* position is given by the following expression [214]:-

$$\frac{Mo}{100} \cdot \frac{k_T}{k_B} \cdot \frac{6}{2}$$

where Mo is the percentage of *ortho* substitution, k_T/k_B the relative rate of nitration of toluene with respect to benzene, and 6/2 a statistical factor inserted because there are six equivalent sites in the benzene nucleus and two equivalent *ortho* sites in the toluene nucleus.

Relative rates of reaction of compounds may be obtained by comparing their absolute rates of reaction determined kinetically or, more commonly, they may be obtained by the "competitive method". The competitive method was introduced by Wibaut [201], albeit unsuccessfully, and was later used with great success by Ingold *et al* [213] for the determination of the relative reactivities of a number of polycyclic aromatic compounds. The method used consisted of nitrating together two compounds in homogeneous solution, having concentrations in excess of that of the nitrating agent. The reaction was allowed to proceed to

completion and the product mixture analysed. The results were treated in the following way. Firstly, an assumption was made that the reactions were carried out in unit volume which does not change appreciably during the process. If x_o and y_o are the initial concentrations of the two compounds, and z_o the initial concentration of nitric acid, then, if the concentrations of the two compounds at time t are x and y, the following relationships may be derived :-

$$-\frac{dx}{dt} = k_x x \{x+y-(x_o+y_o)+z_o\}$$

$$-\frac{dy}{dt} = k_y y \{x+y-(x_o+y_o)+z_o\}$$

where k_x and k_y are the reaction rates of each compound. These equations assume that the reactions are bimolecular and irreversible. On simultaneous integration, these equations give the following expression :-

$$\frac{k_y}{k_x} = \frac{(\log y_\infty - \log y_o)}{(\log x_\infty - \log x_o)}$$

where x_∞ and y_∞ are the final values of x and y respectively, i.e. $x_\infty+y_\infty = x_o+y_o-z_o$. This is a useful form of the expression of the relative rate, and requires only a knowledge of the initial and final concentrations of the reactants. Dewar [200] has written the expression in the form :-

$$\frac{k_y}{k_x} = \frac{\log y_o - \log(y_o - N_y)}{\log x_o - \log(x_o - N_x)}$$

where N_x and N_y represent the total concentrations of the products from each compound. This form of the expression is of use where it is not possible to determine the final concentrations of the reactants.

3.1.4 Theoretical Approach to Reactivity: Use of Molecular Orbital Theory

The prediction of relative reactivities of organic compounds by the use of reactivity indices is a subject which has received considerable attention over the past fifty years. There are two basic approaches to this problem,(a) the "static" or "isolated molecule" method,in which the molecule is considered in its unperturbed state,and (b) the "dynamic" method,in which the molecule is considered in its theoretical transition state.

(a) The Static Method

The "static" or "isolated molecule" method originated from the pioneering work of Wheland and Pauling[199] in 1935 on the orientation effects of substituents in benzene derivatives,and was later extended by Coulson[215] and Longuet-Higgins[216]. The method requires the assumption that electrophiles attack preferentially at positions of high electron density,and nucleophiles attack preferentially at positions of low electron density. Wheland and Pauling proposed that there should be a correlation between reaction rates and the value of the electron density at any site in molecule. Unfortunately,molecular orbital theory indicates that the electron density is unity for all positions of attack on an alternate hydrocarbon,e.g. naphthalene,and that all positions should be equally reactive,which experimentally is generally not the case. Wheland and Pauling[199] therefore considered the molecule in its polarized state,the polarization being caused by

the field of the approaching reagent molecule. Thus the approach of the charged reagent molecule towards the position r in the substrate, having an electron density q_r, was considered to result in a change $\delta\alpha_r$ in the Coulomb integral at that site, so that the new electron density, q_r', was given by the expression :-

$$q_r' = q_r + \pi_{r,r}\delta\alpha_r$$

where $\pi_{r,r}$ was termed the "self-polarizability" of atom r. This parameter is a measure of the ease with which an incoming reagent molecule changes the electron density at a particular position. In 1947, Coulson and Longuet-Higgins[217] derived expressions for self-polarizabilites and for the corresponding changes δE in the π-electron energy of a system :-

$$\delta E = q_r\delta\alpha_r + \tfrac{1}{2}\pi_{r,r}\delta\alpha_r^2$$

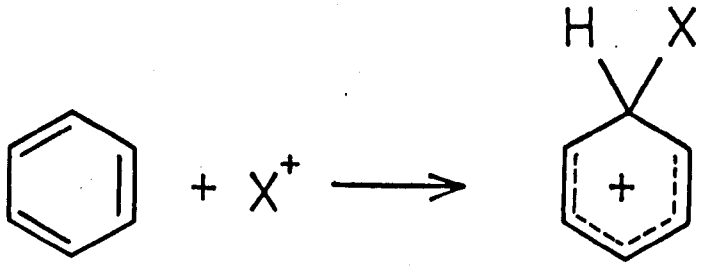
It can be seen that electron densities and self-polarizabilities are related, and when used as reactivity indices they must frequently be considered in combination, in order to avoid misleading results (see *(c)* below).

The "frontier orbital" or "frontier electron" theory was introduced by Fukui[218,219] in 1952. This theory is based on the postulate that the least tightly bound electron in a molecule would react preferentially with an electrophile. For electrophilic reactions, the "frontier orbital" is the highest occupied orbital of the unperturbed ground state of the molecule under attack, and the "frontier electron density" at any site is the contribution to the electron density at that site arising from the pair of electrons occupying that orbital. The positions having

the highest density of these electrons is assumed to be the most reactive. For nucleophilic reactions, the "frontier orbital" is defined as the lowest empty orbital of the same system, and the frontier electron density at a site is the contribution to the electron density at that site that would result from double occupancy of this vacant orbital. This method has had considerable success in predicting the position of attack in alternant hydrocarbons by electrophilic reagents.

(b) The Dynamic Approach

The "dynamic" approach to reactivities is illustrated by the Wheland localisation theory[220], proposed in 1942. This theory considers the transition state in an aromatic substitution reaction to have a pair of electrons localised at the site of substitution and thereby isolated from the conjugated system. Such an example is provided by the electrophilic substitution of benzene, in which attack of the electrophile X^+ at a nuclear site results in a change in hybridisation of the carbon atom at that site from sp^2 to sp^3, and also results in the loss of two electrons from the delocalised π-system to form the bond with the electrophile.



The π-electron energy difference between the unperturbed molecule and the transition state is then referred to as the "localisation energy" for that reaction and,in effect, approximates to the energy of activation for that reaction. In the above case,the π-electron energy of the ground state is 6α+8β,and for the transition state it may be calculated to be 6α+5.464β;therefore the localisation energy for the reaction is -2.536β. In the case of non-symmetrical systems the localisation energies for attack at every reaction site may be calculated,and the position having the lowest localisation energy will therefore be predicted to be the most reactive. This method has the difficulty that localisation energy is only one component of the energy of activation for a particular reaction,and does not include,for example,the contribution from the formation of the σ-bond between the aromatic compound and the attacking species. However,satisfactory correlations of partial rate factors and localisation energies have been obtained for the nitration of a series of polynuclear hydrocarbons [221], suggesting that localisation energies can be taken as indices of reactivity.

Localisation energies may be calculated by the Hückel approximation,although the calculations are lengthy and are best performed by computer. Longuet-Higgins [222] and Dewar [223] devised a method for obtaining approximate localisation energies from the coefficients of the non-bonding molecular orbitals of the atoms adjacent to the site of attack. These values were termed "reactivity numbers",and as with localisation energies,gave satisfactory

correlations with partial rate factors[200].

(c) Comparison of Reactivity Indices

In order to compare the performance of the reactivity indices described above in predicting the preferred sites of substitution,it is worthwhile to examine some examples. Naphthalene is a typical alternate hydrocarbon,and undergoes electrophilic aromatic substitution predominantly at the 1-position. The reactivity indices are given in table 3.1.1.

Table 3.1.1 Reactivity indices for naphthalene from H.M.O.calculations[218,224].

Position	Static			Dynamic	Preferred site of attack. [e]
	ϵ_r [a]	f_r [b]	$\pi_{r,r}$ [c]	L_r [d]	
1	1.000	0.362	0.443	2.299	*1*
2	1.000	0.138	0.405	2.480	*2*

(a) Hückel electron density.

(b) Frontier electron density.

(c) Self-polarizability in units of $1/\beta$.

(d) Localisation energy in units of $-\beta$.

(e) Order of substitution.

The values of the electron densities,being unity for both the 1 and 2 positions,should indicate that both positions are equally reactive,which is not true experimentally. However,as electron densities should be considered in conjunction with self-polarizabilities,the values of the

latter (0.443 for the 1-position,0.405 for the 2-position) indicate that the 1-position should be more favoured towards electrophilic substitution. In the case of naphthalene,the predictions of the localisation energies and the frontier electron densities are consistent with the experimental findings.

Fluoranthene is an example of a non-alternant hydrocarbon in which the electron density is uneven. The reactivity indices are presented in table 3.1.2.

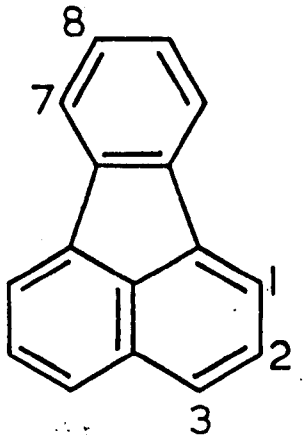


Table 3.1.2 Reactivity indices for fluoranthene from H.M.O.calculations[226].

Position	Static			Dynamic
	ϵ_r	f_r	$\pi_{r,r}$	L_r
1	0.947	0.092	0.440	2.466
2	1.005	0.092	0.400	2.503
3	0.959	0.241	0.462	2.341
7	0.997	0.241	0.427	2.371
8	1.008	0.092	0.410	2.435

It was found experimentally that position 3 was the most reactive site towards electrophilic substitution. This is in agreement with the predictions of the localisation energies, L_r, and of the frontier electron densities, f_r, the latter also predicting that position 7 should be equally reactive. However, the electron density values, ε_r, predict that the 2 and 8 positions should be the most reactive sites, which directly contradicts the experimental findings. The problem was resolved by Greenwood and McWeeny [225] who performed calculations which took into account the polarization of the molecule in the presence of the attacking electrophile. Using the formula $q'_r = q_r + \pi_{r,r}\delta\alpha_r$ for $\delta\alpha_r = 2.0\beta$, the largest electron density of 1.655 was found to be at position 3, with the smallest value of 1.623 at position 2. These workers therefore stated that they considered the electron densities of the ground state to be a poor reflection of the availability of electrons produced by the polarizing effect of an incoming electrophile.

3.2 Partial Rate Factors and Reactivity Indices for the Nitration of Mononitro-1,5-Dimethylnaphthalenes and Mononitro-2,3-Dimethylnaphthalenes in Acetic Anhydride

3.2.1 Introduction

The relative reactivities of 1-nitro-2,3-dimethylnaphthalene, 5-nitro-2,3-dimethylnaphthalene and 4-nitro-1,5-dimethylnaphthalene were investigated by competitive nitration against naphthalene using fuming nitric acid/acetic anhydride as the nitration medium. The kinetic orders of the various reactions were not investigated; the reactions were performed under conditions which would result in first kinetic orders with respect to the concentration of the nitroaromatic compound. The relative rates of nitration of the three mononitrodimethylnaphthalenes with respect to the overall rate of reaction of naphthalene are given in table 3.2.1 together with the isomer proportions of the dinitrodimethylnaphthalenes produced in the reactions.

Table 3.2.1 Relative rates of nitration and isomer proportions of products for mononitrodimethylnaphthalenes (25°).

Compound	k_{rel} [b]	Isomer Proportions(%) [a]							
		1	2	3	4	5	6	7	8 [c]
1-nitro-2,3-DMN [d]	0.70	-	-	-	38	30	*	*	32
5-nitro-2,3-DMN	0.86	42	-	-	58	-	*	*	*
4-nitro-1,5-DMN	0.96	-	*	*	-	-	26	*	74

(a) Estimated error ±3%.

(b) With respect to the *overall* rate of nitration of naphthalene (±5%).

(c) Positions of substitution.

(d) DMN = dimethylnaphthalene.

* Product arising from substitution at this site not observed (a yield, if any, below the limit of analytical detection).

The partial rate factors for each mononitro-dimethylnaphthalene were calculated with respect to a single position in benzene, and are presented in the following tables together with the appropriate reactivity indices derived from H.M.O. calculations.

3.2.2 1-Nitro-2,3-Dimethylnaphthalene

The experimental results (table 3.2.1) show that the 4-position is the most favoured site with respect to nitration, and this finding is in agreement with the predictions of both the "static" and "dynamic" reactivity indices presented in table 3.2.2. The second most reactive site was found to be the 8-position, marginally favoured over the 5-position. The localisation energy (L_r) values for the two α-positions (5 and 8) are practically equal, as are the values for the two β-positions (6 and 7), and are similar to the localisation energies for the α and β positions in naphthalene itself, *viz* α = 2.299, β = 2.480. This indicates that the substituents in the methylated ring do not markedly affect the localisation energies of the positions in the unsubstituted ring. However, of the two α-positions in that ring, the 8-position has the higher electron density (ϵ_r), because it is *"meta"* to the nitro group at the 1-position,

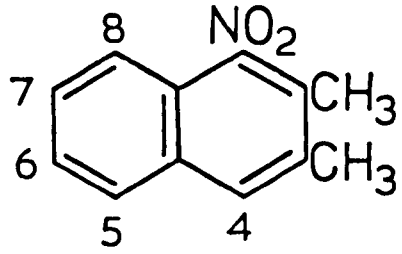


Table 3.2.2 Partial rate factors (PRF) and reactivity indices for the nitration of 1-nitro-2,3-dimethylnaphthalene in acetic anhydride at 25°.

Position	Static			Dynamic	PRF[a]
	ε_r	f_r	$\pi_{r,r}$	L_r	
4	1.045	0.389	0.456	2.177	415
5	1.006	0.336	0.443	2.278	328
6	1.012	0.113	0.405	2.436	*
7	1.006	0.134	0.407	2.443	*
8	1.011	0.335	0.439	2.279	349

(a) Calculated using $k_{naphthalene}/k_{benzene} = 260$ [226]; estimated error ±10%.

and it must be assumed that this effect is predominant in directing the position of substitution in the unsubstituted ring. The 6-position, being *"meta"* to the 8-position, also has a high electron density value but, as can be seen from table 3.2.1, substitution did not occur at this site due presumably to the high localisation energy value.

3.2.3 5-Nitro-2,3-Dimethylnaphthalene

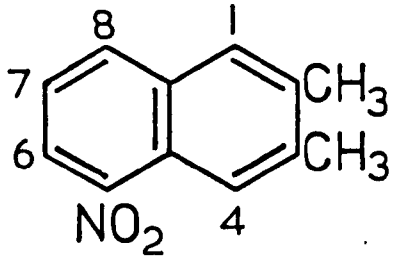


Table 3.2.3 Partial rate factors and reactivity indices for the nitration of 5-nitro-2,3-dimethylnaphthalene in acetic anhydride at 25°.

Position	Static			Dynamic	PRF
	ε_r	f_r	$\pi_{r,r}$	L_r	
1	1.059	0.419	0.450	2.165	563
4	1.072	0.418	0.438	2.167	778
6	0.951	0.100	0.436	2.451	*
7	1.015	0.129	0.401	2.450	*
8	0.961	0.282	0.456	2.339	*

Nitration was found to take place only at the 1 and 4 positions in 5-nitro-2,3-dimethylnaphthalene (table 3.2.1). This finding is consistent with predictions based on the localisation energy calculations, which give the lowest values for electrophilic attack at the 1 and 4 positions (table 3.2.3). However, these calculations do not predict which of these two sites should be more favoured

towards nitration,as the localisation energy values are almost equal. The self-polarizability values indicate that the 1-position might be favoured over the 4-position, and this would also be predicted from consideration of the steric factors. The electron density at the 4-position is higher than at the 1-position,because the former is *"meta"* to a nitro group. This activating effect at the 4-position is quite powerful because the 5-nitro group is relatively unhindered and can therefore lie almost in the plane of the ring,thereby activating those positions *meta* to that nitro group to the maximum extent. Nitration therefore takes place preferentially at the 4-position. The 7-position,which is also *"meta"* to the 5-nitro group, also has a high electron density,but the high localisation energy precludes attack at this site.

3.2.4 4-Nitro-1,5-Dimethylnaphthalene

Nitration of 4-nitro-1,5-dimethylnaphthalene was found to take place only in the non-methylated ring, and only at the positions *ortho* and *para* to the 5-methyl group (table 3.2.1). Attempts to predict the preferred site of attack from the reactivity indices (table 3.2.4) can give misleading results in this case. The localisation energy values correctly indicate that the 8-position should be most favoured towards nitration,but also suggest that the 2 and 6 positions should be equally favoured as the second most reactive site. Similar predictions are obtained from the frontier electron density and self-polarizability calculations. The electron density calculations indicate that the 2-position should be the most

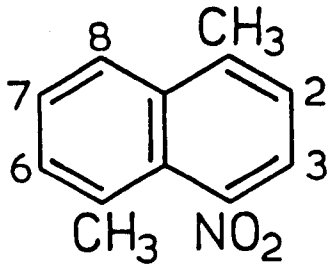


Table 3.2.4 Partial rate factors and reactivity indices for the nitration of 4-nitro-1,5-dimethylnaphthalene in acetic anhydride at 25°.

Position	Static			Dynamic	PRF
	ϵ_r	f_r	$\pi_{r,r}$	L_r	
2	1.068	0.175	0.409	2.284	*
3	0.975	0.104	0.417	2.455	*
6	1.062	0.173	0.414	2.284	359
7	1.006	0.126	0.404	2.439	*
8	1.033	0.349	0.445	2.189	1108

favoured site of electrophilic attack,as this position is *ortho* to a methyl group and *meta* to a nitro group,and that nitration should take place preferentially at the 6-position rather than the 8-position. In cases of disagreement between reactivity indices,particularly those based on the "static" model,earlier discussion has shown that it is necessary to consider the complementary role of electron density and self-polarizablity values in determining the most probable site of attack of an electrophile. It will

be seen from table 3.2.4 that for positions 2,6 and 8 the respective electron density values of 1.068,1.062 and 1.033 are effectively counteracted by the self-polarizability values of 0.409,0.414 and 0.445. Other factors must therefore be taken into account. In this particular case there is a specific *peri*-activating effect of the 8-position by the 1-methyl group. This effect has been observed in the nitration of 1-methylnaphthalene,which gives an unexpectedly high yield of 8-nitro-1-methylnaphthalene[87]. However,no explanation for this latter effect has been given.

3.2.5 Comparison of the Reactivities of Mononitro-1,5-Dimethylnaphthalenes and Mononitro-2,3-Dimethylnaphthalenes

The overall rates of nitration of the three mononitrodimethylnaphthalenes were found to approximate closely to the overall rate of nitration of naphthalene itself. This clearly illustrates the powerful deactivating effect of the nitro group on an aromatic system,since in the above cases the activating effect of two methyl groups was almost exactly neutralised by the presence of one nitro group.

The order of reactivity of the three compounds is 4-nitro-1,5-dimethylnaphthalene>5-nitro-2,3-dimethylnaphthalene>1-nitro-2,3-dimethylnaphthalene. 5-nitro-2,3-dimethylnaphthalene might be expected to react faster than 1-nitro-2,3-dimethylnaphthalene as the former compound has two highly activated α-positions (1 and 4) whereas the latter compound has only one (the 4-position),plus two naphthalene-type α-positions (5 and 8) which have similar localisation energies to the α-positions in naphthalene.

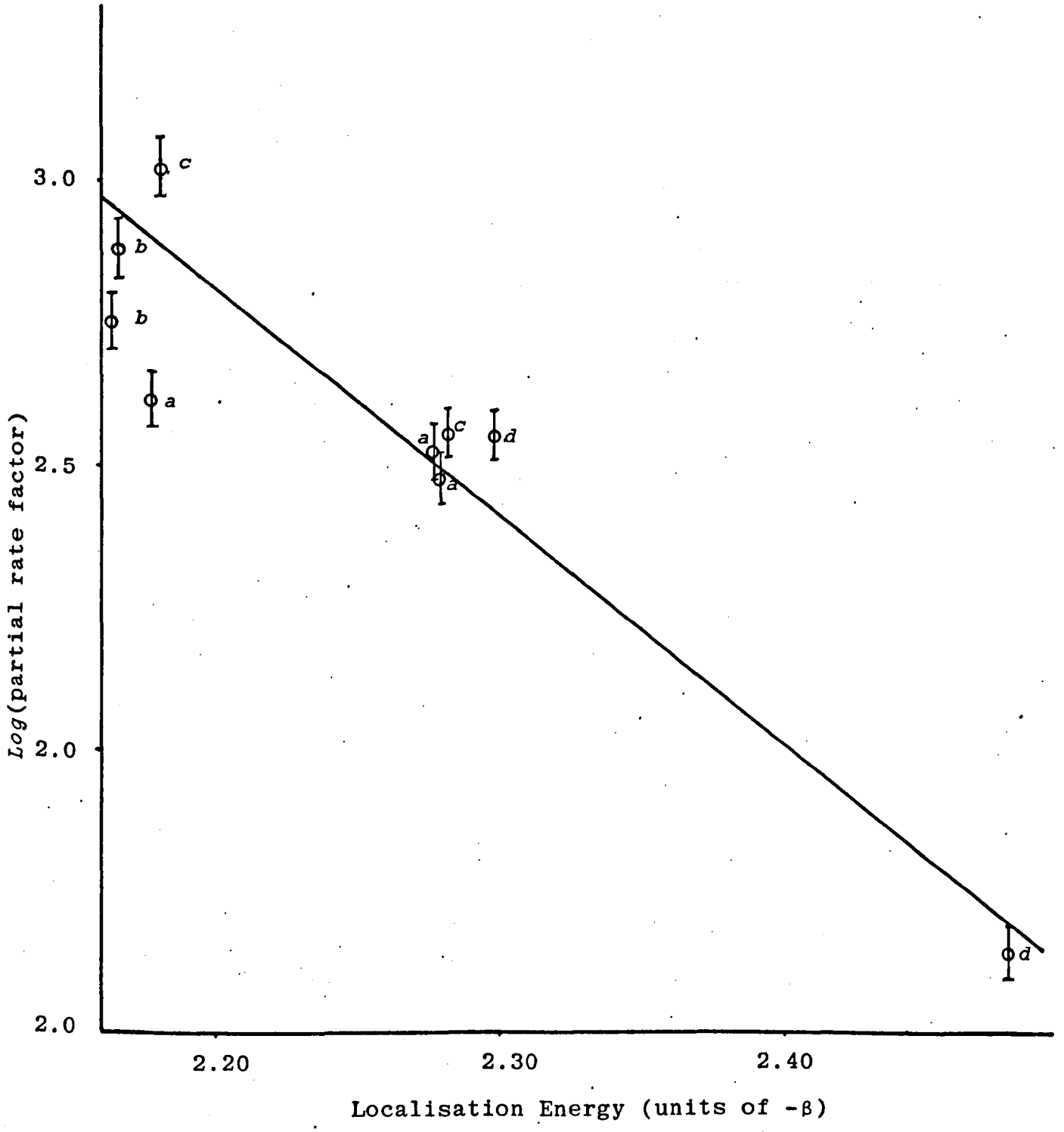


Fig.3.2.1 Graph of *log*(partial rate factor) *vs* localisation energy for positions of substitution in mononitrodimethylnaphthalenes. *(a)* 1-nitro-2,3-dimethylnaphthalene; *(b)* 5-nitro-2,3-dimethylnaphthalene; *(c)* 4-nitro-1,5-dimethylnaphthalene; *(d)* naphthalene.

The reactivity of 4-nitro-1,5-dimethylnaphthalene is greater than either of the mononitro-2,3-dimethylnaphthalenes probably because the former compound possesses a highly activated α-position (the 8-position) which is readily accessible to an incoming electrophile.

A plot of *log*(partial rate factor) *vs* localisation energy for each position of substitution in the three mononitrodimethylnaphthalenes is presented in fig.3.2.1. Points representing the α and β-positions of naphthalene have also been included on the graph for purposes of comparison. The graph is not entirely satisfactory due to the localisation energy values falling into two groups, at *ca* 2.18 and 2.28 (units of -β). However,it can be seen that an empirical relationship does exist between *log*(partial rate factor) and localisation energy values.

3.3 Partial Rate Factors and Reactivity Indices for the Nitration of Dinitro-1,5-Dimethylnaphthalenes and Dinitro-2,3-Dimethylnaphthalenes in Sulphuric Acid

3.3.1 Introduction

The relative reactivities of 1,4-dinitro-2,3-dimethylnaphthalene, 1,5-dinitro-2,3-dimethylnaphthalene, 1,8-dinitro-2,3-dimethylnaphthalene and 4,8-dinitro-1,5-dimethylnaphthalene with respect to nitration in fuming nitric acid/98% sulphuric acid were investigated by competitive nitration against p-nitrotoluene. The kinetic order of each nitration was not investigated, the reactions being assumed to be first order with respect to the concentrations of the nitroaromatics, or second order with respect to the overall reaction. The relative rates of nitration of the four dinitrodimethylnaphthalenes at 25° with respect to the overall rate of reaction of p-nitrotoluene are given in table 3.3.1. In each case only one reaction product was obtained, the proportions of any other products (if formed) being below the limit of analytical detection (*ca* 0.3%).

Table 3.3.1 Relative rates of nitration and positions of substitution for dinitrodimethylnaphthalenes.

Compound	$k_{rel}^{a,b}$	Position of substitution
1,4-dinitro-2,3-DMN	1.38	5
1,8-dinitro-2,3-DMN	1.89	4
1,5-dinitro-2,3-DMN	2.01	4
4,8-dinitro-1,5-DMN	1.26	2

(a) With respect to the overall rate of nitration of p-nitrotoluene.

(b) Estimated error ±15%.

The partial rate factors for each dinitrodimethylnaphthalene were calculated relative to benzene using a value[226] of $k_{p\text{-}nitrotoluene}/k_{benzene}$ of 2.64×10^{-5}. The calculated values are given in the following tables together with the reactivity indices derived from H.M.O.calculations.

3.3.2 1,4-Dinitro-2,3-Dimethylnaphthalene

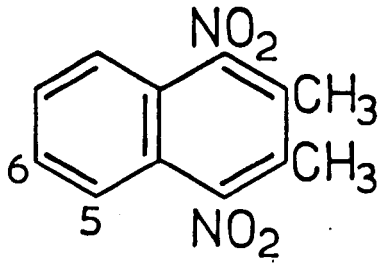


Table 3.3.2 Partial rate factors and reactivity indices for the nitration of 1,4-dinitro-2,3-dimethylnaphthalene in fuming nitric acid/98% sulphuric acid at 25°.

Position	Static			Dynamic	PRF
	ε_r	f_r	$\pi_{r,r}$	L_r	
5	1.008	0.339	0.439	2.291	1.09×10^{-4}
6	1.007	0.133	0.406	2.447	*

Substitution was found to have taken place only at the 5-position, with no evidence for any substitution at the 6-position. The extreme predominance of α-substitution

in this case is consistent with the substitution pattern observed for the nitration of naphthalene under the same conditions where the α/β substitution ratio was found to be 35.3 [226]. The experimental results are consistent with the predictions of both the "static" and "dynamic" reactivity indices. The electron density values for the α and β-positions are very close, but the α-positions are favoured over the β-positions with respect to electrophilic substitution because the former are *"meta"* to the nitro groups at the 1 and 4-positions.

3.3.3 1,5-Dinitro-2,3-Dimethylnaphthalene

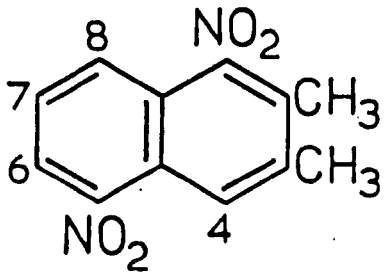


Table 3.3.3 Partial rate factors and reactivity indices for the nitration of 1,5-dinitro-2,3-dimethylnaphthalene in fuming nitric acid/98% sulphuric acid at 25°.

Position	Static			Dynamic	PRF
	ε_r	f_r	$\pi_{r,r}$	L_r	
4	1.051	0.396	0.447	2.200	3.18×10^{-4}
6	0.978	0.118	0.435	2.452	*
7	1.009	0.129	0.402	2.513	*
8	0.964	0.286	0.453	2.352	*

The experimental results show that substitution took place only at the 4-position,a site *ortho* to the 3-methyl group,and therefore highly activated. The predominance of substitution at the 4-position was also observed in the nitration of 1-nitro-2,3-dimethynaphthalene (sec.3.2.2) which also contains a nitro group at the 1-position. This experimental finding is consistent with the predictions of the "static" and "dynamic" reactivity indices,with the exception of the self-polarizabilty values,which marginally favour the 8-position over the 4-position as the most reactive site. This might be expected as the 8-position is *"meta"* to the 1-nitro group. Substitution might also have been expected at the 7-position, which is *meta* to the 5-nitro group,and indeed the electron density at the 7-position is high. However,as in the case of the nitration of 5-nitro-2,3-dimethylnaphthalene,the presence of a nitro group in the non-methylated ring deactivates that ring towards electrophilic substitution, and no substitution takes place at any of the sites in that ring.

3.3.4 1,8-Dinitro-2,3-Dimethylnaphthalene

It was found that substitution only takes place at the 4-position in 1,8-dinitro-2,3-dimethylnaphthalene. The orientation of attack here is comparable to that observed with 1,5-dinitro-2,3-dimethylnaphthalene in that substitution occurred at a position *ortho* to a methyl group. These results are in agreement with the predictions of all the reactivity indices. Although substitution might also have been expected at the 5-position,as this is an α-position

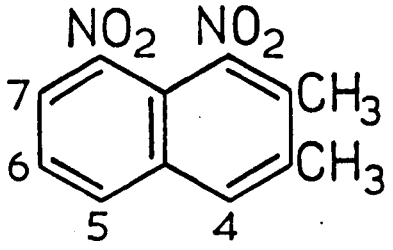


Table 3.3.4 Partial rate factors and reactivity indices for the nitration of 1,8-dinitro-2,3-dimethylnaphthalene in fuming nitric acid/98% sulphuric acid at 25°.

Position	Static			Dynamic	PRF
	ε_r	f_r	$\pi_{r,r}$	L_r	
4	1.041	0.393	0.457	2.187	2.99×10^{-4}
5	0.983	0.312	0.450	2.312	*
6	1.013	0.130	0.403	2.445	*
7	0.952	0.099	0.422	2.456	*

having a low localisation energy,or at the 6-position, which is *meta* to the 8-nitro group and has a high electron density,the presence of the nitro group in the non-methylated ring deactivates that ring towards nitration in a similar manner to the 5-nitro group in 1,5-dinitro-2,3-dimethylnaphthalene.

3.3.5 4,8-Dinitro-1,5-Dimethylnaphthalene

4,8-dinitro-1,5-dimethylnaphthalene is structurally similar to 4-nitrotoluene in that methyl groups are substituted *para* to each other,and in that

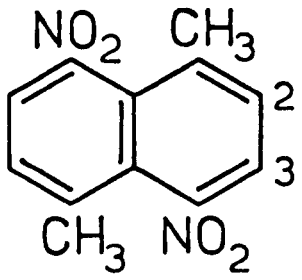


Table 3.3.5 Partial rate factors and reactivity indices for the nitration of 4,8-dinitro-1,5-dimethylnaphthalene in nitric acid/98% sulphuric acid at 25°.

Position	Static			Dynamic	PRF
	ϵ_r	f_r	$\pi_{r,r}$	L_r	
2	1.063	0.170	0.410	2.299	1.00×10^{-4}
3	0.976	0.106	0.417	2.459	*

substitution may take place at two sites only, either *ortho* to a methyl group or *ortho* to a nitro group. Nitration was found to have taken place only at the 2-position in 4,8-dinitro-1,5-dimethylnaphthalene, the site of attack being *ortho* to a methyl group. This result is in accordance with the predictions of the reactivity indices with the exception of the self-polarizability values which marginally favour the 3-position as being the most reactive site.

3.3.6 Comparison of the Reactivities of the Dinitro-1,5-Dimethylnaphthalenes and Dinitro-2,3-Dimethylnaphthalenes

The order of reactivity of the four dinitro-dimethylnaphthalenes was found to be 1,5-dinitro-2,3-dimethyl-

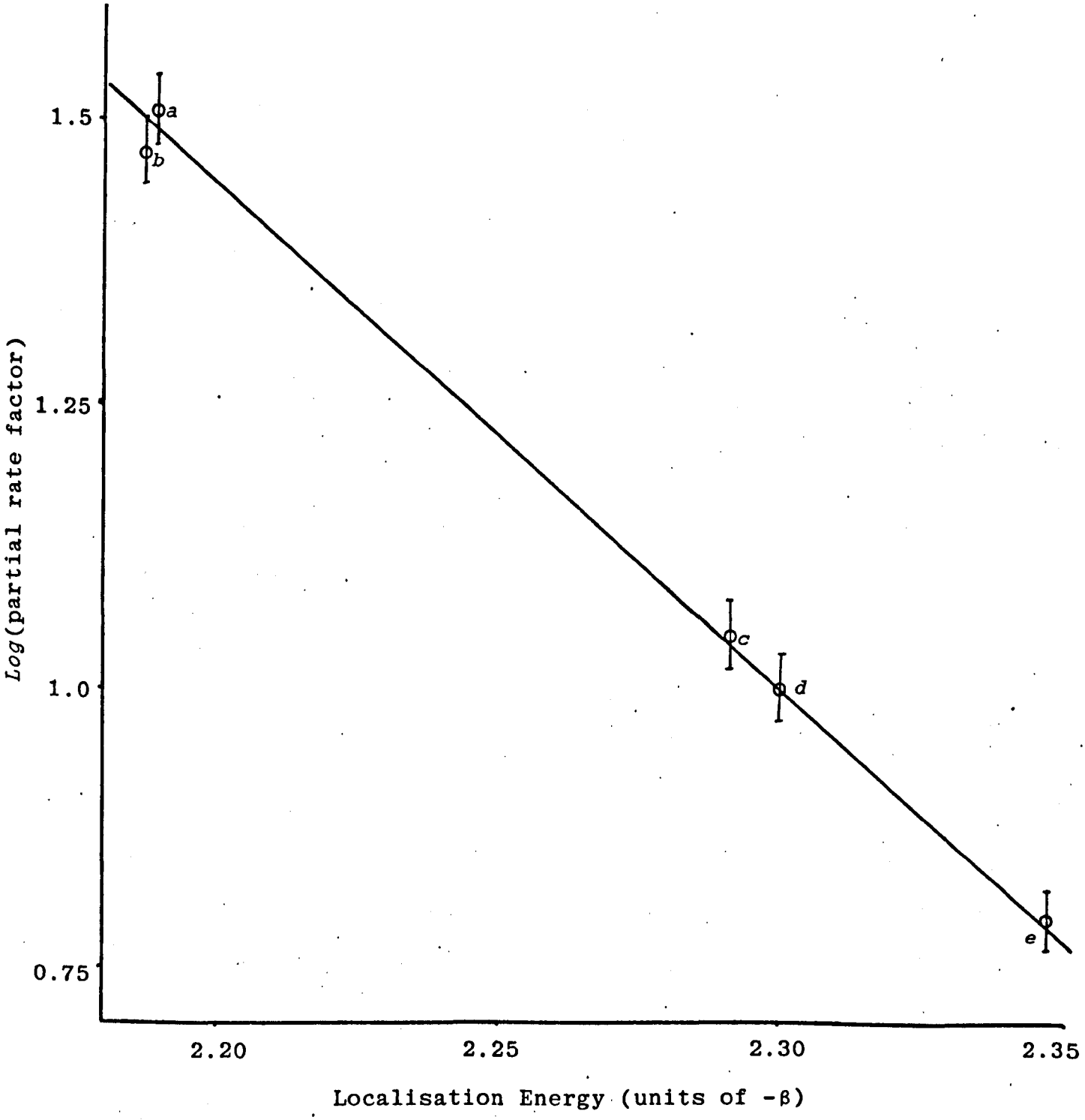


Fig.3.3.1 Graph of *log*(partial rate factor) *vs* localisation energy for positions of substitution in dinitrodimethylnaphthalenes. *(a)* 1,5-dinitro-2,3-dimethylnaphthalene; *(b)* 1,8-dinitro-2,3-dimethylnaphthalene; *(c)* 1,4-dinitro-2,3-dimethylnaphthalene; *(d)* 4,8-dinitro-1,5-dimethylnaphthalene; *(e)* p-nitrotoluene.

naphthalene>1,8-dinitro-2,3-dimethylnaphthalene>1,4-dinitro-2,3-dimethylnaphthalene>4,8-dinitro-1,5-dimethylnaphthalene. In the case of 1,5-dinitro-2,3-dimethylnaphthalene and 1,8-dinitro-2,3-dimethylnaphthalene,substitution takes place at the 4-position for each compound,but the reactivity of the former compound is greater than that of the latter because of the extra activation of the 4-position by the nitro group at the 5-position,to which it is *"meta"*. Of the three dinitro-2,3-dimethylnaphthalenes, 1,4-dinitro-2,3-dimethylnaphthalene was found to have the lowest reactivity due to there being no α-positions activated by methyl groups,unlike the other two dinitro-2,3-dimethylnaphthalenes. 4,8-dinitro-1,5-dimethylnaphthalene was found to have the lowest reactivity of the four dinitro compounds under investigation. There are no activated α-positions available for substitution in this compound,and attack of the electrophile takes place only at the β-positions *ortho* to the methyl groups.

A plot of *log*(partial rate factor) *vs* localisation energy for each compund is presented in fig.3.3.1. As in fig.3.2.1,the points are in two groups,but again there could well be a correlation between partial rate factors and localisation energy values.

3.4 Partial Rate Factors and Reactivity Indices for the Nitration of 2,4,8-Trinitro-1,5-Dimethylnaphthalene and 1,4,5-Trinitro-2,3-Dimethylnaphthalene in Sulphuric Acid

3.4.1 Introduction

The relative reactivities of 1,4,5-trinitro-2,3-dimethylnaphthalene and 2,4,8-trinitro-1,5-dimethylnaphthalene were investigated by competitive nitration against 2,4-dinitrotoluene,using fuming nitric acid/98% sulphuric acid as the nitration medium. The relative rates of nitration of the two trinitrodimethylnaphthalenes at 25°with respect to the overall rate of reaction of 2,4-dinitrotoluene are given in table 3.4.1 together with the isomer proportions of the tetranitrodimethylnaphthalenes produced in the reactions.

Table 3.4.1 Relative rates of nitration and positions of substitution in trinitrodimethylnaphthalenes.

Compound	K_{rel} [a]	Isomer Proportions (%) [b]			
		3	6	7	8
1,4,5-trinitro-2,3-DMN	0.51	-	*	95	5
2,4,8-trinitro-1,5-DMN	10.3	100	*	*	-

(a) Relative to the overall rate of nitration of 2,4-dinitrotoluene; ±25%.

(b) Estimated by NMR spectroscopy; error ±1%.

The partial rate factors for each trinitrodimethylnaphthalene were calculated relative to benzene,using a value of $k_{2,4\text{-dinitrotoluene}}/k_{benzene}$ [226] of 8.34×10^{-9},and are presented

in the following tables together with the reactivity indices derived from H.M.O.calculations.

3.4.2 1,4,5-Trinitro-2,3-Dimethylnaphthalene

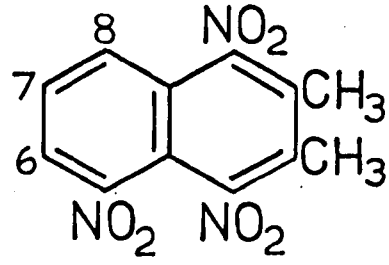


Table 3.4.2 Partial rate factors and reactivity indices for the nitration of 1,4,5-trinitro-2,3-dimethylnaphthalene in fuming nitric acid/98% sulphuric acid at 25°.

Position	Static			Dynamic	PRF [a]
	ε_r	f_r	$\pi_{r,r}$	L_r	
6	0.979	0.117	0.421	2.456	*
7	1.009	0.130	0.403	2.456	2.42×10^{-8}
8	0.986	0.316	0.446	2.324	1.28×10^{-9}

(a) Estimated error ±30%.

Nitration of 1,4,5-trinitro-2,3-dimethylnaphthalene was found to have taken place largely at the 7-position, with only *ca* 5% of the substitution taking place at the 8-position. The experimental results are in contradiction of the predictions of all the reactivity indices,with the exception of the electron density values which correctly predict that the 7-position should be the most favoured with

respect to electrophilic substitution. However, the self-polarizability values tend to complement the electron density values in a similar way to that observed with 4-nitro-1,5-dimethylnaphthalene (sec.3.2.4). In the case of 1,4,5-trinitro-2,3-dimethylnaphthalene, it would appear that the powerful mesomeric effect of the nitro group at the 5-position is the predominant factor directing the orientation of substitution, attack taking place at the 7-position which is *meta* to the 5-position.

3.4.3 2,4,8-Trinitro-1,5-Dimethylnaphthalene

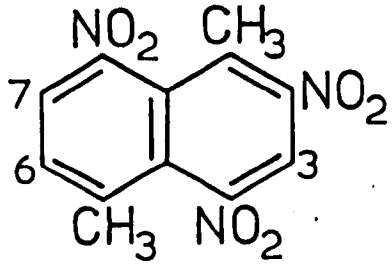


Table 3.4.3 Partial rate factors and reactivity indices for the nitration of 2,4,8-trinitro-1,5-dimethylnaphthalene in fuming nitric acid/98% sulphuric acid at 25°.

Position	Static			Dynamic	PRF [a]
	ϵ_r	f_r	$\pi_{r,r}$	L_r	
3	0.964	0.121	0.428	2.425	*
6	1.057	0.162	0.412	2.312	5.15×10^{-7}
7	0.976	0.110	0.417	2.460	*

(a) Estimated error ±30%.

Substitution was found to have taken place only at the 6-position in 2,4,8-trinitro-1,5-dimethylnaphthalene. This result is in accordance with the predictions of all the reactivity indices with the exception of the self-polarizability values,which favour the 3-position as the most likely position of substitution. This may,however,be ruled out as the 3-position is sterically hindered,and is highly de-activated towards electrophilic substitution by being *ortho* to two nitro groups.

3.4.4 Comparison of the Reactivities of 1,4,5-Trinitro-2,3-Dimethylnaphthalene and 2,4,8-Trinitro-1,5-Dimethylnaphthalene

Despite the large errors in the experimentally obtained partial rate factors,it is clear that the reactivity of 2,4,8-trinitro-1,5-dimethylnaphthalene is greater than that of 1,4,5-trinitro-2,3-dimethylnaphthalene. This is to be expected as in the former case the ring in which substitution takes place contains one methyl and one nitro group,whereas in the latter case substitution takes place in a ring containing one nitro group.

It would not be meaningful to construct a graph of *log*(partial rate factor) *vs* localisation energy for just two compounds. However,the partial rate factor for substitution at the 6-position in 2,4,8-trinitro-1,5-dimethyl-naphthalene of 5.15×10^{-7} (relative to a single position in benzene) for which the localisation energy is -2.312β,is greater than the partial rate factor of 2.42×10^{-8} for substitution at the 7-position in 1,4,5-trinitro-2,3-dimethyl-naphthalene for which the localisation energy is -2.456β. These results are in accordance with the general relationship

between partial rate factors and localisation energies (see sec.3.1.4).

3.5 Experimental Section

3.5.1 Competitive Nitration

(i) Mononitrodimethylnaphthalenes - The following general method was used. A mixture of a mononitrodimethylnaphthalene (0.5g),naphthalene (1g) and 2,4-dinitrotoluene (0.25g) (internal standard) was prepared,and dissolved in acetic anhydride (50ml). The solution was maintained at 25°, with temperature control ±5°. A portion (25ml) of this solution was withdrawn,and hydrolysed in water (300ml). To the remainder of the solution was added during 0.5h a portion (1ml) of a solution of nitric acid (*d* 1.50;0.1ml) in acetic anhydride (20ml) which had been equilibrated in a thermostat at 25°. The reaction mixture was allowed to stand at 25° for 2h,and was then hydrolysed in water (300ml). The products from the hydrolysis of both the reacted and unreacted portions of the mixture were worked up in the following way. The suspensions were neutralised with sodium carbonate,and extracted with ether (4 x 50ml). The ether extracts were washed with water (2 x 100ml),and the washings extracted with ether (50ml). The total ether solutions were dried over calcium chloride (20g),filtered,and the calcium chloride residue washed with ether (30ml). The dried ether extracts were evaporated on a water bath to dryness.

(ii) Dinitrodimethylnaphthalenes - The following general method was used. A mixture of a dinitrodimethylnaphthalene (0.5g),p-nitrotoluene (0.5g) and 1,3,5-trinitrobenzene (internal standard) was prepared,and dissolved in sulphuric acid (*d* 1.84;50ml). The solution was thermostatted at 25° (±0.5°),and a portion (25ml) withdrawn and drowned out in

ice-water (300ml). To the remainder of the solution was added during 0.5h a portion (1ml) of a solution of nitric acid (*d* 1.50;1ml) in sulphuric acid (*d* 1.84;25ml) which had also been thermostatted at 25°. The reaction mixture was allowed to stand at 25° for 2h,and was then drowned out in ice-water (300ml). The products from the reacted and unreacted portions of the original mixture were worked up as follows. The suspensions were neutralised with sodium carbonate,and extracted with ether (5 x 50ml). The ether extracts were washed with water (2 x 100ml),and the washings extracted with ether (2 x 50ml). The combined ether solutions were dried over magnesium sulphate (50g),filtered, and the magnesium sulphate residue washed with ether (50ml). The dried ether extracts were evaporated to dryness on a water bath.

(iii) Trinitrodimethylnaphthalenes - The following general method was used. A mixture of a trinitrodimethylnaphthalene (0.5g), 2,4-dinitrotoluene (1g) and 1,3,5-trinitrobenzene (internal standard) was prepared,and dissolved in sulphuric acid (*d* 1.84;50ml). The solution was maintained at 25° in a thermostat,and a portion (25ml) withdrawn and drowned out in ice-water (300ml). A solution of nitric acid (*d* 1.50;1ml) in sulphuric acid (*d* 1.84;25ml) was prepared,and maintained at 25°. A portion (1ml) of this solution was added during 0.5h to the remainder of the nitroaromatic solution,and the mixture allowed to stand for 2h,after which it was drowned out in ice-water (300ml). The products from the reacted and unreacted portions of the original nitroaromatic mixture were worked up in the following way. The suspensions were

neutralised with sodium carbonate,and extracted with ether (5 x 50ml). The ether extracts were washed with water (3 x 100ml),and the washings extracted with ether (100ml). The combined ether solutions were dried over calcium chloride (50g),filtered,and the calcium chloride residue residue washed with ether (50ml). The dried ether extracts were evaporated to dryness on a water bath. The experiments were performed in triplicate.

3.5.2 *Analytical Method*

(i) Mononitrodimethylnaphthalenes and dinitrodimethylnaphthalenes - The analysis of the product mixtures was carried out by high pressure liquid chromatography,using a Pye-Unicam LCM2 Liquid Chromatograph fitted with a UV detector operating at 254nm. The stationary phase employed was Corasil II packed in a stainless steel column of internal diameter 2mm and length 2m. The eluent was cyclohexane (spectroscopic grade),and the elution rate was 0.4 ml/min. Samples were prepared for analysis by dissolving small quantities (*ca* 50mg) of product in chloroform (1ml),and making the volume up to 50ml with cyclohexane (spectroscopic grade). Samples (10µl) of this solution were injected onto the column,and the chromatogram recorded. The concentrations of the reactants in the mixture were evaluated from calibration curves obtained from the chromatograms of standard mixtures of the reactants containing an internal standard. The ratios of the concentrations of the products in the reaction mixtures were obtained by comparison of their chromatograms with the chromatograms of standard mixtures of the relevant

products. The relative rates of reaction were calculated by the formula given in sec.3.1.3. The partial rate factors were calculated from the product ratios,as described in sec.3.1.3.

(ii) Trinitrodimethylnaphthalenes - The relative concentrations of the starting materials in each product mixture were determined by the high pressure liquid chromatography method described above. Due to the very high retention times of the tetranitrodimethylnaphthalene products on the column,their relative concentrations could not be obtained by the HPLC method. Instead,the products were analysed by NMR spectroscopy using DMSO-d_6 as solvent,and the relative concentrations of the products determined by comparison of the spectra of standard mixtures of the products.

3.5.3 *Theoretical Calculations*

The values of localisation energy (L_r),electron density (ε_r),frontier electron density (f_r) and self-polarizability ($\pi_{r,r}$) for each possible site of attack on each substrate were evaluated by Hückel Molecular Orbital calculations. The calculations were performed on an ICL 1900 computer using the programme "MCAN",based on the McLachlan approximate configuration interaction method [227],taking into account hyperconjugation between the methyl substituents and the ring systems. The values of the parameters h_x and k_{x-y} in the Coulombic integral $\alpha_x = \alpha + h_x\beta$ and the resonance integral $\beta_{xy} = k_{x-y}\beta$ respectively are given in table 3.5.1 below.

Table 3.5.1 Parameters used in the H.M.O. calculations for the nitro-1,5-dimethyl-naphthalenes and nitro-2,3-dimethylnaphthalenes.

Atom	h_x	Bond	k_{x-y}
H(methyl)	-0.5	C-H(methyl)	3.0
H(aromatic)	0.0	C-H(aromatic)	0.0
C	0.0	C-C	1.0
N	2.2	C-N[a]	1.8
O	1.2	C-N[b]	1.2
		N-O	2.4

(a) For nitro groups lying in the plane of the ring,e.g.5-nitro-2,3-dimethylnaphthalene.

(b) For hindered nitro groups lying out of the plane of the ring,e.g.1-nitro-2,3-dimethyl-naphthalene.

Chapter Four. Spectroscopic Properties of Nitro-1,5-Dimethylnaphthalenes and Nitro-2,3-Dimethylnaphthalenes

4.1 Positive and Negative Ion Mass Spectrometry.

4.2 Electronic Spectroscopy.

4.3 Nuclear Magnetic Resonance Spectroscopy.

4.4 Electron Spin Resonance Spectroscopy.

4.1 Positive and Negative Ion Mass Spectrometry

4.1.1 Introductory Survey

(A) Positive Ion Mass Spectra of Nitroaromatic Compounds

The positive ion mass spectra of the simpler nitroaromatic compounds have been investigated in some detail,and their characteristic fragmentation patterns are now well understood[228]. The spectrum of nitrobenzene, the simplest nitroaromatic compound,was investigated in 1956,and it was found that the base peak corresponded to the phenyl cation, $C_6H_5^+$,produced via a simple bond fission giving rise to the loss of the nitro group as $NO_2^{\cdot}$[229]. However,a process involving loss of NO$^{\cdot}$,to yield the phenoxy cation,followed by the ejection of CO was also observed. It was proposed by Beynon *et al*[230] that the key step in this process was the isomerisation of the nitro group to the nitrito form,as shown in fig.4.1.1.

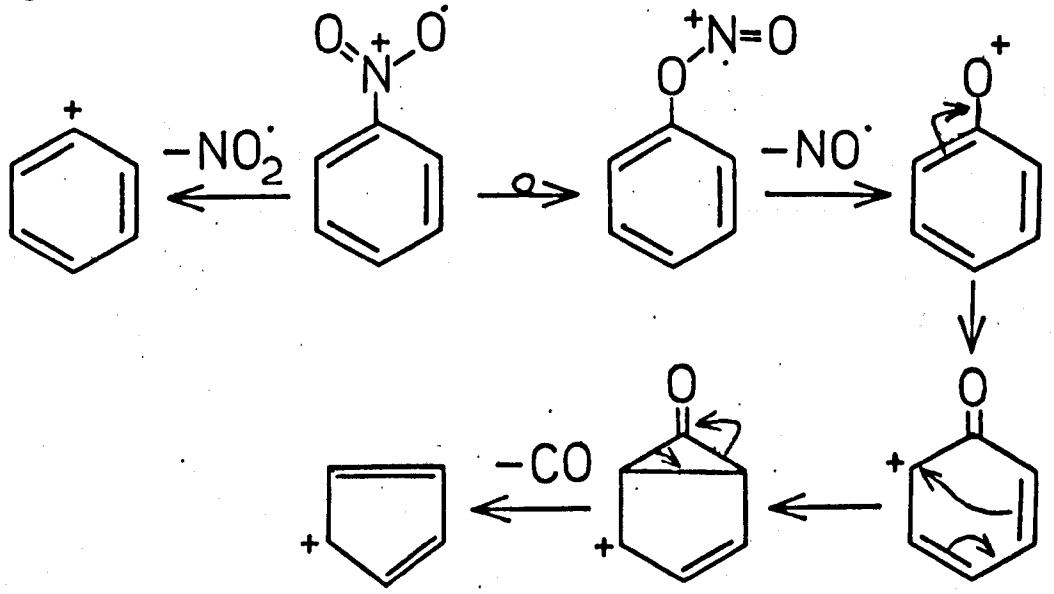


Fig.4.1.1

Simple derivatives of nitrobenzene,e.g.m- and p-nitrotoluene, also undergo primary elimination of NO$^{\cdot}$,presumably via the

nitro→nitrito rearrangement, although, as with nitrobenzene, the loss of $NO_2^{\cdot}$ is of more significance[231]. This is probably because loss of $NO_2^{\cdot}$ requires only the breaking of one bond whereas the loss of NO· requires the formation of a new bond before elimination can take place. The latter process is therefore less energetically favoured than the former. For o-nitrotoluene the major fragmentation process is the elimination of OH· followed by the sequential loss of CO and HCN. This process was thoroughly investigated by Meyerson *et al*[231] who used isotopically labelled carbon and hydrogen in the methyl group of o-nitrotoluene. They established conclusively that the molecule of carbon monoxide which was eliminated from the $[M-OH^{\cdot}]^+$ ion originated from the methyl group, and they proposed the following scheme for the sequential elimination of OH·, CO and HCN :-

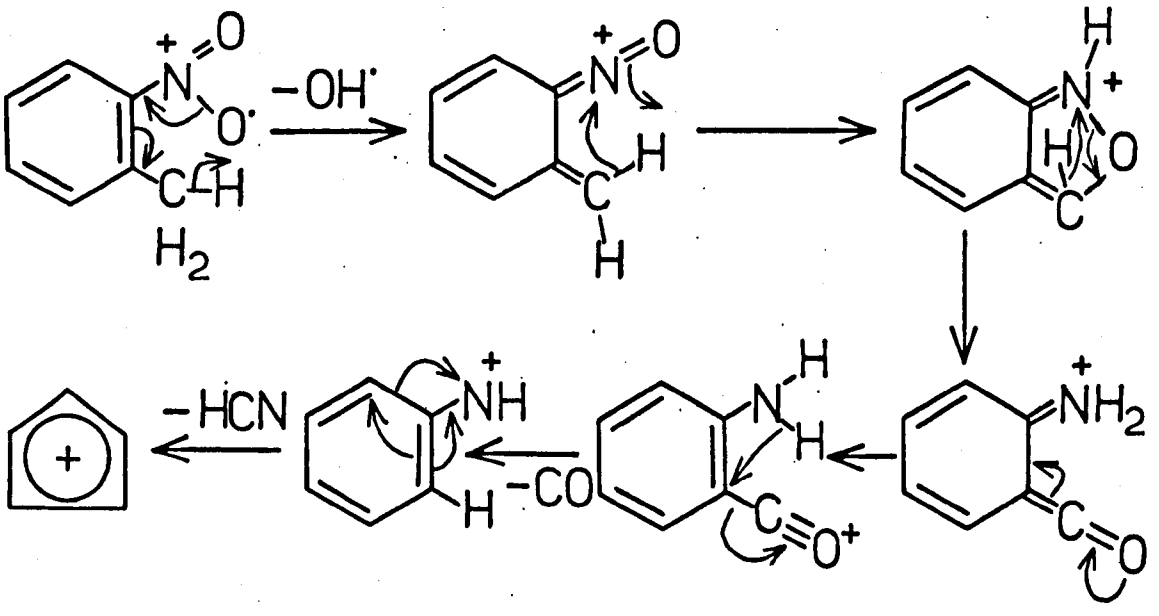


Fig.4.1.2

These workers considered that loss of OH· occurred as a

single step,rather than via a discrete intermediate. For 2,6-dinitrotoluene[230] and 2,4,6-trinitrotoluene[232],in which a methyl group is substituted adjacent to two nitro groups in each case,the primary elimination of two hydroxyl radicals is observed.

The positive ion spectra of the nitro derivatives of naphthalene have received much attention in the literature. 1-nitronaphthalene is of particular interest as the molecular ion undergoes successive loss of CO and NO$^{\cdot}$,the opposite to that observed for nitrobenzene[233]. It has been proposed that an interaction between the nitro group at the 1-position and the carbon atom at the 8-position takes place,and two possible schemes have been postulated[233,234] (fig.4.1.3).

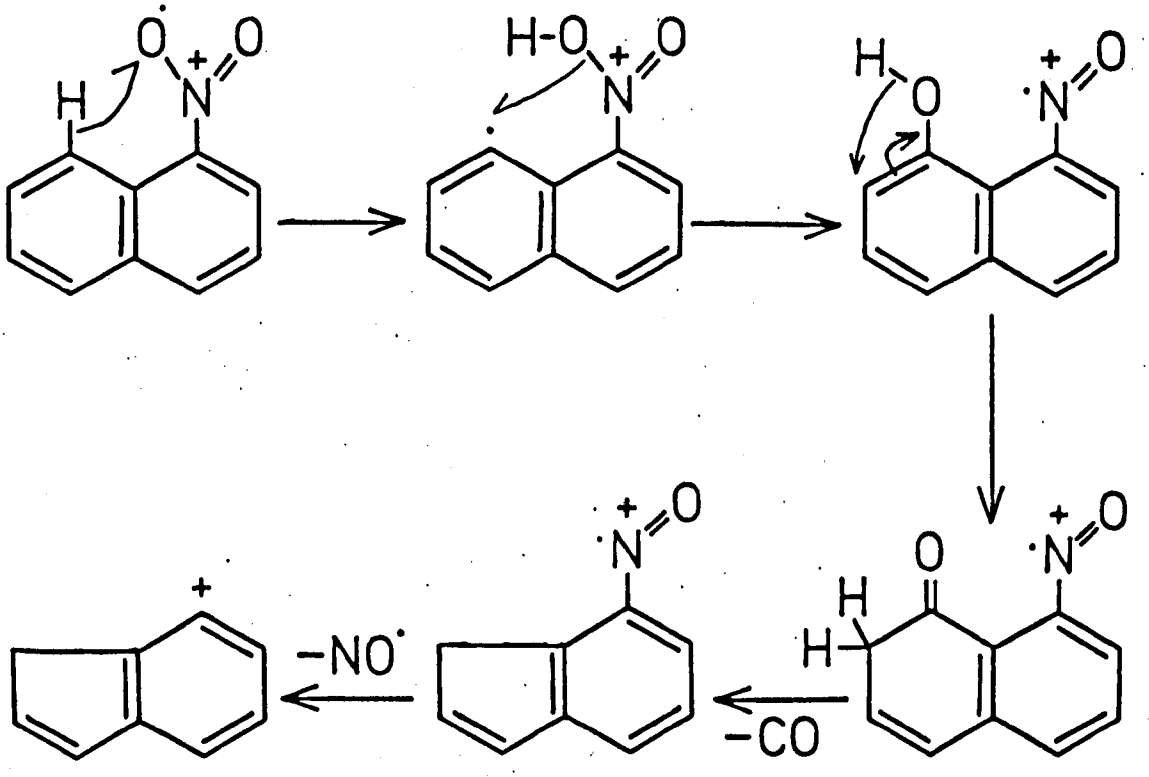


Fig.4.1.3 - Route A

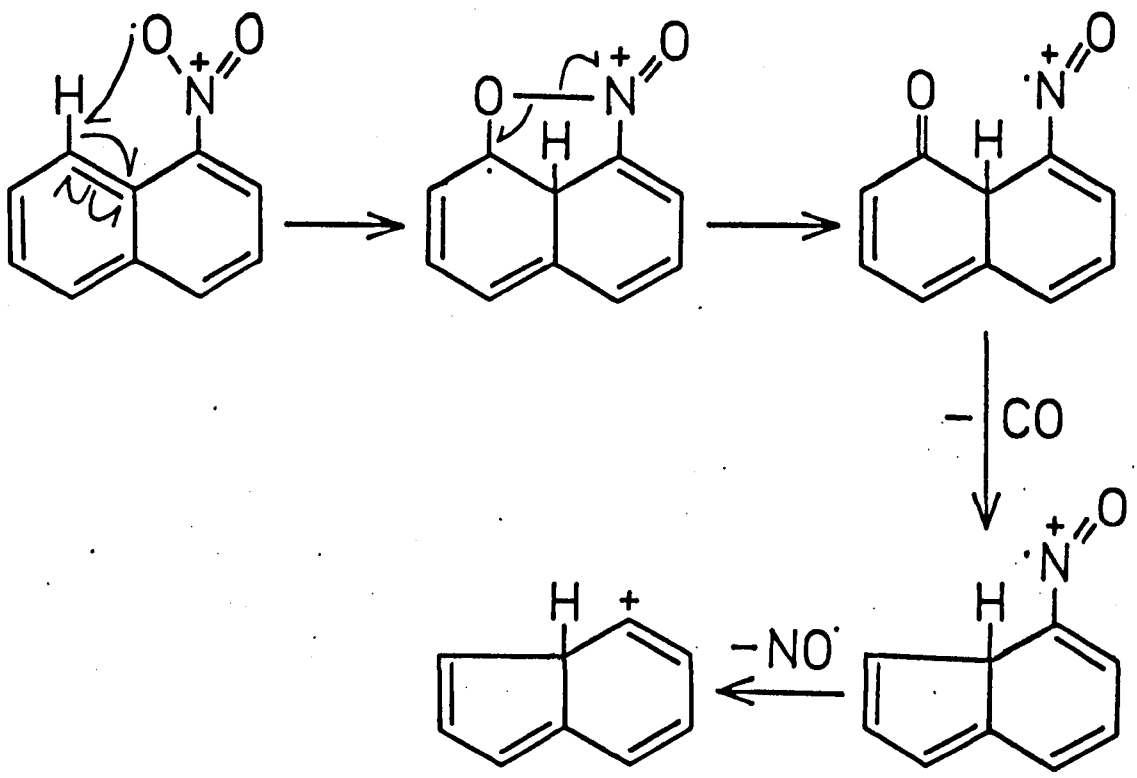


Fig.4.1.3 - Route B

The key step in both of these mechanisms is the bonding of the oxygen atom of the nitro group to the carbon atom at the 8-position. The proposed mechanisms are justified by the observation that for the dinitronaphthalenes the relative intensities of the $[M-CO]^{+}$ peaks decrease with decreasing electron density at the 8-position, being least for 1,7-dinitronaphthalene and greatest for 1,3-dinitronaphthalene [99]. However, the loss of CO from the molecular ion is a minor fragmentation process for the dinitronaphthalenes, the more important route being the sequential loss of two nitrogen dioxide radicals. For 1,8-dinitronaphthalene, the $[M-NO_2^{\cdot}]^{+}$ ion gives rise to the base peak in the spectrum, suggesting that loss of $NO_2^{\cdot}$ is a particularly facile process in this case. The $[M-NO_2^{\cdot}]^{+}$ ion then fragments via loss of $NO^{\cdot}$ and CO. A mechanism for this process has

been proposed [99] (fig.4.1.4).

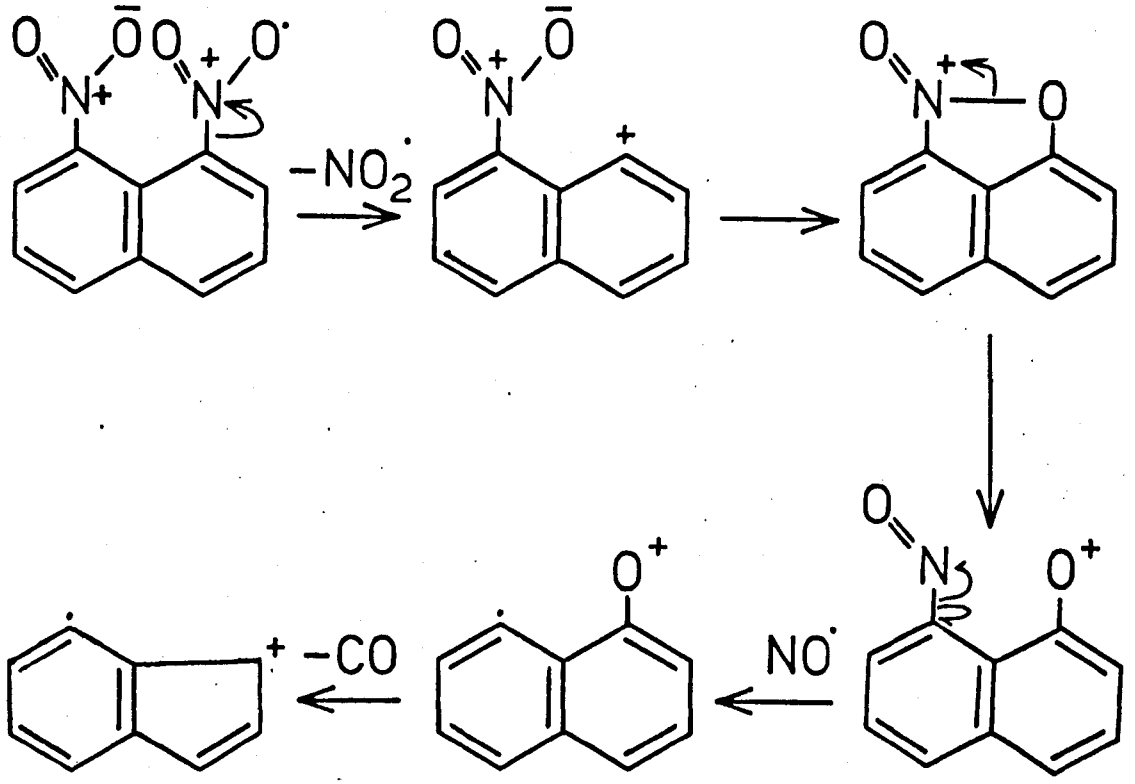


Fig.4.1.4

Primary elimination of $NO_2^{\cdot}$ from the 1-position is followed by attack on that position by the oxygen atom of the 8-nitro group, the latter step being favoured by the electron deficiency of the 1-carbon atom. After loss of NO·, the daughter ion has a structure resembling the phenoxy cation, as derived from nitrobenzene (fig.4.1.1), and loss of CO can then occur. For 1,3-dinitronaphthalene the major fragmentation processes are the loss of OH· and HONO from the molecular ion. This has been explained as being due to a primary rearrangement, as in fig.4.1.3A, in which an ONOH group is formed at the 1-position. Sequential loss of OH· and NO·, or the loss of HONO as a complete fragment, can then occur readily.

Of the alkyl substituted nitronaphthalenes,the nitroacenaphthenes have been particularly comprehensively studied with regard to mass spectrometry[236]. The molecular ions of these compounds,in particular those containing nitro groups which can interact with the aliphatic bridge, fragment via a loss of OH· and HONO,and this is probably due to the formation of discrete intermediates containing the ONOH group,as shown in fig.4.1.5.

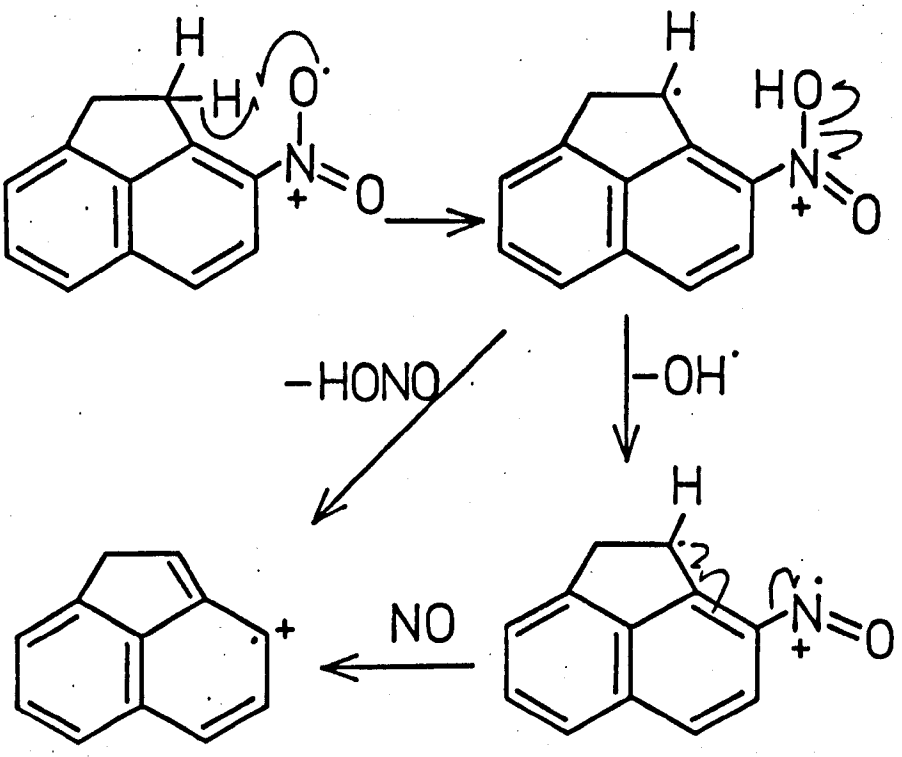


Fig.4.1.5

Those polynitroacenaphthenes containing nitro groups substituted on adjacent *peri* positions,e.g.5,6-dinitro-acenaphthene,undergo sequential loss of $NO_2^{\cdot}$ and NO· from the molecular ion. This is analogous to the fragmentation process observed for 1,8-dinitronaphthalene.

(B) Negative Ion Mass Spectra of Nitroaromatic Compounds

The negative ion mass spectra of nitroaromatic compounds have received considerably less attention than the positive ion spectra of these compounds. The negative ion spectrum of nitrobenzene has been well studied[237], and the main features of the spectrum found to be an intense peak at *m/e* 46, due to the nitrite ion $[NO_2]^-$, and a weak peak at *m/e* 93 corresponding to $[M-NO^{\cdot}]^-$. Bowie and his co-workers[238,239,240] have studied the negative ion spectra of a number of substituted nitrobenzenes, and have concluded that the intensity of the $[M-NO^{\cdot}]^-$ peak increases with the increasing electron withdrawing character of the substituents. Thus the $[M-NO^{\cdot}]^-$ peaks in the negative ion spectra of the dinitrobenzenes are quite intense, whereas for the nitroanilines they are virtually non-existent. Brown and Weber[241] have studied the negative ion spectra of m- and p-dinitrobenzenes obtained with 2-20eV electrons, and have determined that the energy change for the loss of $NO^{\cdot}$ from the molecular ion is greater for p-dinitrobenzene than for m-dinitrobenzene. This is to be expected as a *meta* nitro group can stabilise a phenoxide ion only by inductive electron withdrawal, whereas a *para* nitro group can also stabilise a negative charge by direct resonance interaction, as shown in fig.4.1.6. The loss of $NO^{\cdot}$ is presumably preceded by a nitro→nitrito rearrangement. The negative ion spectrum of 2,4,6-trinitrotoluene has been obtained with 2-8eV electrons, and peaks corresponding to losses of $OH^{\cdot}$, $NO^{\cdot}$, HONO and $NO_2^{\cdot}$ observed[232]. The loss of $OH^{\cdot}$ from the molecular ion undoubtedly proceeds via abstraction of

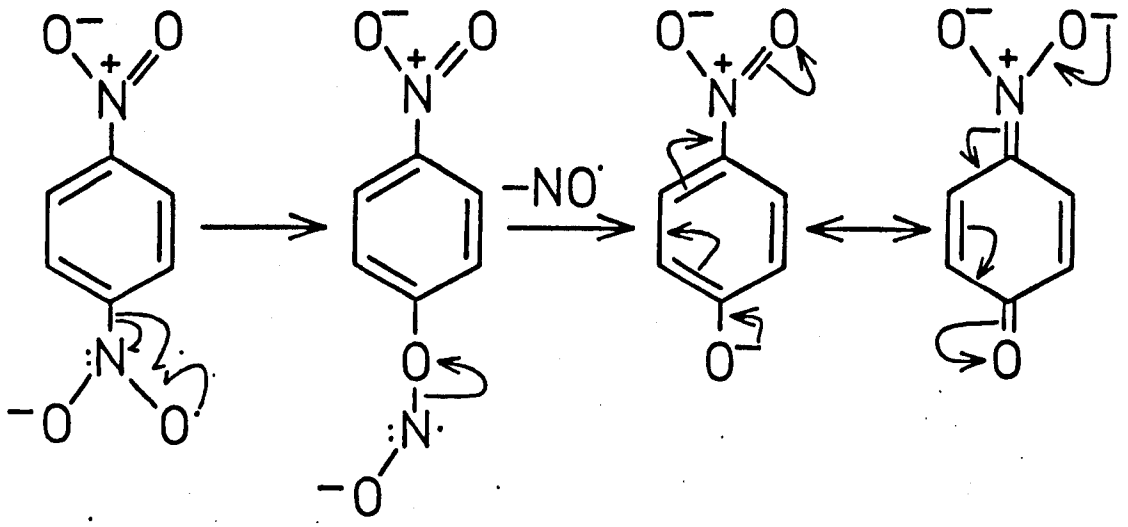


Fig.4.1.6

a hydrogen atom from a methyl group by an adjacent nitro group. Unlike the positive ion spectrum,the sequential loss of two hydroxyl radicals from the molecular ion was not observed in the negative ion spectrum.

Of the compounds based on the naphthalene nucleus,only the nitroacenaphthenes have received attention with regard to negative ion mass spectrometry[236]. Those nitroacenaphthenes having nitro groups substituted *ortho* to the aliphatic bridge undergo elimination of OH· and HONO from their negative molecular ions by an analogous mechanism to that proposed for the comparable eliminations from the positive molecular ions (fig.4.1.5). Primary loss of NO· is favoured for the polynitroacenaphthenes by the presence of a nitro group at an effectively *ortho/para* position with respect to the nitro group from which the loss occurs,e.g.4,6-dinitroacenaphthene. The phenoxide ion that is formed can then be stabilised by resonance interaction,as shown in fig.4.1.7.

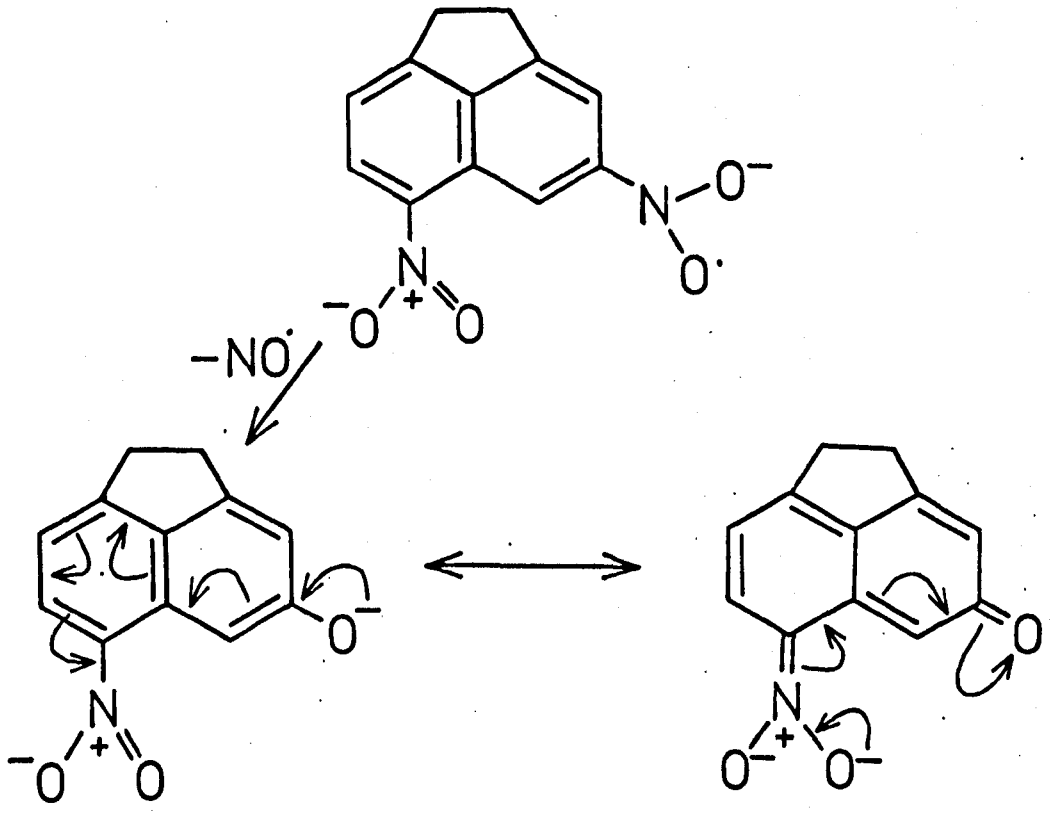


Fig.4.1.7

4.1.2 Positive Ion Mass Spectra of Nitro-2,3-Dimethylnaphthalenes

The positive ion mass spectra of twelve nitro-2,3-dimethylnaphthalenes are presented as computer-processed bar diagrams in figs.4.1.19-30. The most abundant ions in the spectra are listed in table 4.1.1,together with the percentage total ion current carried by each ion. Proposed major fragmentation pathways for each of the twelve compounds, supported where possible by metastable ion evidence,are presented in figs.4.1.35-46. In each case the fragmentation routes have been followed as far as the formation of hydrocarbon species,after which the fragmentation patterns are characteristic of the naphthalene nucleus and are therefore similar in all cases. The fragments giving rise to the base peaks are indicated by double underlining in the diagrams.

The main primary fragmentations were found to be those resulting from the loss of nitrogen dioxide,nitric oxide and hydroxyl radicals. These fragmentations,and the secondary fragmentations associated with them,are discussed below.

(a) Loss of Nitrogen Dioxide and Nitric Oxide

Loss of $NO_2^{\cdot}$ from the molecular ion occurred in the spectra of all the compounds studied. Loss of $NO^{\cdot}$ from the molecular ion was also observed to take place,probably via the nitro→nitrito rearrangement,but,as in the case of simple nitroaromatic compounds,e.g.nitrobenzene [231],the loss was relatively insignificant compared to other primary fragmentations,and the resulting ion was almost always of

Table 4.1.1 Percentage total ion currents (Σi) for primary and secondary fragmentations in the positive ion mass spectra of nitro-2,3-dimethylnaphthalenes.

Compound	$M^{+\cdot}$	$[M-H]^{+}$	$[M-O]^{+\cdot}$	$[M-OH^{\cdot}]^{+}$	$[M-NO^{\cdot}]^{+\cdot}$	$[M-NO_2^{\cdot}]^{+}$	$[M-NO^{\cdot}-CO]^{+\cdot}$	$[M-OH^{\cdot}-NO^{\cdot}]^{+}$	$[M-OH^{\cdot}-CO]^{+}$ [a]	$[M-NO_2^{\cdot}-NO^{\cdot}]^{+\cdot}$ [b]
1-nitro-2,3-DMN	14.0	1.4 *	0.4	2.0 *	2.0 *	4.2 *	1.9 *	2.7 *	5.7 *	-
5-nitro-2,3-DMN	14.3	0.4	0.2	0.2	1.2	5.6 *	1.7 *	2.4 *	2.4	-
1,8-dinitro-2,3-DMN	4.8	0	0.1	0.1	0.1	14.5 *	0	0.2	1.9	8.8 *
1,5-dinitro-2,3-DMN	4.2	0	0.2	0.5 *	0.1	0.1	0	0.2	0.2	1.0
1,4-dinitro-2,3-DMN	8.0	0	0.3	1.1 *	0.7 *	0.5	0.1	0.6	0.7 *	1.5
5,7-dinitro-2,3-DMN	7.5	0.4	0.2	0.4 *	0.1	1.0	0.2	0.3 *	0.5	1.1
5,8-dinitro-2,3-DMN	10.7	0.1	0.2	0.7 *	0.3	0.9	0.1	0.6	0.7	0.8
1,4,5-trinitro-2,3-DMN	1.4	0	0.1	0.1	0.1	10.0 *	0	0	1.7	1.0 *
1,5,7-trinitro-2,3-DMN	9.8	0.1	0.8	3.7 *	0.5	0.2	0	0.3	0.3	0.5
1,6,8-trinitro-2,3-DMN	4.0	0.1	0.2	0.1	0.1	14.2 *	0	0.2	2.1	7.1 *
5,6,8-trinitro-2,3-DMN	1.0	0	0.1	0.3 *	0.1	0.1	0	0.1	0	0.1(*)
1,4,5,7-tetranitro-2,3-DMN	0.1	0	0.1	0.1	0.4	2.4 *	0	0	0.2	0.5(*)

* indicates metastable peak observed for that fragmentation.

(a) The $[M-OH^{\cdot}-CO]^{+}$ percentage total ion current figures are artificially enhanced by C^{13} isotope effects from the $[M-NO_2^{\cdot}]^{+}$ ions.

(b) (*) indicates metastable peak corresponding to $[(M-NO^{\cdot})-NO_2^{\cdot}]^{+}$.

lesser abundance than the ion corresponding to loss of $NO_2^{\cdot}$.

Loss of $NO_2^{\cdot}$ occurred as the major primary fragmentation process in the spectra of both of the mono-nitro-2,3-dimethylnaphthalenes. However, loss of $NO_2^{\cdot}$ from the molecular ions of the polynitro-2,3-dimethylnaphthalenes was found to be predominant only in those compounds where nitro groups are substituted on adjacent *peri*-positions, *viz* 1,8-dinitro-2,3-dimethylnaphthalene, 1,4,5-trinitro-2,3-dimethylnaphthalene, 1,6,8-trinitro-2,3-dimethylnaphthalene and 1,4,5,7-tetranitro-2,3-dimethylnaphthalene. The elimination of $NO_2^{\cdot}$ from the molecular ion is clearly a facile process because it relieves the severe steric strain resulting from the interaction of the *peri* nitro groups. The mechanism of this primary elimination is presumably similar to that postulated for the fragmentation of the molecular ion of 1,8-dinitronaphthalene (sec.4.1.1A). In the latter case, a secondary fragmentation due to loss of $NO^{\cdot}$ also takes place, and this same loss was also observed to take place in the spectra of the four polynitro-2,3-dimethylnaphthalenes named above. Metastable ion evidence was obtained for both the primary and secondary processes in the above cases.

Primary loss of $NO^{\cdot}$ followed by elimination of CO, as in the case of nitrobenzene[229], was observed only for 1-nitro-2,3-dimethylnaphthalene and 5-nitro-2,3-dimethyl-naphthalene (table 4.1.1). In the case of the polynitro-2,3-dimethylnaphthalenes this process was found to be insignificant, the loss of $NO^{\cdot}$ being followed usually by the loss of $NO_2^{\cdot}$. This might be expected as the loss of $NO_2^{\cdot}$

from the $[M-NO^{\cdot}]^{+}$ ion requires the breaking of one bond, whereas the loss of CO requires the breaking of two bonds, and could therefore be less energetically favoured.

(b) Loss of Hydroxyl Radical

Primary elimination of $OH^{\cdot}$ was observed in the spectra of both of the mononitro-2,3-dimethylnaphthalenes. In the case of the polynitro-2,3-dimethylnaphthalenes the loss of $OH^{\cdot}$ and $NO_2^{\cdot}$ from the molecular ion were competing processes. It is interesting to note that the occurrence of metastable ions for the two processes is mutually exclusive (see table 4.1.1). Loss of $OH^{\cdot}$ from the molecular ion of 1-nitro-2,3-dimethylnaphthalene was of particular significance as it was followed by the sequential loss of CO and HCN,as confirmed by metastable ion evidence (fig.4.1.35). This process must follow an analogous route to that proposed for the fragmentation of the structurally related o-nitrotoluene,where the molecule of CO eliminated is derived from the carbon atom in the methyl group (sec.4.1.1A). This fragmentation route was also observed for 1,4-dinitro-2,3-dimethylnaphthalene in which both the nitro groups are substituted *ortho* to methyl groups. Sequential loss of $OH^{\cdot}$ and CO from the molecular ion was also observed for 1,5-dinitro-2,3-dimethylnaphthalene and 1,5,7-trinitro-2,3-dimethylnaphthalene,both of these compounds containing one nitro group substituted *ortho* to a methyl group,but the subsequent loss of HCN was not observed,probably due to competing processes which render the loss of HCN from the $[M-OH^{\cdot}-CO]^{+}$ ion an insignificant fragmentation route.

Metastable ion evidence showed that sequential

loss of OH· and NO· from the molecular ion,i.e.overall loss of nitrous acid (HONO) occurred for all the nitro-2,3-dimethylnaphthalenes in which primary loss of OH· was a significant process. There was no metastable ion evidence, however,for direct loss of HONO. In the case of 1-nitro-2,3-dimethylnaphthalene,in which a nitro group is substituted *ortho* to a methyl group,the fragmentation route leading to loss of HONO (fig.4.1.8A) must be regarded as being competitive with the sequential loss of OH·and CO (fig.4.1.8B).

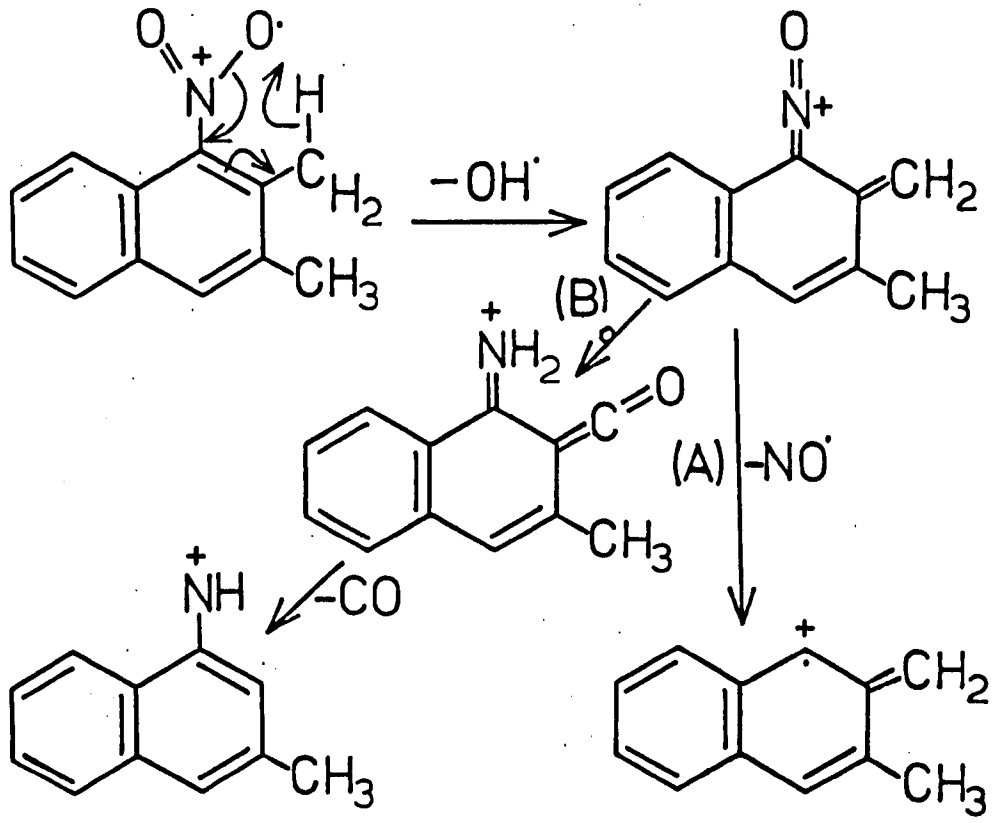


Fig.4.1.8

In the case of those compounds not having nitro groups substituted *ortho* to methyl groups,but having one nitro group substituted at a *peri* position,e.g.5-nitro-2,3-dimethylnaphthalene,the loss of HONO probably proceeds via an interaction with a hydrogen atom on an adjacent *peri* position to that of the nitro group,as shown in fig.4.1.9.

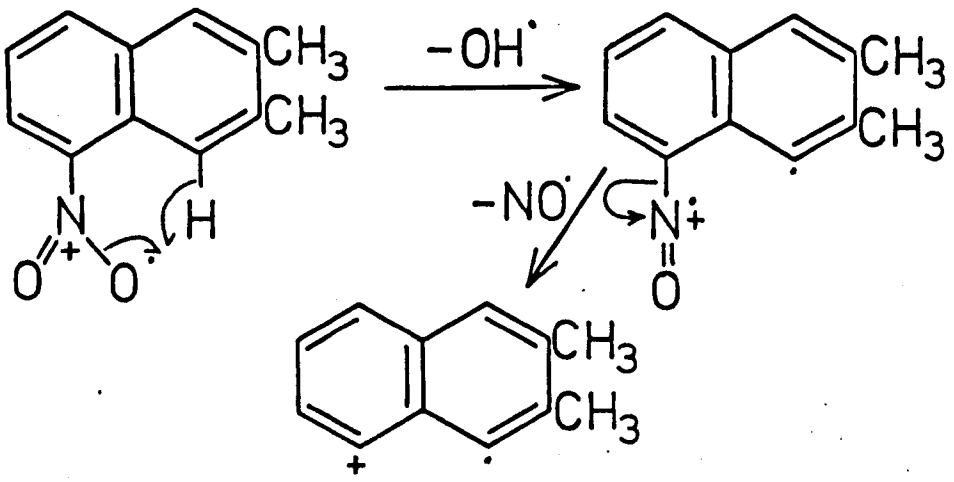


Fig.4.1.9

(c) Loss of Carbon Monoxide

Although elimination of CO from the molecular ion is an important fragmentation process for nitronaphthalenes substituted at the 1-position and unsubstituted at the 8-position [99], no such primary loss was observed for any of the structurally similar nitro-2,3-dimethylnaphthalenes, although losses of CO were frequently observed as secondary eliminations. As an example, the primary fragmentation of 1-nitronaphthalene may be compared to the primary fragmentations of 1-nitro-2,3-dimethylnaphthalene and 5-nitro-2,3-dimethylnaphthalene, all of which contain α-nitro groups. The key step in the primary elimination of CO from 1-nitronaphthalene is the transfer of an oxygen atom from the nitro group at the 1-position to the carbon atom at the 8-position (fig.4.1.3). In the case of 5-nitro-2,3-dimethylnaphthalene however, the loss of OH· takes preference (fig.4.1.9), probably because transfer of the oxygen atom to the 4-position is prevented because of the high electron density at this site (see table 3.2.3) arising from the electron-donating methyl group at the 3-position. In the case of 1-nitro-2,3-dimethylnaphthalene, the nitro group is

twisted out of the plane of the ring by the methyl group at the 2-position,and thus transfer of an oxygen atom to the 8-position is inhibited.

4.1.3 Positive Ion Mass Spectra of Nitro-1,5-Dimethylnaphthalenes

The positive ion mass spectra of four nitro-1,5-dimethylnaphthalenes are presented in figs.4.1.31-34,and the proposed major fragmentation pathways for each compound are given in figs.4.1.47-50. The more important ions are listed in table 4.1.2 together with the percentage total ion current carried by each ion.

(a) Loss of Nitrogen Dioxide and Nitric Oxide

Unlike the polynitro-2,3-dimethylnaphthalenes, none of the polynitro-1,5-dimethylnaphthalenes contain nitro groups substituted on adjacent *peri* positions,and consequently the primary elimination of $NO_2^{\cdot}$ was not observed as a major process for the latter compounds. The total ion current carried by the $[M-NO_2^{\cdot}]^{+\cdot}$ ion decreased sharply with the increased substitution of nitro groups. Loss of $NO^{\cdot}$ from the molecular ion was of lesser significance than the loss of $NO_2^{\cdot}$ for the mononitro and polynitro-1,5-dimethylnaphthalenes. The sequential loss of $NO^{\cdot}$ and CO was observed only for 4-nitro-1,5-dimethylnaphthalene,the process involved probably being similar to that postulated for the comparable loss from nitrobenzene (fig.4.1.1).

(b) Loss of Hydroxyl Radical and Nitrous Acid

Loss of the hydroxyl radical was found to be the most important primary fragmentation process in the spectra of all the nitro-1,5-dimethylnaphthalenes investigated. The elimination of $OH^{\cdot}$ must proceed via a route analogous to that postulated for the primary elimination of $OH^{\cdot}$ from o-nitrotoluene,as in all the compounds studied each nitro

Table 4.1.2 Percentage total ion currents for primary and secondary fragmentations in the positive ion mass spectra of nitro-1,5-dimethylnaphthalenes.

Compound	$M^{\cdot+}$	$[M-O]^{\cdot+}$ [a]	$[M-OH^{\cdot}]^{+}$	$[M-NO^{\cdot}]^{+}$	$[M-NO_2^{\cdot}]^{+}$	$[M-OH^{\cdot}-CO]^{+}$	$[M-NO^{\cdot}-CO]^{+}$	$[M-OH^{\cdot}-NO^{\cdot}]^{+}$
4-nitro-1,5-DMN	6.4	2.6	15.6 *	0.9	2.8 *	2.3 *	0.4	2.9 *
4,8-dinitro-1,5-DMN	5.7	1.3	12.0 *	0.2	0.5	0.5	0	1.9 *
2,4,8-trinitro-1,5-DMN	8.3	1.2	6.9 *	0	0.1	0.2	0	0.4 *
2,4,6,8-tetranitro-1,5-DMN	1.7	0.4	2.0 *	0	0.2	0.2	0	0.4

* indicates metastable peak observed for that fragmentation.

(a) The $[M-O]^{\cdot+}$ figures are artificially enhanced by C^{13} isotope effects from the intense $[M-OH^{\cdot}]^{+}$ peaks.

group can interact sterically with a methyl group. Thus 4-nitro-1,5-dimethylnaphthalene was observed to undergo loss of one OH radical from the molecular ion,whereas 4,8-dinitro-1,5-dimethylnaphthalene and 2,4,8-trinitro-1,5-dimethylnaphthalene were observed to undergo sequential loss of two and three OH radicals respectively. In the case of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene,the sequential loss of only three OH radicals was observed.

The initial fragmentation of 4-nitro-1,5-dimethylnaphthalene was found to be similar to that of 1-nitro-2,3-dimethylnaphthalene in that loss of OH· was followed by either the loss of NO· or by the sequential loss of CO and HCN,and it is likely that the processes involved were similar for both compounds (*cf* fig.4.1.8). Loss of CO from the $[M\text{-}OH\cdot]^+$ ion of 4,8-dinitro-1,5-dimethylnaphthalene was of much less significance than for 4-nitro-1,5-dimethylnaphthalene. This is presumably because the key step in the process,i.e.the conversion of the methylene group at the 5-position to a carbonyl group (*cf* fig.4.1.2),was inhibited by the nitro group at the 8-position stabilising the methylene group by resonance interaction (fig.4.1.10).

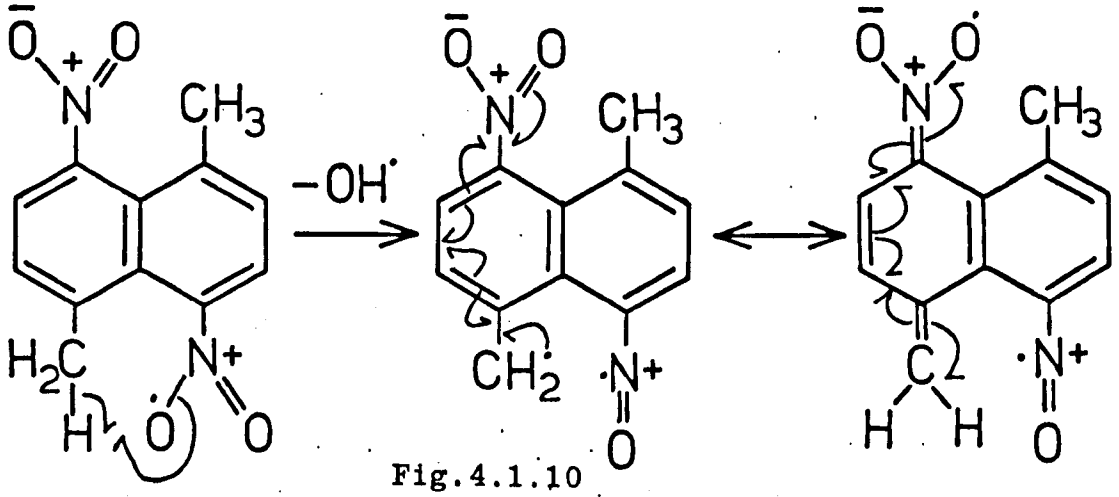


Fig.4.1.10

In this case loss of loss of NO· from the $[M-OH\cdot]^+$ ion predominated over the loss of CO from the same ion.

For the polynitro-1,5-dimethylnaphthalenes loss of nitrous acid was the most important feature of the fragmentation processes. The loss of nitrous acid always occurred as a combination of losses of OH· and NO·, the loss of OH· being the primary process. In no case was loss of OH· preceded by the loss of NO·. Thus 2,4,8-trinitro-1,5-dimethylnaphthalene was found to undergo the loss of three molecules of nitrous acid by the sequential loss of three hydroxyl radicals followed by the loss of three nitric oxide radicals. There was no metastable ion evidence for the loss of HONO as a complete fragment in any case.

4.1.4 Negative Ion Mass Spectra of Nitro-2,3-Dimethylnaphthalenes

The negative ion mass spectra of twelve nitro-2,3-dimethylnaphthalenes are presented in figs.4.1.19-30, and the proposes major fragmentation pathways for each compound given in figs.4.1.51-62. The more important primary and secondary fragmentations are listed in table 4.1.3 together with the percentage total ion current carried by each ion. The basic characteristic of the negative ion mass spectra of nitroaromatic compounds is that stable,high molecular weight ions tend to be formed, and therefore the intensities of the peaks for the lower molecular weight daughter ions tend to be small. Consequently,it has not been possible to propose fragmentation pathways as extensive as those proposed for the positive ion spectra.

The most important primary fragmentations involve loss of hydroxyl radical,nitrous acid,nitric oxide and nitrogen dioxide. In addition,an intense peak corresponding to the nitrite ion was observed in the spectra of all the compounds under investigation.

(a) Loss of Nitric Oxide

The elimination of NO· from the negative molecular ion was an important process for the nitro-2,3-dimethylnaphthalenes. However,table 4.1.3 shows up interesting variations in the percentage total ion current,Σi,carried by the $[M-NO\cdot]^-$ ion. For the purposes of comparison,the values for the dinitro and trinitro derivatives of 2,3-dimethylnaphthalene are given below,along with the

Table 4.1.3 Percentage total ion currents for primary and secondary fragmentations in the negative ion mass spectra of nitro-2,3-dimethylnaphthalenes.

Compound	$M^{-\cdot}$	$[M-H]^{-\cdot}$	$[M-O]^{-\cdot}$	$[M-OH^{\cdot}]^{-}$	$[M-NO^{\cdot}]^{-}$	$[M-NO_2^{\cdot}]^{-}$	$[M-OH^{\cdot}-NO^{\cdot}]^{-\cdot}$	$[M-OH^{\cdot}-CO]^{-}$ [d]	$[M-NO^{\cdot}-NO^{\cdot}]^{-\cdot}$	$[M-NO_2^{\cdot}-NO^{\cdot}]^{-\cdot}$ [e]	NO_2^{-}
1-nitro-2,3-DMN	20.6	0.8	1.3	2.0	10.9	0.8	0.7 *	1.4 *	-	-	46.8
5-nitro-2,3-DMN	50.6	0.9	0.9	0.5	3.4	0.1	0.1	0.2	-	-	30.7
1,8-dinitro-2,3-DMN	13.1	0.3	0	0.1	1.0	9.1 *	0.1	1.4	0.1	4.8 *	60.3
1,5-dinitro-2,3-DMN	32.8	0.2	0.3	0.9 *	8.5 *	0.6	0.2 * [a,c]	0.2	1.1 *	0.2	45.0
1,4-dinitro-2,3-DMN	21.0	0	0.6	2.0 *	17.8 *	1.4	0.1 * [a,b,c]	0.4 *	0.4	0.2	43.0
5,7-dinitro-2,3-DMN	23.8	0.2	0.2	0.1	16.5 *	0.4	0	0.1	1.8 *	0.5	47.7
5,8-dinitro-2,3-DMN	48.7	0.6	0.4	0.1	19.5 *	1.0	0.1	0.5	0.2	0.4	14.6
1,4,5-trinitro-2,3-DMN	1.4	0	0.6	0.2	2.4	9.4 *	0.2	1.7	0.5	1.0 *	45.1
1,5,7-trinitro-2,3-DMN	18.4	1.4	0.6	2.2 *	30.6 *	3.2 *	1.9 * [a,c]	0.8	3.6 *	2.9(*)	9.6
1,6,8-trinitro-2,3-DMN	3.6	1.5	0	0	1.5	9.4 *	0.2	1.9	0.5	8.5 *	50.9
5,6,8-trinitro-2,3-DMN	5.3	1.6	0.4	0	16.9 *	9.0 *	0.2	1.6	0.1	5.1(**)	14.6
1,4,5,7-tetranitro-2,3-DMN	0.1	0	0.1	0	1.7	14.3 *	0.1	2.0	0.2	26.5(**)	14.3

(a) Corresponding to $[(M-NO^{\cdot})-OH^{\cdot}]^{-\cdot}$. *(b)* Corresponding to $[(M-OH^{\cdot})-NO^{\cdot}]^{-\cdot}$. *(c)* Corresponding to $[M-HONO]^{-\cdot}$. *(d)* The $[M-OH^{\cdot}-CO]^{-}$ are artificially enhanced by isotope effects from the $[M-NO_2^{\cdot}]^{-}$ ion. *(e)* (*) indicates metastable peak observed corresponding to $|(M-NO^{\cdot})-NO_2^{\cdot}|^{-\cdot}$.

appropriate molecular framework.($X=NO_2$).

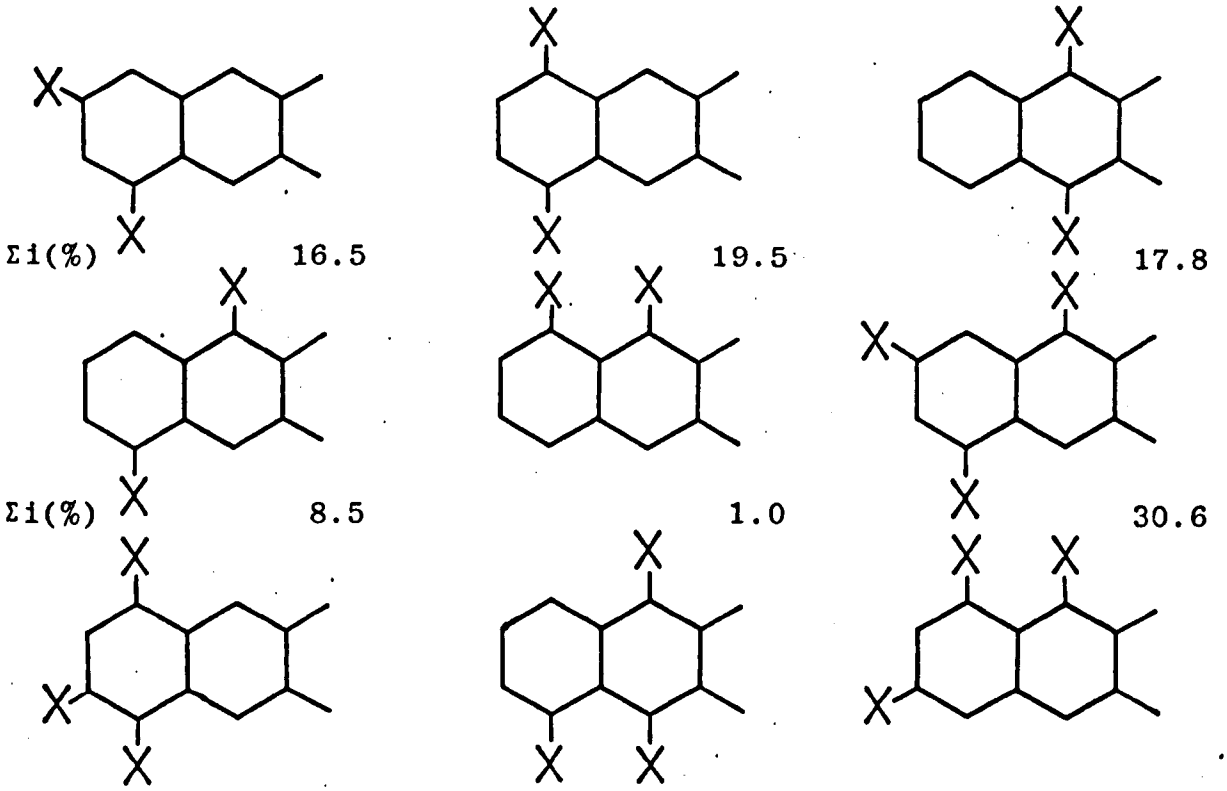


Fig.4.1.11

It is of some significance that the compounds which have the lowest value of Σi for the $[M-NO^{\cdot}]^-$ ion,*viz* 1,8-dinitro-2,3-dimethylnaphthalene and 1,6,8-trinitro-2,3-dimethylnaphthalene,also have the highest values of Σi for the NO_2^- ion (see table 4.1.3). Thus it would appear that steric interaction between *peri*-substituted nitro groups enhances the loss of NO_2^- and hence inhibits the loss of $NO^{\cdot}$. 1,4,5-trinitro-2,3-dimethylnaphthalene also possesses *peri*-substituted nitro groups which can sterically interact,and although it too exhibits a very low Σi value for the NO_2^- species,this latter value is not as great as in the cases of 1,8-dinitro-2,3-dimethylnaphthalene and 1,6,8-trinitro-

2,3-dimethylnaphthalene.

The values of Σi for the $[M-NO^{\cdot}]^-$ ions of 1,4-dinitro-2,3-dimethylnaphthalene (17.8%) and 1,5-dinitro-2,3-dimethylnaphthalene (8.5%) were relatively high. Thus for 1-substituted compounds in which there is no steric interaction with an adjacent *peri*-nitro group, the loss of NO· is a relatively facile process. The mechanism for loss of NO· most probably involves an initial nitro→nitrito rearrangement followed by bond cleavage, as shown in fig.4.1.6. However, for 1,5,7-trinitro-2,3-dimethylnaphthalene, which also falls into the above class, the Σi value for the $[M-NO^{\cdot}]^-$ ion was found to be abnormally high (30.6%). This must be attributed to the fact that the phenoxide-type ion formed on loss of NO· from the molecular ion can possess structures which are stabilised by resonance interaction. Thus for elimination from the 7-position, the resultant ion would be stabilised by resonance with the nitro group at the 1-position, as shown in fig.4.1.12.

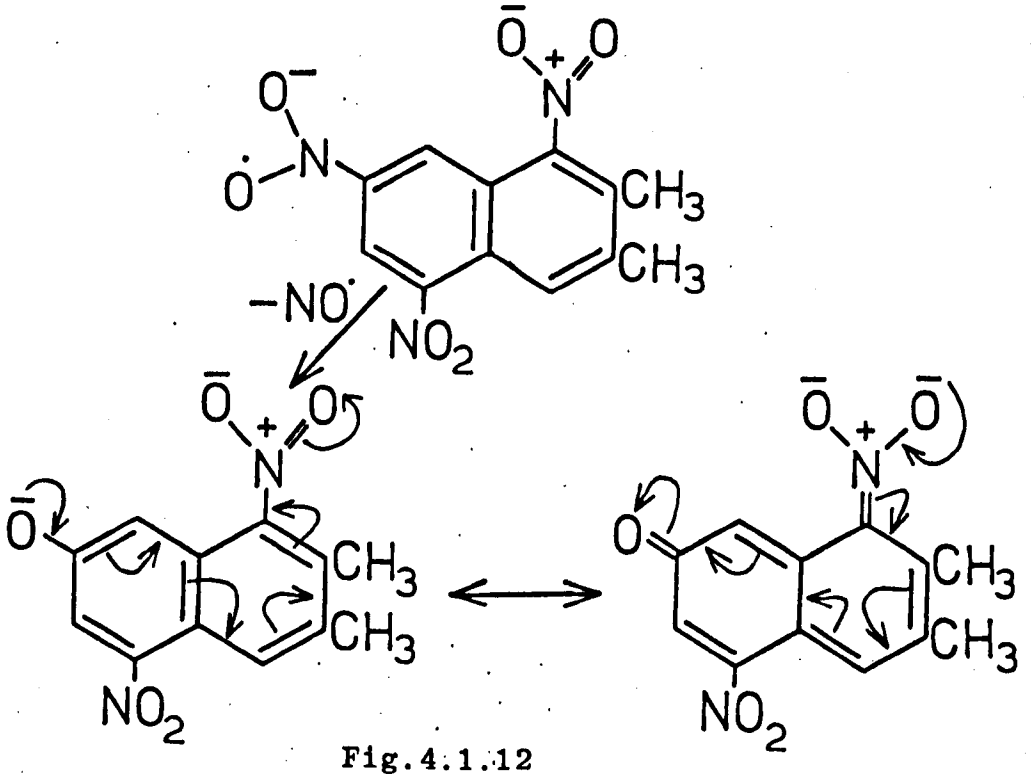


Fig.4.1.12

Also, loss of NO· from the 1-position would yield an ion stabilised by resonance interaction with the 7-nitro group, and loss of NO· from the 5-position would yield an ion stabilised by resonance interaction with the 1-nitro group.

Brown and Weber[241] have reported that for *meta* and *para*-dinitrobenzene, loss of NO· from the negative molecular ion leads to the formation of a more stable $[M-NO\cdot]^-$ ion for the *para* isomer than for the *meta* isomer. This was attributed to the ability of the *para*-nitro group to stabilise the negative charge of the phenoxide ion by direct resonance interaction, whereas the *meta*-nitro group can only provide stabilisation by inductive effects. Therefore, for 5,7-dinitro-2,3-dimethylnaphthalene and 5,8-dinitro-2,3-dimethylnaphthalene, in which the nitro groups are orientated respectively *meta* and *para*, it would be expected that the $[M-NO\cdot]^-$ ion would be more stable, i.e. carry a greater percentage total ion current, in the latter rather than the former case. This was in fact found to be the case, the Σi values for 5,7-dinitro-2,3-dimethylnaphthalene and 5,8-dinitro-2,3-dimethylnaphthalene being 16.5 and 19.5% respectively. Further evidence for the greater stability of the $[M-NO\cdot]^-$ ion of 5,8-dinitro-2,3-dimethylnaphthalene was given by the observation that the subsequent fragmentations of that ion were relatively insignificant (fig.4.1.57), whereas for 5,7-dinitro-2,3-dimethylnaphthalene, the $[M-NO\cdot]^-$ ion was found to undergo a fairly facile fragmentation process (fig.4.1.56).

(b) Loss of Nitrogen Dioxide

Elimination of $NO_2^{\cdot}$ was the most important primary

fragmentation for 1,8-dinitro-2,3-dimethylnaphthalene, 1,4,5-trinitro-2,3-dimethylnaphthalene, 1,6,8-trinitro-2,3-dimethylnaphthalene and 1,4,5,7-tetranitro-2,3-dimethylnaphthalene,i.e.compounds having nitro groups substituted on adjacent *peri*-positions. Thus it would appear that steric crowding at the *peri*-positions favours loss of the $NO_2^{\cdot}$ radical,probably because interaction prevents the nitro→nitrito rearrangement which is the precursor to the loss of NO·,a process which would be in competition with the loss of $NO_2^{\cdot}$. 5,6,8-trinitro-2,3-dimethylnaphthalene also possesses sterically hindered nitro groups,and here again the loss of $NO_2^{\cdot}$ is much more significant than for those compounds not possessing adjacent nitro groups.

For each of the above compounds there was metastable ion evidence for the loss of NO· after the loss of $NO_2^{\cdot}$. The following scheme is proposed for 1,8-dinitro-2,3-dimethylnaphthalene,where loss of $NO_2^{\cdot}$ is followed by a nitro→nitrito rearrangement and subsequent loss of NO·.

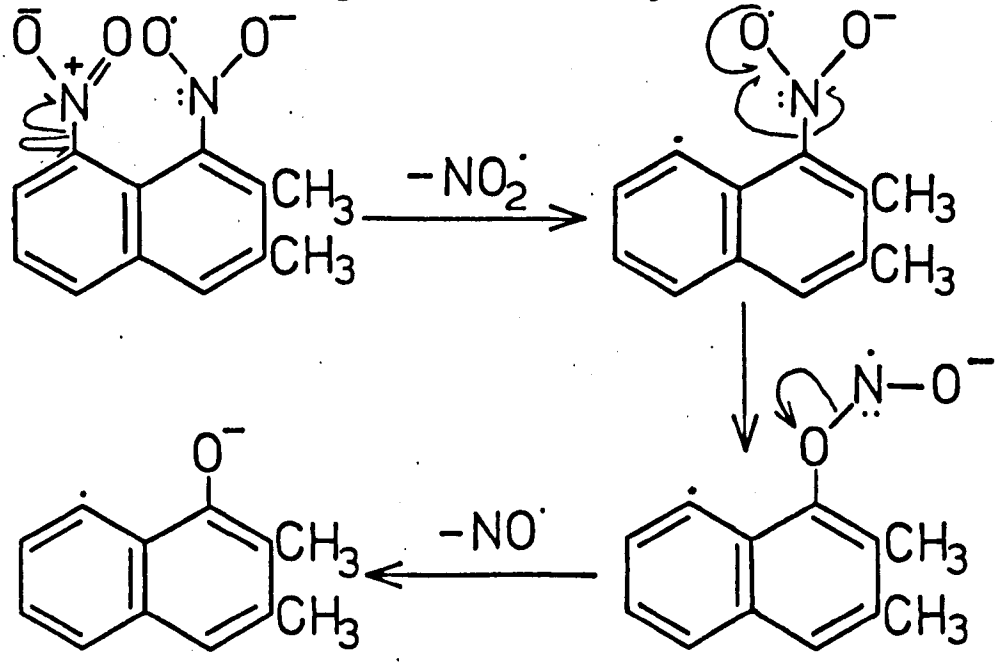


Fig.4.1.13

(c) Loss of Hydroxyl Radical and Nitrous Acid

Loss of hydroxyl radical from the molecular ion was only found to be of significance for 1-nitro-2,3-dimethylnaphthalene, 1,4-dinitro-2,3-dimethylnaphthalene and 1,5,7-trinitro-2,3-dimethylnaphthalene. As all these compounds have structures with a nitro group substituted *ortho* to a methyl group,it must be concluded that primary elimination of OH$^{\bullet}$ in these cases proceeded via an interaction between the nitro and methyl groups similar to that postulated for the loss of OH$^{\bullet}$ from the positive molecular ions (sec.4.1.2b).

Metastable ion evidence for the loss of CO from the $[M\text{-}OH^{\bullet}]^-$ ion was only observed for 1-nitro-2,3-dimethylnaphthalene and 1,4-dinitro-2,3-dimethylnaphthalene. A similar process was observed in the positive ion spectra of these two compounds. However,there was no evidence for the loss of HCN from the $[(M\text{-}OH^{\bullet})\text{-}CO]^-$ ions in the negative ion spectra. For these two compounds,the primary fragmentation processes must have involved the formation of intermediate ions containing the HONO group,as metastable ion evidence was obtained for the direct loss of HONO from the molecular ions. The proposed process is illustrated for 1-nitro-2,3-dimethylnaphthalene in fig.4.1.14. Direct loss of HONO from the molecular ion was also observed for 1,5-dinitro-2,3-dimethylnaphthalene and 1,5,7-trinitro-2,3-dimethylnaphthalene. However,for these compounds,and also for 1,4-dinitro-2,3-dimethylnaphthalene, there was definite metastable ion evidence for the formation of $[M\text{-}HONO]^-$ ions via elimination of OH$^{\bullet}$ from the $[M\text{-}NO^{\bullet}]^-$

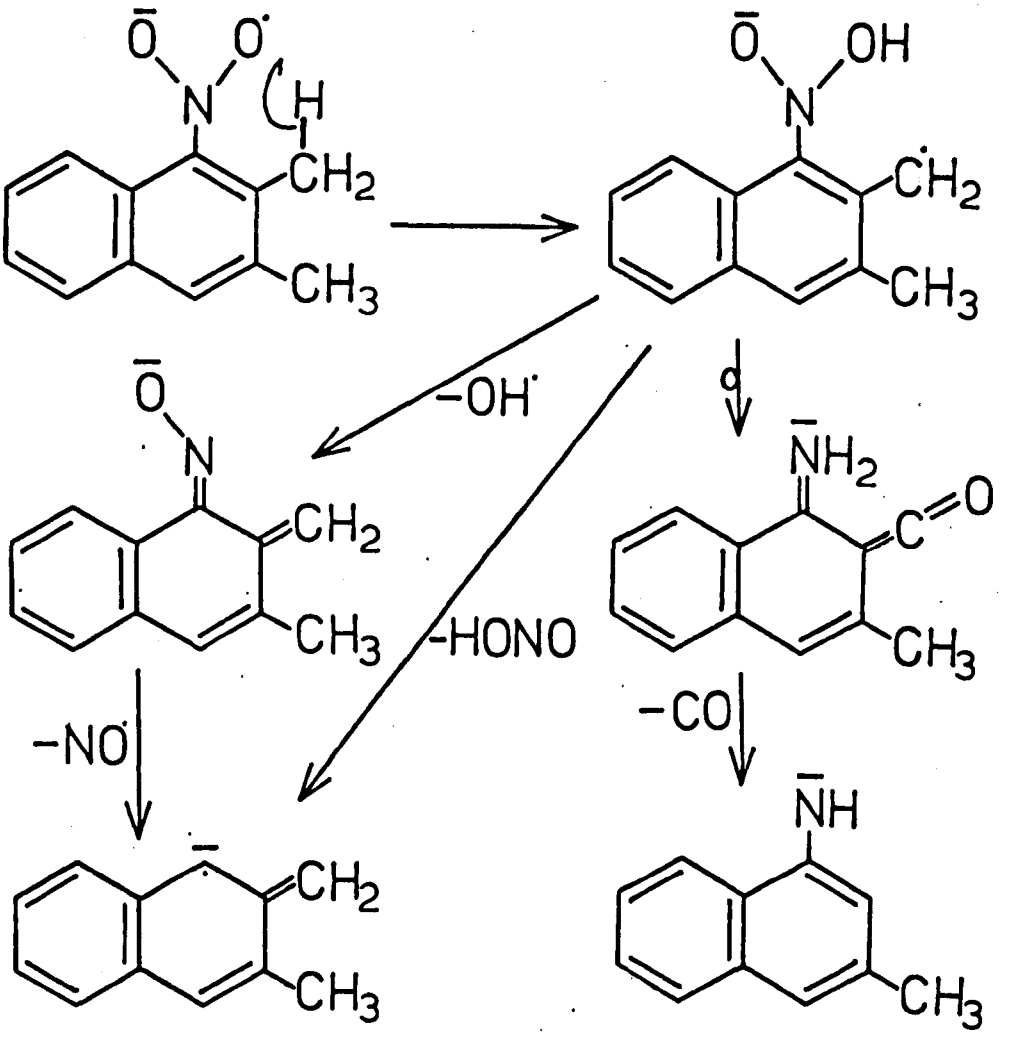


Fig.4.1.14

ions. This suggests that for these three compounds, the $[M-HONO]^-$ ions could exist in two different forms, one derived by loss of HONO as above, and the other derived by the elimination of NO· from one nitro group followed by elimination of OH· via an interaction between another nitro group and a methyl group.

(d) Formation of the Nitrite Ion

Intense peaks corresponding to the nitrite ion, NO_2^-, were observed in the negative ion spectra of all the nitro-2,3-dimethylnaphthalenes. There appeared to be no simple correlation between the structure of the parent ions and the percentage total ion current carried by the nitrite ion. In no case was any metastable ion observed for the

formation of the nitrite ion,which suggests that the process involved must be exceedingly rapid,e.g.dissociative electron capture.

4.1.5 Negative Ion Mass Spectra of Nitro-1,5-Dimethylnaphthalenes

The negative ion mass spectra of four nitro-1,5-dimethylnaphthalenes are shown in figs.4.1.31-34,and the proposed major fragmentation pathways for each compound are given in figs.4.1.63-66. The more important primary and secondary fragmentations are listed in table 4.1.4, together with the percentage total ion current carried by each ion.

The fragmentation patterns of the nitro-1,5-dimethylnaphthalenes were found to be more complex than those of the nitro-2,3-dimethylnaphthalenes,as in addition to the primary elimination of hydroxyl radical,nitrous acid, nitric oxide and nitrogen dioxide,the primary elimination of methyl radical was also observed. These are discussed below.

(a) Loss of Nitric Oxide

As was found for the nitro-2,3-dimethylnaphthalenes, the loss of NO· was a major process in the primary fragmentation of the negative molecular ions of the nitro-1,5-dimethylnaphthalenes. The percentage total ion current carried by the $[M-NO\cdot]^-$ ions of the four compounds was least for 2,4,6,8-tetranitro-1,5-dimethylnaphthalene where there was considerable competition from the primary losses of OH· and NO_2·. It is interesting that for the two structurally similar compounds 4-nitro-1,5-dimethylnaphthalene and 4,8-dinitro-1,5-dimethylnaphthalene,the Σi value for the $[M-NO\cdot]^-$ ion of the former compound (3.2%) is much lower than that for the latter compound (14.7%). This difference

Table 4.1.4 Percentage total ion currents for primary and secondary fragmentations in the negative ion mass spectra of nitro-1,5-dimethylnaphthalenes.

Compound	$M^{-\cdot}$	$[M-CH_3^{\cdot}]^-$	$[M-O]^{-\cdot}$	$[M-OH]^-$	$[M-NO^{\cdot}]^-$	$[M-NO_2^{\cdot}]^-$	$[M-HONO]^{-\cdot}$	$[M-OH^{\cdot}-CO]^{-}$ [d]	$[M-NO^{\cdot}-NO]^{-\cdot}$	$[M-NO_2^{\cdot}-NO]^{-\cdot}$	$[M-NO^{\cdot}-OH_2]^-$	NO_2^-
4-nitro-1,5-DMN	18.3	0.2	0.6	0.3	3.2*	0.8	0.1	0.4	-	-	0.1	70.0
4,8-dinitro-1,5-DMN	30.9	2.7*	0.1	0.2*	14.7*	0.6*	1.0*[a]	0.3*[e]	1.0*	0.2*[f]	2.0*	32.3
2,4,8-trinitro-1,5-DMN	3.9	6.0*	0.7	3.0*	9.6*	3.6*	1.6*[abc]	2.5*[e]	0.9*	0.4	1.7*	21.0
2,4,6,8-tetranitro-1,5-DMN	1.5	1.9*	0.4	2.6*	2.6	2.1*	0.7*[abc]	1.7*[e]	0.4	0.3	0.4	15.0

* indicates metastable ion peak for that fragmentation.

(a) Metastable ion corresponding to $[M-HONO]^{-\cdot}$. *(b)* Corresponding to $[(M-NO^{\cdot})-OH^{\cdot}]^{-\cdot}$. *(c)* Corresponding to $[(M-OH^{\cdot})-NO^{\cdot}]^{-\cdot}$. *(d)* *M/e* values of $[(M-OH^{\cdot})-CO]^-$ are also numerically equal to $[(M-CH_3^{\cdot})-NO^{\cdot}]^{-\cdot}$. *(e)* Metastable ion corresponding to $[(M-CH_3^{\cdot})-NO^{\cdot}]^{-\cdot}$. *(f)* Corresponding to $[(M-NO^{\cdot})-NO_2^{\cdot}]^{-\cdot}$.

is even more marked when one considers that the molecular ion of the latter compound is much more stable than that of the former compound. A possible reason for the low Σi value for the $[M-NO^{\cdot}]^{-}$ ion of 4-nitro-1,5-dimethylnaphthalene is that the phenoxide ion formed as a result of the NO· loss is unstable on account of the electron donating effect of the methyl group at the position *para* to the O^{-} entity :-

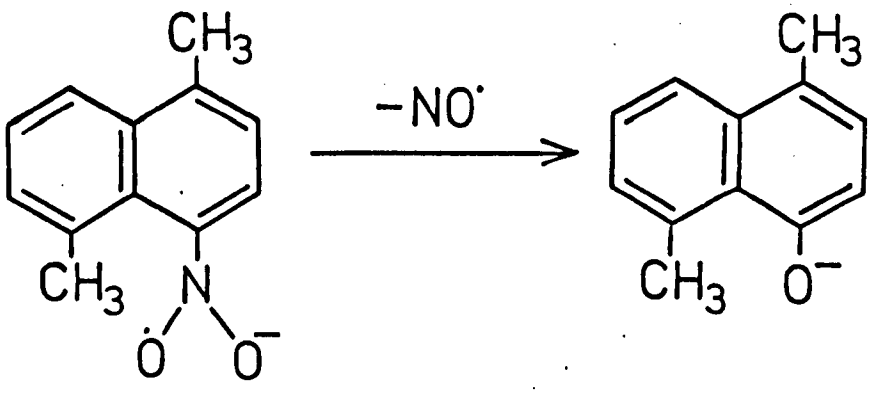


Fig.4.1.15

In the case of 4,8-dinitro-1,5-dimethylnaphthalene there will be a nitro group *peri* to the methyl group which is *para* to the O^{-} entity,and steric interaction between the two groups may reduce the electron donating effect of the methyl group. Hence the $[M-NO^{\cdot}]^{-}$ ion for 4,8-dinitro-1,5-dimethylnaphthalene will be the more stable.

For the polynitro-1,5-dimethylnaphthalenes,the primary loss of NO· was followed by the further loss of NO·, a similar fragmentation pattern to that observed in the negative ion spectrum of 2,4,6-trinitrotoluene[232]. For those compounds containing nitro groups substituted *ortho* to methyl groups,there was metastable ion evidence for the loss of OH· from the $[M-NO^{\cdot}]^{-}$ ion,i.e.loss of nitrous acid

from the molecular ion. However,the two fragmentations involved in this process probably took place from different parts of the molecule,*cf* sec.4.1.3(c).

For 4,8-dinitro-1,5-dimethylnaphthalene and 2,4,8-trinitro-1,5-dimethylnaphthalene,loss of water from the $[M-NO^{\cdot}]^{-}$ ion was observed,and confirmed by metastable ion evidence. Loss of water as part of a fragmentation process is unusual for nitroaromatic compounds,and where it is observed there is usually a specific driving force favouring the loss[242,243]. In the cases observed here,the loss of water probably occurred as a synchronous loss of $OH^{\cdot}$ and $H^{\cdot}$ rather than as a complete H_2O fragment,the driving force for the process possibly being the achievement of a stable quinoidal structure. This process is illustrated for 4,8-dinitro-1,5-dimethylnaphthalene in fig.4.1.16.

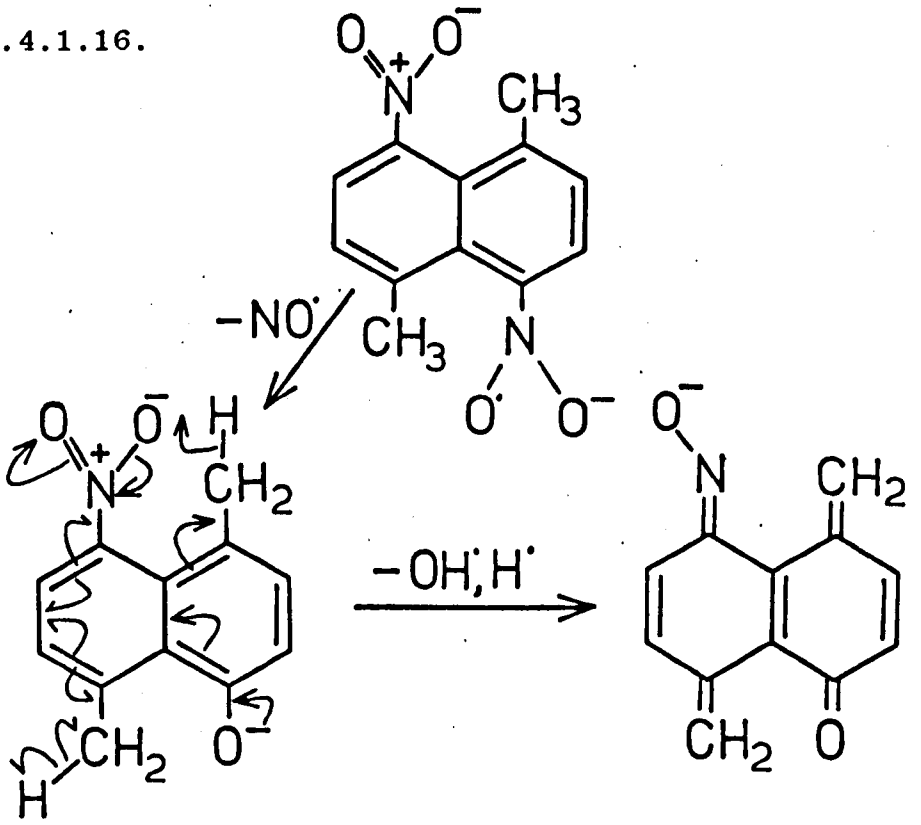


Fig.4.1.16

(b) Loss of Hydroxyl Radical and Nitrous Acid

Loss of OH· from the molecular ion was observed for all the nitro-1,5-dimethylnaphthalenes. As each of the compounds contain nitro groups which can interact with methyl groups, the process by which OH· is eliminated is probably similar to the process postulated for the elimination of OH· from the negative molecular ion of 1-nitro-2,3-dimethylnaphthalene (sec.4.1.4c). The elimination of OH· was more facile for those compounds containing nitro groups substituted *ortho* to methyl groups than for those compounds in which nitro groups are substituted on adjacent *peri*-positions to methyl groups.

For 4-nitro-1,5-dimethylnaphthalene, peaks were observed corresponding to the sequential loss of OH· and CO, although no metastable ion evidence could be obtained owing to the general weakness of the spectrum. For the polynitro-1,5-dimethylnaphthalenes, the primary loss of OH· was followed by loss of NO·, i.e. loss of nitrous acid. This process probably involved the intermediate formation of an ONOH group, as metastable ion evidence was obtained for the loss of HONO as a complete fragment. The sequential loss of two hydroxyl radicals from the molecular ion, which was observed in the positive ion spectra of the polynitro-1,5-dimethylnaphthalenes, was not observed in the negative ion spectra of these compounds.

(c) Loss of Nitrogen Dioxide

As in the case of the positive ion spectra, loss of $NO_2^{\cdot}$ was not the major fragmentation process in the negative ion spectra of any of the nitro-1,5-dimethyl-

naphthalenes. Loss of $NO_2^{\cdot}$ was however of much greater significance for 2,4,8-trinitro-1,5-dimethylnaphthalene and for 2,4,6,8-trinitro-1,5-dimethylnaphthalene than for 4-nitro-1,5-dimethylnaphthalene and 4,8-dinitro-1,5-dimethylnaphthalene,a similar phenomenon to that observed for the primary loss of $OH^{\cdot}$.

(d) Loss of Methyl Radical

The loss of methyl radical from the molecular ion was observed only in the negative ion spectra of the nitro-1,5-dimethylnaphthalenes. It was not observed in the negative ion spectra of the nitro-2,3-dimethylnaphthalenes. A possible explanation is that the spin densities at nuclear sites substituted by methyl groups in the radical anions of nitro-1,5-dimethylnaphthalene are higher than in the radical anions of nitro-2,3-dimethylnaphthalenes. For example,the H.M.O.spin density at the 1-position in the radical anion of 4-nitro-1,5-dimethylnaphthalene is 0.139, whereas the H.M.O.spin density at the 2-position in the radical anion of 1-nitro-2,3-dimethylnaphthalene is only 0.040. Thus the greater repulsion between the methyl group and the naphthalene nucleus in the case of the nitro-1,5-dimethylnaphthalenes probably facilitates the breaking of the $C-CH_3$ bond for these compounds.

The primary loss of $CH_3^{\cdot}$ was of less significance for 4-nitro-1,5-dimethylnaphthalene than for 4,8-dinitro-1,5-dimethylnaphthalene and 2,4,8-trinitro-1,5-dimethylnaphthalene. As in the latter two compounds all four *peri* positions are occupied,a possible driving force for the elimination of $CH_3^{\cdot}$ could be the relief of the strain on

the naphthalene skeleton caused by the steric crowding at the *peri* sites.

For the polynitro-1,5-dimethylnaphthalenes, there was metastable ion evidence for the loss of NO· from the $[M-CH_3]^-$ ion. This process was possibly favoured by the formation of a semiquinone-type ion which could be stabilised by resonance interaction. This process is illustrated for 4,8-dinitro-1,5-dimethylnaphthalene in fig.4.1.17.

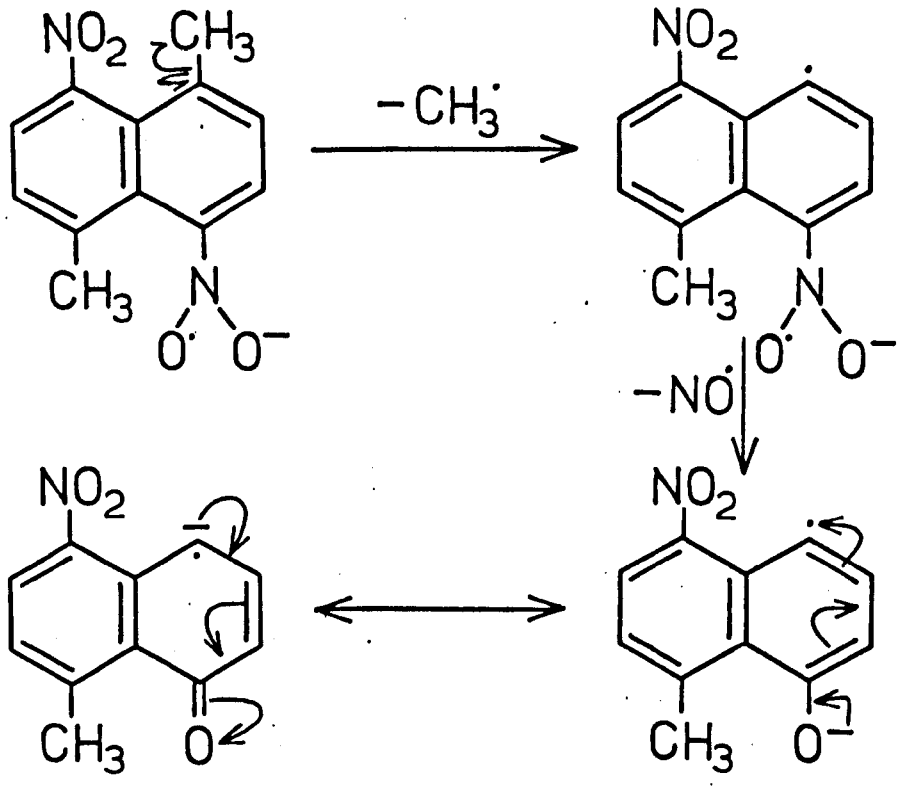


Fig.4.1.17

(e) Formation of the Nitrite Ion

As in the case of the negative ion spectra of the nitro-2,3-dimethylnaphthalenes, the nitrite ion gave rise to an intense peak in the spectra of all the nitro-1,5-dimethylnaphthalenes. The only correlation between

the structure of the parent ion and the percentage total ion current carried by the nitrite ion was that the latter decreased with increasing substitution of nitro groups, changing from 70.0% for 4-nitro-1,5-dimethylnaphthalene to 15.0% for 2,4,6,8-tetranitro-1,5-dimethylnaphthalene.

4.1.6 Comparison of the Positive and Negative Ion Mass Spectra

In comparing the two types of spectra, the first observation that must be made is that the molecular anions are more stable than the molecular cations (see tables 4.1.1, 4.1.2, 4.1.3, 4.1.4). This is consistent with the electron deficient character of nitroaromatic compounds, in that they can more easily stabilise a negative charge than a positive charge.

In general, the positive and negative mass spectra show marked similarities in the types of species lost from the molecular ion, e.g. $OH^{\cdot}$, $NO^{\cdot}$, $NO_2^{\cdot}$. Certain losses were favoured by the same structural factors in each type of spectrum. Thus for the positive and negative ion spectra of the polynitro-2,3-dimethylnaphthalenes, the loss of $NO_2^{\cdot}$ was favoured by the compounds having nitro groups substituted on adjacent *peri*-positions. However, the tendency to lose one type of species rather than another was different, e.g. the loss of $OH^{\cdot}$ from the molecular ion was more significant than the loss of $NO^{\cdot}$ in the positive ion spectra, but in the negative ion spectra the reverse situation was observed. In some cases the difference in the tendency to lose a particular species can be extreme. The loss of $CH_3^{\cdot}$ was observed as a prominent primary process in the negative ion spectra of the nitro-1,5-dimethylnaphthalenes, but not at all in the positive ion spectra of the same compounds. A possible explanation is that in the negative molecular ions of nitro-1,5-dimethylnaphthalenes, the naphthalene π-system contains eleven electrons, and therefore elimination

of a methyl radical would leave an "aromatic" system of ten π-electrons. This is illustrated for 4-nitro-1,5-dimethylnaphthalene in fig.4.1.18.

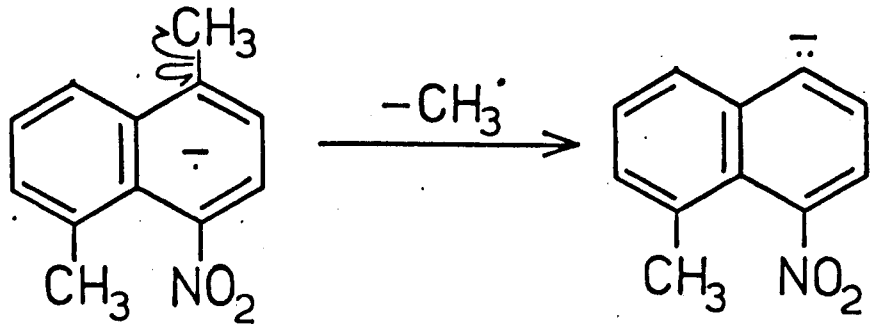
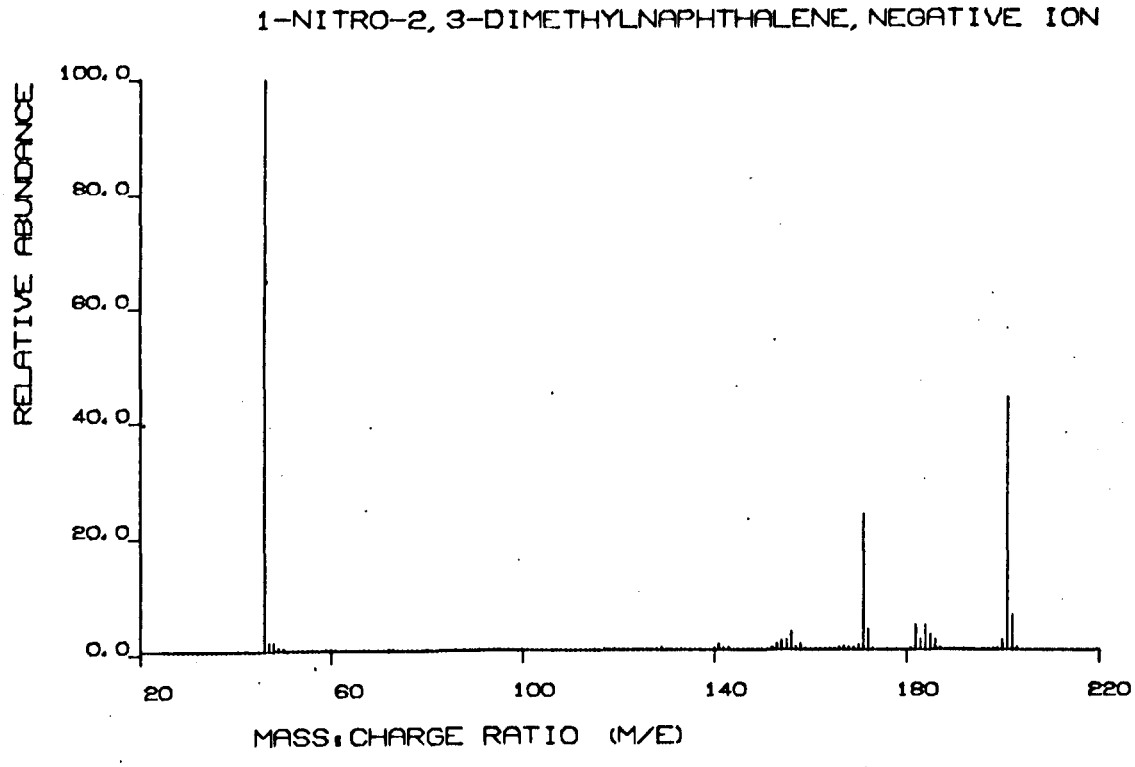


Fig.4.1.18

However, for the corresponding positive molecular ion, there would be nine electrons in the naphthalene π-system, and the loss of a methyl radical would leave a "non-aromatic" system of eight π-electrons. Thus elimination of a methyl radical is unlikely in the latter case.

4.1.7 Experimental Section

The positive ion mass spectra were recorded on an AEI MS9 mass spectrometer, using a source pressure of *ca* 10^{-6} *Torr* and temperature of *ca* 200°. The negative ion mass spectra were recorded on an AEI MS902 mass spectrometer, using a source pressure of *ca* 10^{-6} *Torr* and temperature of *ca* $150\text{-}220^{\circ}$. Assignment of the negative ion peaks was assisted by the use of an AEI "Massmaster" modified for use with negative ion mass spectra.


1-NITRO-2, 3-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
60
100
140
180
220
MASS:CHARGE RATIO (M/E)

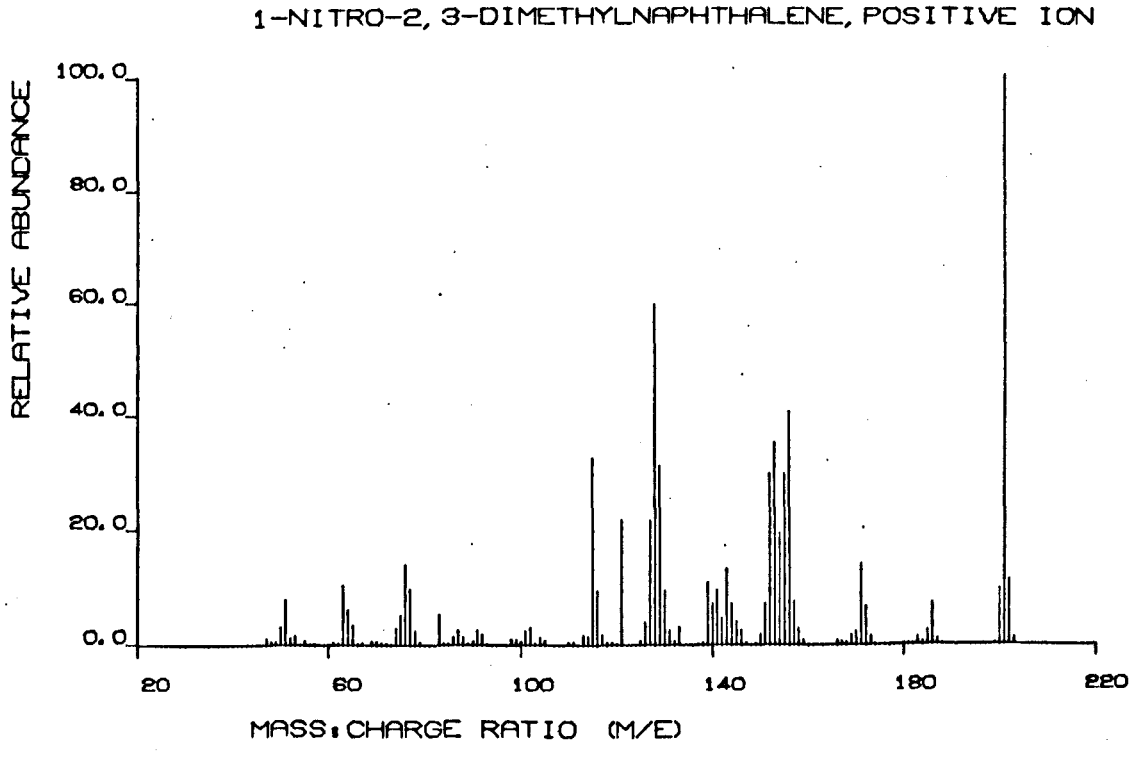
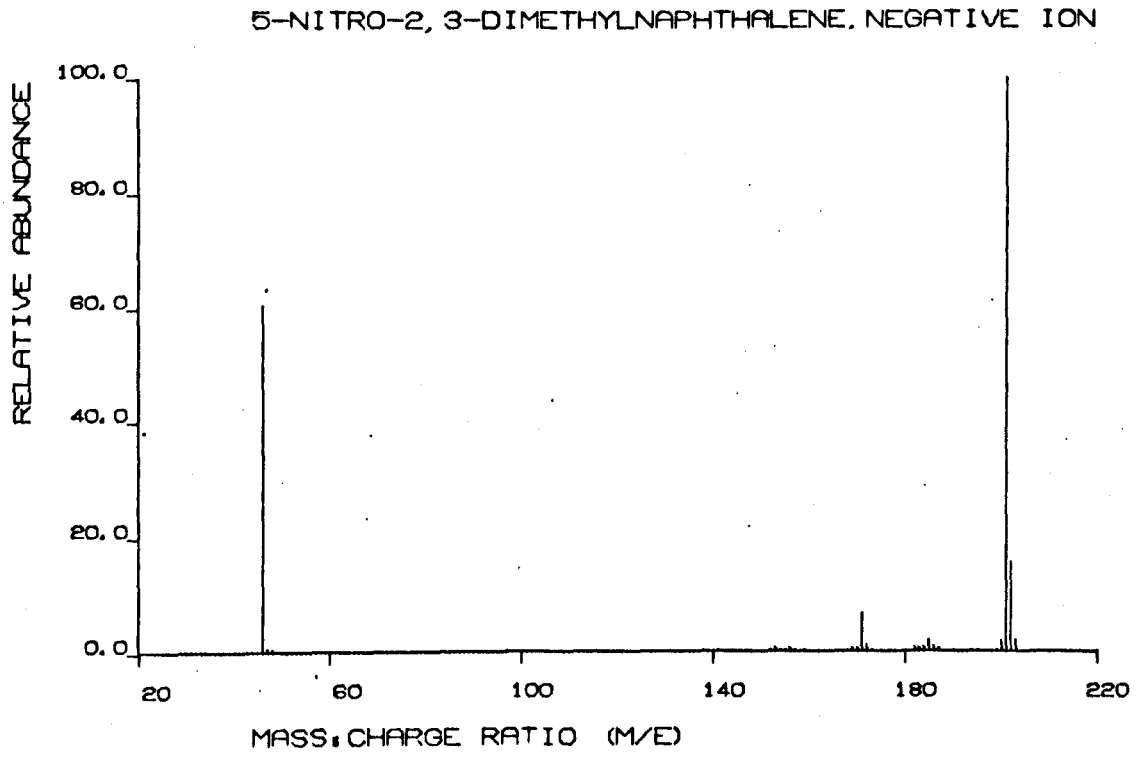

1-NITRO-2, 3-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
60
100
140
180
220
MASS:CHARGE RATIO (M/E)

Fig.4.1.19


5-NITRO-2, 3-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
60
100
140
180
220
MASS:CHARGE RATIO (M/E)

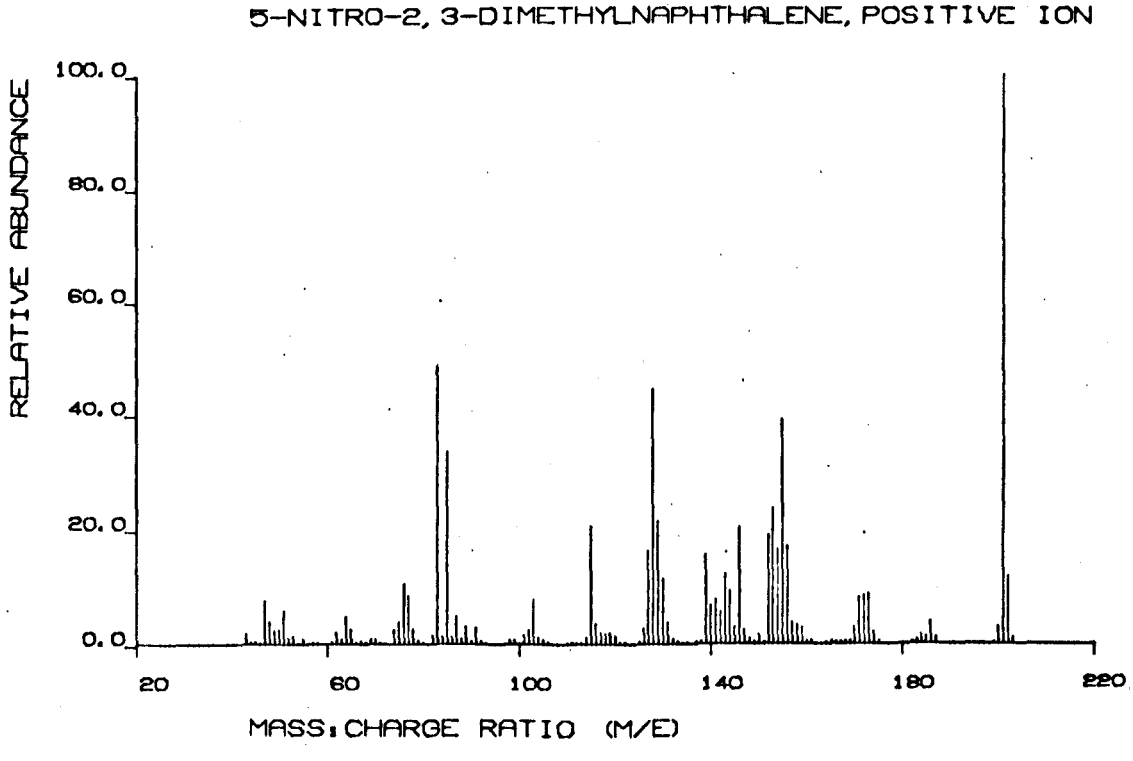
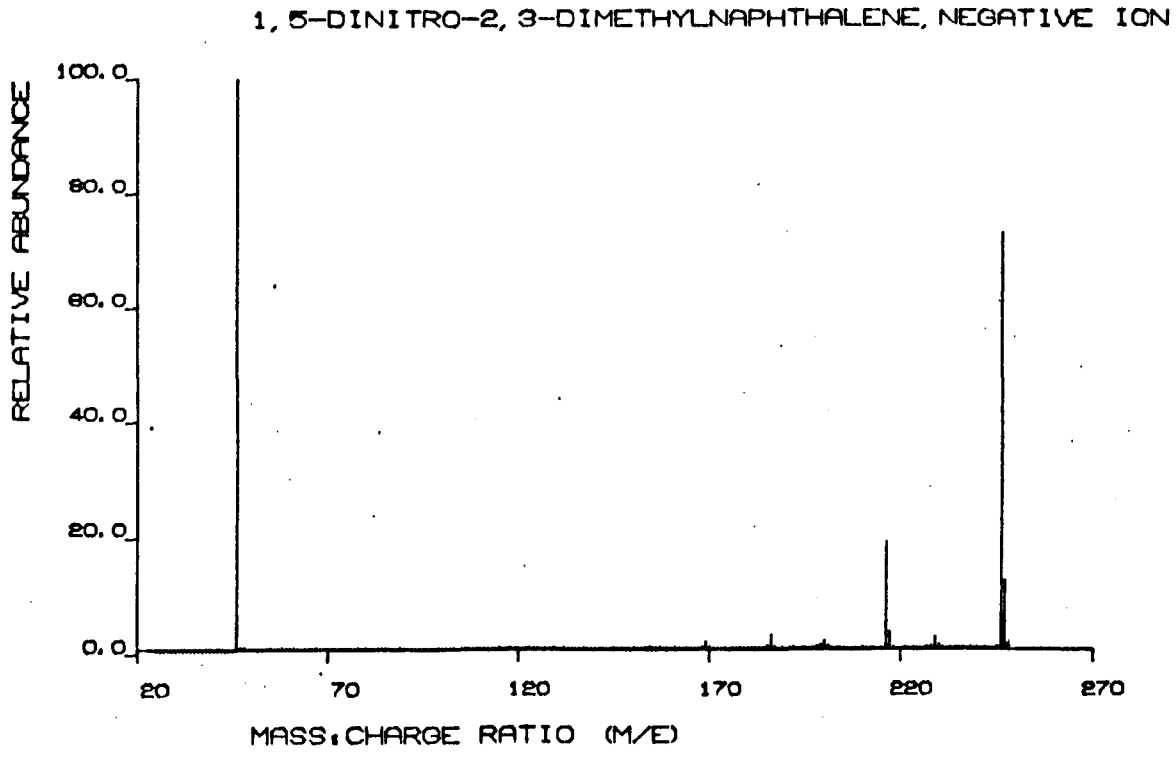

5-NITRO-2, 3-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
60
100
140
180
220
MASS:CHARGE RATIO (M/E)

Fig.4.1.20


1, 5-DINITRO-2, 3-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
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40.0
20.0
0.0
20
70
120
170
220
270
MASS:CHARGE RATIO (M/E)

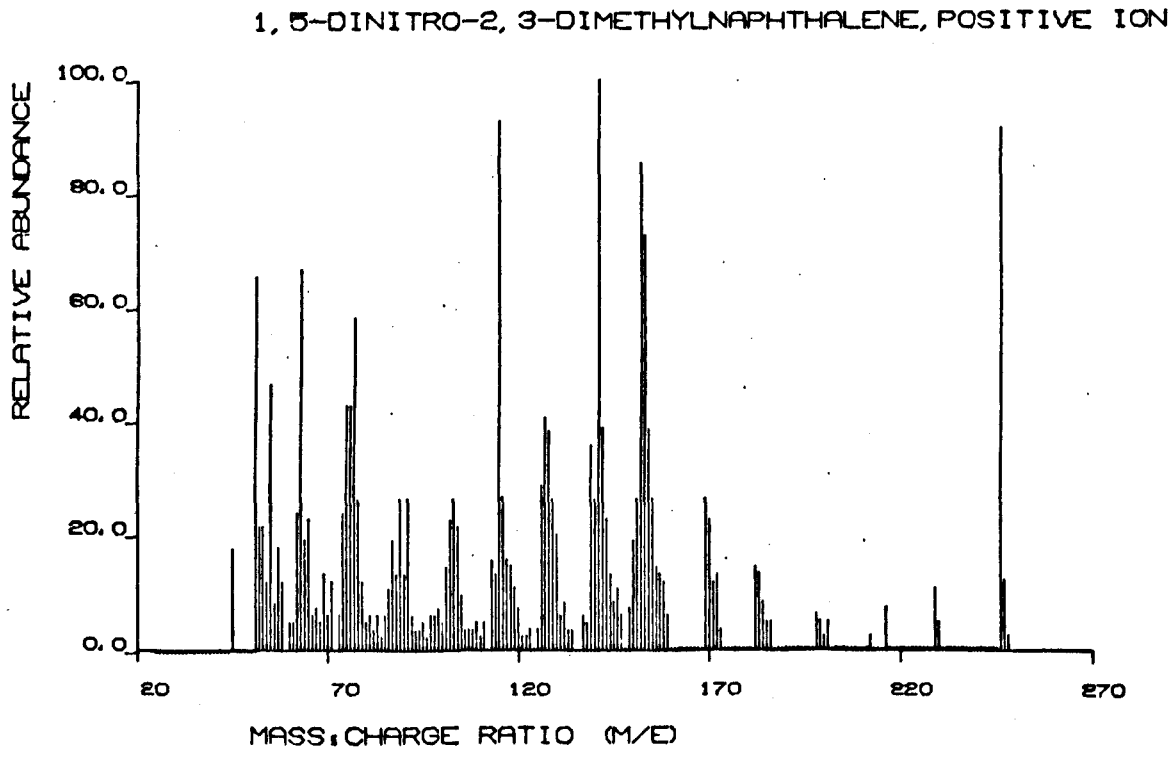
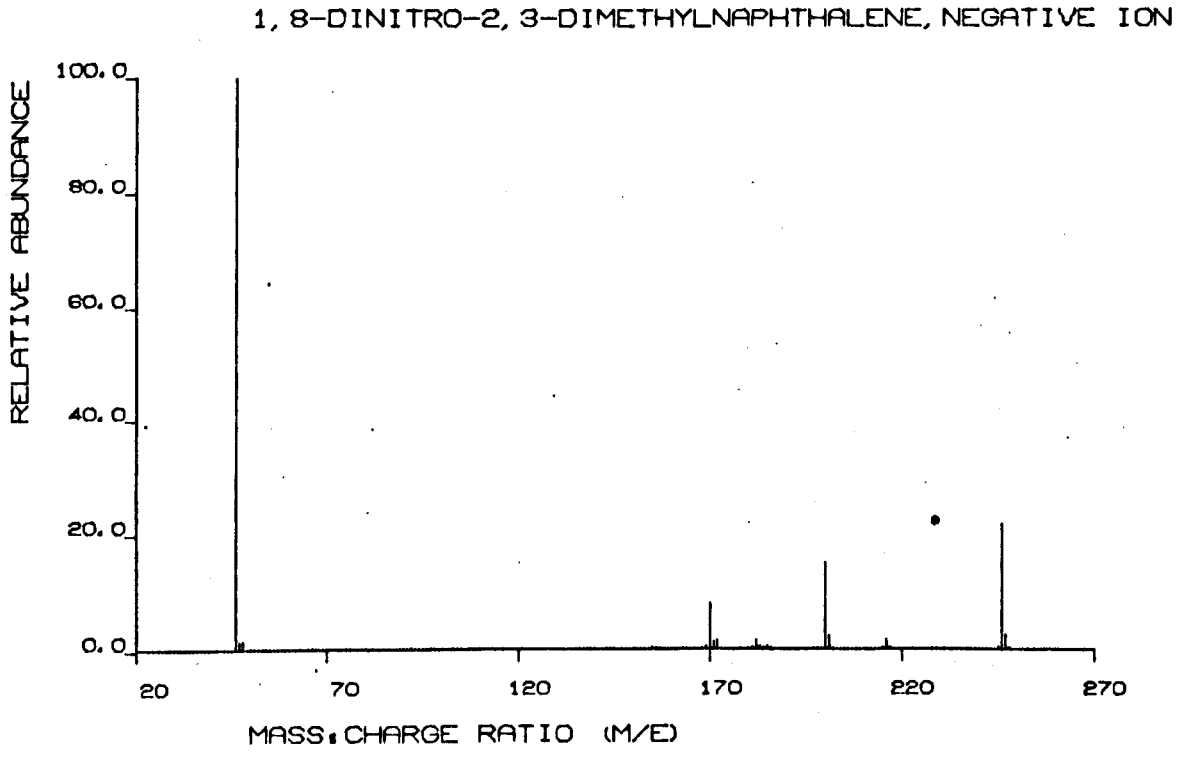

1, 5-DINITRO-2, 3-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
70
120
170
220
270
MASS:CHARGE RATIO (M/E)

Fig.4.1.21


1, 8-DINITRO-2, 3-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
70
120
170
220
270
MASS: CHARGE RATIO (M/E)

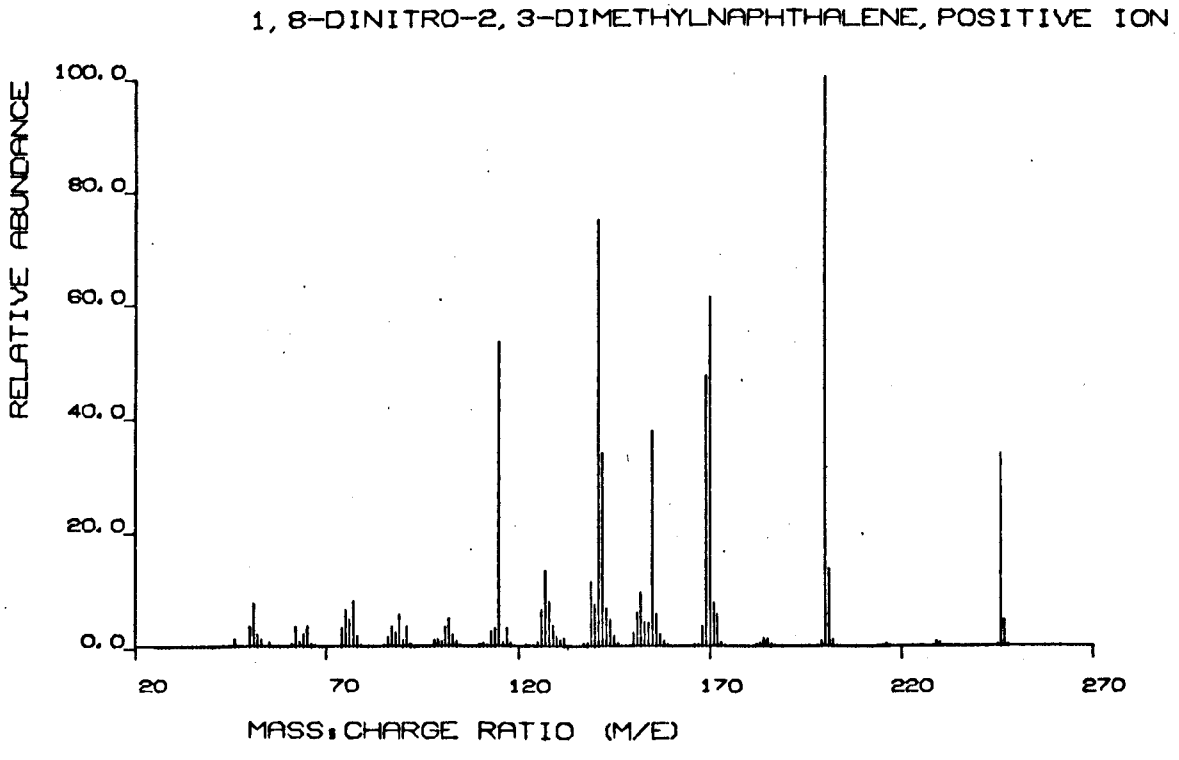
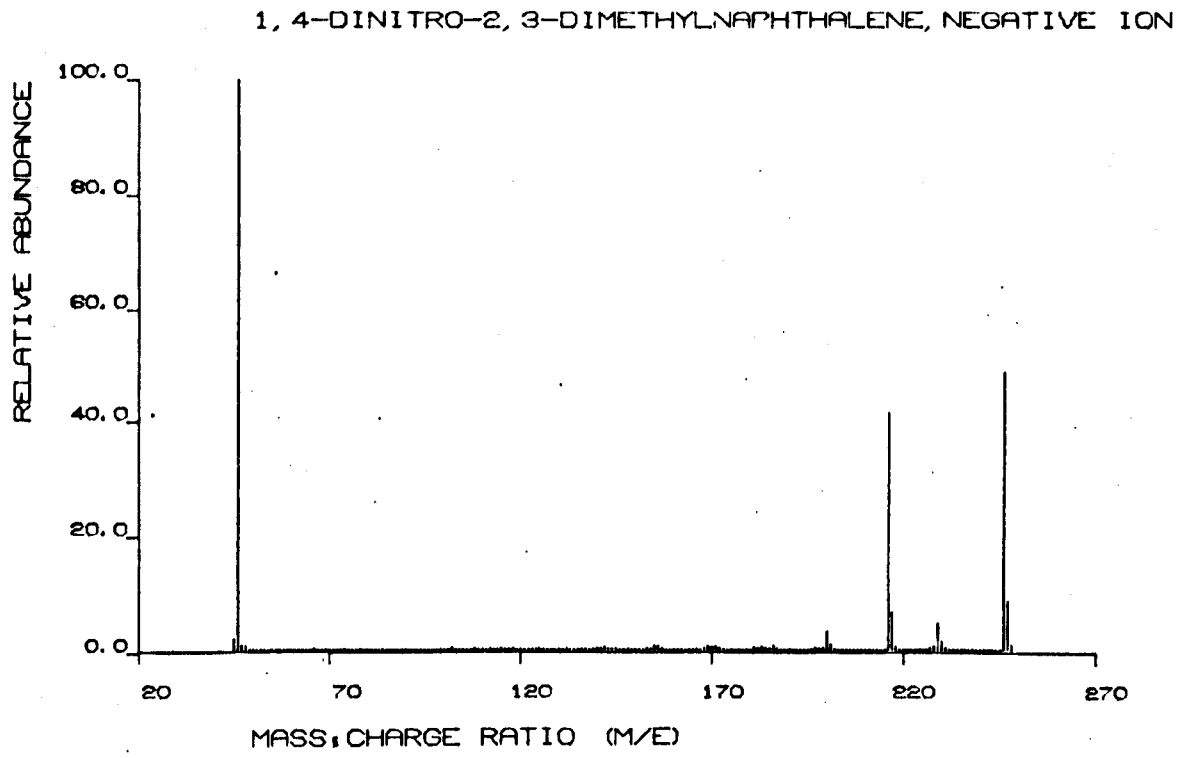

1, 8-DINITRO-2, 3-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
70
120
170
220
270
MASS: CHARGE RATIO (M/E)

Fig.4.1.22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RELATIVE ABUNDANCE
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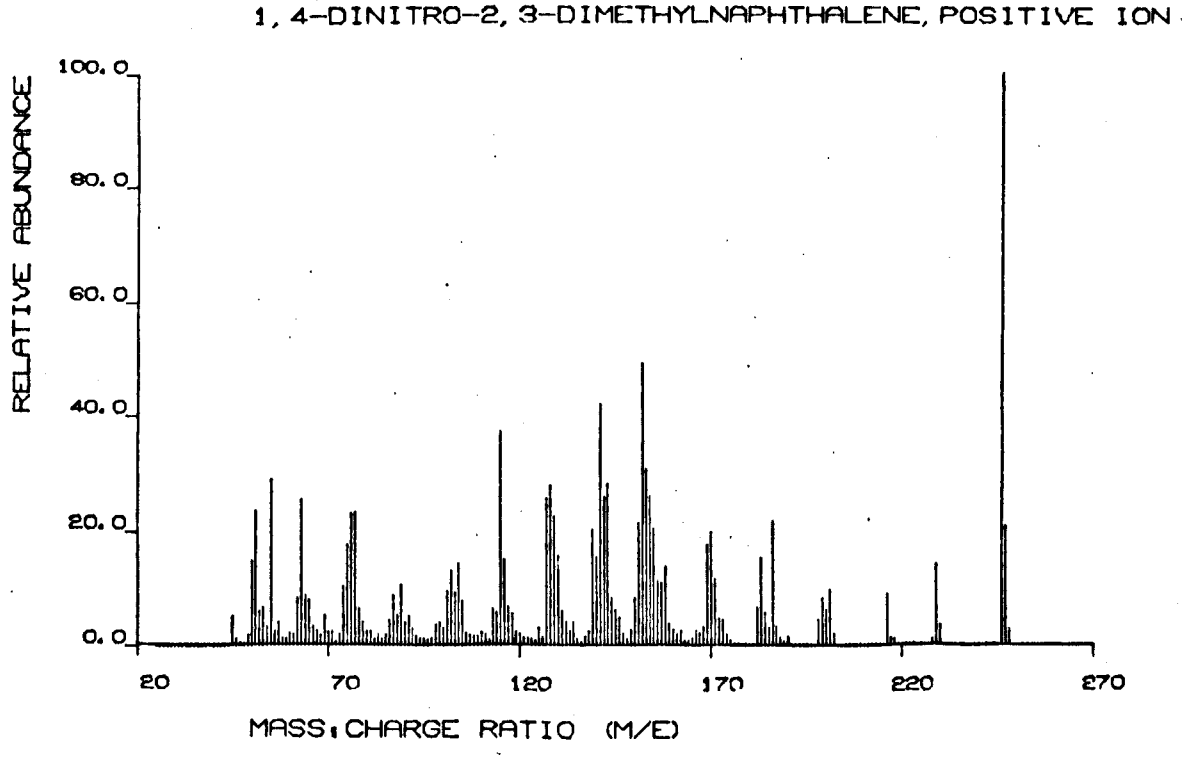
40.0
20.0
0.0
20
70
120
170
220
270
MASS:CHARGE RATIO (M/E)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RELATIVE ABUNDANCE
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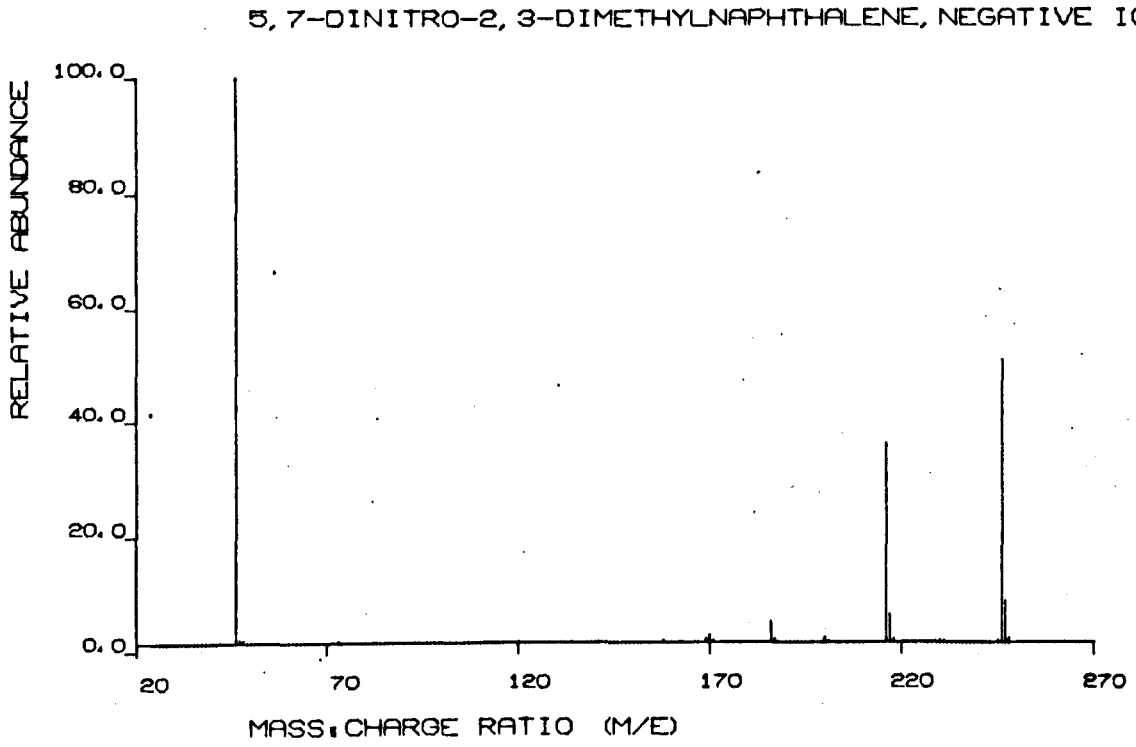
80.0
60.0
40.0
20.0
0.0
20
70
120
170
220
270
MASS:CHARGE RATIO (M/E)

Fig.4.1.23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RELATIVE ABUNDANCE
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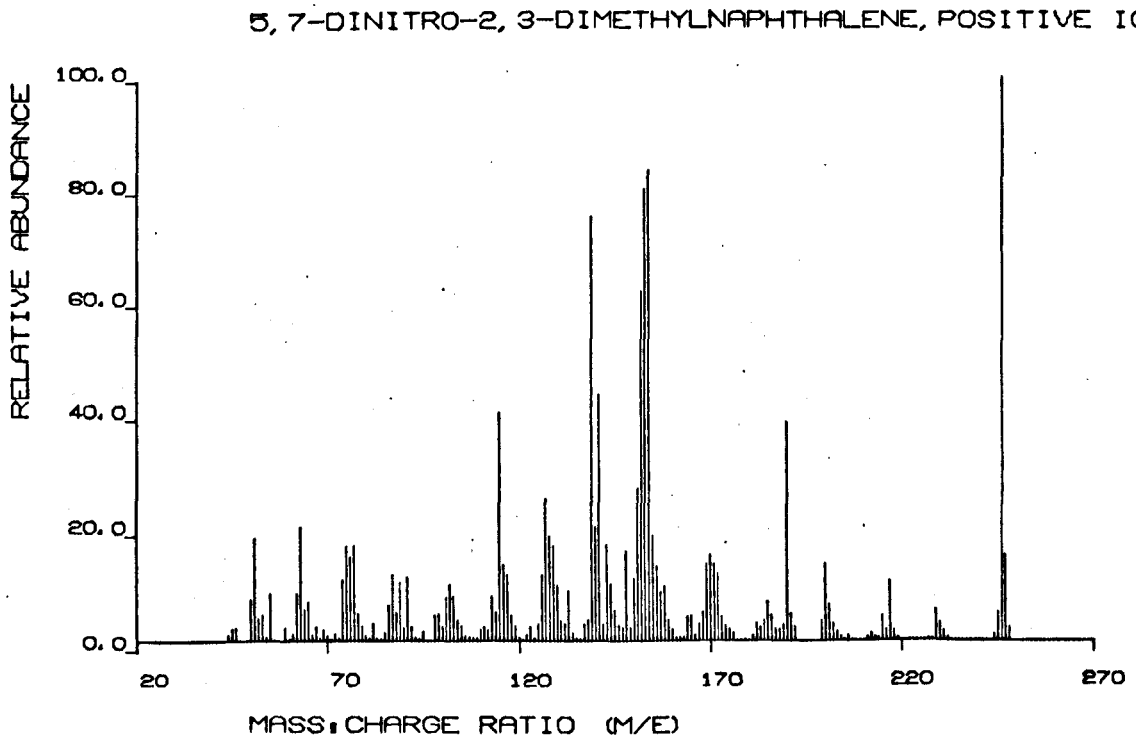
40.0
20.0
0.0
20
70
120
170
220
270
MASS:CHARGE RATIO (M/E)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RELATIVE ABUNDANCE
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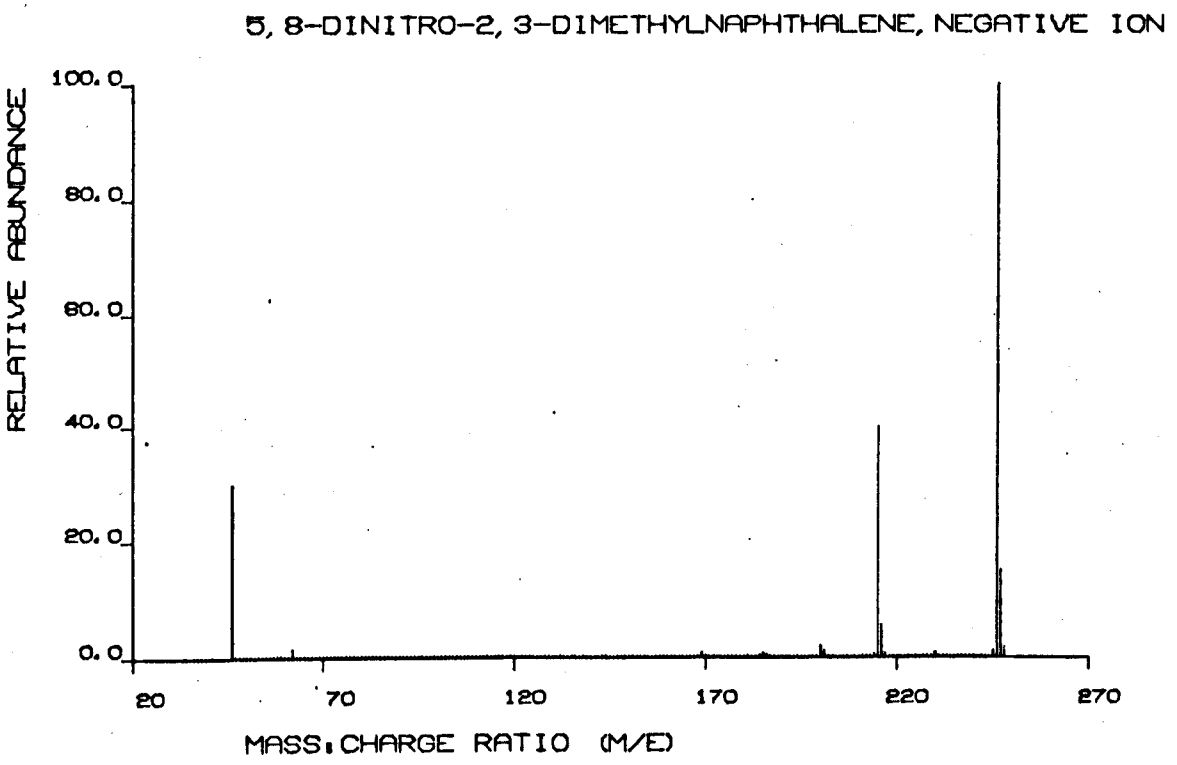
0.0
20
70
120
170
220
270
MASS:CHARGE RATIO (M/E)

Fig.4.1.24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RELATIVE ABUNDANCE
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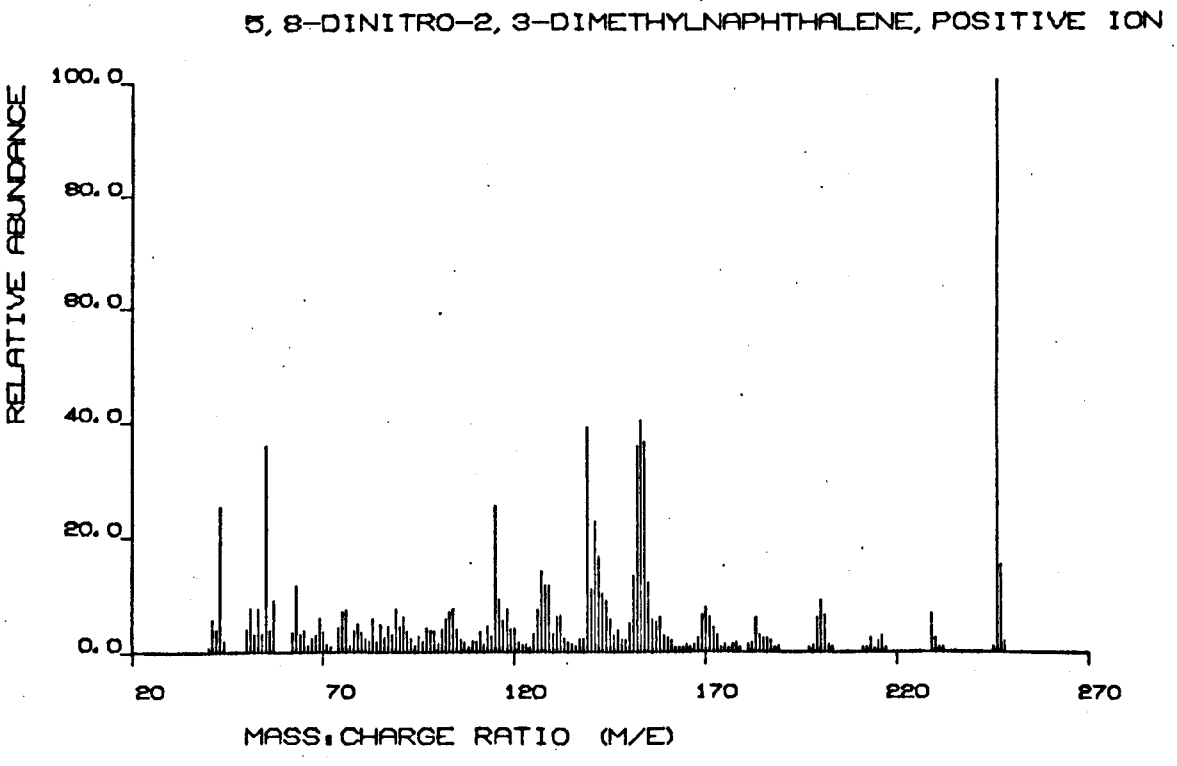
40.0
20.0
0.0
20
70
120
170
220
270
MASS:CHARGE RATIO (M/E)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RELATIVE ABUNDANCE
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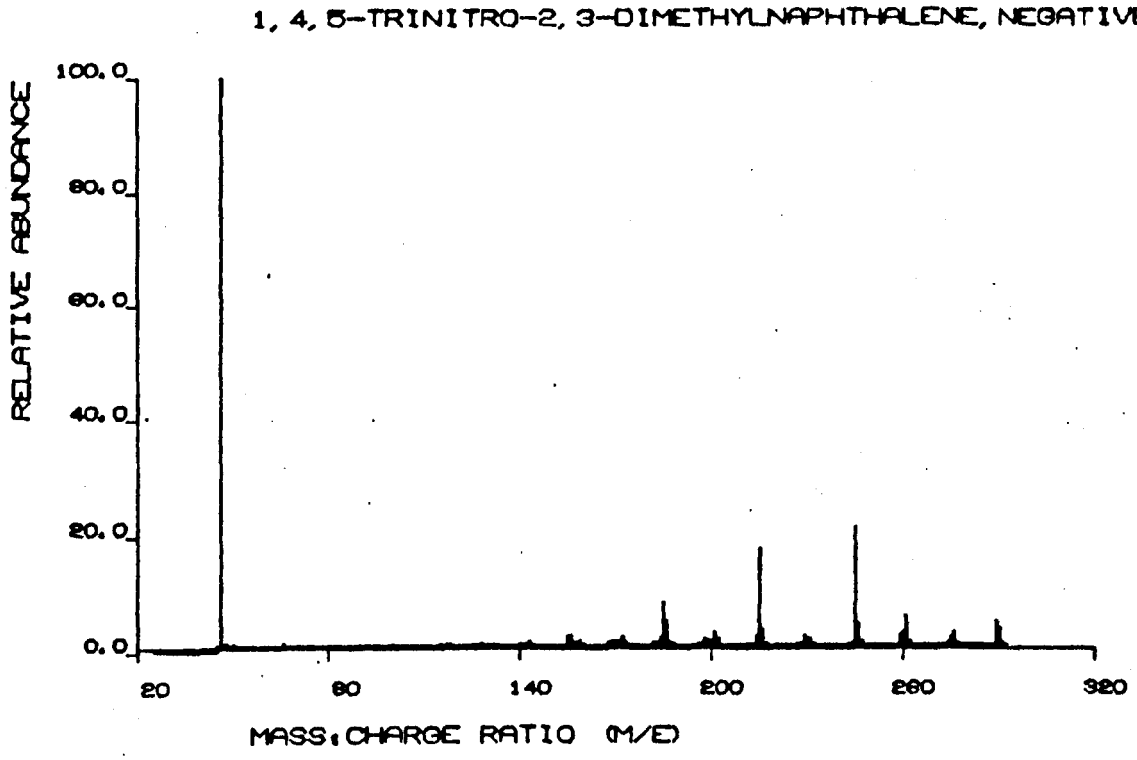
20
70
120
170
220
270
MASS:CHARGE RATIO (M/E)

Fig.4.1.25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RELATIVE ABUNDANCE
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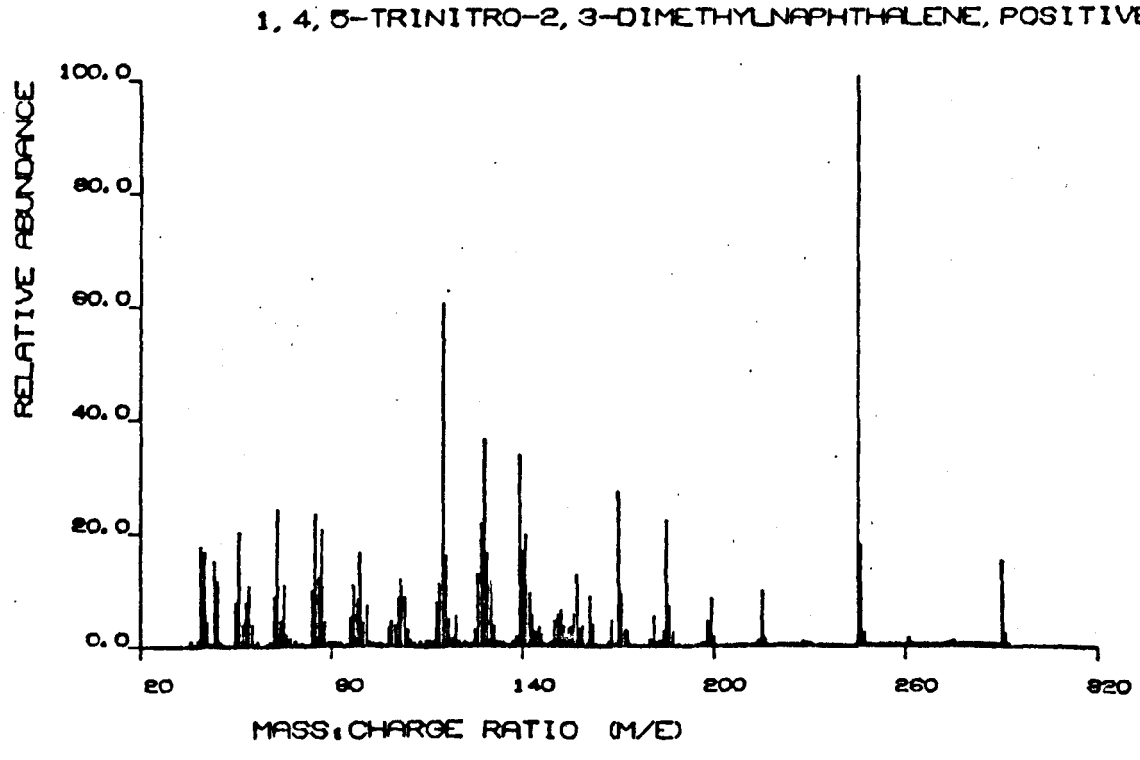
40.0
20.0
0.0
20
80
140
200
260
320
MASS-CHARGE RATIO (M/E)


1, 4, 5-TRINITRO-2, 3-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
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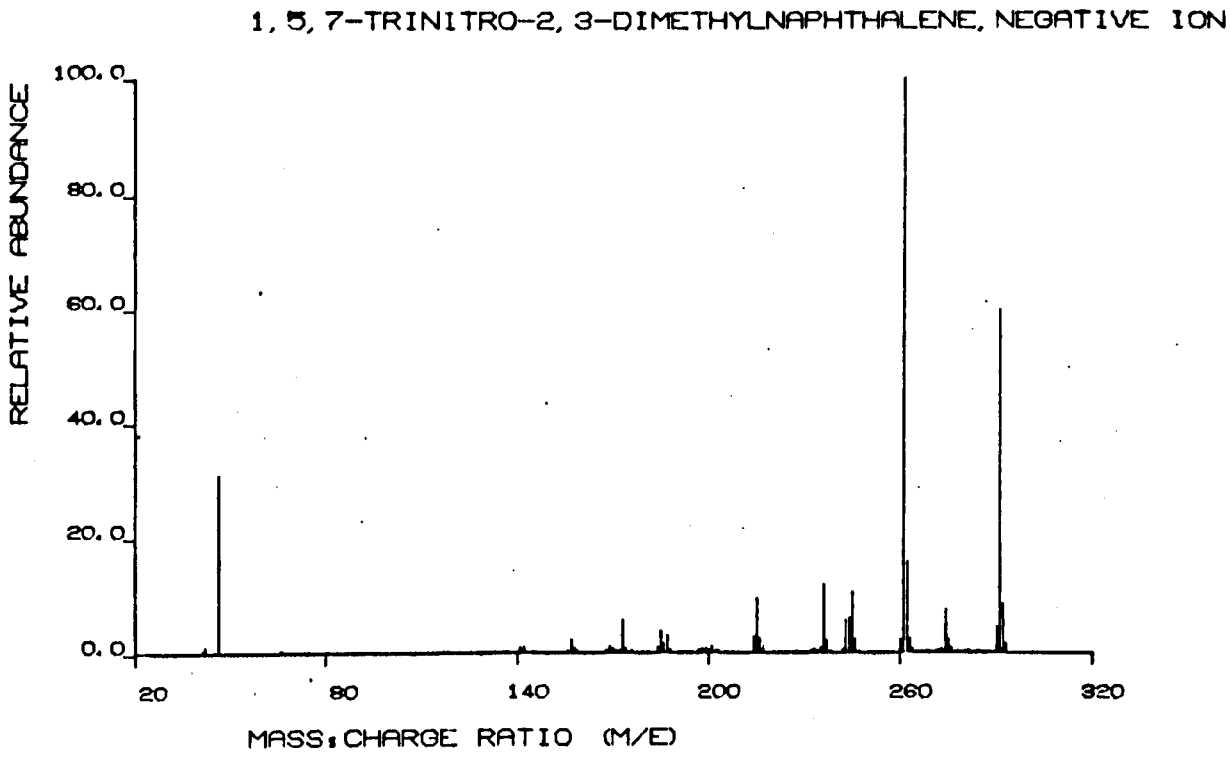
20.0
0.0
20
80
140
200
260
320
MASS-CHARGE RATIO (M/E)

Fig.4.1.26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RELATIVE ABUNDANCE
100.0
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60.0
40.0
20.0
0.0
20
80
140
200
260
320
MASS:CHARGE RATIO (M/E)

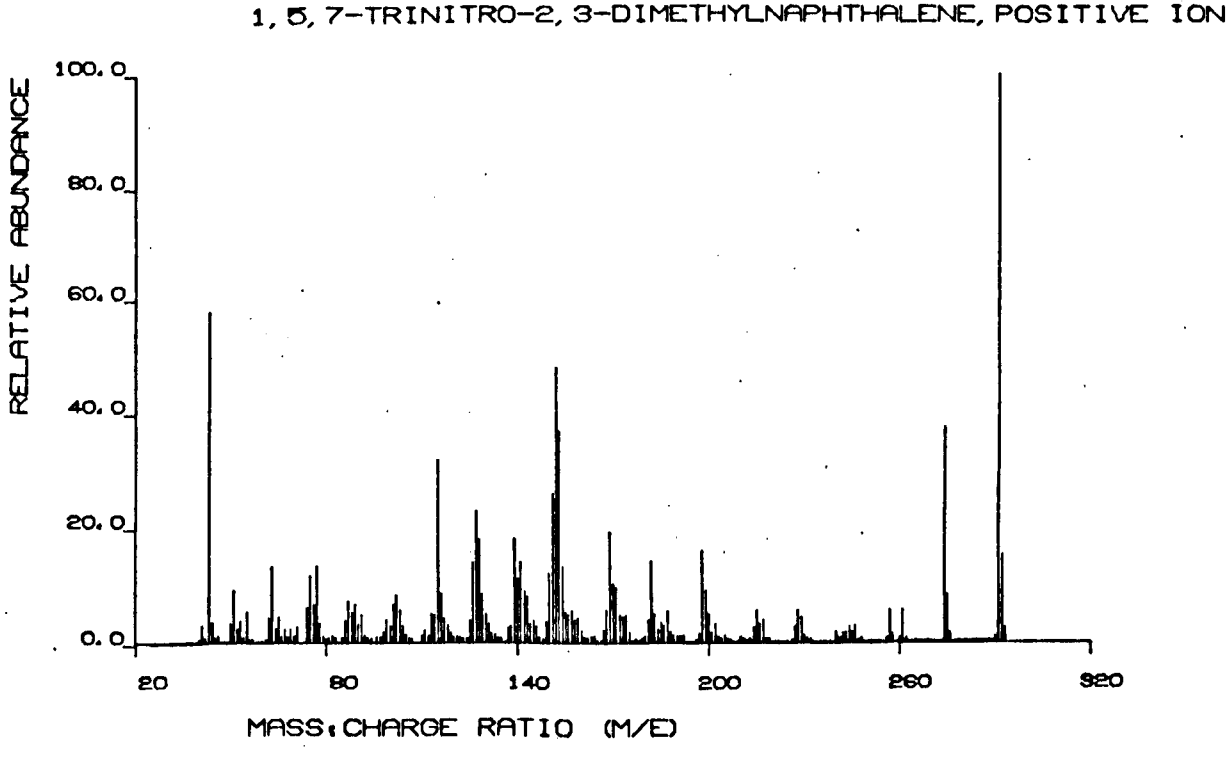
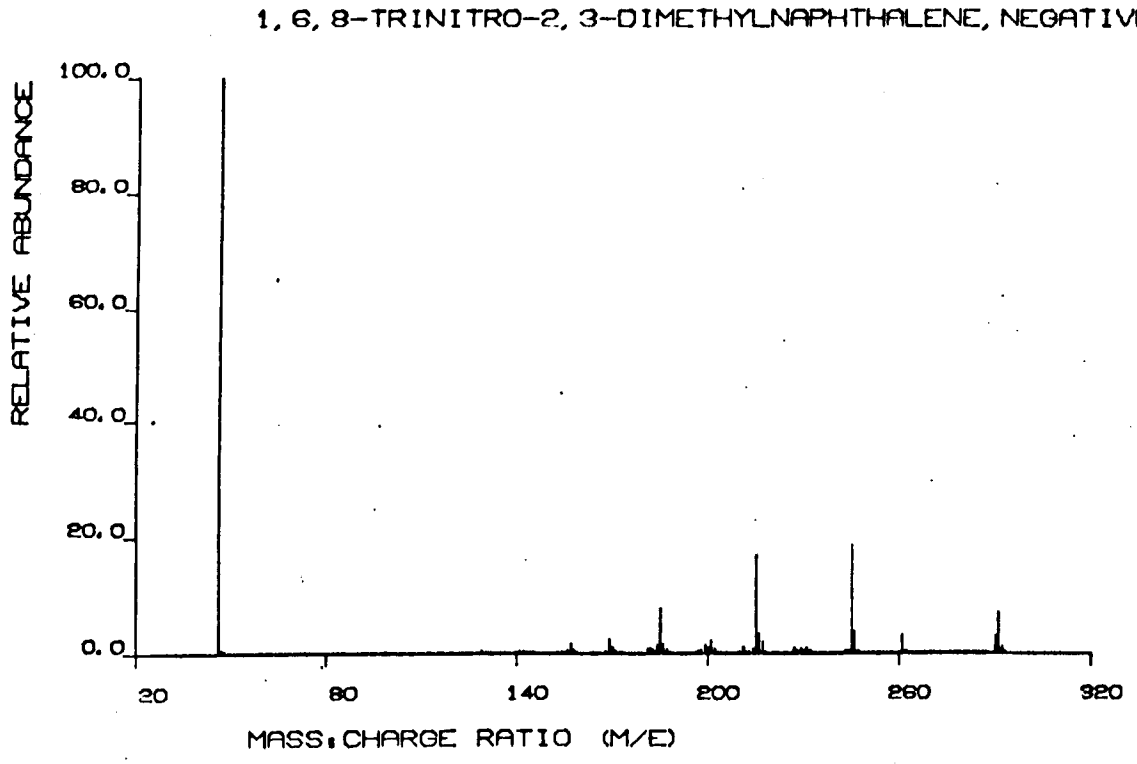

1, 5, 7-TRINITRO-2, 3-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
80
140
200
260
320
MASS:CHARGE RATIO (M/E)

Fig.4.1.27


1, 6, 8-TRINITRO-2, 3-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
80
140
200
260
320
MASS:CHARGE RATIO (M/E)

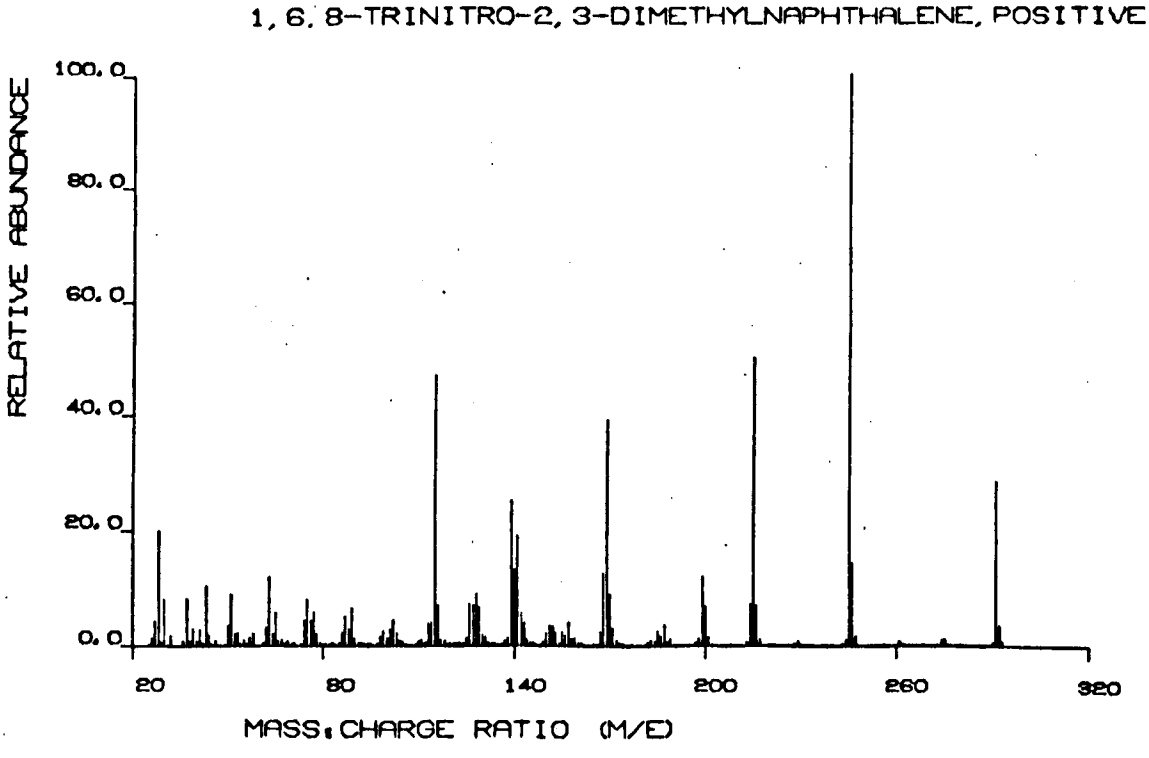
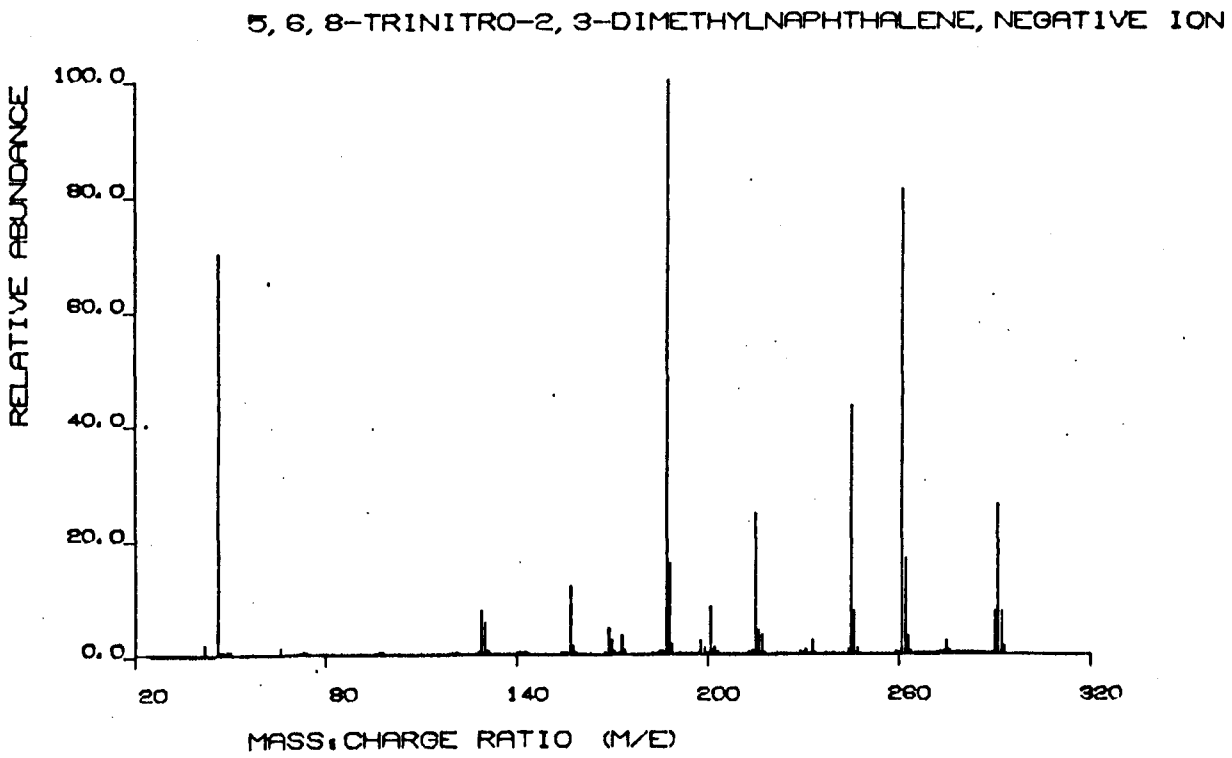

1, 6, 8-TRINITRO-2, 3-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
80
140
200
260
320
MASS:CHARGE RATIO (M/E)

Fig.4.1.28


5, 6, 8-TRINITRO-2, 3-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
80
140
200
260
320
MASS:CHARGE RATIO (M/E)

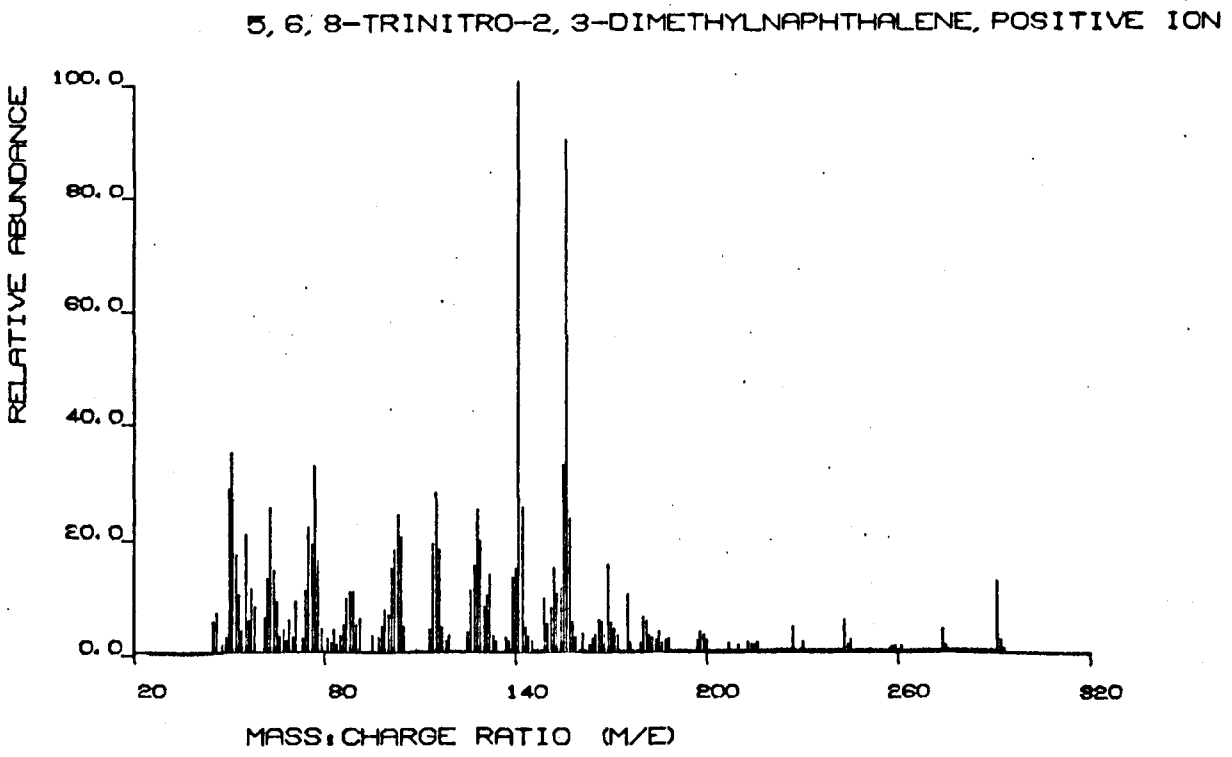
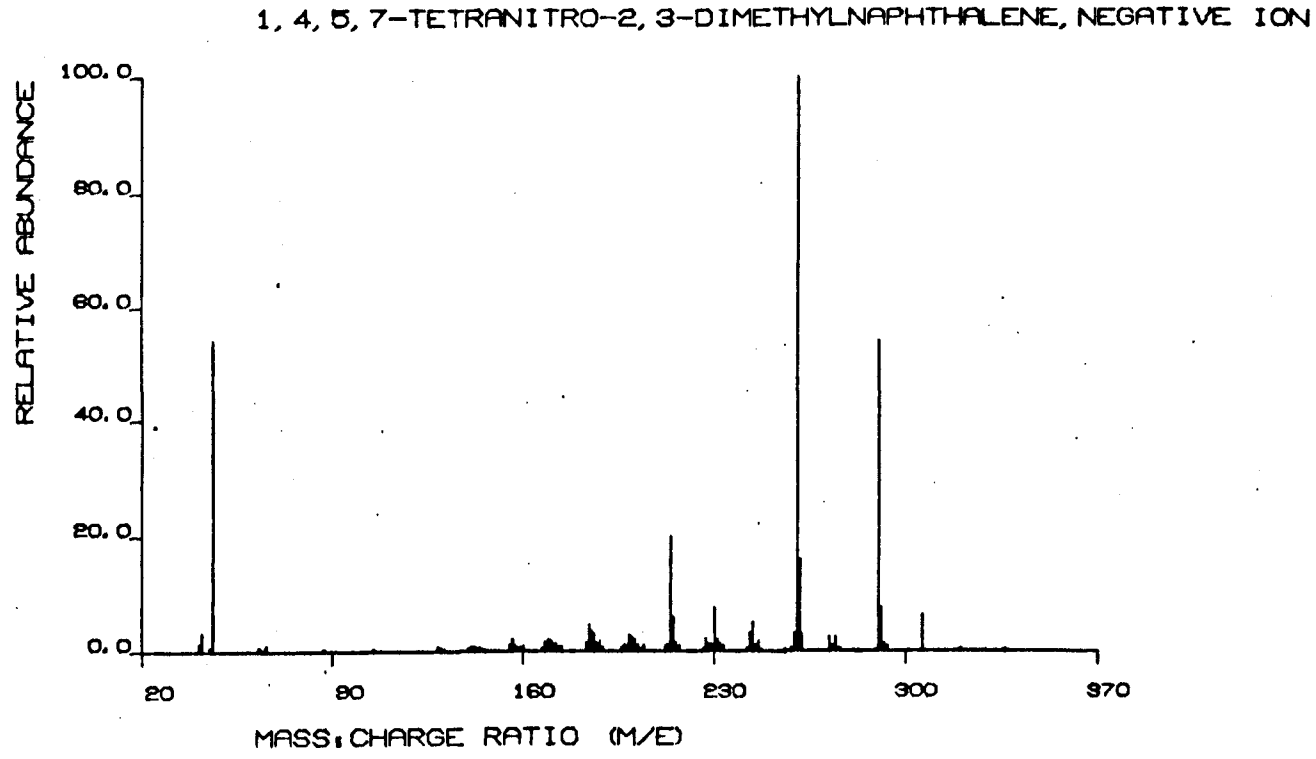

5, 6, 8-TRINITRO-2, 3-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
80
140
200
260
320
MASS:CHARGE RATIO (M/E)

Fig.4.1.29


1, 4, 5, 7-TETRANITRO-2, 3-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
90
160
230
300
970
MASS:CHARGE RATIO (M/E)

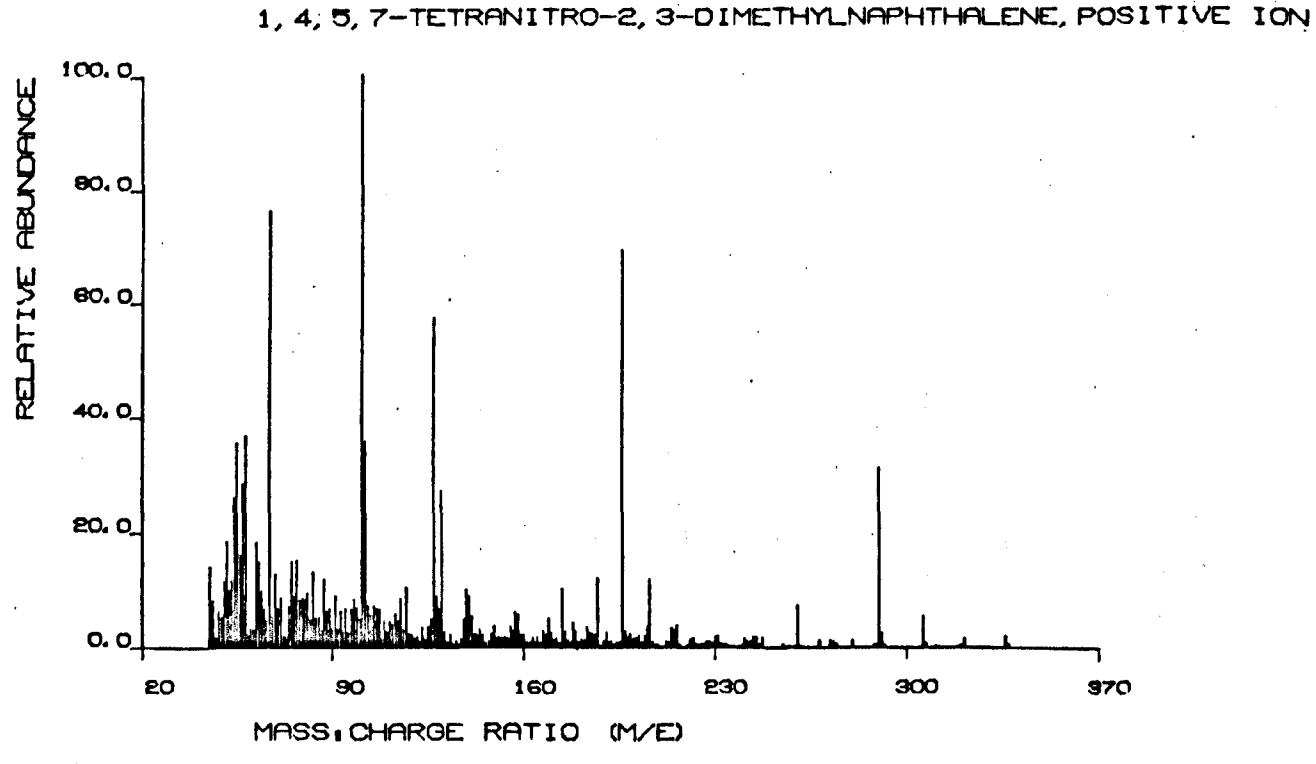
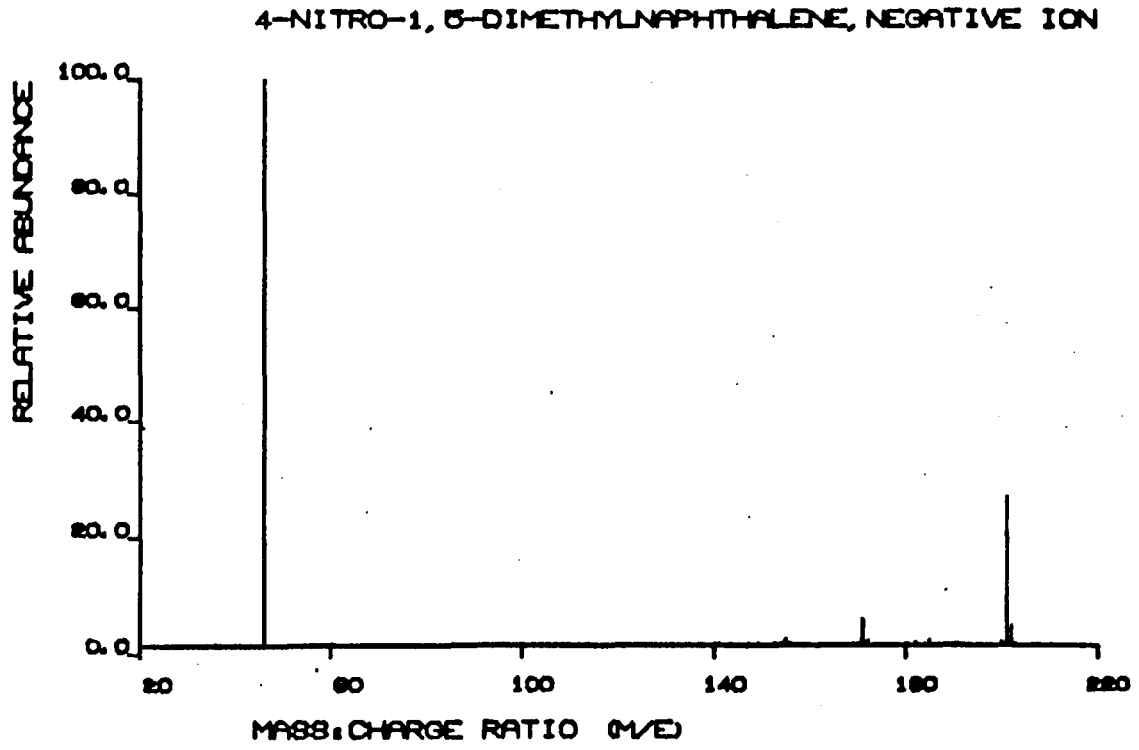

1, 4, 5, 7-TETRANITRO-2, 3-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
90
160
230
300
970
MASS:CHARGE RATIO (M/E)

Fig.4.1.30


4-NITRO-1,5-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
60
100
140
180
220
MASS:CHARGE RATIO (M/E)

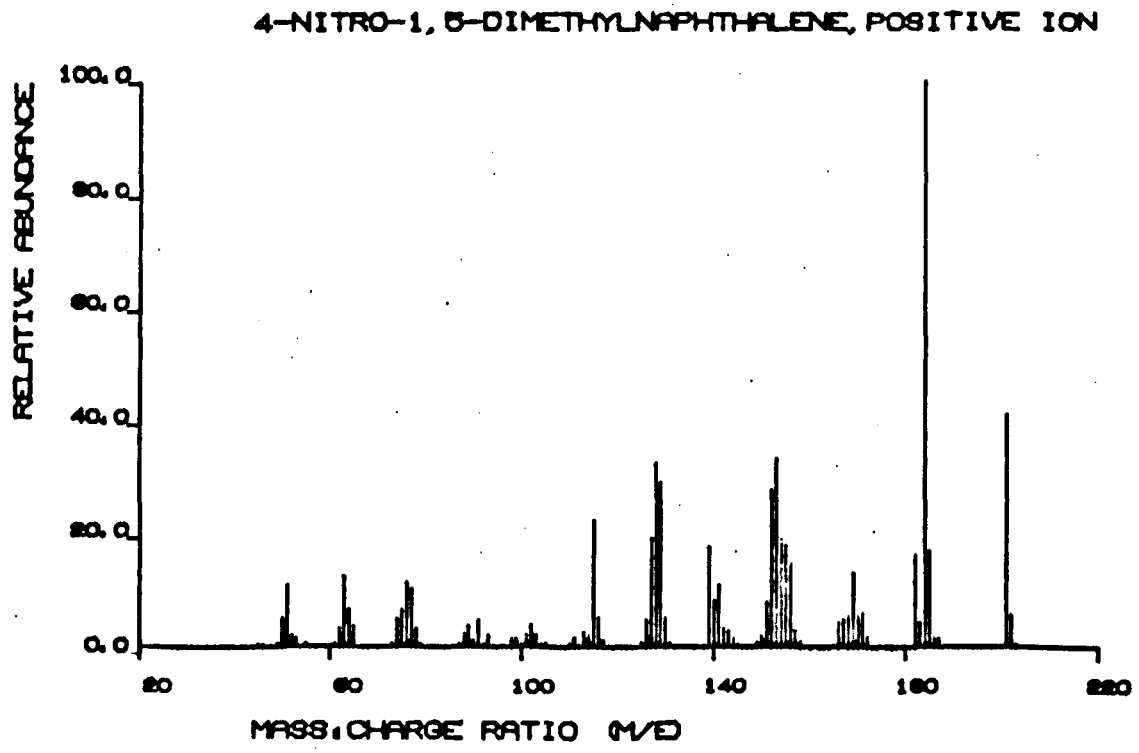
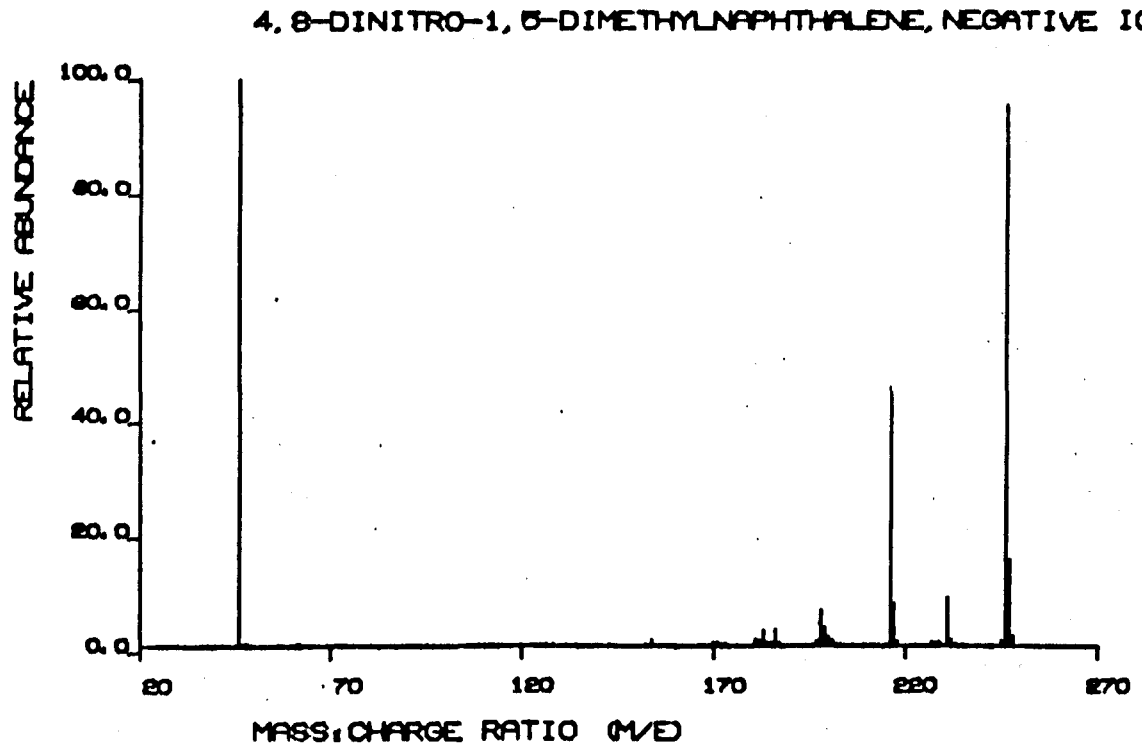

4-NITRO-1,5-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
60
100
140
180
220
MASS:CHARGE RATIO (M/E)

Fig.4.1.31


4,8-DINITRO-1,5-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
50
70
120
170
220
270
MASS:CHARGE RATIO (M/E)

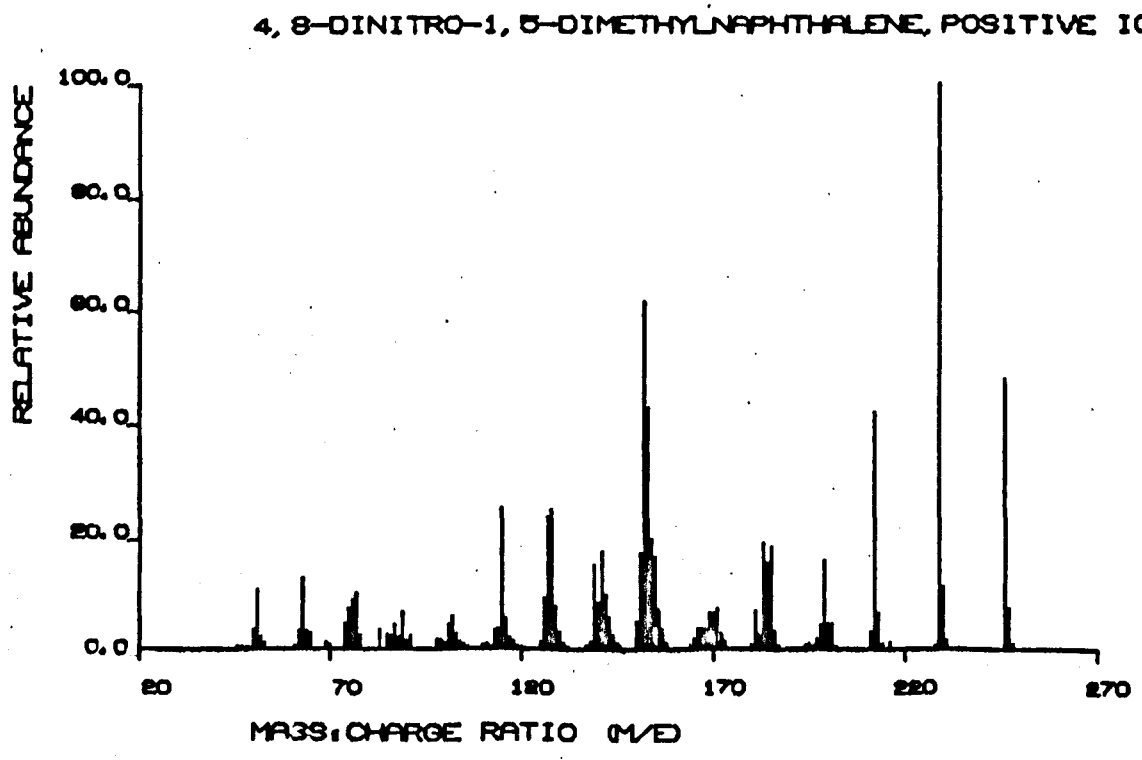
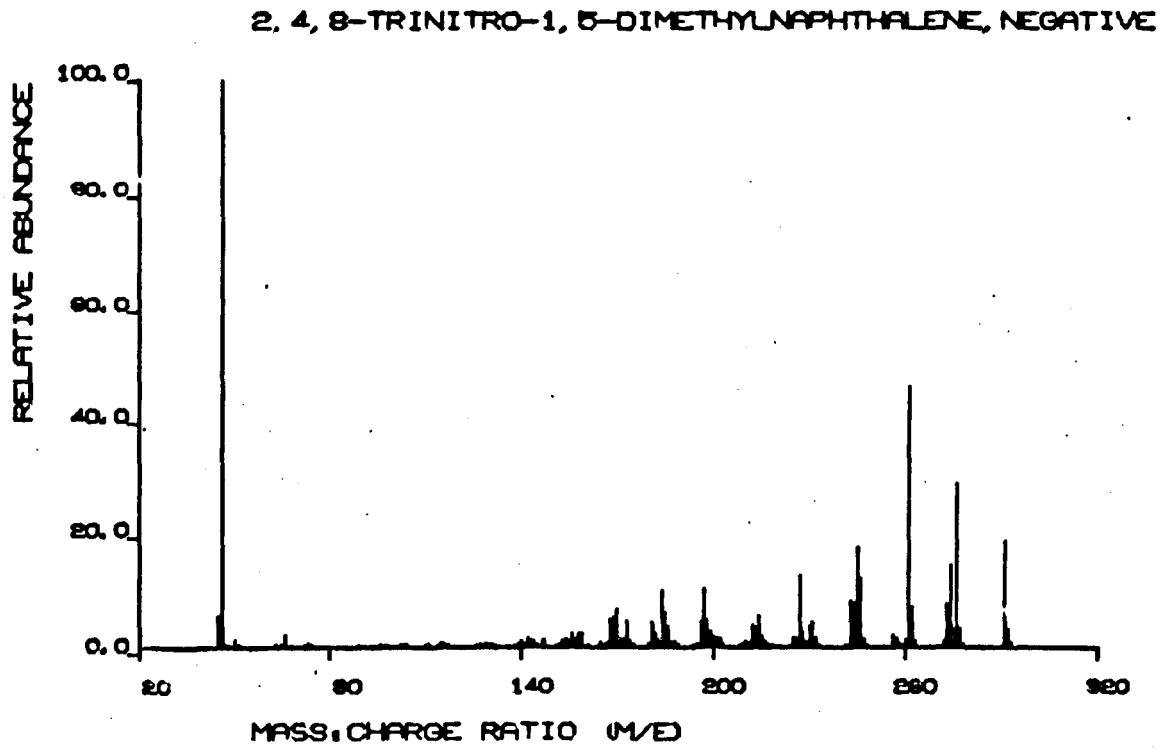

4,8-DINITRO-1,5-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
50
70
120
170
220
270
MASS:CHARGE RATIO (M/E)

Fig.4.1.32


2, 4, 8-TRINITRO-1, 5-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
80
140
200
260
320
MASS:CHARGE RATIO (M/E)

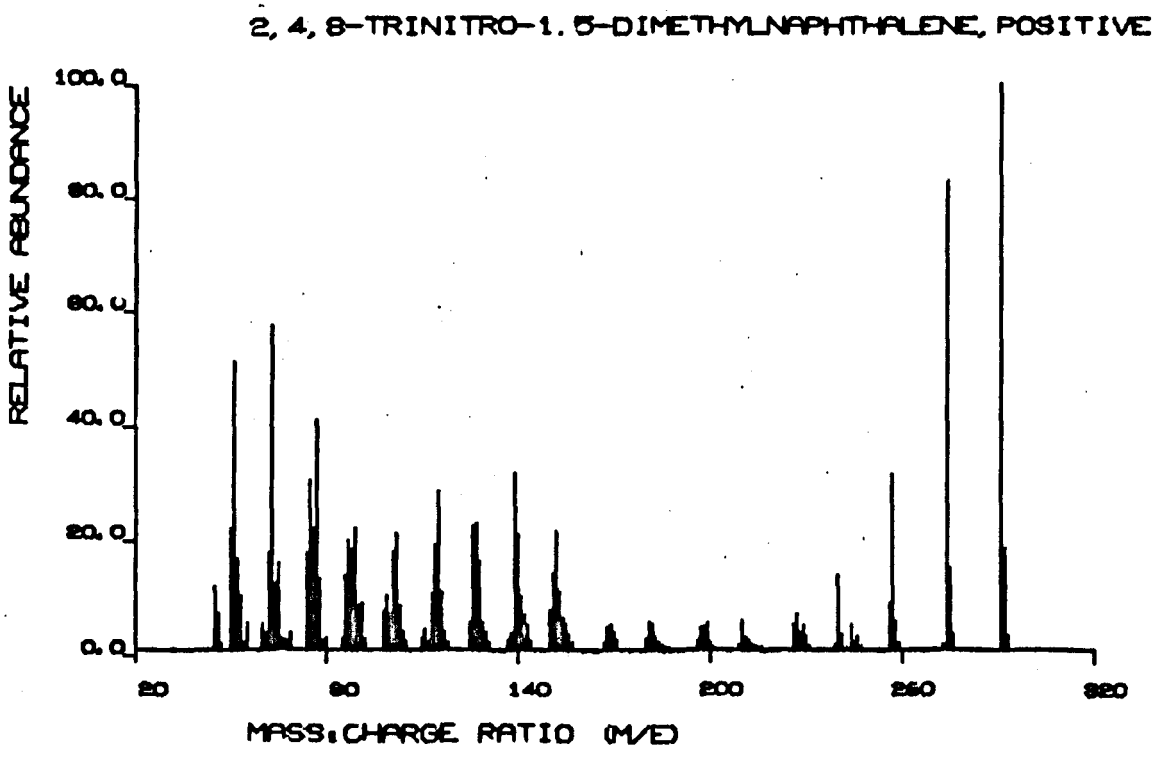
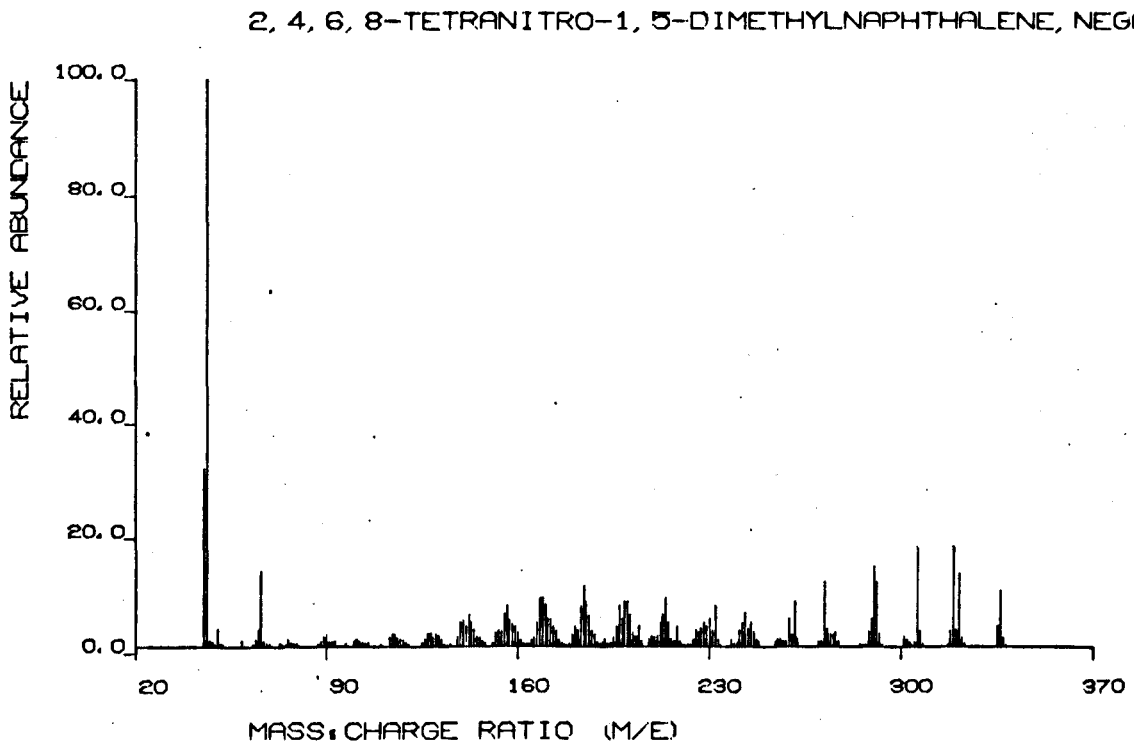

2, 4, 8-TRINITRO-1. 5-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
80
140
200
260
320
MASS:CHARGE RATIO (M/E)

Fig.4.1.33


2, 4, 6, 8-TETRANITRO-1, 5-DIMETHYLNAPHTHALENE, NEGATIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
90
160
230
300
370
MASS: CHARGE RATIO (M/E)

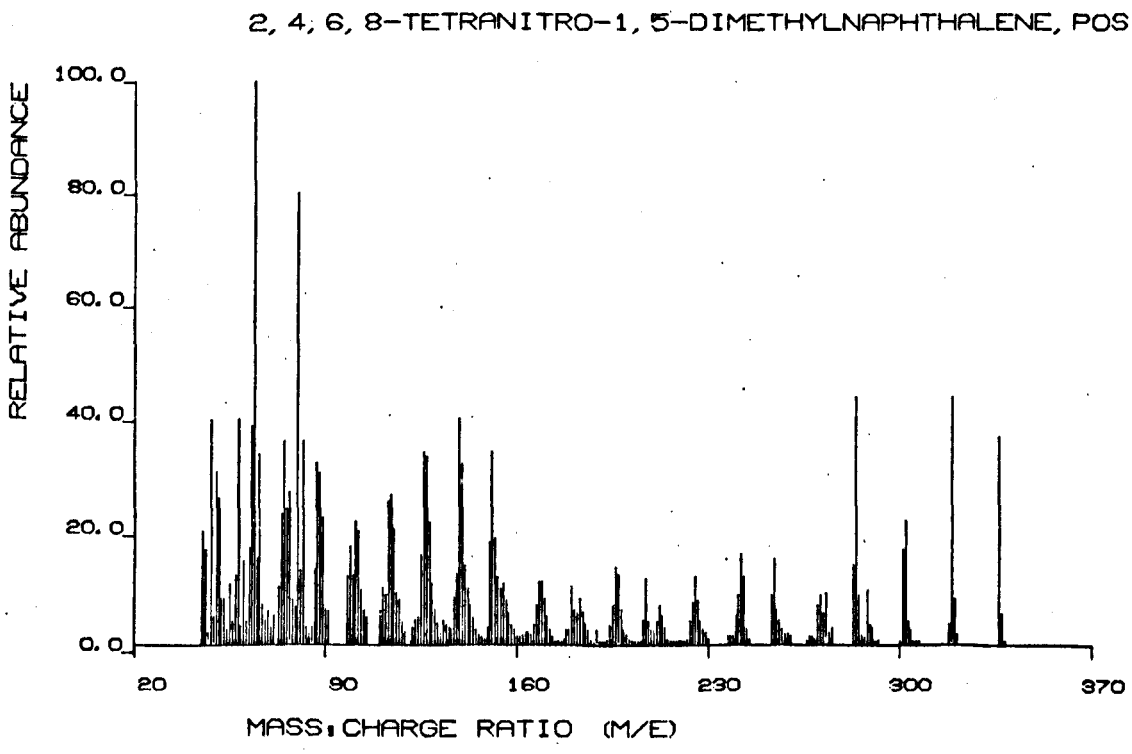

2, 4, 6, 8-TETRANITRO-1, 5-DIMETHYLNAPHTHALENE, POSITIVE ION
RELATIVE ABUNDANCE
100.0
80.0
60.0
40.0
20.0
0.0
20
90
160
230
300
370
MASS: CHARGE RATIO (M/E)

Fig.4.1.34

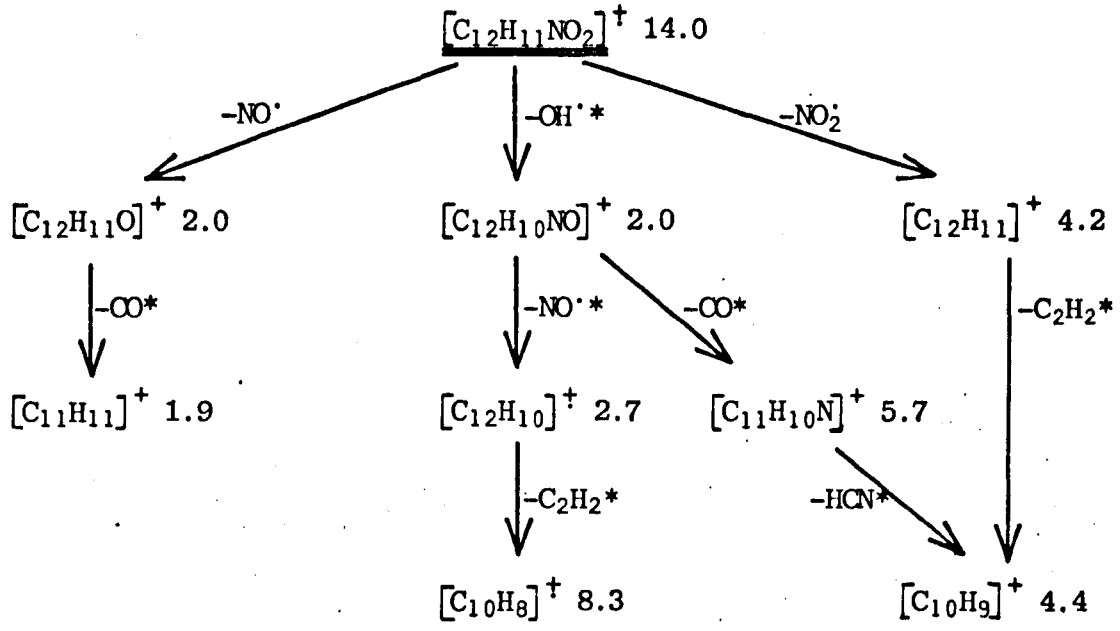


Fig.4.1.35 1-nitro-2,3-dimethylnaphthalene,positive ion.

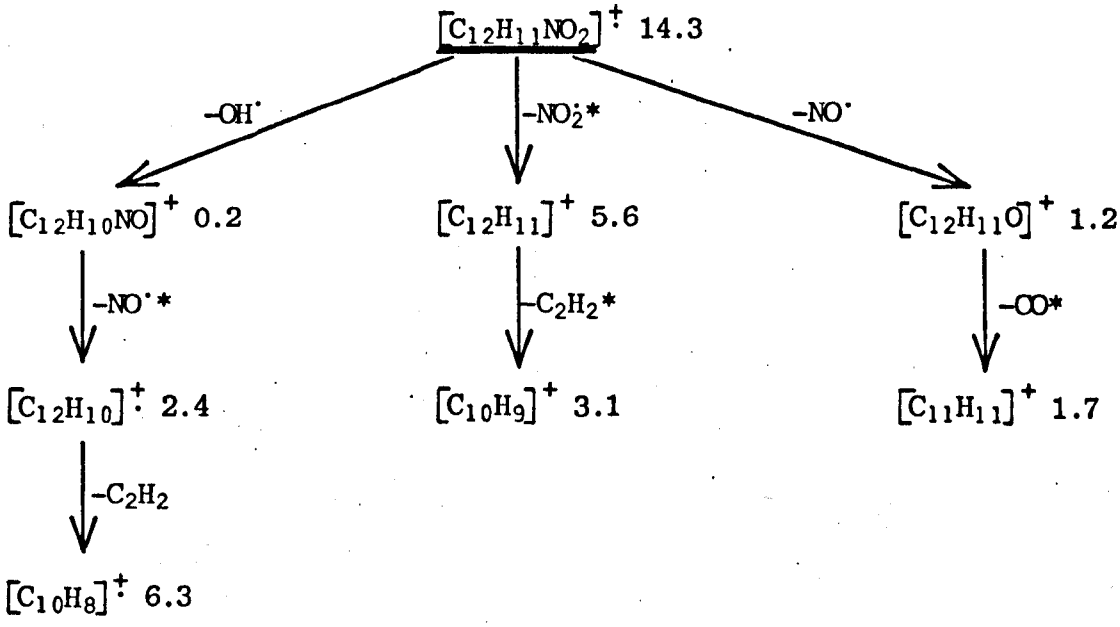


Fig.4.1.36 5-nitro-2,3-dimethylnaphthalene,positive ion.

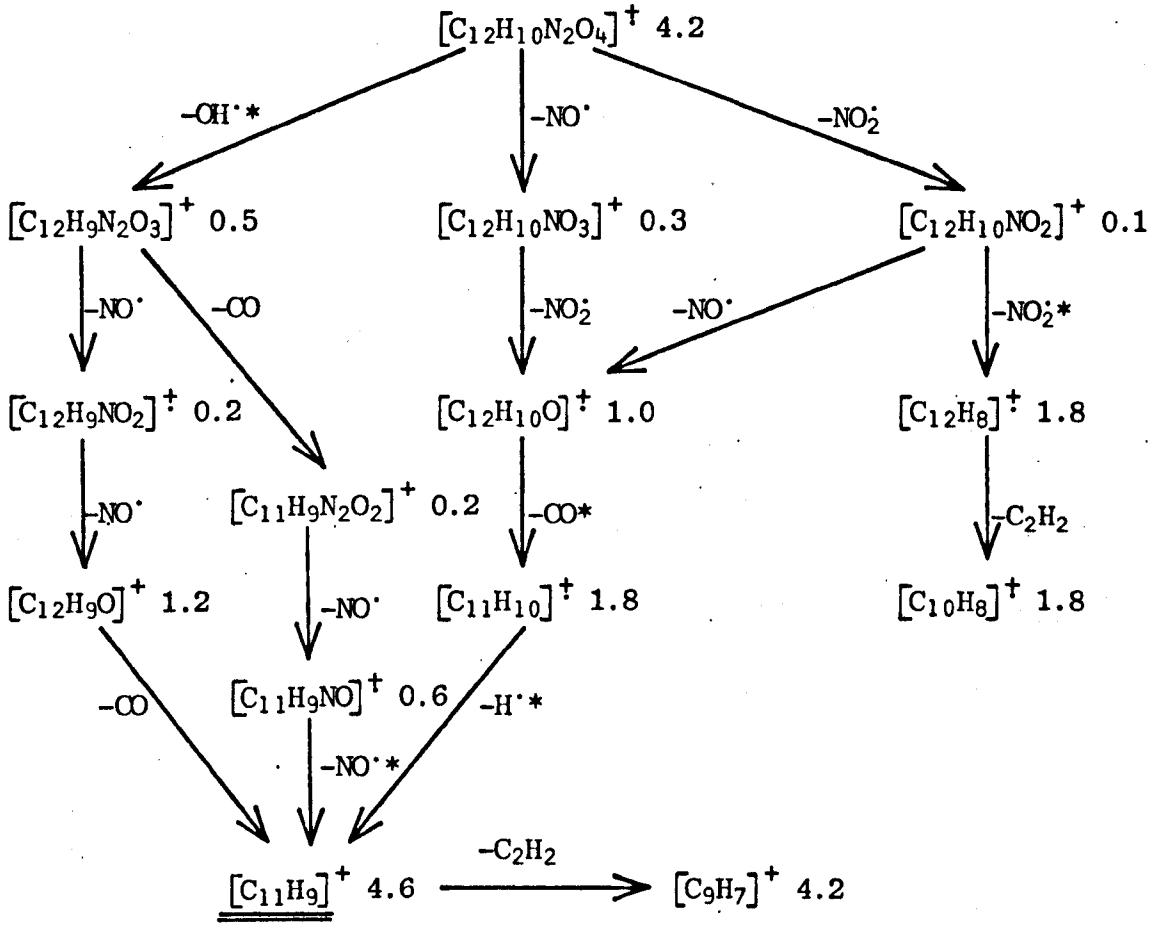


Fig.4.1.37 1,5-dinitro-2,3-dimethylnaphthalene,positive ion.

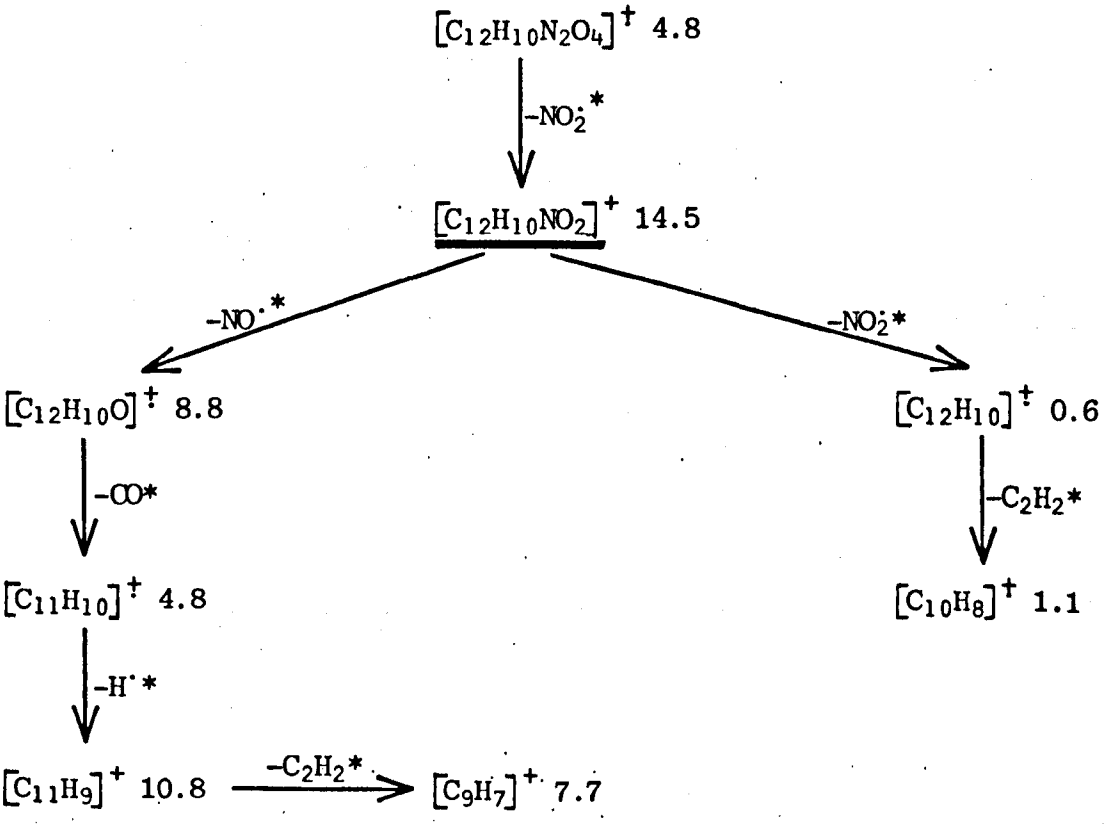


Fig.4.1.38 1,8-dinitro-2,3-dimethylnaphthalene,positive ion.

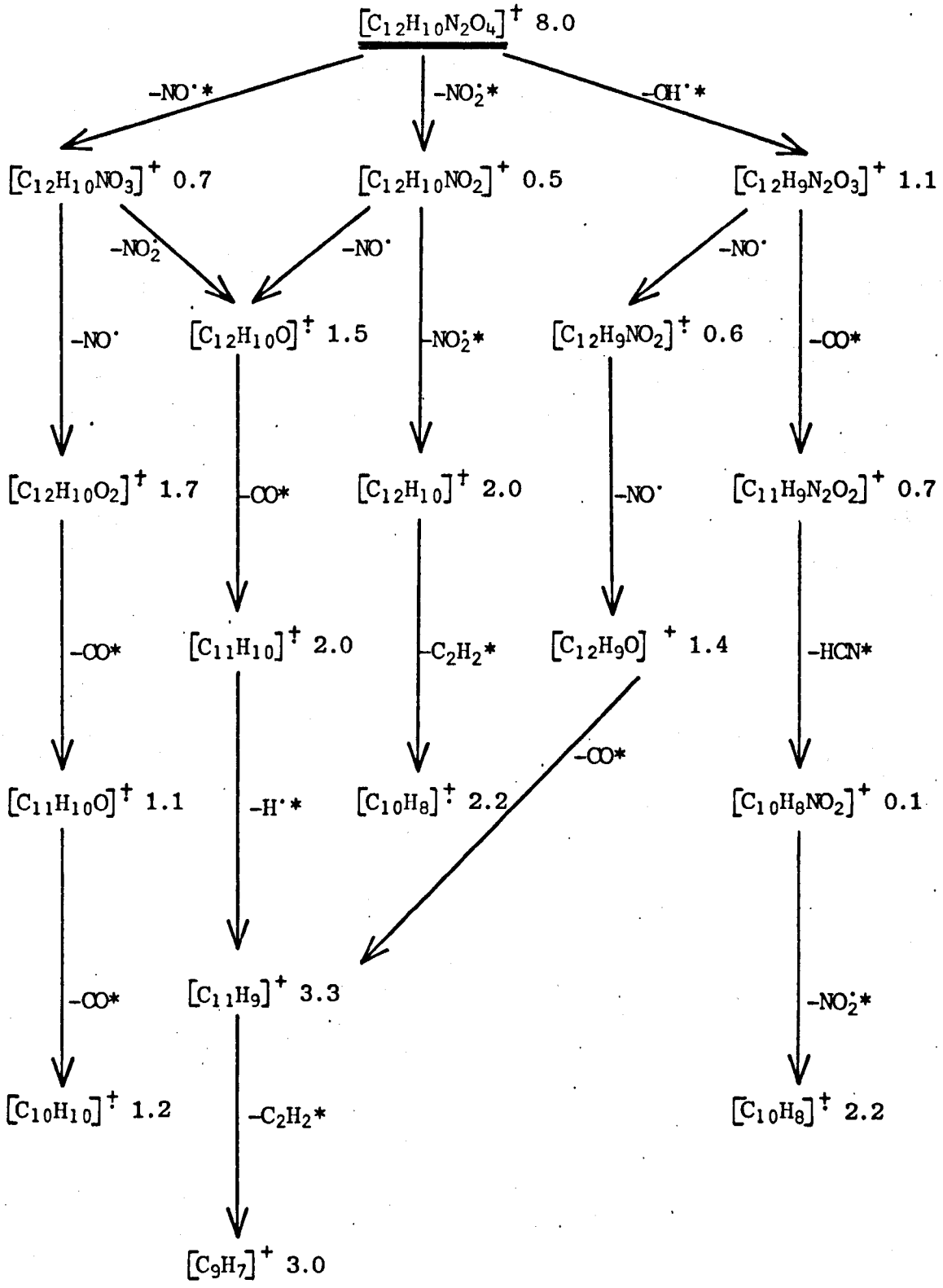


Fig.4.1.39 1,4-dinitro-2,3-dimethylnaphthalene,positive ion.

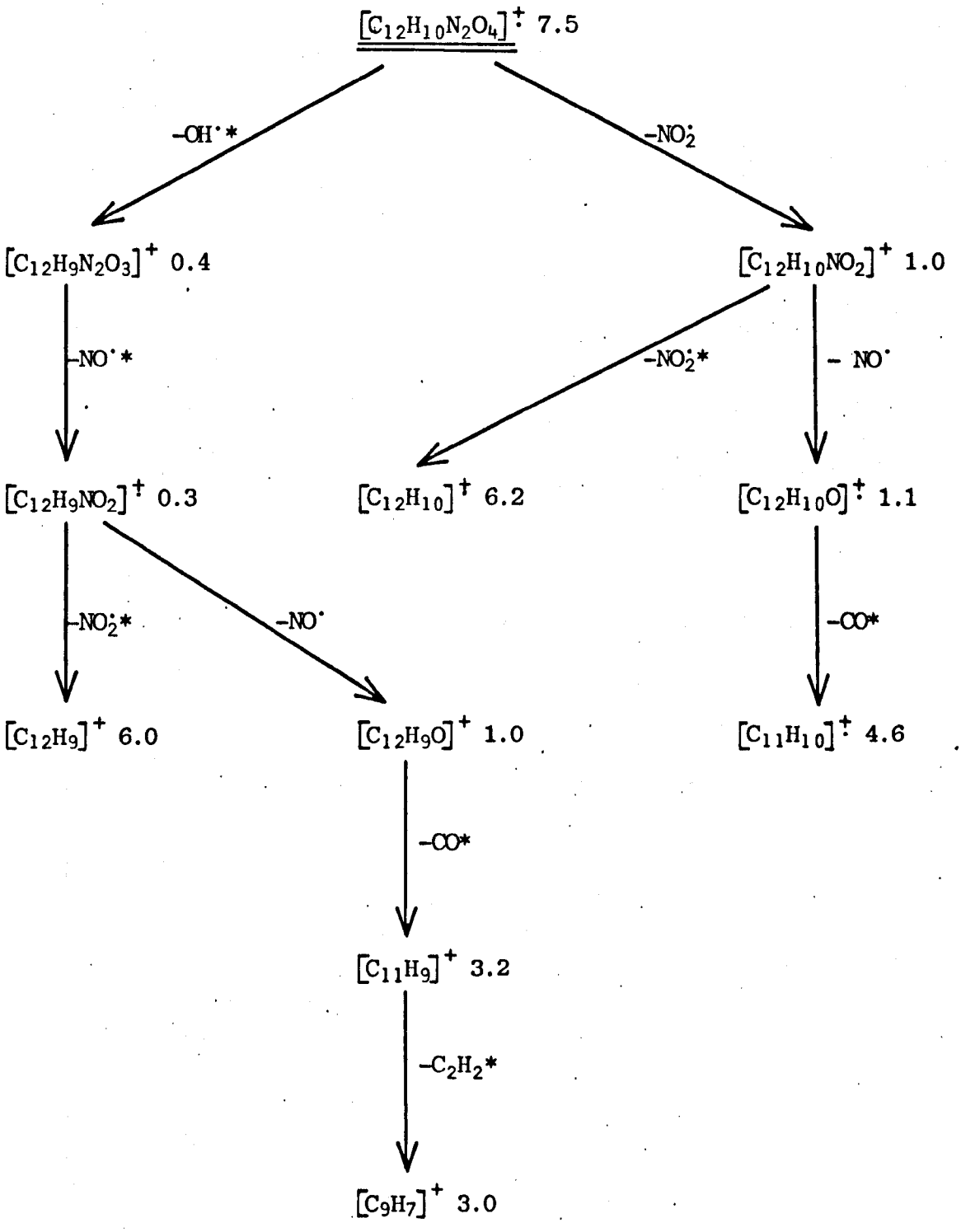


Fig.4.1.40 5,7-dinitro-2,3-dimethylnaphthalene,positive ion.

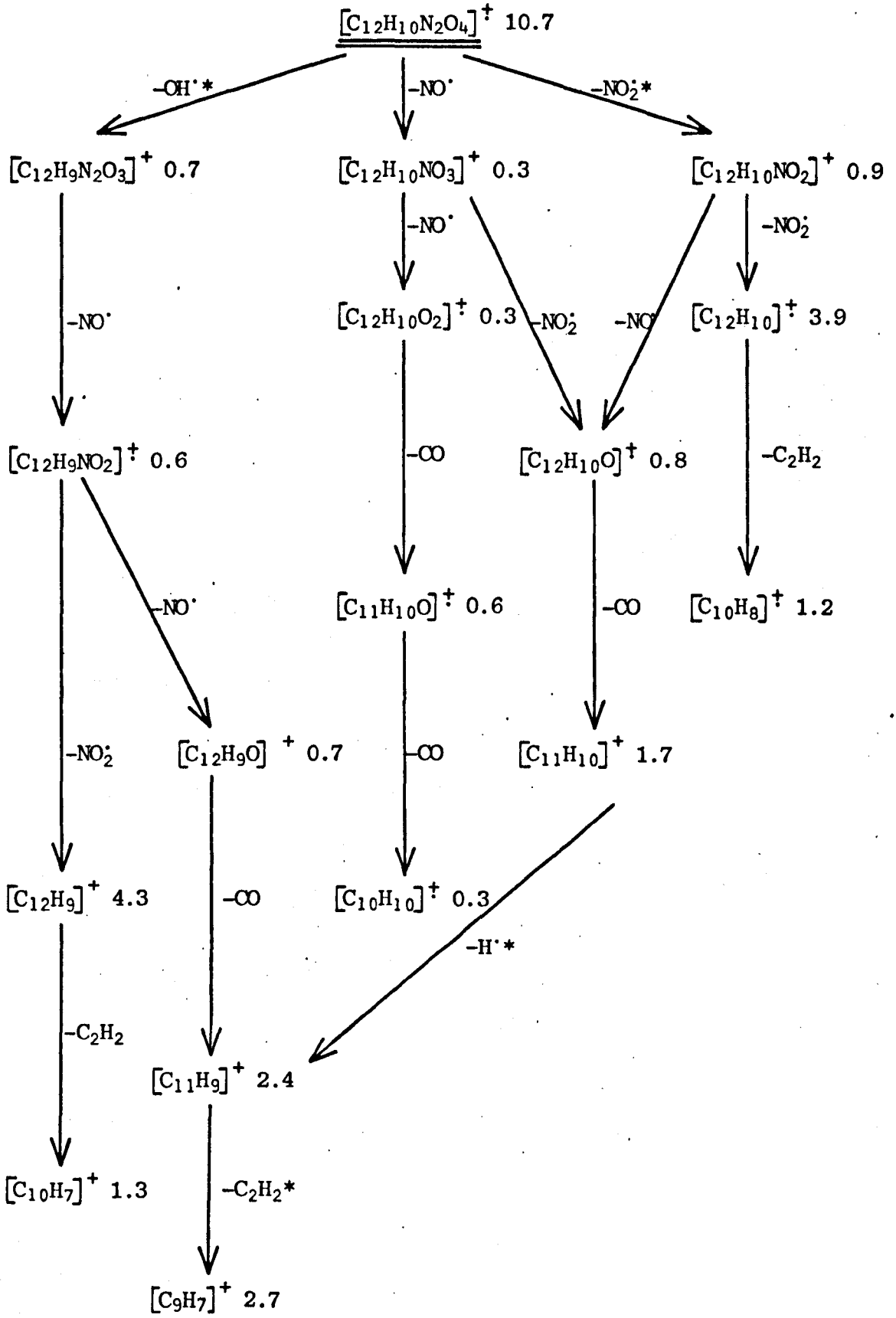


Fig.4.1.41 5,8-dinitro-2,3-dimethylnaphthalene,positive ion.

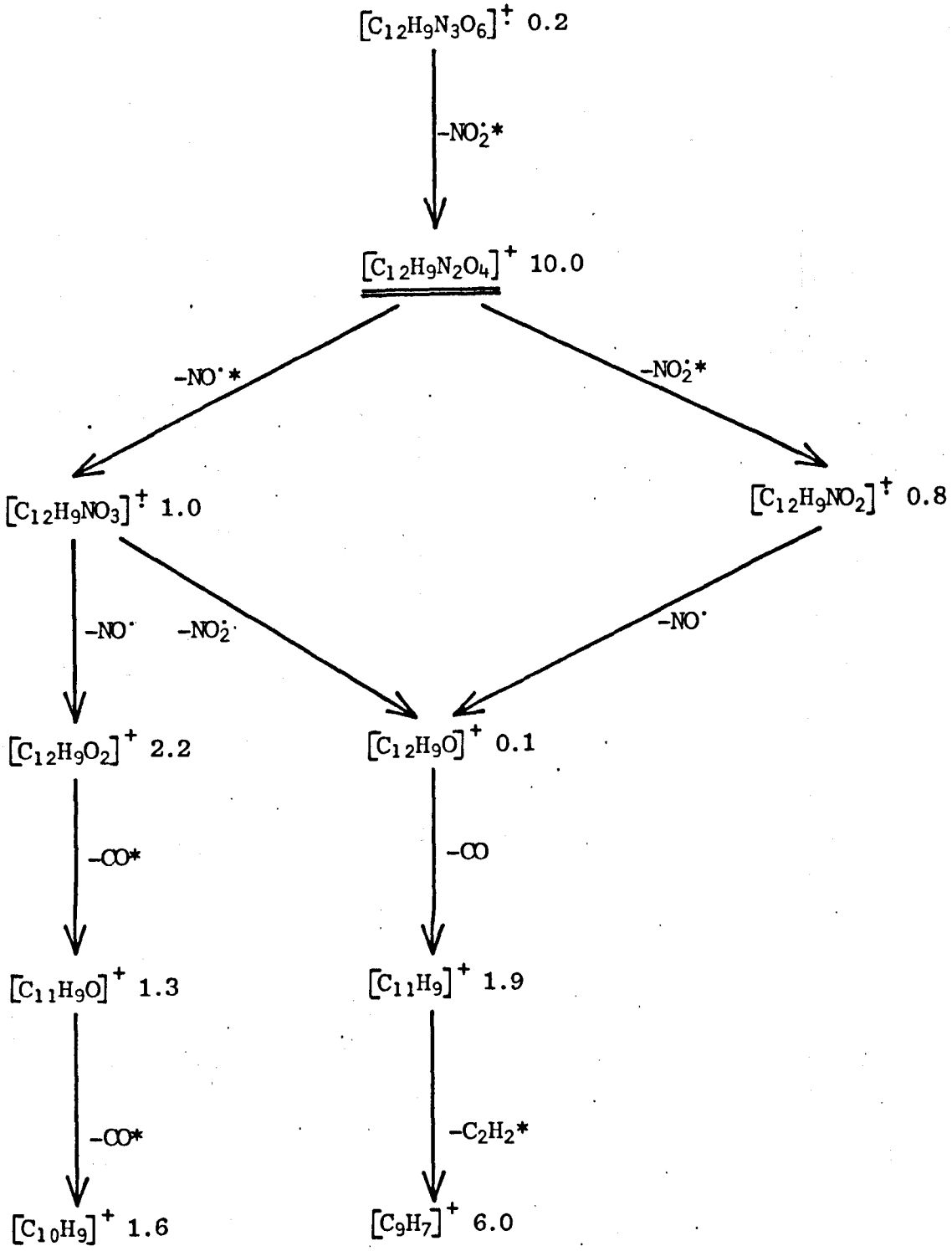


Fig.4.1.42 1,4,5-trinitro-2,3-dimethylnaphthalene, positive ion.

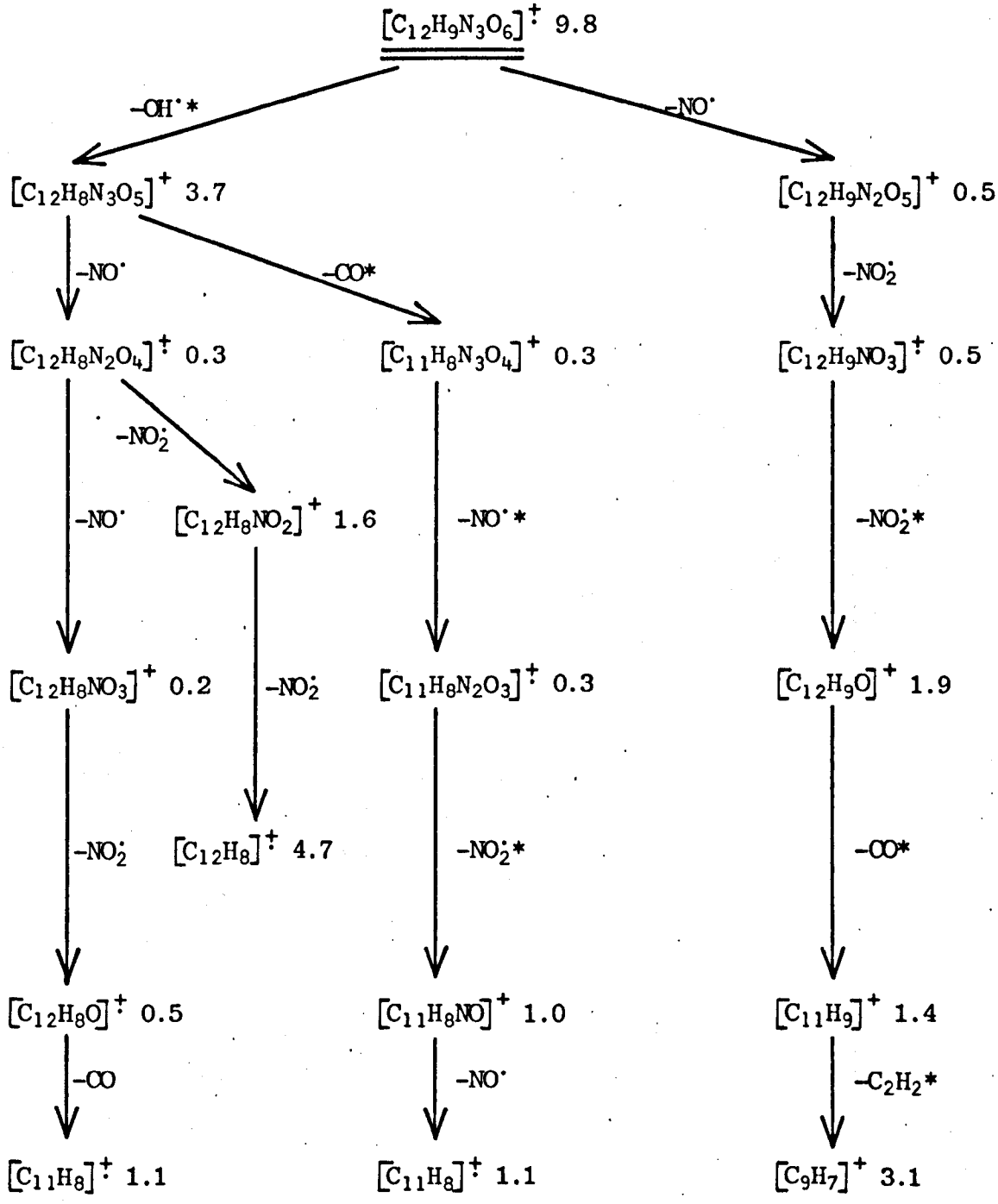


Fig.4.1.43 1,5,7-trinitro-2,3-dimethylnaphthalene, positive ion.

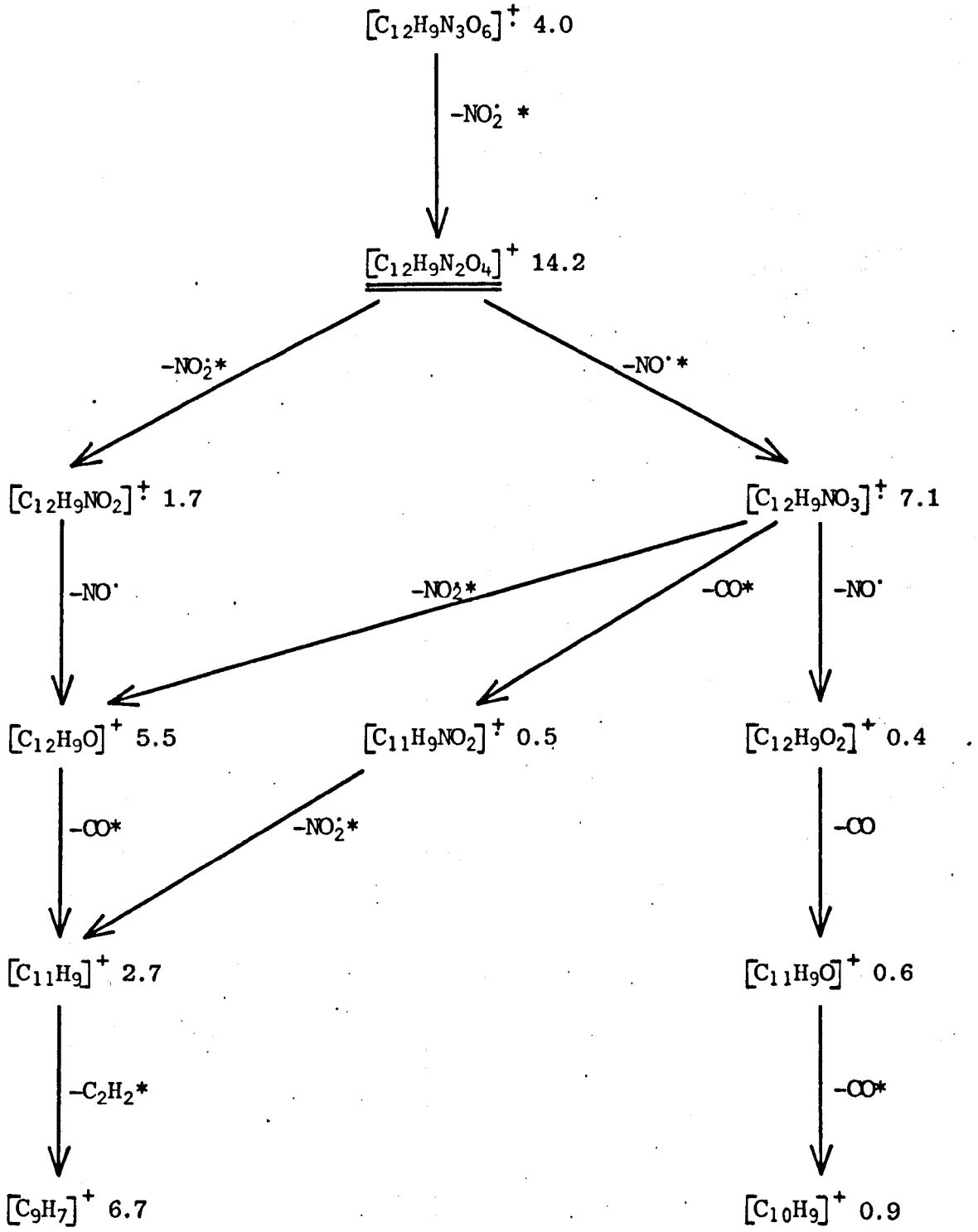


Fig.4.1.44 1,6,8-trinitro-2,3-dimethylnaphthalene, positive ion.

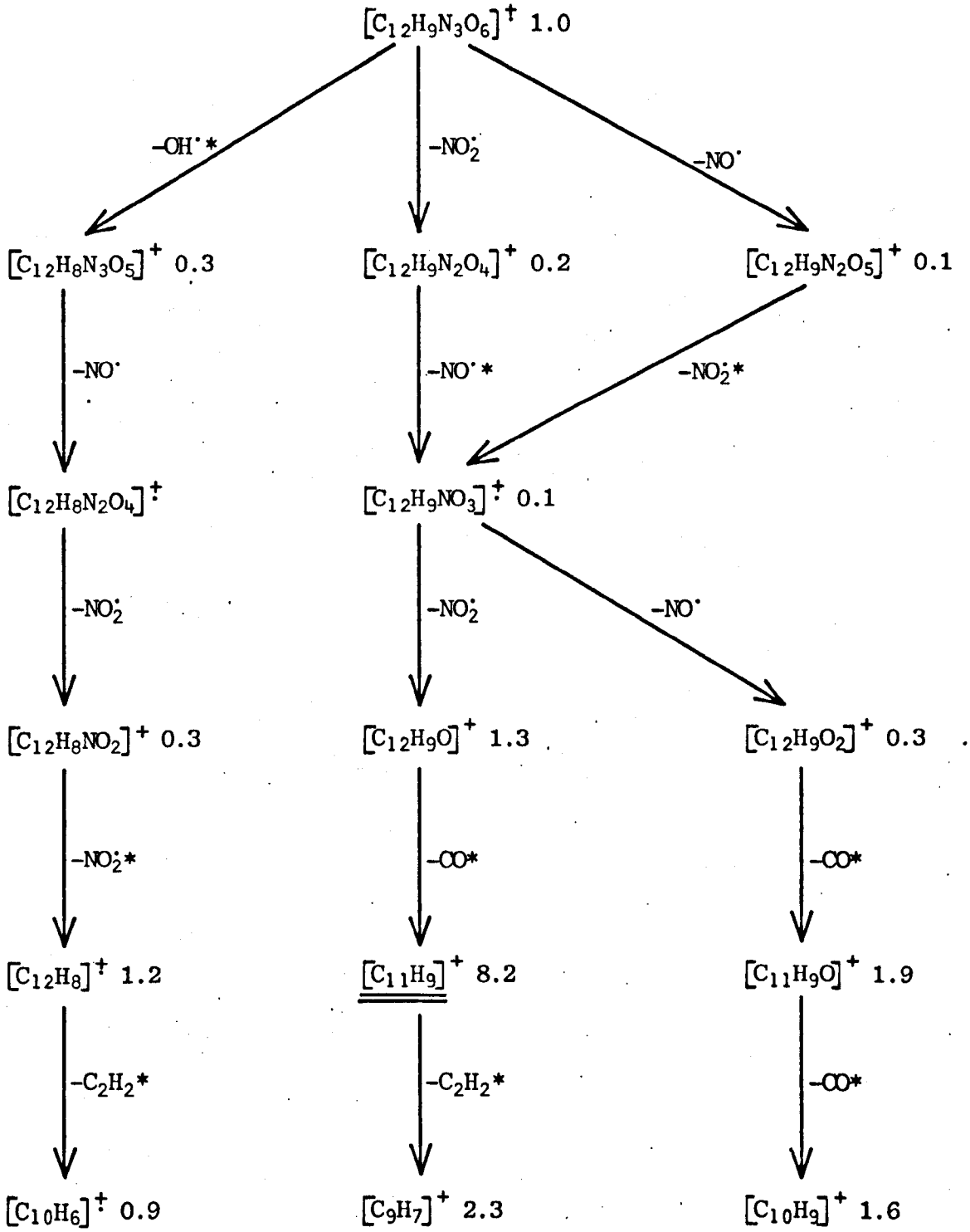


Fig.4.1.45 5,6,8-trinitro-2,3-dimethylnaphthalene, positive ion.

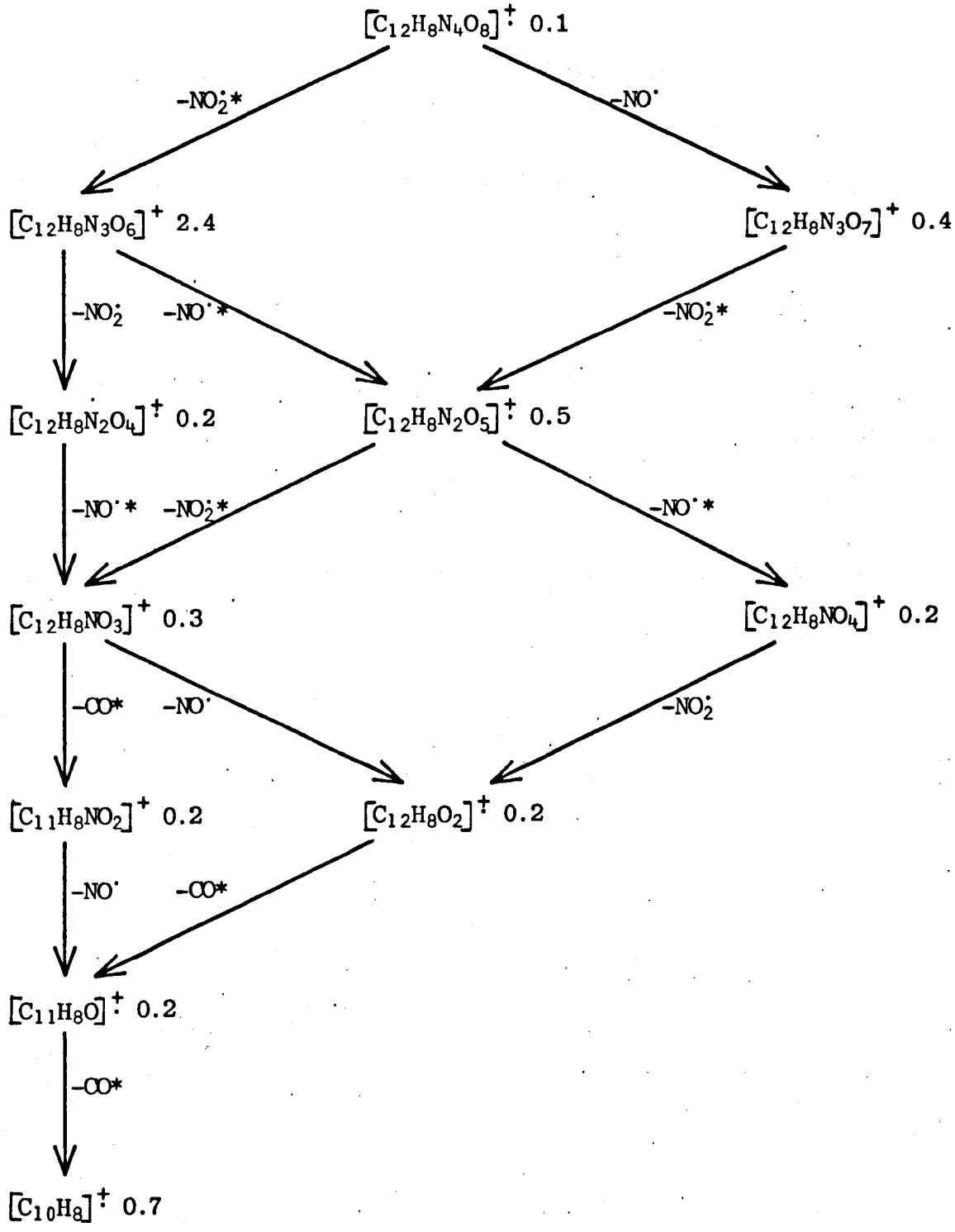


Fig.4.1.46 1,4,5,7-tetranitro-2,3-dimethylnaphthalene, positive ion.

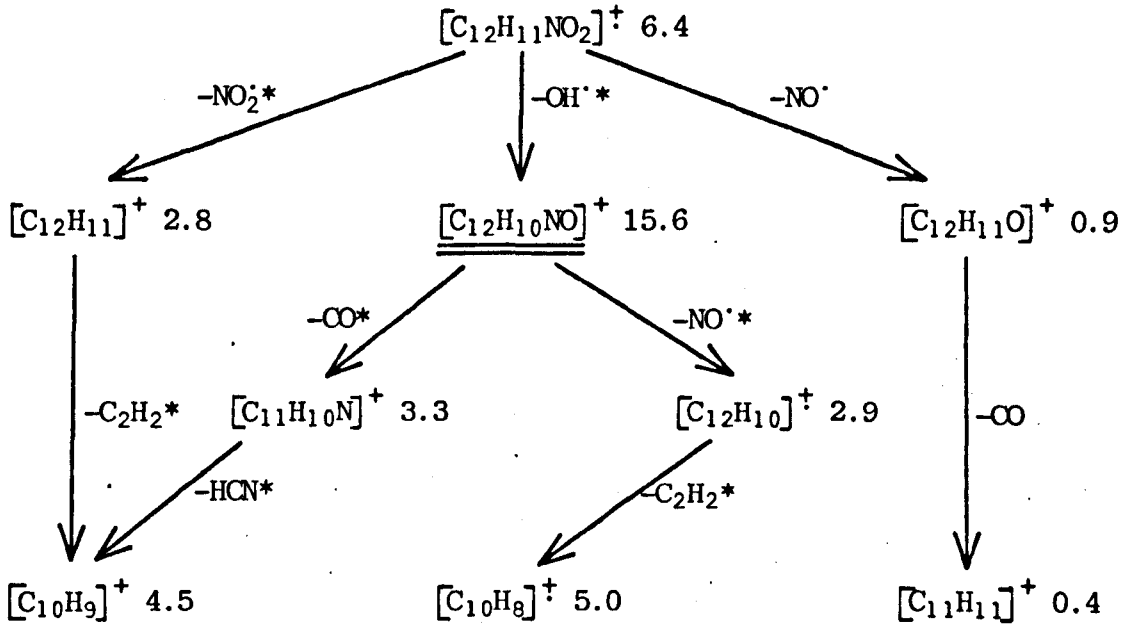


Fig.4.1.47 4-nitro-1,5-dimethylnaphthalene,positive ion.

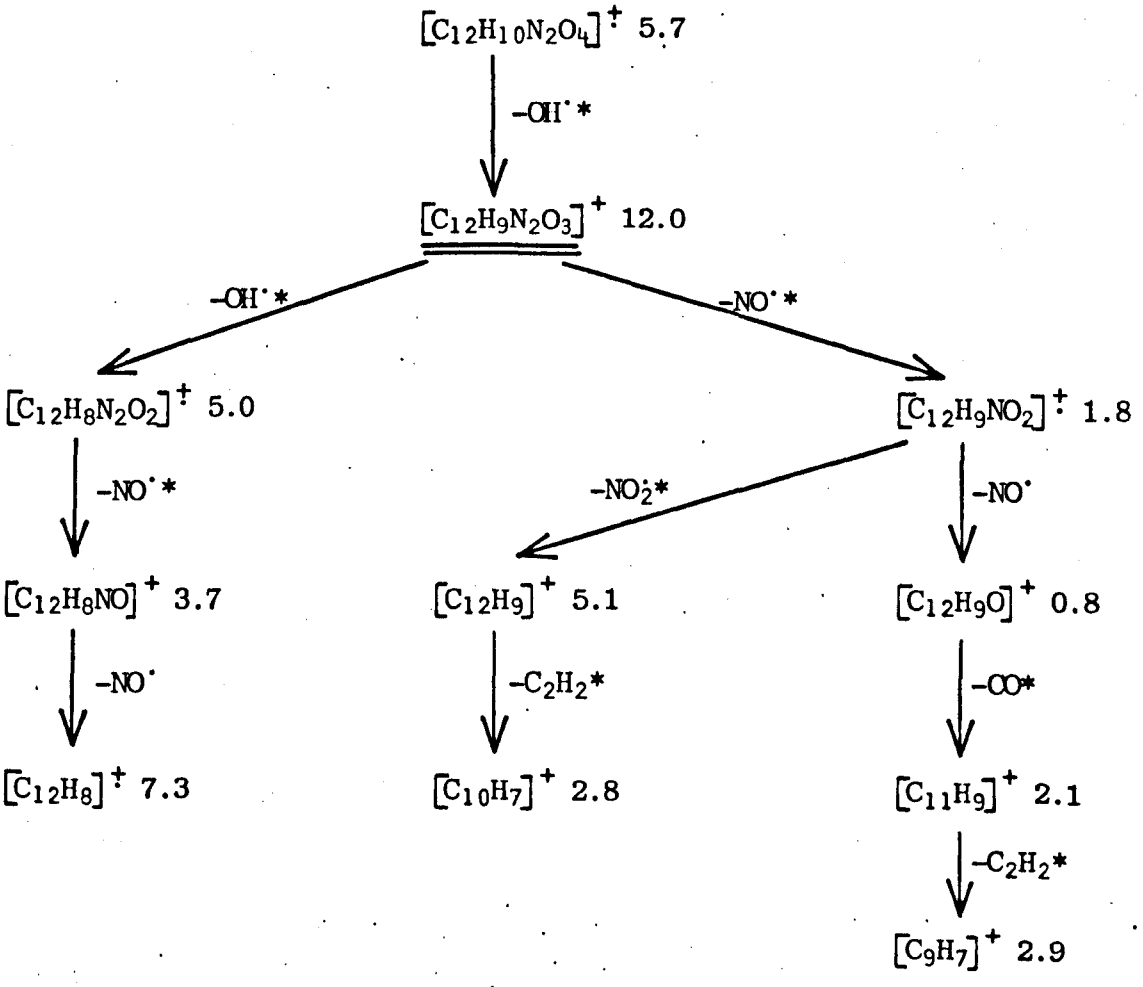


Fig.4.1.48 4,8-dinitro-1,5-dimethylnaphthalene,positive ion.

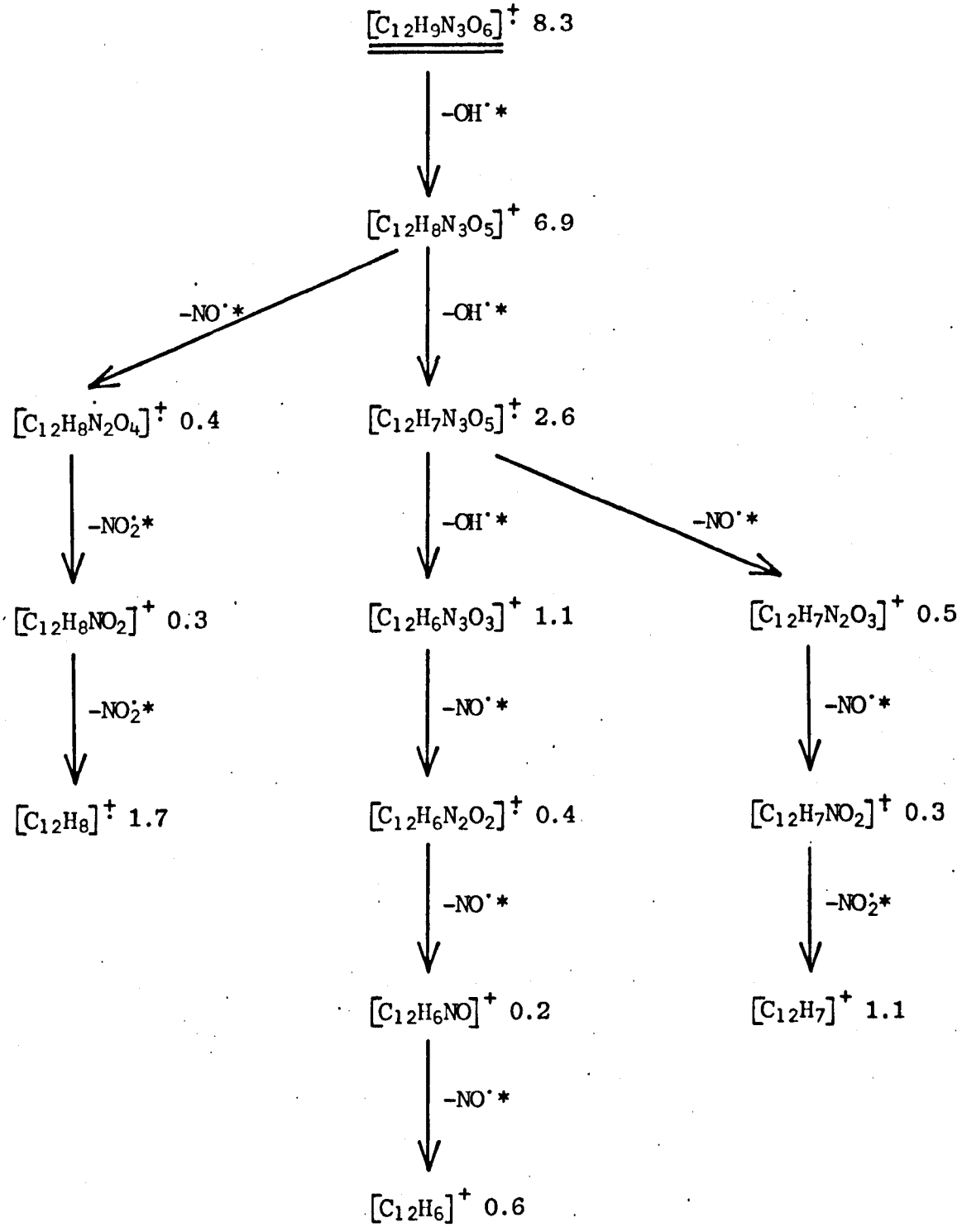


Fig.4.1.49 2,4,8-trinitro-1,5-dimethylnaphthalene, positive ion.

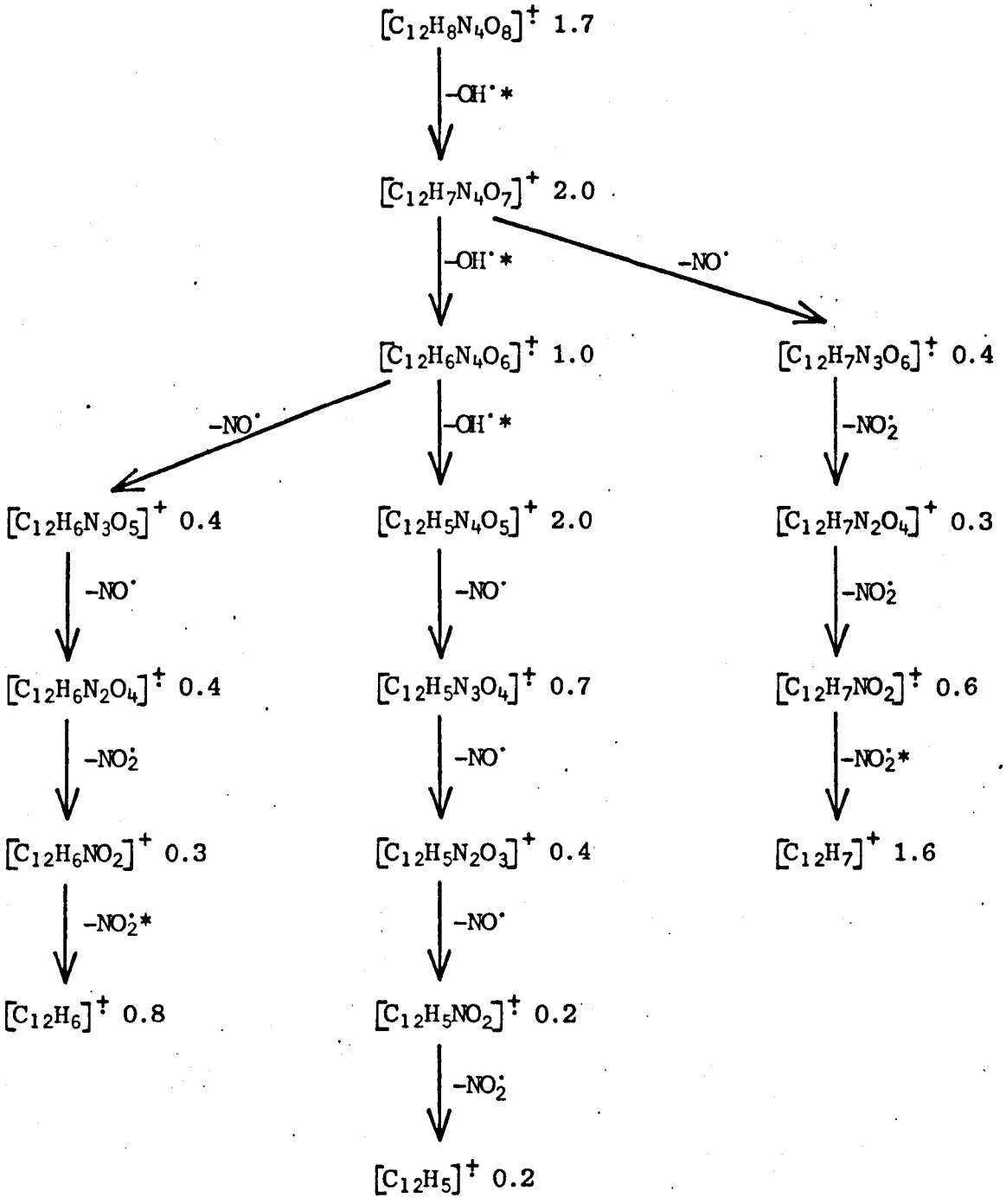


Fig.4.1.50 2,4,6,8-tetranitro-1,5-dimethylnaphthalene, positive ion.

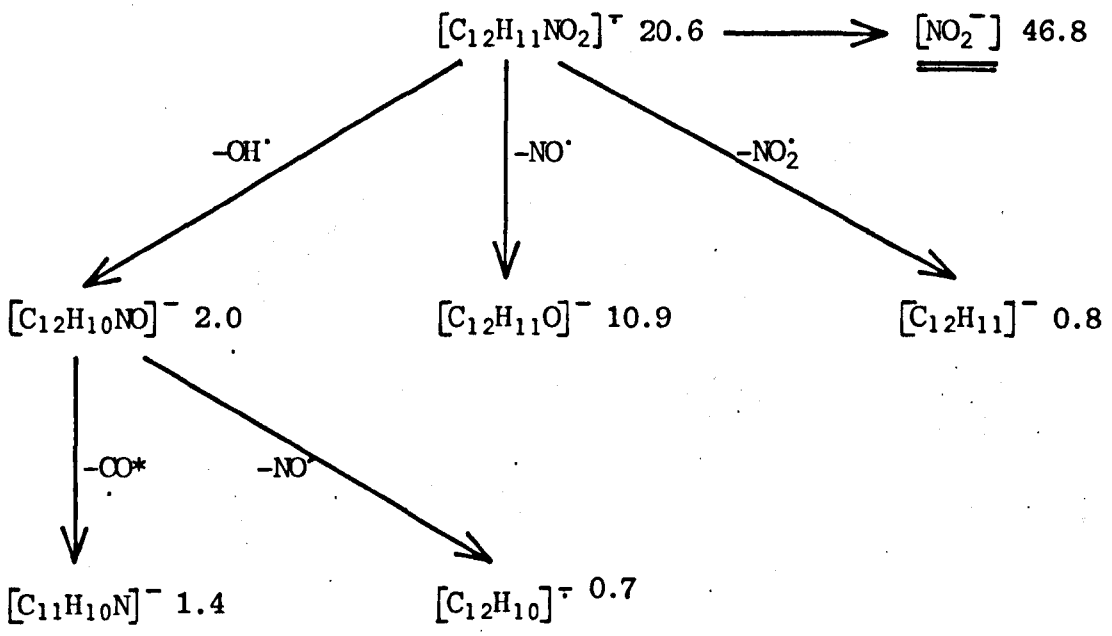


Fig.4.1.51 1-nitro-2,3-dimethylnaphthalene,negative ion.

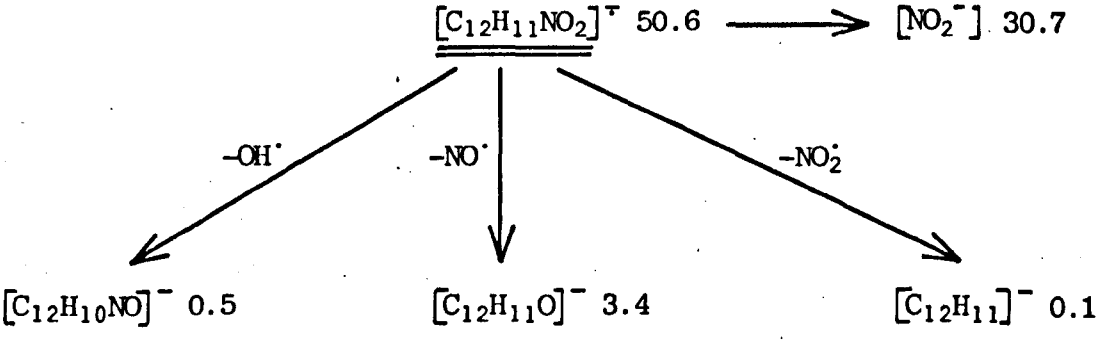


Fig.4.1.52 5-nitro-2,3-dimethylnaphthalene,negative ion.

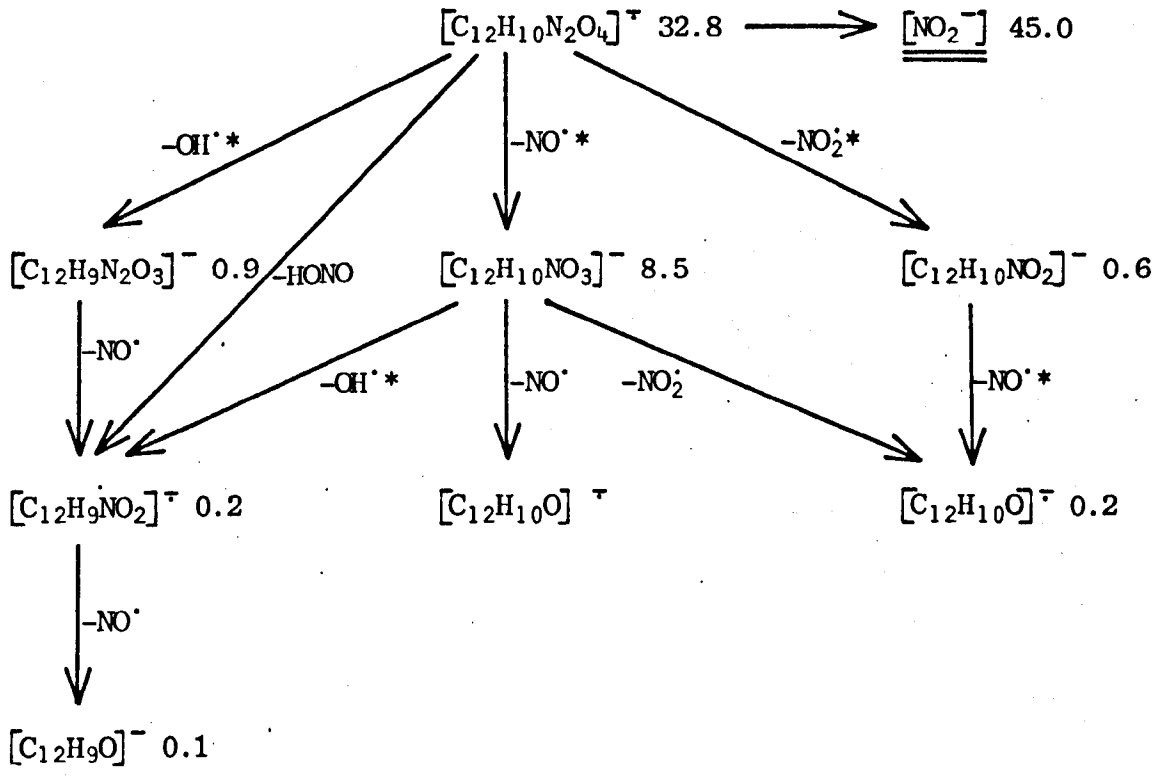


Fig.4.1.53 1,5-dinitro-2,3-dimethylnaphthalene,negative ion.

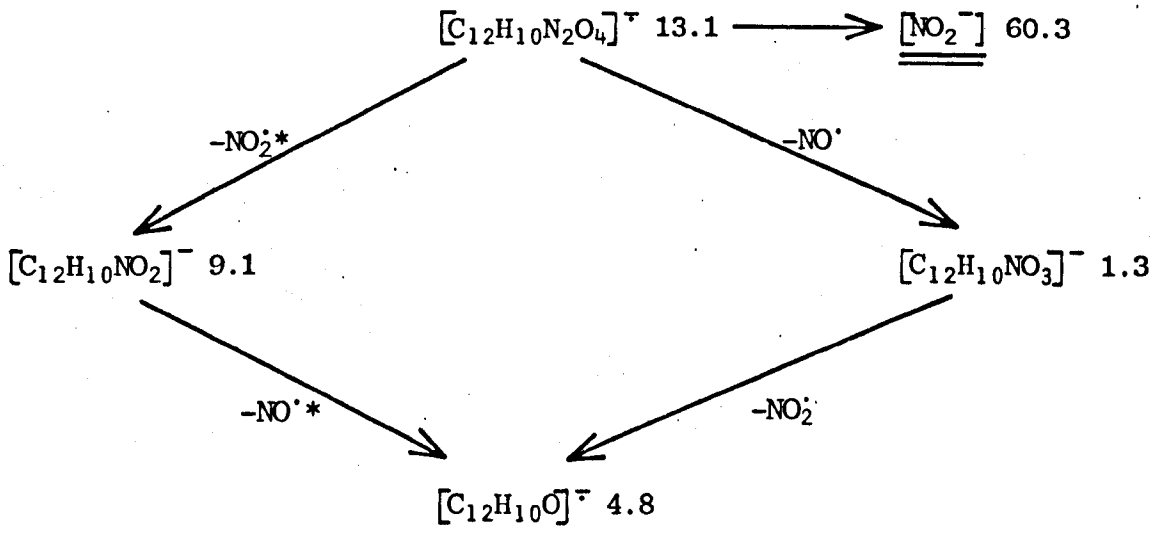


Fig.4.1.54 1,8-dinitro-2,3-dimethylnaphthalene,negative ion.

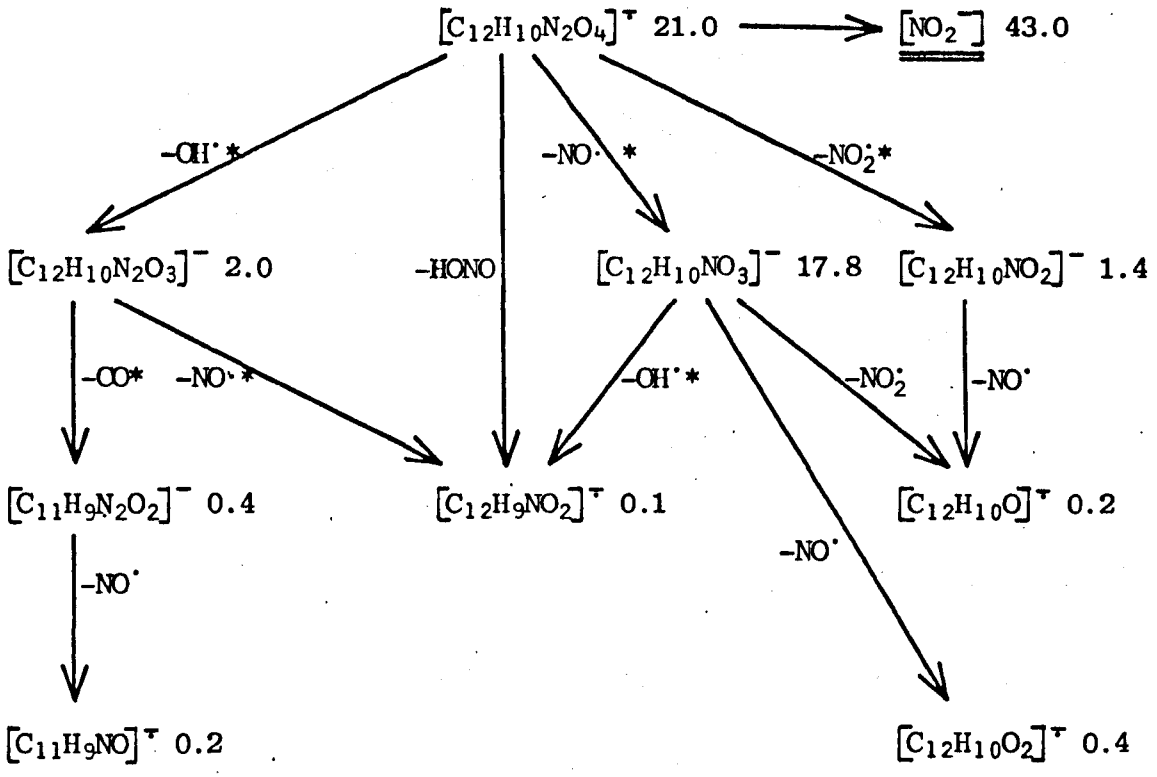


Fig.4.1.55 1,4-dinitro-2,3-dimethylnaphthalene,negative ion.

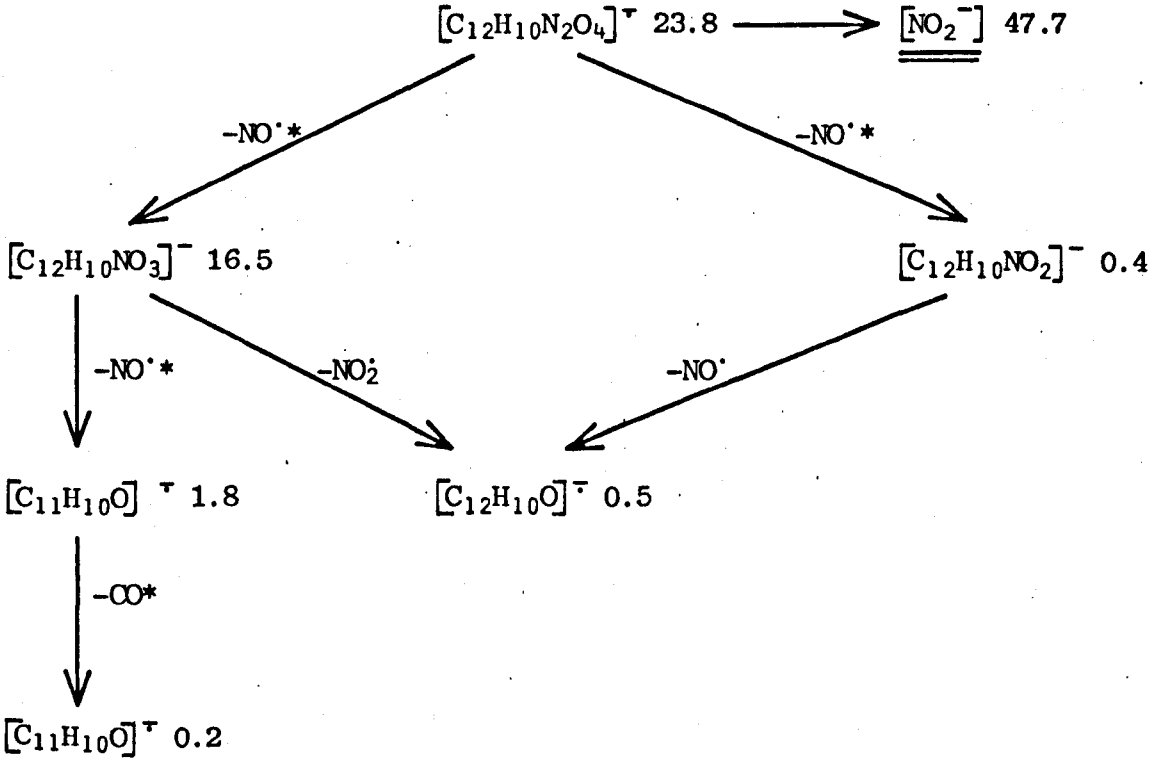


Fig.4.1.56 5,7-dinitro-2,3-dimethylnaphthalene,negative ion.

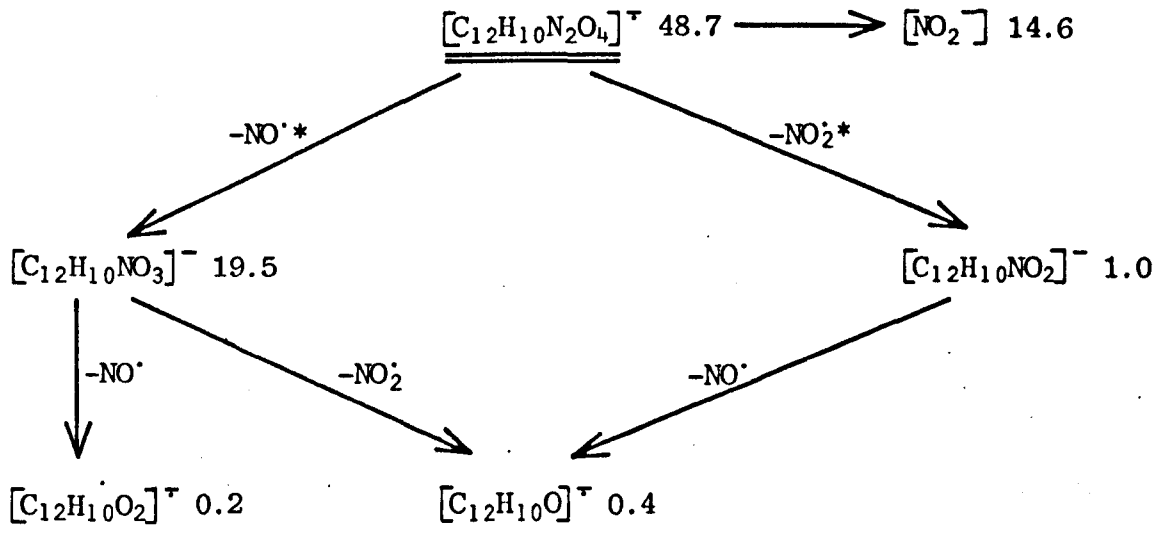


Fig.4.1.57 5,8-dinitro-2,3-dimethylnaphthalene,negative ion.

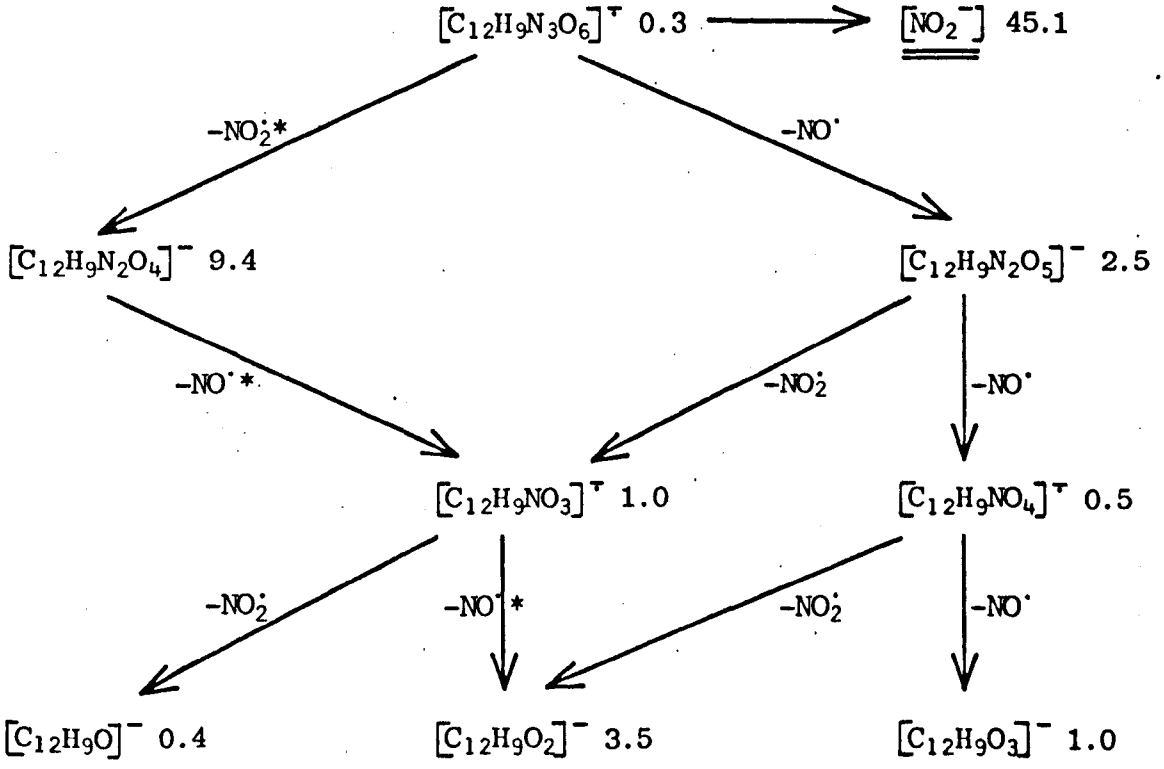


Fig.4.1.58 1,4,5-trinitro-2,3-dimethylnaphthalene, negative ion.

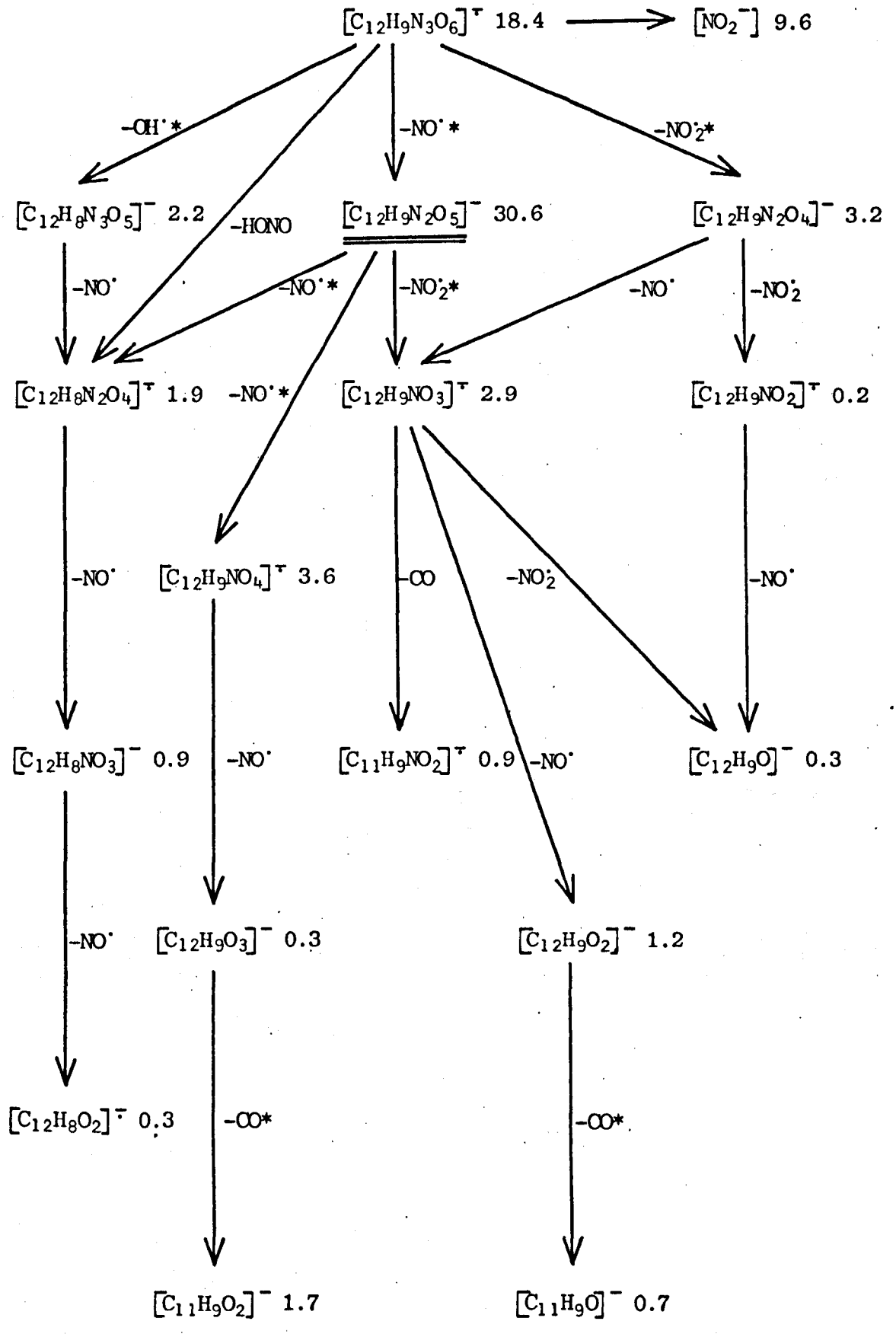


Fig.4.1.59 1,5,7-trinitro-2,3-dimethylnaphthalene, negative ion.

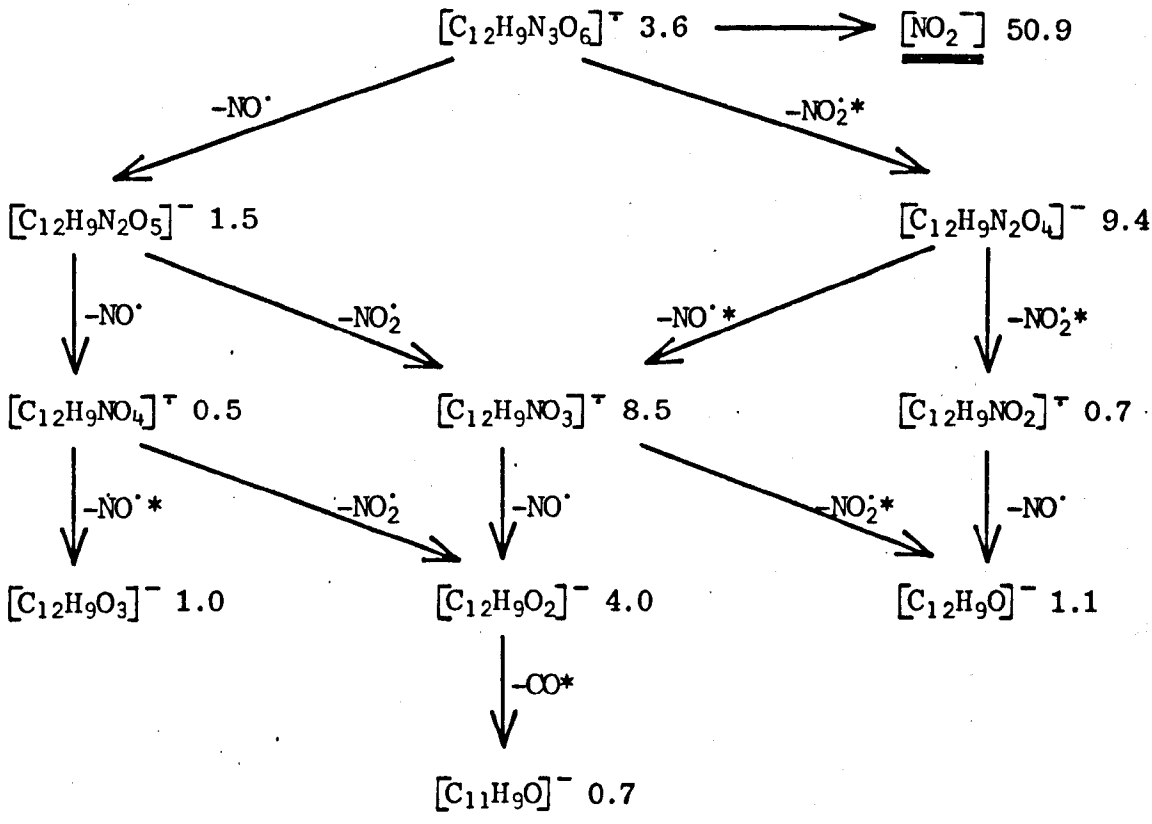


Fig.4.1.60 1,6,8-trinitro-2,3-dimethylnaphthalene, negative ion.

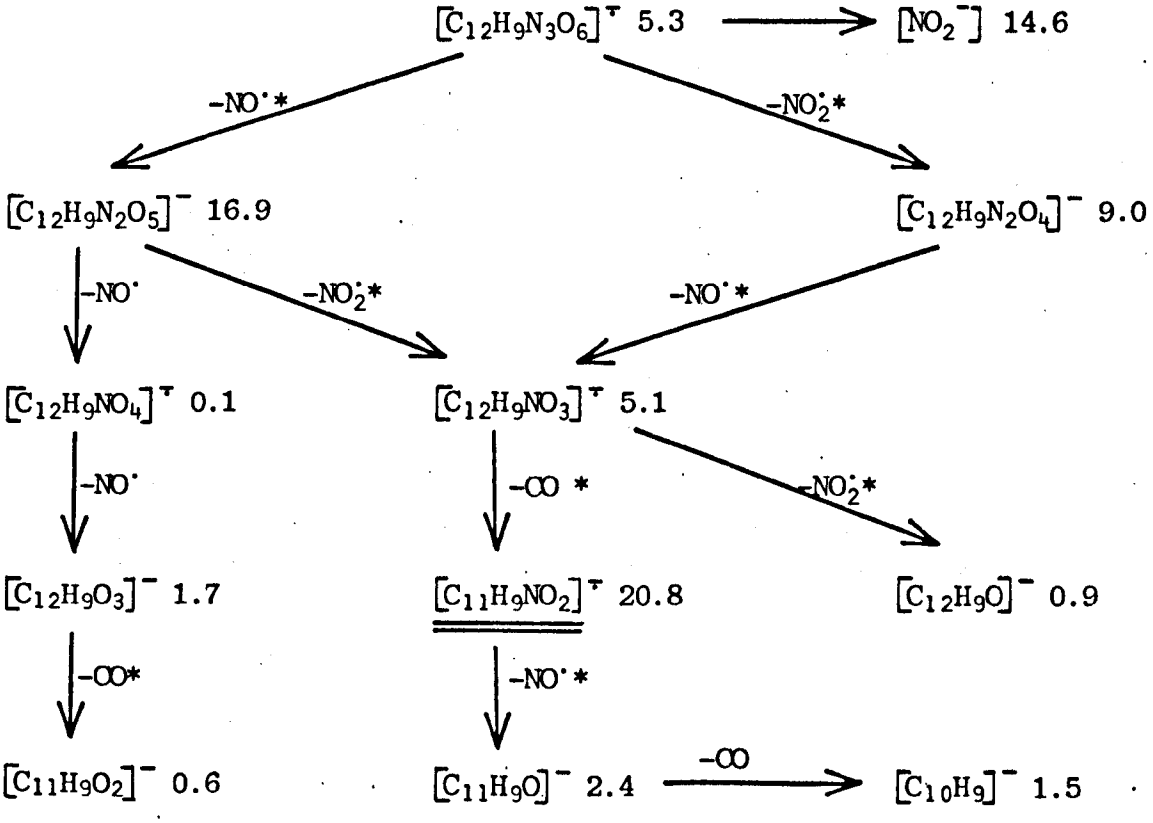


Fig.4.1.61 5,6,8-trinitro-2,3-dimethylnaphthalene, negative ion.

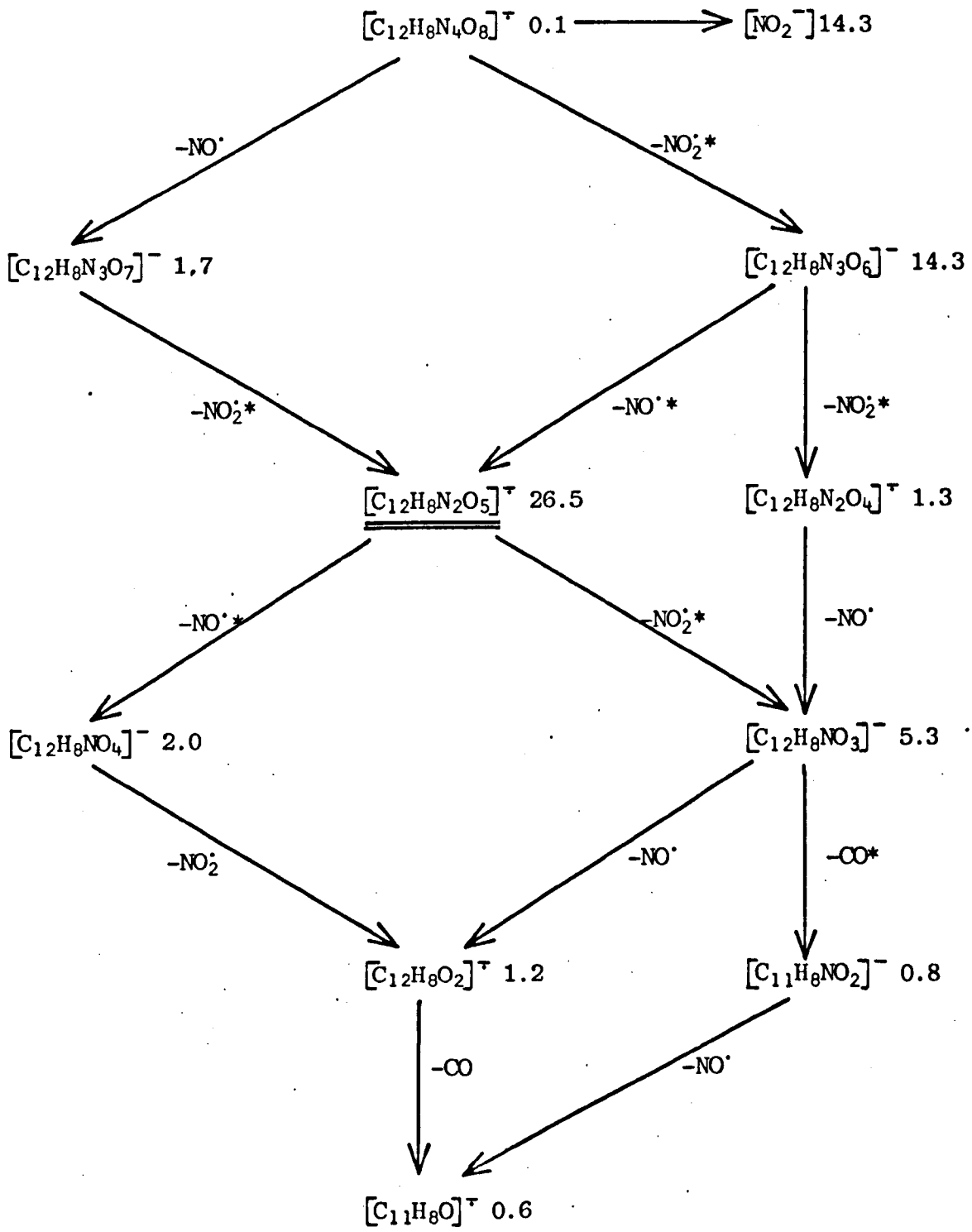


Fig.4.1.62 1,4,5,7-tetranitro-2,3-dimethylnaphthalene, negative ion.

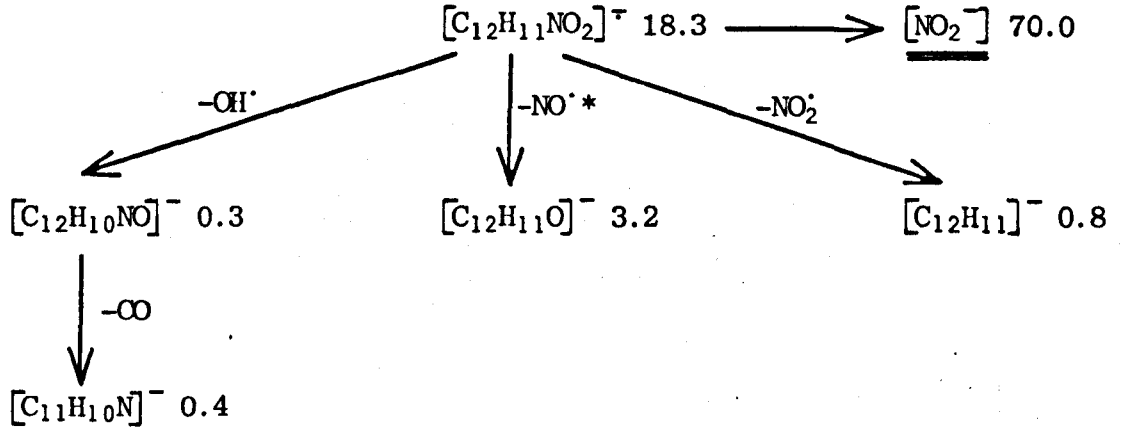


Fig.4.1.63 4-nitro-1,5-dimethylnaphthalene,negative ion.

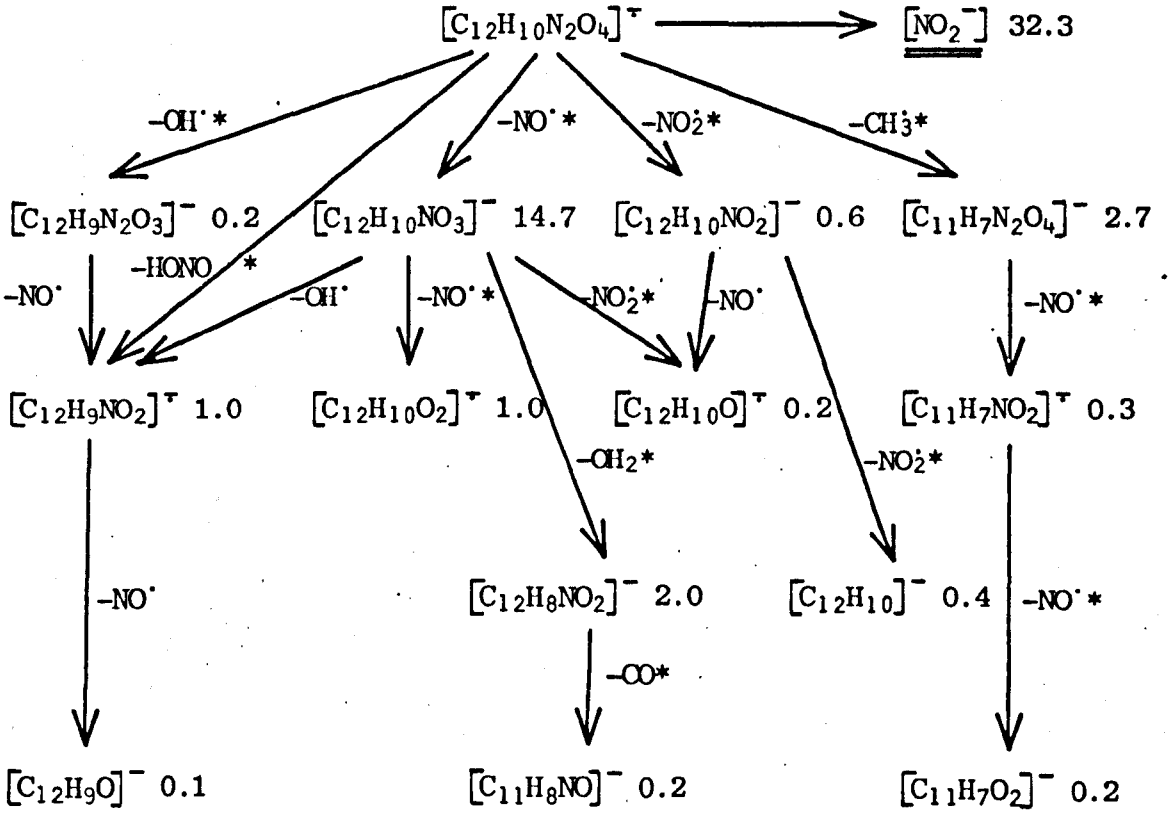


Fig.4.1.64 4,8-dinitro-1,5-dimethylnaphthalene,negative ion.

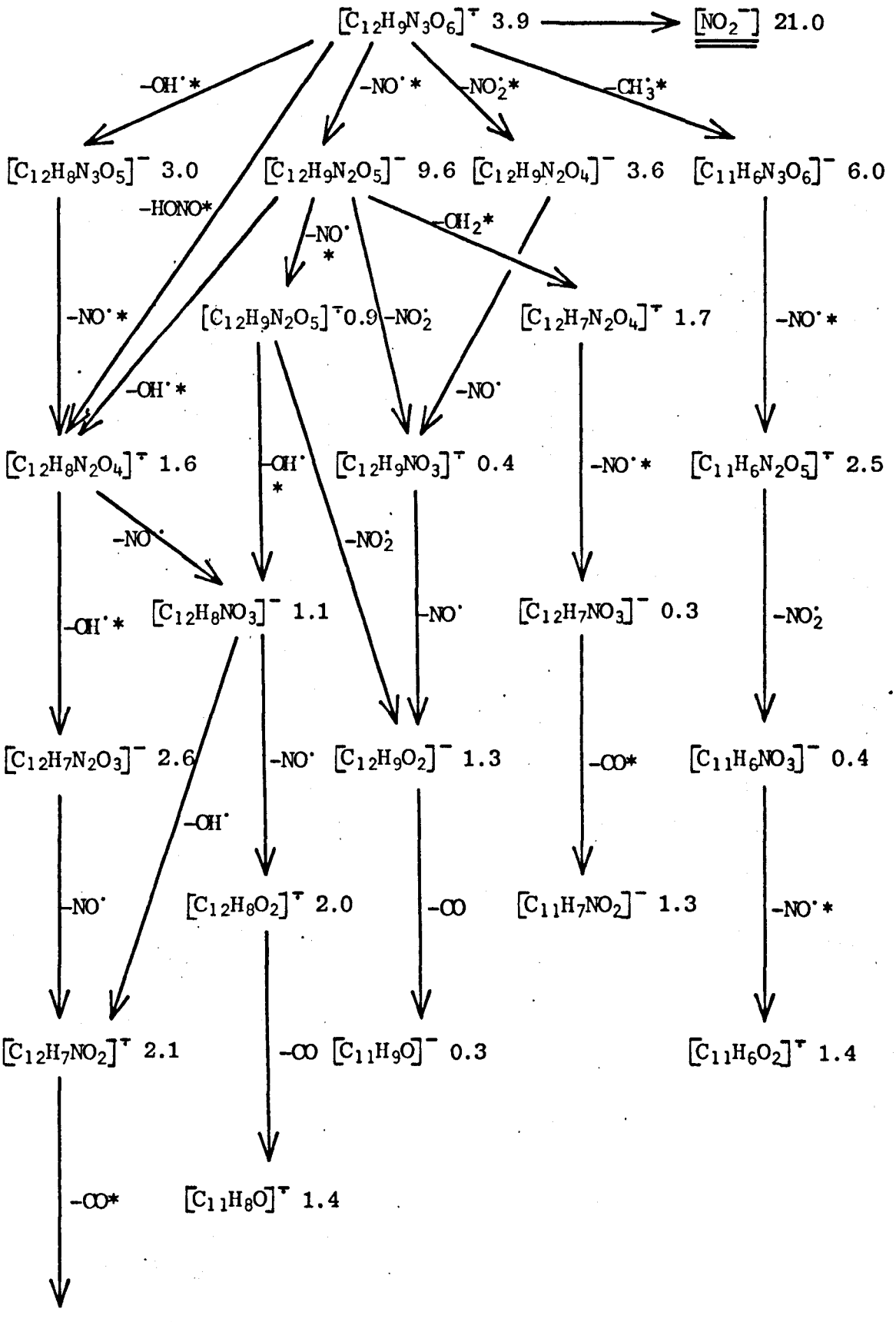


Fig.4.1.65 2,4,8-trinitro-1,5-dimethylnaphthalene, negative ion.

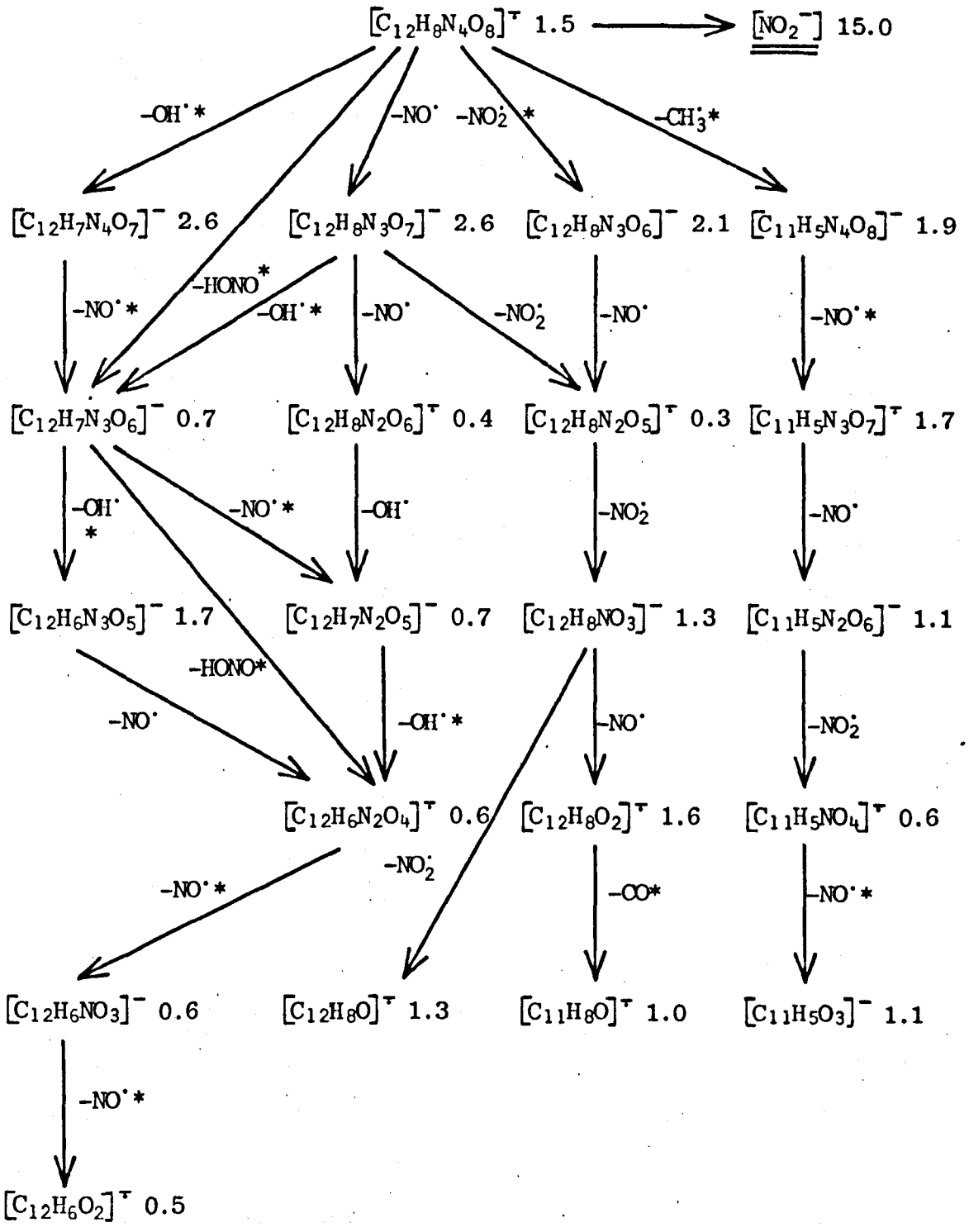


Fig.4.1.66 2,4,6,8-tetranitro-1,5-dimethylnaphthalene, negative ion.

4.2 Electronic Spectroscopy

4.2.1 Introductory Survey

The electronic spectra of the simpler nitroaromatic compounds have been studied in some detail[244,245,246]. The characteristic features may be illustrated by considering the spectrum of the simplest nitroaromatic compound, nitrobenzene. This consists of three bands in the accessible UV region, at λ_{max} 250, 280 and 330nm[247] (saturated hydrocarbon solvent). The shortest wavelength band has a high intensity ($log\varepsilon_{max}$ 3.94), and corresponds to the $^1L_a \leftarrow {}^1A$ transition of benzene (using the Platt notation[248]). This band has been described by Nagakura[247] as an "intramolecular charge-transfer band". The medium intensity band at 280nm ($log\varepsilon_{max}$ 2.81) corresponds to the $^1L_b \leftarrow {}^1A$ band of benzene, and consists primarily of a transition from the bonding to the anti-bonding π-orbitals of the ring system, with a smaller "charge-transfer" contribution. The low intensity band at 330nm ($log\varepsilon_{max}$ 2.15) is due to the localised n-π* transition of the nitro group. The bands which appear in the spectra of nitroaromatic compounds are subject to variation in position and intensity dependent on the steric hindrance to the coplanarity of the nitro group and the ring. The 250nm band of nitrobenzene undergoes a considerable hypochromic effect when bulky groups are substituted *ortho* to the nitro group, e.g. nitrobenzene has a $log\varepsilon_{max}$ of 3.94 at 250nm, whereas o-nitrotoluene has a $log\varepsilon_{max}$ of 3.78 and 2-nitro-m-xylene has a $log\varepsilon_{max}$ of 3.18[249,250]. This is because the twisting of the nitro group out of the plane of the ring reduces the π-π overlap between the nitro

group and the ring system,thereby inhibiting the transfer of charge. The 280nm band,having only a low charge-transfer character,does not fall in intensity with the increase of the interplanar angle between the nitro group and the ring to the same extent as the 250nm band[251], although a hypsochromic effect does occur. This is probably because a reduction in the extent of conjugation raises the energy of the excited state relative to the ground state. The n-π^* band at 330nm is subject to bathochromic and hypsochromic effects as the nitro group is twisted out of the plane of the ring. Thus for nitrobenzene,the 330nm band has a $log\varepsilon_{max}$ of 2.15,and for nitromesitylene the band has a $log\varepsilon_{max}$ of 2.60,λ_{max} 335nm. This may be attributed to the energy of the excited state being lowered by the π-electrons of the nitro group being localised rather than delocalised into the ring π-system.

The electronic spectra of 1-nitronaphthalene and 2-nitronaphthalene have been investigated[254]. As in the case of nitrobenzene,the spectra feature three bands in the accessible UV region; λ_{max} 1-nitronaphthalene 213,243 and 327nm; λ_{max} 2-nitronaphthalene 210,259 and 303nm. The most significant difference between the spectra of the two compounds is the molar extinction coefficients of the bands,being a factor of two greater for 2-nitronaphthalene than for 1-nitronaphthalene. In the case of 2-nitro-naphthalene,the substituent nitro group is coplanar with the ring,and there is a more extended conjugated system in this case than in the case of 1-nitronaphthalene where there is a degree of steric interaction between the nitro

group and the hydrogen atom at the 8-position.

4.2.2 The Electronic Spectra of the Nitro-1,5-Dimethylnaphthalenes and Nitro-2,3-Dimethylnaphthalenes

The electronic spectra of the nitro-1,5-dimethylnaphthalenes and nitro-2,3-dimethylnaphthalenes were found to consist of three bands in the 210-370nm region. The wavelengths and molar extinction coefficients of these bands are listed in table 4.2.1. For convenience, these bands will be referred to as Band I, Band II and Band III, corresponding to the low, medium and high wavelength bands respectively.

(i) Band I

With respect to their electronic spectra, the nitro-2,3-dimethylnaphthalenes may be divided into two classes. The first class includes those compounds in which all the nitro groups are *peri*-substituted, i.e. 1-nitro-2,3-dimethylnaphthalene, 5-nitro-2,3-dimethylnaphthalene, 1,8-dinitro-2,3-dimethylnaphthalene, 1,5-dinitro-2,3-dimethylnaphthalene, 1,4-dinitro-2,3-dimethylnaphthalene and 1,4,5-trinitro-2,3-dimethylnaphthalene. The second class includes all those compounds containing β-substituted nitro groups, i.e. 5,7-dinitro-2,3-dimethylnaphthalene, 1,5,7-trinitro-2,3-dimethylnaphthalene, 1,6,8-trinitro-2,3-dimethylnaphthalene, 5,6,8-trinitro-2,3-dimethylnaphthalene and 1,4,5,7-tetranitro-2,3-dimethylnaphthalene. For the first group, a general hypsochromic shift of the Band I maximum was observed with increasing substitution by nitro groups. For the mononitro isomers, the extinction coefficient at the Band I maximum of 5-nitro-2,3-dimethylnaphthalene was found to be greater than that of 1-nitro-2,3-dimethyl-

Table 4.2.1 Main bands and molar extinction coefficients ($l.mol^{-1}cm^{-1}$) of the electronic spectra of nitro-1,5-dimethylnaphthalenes and nitro-2,3-dimethylnaphthalenes.

Compound	Band I [c]		Band II		Band III	
2,3-DMN	268	*(3.77)*	306	*(3.08)*	-	
1-nitro-2,3-DMN	268	*(3.97)*	307	*(3.42)*	340	*(3.18)*
5-nitro-2,3-DMN	259	*(4.13)*	315	*(3.78)*	335	*(3.65)*
1,8-dinitro-2,3-DMN	236	*a*	308	*(3.70)*	*b*	
1,5-dinitro-2,3-DMN	239	*a*	330	*(3.85)*	*b*	
1,4-dinitro-2,3-DMN	257	*(4.30)*	307	*(3.70)*	342	*(3.48)*
5,7-dinitro-2,3-DMN	259	*(4.62)*	280	*(4.48)*	320	*(3.40)*
1,4,5-trinitro-2,3-DMN	233	*a*	297	*(4.00)*	*b*	
1,5,7-trinitro-2,3-DMN	257	*(4.70)*	286	*(4.45)*	345	*(3.85)*
1,6,8-trinitro-2,3-DMN	262	*(4.59)*	275	*(4.38)*	354	*(3.95)*
5,6,8-trinitro-2,3-DMN	255	*(4.68)*	277	*(4.54)*	255	*(3.90)*
1,4,5,7-tetranitro-2,3-DMN	258	*(4.74)*	276	*(4.30)*	353	*(4.04)*
1,5-DMN	297	*(3.78)*	316	*(3.15)*	-	
4-nitro-1,5-DMN	248	*(4.23)*	289	*(3.86)*	345	*(3.40)*
4,8-dinitro-1,5-DMN	240	*(4.68)*	303	*(4.14)*	345	*(3.95)*
2,4,8-trinitro-1,5-DMN	248	*(4.75)*	310	*(4.23)*	340	*(4.08)*
2,4,6,8-tetranitro-1,5-DMN	250	*(4.80)*	311	*(4.34)*	325	*(4.01)*

(a) Peak appeared as small shoulder on the tail of the $^1B_b \leftarrow {}^1A$ peak. *(b)* Peak obscured by broad Band II peak. *(c)* Wavelengths in nm; molar extinction coefficients expressed as $log\,\varepsilon$.

naphthalene. This result is not unexpected as this band has a high charge-transfer character (corresponding to the 250nm band of nitrobenzene),and the nitro group in 5-nitro-2,3-dimethylnaphthalene is less hindered than in 1-nitro-2,3-dimethylnaphthalene,with the effect that a greater degree of π-π overlap can take place. However,whereas for nitrobenzene derivatives in which the nitro group is unhindered there is a hypsochromic shift of the Band I maximum relative to nitrobenzene derivatives in which the nitro group is unhindered,the opposite effect was observed for the mononitro-2,3-dimethylnaphthalenes (see table 4.2.1). This appears to be a specific effect for 1-nitronaphthalene derivatives in which the nitro group is *ortho* to a methyl group[252]. This effect also appears to have operated for 1,4-dinitro-2,3-dimethylnaphthalene,for which the Band I maximum exhibits only a small hypsochromic shift with respect to 1-nitro-2,3-dimethylnaphthalene,in marked contrast to the large hypsochromic shift observed for the relatively less hindered 1,5-dinitro-2,3-dimethylnaphthalene (see table 4.2.1). For 1,8-dinitro-2,3-dimethylnaphthalene there was a hypsochromic shift of 32nm with respect to 1-nitro-2,3-dimethylnaphthalene. A similar hypsochromic shift (30nm) was observed for 1,8-dinitronaphthalene relative to 1-nitronaphthalene[253]. Clearly the high degree of steric hindrance between the adjacent *peri* substituted nitro groups resulted in the energy of the excited (charge-transfer) state being increased to a greater extent than the ground state. This effect was also observed for 1,4,5-trinitro-2,3-dimethylnaphthalene,in which all the

nitro groups are hindered (see table 4.2.1). For the second class of nitro-2,3-dimethylnaphthalenes, in which there is a β-nitro group, the position and intensity of the Band I maxima did not vary greatly (λ_{max} 252-262nm; $log\varepsilon_{max}$ 4.59-4.74). It is known that the extinction coefficient at the Band I maximum of 2-nitronaphthalene is three times greater than that of 1-nitronaphthalene[254], due to the unhindered β-nitro group being able to lie in the plane of the ring system, thereby facilitating the transfer of charge in the Band I transition. Clearly, for the nitro-2,3-dimethylnaphthalenes under consideration, the enhancement to the Band I transition afforded by the β-nitro group was so great that the presence of hindered α-nitro groups had relatively little effect on the intensity of the Band I maxima.

For the nitro-1,5-dimethylnaphthalenes, a hyperchromic effect effect was observed with increasing substitution of nitro groups. For 4-nitro-1,5-dimethylnaphthalene, the Band I maximum occurred at 248nm. Addition of an α-nitro group to give 4,8-dinitro-1,5-dimethylnaphthalene resulted in a hypsochromic shift of the band to 240nm. The addition of β-nitro groups to 4,8-dinitro-1,5-dimethylnaphthalene, to give 2,4,8-trinitro-1,5-dimethylnaphthalene and 2,4,6,8-tetranitro-1,5-dimethylnaphthalene, resulted in bathochromic shifts of the Band I maxima to 248 and 250nm respectively. This bathochromic shift is probably a characteristic effect of β-nitro groups in naphthalene systems, *cf* 1-nitronaphthalene and 2-nitronaphthalene for which the Band I maximum occurs at longer

wavelength in the latter case[253].

(ii) Band II

For the purposes of discussion, the nitro-2,3-dimethylnaphthalenes may again be divided into the two classes detailed above. For the first class, in which all the nitro groups are substituted on *peri*-positions, there was a general hypsochromic effect with increasing substitution of nitro groups. As Band II results from a π-π^* transition associated with the naphthalene π-system, the energy requirement of this transition should be reduced, i.e. the band maxima shifted to longer wavelength, with increasing conjugation of the π-system. Thus the molar extinction coefficient and λ_{max} value for the Band II transitions were found to be higher for 5-nitro-2,3-dimethylnaphthalene than for 1-nitro-2,3-dimethylnaphthalene, the extent of conjugation being greater in the former compound on account of the nitro group being closer to coplanarity with the ring than in the latter compound. For 1,4-dinitro-2,3-dimethylnaphthalene and 1,8-dinitro-2,3-dimethylnaphthalene, in which the nitro groups are severely hindered and cannot achieve coplanarity with the ring system, the Band II maxima were found to occur at practically the same λ_{max} value as 1-nitro-2,3-dimethylnaphthalene, whereas for 1,5-dinitro-2,3-dimethylnaphthalene, which has one relatively unhindered nitro group, the Band II maximum exhibited a marked bathochromic shift with respect to 1-nitro-2,3-dimethylnaphthalene. For 1,4,5-trinitro-2,3-dimethyl-naphthalene, in which all three nitro groups are hindered, the Band II maximum occurred at slightly shorter wavelength

than for 1-nitro-2,3-dimethylnaphthalene.

For the second class of nitro-2,3-dimethyl-naphthalenes,the effect of the β-nitro group on the Band II maxima was similar to the effect on the Band I maxima,in that variations in the position and intensity of the band were markedly reduced. Thus the Band II maximum of the relatively planar 1,5,7-trinitro-2,3-dimethylnaphthalene exhibited only small bathochromic and hyperchromic effects with respect to the relatively non-planar 1,6,8-trinitro-2,3-dimethylnaphthalene (see table 4.2.1).

For the nitro-1,5-dimethylnaphthalenes,there is a bathochromic shift and hyperchromic effect on increasing the extent of substitution of nitro groups. This would appear to be consistent with a hyperconjugative effect operating,which would increase with increasing substitution of nitro groups. Thus the extent of conjugation of 4,8-dinitro-1,5-dimethylnaphthalene should be greater than for 4-nitro-1,5-dimethylnaphthalene (fig.4.2.2).

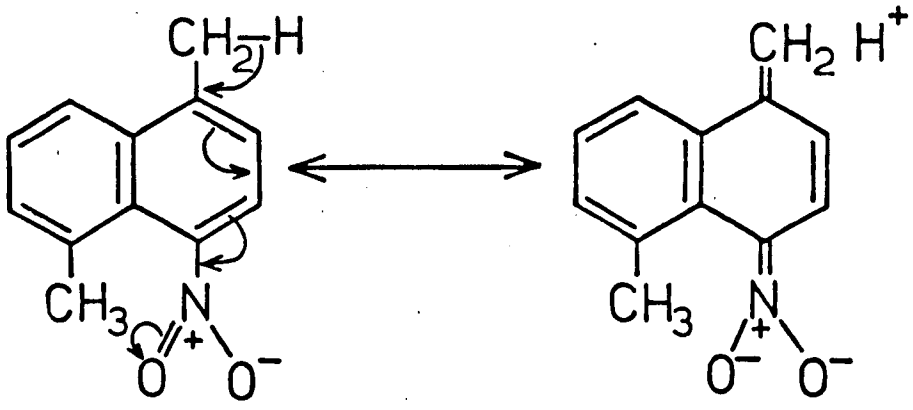


Fig.4.2.2a

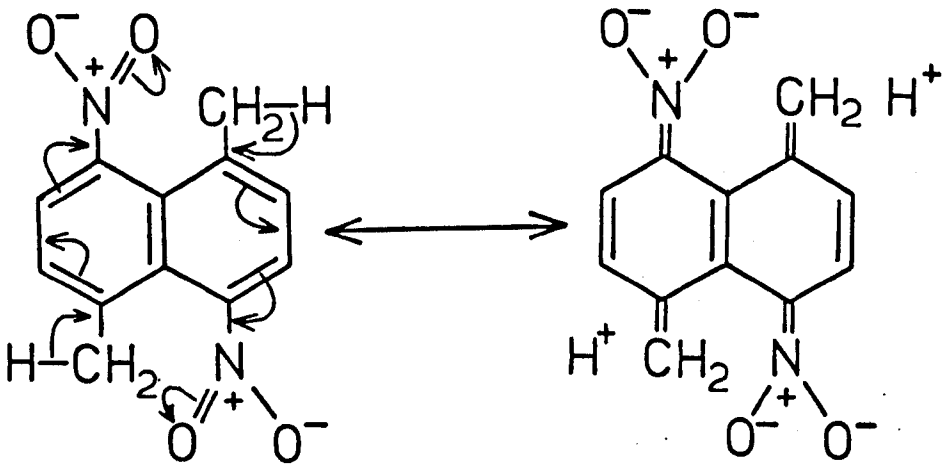


Fig.4.2.2b

The introduction of β-nitro groups,to give 2,4,8-trinitro-1,5-dimethylnaphthalene and 2,4,6,8-tetranitro-1,5-dimethylnaphthalene was found to produce smaller bathochromic and hyperchromic effects. This would be expected as β-nitro groups would be hindered by α-methyl groups,and could not provide an increase in conjugation as great as for *peri*-substituted nitro groups.

(ii) Band III

The Band III transitions exhibited the lowest molar extinction coefficients of the three bands studied. Band III corresponds to localised n-π* transitions of the nitro group,i.e.transfer of an electron from the non-bonding orbitals on the oxygen atoms to the antibonding π-orbitals of the nitro group π-system. Consequently,the Band III maxima will exhibit a hypsochromic shift where the nitro group π-electrons are delocalised into the naphthalene π-system,and a bathochromic shift where the nitro group is sterically hindered,and its π-electrons are localised. Thus the wavelength of the Band III maximum for 1-nitro-2,3-dimethylnaphthalene was found to

be greater than that for 5-nitro-2,3-dimethylnaphthalene, the nitro group of the former being more hindered than the latter. The wavelength of the Band III maximum is also dependent upon the stability of the ground state,which can be enhanced where resonance stabilisation is possible, e.g.by nitro groups being orientated *meta* to each other. Thus in the nitro-2,3-dimethylnaphthalene series,the Band III maximum occurs at shortest wavelength for 5,7-dinitro-2,3-dimethylnaphthalene. In the nitro-1,5-dimethylnaphthalene series,the Band III maxima of 2,4,8-trinitro-1,5-dimethylnaphthalene and 2,4,6,8-tetranitro-1,5-dimethylnaphthalene, which both contain *meta*-orientated pairs of nitro groups, were found to exhibit a hypsochromic shift with respect to 4-nitro-1,5-dimethylnaphthalene and 4,8-dinitro-1,5-dimethylnaphthalene.

4.2.3 Experimental Section

The spectra were recorded in cyclohexane (spectroscopic grade) at room temperature using a Pye-Unicam SP8000 UV Spectrophotometer with 10mm path length silica cells. The wavelengths of the peak maxima and the corresponding molar extinction coefficients are given in table 4.2.1.

4.3 Nuclear Magnetic Resonance Spectroscopy

4.3.1 Introductory Survey

NMR spectroscopy is a powerful tool in the investigation of substitution patterns in nitroaromatic compounds. However, interest has recently centred on the quantitative effect of the nitro group upon the chemical shifts of protons in a nitroaromatic compound[190]. The chemical shift of a proton is largely dependent upon its local diamagnetic shielding, which is in turn dependent upon the electron density at its site of substitution. A nitro group affects the chemical shift of a proton in a number of ways. Firstly, an electrostatic effect[255] due to the dipole of the nitro group causes a polarization of the electrons in a C-H bond, with consequent deshielding of the proton concerned. Secondly, an inductive effect deshields protons substituted close to the nitro group by inductive withdrawal of electrons along the sigma-bonds. Thirdly, a mesomeric effect strongly deshields protons substituted *ortho* and *para* to a nitro group by resonance interaction via the aromatic π-system. Lastly, a diamagnetic anisotropic effect strongly shields a proton sited above or below the plane of the nitro group. Little published information is available regarding theoretical estimates of the diamagnetic anisotropy of the nitro group[256]. However, fig.4.3.1 may be taken to be a fair representation of the shielding zones of the nitro group.

A number of quantitative studies of proton chemical shifts in nitroaromatic compounds have been made. Yamaguchi[256] has investigated the NMR spectra of nitrotoluenes

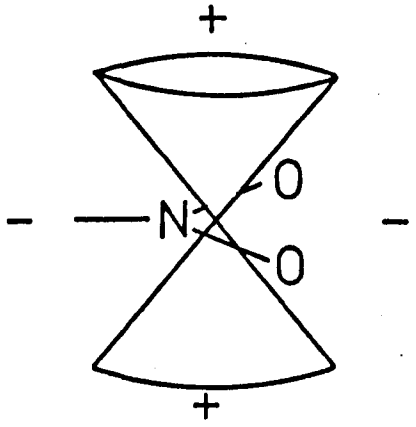


Fig.4.3.1

and nitroxylenes,and has estimated the effect on the chemical shifts of the methyl group by *ortho*,*meta* and *para* nitro groups to be -0.25,-0.13 and -0.12 ppm respectively. The shift due to the *ortho*-interaction is large because the diamagnetic anisotropic effect can operate very strongly in this case. However,this effect is dependent upon the orientation of the nitro group,and this has been demonstrated by investigations of the methyl derivatives of 1- and 2-nitronaphthalenes[257]. Thus for 1-methyl-2-nitronaphthalene,the chemical shift of the methyl group was lowered by 0.16 ppm with respect to 1-methylnaphthalene. This is comparable to the *ortho*-nitro group effect experienced in nitroxylenes (see above). For 2-methyl-1-nitronaphthalene,there was no alteration of the chemical shift of the methyl group with respect to 2-methyl-naphthalene. This may be attributed to steric hindrance of the 1-nitro group by the 8-proton,which orientates the nitro group such that the 2-methyl group lies in a shielding zone,thus neutralising the other deshielding effects of the nitro group,i.e.inductive,mesomeric and electrostatic. In the case of 8-methyl-1-nitronaphthalene,the steric hindrance of the nitro group by the methyl group is such that the methyl group is situated within the strongest

region of the nitro group shielding "cone",and its chemical shift is raised by 0.15 ppm with respect to 1-methyl-naphthalene.

The effect of nitro group anisotropy is greater for aromatic protons. Thus the 8-proton of 1-nitro-naphthalene is shifted by 0.79 ppm to lower field by the presence of the 1-nitro group,but this is reduced to 0.025 ppm by the substitution of a methyl group at the 2-position, which markedly affects the orientation of the 1-nitro group. The steric hindrance to the 1-nitro group also affects the "quinoidal" or *para* resonance interaction with the 4-proton,the chemical shift of which is lowered by 0.33 ppm with respect to naphthalene,but this is reduced to 0.14 ppm by the presence of a methyl group at the 2-position. Clearly a number of factors have to be taken into account when considering the quantitative effect of a nitro group upon the chemical shifts of protons in a nitroaromatic compound.

4.3.2 NMR Spectra of Nitro-2,3-Diethylnaphthalenes

The chemical shifts of the aromatic and methyl protons of fourteen nitro-2,3-dimethylnaphthalenes, recorded in deuterochloroform solvent, are presented in table 4.3.1. In the case of three and four proton interactions, it has not been possible to obtain the chemical shifts of the protons involved.

Table 4.3.1 Chemical shifts for nitro-2,3-dimethylnaphthalenes recorded in deuterochloroform (ppm; with respect to TMS as 10.00).

Compound	Aromatic						Methyl	
	1	4	5	6	7	8	2	3
1-nitro-2,3-DMN	-	*	(2.20 -2.60,m,5H)				7.67	7.54
5-nitro-2,3-DMN	*	*	-	(1.60-2.60,m,5H)			7.55	7.54
1,8-dinitro-2,3-DMN	-	1.80	(2.0-2.50,m,4H)			-	7.51	7.45
1,5-dinitro-2,3-DMN	-	1.50	-	(1.50-2.50,m,4H)			7.60	7.45
1,4-dinitro-2,3-DMN	-	-	2.31	2.31	2.31	2.31	7.58	7.58
5,7-dinitro-2,3-DMN	2.08	1.60	-	1.10		1.10	7.43	7.47
5,8-dinitro-2,3-DMN	2.01	2.01	-	1.82	1.82	-	7.48	7.48
1,4,5-trinitro-2,3-DMN	-	-	-	(1.75-2.30,m,3H)			7.55	7.50
1,5,7-trinitro-2,3-DMN	-	1.46	-	1.05[a]	-	1.22[a]	7.54	7.35
1,5,8-trinitro-2,3-DMN	-	1.88	-	1.67	1.67	-	7.48	7.38
1,6,8-trinitro-2,3-DMN	-	1.84	1.22[a]	-	1.05[a]	-	7.46	7.35
5,6,8-trinitro-2,3-DMN	1.61	2.35	-	-	1.22	-	7.45	7.40
1,4,5,7-tetranitro-2,3-DMN	-	-	-	1.07[a]		1.22[a]	7.37	7.44
1,4,5,8-tetranitro-2,3-DMN	-	-	-	1.80	1.80	-	7.42	7.42

* Singlet - could not be resolved from complex multiplet.

(a) AB quartet, J_{AB} 2Hz.

(A) Methyl Protons

In general,it may be seen that the chemical shifts of the methyl protons vary with variation in the substitution pattern of nitro groups,but to a far smaller extent than the chemical shifts of the aromatic protons. This is undoubtedly because the methyl protons are effectively "insulated" from the aromatic system,and thus the mesomeric effects of the nitro group are reduced to a minimum. For the purposes of discussion,the fourteen nitro-2,3-dimethylnaphthalenes may be divided into three classes,*viz* those in which the 1- and 4-positions are unsubstituted,those in which the 1-position is substituted,and those in which both the 1- and 4-positions are substituted.

The first class of compounds comprises 5-nitro-2,3-dimethylnaphthalene, 5,7-dinitro-2,3-dimethylnaphthalene, 5,8-dinitro-2,3-dimethylnaphthalene and 5,6,8-trinitro-2,3-dimethylnaphthalene. Due to the different dilutions used in each case,the estimated accuracy of the chemical shifts is only *ca* ±0.04 ppm. However,a general decrease in the chemical shifts of the methyl protons with increased substitution of nitro groups is apparent. The difference in chemical shift of the two methyl groups in any compound is only 0.05 ppm at maximum,indicating that the *direct* effect of nitro groups in the non-methylated ring on the methyl groups is very slight.

The second class of compounds,i.e.those in which the 1-position is substituted,may be divided into two groups,(A) those in which the 8-position is unsubstituted and (B) those in which the 8-position is substituted.

Group A comprises 1-nitro-2,3-dimethylnaphthalene, 1,5-dinitro-2,3-dimethylnaphthalene and 1,5,7-trinitro-2,3-dimethylnaphthalene. Group B comprises 1,8-dinitro-2,3-2,3-dimethylnaphthalene, 1,5,8-trinitro-2,3-dimethyl-naphthalene and 1,6,8-trinitro-2,3-dimethylnaphthalene. These are illustrated in fig.4.3.2,together with the chemical shift differences of the methyl groups ($X=NO_2$).

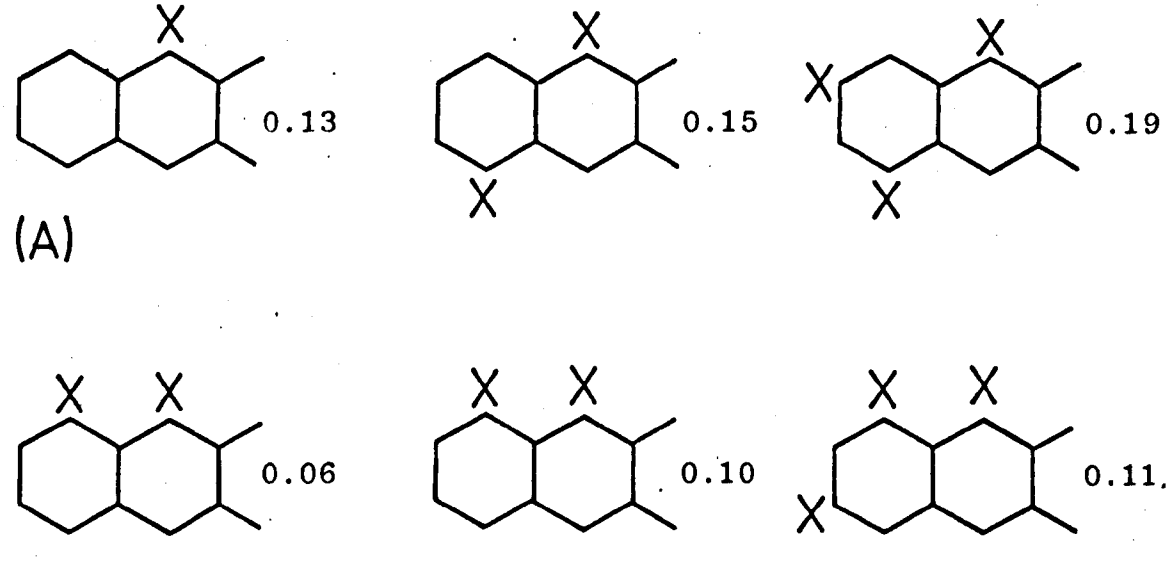


Fig.4.3.2

The most interesting feature of this class of compound is that the 2-methyl group has a higher chemical shift than the 3-methyl group. This phenomenon has been reported by Wells[257] for 1-nitro-2,3-dimethylnaphthalene,and is confirmed in the present work by the observation that the 3-methyl group resonance,which is broadened due to coupling with the 4-proton,is at lower field than the 2-methyl group resonance,which appears as a sharp peak. However,for group A,the separation between the methyl resonances (average 0.16 ppm) is greater than for group B (average 0.09 ppm). The most important effect of the 1-nitro group

upon the chemical shift of the 2-methyl group is that of diamagnetic anisotropy. In the case of group A,the 1-nitro group is hindered by the 8-proton,and is therefore twisted out of the plane of the ring to such an extent that the 2-methyl group lies within the shielding "cone" of the nitro group (*cf* 1-nitro-2-methylnaphthalene above). This therefore raises the chemical shift of the 2-methyl group with respect to the 3-methyl group. In the case of group B, the 1-nitro group is severely hindered by the 8-nitro group,and the plane of the 1-nitro group may be almost perpendicular to the plane of the ring. The fact that the chemical shift difference of the 2- and 3-methyl groups is lower in these cases appears to indicate that the change in orientation of the 1-nitro group results in the 2-methyl group being in a weaker region of the nitro group's shielding "cone",and therefore its chemical shift would be raised less with respect to the 3-methyl group than in the case of group A.

The third class of compounds,in which both the 1- and 4-positions are substituted,comprises 1,4-dinitro-2,3-dimethylnaphthalene, 1,4,5-trinitro-2,3-dimethylnaphthalene, 1,4,5,7-tetranitro-2,3-dimethylnaphthalene and 1,4,5,8-tetranitro-2,3-dimethylnaphthalene. It is interesting to observe that the chemical shifts of the methyl protons of 1,4-dinitro-2,3-dimethylnaphthalene are higher than those of 5,8-dinitro-2,3-dimethylnaphthalene. As the former compound has nitro groups substituted *ortho* to both methyl groups,whereas the latter does not,this confirms the observation made above that a methyl group at the 2-position

lies in a shielded region of the shielding "cone" of the nitro group at the 1-position. The addition of a nitro group at the 5-position in 1,4-dinitro-2,3-dimethyl-naphthalene to give 1,4,5-trinitro-2,3-dimethylnaphthalene causes the chemical shift of the 3-methyl group to be lowered by 0.05 ppm with respect to the 2-methyl group. A similar change in chemical shifts of the methyl groups (0.07 ppm) is observed for 1,4,5,7-tetranitro-2,3-dimethyl-naphthalene. For both these compounds the 4-nitro group is more hindered than the 1-nitro group,and thus the nitro-group shielding effect is less for the 3-methyl group than for the 2-methyl group,for the reasons given in the preceding paragraph. For 1,4,5,8-tetranitro-2,3-dimethyl-naphthalene,both the 1- and 4-nitro groups are severely hindered,and it is interesting to note that the chemical shift of the single methyl resonance is of intermediate value between the chemical shifts of the methyl resonances of the isomer 1,4,5,7-tetranitro-2,3-dimethylnaphthalene.

(B) Aromatic Protons

The chemical shifts of the aromatic protons of the nitro-2,3-dimethylnaphthalenes vary considerably with the pattern of substitution of nitro groups. This is undoubtedly because the aromatic protons,being bonded to the aromatic nucleus,are particularly susceptible to mesomeric effects via the aromatic π-system. This effect is illustrated by reference to the chemical shifts of the 4-protons in those compounds substituted at the 1-position, i.e.the compounds shown in fig.4.3.2. For 1,5-dinitro-2,3-dimethylnaphthalene and 1,5,7-trinitro-2,3-dimethyl-

naphthalene (group A),the chemical shift of the 4-proton is 1.50 and 1.46 respectively. For 1,8-dinitro-2,3-dimethylnaphthalene, 1,5,8-trinitro-2,3-dimethylnaphthalene and 1,6,8-trinitro-2,3-dimethylnaphthalene,the chemical shift of the 4-proton is 1.80,1.88 and 1.84 respectively. This is clearly due to a variation in the "quinoidal" or *para* resonance interaction of the 1-nitro group with the 4-proton,which is illustrated in fig.4.3.3 for 1,5,7-trinitro-2,3-dimethylnaphthalene and 1,5,8-trinitro-2,3-dimethylnaphthalene.

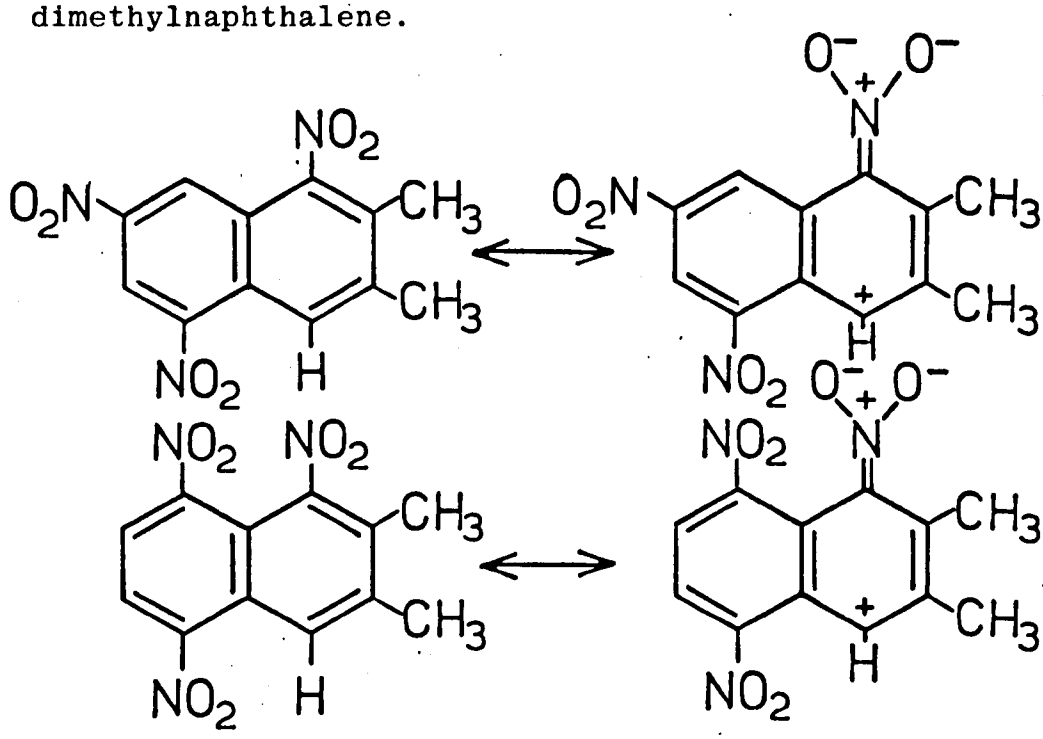


Fig.4.3.3

In these two cases,the 4-proton is subject to the same diamagnetic anisotropic effect from the 5-nitro group,and so the difference in chemical shift of the 4-proton (0.42 ppm) must be attributed to the hindrance of the 1-nitro group being greater for 1,5,8-trinitro-2,3-dimethylnaphthalene than for 1,5,7-trinitro-2,3-dimethylnaphthalene,resulting

in the "quinoidal" interaction being greater in the former than in the latter case.

In the case of unhindered β-nitro groups, the diamagnetic anisotropic effect is very powerful. Thus the lowest chemical shifts of aromatic protons are observed for protons *ortho* to β-nitro groups, e.g. in 1,5,7-trinitro-2,3-dimethylnaphthalene, 1,6,8-trinitro-2,3-dimethylnaphthalene and 1,4,5,7-tetranitro-2,3-dimethylnaphthalene (see table 4.3.1). This is clearly because the β-nitro group is almost coplanar with the ring (see sec.4.2.1), and the protons *ortho* to it lie within the strongest region of the nitro group's "deshielding zone" (fig.4.3.1). All α-nitro groups are hindered, and the strength of their interactions with *peri*-protons will be dependent upon the degree of hindrance. This may be illustrated by comparing the chemical shifts of the *peri*-protons in 5,8-dinitro-2,3-dimethylnaphthalene and 1,4-dinitro-2,3-dimethyl-naphthalene, which are 2.01 and 2.31 respectively. The nitro groups in the latter compound will be forced out of the plane of the ring to a greater extent than in the former compound, with the expected result that the *peri*-protons in the latter compound will be "deeper" into the shielding "cone" of the nitro groups and hence be more strongly shielded than the *peri*-protons in the former compound.

4.3.3 NMR Spectra of Nitro-1,5-Dimethylnaphthalenes

The chemical shifts of the aromatic and methyl protons of seven nitro-1,5-dimethylnaphthalenes, recorded in deuterochloroform, are presented in table 4.3.2

Compound	Aromatic						Methyl	
	2	3	4	6	7	8	1	5
4-nitro-1,5-DMN	(2.10-2.90,m,5H)						7.33	7.52
4,6-dinitro-1,5-DMN	2.25[a]	2.10[a]	-	-	2.15[b]	1.90[b]	7.20	7.50
4,7-dinitro-1,5-DMN	2.51[b]	2.22[b]	-	1.70[c]	-	1.10[c]	7.18	7.40
4,8-dinitro-1,5-DMN	2.50[d]	2.10[d]	-	2.50[d]	2.10[d]	-	7.40	7.40
2,4,7-trinitro-1,5-DMN	-	1.70	-	1.55[c]	-	0.80[c]	6.98	7.30
2,4,8-trinitro-1,5-DMN	-	1.80	-	2.30[b]	1.90[b]	-	7.35	7.35
2,4,6,8-tetranitro-1,5-DMN	-	1.65	-	-	1.65	-	7.30	7.30

(a) AB quartet, J_{AB} 9Hz. *(b)* AB quartet, J_{AB} 7Hz.

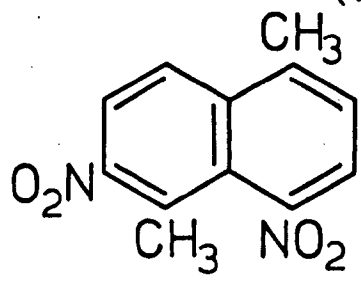
(c) AB quartet, J_{AB} 2Hz. *(d)* AB quartet, J_{AB} 8Hz.

(A) Methyl Protons

The methyl groups in nitro-1,5-dimethylnaphthalenes are substituted on *peri*-positions, and are therefore subject to three main types of interaction with nitro groups :- (1) resonance or "quinoidal" interaction with *para*-nitro groups, (2) *ortho*-interaction, and (3) *peri*-interaction. The "quinoidal" effect, which is powerful for aromatic protons (see sec.4.3.2B), is a relatively weak deshielding effect for methyl groups. The *ortho*-interaction, which raises the chemical shift of β-methyl groups in naphthalene systems, tends to lower the chemical shift of α-methyl

groups[257]. The *peri*-interaction,which is the most powerful effect,raises the chemical shift of a methyl group substituted on an adjacent *peri*-position to a nitro group. These three effects are demonstrated by the chemical shift values for 4,6-dinitro-1,5-dimethylnaphthalene,shown in fig.4.3.4.

(7.20)



(7.50)

Fig.4.3.4

Analysis of the NMR spectrum of this compound revealed that the 5-methyl group,being adjacent to two nitro groups, and therefore providing a sharp resonance,had a higher chemical shift value than the 1-methyl group which,being *ortho* to an aromatic proton,had a broadened resonance. The chemical shift of the 1-methyl group is lowered by the "quinoidal" effect of the 4-nitro group. The chemical shift of the 5-methyl group is reduced by being *ortho* to the 6-nitro group,but this was more than counterbalanced by the enhancing effect of the *peri*-interaction of the 4-nitro group. That the *peri*-interaction is more powerful than the *ortho*-interaction is demonstrated by comparing the chemical shifts of the methyl protons in the isomers 2,4,7-trinitro-1,5-dimethylnaphthalene and 2,4,8-trinitro-1,5-dimethylnaphthalene,as shown in fig.4.3.5.

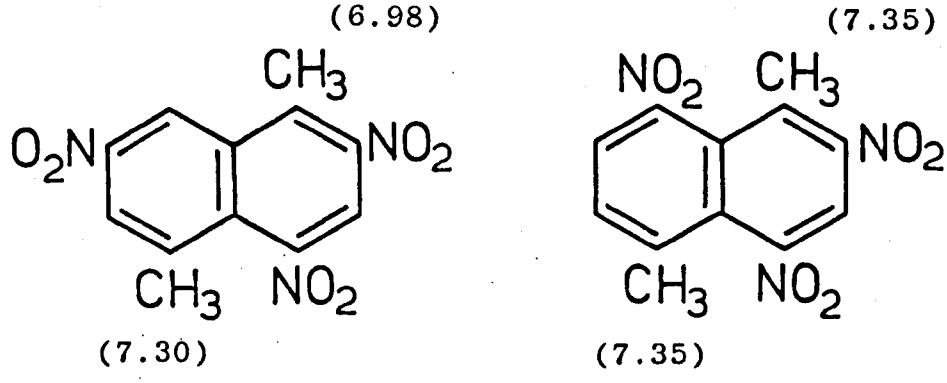


Fig.4.3.5

In the case of 2,4,8-trinitro-1,5-dimethylnaphthalene, the methyl groups are both substituted *peri* to nitro groups,and although the 1-methyl group is *ortho* to the 2-nitro group,the effect upon the chemical shift is so slight with respect to the enhancing *peri*-interaction of the 8-nitro group that the resonances appear as a slightly broadened singlet. In the case of 2,4,7-trinitro-1,5-dimethylnaphthalene,the 5-methyl group is *peri* to the 4-nitro group,and has a similar chemical shift to the 5-methyl group of 2,4,8-trinitro-1,5-dimethylnaphthalene. The 1-methyl group,however,has a nitro group substituted *ortho* to it,but does not have a nitro group substituted *peri* to it,and the loss of the *peri*-interaction causes the chemical shift of the 1-methyl group to be lowered by 0.32 ppm with respect to the 5-methyl group.

(B) Aromatic Protons

The effect of nitro group substitution upon the chemical shifts of aromatic protons for the nitro-1,5-dimethylnaphthalenes is similar to that found for the nitro-2,3-dimethylnaphthalenes,with the exception that

there are no examples of "quinoidal" interactions or *peri*-interactions between the nitro groups and aromatic protons for the nitro-1,5-dimethylnaphthalenes. Thus the lowest chemical shifts were observed for protons *ortho* to unhindered β-nitro groups, i.e. the 6- and 8-protons of 4,7-dinitro-1,5-dimethylnaphthalene and 2,4,7-dinitro-1,5-dimethylnaphthalene, for similar reasons to those given in section 4.3.2B. The chemical shifts of other protons *ortho* to nitro groups were found to be dependent upon the degree of steric hindrance of the nitro group. Thus the 3-proton in 4,6-dinitro-1,5-dimethylnaphthalene, which is *ortho* to a *peri*-nitro group hindered by a *peri*-methyl group, has a lower chemical shift than the 7-proton in the same compound, which is *ortho* to a nitro group hindered by an *ortho*-methyl group.

4.3.4 Experimental Section

The NMR spectra of the compounds were recorded on a Perkin-Elmer R10 NMR spectrometer operating at 60.004MHz, with a probe temperature of 33.5°. The solvent used was deuterochloroform (99.5%). Solutions were prepared having concentrations of *ca* 10%; where the solubilities of the samples were too low to permit this, saturated solutions were used. Tetramethylsilane was used as an internal reference (10.00 ppm).

4.4 Electron Spin Resonance Spectroscopy

4.4.1 Introductory Survey

The electron-deficient π-system in polynitro-aromatic compounds results in the ready acceptance of an electron to form a radical anion. Such radical anions give rise to ESR spectra which on analysis can allow the determination of the π-electron spin densities at the magnetically active sites in the radical anion[258,259].

The ESR spectra of the radical anions of nitrobenzene, the dinitrobenzenes and trinitrobenzenes have been investigated[260,261,262]. In the case of nitrobenzene, the magnetically active nuclei are N^{14} (nitro group) and and H^1 (aromatic protons). The coupling constant of the N^{14} nucleus was found to be much greater than that of the aromatic protons, and thus the spectrum consists of a triplet split by coupling with other nuclei[263]. The coupling constant of the N^{14} nuclei was also found to be greater than the H^1 nuclei in the dinitrobenzenes. For the nitrotoluenes, the coupling constant of the N^{14} nucleus is larger, and that of the methyl protons smaller, for *ortho*-nitrotoluene than for *para*-nitrotoluene[264]. Thus for *ortho*-nitrotoluene, a_N=11.00, a_{CH_3}=3.12*g*; for *para*-nitrotoluene, a_N=10.79, a_{CH_3}=3.98*g*. It appears that the twisting of the nitro group out of the plane of the ring by steric hindrance generally increases the coupling constant of the N^{14} nucleus with respect to the coplanar case. The dinitronaphthalenes have attracted some interest, as for 1,8-dinitronaphthalene the coupling constants of the N^{14} nuclei are higher than for the other dinitronaphthalenes[259,265]. As in this case there is

considerable steric interaction between the nitro groups, the effect upon the N^{14} coupling constants must be the same as that observed in the case of *ortho*-nitrotoluene.

4.4.2 ESR Spectra of Nitro-1,5-Dimethylnaphthalenes and Nitro-2,3-Dimethylnaphthalenes

The ESR spectra of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene and 1,4-dinitro-2,3-dimethylnaphthalene are shown in figs.4.4.1 and 4.4.2 respectively. Due to the high multiplicities involved,i.e.525 for the former and 315 for the latter compound,it was not possible to obtain fully resolved spectra in either case,and hence it was not possible to obtain the coupling constants for the nitrogen atoms and aromatic protons in either compound. However,it can be seen that the two spectra exhibit a septet pattern,which implies that the largest coupling constants are those of the methyl protons. This may be contrasted to the case of the nitrotoluenes[264],in which the coupling constants of the nitrogen atoms are considerably higher those of the methyl protons.

4.4.3 Experimental Section

The radical anions of the two nitrodimethylnaphthalenes were prepared by chemical reduction with sodium metal,using the method described by Wells and Wilson[258]. The solvent used was tetrahydrofuran,which was thoroughly degassed,and dried by being allowed to stand in the presence of sodium/potassium alloy. The sample tube was prepared at a pressure of *ca* 10^{-6} *Torr*, and was maintained in liquid nitrogen until required. The spectra were recorded on a Varian E-3 ESR Spectrometer, using a field strength of 3000*g*,a frequency of 9GHz,and a temperature of -50°.

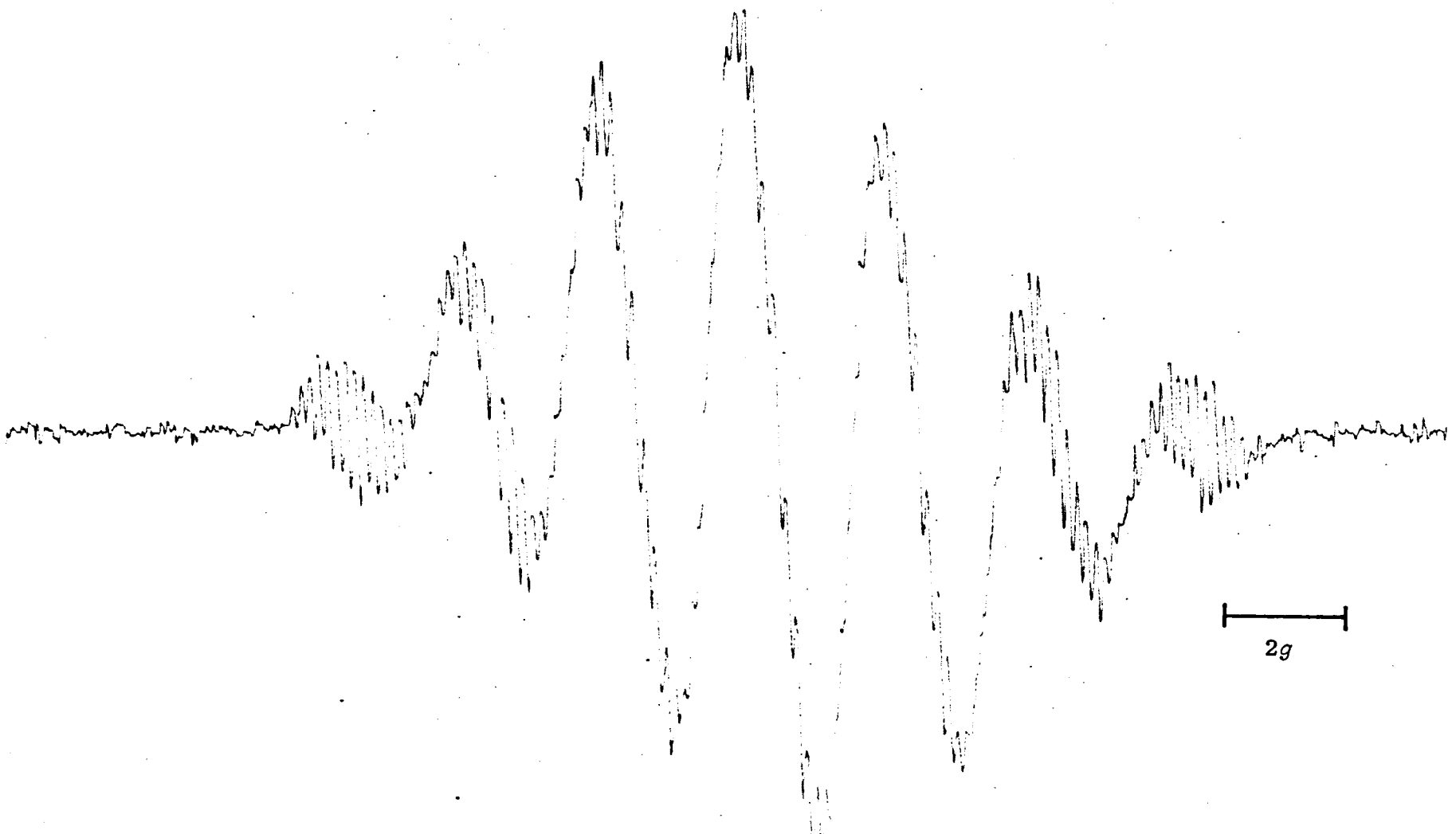


Fig.4.4.1 ESR spectrum of the radical anion of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene.

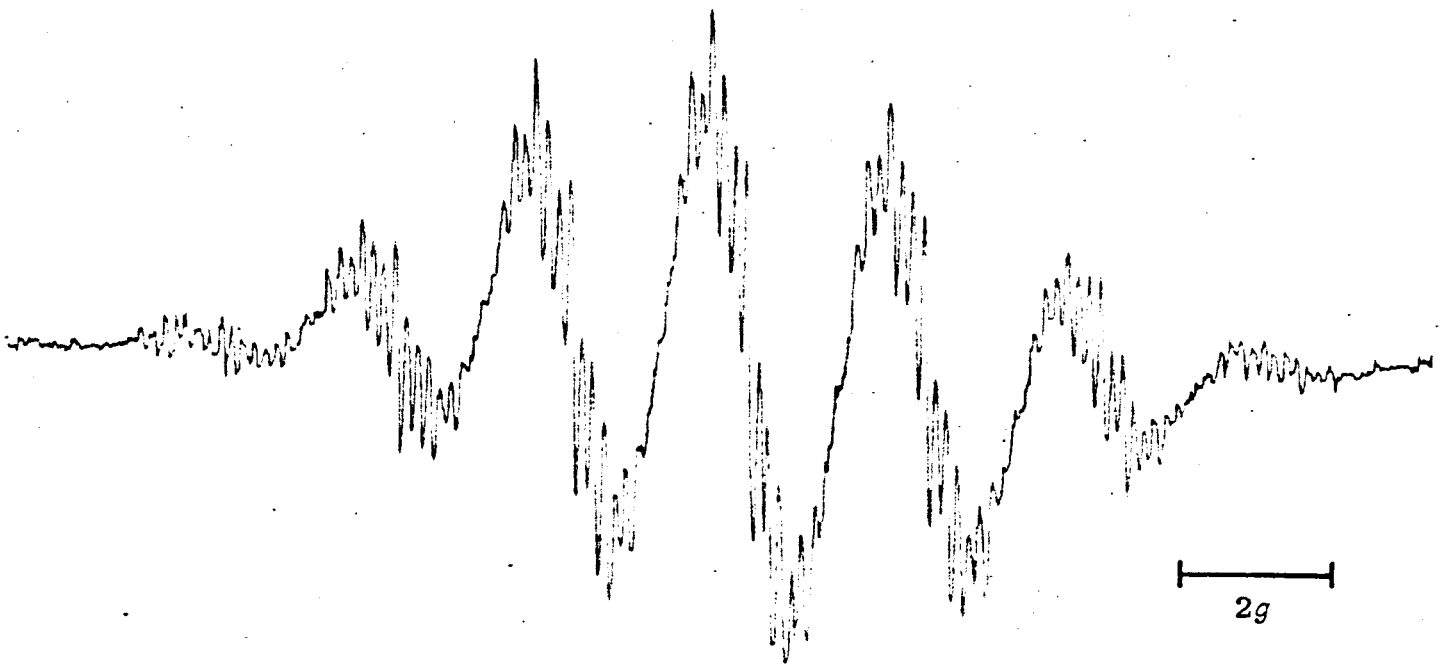


Fig.4.4.2 ESR spectrum of the radical anion of 1,4-dinitro-2,3-dimethylnaphthalene.

Appendices

A.1 Miscellaneous Reactions.

A.2 Courses attended during the period of this study.

A.1 Miscellaneous Reactions

A.1.1 Nitration of *Trans*-5,5'-Dimethyl-4,4'-Dinitro-*Bis*-1,2(1-Naphthyl)Ethene

In an attempt to synthesise compounds with structures analogous to that of the thermally stable explosive 2,2',4,4',6,6'-hexanitrostilbene, the nitration of *trans*-5,5'-dimethyl-4,4'-dinitro-*bis*-1,2(1-naphthyl) ethene (see sec.2.3.1), using nitric acid in acetic anhydride, was investigated. It appeared, however, that nitration occurred preferentially at the ethylenic bridge, as opposed to the aromatic ring system, and that the structure of the product was best described by that shown in fig.A.1.

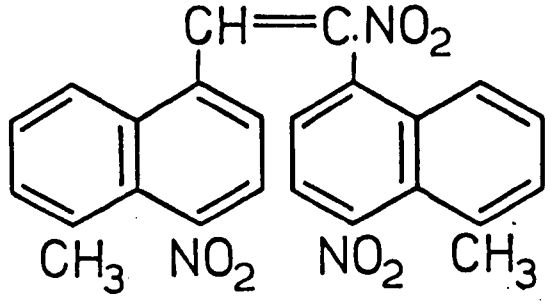


Fig.A.1

A.1.2 Reduction of *Trans*-5,5'-Dimethyl-4,4'-Dinitro-*Bis*-1,2(1-Naphthyl)Ethene

In an attempt to bring about a nitro-to-amino group reduction in *trans*-5,5'-dimethyl-4,4'-dinitro-*bis*-1,2(1-naphthyl)ethene, the compound was treated with hydrazine hydrate in the presence of palladium catalyst. However, the product was found to be 4,4'-diamino-5,5'-dimethyl-*bis*-1,2(1-naphthyl)ethane (fig.A.2), resulting

from reduction of both the nitro groups and the ethylenic linkage.

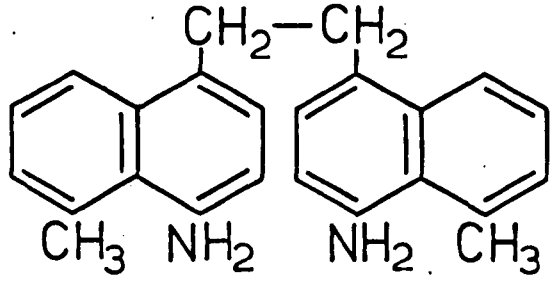


Fig.A.2

A.1.3 Experimental Section

(i) Nitration of trans-*5,5'-dimethyl-4,4'-dinitro*-bis-*1,2-(1-naphthyl)ethene* (43)

(43)(0.1g) was dissolved in acetic anhydride (7ml) and nitric acid (*d* 1.42;1ml) added dropwise,with stirring, whilst cooling in an ice-bath. After standing at 20° for 2h,the solution was poured into water (200ml). A solid was obtained (0.09g) which was chromatographed on a silica gel column (340 x 20mm),using chloroform as eluent, to yield *trinitro-5,5'-dimethyl*-bis-*1,2(1-naphthyl)ethene* (0.054g,48%),mp 202°. (Found: C,64.8; H,3.8; N,9.7. $C_{24}H_{17}N_3O_6$ requires C,65.0; H,3.8; N,9.5%); τ($CDCl_3$) 0.8 (1H,s),2.0-2.8(10H,m),7.39(3H,s) and 7.45(3H,s); *m/e* 443 (M^+).

(ii) Reduction of trans-*5,5'-dimethyl-4,4'-dinitro*-bis-*1,2-(1-naphthyl)ethene* (43)

(43)(0.5g) was dissolved in 95% ethanol (50ml),10% palladium on charcoal catalyst added,and the mixture refluxed with hydrazine hydrate (7ml) for 5h. Hot filtration,followed

by cooling, produced lime green crystals of *4,4'-diamino-5,5'-dimethyl*-bis-*1,2(1-naphthyl)ethane* (0.25g, 59%), mp 196°. (Found: C, 84.6; H, 6.9; N, 8.5. $C_{24}H_{24}N_2$ requires C, 84.7; H, 7.1; N, 8.2%); τ($CDCl_3$) 2.1-2.7(3h,m), 2.9 and 3.4(2H, ABq, J_{AB} 7Hz), 5.80(2H, broad singlet), 6.75(2H, s) and 7.00(3H, s); *m/e* 340 (M^+), high resolution mass spectrometry gave the molecular formula as $C_{24}H_{24}N_2$.

A.2 Courses attended during the period of this study in fulfilment of C.N.A.A.regulations

1970-1971

Quantum Theory (6 lectures).

Intoduction to Chromatography (6 lectures).

K.P.Computer Course (Algol Programming) (10 lectures).

1971-1972

Practical Mass Spectrometry (6 lectures).

Chemical Instrumentation (6 lectures).

1972-1973

NMR and ESR Spectroscopy (36 lectures).

1974 - Symposium on Liquid-Liquid Chromatography (Kingston Polytechnic),1 day.

During the period of this study I have given a research colloquium and have attended various research colloquia given by internal and external lecturers at Kingston Polytechnic.

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