STUDIES OF SOME ELECTRON DEFICIENT AROMATIC SYSTEMS

by

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SUMMARY

A study has been made of the properties of the electron deficient π-systems in the compounds 3,5,6,8-tetranitroacenaphthene (T.N.A.), 2,5-dinitro-1,8-naphthalic anhydride (2,5-D.N.N.A.), 3,6-dinitro-1,8-naphthalic anhydride (3,6-D.N.N.A.), 4,5-dinitro-1,8-naphthalic anhydride (4,5-D.N.N.A.), 2,4,5-trinitro-1,8-naphthalic anhydride (Tri.N-1,8-N.A.), 1,6,8-trinitro-2,3-naphthalic anhydride (Tri.N-2,3-N.A.) and 2,4,5,7-tetranitro-1,8-naphthalic anhydride (T.N.N.A.).

Measurements on the visible absorption spectra of the donor-acceptor (charge-transfer) complexes formed between aromatic hydrocarbons and the above compounds have shown that the electron acceptor ability increases in the order T.N.A. $<$ 2,5-D.N.N.A. $\sim$ 3,6-D.N.N.A. $\sim$ 4,5-D.N.N.A. $<$ Tri.N-2,3-N.A. $\sim$ Tri.N-1,8-N.A. The electron acceptor ability of T.N.N.A. could not be determined by this method. The extent of electron transfer in the complexes formed with N,N,N',N'-tetramethyl-p-phenylene diamine has been investigated by electron spin resonance spectroscopy and the results have confirmed that T.N.A. is the weakest acceptor.

The association constants for the formation of complexes between T.N.A. and various methyl benzenes have been determined by nuclear magnetic resonance spectroscopy and the association constant and the heat of formation of the 3,6-D.N.N.A.-pyrene complex has been determined by visible spectroscopy. The values are comparable with those for other electron donor-acceptor systems.

The electron spin resonance spectra of the radical anions of all the compounds, except 3,6-D.N.N.A. and Tri.N-2,3,-N.A., have been analysed and the experimentally determined spin densities have been found to be in good agreement with the values calculated by the Huckel and McLachlan molecular orbital methods. The relative spin densities at the proton sites in 3,6-D.N.N.A. have been estimated by a nuclear magnetic resonance method and found to agree qualitatively with the calculated values.

The reactions of the compounds with the bases - methoxide ion, sulphite ion, amines - have been investigated, and the products have been characterised and correlated with the strength of the base used in the reaction. A possible mechanism for the reaction of 3,6-D.N.N.A. with the methoxide ion has been proposed.

The preparation of the compounds under study have been described and the nuclear magnetic resonance, infrared and mass spectra have been recorded. The infrared and mass spectra have been discussed in terms of the structure of the compounds. The infrared spectra of the complexes formed with aromatic hydrocarbons have also been recorded and shown to be basically composites of the spectra of the individual components.

A number of computer programs relevant to the present work and of general chemical application have been written and are presented as an appendix to the thesis.

CHAPTER 1

INTRODUCTORY SURVEY

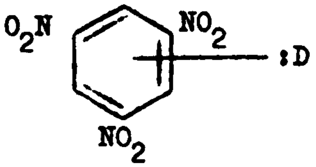
1. Introduction
2. Charge-Transfer Interaction
3. Radical Anion Formation
4. Sigma-Complex Formation

1. Introduction

The object of the present work is to investigate the properties of electron deficient aromatic systems based on the naphthalene skeleton in an attempt to compare the results with the much studied benzenoid systems. In order to set the present study in context a review of some of the principle features of the properties and reactions of electron deficient molecules will be presented.

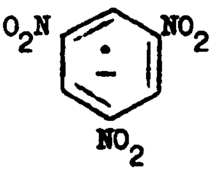
Electron deficient molecules are often capable of interacting with electron rich molecules, and the type or class of interaction is dependent upon the extent of electron transfer from the electron rich donor to the electron deficient acceptor. In view of this, the following introductory survey on the reactions of electron deficient systems is divided into sections based on the degree of electron transfer between the interacting species.

The first section is concerned primarily with charge-transfer complexes formed as a result of partial transfer of electronic charge from the donor to the acceptor



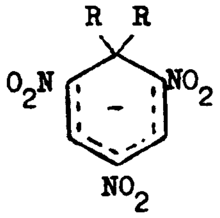
Charge-Transfer Interaction

The second section deals with reactions involving a further degree of interaction, namely the complete transfer of an electron from the donor to the acceptor leading to the formation of radical anions.



Radical Anion Formation

The final section deals with sigma-complex formation in which donation of a lone pair of electrons from the donor to the acceptor results in the formation of a covalent bond between the two species. The product of this type of interaction is a species in which the benzenoid resonance is no longer intact.



Sigma-Complex Formation

2. Charge-Transfer Interaction

A charge-transfer complex is formed by the weak interaction of molecules which are capable of acting as electron donors with molecules which function as electron acceptors. These complexes consist of integral molar ratios of the components.

There are two main classes of electron donors, the first includes alkenes, alkynes and aromatic hydrocarbons. These are termed π -donors since the electrons available for donation are delocalised in the π -orbitals of the donor. The second class of donors are the n-donors. These are molecules containing non-bonding electrons which are available for coordination. Examples of such donors are alcohols, iodides, sulphides and nitrogen bases.

A wide variety of molecules show acceptor properties but this particular study is confined to organic acceptors. Hydroxylic organic compounds interact with many n-donors with the formation of hydrogen bonds. Since this type of interaction usually results in alterations of the O-H stretching frequency, infrared spectroscopy is a suitable method for studying this type of complex.

Many compounds which react as dienophiles in the Diels-Alder reaction also form complexes with unsaturated aliphatic and aromatic substances. An example of this is the production of highly coloured adducts from the fusion of maleic anhydride with polymethylbenzenes[1]. Many of the compounds termed π -acceptors are ethylenes which are substituted with highly electronegative groups. The acceptor strength of these compounds is related to the electron withdrawing power of the substituents. Tetracyanoethylene[2], one of the strongest π -acceptors known, falls into this class of compound.

The nitro group is strongly electron withdrawing and due to this effect polynitroaliphatic and polynitroaromatic compounds show acceptor properties. A large number of coloured solid adducts of polynitroaromatic acceptors have been formed. The complexes formed with picric acid and sym-trinitrobenzene have been known for many years and have been well studied[3]. Rather less work, however, has been done on nitro substituted polycyclic aromatic compounds and probably 2,4,7-trinitrofluorenone has been the most extensively studied in this class of compound[4]. Other examples of acceptors in this class are the dinitronaphthalenes studied by Emslie and Foster[5] and 3-nitro-1,8-naphthalic anhydride studied by Ilmet and Berger[6].

(i) The Bonding in Charge-Transfer Complexes

Many changes in the theories of bonding in complexes have occured during the last fifty years. In 1927 Pfeiffer[7] postulated the existance of secondary valence forces within the aromatic nucleus which were susceptible to saturation through interaction with quinones and various other molecules. This theory triggered off much discussion and several new ideas have followed on the theory of bonding in molecular complexes.

(a) The covalent bond theory

In 1929 Bennett and Willis[8] rejected the ideas of Pfeiffer in favour of a theory of covalent bonding between the components. The covalent bond was presumed to link the nitrogen atom of a nitro group to the carbon of the aromatic ring of the donor. The fact that complexes were formed in simple molar ratios seemed to support the covalent bonding theory but it soon became unreasonable when it was discovered that the separation between the components was much larger than that actually observed in covalent bonding.

(b) The polarization aggregate theory

Briegleb[9] in 1932 postulated that complex formation was due to interactions resulting from the electrostatic attraction between polar molecules with permanent dipoles and non-polar molecules which are subject to polarization through induction. This theory is consistent with observed changes in the heats of formation of trinitrobenzene complexes with various aromatic hydrocarbons[10]. However it cannot explain the formation of complexes with iodine as the acceptor[10].

(c) Collision theory

In 1940, Gibson and Loeffler[11] and Hammick and Yule[12] suggested that colour producing collisions between components of a complex in solution are comparable to normal impacts between liquid molecules except for added restrictions in the orientations of the colliding molecules. It is presumed that the colour phenomena are associated with the drift of electrons from one component to the other when the reactive centres are appropriately located. This interaction theory is supported by the fact that when solutions of aromatic amines in nitroaromatics are subjected to increased pressure at constant temperature an intensification of the colour is observed[11].

(d) The ionic complex theory

In 1942 Weiss[13] suggested an aromatic donor-acceptor complex to be the product of a single electron transfer

$$D{:} \; + \; A \longrightarrow [\cdot D]^{+} \;\; [\cdot A]^{-}$$

He explained the characteristic complex colours on the basis that the ions $D^{+\cdot}$ and $A^{-\cdot}$ are odd electron molecules which, in general, have low excitation energies. Complexes between dienes and dienophiles, which may serve as Diels-Alder reaction intermediates, have also been formulated as ion pairs resulting from the transfer of a single electron.

The term "intermolecular semi-polar bond" has been used[14] to describe the bonds between the components of the complex.

(e) The concept of complex resonance

Weiss's arguments have received much criticism[15] and in 1949 Brackman[16] put forward his concept of resonance which requires only partial ionic character and which seems to be in more accord with the known properties of most aromatic donor-acceptor interaction products. According to this theory the donor compound can share an electron pair with the acceptor by a process comparable to Lewis acid-base interaction. The complex structure is regarded as a resonance hybrid

$$D{:}\ A \rightleftharpoons \overset{+}{D}\ {:}\ \overset{-}{A}$$

The crystal structure of the p-iodoaniline-sym-trinitrobenzene complex[17] serves as indication that the contribution of the dative form is of small but significant structural influence. The colour of the complex is not discretely determined by either component but it is a characteristic feature of the complex itself.

(f) The Mulliken theory

The description of charge-transfer complexes which is most generally accepted is the valence bond approach suggested by Mulliken[18] in 1952. This theory describes the relatively weak interactions between an electron donor, D, and an electron acceptor, A, in terms of a ground state wavefunction, ψ_N, and an excited state wavefunction ψ_E such that

$$\psi_N(AD) = a\psi_0(A,D) + b\psi_1(A^- - D^+) \qquad (1)$$

$$\psi_E(AD) = a^*\psi_1(A^- - D^+) - b^*\psi_0(A,D) \qquad (2)$$

where a and b are coefficients such that $a \sim a^*$, $b \sim b^*$ and $a^2 \gg b^2$. The wavefunction ψ_0 has been termed by Mulliken the no-bond function and it represents bonding derived from physical forces such as dipole-dipole interactions and London dispersion forces. The wavefunction ψ_1 has been termed the dative function and this corresponds to complete electron transfer from the donor to the acceptor. A loosely bound molecular complex is regarded as a resonance hybrid between the no-bond form and the dative form with the no-bond form providing the major contribution to the hybrid structure.

The transition from the ground to the excited state, which accompanies the absorption of light of appropriate wavelength, corresponds to the transfer of an electron from the donor to the acceptor. The corresponding spectrum, which is considered to be characteristic of the complex as a whole[14], is called an <u>intermolecular charge-transfer</u> spectrum. The coordinations products themselves being termed <u>charge-transfer</u> complexes.

(g) The molecular orbital method

As an alternative to the valence bond approach postulated by Mulliken, a simple molecular orbital approach was put forward in 1961 by Dewar[19]. The charge-transfer absorption band is assumed to result from a transition from the highest occupied molecular orbital of the donor to the lowest vacant molecular orbital of the acceptor. It can be shown that the energy of charge-transfer, E_{CT}, is given by

$$E_{CT} = Bj - \alpha_0 - X_i\beta + P \qquad (3)$$

where α_0 is the coulombic integral for an sp^2 hybridised carbon atom and β is the resonance integral for a carbon-carbon bond in benzene. The molecular orbital parameter, X_i, is calculated and relates to the highest occupied molecular orbital of the donor. Bj represents the energy of the lowest vacant molecular orbital of the acceptor. The energy term P which represents the perturbation of the donor and acceptor energy levels is small and usually

A more detailed treatment has been given by Murrell[20] who has attempted to demonstrate a relationship between the stability of a charge-transfer complex and the intensity of the charge transfer band.

(ii) The Energy of the Charge-Transfer Transition

The transition from the ground state to the excited state of a complex is brought about by the absorption of light of a particular wavelength. This absorption, which causes the promotion of an electron from a molecular orbital of the donor to a molecular orbital of the acceptor, can be conveniently monitored using ultraviolet and visible spectroscopic techniques. This is of significance since the wavelength of the maximum in the charge-transfer absorption band leads simply to the energy of charge-transfer. Since the charge-transfer process requires the transfer of an electron from the donor to the acceptor, the transition energy may be expected to be a function of the ionisation potential of the donor, I^D, and the electron affinity, E^A, of the acceptor.

It has been shown by McConnell[21] that, for complexes of iodine with a wide range of weak donors, an approximately linear relationship exists between the ionisation potential of the donor and the frequency, ν_{CT}, of the charge-transfer transition such that:

$$h\nu_{CT} = I^D - E^A - W \qquad (4)$$

where h is Planck's constant and W is the dissociation energy of the excited state of the complex. Subsequently, several relationships between the energy of charge-transfer and the donor ionisation potential for various acceptors have been proposed, all of which take the general form

$$h\nu_{CT} = aI^D + b \qquad (5)$$

where a and b are constants for the acceptor being studied.

For weak complexes it can be shown[22] that the ionisation potential is related to the energy of the charge-transfer transition by the equation

$$h\nu_{CT} = I^D - C_1 + \frac{C_2}{I^D - C_1} \qquad (6)$$

where C_1 and C_2 are constants for a given acceptor.

This equation describes a parabola, and would, at first sight, appear to be in conflict with the more simple linear equations (4) and (5). The fact that the range of measured values of the donor ionisation potential is relatively small means that the segment of the parabola over which the results have been applied approximates to a straight line. This, together with the fact that the charge-transfer band is broad which makes an accurate evaluation of ν_{CT} difficult, is sufficient to justify the use of the more simple linear equations (4) and (5).

Experimental determinations of ionisation potentials vary somewhat depending on the method of measurement. Direct photoionisation experiments seem to be the most reproducible source of ionisation potentials and figure 1 shows some typical plots of the energy of the charge-transfer transition against the donor ionisation potential[3]. The linearity of the plots is reasonable. However some of the points which deviate from the least squares line may be accounted for by experimental error but there seems little doubt that many of the discrepancies are real. Nevertheless despite such inherent errors this type of plot has been used to estimate unknown donor ionisation potentials.

The variation in ν_{CT} throughout a set of complexes of a given acceptor with different donors may be paralleled in a corresponding set of complexes with a different acceptor. Plots of

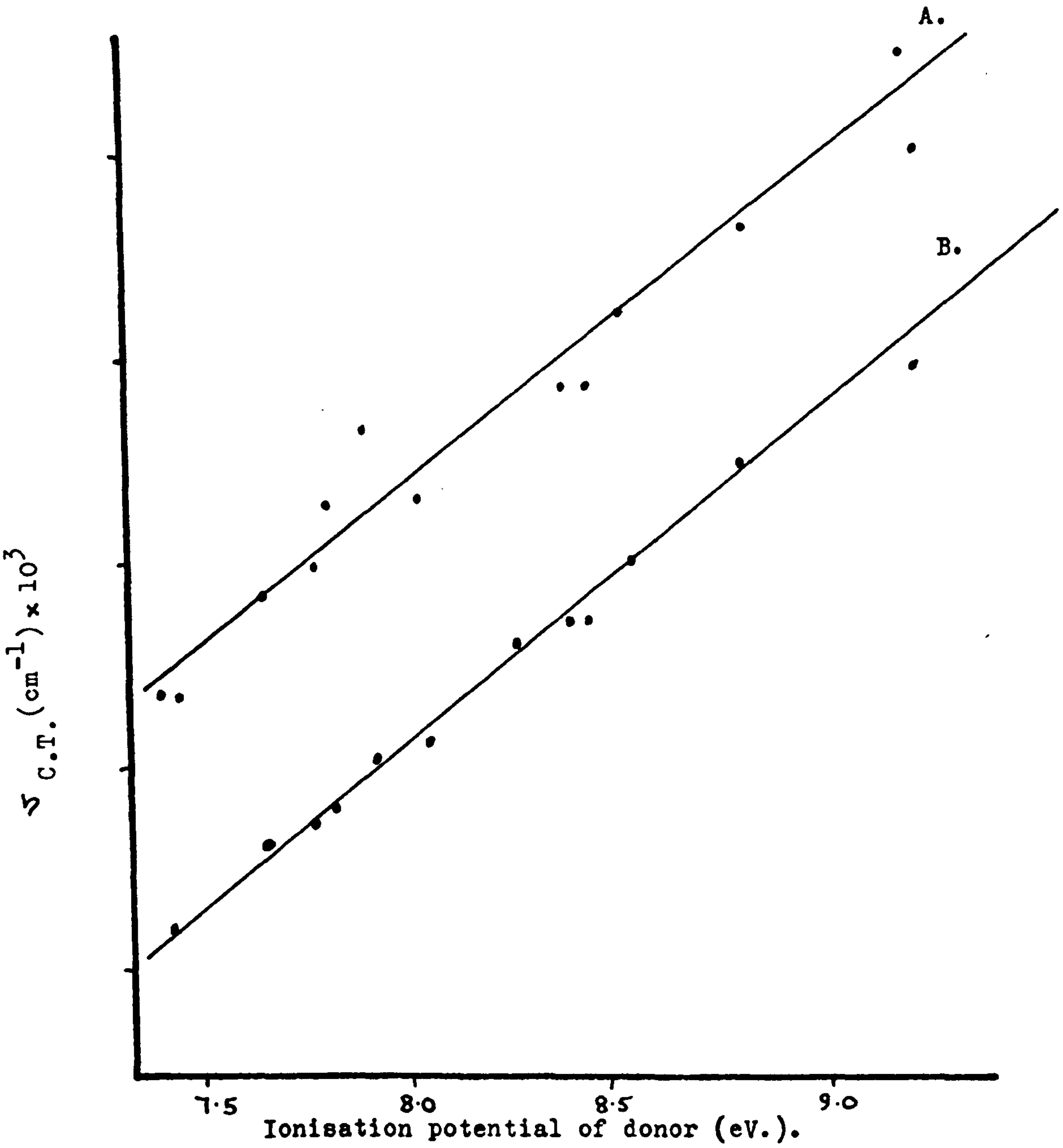


Figure 1 A plot of $\nu_{C.T.}$ against the ionisation potential for a series of donors with the acceptors (A) 1,3,5 - trinitrobenzene and (B) chloranil.

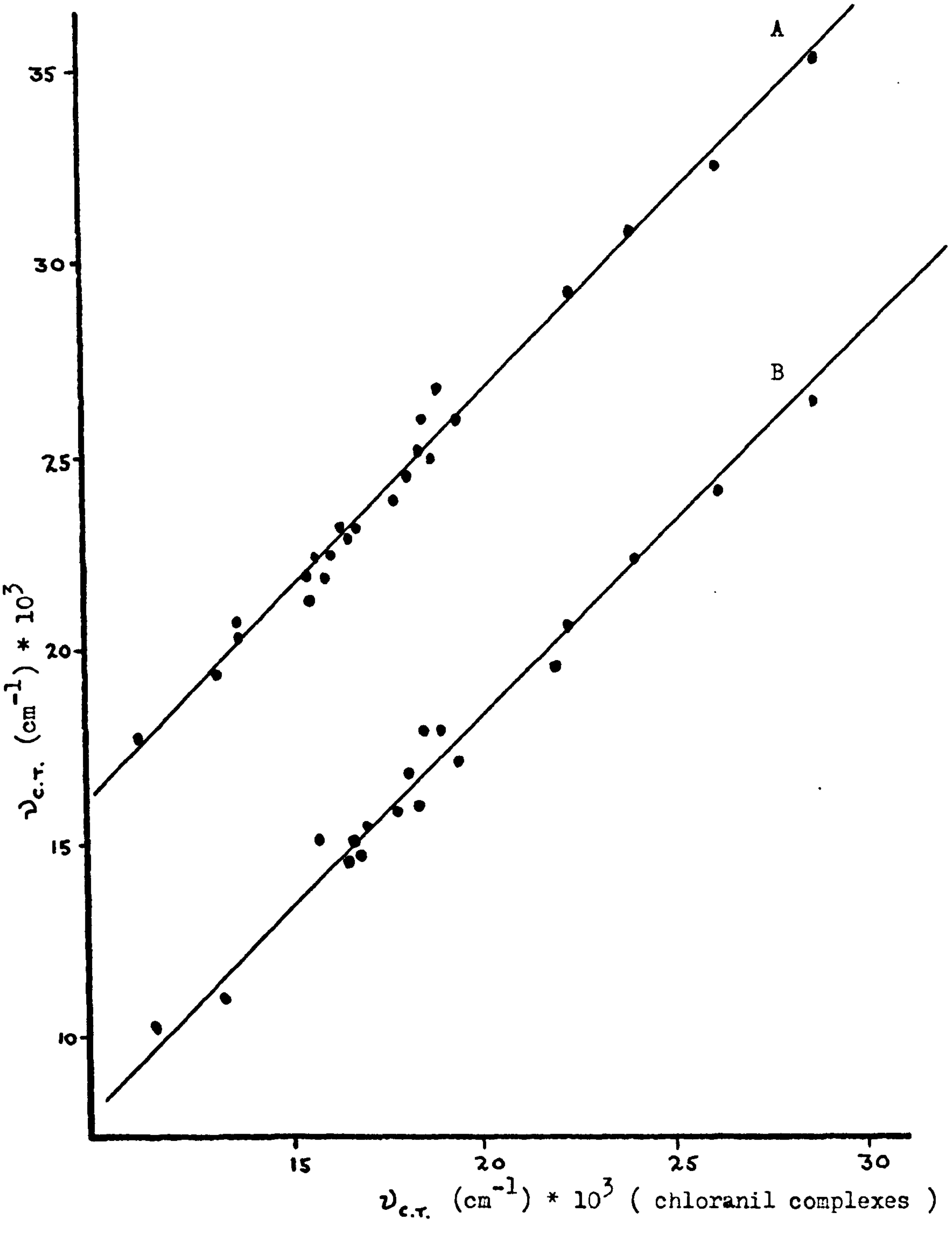
this type, as shown in figure 2, provide useful evidence for the presence of charge-transfer complexes when the appropriate ionisation potentials of the donors are not available[3]. In many cases, where both the acceptors are π -acceptors, this type of plot shows a gradient of unity. This corresponds to an equal value of the constant a in equation (5) for both the acceptors. In certain cases, the gradient obtained from such plots is significantly different to unity. Such an example being a plot of ν_{CT} for iodine complexes against ν_{CT} for the corresponding complexes with a π -acceptor[23]. Theoretically this case can be understood in terms of the difference in overlap for the two acceptors resulting in different values of the constant a in equation (5) for each acceptor.

A measure of the ionisation potential of a donor compound may be obtained from the half wave oxidation potential, $\epsilon_{\frac{1}{2}}^{OX}$. It is a requirement of the method[3] that there is an electrochemical equilibrium at the electrode and that the wave is reversible.

It has been shown[24.25] that if the difference in the diffusion of the compound and its positive ion is small and entropy changes are small then

$$\epsilon_{\frac{1}{2}}^{OX} = I^{D} + \Delta Fsolv + \text{constant} \qquad (7)$$

where Δ Fsolv is the difference in the solvation energy between the compound and its positive ion. If, for a series of compounds, it is assumed that variations in the ionisation potential are much greater than in ΔFsolv, the half wave oxidation potential may be used as a measure of the electron donating ability of the donor. Plots of ν_{CT} against $\epsilon_{\frac{1}{2}}^{OX}$ result in good straight lines[25] (see figure 3). Since polarographic data often extends to compounds for which no direct ionisation potential data is available such results are of considerable interest.



<u>Figure 2</u> Plots of $\nu_{c.T.}$ for a series of complexes of (A) 1,3,5 - trinitrobenzene and (B) tetracyanoethylene against $\nu_{c.T.}$ for the corresponding complexes of chloranil.

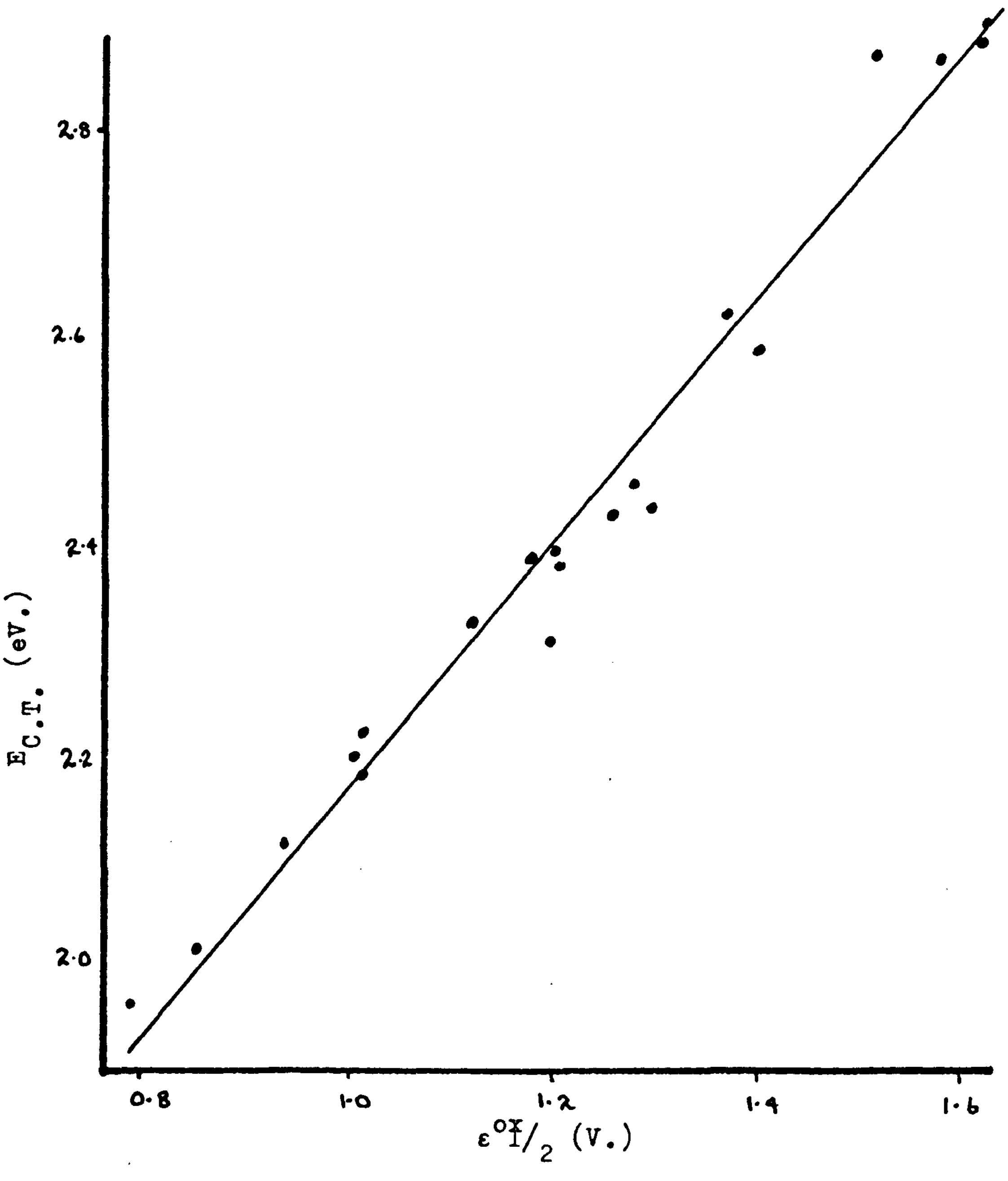


Figure 3 A plot of the charge - transfer transition energies of 2,4,7 - trinitrofluorenone complexes against $\varepsilon^{ox}_{1/2}$ for the respective donors.

The correlation between the energy of charge-transfer and the electron affinity of the acceptor as is implied by equation (4) has not been studied to any great extent. This being mainly due to the lack of reliable data on the electron affinity of acceptors. The methods available for the determination of the electron affinity of acceptors have been comprehensively reviewed by Briegleb[26] and will only be outlined in this discussion.

Since it has been shown that the half wave oxidation potential is related to the ionisation potential of the donor (equation 7), it seems reasonable that the half wave reduction potential might be related to the electron affinity of the acceptor. It has been shown, for two acceptors of similar type that, if the difference in solvation energy between the compound and its negative ion is assumed constant, the following relationship holds:

$$E^A(A_1) - E^A(A_2) = \epsilon(A_1) - \epsilon(A_2) \qquad (8)$$

where ϵ is the reduction potential of the acceptor and is equal to the half wave reduction potential within experimental error. Thus if the electron affinity of one acceptor is known then others may be derived from a knowledge of their reduction potentials.

A very similar equation relates the electron affinity of an acceptor to the energy of the charge-transfer transition.

$$E^A(A_1) - E^A(A_2) = h\nu_{CT}(A_1) - h\nu_{CT}(A_2) \qquad (9)$$

Equation (9) relies on the same assumption as equation (8) and should only be used for comparisons between complexes of the same bond type.

However, since the reliance which can be placed on the value of the electron affinity of any standard acceptor is uncertain, the results obtained for electron affinities using equations (8) and (9), and indeed by most available methods, must be viewed with caution.

Plots of the frequency of the charge-transfer transition against the half wave reduction potential show more scatter than do the analagous plots against the half wave oxidation potential. This suggests that the assumption that the difference in the solvation energy between a compound and its negative ion is constant for different systems is less reliable than when dealing with positive ions in oxidation potential measurements. Thus ionisation potential measurements are usually more reliable than electron affinity measurements when methods which rely on this assumption are used.

It is unfortunate that the electron affinity presents so many difficulties in its determination since it would offer a direct measure of electron acceptor ability. However it can be seen from equation (3) that Bj, the energy of the lowest vacant molecular orbital of the acceptor, is directly related to the energy of charge-transfer and should provide a measure of the acceptor strength.

It can be seen, from equation (3), that by plotting the energy of charge-transfer against the calculated molecular orbital parameter, Xi for a series of complexes of a single acceptor with several donors a straight line should be observed. An illustrative plot of E_{CT} against Xi for trinitrofluorenone complexes[27] is given in figure 4. If the energy function, P, is omitted from equation (3) we have

$$E_{CT} = (Bj - \alpha_0) - X_1\beta \qquad (10)$$

and, hence the gradient of the plot leads to a value of the negative resonance integral for a carbon-carbon bond in benzene and the intercept leads to a value of the lowest vacant molecular orbital

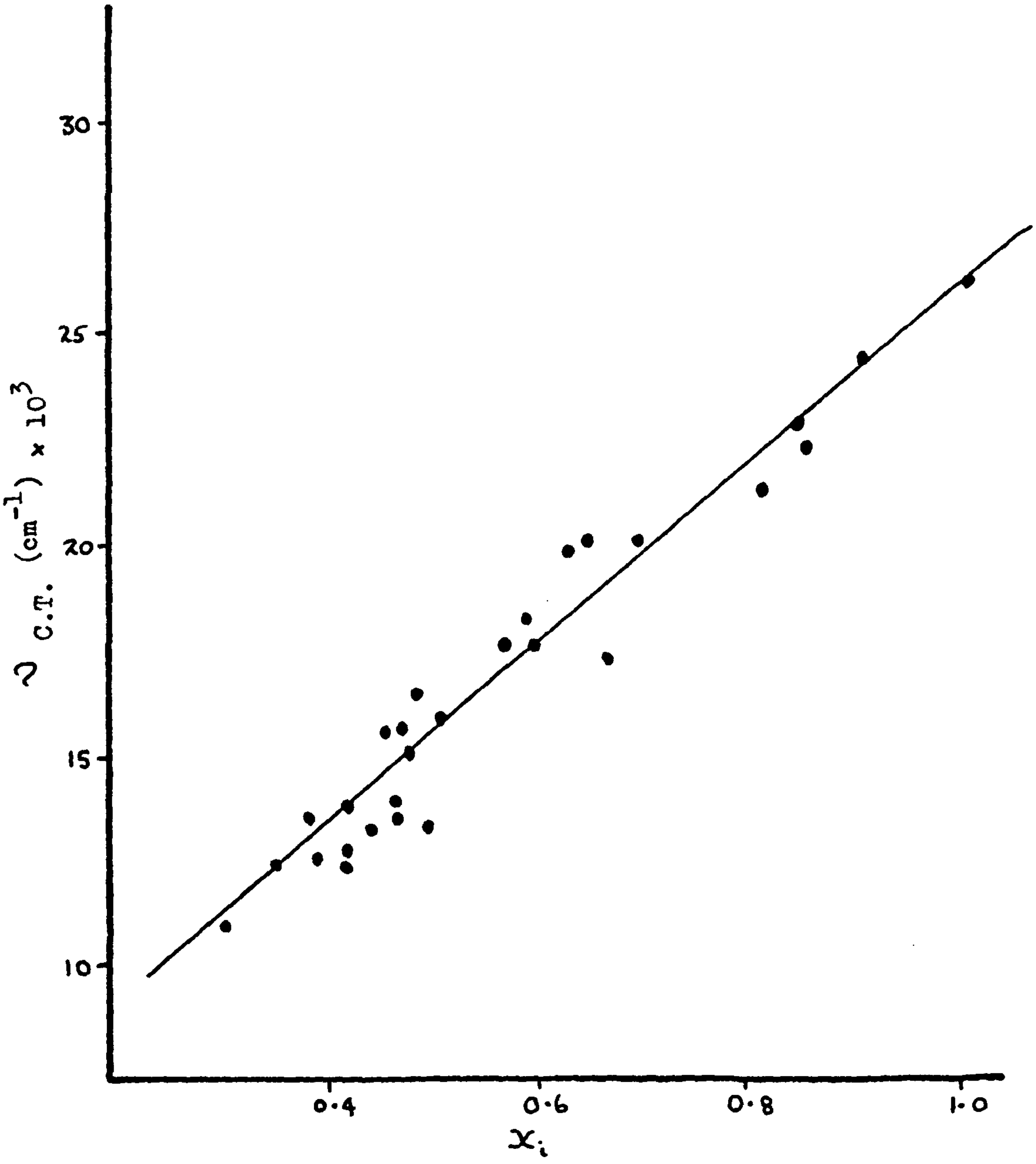


Figure 4 Plot of charge - transfer transition energies for a series of tetracyanoethylene - donor complexes against the Huckel coefficients (x_i) for the donors.

of the acceptor reduced by the value of the coulombic integral for an sp^2 hybridised carbon atom. By analogy with equation (3), it can be seen that the intercept is, more accurately, given by

$$Bj - \alpha_o - P$$

where P is an energy term. Calculations have been carried out to eliminate α_o and P from this intercept but the determination of P is difficult. However the values of $(Bj - \alpha_o)$ obtained from the simple treatment outlined above give a reliable relative measure of the electron acceptor ability of molecules. The resonance integral, β, has been shown not to be constant, as expected, but to show a dependence on the class of donor and on the particular acceptor being investigated.

(iii) <u>The Effect of Solvent on the Energy of Charge Transfer</u>

The wavelength at which a charge-transfer absorption band occurs is very dependent upon the solvent used in the determination. Kosower[28] has suggested that for 4-carbomethoxy-1-ethyl pyridinium iodide the energy of the charge-transfer transition, expressed in kilocalories per mole, and termed the Z value, can be taken as a standard measure of the ionising power of a solvent.

In general solvents may be divided into protic and aprotic solvents and in each case the position of the charge-transfer band in non-ionic complexes has been shown to be reasonably linearly dependent on the solvent Z value[29].

For protic solvents, where the Z value is high, the larger values of Z correlate with the larger values of the energy of charge-transfer for a given complex. At first sight this is unexpected since the upper states are more ionic. However, in the ground state, these complexes will be strongly solvated by such solvents. By application of the Franck-Condon Principle there will be no reorientation of this solvent cage to minimise the energy of the excited state at the instant of excitation, and the fact that the more ionising solvents cause a shift to shorter wavelength suggests that the solvation in the ground state results mainly from the localised fields in the constituent molecules, rather than from the small dipole due to the contribution of the dative structure.

Aprotic solvents of low Z value will not provide an effective solvent cage and although this will lead to an absence of orientation strain, dispersion forces and polarisation of the solvent molecules by the solute dipoles will be operative. The increase in solute dipole as a result of the optical transition will result in a shift to longer wavelength as the Z-value of the solvent increases.

Recently studies of gas phase charge-transfer complexes have shown that in all cases there is a considerable blue shift in the position of the charge-transfer band in the gas phase relative to its position in the liquid phase. Prochorow and Tramer[30] have attempted to explain this shift as being caused jointly by a dielectric shift and a cage effect of comparable magnitude. Kroll[31] has studied several charge-transfer complexes in the gas phase and shown that as well as the blue shift observed in going from liquid to gas phase, the extinction coefficient is decreased whilst the charge-transfer association constant is increased by about a factor of three. He also suggests that the shifts are due to changes in the dielectric medium.

(iv) Methods for the Determination of Association Constants

The value of the association constant for the equilibrium between an electron donor and an electron acceptor is important as a measure of the extent of interaction between the donor and acceptor.

It is usual to assume, in the determination of the association constant, that, initially at least, the interaction gives rise to only one species of complex. Thus for the equilibrium

$$D + A \rightleftharpoons DA$$

assuming the activities of the reacting species to be unity the association constant, K_c^{AD}, is given by

$$K_c^{AD} = \frac{[AD]}{[A][D]} \qquad (11)$$

where the quantities in square brackets represent the concentrations of the reacting species at equilibrium. Equation (11) is the basic expression used in the various methods outlined below. The following account briefly summarises the main methods used in the determination of association constants.

(a) <u>Electronic spectroscopy</u>

Ultraviolet and visible spectroscopic techniques have been greatly used for the determination of association constants. The observation of Brackman[16] that a complex retains the absorptions of the components together with one or more absorptions characteristic of the complex as a whole was important and was followed up by the work of Benesi and Hilderbrand[32]. These workers derived the following standard equation, which is usually termed the <u>Benesi Hilderbrand equation</u>

$$\frac{[A_0]}{OD} = \frac{1}{K_c^{AD}\,\epsilon_\lambda^{AD}} \cdot \frac{1}{[D_0]} + \frac{1}{\epsilon_\lambda^{AD}} \qquad (12)$$

Equation (12) was derived for 1:1 complex formation under the conditions of $[D_0] \gg [A_0]$ where $[D_0]$ and $[A_0]$ are the initial donor and acceptor concentrations, OD is the optical density of the charge-transfer absorption at the wavelength, λ, being studied and ϵ_{λ}^{AD} is the extinction coefficient of the charge-transfer absorption at the wavelength λ. A plot of $[A_o]/OD$ against $1/[D_o]$ for a series of solutions should be linear and leads to values of the extinction coefficient and the association constant. The equation has its disadvantages since it requires the determination of a small intercept by extrapolation to concentrated solutions, and various refinements have been suggested by Scott[33], and Foster, Hammick and Wardley[34].

(b) Nuclear magnetic resonance spectroscopy

The nuclear magnetic resonance absorption resulting from a magnetic nucleus is dependent on the environment of the particular nucleus. If the environment is changed, e.g. by complexing, a shift in the position of the signal will be observed. It can be shown that on complexing the upfield shift of the acceptor signal, Δ, is related to the association constant, K_c^{AD}, by the equation

$$\frac{1}{\Delta} = \frac{1}{K_c^{AD}} \cdot \frac{1}{\Delta_o^{AD}} \cdot \frac{1}{[D_o]} + \frac{1}{\Delta_o^{AD}} \qquad (13)$$

where Δ_o^{AD} is the shift of the pure complex relative to the pure acceptor. Equation (13), originally derived from hydrogen bonding studies, was first used in the study of charge-transfer complexes by Hanna and Ashbaugh[35]. The equation is analagous to the Benesi-Hilderbrand equation for optical determinations and has the same disadvantage of requiring extrapolation to concentrated solution to obtain a small intercept. Foster and Fyfe[36] suggested a rearrangement, similar to that of Foster, Hammick and Wardley[34] for the optical method, to the form

$$\Delta/[D_o] = -\Delta K_c^{AD} + \Delta_o^{AD} K_c^{AD} \qquad (14)$$

Equation (14) indicates that for a series of solutions in which $[D_0] \gg [A_0]$ a plot of $\Delta / [D_0]$ against Δ should be linear. The line has a gradient equal to the negative value of the association constant and the value of the shift of the pure complex, Δ_0^{AD}, may be obtained from the intercept by extrapolation to infinitely dilute solution.

(c) Infrared spectroscopy

In principle, the procedures used in electronic spectroscopy can be applied to the infrared absorptions of solutions containing electron donors and electron acceptors in equilibrium with the complex species[37]. Since the intermolecular stretching frequencies of the complex species are not normally accessible, measurements are made on a band which occurs in one or other of the components and in the complex. For the method to be applied there must be sufficient difference in the intensity of the absorption by these two species at some wavelength. The method which has also been applied to Raman lines[38] is only rarely used.

(d) Distribution methods

It has proved convenient in making quantitative studies of certain types of donor acceptor complexes to measure the distribution of one component, often the donor, between a liquid phase in which only that component is appreciably soluble and a liquid phase which contains all the components. Analysis of the free donor concentration in each of the layers with a knowledge of the distribution coefficient can lead to a value of the association constant for complex formation[39].

(e) Polarography

The reversible one electron reduction of organic acceptors in aprotic solvents is modified when a donor is added to the system and this change can be related to the association constant for complex formation. The results, which seem sensitive to the supporting electrolyte, do not correlate closely with values obtained from optical data[40,41].

Other methods, including osmometry[42], viscosity[43] measurements, solubility measurements[44] and surface tension measurements[45] have all been used in the determination of association constants for complex formation, but they are rather more specialised and have only been used in specific cases.

(v) Paramagnetism in complexes

The observations of Kainer, Bijl and Rose Innes[46] indicated that in certain cases charge-transfer complexes could be paramagnetic. They showed that adducts of p-phenylene diamine (P.P.D.) and N,N,N',N'-tetramethyl-p-phenylene diamine (T.M.P.D.) with tetrahalobenzoquinones and other strong acceptors exhibited electron spin resonance signals.

Paramagnetism in complexes was explained[46,47] by assuming that the radical anion derived from the acceptor, $A^{\overline{\cdot}}$, and the radical cation derived from the donor, $D^{\dot{+}}$, each have an unpaired electron and are in the doublet state. When these ions are held together in the complex the unpaired electrons may interact to give a singlet or triplet state. Often the triplet state is of too high energy to be significantly populated, but in complexes formed from donors of low ionisation potential and acceptors of high electron affinity the triplet state may be accessible. In such cases the complex is paramagnetic. The electron spin resonance signal of certain solid adducts of the tetrahaloquinones and T.M.P.D. have been resolved[48,49] and the spectral lines identify with the radical cations of the donor $D^{\dot{+}}$ and the radical anions of the acceptor $A^{\overline{\cdot}}$.

Eastman[50] has observed an electron spin resonance signal from a perylene-quinone complex but the spectrum of this type of complex does not, in general, exhibit any hyperfine structure and it is difficult to identify the species giving rise to the signal.

Radical anion formation is enhanced in solution since ion-solvent interactions lower the free energy of the radical ion state. This allows the triplet state to be populated to a greater extent.

The relative strengths of the electron spin resonance signals from complexes formed from various acceptors with P.P.D. and T.M.P.D. have been investigated using a radical with a simple doublet ground state as a reference standard[51].

The results for the various acceptors are shown in the table.

<u>Relative strengths of the electron spin resonance absorption per molecule of complex at 90° K[51]</u>

Acceptor	P.P.D. Complexes	T.M.P.D. Complexes
p-Benzoquinone	0.0	0.1
p-Chloranil	0.2	0.2
p-Bromanil	0.3	2.0
p-Iodanil	7.0	20.0
o-Bromanil	3.0	40.0

It has been deduced that the factors which lead to an increase in the population of the triplet level and hence the strength of the electron spin resonance signal are:

(1) Increased ease of reduction of the acceptor.

(2) Increased bulkiness of the substituents on the donor and acceptor nuclei leading to a corresponding decrease in the overlap of the

orbitals $A^{\overset{-}{\cdot}}$ and $D^{\overset{+}{\cdot}}$ which contain the unpaired electrons.

Several complexes formed with polycyclic aromatic hydrocarbons as donors and inorganic molecules as acceptors[52,53,54] have been reported to show electron spin resonance signals but these are outside the scope of this review.

2. Radical Anion Formation

It can be seen from the previous section that complex formation in certain cases can lead to the formation of a paramagnetic species and to radical anion formation. Although the electron spin resonance spectrum can be obtained from the species $D^{\dot{+}}$ and $A^{\dot{-}}$ formed by one electron transfer from the donor to the acceptor, it is often not possible to resolve the fine structure in the spectra of radical anions formed by charge-transfer complexation. Hence it is not possible to obtain direct experimental evidence on the electron distribution within either the donor or the acceptor molecule. In order to gain this information it is necessary to generate the radical anions by other means.

Electron deficient aromatic systems can be converted relatively easily into radical anions by the addition of an electron from a donor molecule. It has been observed that 4-nitrotoluene gives a high concentration of radical anions when dissolved in *tert*-butanol to which potassium-*tert*-butoxide has been added[55]. However trinitrobenzene under similar conditions gives only a very small concentration of radical anion and this is explained as being due to sigma-complex formation[55].

There are several methods available for the preparation of radical anions and one of the earliest and originally most commonly used is chemical reduction using an alkali metal. Although the mechanism of this reaction is simple the expected anion is not always produced. Sometimes an ion-pair is obtained which introduces complications into the interpretation of the spectrum. Recently photolytic reduction[56] has been employed, particularly in the reduction of aromatic ketones, but the *in situ* electrolytic reduction method introduced by Geske and Maki[57] is perhaps the best and most widely used. This last method is superior to chemical methods because it does not normally lead to any anomalies in the electron density in the aromatic system.

Modern electron spin resonance spectrometers can resolve linewidths of 0.1 gauss or less and the hyperfine structure resulting from the interaction of the magnetic moment of the unpaired electron with the magnetic nuclei in the radical can lead to a "mapping" of the unpaired electron density throughout the radical. Several methods, based on the valence bond and molecular orbital approximations, are available for the calculation of the unpaired electron density throughout the radical. The molecular orbital method is the approach normally adopted but the valence bond method of Karplus has several advantages[58]. A theoretical treatment, such as the molecular orbital method, derived for use with aromatic hydrocarbons is not strictly valid in systems where there is a considerable degree of delocalisation of the π -electrons into substituent groups. Nevertheless Reiger and Fraenkel[59] have been remarkably successful in correlating a vast amount of data on hyperfine interactions in nitroaromatic radical anions using the Huckel Linear Combination of Atomic Orbitals theory and the approximate configuration interaction theory of McLachlan.

Most of the early studies of radicals in solution concerned highly stable species such as radicals derived from substituted cyclopentadienyls[60,61] hydrazyls[62,63] carbazyls[64,65] and nitric oxide[66]. However, electron deficient aromatic systems, and particularly nitroaromatic compounds, can readily be converted into radical anions because of their ease of reduction. As a result extensive investigations have been made into such systems[59,67,68].

The reduction of a nitroaromatic compound usually leads to a stable radical anion but the anion formed is susceptible to both oxidation and reduction. Oxidation to the parent nitro compound occurs easily and may be accomplished simply by exposure to air or by addition of an acceptor stronger than the parent nitro compound. Reduction of a nitroaromatic radical anion may yield a nitroso compound, hydroxylamine, amine or condensation products. Hence considerable care must be exercised during the preparation to ensure that the correct conditions are employed to obtain the stable radical anion.

Maki and Geske[69] who made the first systematic study of electrolytically produced nitroaromatic radical anions commented on various semi-empirical correlations. For instance, it was observed that changes in the nitrogen hyperfine coupling constant could be related to changes in the half wave one electron reduction potentials and also to the Hammett σ function. The addition of electrophilic substituents caused a decrease in the half wave reduction potential which was paralleled by a decrease in the nitrogen hyperfine coupling constant. Nucleophilic substituents were found to have the opposite effects.

The values of the nitrogen hyperfine coupling constants are also solvent dependent, being greatest when measured in a solvent of high dielectric constant[70,71,72]. The ring proton coupling constants are however only slightly affected by changes in solvent. Reiger and Fraenkel[59] suggest that the main effect of the solvent is on the electron distribution within the nitro group, the point at which local solvent complexes are most likely.

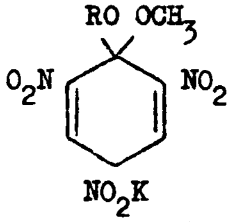
The extent to which radical anions are involved in the mechanism of σ-complex formation is uncertain. Electron spin resonance spectra have been observed during the reaction of trinitrobenzene with diethylamine[73,74] in the presence and absence of acetone and from trinitrobenzene in the presence of basic acetone[71]. However the origin and role of these paramagnetic species is not fully understood.

It has been shown that irradiation can lead to the production of radical anions, and spectra have been obtained in this way from a solution of nitrobenzene in methanolic methoxide[75] and from chloroform solutions of trinitrobenzene containing the cyanide ion[76]. However it is likely that these species are in low concentration and have little significance in σ-complex formation.

A more detailed account of the theory related to the investigation of radical anions derived from nitroaromatic compounds is given in chapter 3 section 1, and details of the methods of calculation of the theoretical π-electron densities are given in chapter 7 section 1.

3. Sigma Complex Formation

At the turn of the century Jackson[77,78] and Meisenheimer[79] reported bright coloured products resulting from the reaction of an alkoxide with 2,4,6-trinitroanisole. Meisenheimer suggested the structure of the product to be



(I)

This type of product resulting from the transfer of a lone pair of electrons from a donor molecule to an acceptor molecule has been the subject of detailed studies over the past decade. Recent nuclear magnetic resonance spectroscopic studies[80,81] have shown that the structure (I) suggested by Meisenheimer was largely correct. This type of sigma-complex has subsequently come to be known as a Meisenheimer complex.

(i) Methods of Investigating Meisenheimer Complexes

The increase in the availability of spectroscopic techniques has greatly facilitated the study of this type of sigma-complex formation and electronic and nuclear magnetic resonance spectroscopy have been of particular value.

(a) Electronic spectroscopy

In the interaction of a nitroaromatic compound with any one of a variety of bases a characteristic absorption of light in the visible region is observed. The visible spectra of a large number of nitroaromatic/anion type systems have been studied[82-86], and, apart from the adducts formed from sym-trinitrobenzene with the hydroxide ion and the sulphite ion, the observed spectra show very marked similarities.

These are:

(i) Two distinct maxima in the region 400 - 850 nm.

(ii) The molar extinction coefficient of the low energy band is about half that of the high energy band and has a value around 2×10^4 l. mole^{-1} cm^{-1}.

(iii) The band profiles are very similar.

The positions of the bands, their separation and extinction coefficients are dependent on the solvent system used. Foster and Fyfe[87] have reported that in the 2,4,6-trinitroanisole/alkoxide system the high energy band shifts to longer wavelengths on increasing the ionising power of the solvent. Similar effects have been reported[88] for the sym-trinitrobenzene/cyanide ion system and the 1,3-dinitrobenzene/acetonate ion system. No simple relationship has been observed however between the position of the absorbance maximum and a single function of the solvent such as the dielectric constant.

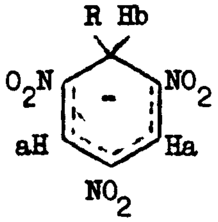
In the case of the adducts formed from sym-trinitrobenzene with the hydroxide and sulphite ions, the spectrum shows a single sharp maximum plus a shoulder on the long wavelength side of the peak maximum[76,89].

From the results of a visible spectroscopic study of the interaction of sym-trinitrobenzene with various anions Ainscough and Caldin[90] have suggested the product of the reaction to be a charge-transfer complex of unspecified geometry rather than a Meisenheimer complex of structure (I). Pollett and Saunders[86] however suggested that the complex between sym-trinitrobenzene and the acetonate ion contains the ion situated above one of the ring carbon atoms and donating a lone pair on the methylene group to the lowest available π^* orbital of the benzene ring to form a dative sigma-bond.

(b) Nuclear magnetic resonance spectroscopy

The change in the environment of the ring proton at the site of sigma-complex formation is easily detectable by nuclear magnetic resonance spectroscopy and has led to this technique being greatly used in the investigation of Meisenheimer complexes.

The nuclear magnetic resonance spectrum of the species resulting from the interaction of sym-trinitrobenzene and a variety of anions and aliphatic amines can be rationalised in terms of sigma-complex formation but not on the basis of π -complex formation[80,81,91-95]. The structure of the product is very similar to that initially proposed by Meisenheimer



II

The ring protons (H a) resonate in the range 1·1 to 1.3 and appear as a doublet with a coupling constant of approximately 1 Hz., while the proton (H b) bonded to the carbon atom at which attack of the anion takes place resonates in the range 3.7 to 4.1 and appears as a broad triplet showing the same coupling constant.

In the case of interactions of sym-trinitrobenzene with aliphatic amines simultaneous measurements of both the nuclear magnetic resonance spectrum and the visible spectrum have been taken[93,96] and it appears that the species giving rise to the visible absorption is the same as that giving rise to the nuclear magnetic resonance spectrum.

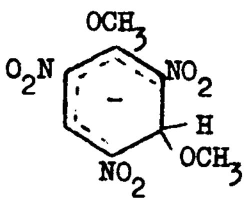
At ratios of anion to trinitrobenzene greater than unity the addition of the second anion to the adduct can easily be observed by nuclear magnetic resonance spectroscopy[81,97].

(c) Infrared spectroscopy

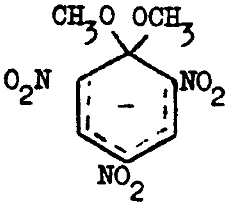
Although infrared spectroscopy does not offer such direct structural evidence as does nuclear magnetic resonance spectroscopy, evidence has been deduced from the infrared spectrum of the product of the reaction of trinitroanisole with methoxide to support sigma-complex formation[98]. The outstanding feature of the spectrum of such complexes is a series of five or six strong bands in the region between 1225 and 1040 cm^{-1} which correspond to the strong characteristic bands of a ketal[99]. This correspondance with the ketal spectrum clearly indicates that the complexes do have the covalent Meisenheimer complex structure. The transfer of negative charge to the ring which would accompany formation of either a charge-transfer complex or a Meisenheimer complex will lead to a decreased N-O bond order and to the lowering of the symmetric and asymmetric N-O stretching frequencies. As expected the strong asymmetric N-O stretching band at 1552 cm^{-1} in the picryl compound does not occur in the spectra of the complexes. The complexes show a new band at either 1513 or 1481 cm^{-1}. The N-O symmetric stretching band at 1347 cm^{-1} is also missing in the complexes and is replaced by a strong band near 1300 cm^{-1} which can be assigned to the nitro group[100].

(d) Calorimetry

Recently a calorimetric method has been used to show the presence of transient intermediates in the formation of Meisenheimer complexes[101]. Using this technique the complexes of structure III and IV have been shown to be present in the reaction of trinitroanisole with sodium methoxide in methanol solution.



III



IV

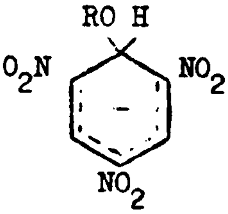
The method also leads to values of the enthalpy of formation of the species involved and these have been determined as -1.48 Kcal mole^{-1} for structure III and as -4.86 Kcal mole^{-1} for structure IV.

(ii) Reactions of Electron Deficient Aromatic Species with Bases

The reactions of polynitroaromatic compounds with bases such as alkaxide[80,81], sulphite[89,102-104], hydroxide[105-107], and cyanide[88,108-114] ions have been extensively studied. The reaction of sym-trinitrobenzene with alkoxides has received particular attention and the results reviewed in detail[76,87,115]. Only the major conclusions on the reactions will be summarised at this time.

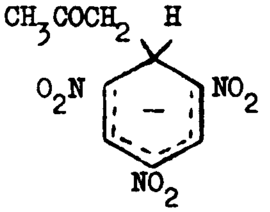
(a) Reactions with alkoxides

Crampton and Gold[80] and Foster and Fyfe[81] have shown by nuclear magnetic resonance spectroscopy that the product of the reaction of sym-trinitrobenzene with alkoxides is a sigma-complex and has the structure V as shown



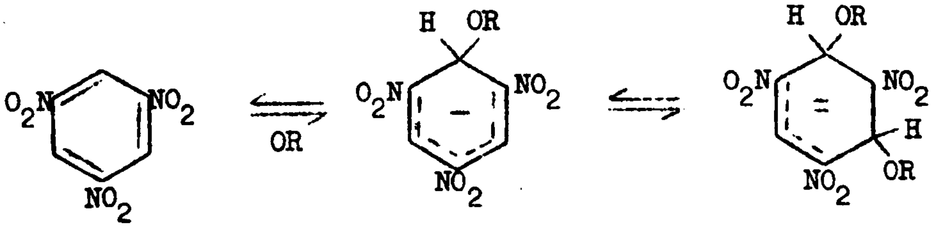
V

This product has been shown to be susceptible to solvolysis[81] and on addition of acetone the sigma-complex having a structure VI is produced.



VI

If the product of structure V is allowed to react with an excess of alkoxide a change is observed in the nuclear magnetic resonance spectrum which is consistent with the formation of a 2:1 adduct of structure VII. The equilibria involved may be represented as shown:



VII

The reactions of trinitroanisole with alkoxides have also been studied and a reaction scheme exactly analagous to that for trinitrobenzene has been proposed[81].

The structure VII and the equivalent structure for trinitroanisole had both previously been proposed on the basis of visible spectroscopic evidence[116] and the results from nuclear magnetic resonance spectroscopy elegantly confirmed previous thinking. The solid product isolated from the reaction of trinitroanisole with excess alkoxide was shown to have a structure analagous to structure V[81] i.e. only a 1:1 sigma complex.

The reactions of the dinitrobenzenes are very similar to those described for trinitrobenzene. However Foreman and Foster[117] have pointed out some interesting reactions of 1-substituted-3,5-dinitrobenzenes. It has been shown by nuclear magnetic resonance that both 3,5-dinitrobenzonitrile and 3,5-dinitrobenzotrifluoride form Meisenheimer complexes with methoxide in solution, the attack generally being at the 2-position. However, with other, particularly more bulky, nucleophiles attack is at the 4-position. In the case where the substituent at the 1-position is iodide (-I) or ethyl carboxylate (-COOEt), the addition of methoxide to a solution of the nitro compound in dimethylsulphoxide produced a deep red colouration characteristic of a Meisenheimer complex. In both cases the original nuclear magnetic resonance absorption collapsed immediately on addition of methoxide but on long standing the original peaks reappeared, however no peaks assignable to Meisenheimer complex formation were observed.

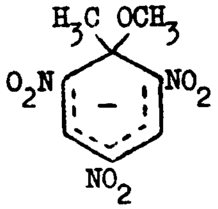
The reactions of polycyclic nitroaromatic compounds have not been so extensively studied as the monocyclic compounds but Meisenheimer complexes derived from the reactions of 1-methoxy and 1-ethoxy-dinitronaphthalene with methoxide ions and ethoxide ions have been reported[118].

Foster[119] has shown that these Meisenheimer complexes undergo a solvolysis with acetone exactly analagous to the solvolysis reaction of the trinitrobenzene/alkoxide Meisenheimer complex.

The reaction of 9-nitroanthracene with methoxide results in Meisenheimer complex formation by addition of the methoxide ion at the 10-position[119], again the complex is susceptible to solvolysis in acetone solution.

The reaction of 9-nitro-10-methoxyanthracene with methoxide is analagous to the reaction of trinitroanisole and Meisenheimer complex formation results from an addition of the methoxide ion at the 10-position[119].

The reactions of trinitrotoluene with bases are less well understood. Hantzsch and Kissel[110] by treating trinitrotoluene with potassium methoxide obtained an addition product, which subsequent to the work of Meisenheimer was ascribed the structure VIII.



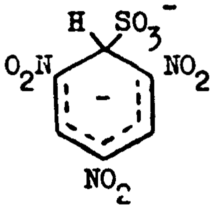
VIII

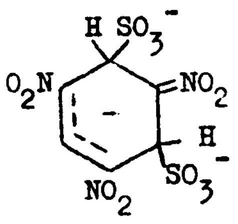
Further studies by Hantzsch and Picton showed that these salts were decomposed by inorganic acids and oxides of nitrogen were evolved[120]. Solid products were simultaneously precipitated and among those isolated were stilbene derivatives and products of oxidation of the methyl group.

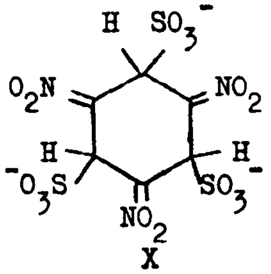
Copisarow[121] attempted an analysis of the products formed in the reaction of trinitrotoluene with alkoxides or alkali metal hydroxides and isolated nitro-nitroso derivatives of dibenzyl and stilbene and also an azoxy compound. Many similar coupled structures have been proposed as being produced in the reaction and even in more recent work doubt still exists as to the precise nature of the products. It has been proposed[122,123] that trinitrotoluene reacts with methoxide to give a benzyl type anion. However, Servis[97] has suggested this to be unlikely and that an addition, to give a Meisenheimer complex, at the 3-position is more probable. However no evidence has been found for this product and the results of Servis tend to suggest radical formation in the system. No further evidence as to the precise nature of this reaction seems to have been proposed.

(b) Reactions with sulphite ions

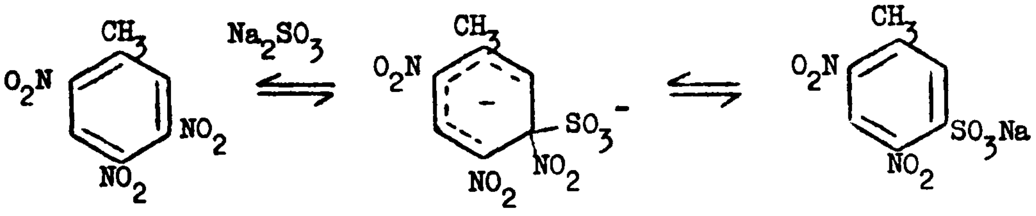
In 1924 Muraour[102] reported that trinitrobenzene and trinitrotoluene would dissolve in aqueous solutions of sodium sulphite to give highly coloured solutions from which the parent nitro compounds can be reformed. It has been shown by Henry that if the sulphite concentration is greater than that of trinitrobenzene a solid crystalline complex of stoichiometry T.N.B: $2Na_2SO_3$ can be isolated[103]. He has suggested that the structures of the species in solution, as the concentration of the sulphite is increased, are analagous to those in the reaction of trinitrobenzene with alkoxides.


VIII


IX


X

Crampton has provided evidence for 1:1 and 2:1 complex formation, using visible and nuclear magnetic resonance spectroscopic techniques, in the reaction of sulphite with 1-substituted-2,4,6-trinitrobenzenes[104]. However, Norris has shown[89], by the method of continuous variation, that the 1:1 adduct predominates in dilute solution. It is interesting to note that the reaction of trinitrotoluene with sodium sulphite is of great practical importance, since it is the simplest and most frequently used way of removing unsymmetrical isomers from crude sym-trinitrotoluene. It has been suggested by Urbanski[124] that the reaction may involve a Meisenheimer complex intermediate

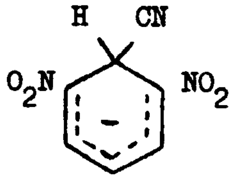


The reaction of sym-trinitrotoluene under these conditions is very slow and hence the separation procedure. It is by no means certain that a reaction of the same type occurs in the symmetrical isomer.[124]

(c) Reactions with cyanide and hydroxide ions

Several references have been made to the reaction of trinitrobenzene with cyanide ions[88,108-114] which results in a deep red coloured solution. Norris[88] made a detailed study of this reaction and showed that it resulted in the formation of a 1:1 complex. He determined the equilibrium constant of the reaction in various solvents and on the basis of the visible and infrared data he suggested the complex to be of Meisenheimer type rather than a charge-transfer complex.

It has been shown[109,111] that the product of the reaction of 1,3-dinitrobenzene in methanol with potassium cyanide is 2-nitro-6-methoxybenzonitrile, the reaction mixture being purple in colour. It seems plausible that the purple colour results from the formation of a Meisenheimer complex, of structure XI, as the first stage of a nucleophilic substitution reaction.



XI

It has been shown[105-107] that the products of the reaction of trinitrobenzene with hydroxide ion in aqueous solution are initially analagous to those resulting from the reaction with sulphite ion and are represented in structures VIII, IX and X. Aqueous solutions of trinitrobenzene in the presence of hydroxide ion undergo a slow irreversible reaction with time, the products include 3,5-dinitrophenol and 33,'55'-tetranitroazoxybenzene[125].

It has been reported that the addition of hydroxide ions to 2,4,6-trinitrotoluene yields the carbanion formed by loss of a proton from the methyl group[126,127].

Evidence for sigma-complex formation has been reported as resulting from the reaction of electron deficient aromatic species with other anions. In the reaction of azide ions with 4-fluoronitrobenzene in dimethylformamide solution sigma-complex formation has been shown to have resulted from the reaction with dimethylamine formed from the solvent[128].

The reactions of polynitrobenzenes with iodide, bromide and thiocyanate yield coloured products but these have been shown by Briegleb[129] to result from weak charge-transfer interaction and not from Meisenheimer complexes.

(iii) Reactions of Electron Deficient Aromatic Species with Amines

Most of the work on the reactions of electron deficient aromatic species with amines has been concentrated on the reactions of trinitrobenzene with various amines. Aromatic amines, unlike aliphatic amines, do not appear to react chemically with trinitrobenzene but rather form donor-acceptor complexes in both ionising and non-ionising solvents[130,131]. Alan, Brook and Caldin[132] have attempted to follow the kinetics of the interaction but the rate of reaction was found to be too rapid to permit measurements to be made. The interaction of di- and trinitrotoluenes with the aromatic amine N,N,N',N'-tetramethyl-p-phenylene diamine also resulted in complex formation rather than in chemical reaction[133,134].

The addition of aliphatic amines to solutions of trinitrobenzene gives rise to intensely coloured solutions. However in contrast to aromatic amines, this colour does not usually appear to completely result from charge-transfer complex formation.

Yada, Tanaka and Nagakuru[135], however, have shown that the interaction of iodine with aliphatic amines leads to charge-transfer complex formation and Foster[136] observed similar behaviour in the reaction between trinitrobenzene and aliphatic amines in solvents of low ionising power and again suggested charge-transfer complex formation to have occured.

The course of the reaction seems to be dependent on the particular amine and on the solvent. Foster[82] showed in a spectrophotometric study of trinitrobenzene with a series of aliphatic amines in chloroform and dioxan, that a fast reaction took place, possibly charge-transfer complex formation, followed by a slow chemical reaction. The continuous variation method of Job[137] showed that for small aliphatic amines (methyl-, ethyl-, dimethyl- and diethylamine) the molar ratio of amine to trinitrobenzene is 3:1 whereas for trimethylamine and sec-butylamine the molar ratio is 1:1. The stoichiometry appears also to be dependent on the solvent system used. In ethanol, 1:1 adduct formation takes place[131] in acetone the ratio is 2:1,[132] and in chloroform 3:1[135]. In almost every case the initial colour formation was complicated by further slow reactions.

Muller and Wynne-Jones[73] have detected a weak electron spin resonance signal from trinitrobenzene with several different aliphatic amines in a variety of protic solvents and have suggested that the signal is derived from the trinitrobenzene radical anion. However, other workers[138,139] have detected similar signals in similar systems but have not been so categorical as to the origin of the signal.

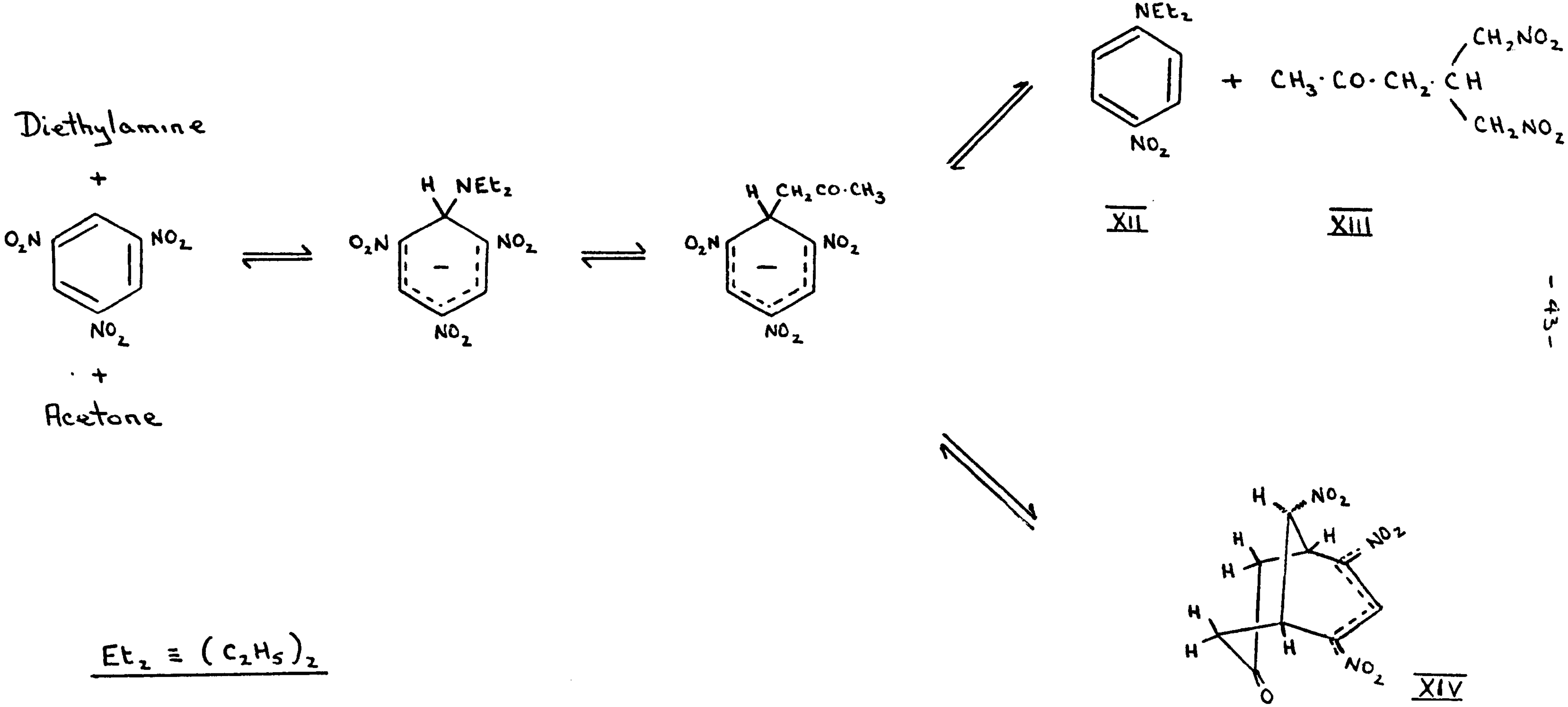
An interesting sequence of reactions is observed when trinitrobenzene reacts with aliphatic amines in ketonic solvents.

The products of this reaction have been elegantly elucidated by nuclear magnetic resonance spectroscopy[139]. The reaction scheme for the interaction of trinitrobenzene with diethylamine in acetone solution is shown in figure 5.

It is interesting to note that the reaction proceeds to give structures XII, p-nitro-N,N-diethylaniline, and XIII, a secondary amine, which probably would not be expected as products of this reaction.

The structure XIV was not finally elucidated until sometime after the original work and three groups of workers[140-142] all postulated the same structure on the basis of nuclear magnetic resonance spectroscopic evidence.

The products of the reactions of the nitrotoluenes with amines have not been so extensively studied. However, Miller and Wynne-Jones[131] have shown that both trinitrotoluene and trinitro-m-xylene will dissolve in pyridine (which has been shown to react like an aliphatic amine[132]) to give an immediate colouration and the resulting solution exhibited electrical conductivity. No firm conclusions were drawn about the nature of this reaction but it was pointed out that the system was complicated by proton transfer reactions.



$Et_2 \equiv (C_2H_5)_2$

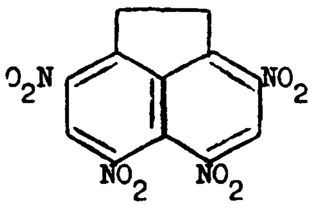
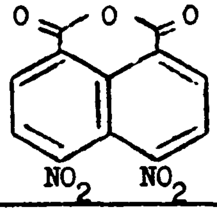
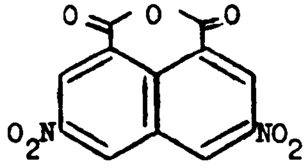
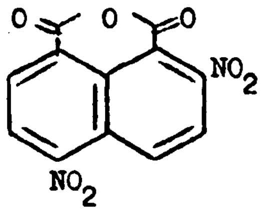
CHAPTER 2

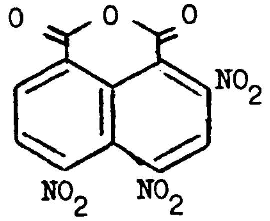
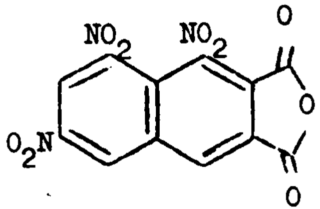
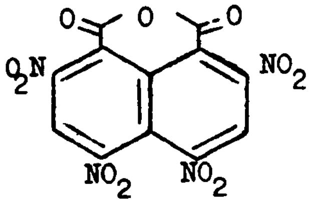
OVERALL ELECTRON ACCEPTOR ABILITY

1. Introduction
2. Relative Acceptor Strengths
3. Thermodynamic Properties of Selected Complexes
4. Electron Transfer in Complexes with N,N,N',N'-Tetramethyl-p-phenylene diamine
5. Infrared Studies of Charge-Transfer Complex Formation.

(1) Introduction

The compounds which form the basis of the investigation reported herein are based on the naphthalene skeleton substituted with nitro groups and with the anhydride group. The compounds studied are represented in the table below by both their structure and name and also by an abbreviation which serves to identify the compound throughout the text. Brief reference is given to the solubility of each compound since this property has largely governed the extent of the investigation.

NAME AND STRUCTURAL FORMULA	ABBREVIATION	SOLUBILITY PROPERTIES
3,5,6,8-tetranitroacenaphthene 	T.N.A.	Sparingly soluble in dichloromethane very sparingly soluble in chloroform
4,5-dinitro-1,8-naphthalic anhydride 	4,5-D.N.N.A.	Insoluble in halogenated hydrocarbons
3,6-dinitro-1,8-naphthalic anhydride 	3,6-D.N.N.A.	Very sparingly soluble in halogenated hydrocarbons soluble in 'complexing' solvents
2,5-dinitro-1,8-naphthalic anhydride 	2,5-D.N.N.A.	Very sparingly soluble in halogenated hydrocarbons

NAME AND STRUCTURAL FORMULA	ABBREVIATION	SOLUBILITY PROPERTIES
2,4,5-trinitro-1,8-naphthalic anhydride 	Tri.N-1,8-N.A.	Insoluble in halogenated hydrocarbons
1,6,8-trinitro-2,3-naphthalic anhydride 	Tri.N-2,3-N.A.	Insoluble in halogenated hydrocarbons
2,4,5,7-tetranitro-1,8-naphthalic anhydride 	T.N.N.A.	Insoluble in halogenated hydrocarbons

In any study of electron deficient aromatic systems it is of interest to have a knowledge of the relative acceptor strengths of the compounds involved. The acceptor strength of the nitroaromatic compounds were compared by methods which are dependent on the determination of the wavelength of maximum absorption of the charge-transfer complexes formed with common donors. The variation of the charge-transfer maximum with solvent was also investigated.

The values of the association constants for the charge-transfer equilibria between T.N.A. and various methyl benzenes were determined by nuclear magnetic resonance spectroscopy. It was not possible to make a comparative study with the other compounds since the others were not sufficiently soluble in an 'inert' solvent to allow the nuclear magnetic resonance measurements to be made. Even with T.N.A. it was not possible to use homologues higher than mesitylene since the complexes were insoluble.

The value of the association constant, and other thermodynamic parameters, for the equilibrium between 3,6-D.N.N.A. and pyrene was determined by visible spectroscopy. Again, no comparison with other nitroaromatic compounds was possible because either the parent compound or the complex was insoluble.

The complexes formed between the nitroaromatic compounds and N,N,N',N'-tetramethyl-*p*-phenylene diamine were investigated by electron spin resonance spectroscopy in an attempt to determine the extent of electron transfer from the donor to the acceptor molecule.

A brief investigation of the infrared spectra of the complexes formed between the acceptor molecules and anthracene has also been made.

(2) Relative Acceptor Strengths

(a) Experimental techniques

(i) Preparation of solid complexes

The nitroaromatic anhydride (1 gm) was dissolved in a minimum quantity of hot acetic anhydride and this solution was added to a hot solution of chloroform containing an equimolar quantity of the chosen donor (see Table 1). The resulting mixture was cooled and the solid which precipitated was filtered off, washed with petroleum ether (40° - 60°) and dried under vacuum. The results of elemental analysis on the complexes suggested 1:1 complex formation to have taken place.

In the case of the T.N.A. complexes, the solvent used for initially dissolving T.N.A. was a 1:1 mixture of nitromethane and chloroform.

It can be seen from Table 1 that the complexes of T.N.N.A. and certain of the complexes of 4,5-D.N.N.A. and Tri.N-1,8-N.A. could not be isolated in the solid state.

(ii) Spectrophotometric methods

The visible absorption spectra of the solid state complexes were recorded on a Unicam S.P. 800 spectrophotometer fitted with a Unicam diffuse reflectance attachment.

The visible absorption spectra of the complexes of 3,6-D.N.N.A., 2,5-D.N.N.A., T.N.A. and sym-trinitrobenzene (T.N.B.) in chloroform solution were obtained using a Unicam S.P. 800 spectrophotometer. A chloroform solution of each acceptor was mixed with a chloroform solution of the required donors (see Table 2) and for the 3,6-D.N.N.A., 2,5-D.N.N.A. and T.N.A. complexes in solution the spectra were recorded in 4 cm matching silica cells using a solution of the acceptor at the same concentration in the reference beam. A similar technique was used for the T.N.B. complexes in solution using 1 cm matching silica cells.

(b) Results

The charge-transfer band observed in the solid state was extremely broad which made it difficult to obtain an accurate position of the charge-transfer maximum. The results, given in Table 1, are estimated to an accuracy of ± 10 nm.

The results obtained from the solution spectra are given in Table 2. The results for the complexes formed with T.N.B. and 3,6-D.N.N.A. are estimated to an accuracy of ± 5 nm., whereas, owing to solubility problems, those for the complexes of T.N.A. and 2,5-D.N.N.A. are estimated to an accuracy of ± 10 nm. The values obtained for the T.N.B. complexes compare well with previously reported values from the literature.[143, 144, 145]

(c) Discussion

A convenient method of determining the acceptor strength of a compound is to use the dependence of the energy of charge-transfer on the molecular orbital coefficients of the donor involved.[19, 146] The charge-transfer transition occurs when an electron initially occupying an orbital i of the donor (D) is promoted into one of the empty orbitals j of the acceptor (A). The transition energy (Eij) for this process is given by:

$$Eij = Aj - Di \qquad (15)$$

where Aj is the energy of the orbital j of the acceptor and Di is the energy of the orbital i of the donor. If the donor is a polycyclic aromatic hydrocarbon the orbital energies are given in the simple molecular orbital theory by:

$$Di = \alpha_0 + \beta x_i \qquad (16)$$

where α_0 is the coulombic integral for an sp^2 hybridised carbon atom and β is the resonance integral for a carbon-carbon bond in

TABLE 1 The charge transfer maxima (λ_{max} nm.) and the energy of charge transfer ($E_{C.T.}$ eV) for a series of solid state donor-acceptor complexes

DONOR ACCEPTOR		Naphthalene	Phenanthrene	Chrysene	1,2,5,6-Dibenzanthracene	1,2-Benzanthracene	Pyrene	Anthracene	3,4-Benzopyrene	Perylene
4,5-D.N.N.A.	λ_{max}	450	450	COMPLEXES			560	560	610	620
	$E_{C.T.}$	2.76	2.76	UNSTABLE			2.21	2.21	2.03	2.00
3,6-D.N.N.A.	λ_{max}	390	390	450	470	470	490	500	550	570
	$E_{C.T.}$	3.14	3.14	2.76	2.64	2.64	2.53	2.48	2.26	2.18
2,4,5-Tri.N-1,8-N.A.	λ_{max}	460	470	COMPLEXES			570	600	640	670
	$E_{C.T.}$	2.70	2.64	UNSTABLE			2.18	2.07	1.94	1.85
1,5,8-Tri.N-2,3-N.A.	λ_{max}	440	450	490	530	560	550	550	610	640
	$E_{C.T.}$	2.82	2.76	2.53	2.34	2.21	2.25	2.25	2.03	1.94
T.N.A.	λ_{max}	400	400	430	465	470	460	480	510	550
	$E_{C.T.}$	3.10	3.10	2.88	2.67	2.64	2.70	2.58	2.43	2.26
T.N.N.A.		SOLID STATE COMPLEXES UNSTABLE								
T.N.B.	λ_{max}	400	410	450	450	460	475	490	520	530
	$E_{C.T.}$	3.10	3.02	2.76	2.76	2.70	2.61	2.53	2.38	2.34
CALCULATED VALUE OF X_i		0.618	0.605	0.520	0.473	0.452	0.445	0.414	0.371	0.347

TABLE 2 The charge transfer maxima (λ_{max} nm.) and the energy of charge transfer ($E_{C.T.}$ eV) for a series of donor-acceptor complexes in chloroform solution.

DONOR ACCEPTOR		Naphthalene	Phenanthrene	Chrysene	1,2,5,6-Dibenzanthracene	1,2-Benzanthracene	Pyrene	Anthracene	3,4-benzopyrene	Perylene
3,6-D.N.N.A.	λ_{max}	410	410	460	490	510	510	525	570	600
	$E_{C.T.}$	3.04	3.04	2.70	2.53	2.43	2.43	2.36	2.18	2.07
2,5-D.N.N.A.	λ_{max}	420	420	460	500	520	520	525	570	600
	$E_{C.T.}$	2.95	2.95	2.70	2.48	2.38	2.38	2.36	2.18	2.07
T.N.A.	λ_{max}	370	370	420	420	450	455	470	490	500
	$E_{C.T.}$	3.37	3.37	2.95	2.95	2.76	2.72	2.64	2.53	2.48
T.N.B.	λ_{max}	370	370	420	430	440	445	460	475	480
	$E_{C.T.}$	3.37	3.37	2.95	2.88	2.84	2.80	2.70	2.62	2.58
Calculated value of Xi		0.618	0.605	0.520	0.473	0.452	0.445	0.414	0.371	0.347

benzene, Xi is a theoretically calculated molecular orbital parameter.

The first charge-transfer band is defined as being derived from a transition of an electron from the highest occupied orbital of the donor to the lowest vacant orbital of the acceptor and the energy of this transition is given by:

$$\begin{aligned} Eij &= (A - \alpha) - \beta Xi & \text{(17a)} \\ &= K - \beta Xi & \text{(17b)} \end{aligned}$$

where K is a constant related to the lowest vacant molecular orbital of the acceptor. The value of the parameter Xi, for the highest occupied molecular orbital of the donor, has been calculated by Coulson and Daudel.[147] Equation 17b suggests that Eij should be a linear function of the quantity Xi regardless of the values of K and β. The equation requires also that the slopes of the lines obtained from data for complexes with different acceptors should be the same, being equal to β, the resonance integral of the carbon-carbon bond in benzene.

Plots of the molecular orbital energy Xi against the energy of charge-transfer for each of the acceptors with a series of donors were constructed and their slopes and intercepts computed using a least squares method. Some typical plots are shown in figure 6. The results are listed in Table 3 for the solid state complexes and in Table 4 for the complexes in chloroform solution. In Tables 3 and 4 the acceptors are listed in order of decreasing orbital energy which corresponds to the order of increasing acceptor strength.

It can be seen from Tables 3 and 4 that the value of the resonance integral β is not quite constant as predicted by the theory. This, however, is in agreement with the results of Nepras and Zahradnik[148,149] who have shown that the value of β is somewhat dependent on both the class of the donor and on the particular acceptor being investigated.

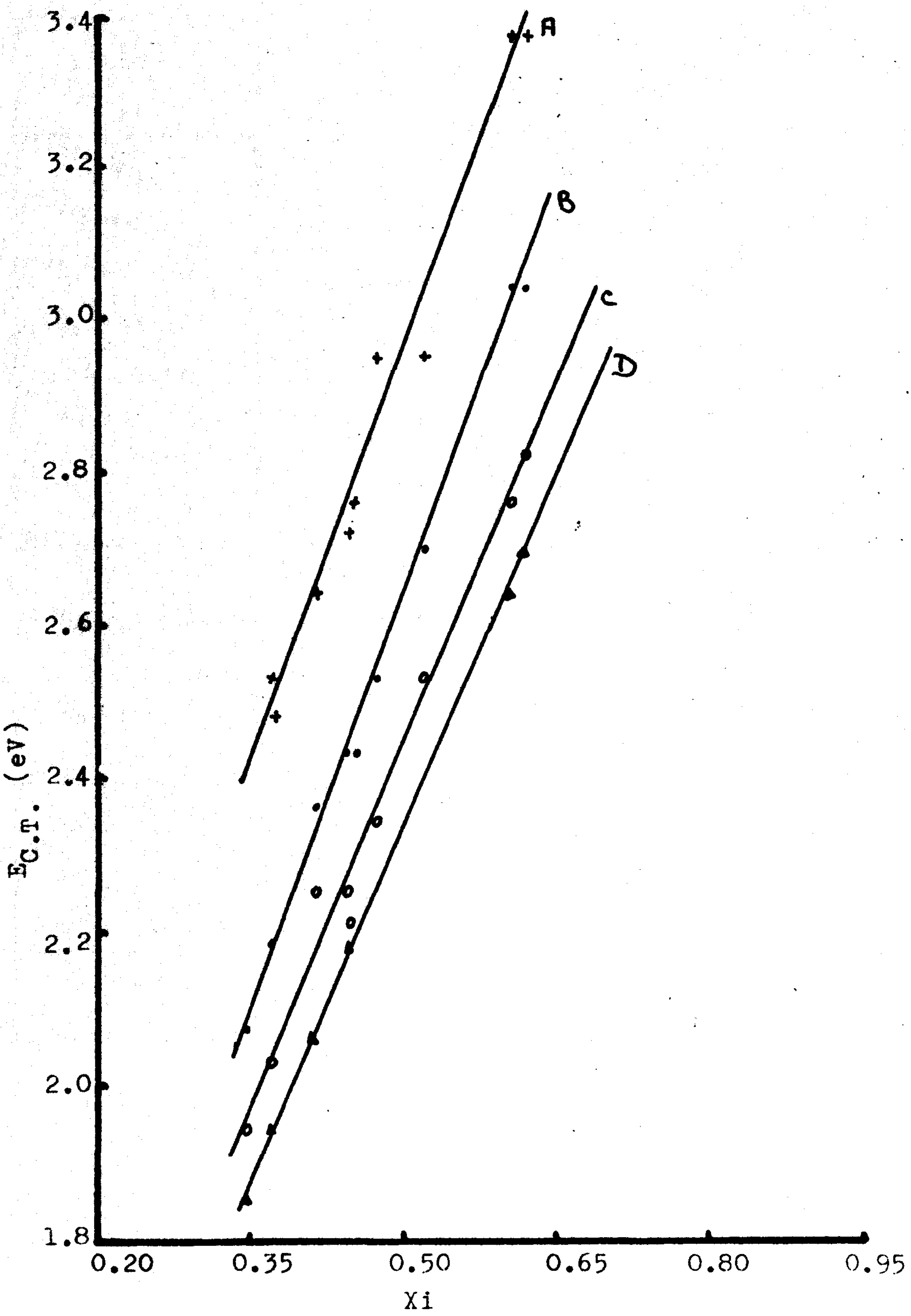


Figure 6 Plots of the energy of the charge - transfer transition (eV) against Xi for complexes of (A) T.N.A. (B) 3,6 - D.N.N.A. in chloroform solution (C) Tri.N -1,8- N.A. and (D) Tri.N -2,3- N.A. in the solid state.

TABLE 3 Summary of Results from Solid State Complexes

Acceptor	Resonance Integral β	Intercept	Energy of the L.V.M.O. of Acceptor
T.N.B.	-2.78 ± 0.2	-0.496	$(\alpha + 1.38) \pm 0.1$
T.N.A.	-3.03 ± 0.2	-0.423	$(\alpha + 1.28) \pm 0.1$
3,6-D.N.N.A.	-3.58 ± 0.15	-0.265	$(\alpha + 0.95) \pm 0.05$
4,5-D.N.N.A.	-2.95 ± 0.15	-0.319	$(\alpha + 0.94) \pm 0.05$
Tri.N-2,3-N.A.	-3.23 ± 0.2	-0.256	$(\alpha + 0.83) \pm 0.05$
Tri.N-1,8-N.A.	-3.08 ± 0.15	-0.258	$(\alpha + 0.80) \pm 0.05$

TABLE 4 Summary of Results from Complexes in Chloroform Solution

Acceptor	Resonance Integral β	Intercept	Energy of the L.V.M.O. of Acceptor
T.N.B.	-3.13 ± 0.2	-0.457	$(\alpha + 1.43) \pm 0.1$
T.N.A.	-3.62 ± 0.3	-0.323	$(\alpha + 1.17) \pm 0.15$
2,5-D.N.N.A.	-3.42 ± 0.2	-0.255	$(\alpha + 0.87) \pm 0.1$
3,6-D.N.N.A.	-3.56 ± 0.15	-0.239	$(\alpha + 0.85) \pm 0.05$

Another method for the comparison of acceptor strengths involves the comparison of the magnitudes of the energy of charge-transfer of several acceptors with a specific donor, the smaller the charge-transfer energy the stronger the electron acceptor ability. In Table 5 a comparison is made using this method with pyrene, anthracene and naphthalene as donors for the solid state complexes, and a similar comparison is made, in Table 6, for complexes in chloroform solution.

It can be seen from a comparison of Tables 3 and 5 that the order of acceptor strengths compare reasonably well, except that the order for T.N.A. and T.N.B. and for 4,5-D.N.N.A. and Tri.N-2,3-N.A. is reversed. A similar comparison can be made between Tables 4 and 6 and again the order of acceptor strengths compare reasonably well except that in this case the order for 3,6-D.N N.A. and 2,5-D.N.N.A. is reversed.

The molecular orbital approach results (see Tables 3 and 4) would be expected to be the more reliable for the determination of relative acceptor strengths since the method is based on a statistical average of the charge-transfer energies of an acceptor with several donors, whereas the method of comparison of charge-transfer energies is only based on a single measurement.

It has been shown by McConnell <u>et al</u>[21] that there is an approximately linear relationship between the ionisation potential of the donor, I^D, and the energy of charge-transfer, $E_{C.T.}$, for the complexes of iodine with weak donors:

$$E_{C.T.} = h\nu_{C.T.} = I^D - E^A - W \qquad (18)$$

where EA is the electron affinity of the acceptor and W is the dissociation energy of the excited state of the complex. This

TABLE 5 The Charge Transfer Energies (in eV) for the Acceptors with a Single Donor in the Solid State

Donor Acceptor	Pyrene	Anthracene	Naphthalene
T.N.A.	2.70	2.58	3.10
T.N.B.	2.61	2.53	3.10
3,6-D.N.N.A.	2.53	2.48	3.14
Tri.N-2,3-N.A.	2.25	2.25	2.82
4,5-D.N.N.A.	2.21	2.21	2.76
Tri.N-1,8-N.A.	2.18	2.06	2.70

TABLE 6 The Charge Transfer Energies (in eV) for some Acceptors with a Single Donor in Chloroform Solution

Donor Acceptor	Pyrene	Anthracene	Naphthalene
T.N.B.	2.80	2.70	3.37
T.N.A.	2.72	2.64	3.37
3,6-D.N.N.A.	2.43	2.36	3.04
2,5-D.N.N.A.	2.38	2.36	2.95

equation may be generalised into the form

$$h\nu_{C.T.} = a\,I^{D} + b \qquad (19)$$

Based on equation (19) a plot of $\nu_{C.T.}$ for a set of complexes of a series of donors with one acceptor against the corresponding value of $\nu_{C.T.}$ for a set of complexes of the same donors with a second acceptor should be a straight line. The gradient of the plot is related to the parameter a in equation 19 and takes a value of unity if both acceptors are of the same type. Such a plot is shown in figure 7 where the charge-transfer energies of a series of 3,6-D.N.N.A. complexes and 4,5-D.N.N.A. complexes are plotted against the corresponding charge-transfer energies of the same series of T.N.B. complexes.

The parameter b in equation 19 can be seen, by comparison with equation 18, to be related to the electron affinity of the acceptor. The electron affinity of an organic molecule directly governs its electron acceptor properties and the greater the electron affinity the stronger are the electron acceptor powers of the molecule.

The methods of determining electron affinities have been reviewed in detail by Briegleb[26]. Several equations have been derived in this work and the ones used in the present determinations are listed below.

$$\nu_{C.T.} = 0.701\nu_{o} + 0.81 - EA \qquad (20)$$

$$(\nu_{C.T.})_{i} = (\nu_{C.T.})_{j} = EA_{j} - EA_{i} \qquad (21)$$

$$EA = -1.04\,\epsilon_{\frac{1}{2}}^{Red} + 1.39 \qquad (22)$$

For pyrene complexes

$$\epsilon_{\frac{1}{2}}^{Red} = \nu_{C.T.} - 2.09 \qquad (23)$$

For pyrene complexes

$$\nu_{CT} = -EA + 3.51 \qquad (24)$$

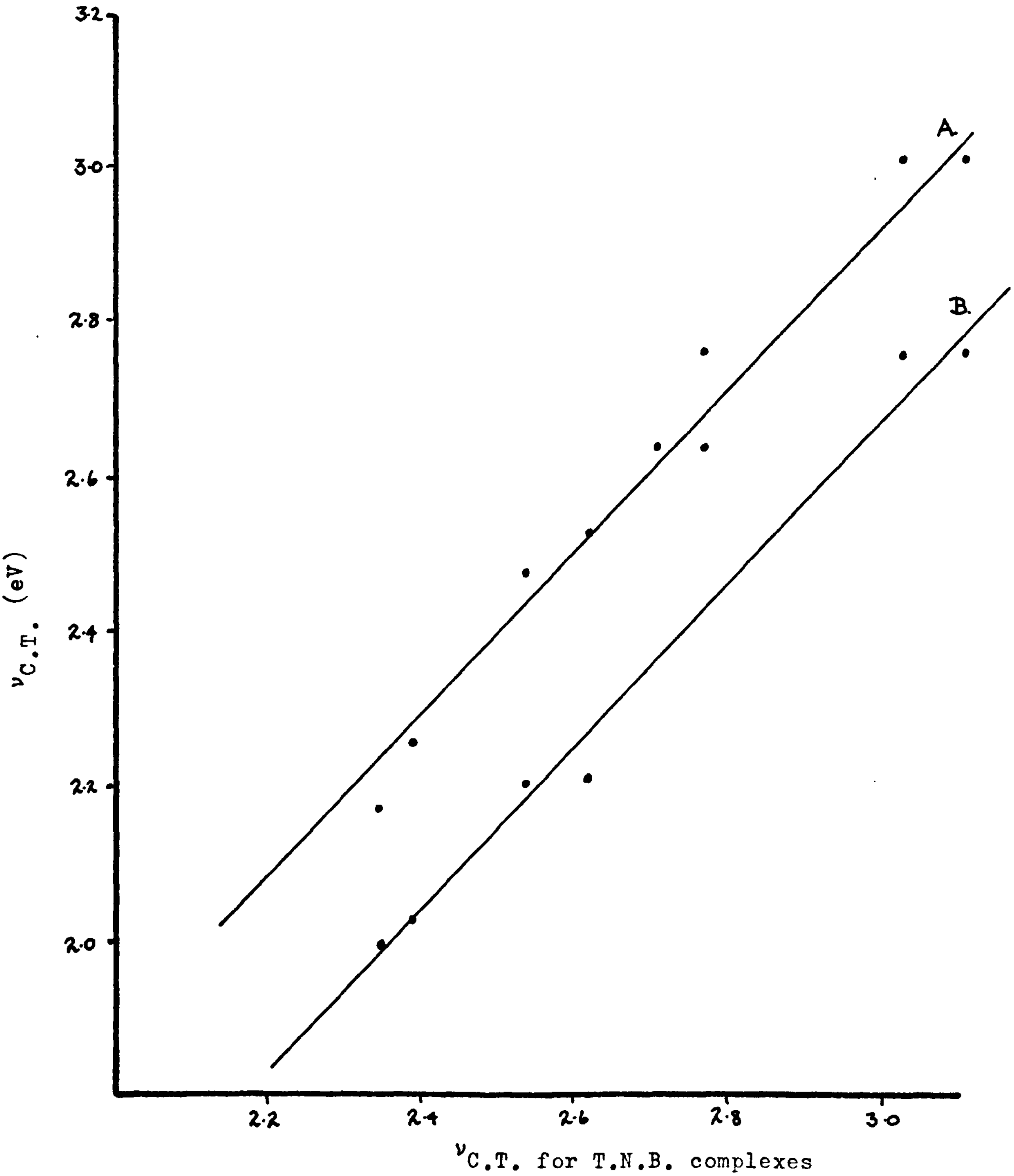


Figure 7 Plots of $\nu_{C.T.}$ for a series of complexes of (A) 3,6 - D.N.N.A. and (B) 4,5 - D.N.N.A. against $\nu_{C.T.}$ for the corresponding complexes of T.N.B. in the solid state.

The energies of the charge-transfer transitions in the complexes of the acceptors with pyrene both in the solid state and in chloroform solution are listed in Table 7. The method of calculation using equation 21 requires the use of a standard electron affinity and that of T.N.B. is used for this purpose. Hence the energy of the charge-transfer transition in the complex between T.N.B. and pyrene both in the solid state and in chloroform solution is included in Table 7.

The mean value of the electron affinities as determined by the various methods were calculated and the results as derived from the solid state complexes are listed in Table 8 and as derived from the complexes in chloroform solution in Table 9. The compounds are listed in Tables 8 and 9 in order of increasing electron affinity which corresponds to increasing acceptor strength.

By comparing Tables 3 and 8 it can be seen that the order derived from the molecular orbital approach compares favourably with the electron affinity results when derived from the solid state complexes. The only difference being the exchange in relative position of 4,5-D.N.N.A. and Tri.N-2,3-N.A. In the results derived from the solution studies it can be seen by comparing Tables 4 and 9 that the electron affinity results reverse the relative positions of 2,5-D.N.N.A. and 3,6-D.N.N.A. from that observed by the molecular orbital method. However the acceptor strength of 2,5-D.N.N.A. and 3,6-D.N.N.A. are shown, by both methods, to be very similar and the reversal is probably insignificant. A similar argument may be proposed for the reversal of 4,5-D.N.N.A. and Tri.N-2,3-N.A. on the electron affinity results. However, by comparison with the electron affinity of 3,6-D.N.N.A. the result for the electron affinity of 4,5-D.N.N.A. seems rather high.

TABLE 7 Charge Transfer Energies of Some Acceptors with Pyrene in the Solid State and in Chloroform Solution

Acceptor	Charge Transfer Energy (eV)	
	Solid State	Solution
4,5-D.N.N.A.	2.21	-
3,6-D.N.N.A.	2.53	2.43
2,5-D.N.N.A.	-	2.38
Tri.N-1,8-N.A.	2.18	-
Tri.N-2,3-N.A.	2.25	-
T.N.A.	2.70	2.72
T.N.B.	2.61	2.80

TABLE 8 Calculated Electron Affinities from Solid State Results

Acceptor	I*	II*	III*	IV*	Mean
T.N.A.	0.72	0.61	0.71	0.81	0.71
3,6-D.N.N.A.	0.89	0.78	0.92	0.98	0.89
Tri.N-2,3-N.A.	1.17	1.06	1.25	1.26	1.18
4,5-D.N.N.A.	1.21	1.10	1.18	1.30	1.20
Tri.N-1,8-N.A.	1.24	1.13	1.22	1.33	1.23

TABLE 9 Calculated Electron Affinities from Solution Results

Acceptor	I*	II*	III*	IV*	Mean
T.N.A.	0.70	0.78	0.73	0.85	0.77
3,6-D.N.N.A.	0.99	1.07	1.05	1.14	1.06
2,5-D.N.N.A.	1.04	1.12	1.08	1.19	1.11

* I - Derived from equation 20

II - Derived from equation 21

III - Derived from equation 22 and equation 23

IV - Derived from equation 24

Examination of the electron affinity results and the results derived from the molecular orbital method suggest that T.N.A. is a slightly stronger electron acceptor than T.N.B.. The nitroaromatic anhydrides are stronger acceptors than T.N.A., as might be expected, and the acceptor strength increases with increasing number of nitro groups. The results from the molecular orbital method on the solid state complexes suggest that 3,6-D.N.N.A. and 4,5-D.N.N.A. are very similar in acceptor strength and likewise 3,6-D.N.N.A. and 2,5-D.N.N.A. from the solution results. Thus it can be concluded that the dinitronaphthalic anhydrides show similar acceptor strengths, and that the acceptor strength of the nitroaromatic anhydrides is dependent on the number rather than the relative positioning of the nitro groups on the naphthalene skeleton. This fact is borne out in the trinitronaphthalic anhydrides which show almost identical acceptor strength, their acceptor strength being greater than that of the dinitronaphthalic anhydrides.

It would appear, at first sight, that this result differs from the results obtained in a spectroscopic study of the isomeric dinitronaphthalenes[5]. In this study the association constants for the charge-transfer equilibria and the free energy of formation of the complexes varied to an observable extent and this variation was correlated with the relative positioning of the nitro groups on the naphthalene ring. However, the determination of association constants is a sensitive method and if it could be applied in the case of the isomeric dinitronaphthalic anhydrides a similar trend may be observed.

The effect on the acceptor properties of increasing the number of nitro groups in a nitroaromatic anhydride is further shown up by a comparison of the present results for 3,6-D.N.N.A. with those of Berger[150] for 3-nitronaphthalic anhydride. The calculated energies of the lowest vacant molecular orbital of the acceptors are shown in the table along with the corresponding values for T.N.B..

Acceptor	Resonance Integral β	Energy of L.V.M.O. of Acceptor
*T.N.B.	-3.13	$\alpha + 1.43$
T.N.B.	-3.00	$\alpha + 1.38$
N.N.A.	-3.58	$\alpha + 1.128$
*3,6-D.N.N.A.	-2.39	$\alpha + 0.85$

* Values obtained in the present study

N.N.A. = 3-nitro-1,8-naphthalic anhydride

It can be seen that the addition of an extra nitro group markedly lowers the energy of the lowest vacant molecular orbital of the nitroaromatic anhydride and hence increases its electron acceptor ability.

(3) Thermodynamic Properties of Selected Complexes

To enable a more strict comparison between the acceptor strengths of the nitroaromatic compounds at present being investigated and the acceptor strengths of known acceptor molecules it is convenient to determine the association constant for the equilibrium

$$D + A \rightleftharpoons DA$$

If the association constant is measured at various temperatures then information on the enthalpy of formation of the complexes can be obtained. A measure of the degree of ionic character of the complex can also be derived.

Two of the main methods for evaluating association constants involve the use of visible spectroscopy and nuclear magnetic resonance spectroscopy. In the visible spectroscopic method the equation of Foster, Hammick and Wardley[34], based on the Benesi-Hilderbrand equation, is commonly used:

$$\frac{OD}{[D_o]} = -K_c^{AD}.OD + K_c^{AD}[A_o]\,\epsilon_{\lambda}^{AD} \qquad (25)$$

In the nuclear magnetic resonance method the equation introduced into the field of charge-transfer complexes by Hanna and Ashbough[35] and subsequently modified by Foster and Fyfe[36] is used:

$$\Delta / [D] = -K_c^{AD}.\Delta + \Delta_o K_c^{AD} \qquad (26)$$

In the present work, it was not possible to determine association constants for equilibria involving all the compounds under study owing to the general insolubility of the parent compounds and their complexes. However the association constant for the equilibrium between 3,6-D.N.N.A. and pyrene was measured by visible spectroscopy and that for the equilibria between T.N.A. and various methyl benzenes by nuclear magnetic resonance spectroscopy. The results obtained for these two acceptors are representative for the group as a whole, and with a knowledge of the relative electron acceptor strengths as evaluated by the methods outlined in the previous section, it would be possible to extrapolate, to a first approximation, the findings on the values of the association constants to the other acceptors.

(a) 3,6-D.N.N.A.-Pyrene Complex

(i) Experimental

The method of continuous variations[137] was applied to the 3,6-D.N.N.A.-pyrene equilibrium in chloroform solution at each temperature at which the equilibrium constant was determined. The measurements were made on a Unicam S.P. 500 spectrophotometer with a constant temperature cell compartment, temperature control was to within ± 0.1°C.

The determination of the association constants at 2.9°C, 27.5°C and 41.0°C were made using the same spectrophotometer. A graph of the temperature of the cell compartment against time was plotted to determine the time required to reach equilibrium and each sample was allowed to attain equilibrium before the measurements were taken at a wavelength of 510 nm. Each reading was repeated 3 times and the average value taken.

(ii) Results

The method of continuous variations showed that the overall stoichiometry of the complex formed between 3,6-D.N.N.A. and pyrene, at each of the temperatures, was 1:1. A typical plot of the results from the method of continuous variations for the 3,6-D.N.N.A.-pyrene equilibrium is shown in figure 8. The results from the determinations of the association constant at each of the three temperatures are given in Table 10. The plots of $OD/[D_0]$ against OD at each of the three temperatures are shown in figure 9. The slope and intercept of the plots were computed by a least squares method. The values of the association constants and extinction coefficients at the three

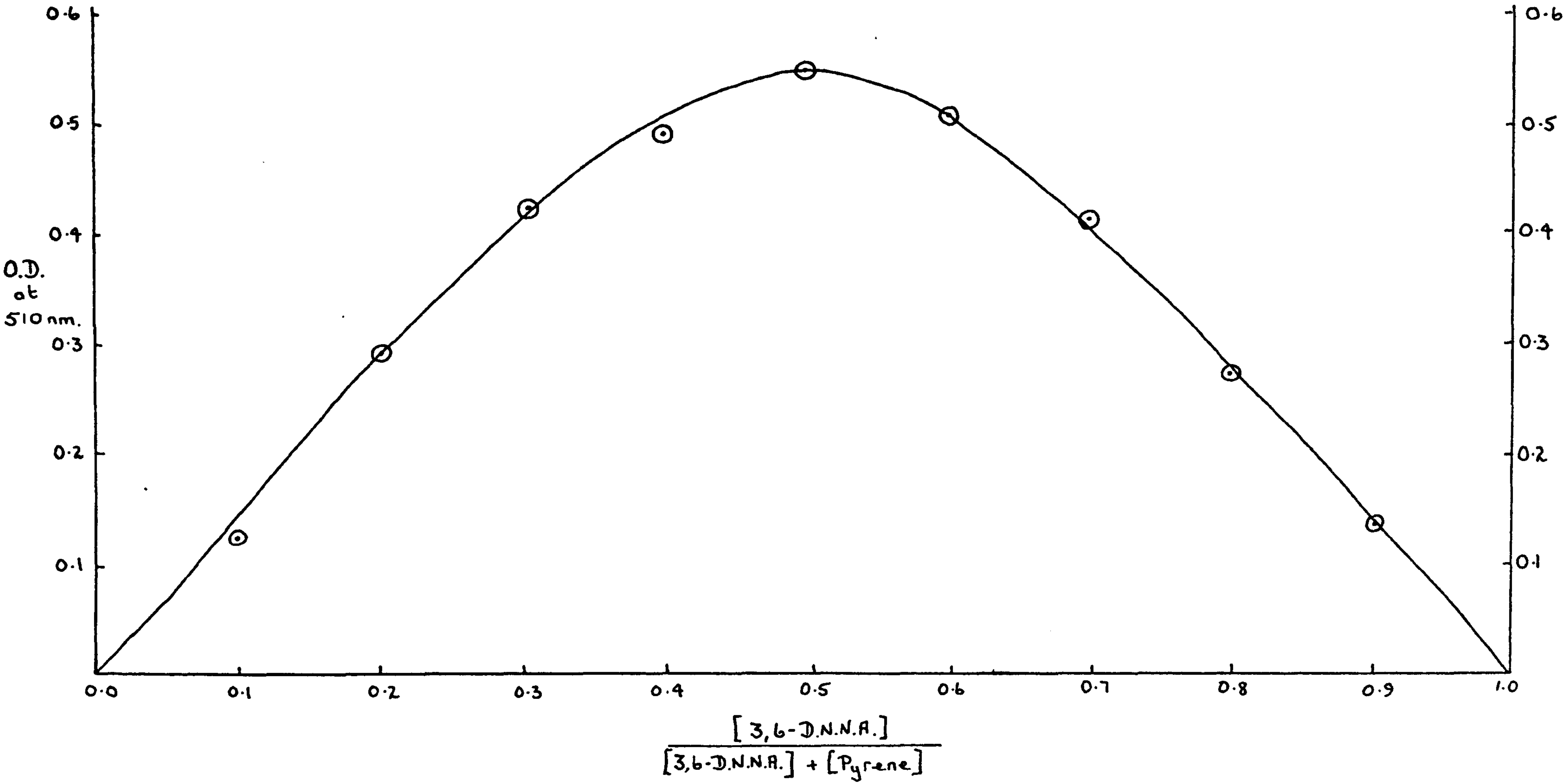


Figure 8 Job plot for the 3,6, - D.N.N.A. - pyrene charge - transfer complex equilibrium at 27.5°C.

TABLE 10 3,6-D.N.N.A./Pyrene Complexes

Temperature 2.9°C Constant Acceptor Conc 2.20 x 10^{-4}M

Optical Density	Donor Concentration M	O.D./Donor Conc M^{-1}
0.642	2.667 x 10^{-1}	2.407
0.628	2.401 x 10^{-1}	2.616
0.590	2.134 x 10^{-1}	2.765
0.561	1.867 x 10^{-1}	3.004
0.528	1.600 x 10^{-1}	3.299
0.500	1.334 x 10^{-1}	3.749
0.450	1.067 x 10^{-1}	4.218
0.392	0.800 x 10^{-1}	4.899
0.302	0.533 x 10^{-1}	5.661
0.179	0.267 x 10^{-1}	6.711
Temperature 27.5°C	Constant Acceptor Conc	2.50 x 10^{-4}M
0.460	2.663 x 10^{-1}	1.727
0.435	2.397 x 10^{-1}	1.815
0.401	2.131 x 10^{-1}	1.882
0.373	1.864 x 10^{-1}	2.001
0.336	1.598 x 10^{-1}	2.103
0.302	1.332 x 10^{-1}	2.268
0.255	1.065 x 10^{-1}	2.394
0.202	0.799 x 10^{-1}	2.528
0.147	0.532 x 10^{-1}	2.760
Temperature 41.0°C	Constant Acceptor Conc	3.19 x 10^{-4}M
0.381	2.669 x 10^{-1}	1.427
0.354	2.402 x 10^{-1}	1.474
0.332	2.134 x 10^{-1}	1.555
0.289	1.869 x 10^{-1}	1.595
0.268	1.602 x 10^{-1}	1.673
0.230	1.335 x 10^{-1}	1.723
0.190	1.068 x 10^{-1}	1.780
0.148	0.801 x 10^{-1}	1.848
0.102	0.534 x 10^{-1}	1.911

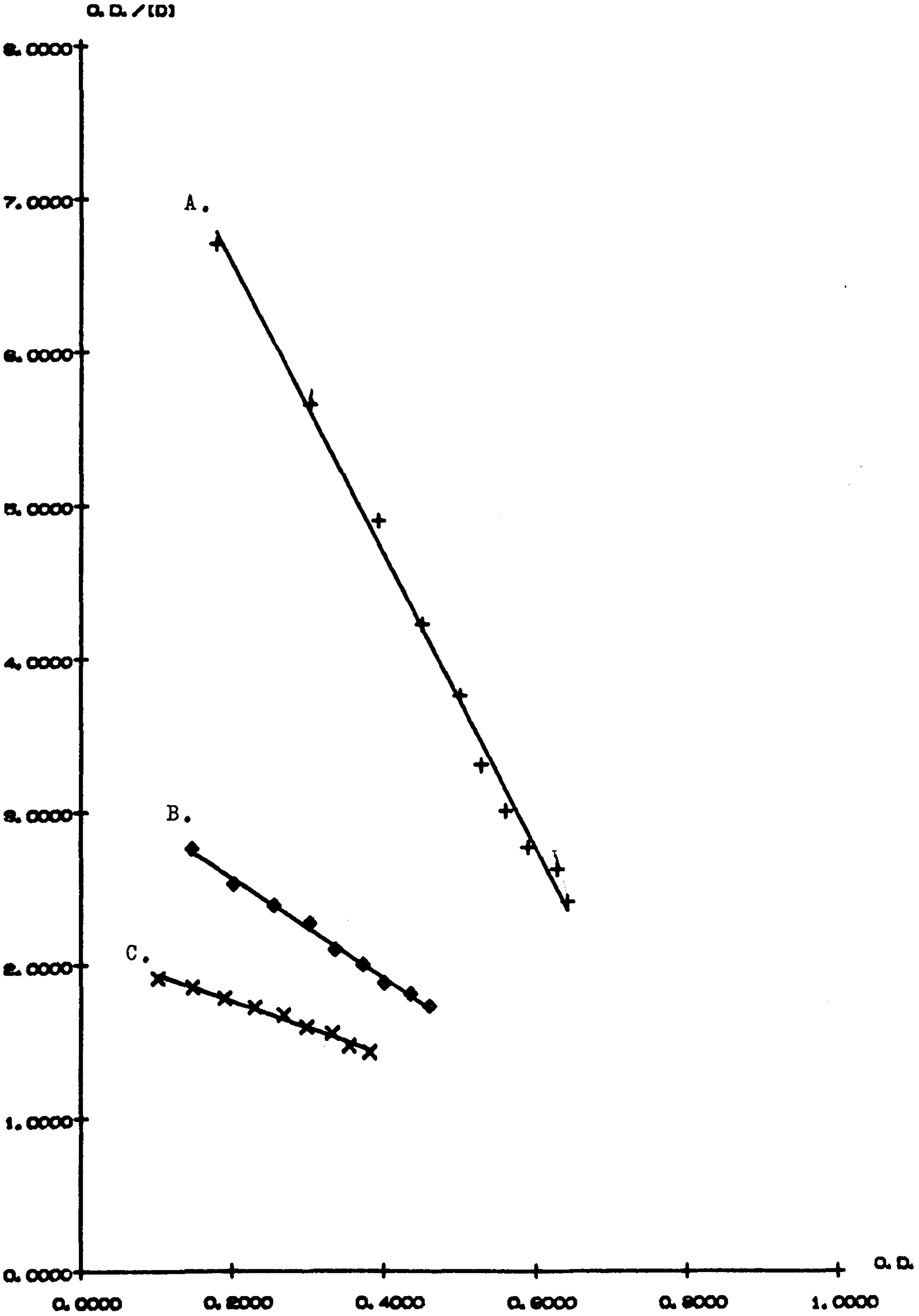


Figure 9 Plots of O.D./[D_o] against O.D. for 3,6 - D.N.N.A. - pyrene complex formation at (A) 2.9°C. (B) 27.5°C. and (C) 41.0°C. all in chloroform solution.

temperatures derived from measurements taken at the charge-transfer maximum wavelength of 510 nm. are given below.

Temperature °C	Association Constant l. mole^{-1}	Extinction Coefficient l. mole^{-1} cm^{-1}
2.9	9.56 ± 0.25	4040
27.5	3.27 ± 0.10	3920
41.0	1.73 ± 0.07	3820

The bonding enthalpy $(-\Delta H)$ for the complex can be obtained by using the integrated form of the van't Hoff equation

$$\log K = \frac{-\Delta H}{2.303\ RT} + \text{constant} \qquad (27)$$

A plot of log K against the reciprocal of the absolute temperature, T, should yield a straight line the slope of which will be $-\Delta H/2.303\ R$, where R is the gas constant. This plot is shown in figure 10 and the bonding enthalpy derived from the slope has a value of -7.32 ± 0.5 Kcal mole^{-1}.

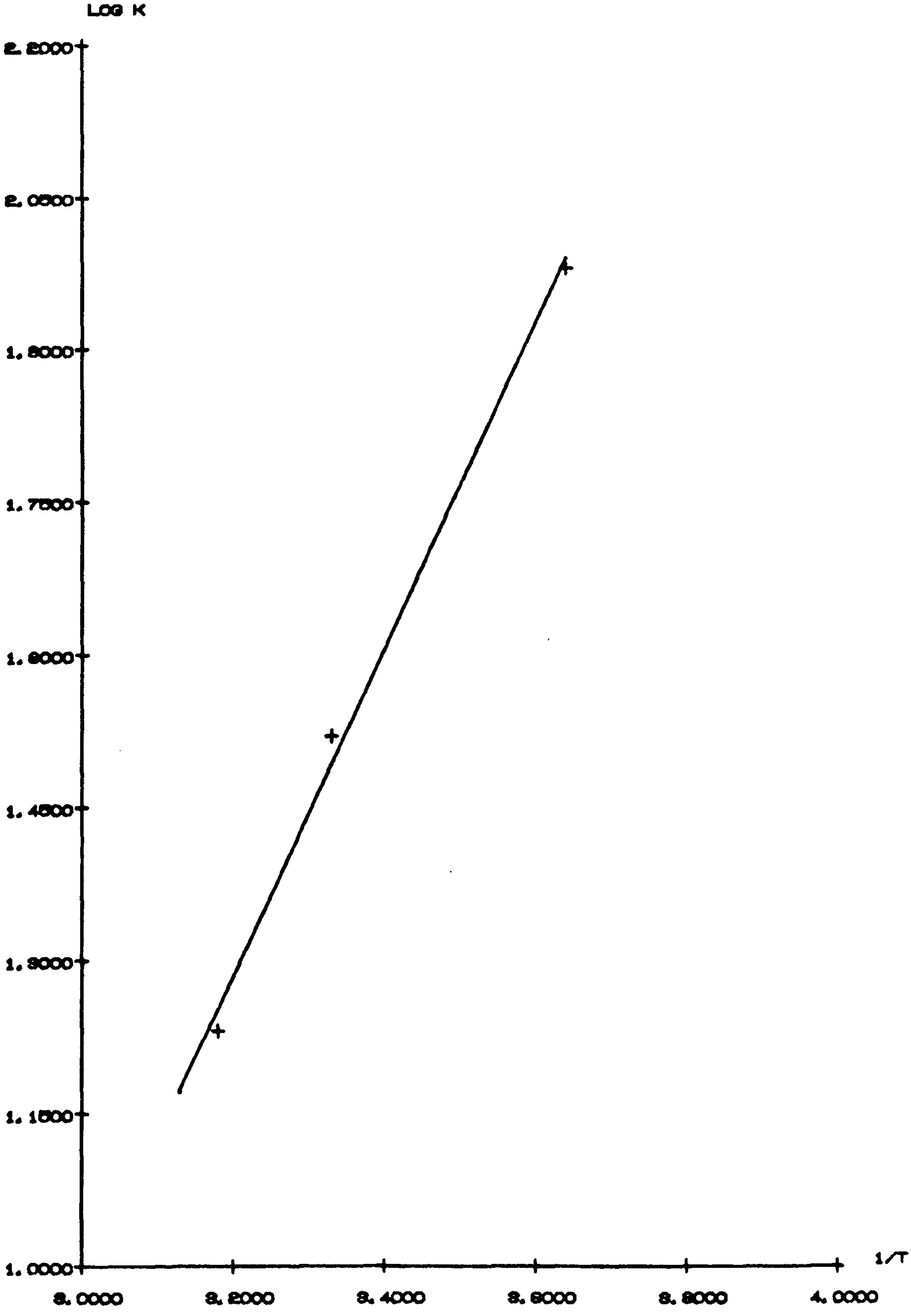
The oscillator strength, f, and the transition dipole moment, μ_{EN}, of the charge-transfer transition in the 3,6-D.N.N.A.-pyrene complex were obtained (see Table below) from equations 28 and 29 respectively[151].

$$f = 1.7 \times 10^{-9} . \epsilon_{\lambda}^{AD} . \bar{\nu}_{max} \qquad (28)$$

$$\mu_{EN}^{2} = \frac{1.7 \times 10^{-9}}{3.5 \times 10^{-7}} . \epsilon_{\lambda}^{AD} \qquad (29)$$

where $\bar{\nu}_{max}$ is the position of the charge-transfer maximum in cm^{-1} and ϵ_{λ}^{AD} is the extinction coefficient at the maximum wavelength λ of the charge-transfer absorption.

Figure 10 Plot of log K against 1/T for the 3,6 - D.N.N.A. - pyrene charge - transfer complex equilibrium.



The extent of electron transfer from the donor to the acceptor in the complex is given by the ratio (b/a) of the coefficients in Mulliken's equation[130] for the wavefunction of the ground state of the complex (equation 1). The ratio can be evaluated from the experimentally measured enthalpy of formation ($-\Delta H$) using the equation

$$-\Delta H = E_{C.T.} \frac{b^2}{a^2}$$

where $E_{C.T.}$ is the energy of the charge-transfer transition expressed in kilocalories per mole.

3,6-D.N.N.A.-Pyrene Complex at 27.5°C

Oscillator Strength f	Transition Dipole Moment μ_{EN}	b/a
0.14	19.04	0.354

(iii) Discussion

The value of the experimentally determined oscillator strength for a series of $\pi - \pi$ complexes ranges from 0.02 to 0.15, the most frequently accuring value being of the order of 0.1[152,153]. The value of 0.14 observed in this study, although somewhat higher than the usual value, still occurs within the range of experimental values.

Similarly the values for the enthalpy of formation, transition dipole moment and the ratios of the coefficients (b/a) observed in this study fall comfortably within a range of previously obtained values for $\pi - \pi$ complexes.[152,153,154]

The position of maximum absorbance in a charge-transfer absorption band is generally dependent upon the solvent medium around the complex. In order to ascertain whether the complexes formed between 3,6-D.N.N.A. and T.N.A. with pyrene exhibited this effect the spectra of the complexes were recorded in a number of solvents. The wavelengths of the charge-transfer maxima are summarised in the table below.

Solvent	Refractive Index	λ_{max} (n.m) 3,6-D.N.N.A. Complexes	λ_{max} (n.m) T.N.A. Complexes
Chloroform	1.445	510	455
Dichloromethane	1.425	505	450
Acetic Anhydride	1.391	480	430
Nitromethane	1;382	485	435
Acetone	1.359	475	-

The correlation plots of refractive index against the wavelength of the charge-transfer maximum are shown in figure 11 for 3,6-D.N.N.A. complexes (A) and T.N.A. complexes (B). The results follow the generally accepted trend of a decrease in the wavelength of the charge-transfer maximum as the refractive index of the solvent decreases. However, it has been pointed out[155] that although the refractive index of the solvent appears to be significant it is expected that other factors also influence the solvent shift.

This variation in the position of the charge-transfer maximum with solvent is reflected in the variation of association constant with solvent and comparisons of association constants obtained under differing conditions must be made with extreme caution.

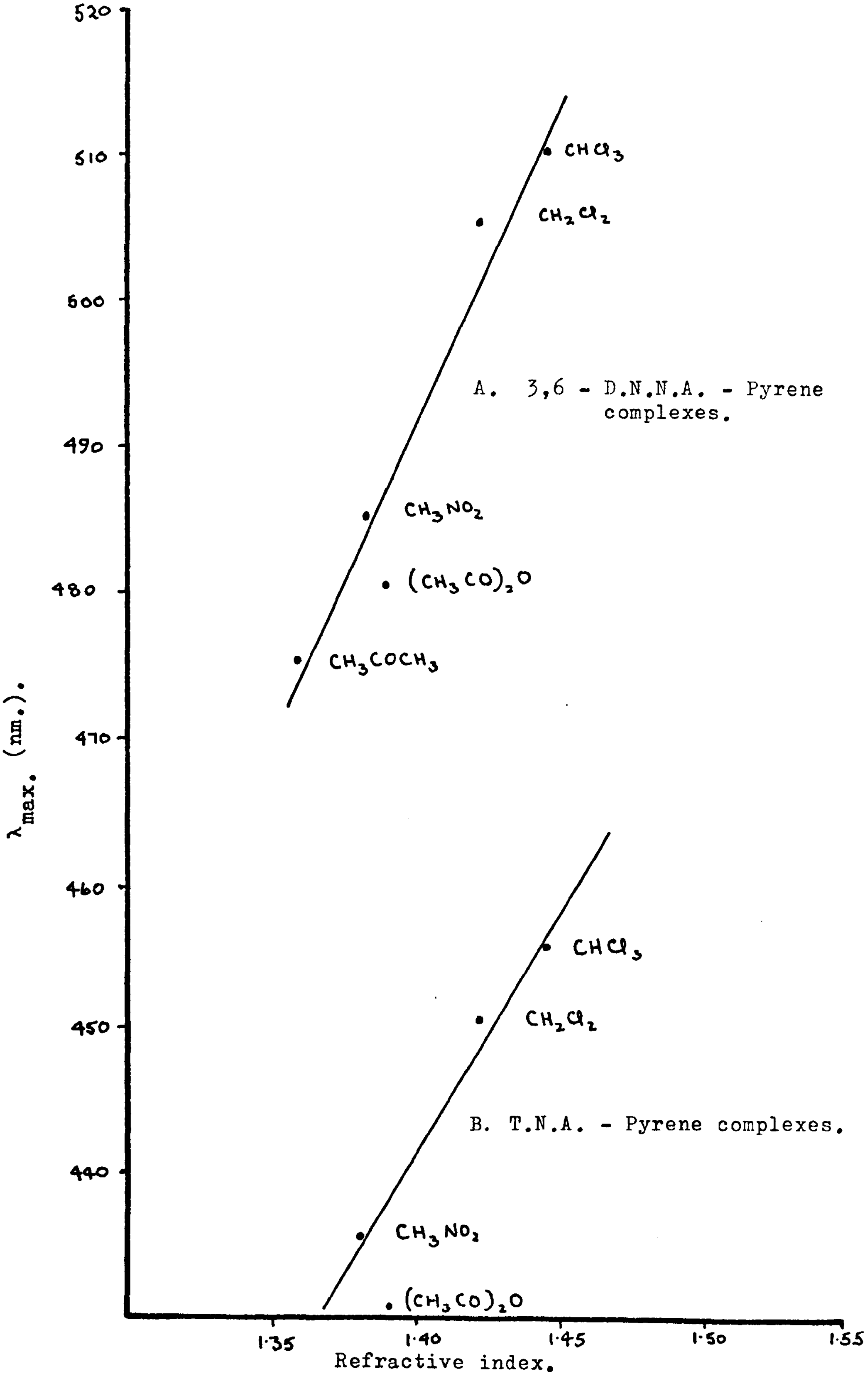


Figure 11 A correlation plot of the refractive index of the solvent against the wavelength maximum of the charge - transfer transition ($\lambda_{max.}$).

The table below shows the values of the association constants for complexes of pyrene with various acceptors in chloroform solution.

Acceptor	Temperature of Determination °C	Association Constant $1\ mole^{-1}$	Ref.
Pyromellitic dianhydride	25	18.3	155
Tetracyanobenzene	23	12.7	156
Tricyano-s-triazine	23	8.4	156
Trinitrobenzene	23	8.1	156
Tetrachlorophthalic anhydride	23	6.1	156
Tetrachlorophthalo nitrile	23	5.7	156
3-nitronaphthalic anhydride	25	4.4	6
Tetracyanoethylene	25	2.8	157
3,6-D.N.N.A.	27.5	3.3	This work

The values appear to vary widely and it is of interest to note that the association constant for the complex of pyrene with tetracyanoethylene, a known strong acceptor, is the smallest shown.

The value of the association constant of the 3,6-D.N.N.A.-pyrene complex derived in this study is similar to the value, derived by Ilmet and Berger[6], for the 3-nitronaphthalic anhydride - pyrene complex. It might have been expected, however, that the association constant for the dinitro compound would have been greater than that of the mononitro compound since the dinitro compound has been shown to be a stronger electron acceptor. It is well known that the determination of association constants depends to a great extent on the precise conditions used and also that the geometry of the complex markedly affects the value of the association constant[156]. Hence for a reliable comparative study the same conditions and a series of structurally related compounds should be used.

(b) T.N.A.-Methyl benzene Complexes

(i) Experimental

All determinations were made on dichloromethane solutions. In each determination a saturated solution of T.N.A. in dry distilled dichloromethane was used and the donors (benzene, toluene, *p*-xylene and mesitylene) were distilled immediately prior to use. The solutions were made up gravimetrically and the nuclear magnetic resonance measurements were made using a Perkin Elmer R.10 spectrometer operating at 60.004 MHz with a probe temperature of 33.5°C. The position of the lines due to the 'aromatic' and 'aliphatic' protons were measured relative to an internal T.M.S. reference. Each measurement was made in triplicate and the average value taken. The estimated accuracy in the chemical shift measurements was ±0.5 Hz.

(ii) Results

The nuclear magnetic resonance spectrum of T.N.A. in dichloromethane solution shows two resonances, one at 0.75τ due to the 'aromatic' protons and one at 5.75 τ due to the 'aliphatic' bridge protons. The integrated intensity ratio of the two signals was 1:2 respectively. The complexes with benzene, toluene, *p*-xylene and mesitylene were studied and in each case a plot of $\Delta/[D_0]$ against Δ for both the aromatic protons and the aliphatic protons was computed. A typical plot is shown in figure 12. The root mean square deviation in the value of the association constant and the value of Δ_0 was obtained. The results are summarised in Table 11.

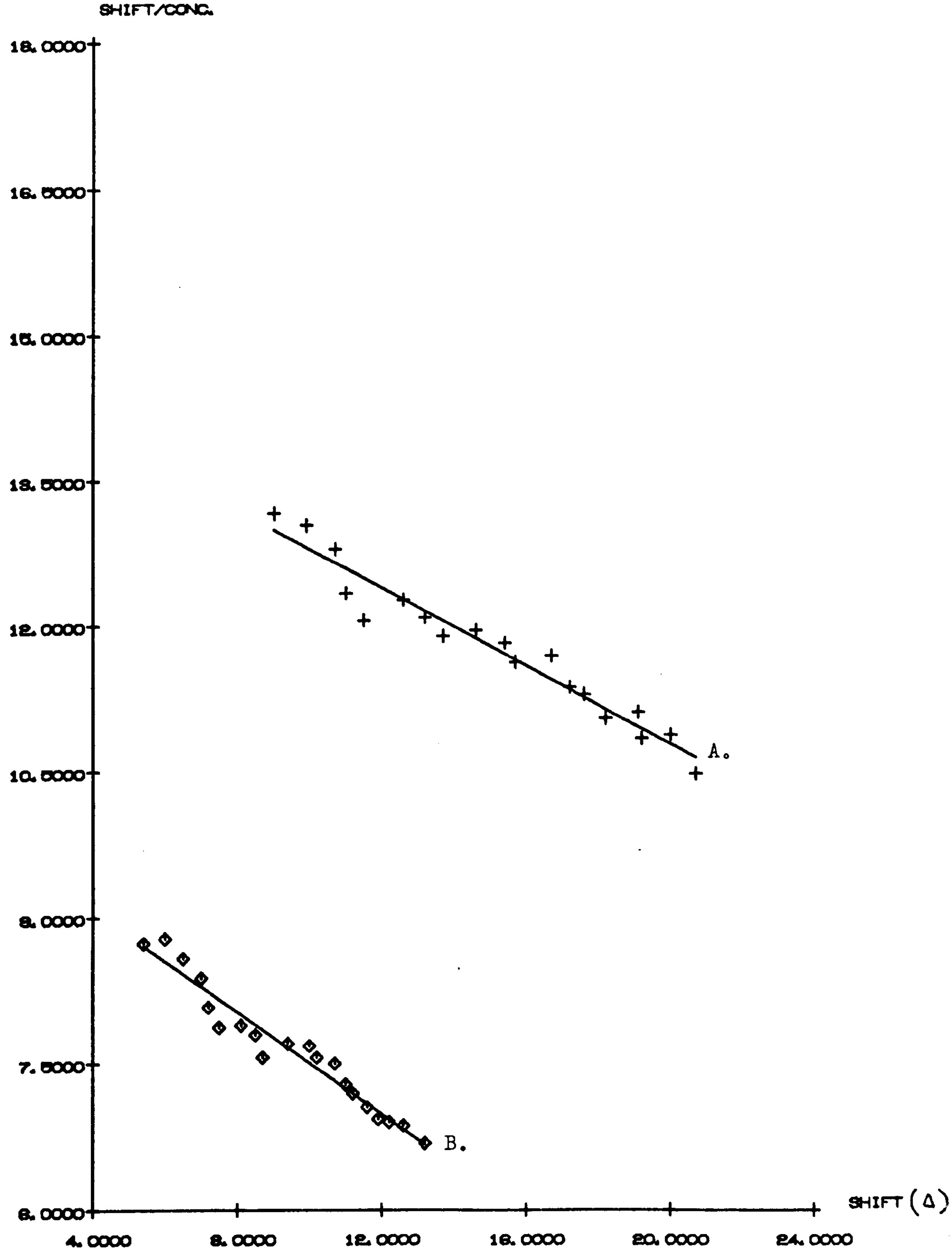


Figure 12 Plots of $\Delta / [D_o]$ against Δ for the T.N.A. - toluene complex derived from (A) the aliphatic proton shift and (B) the aromatic proton shift.

TABLE 11 The Maximum Observed Shifts, Δ_{max}, the Calculated Shifts for the Pure Complex, Δ_o, both with respect to the acceptor and the Association Constants determined from both 'Aromatic' and 'Aliphatic' Acceptor Protons for T.N.A. Complexes in Dichloromethane at 33.5°C

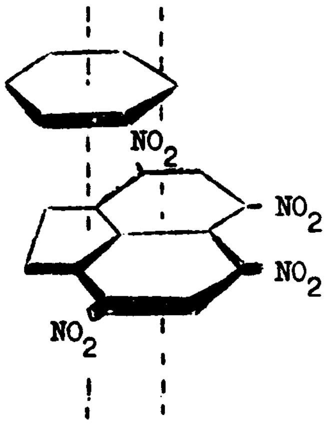
Donor	Range of Concentrations moles/kg	From Aromatic Protons			From Aliphatic Protons		
		Δ_{max} Hz	Δ_o Hz	K kgs/mole	Δ_{max} Hz	Δ_o Hz	K kgs/mole
Benzene	0.2 - 2.6	13.9	33 ± 4	0.25 ± 0.04	22.8	59 ± 6	0.23 ± 0.02
Toluene	0.2 - 2.0	13.2	39 ± 2	0.26 ± 0.02	20.7	74 ± 4	0.21 ± 0.01
p-Xylene	0.1 - 1.8	13.9	33 ± 3	0.36 ± 0.04	22.0	67 ± 3	0.27 ± 0.01
Mesitylene	0.2 - 0.8	7.0	26 ± 4	0.46 ± 0.08	11.4	49 ± 4	0.39 ± 0.03

The complexes of trinitrobenzene with p-xylene and mesitylene were studied in dichloromethane solution to provide a comparison with the T.N.A. results. The trinitrobenzene results are summarised in Table 12.

(iii) Discussion

A comparison of the values obtained for the association constants for the trinitrobenzene complexes with the average values of the T.N.A. complexes (see Table 13) in dichloromethane solution shows that the values for the T.N.A. complexes are greater than the corresponding values for the trinitrobenzene complexes. This is in agreement with the results obtained from the charge-transfer band maxima determinations in the visible spectrum and also shows T.N.A. to be a slightly stronger acceptor than trinitrobenzene.

The differences in the values of Δ_0 obtained from the 'aromatic' and 'aliphatic' protons offer some evidence for the relative orientation of the components in the complex. It must be assumed that the protons most perturbed, i.e. those having the largest Δ_0 value, are those lying closest to the centre of the two component system. The relative magnitude of the Δ_0 values suggest that the donor is lying over the aliphatic bridge. Structures I and II show configurations which could account for the observations, but other, less symmetrical configurations are also possible.



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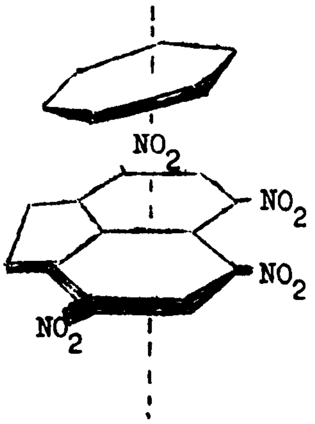

II

TABLE 12 The Maximum Observed Shift, Δ_{max}, the Calculated Shift for the Pure Complex, Δ_{o}, both with respect to the Acceptor and the Association Constants for Trinitrobenzene Complexes in Methylene Dichloride at 33.5°C

Donor	Range of Concentration moles/kg	Δ_{max} Hz	Δ_{o} Hz	K kgs/mole
p-Xylene	0.4 - 2.0	21.1	69.0 ± 7	0.23 ± 0.02
Mesitylene	0.3 - 1.8	20.8	63.0 ± 3	0.28 ± 0.01

TABLE 13 Comparison of Average K Value for T.N.A. with K Value for T.N.B. for Complexes in Methylene Dichloride at 33.5°C

Donor	Average* K Value for T.N.A. kgs/mole	K Value for T.N.B. kgs/mole
p-Xylene	0.31	0.23
Mesitylene	0.43	0.28

*K = $\frac{\text{Karomatic} + \text{Kaliphatic}}{2}$

This type of orientation would seem reasonable since the nitro groups in the <u>peri</u> positions will be twisted out of the plane of the ring and so would cause considerable steric interaction if the donor molecule was positioned over that part of the ring. Also, it has been shown[158] that in the case of the complexes of benzene with the isomeric trinitrotoluenes the benzene molecule lies preferentially over the least sterically crowded part of the trinitrotoluene molecule.

It is interesting to note that the values of the association constants derived from the aromatic proton resonance appear to be larger than the corresponding values derived from the aliphatic proton resonance. This difference is consistent with recently reported work[159] for a number of donor-acceptor systems including that of benzene-2,4,6-trinitrotoluene. The magnitude of the difference in this latter system is dependent upon the solvent used, and is relatively large in non-polar solvents such as cyclohexane and carbon tetrachloride but is within the experimental error of the measurement in more polar solvents such as 1,2-dichloroethane and dichloromethane[160]. Since there appears to be a difference between the association constants for the methylbenzene-T.N.A. system in dichloromethane, it is to be expected that the difference would become more marked if it were possible to do the determination in cyclohexane or carbon tetrachloride solution.

These differences in the association constants must make the meaning of the results somewhat doubtful, particularly since the reason for the differences are not entirely clear at present.

(4) Electron Transfer in Complexes with N,N,N',N'-Tetramethyl-p-phenylene diamine

(a) Introduction

Electron acceptors such as the quinones, bromanil chloranil etc. can interact with N,N,N',N'-tetramethyl-p-phenylene diamine (T.M.P.D.) to form adducts in which one electron transfer from the donor to the acceptor occurs and the corresponding radical ions are formed. As part of the studies on the acceptor properties of the nitroaromatics, the electron spin resonance spectra of the complexes formed with T.M.P.D. have been recorded to determine whether the compounds are sufficiently powerful acceptors to produce the corresponding radical ions.

An investigation by visible spectroscopy[134] on the complexes of T.M.P.D. with various acceptors has shown that the extent of electron transfer is dependent upon the acceptor strength and the polarity of the solvent. In cyclohexane, irrespective of the acceptor strength only charge-transfer complex formation takes place whereas in methanol and with acceptors such as chloranil, the absorption of the T.M.P.D.$^{\dot{+}}$ radical cation is observed together with, in certain cases, an absorption corresponding to the free radical anion, $A^{\dot{-}}$, of the acceptor.

The chloranil-T.M.P.D. complex in a mixture of chloroform and ethanol has been studied by electron spin resonance spectroscopy[161]. The spectrum obtained was a superposition of the spectrum of the chloranil radical anion and the spectrum of the T.M.P.D.$^{+\bullet}$ radical cation. The signal from the chloranil radical anion decreased with time while that from the T.M.P.D.$^{+\bullet}$ radical cation appeared stable.

The diethylamine-chloranil system has also been studied and the electron spin resonance signal was shown to increase with solvent polarity[161]. The signal, apparently due to the chloranil radical anion[162], showed no fine structure and, in this case, did not decrease with time.

(b) Experimental

T.M.P.D.-dihydrochloride was dissolved in water, neutralised with potassium hydroxide solution and extracted with ether. The ether was removed under vacuum and the white powder sublimed onto a cold finger. The white solid was used immediately on purification. Solid complexes were prepared between T.M.P.D. and each of the acceptors, except T.N.N.A., and their electron spin resonance spectrum was recorded in the solid state and in dimethyl sulphoxide solution on either a Varian E3 or E9 spectrometer.

In the case of T.N.N.A. the spectrum of a solution of the complex in dimethyl sulphoxide was obtained.

(c) Results

In the case of the solid complexes, the spectra showed a broad band of total width 90 gauss. The spectrum shown in figure 13 is derived from the T.N.A.- T.M.P.D. complex and superimposed on the spectrum is the signal from diphenyl picryl hydrazyl (D.P.P.H.). It can be seen that the g-value of the two species are virtually identical with a value of 2.0036.

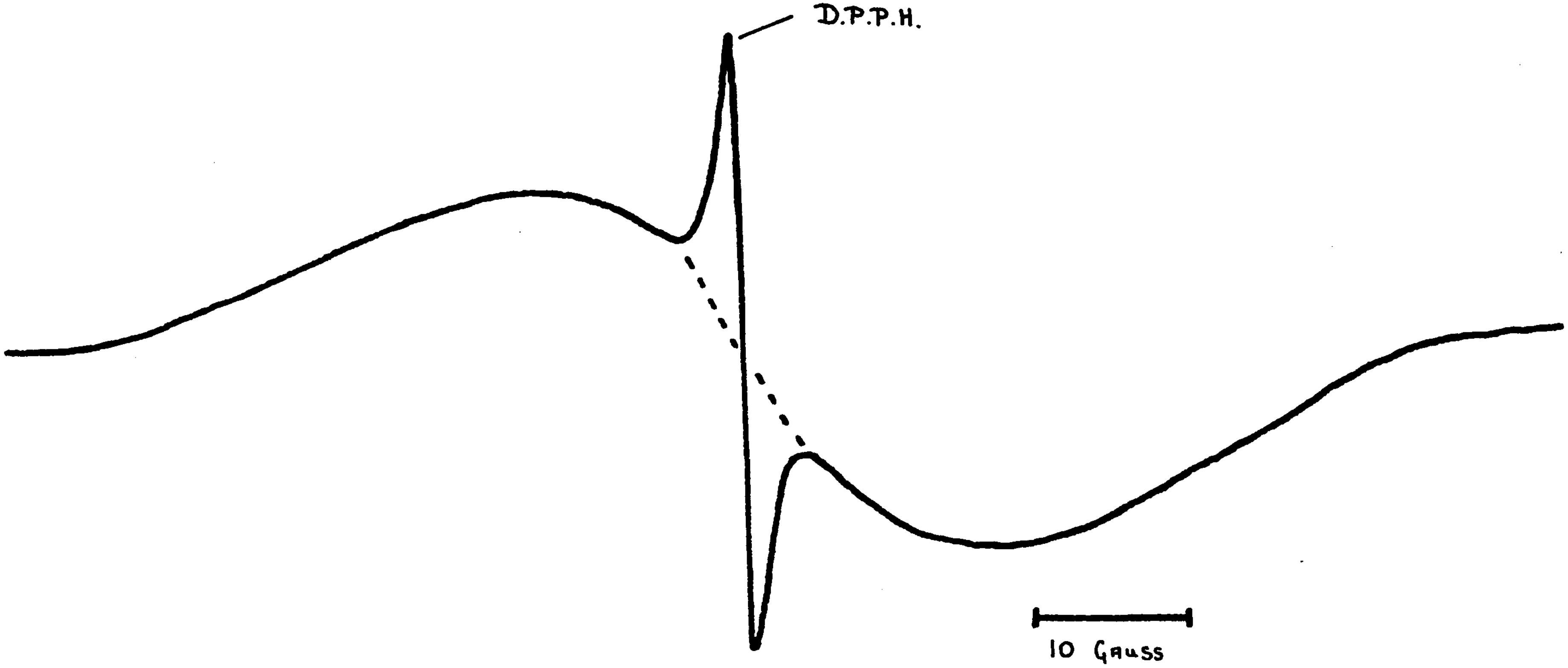

Figure 13 The electron spin resonance spectrum of the T.N.A. - T.M.P.D. complex in the solid state with a superimposed D.P.P.H. spectrum.

The spectrum of the T.N.A.-T.M.P.D. complex in dimethylsulphoxide solution is shown in figure 14. It consists of a single line of linewidth* 2 gauss.

The spectrum of each of the complexes of the anhydrides with T.M.P.D. in dimethylsulphoxide solution consists of 61 distinct lines of linewidth 0.2 gauss. The total width of the spectrum being 95 gauss. The spectrum observed from the Tri.N-1,8-N.A.-T.M.P.D. complex in dimethylsulphoxide solution is shown in figure 15 as a typical example.

(d) Discussion

Comparison of the spectra derived from the anhydride complexes in dimethylsulphoxide solution with that of the T.M.P.D.$^{+\cdot}$ radical cation[163] shows that the spectra are identical. The spectra observed from the complexes in the solid state have a width of 90 gauss, and since this compares well with the width of 95 gauss observed from the spectrum of the T.M.P.D.$^{+\cdot}$ radical cation in solution it is likely that the T.M.P.D.$^{+\cdot}$ radical cation is contributing to the signal in the solid state.

The observation of a spectrum in the solid state suggests that the dative state and the no-bond state in the complexes are very close in energy and that the energy gap between the states is sufficiently small such that the triplet level has a significant thermal population. Similar observations have been made for the solid chloranil and

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* Linewidths are quoted as the distance between the derivative extrema.

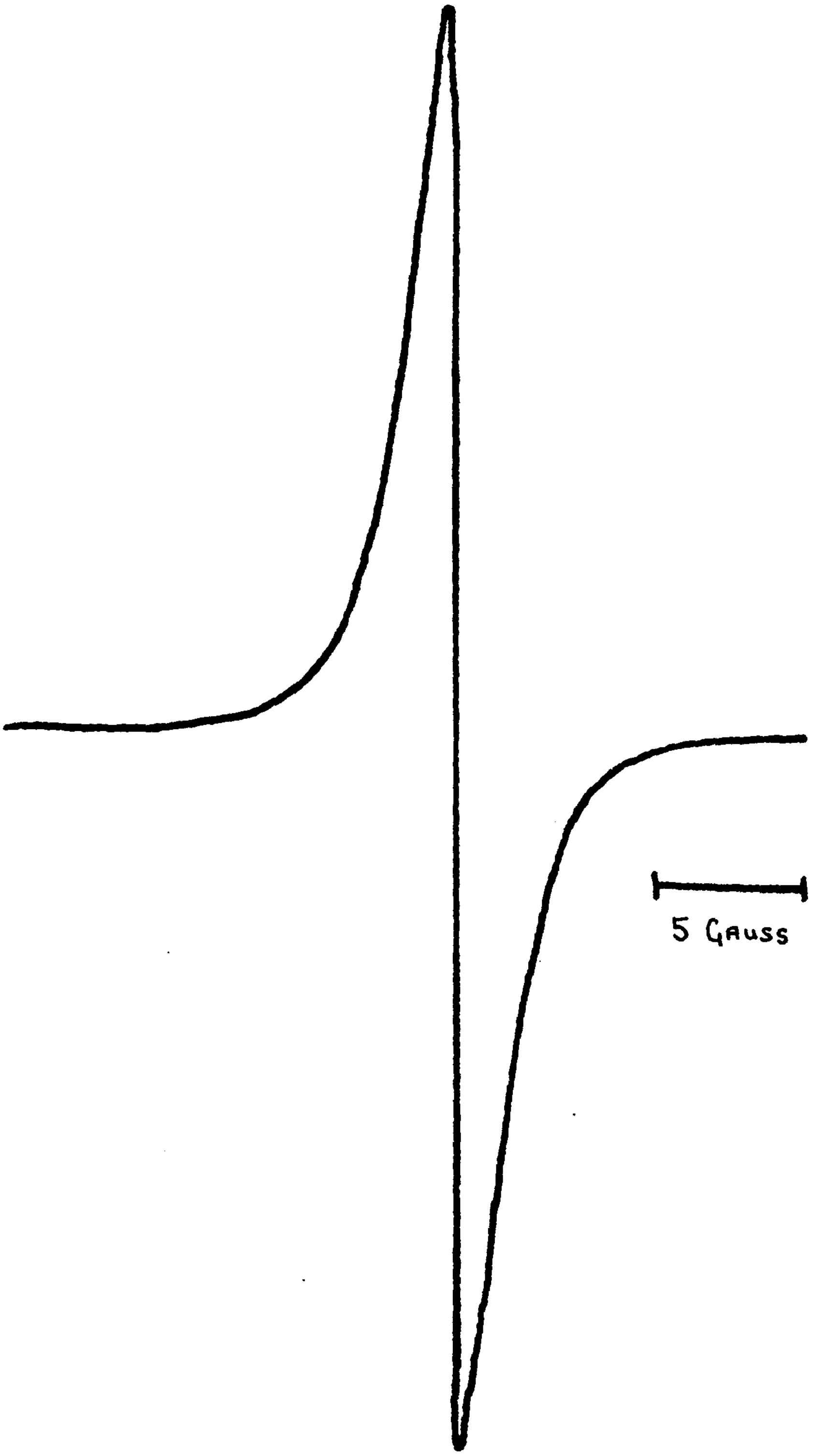


Figure 14 The electron spin resonance spectrum of the T.N.A. - T.M.P.D. complex in dimethylsulphoxide solution.

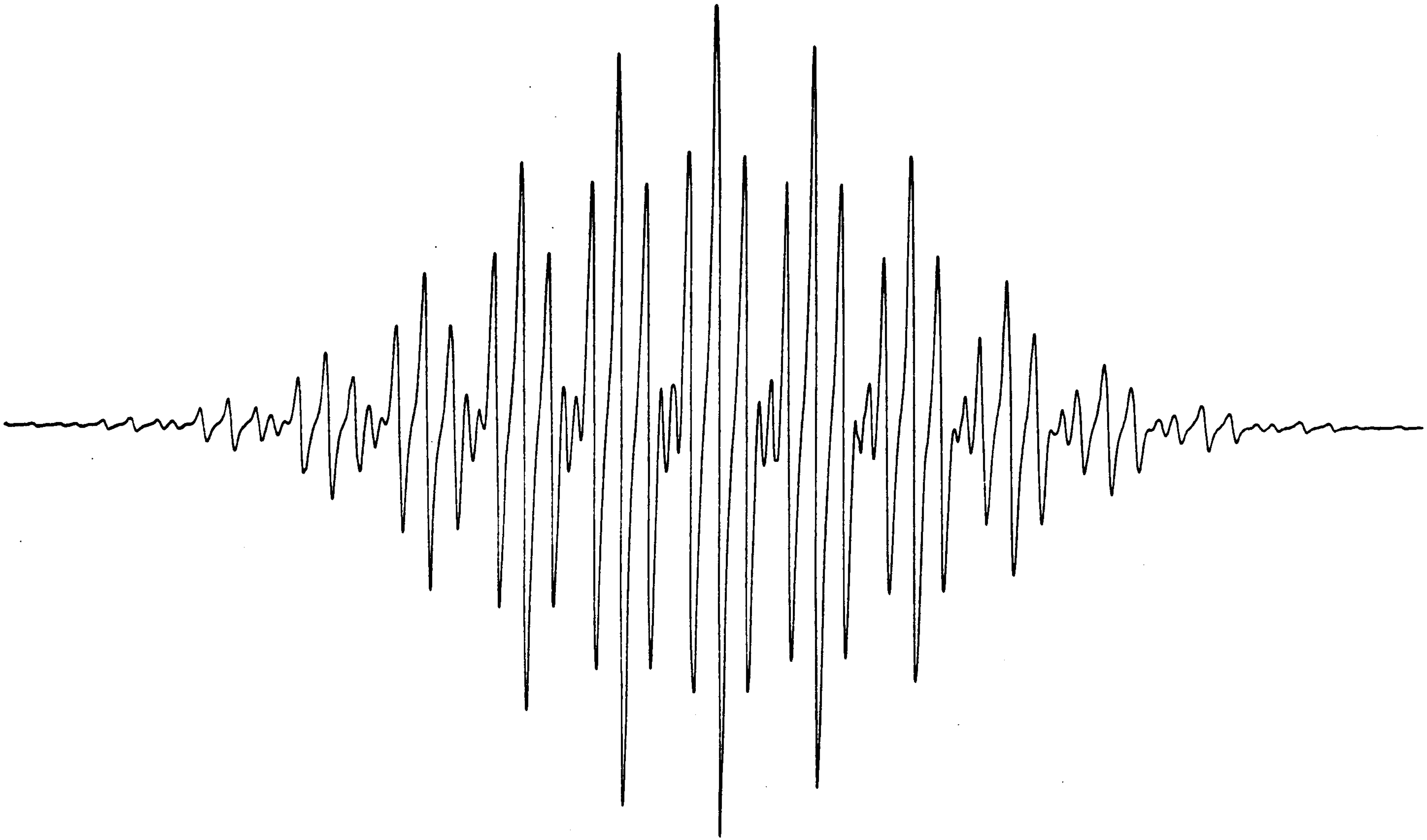


Figure 15 The electron spin resonance spectrum of the Tri.N.-1,8-N.A. - T.M.P.D. complex in dimethylsulphoxide solution.

bromanil complexes with T.M.P.D.[46,51].

In solution the presence of ion-solvent interactions will result in a lowering of the free energy of the radical ion state which may be visualised as being formed via the charge-transfer complex, namely

$$D + A \rightleftharpoons DA$$

$$DA \rightleftharpoons D^{\dot{+}} + A^{\dot{-}}$$

In the case of the anhydride complexes the observation of the spectrum due to the T.M.P.D.$^{\dot{+}}$ radical cation suggests this stabilisation takes place. It has been shown, in Chapter 3, that the stability of the radical anions, derived from the nitroaromatic compounds at present under investigation, is decreased as the temperature is increased. Hence, since the spectra of the complexes formed with T.M.P.D. were recorded at room temperature, instability is probably the reason for the absence of a signal due to the acceptor radical anion. It has been shown for the chloranil complex with T.M.P.D.[161] that although the signal due to the chloranil radical anion is initially apparent it is unstable under the conditions of the experiment and rapidly decays.

The origin of the unresolved single line spectrum derived from the T.N.A.-T.M.P.D. complex in dimethylsulphoxide solution is not clear. However it may be due to the T.N.A. radical anion since the total width of the spectrum compares reasonably well with that of the resolved spectrum of the T.N.A. radical anion, (see Chapter 3). The present results on the T.N.A.-T.M.P.D. complex are similar to those observed from the diethylamine complex with chloranil where a poorly resolved signal due to the acceptor radical anion was observed[162].

The observation that complexation of the nitroaromatic anhydrides with T.M.P.D. gives a resolved T.M.P.D.$^{\dot{+}}$ spectrum whereas complexation of T.N.A. with T.M.P.D. produces an unresolved spectrum is probably indicative of a greater degree of charge separation in the former complexes. This would be in agreement with the observation that T.N.A. is a weaker electron acceptor than are the nitroaromatic anhydrides.

(5) Infrared Studies of Charge-Transfer Complex Formation

The infrared spectra of $\pi - \pi$ complexes often only show small differences when compared with the sum of the spectra of their individual components[11,151,164,165,166]. This type of behaviour has been observed in the chloranil-hexamethylbenzene system[167]. However it has been shown[168] that in certain complexes of polynitroaromatics with aromatic hydrocarbons the out of plane C-H bending modes are particularly sensitive to complex formation. Generally such changes are more marked in complexes involving sigma-donors and sigma-acceptors such as the amine-iodine complexes[169-172].

In this section the infrared spectra of the complexes formed between the acceptors at present under investigation with anthracene as the donor are investigated. Under low resolution, the spectra of the complexes appear as the sum of their components. However, under high resolution some interesting shifts in the position of the absorptoon bands are observed. The trends in all the complexes studied are identical and the T.N.A.-anthracene complex is taken as a typical example.

(a) Experimental

The spectra of the donor, acceptor and the complex were recorded as 0.5% potassium bromide discs on a Perkin Elmer 457 spectrometer under high resolution.

(b) Results

The observed spectra are shown in figure 16. The spectra were recorded in the range 1700 - 700 cm^{-1} and spectrum A is that of T.N.A., spectrum B that of anthracene and spectrum C that of the complex. The positions of the

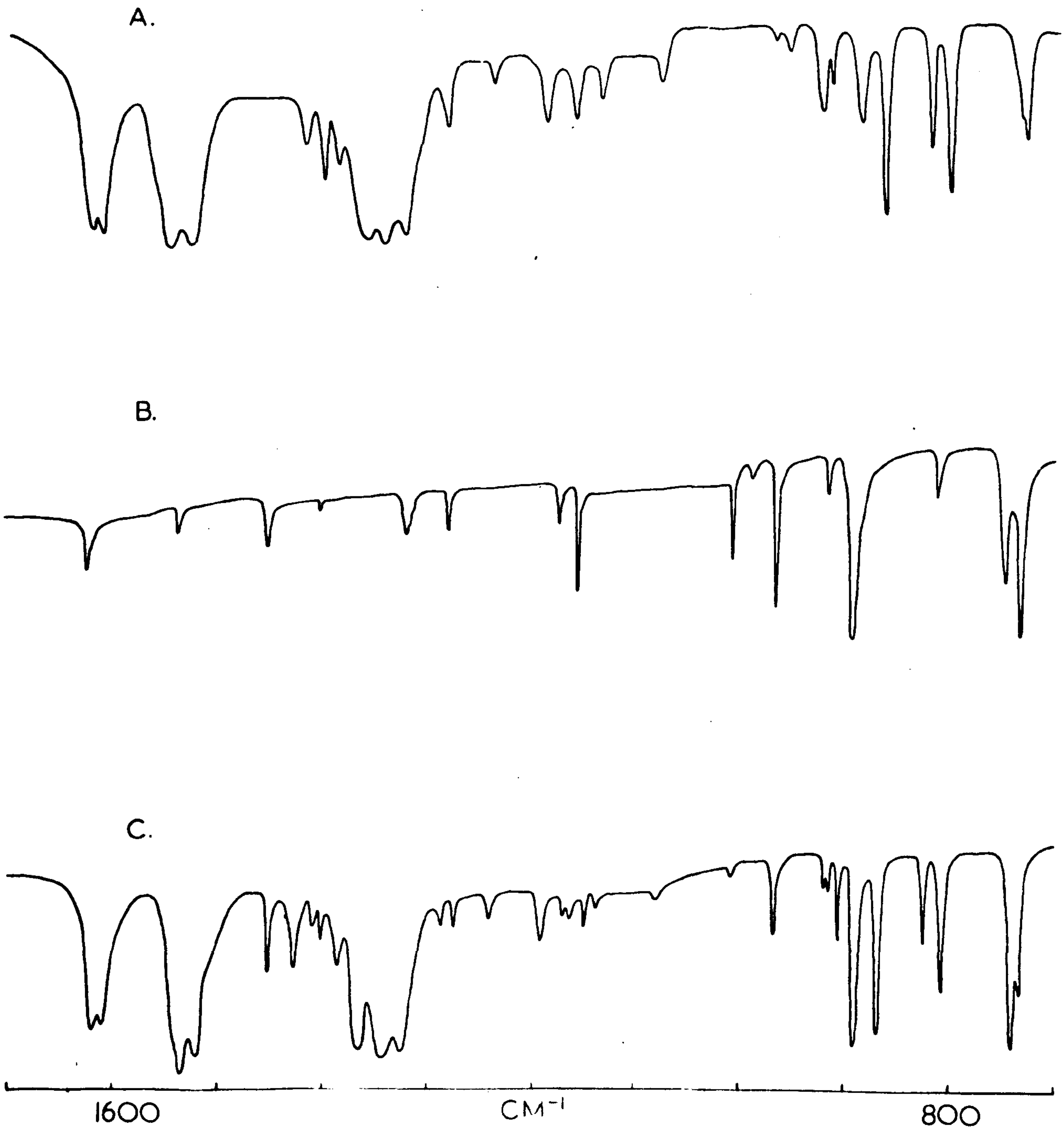


Figure 16 The infrared spectra recorded as 0.5% potassium bromide discs of (A) T.N.A., (B) anthracene and (C) the T.N.A.-anthracene complex

bands with their respective intensities are listed in Table 14.

(c) Discussion

The trend of the results is in agreement with the generally agreed pattern for π -π complexes in that the bands of the donor partner shift to higher wavenumbers and those of the acceptor partner shift to lower wavenumbers.

Of particular interest is the shift of the strong bands of T.N.A. at 1550 cm^{-1} and 1530 cm^{-1} to 1535 cm^{-1} and 1520 cm^{-1} respectively. These bands, probably associated with the symmetric stretching vibrations of the nitrogroups appear sensitive to complex formation while the bands due to the asymmetric stretching frequencies at 1620 cm^{-1} and 1613 cm^{-1} are affected to a lesser extent.

The only other shift of real significance is that of the strong band at 928 cm^{-1} in the spectrum of T.N.A. which appears in the complex as a band at 904 cm^{-1}. This band is probably due to the C-H bending mode in T.N.A. and the shift is consistent with previously observed shifts in this region[168].

Many of the other shifts are very small and in the absence of a detailed study it is difficult to comment on their origin, particularly since it is known that differences which are observed in the solid phase may be due to crystal packing effects[168].

TABLE 14 Infrared Spectral Bands with their respective Intensities for T.N.A., Anthracene and the Complex

T.N.A.		Anthracene		Complex	
Band (cm^{-1})	Intensity	Band (cm^{-1})	Intensity	Band (cm^{-1})	Intensity
1620	s	1621	w	1620	s
1613	s			1609 7	ss
1550	vs				
1530	vs	1535	w	1535	vs
				1520	vs
		1448	m	1451	m
1426	m			1427	m
1405	m			1408	w
				1401	w
1386	m			1384	m
1370	vs			1370	vs
1360	vs			1360	vs
1345	vs			1345	vs
1325	vs	1318	w	1324	vs
1287	m			1286	w
		1274	w	1274	w
1243	w			1240	w
1189	m			1188	m
1163	m			1163	w
		1153	w	1159	w
				1147	w
1138	w			1136	w
1082	w			1080	w
		1008	m	1008	m
		987	w		
		636	m	965	m
928	m				
919	m	913	w	917	w
				904	m
891	s	892	s	892	vs
869	vs	869	w	868	vs
827	s			825	s
		811	m		
808	s			807	s
740	s	745	s	740	vs
		733	vs	734	vs

CHAPTER 3

RELATIVE ELECTRON DENSITIES AT PARTICULAR SITES IN THE π-SYSTEMS

1. An electron spin resonance study of the radical anions derived from some nitroaromatic compounds

2. Relative electron densities at the proton sites in 3,6-D.N.N.A.

(1) An Electron Spin Resonance Study of the Radical Anions derived from some Nitroaromatic Compounds

(a) Introduction

In any attempt to correlate the reactions of the molecules at present under study with the reactions of other electron deficient aromatic systems it would be useful to have some knowledge of the π -electron density at the reaction site. Such information is obtained experimentally from electron spin resonance spectroscopy and theoretically by applying molecular orbital calculations.

In the experimental method the radical anion of the compound is prepared either by chemical reduction with alkali metals[138,173-175], electrolytically[57,69,176] or photolytically[177,178] and the electron spin resonance spectrum of the radical anion recorded. The extra unpaired electron in the radical anion is assumed to be in a π -orbital and delocalised over the whole molecular framework. By analysis of the spectrum, the magnitude of the interaction (the coupling constant) between the unpaired electron and the molecular sites within the framework can be determined. The unpaired spin density at the individual sites can then be estimated using the McConnell equation[179].

Theoretically the π -electron densities can be estimated using the Huckel Linear Combination of Atomic Orbitals method, (L.C.A.O.)[180], and by the approximate configuration interaction treatment of McLachlan[181].

The experimental values of the π -electron densities derived from the spectrum can be compared with the values calculated from the molecular orbital theory, and, in the cases where comparison is good the theoretical results, which provide the electron density at each atomic site in the molecule, can be assumed reasonable.

(b) Experimental and Results

The radical anions of the nitro compounds were prepared using the apparatus as shown in the diagram, figure 17.

The solvent, 1,2-dimethoxyethane, was trap to trap distilled under vacuum from alumina and sodium hydroxide pellets onto sodium and anthracene and the solution was thoroughly degassed and stored on the vacuum line. The nitro compound (2 mg) and a piece of sodium metal (0.5 gm) were put into the apparatus prior to sealing, and the apparatus was connected to a vacuum line and evacuated, the pressure being $< 10^{-3}$ torr. The sodium was gently warmed until a sodium mirror sublimed onto the walls of the glass tube, and the end of the tube was sealed off to isolate any impurities. Dimethoxyethane was distilled over into the central tube and degassed several times, the apparatus was then sealed and removed from the vacuum line. The solvent was shaken with the sodium mirror and then poured onto the nitro compound and the anion which was formed was kept at liquid nitrogen temperature until its spectrum was recorded.

The theoretical calculations were carried out using an Elliott 4120 computer. The values of the electron densities calculated by both the Huckel and McLachlan methods were obtained from the program called McLachlan. The simulated spectrum was computed using the program SIMUL. For further details of the methods of calculation and the computer program reference should be made to chapter 7 sections 1 and 2 respectively.

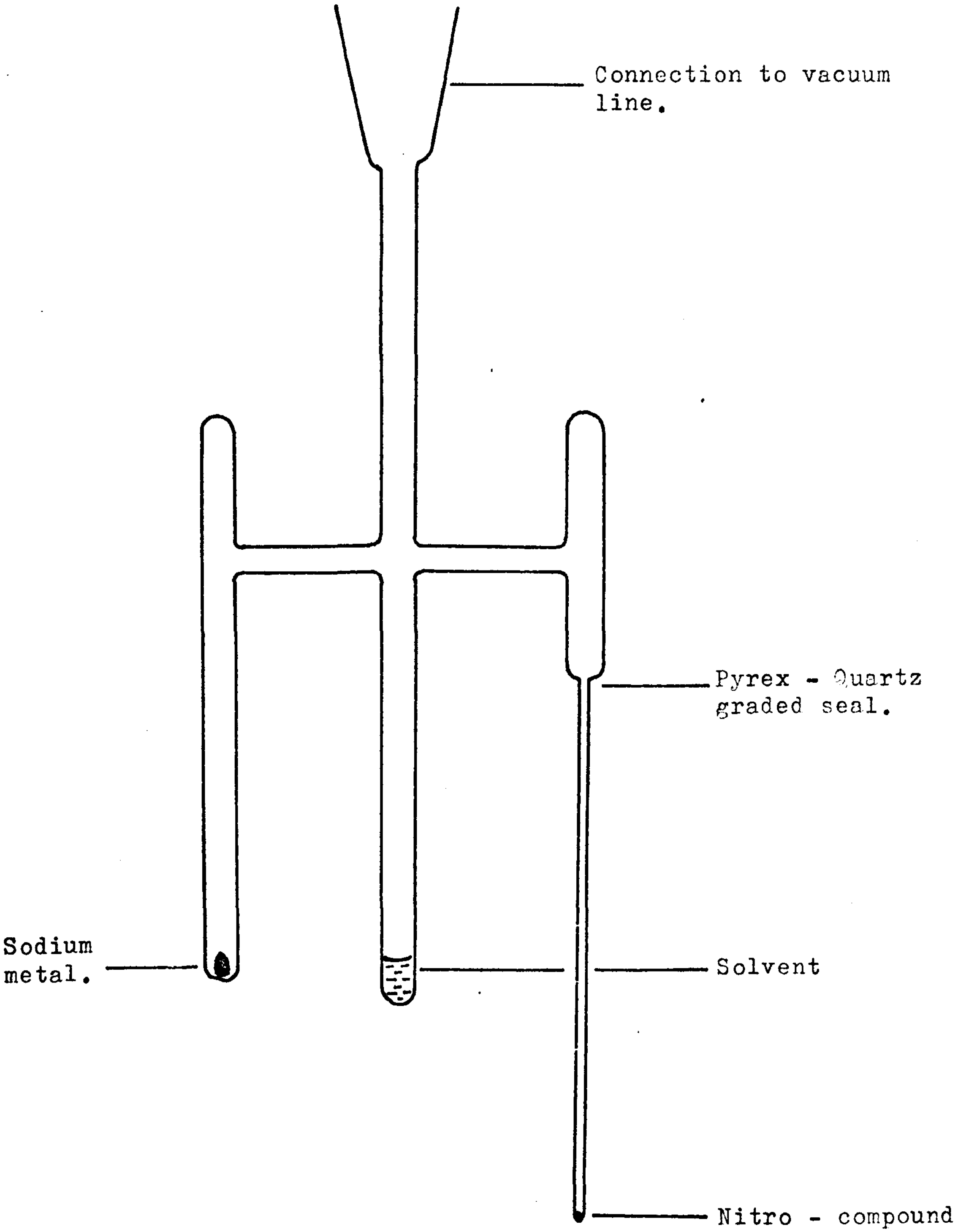


Figure 17 The apparatus for the preparation of the radical anions.

(i) Molecular orbital calculations

The Huckel[180] L.C.A.O. molecular orbital method and the McLachlan procedure[181] for approximately introducing configuration interaction have been used to estimate the π -electron spin densities at specific nuclei in the radical anions.

The first task in performing M.O. calculations on the compounds at present under study is the proper choice of Coulomb and resonance integrals for the nitro group, the anhydride group and the acenaphthene bridge.

The expressions commonly used for the Coulombic and resonance integrals for heteroatoms are:

$$\alpha_x = \alpha_o + h_x\beta_o \qquad (30)$$

$$\beta_{cx} = K_{cx}\beta_o \qquad (31)$$

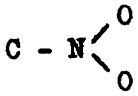
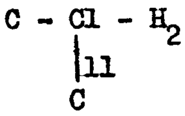
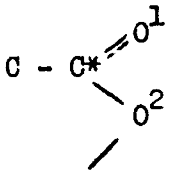
where α_o and β_o are the values of the Coulombic and resonance integrals used for carbon atoms in the benzene ring system and where h_x and K_{cx} are constants for the heteroatom in question. The values of h_x and K_{cx} to be used with a particular heteroatom X are not easy to obtain, The ideal procedure to deduce their values would be to correlate some experimental property and a calculated quantity in a series of related compounds containing the heteroatom in question. Then systematic variation of h_x and K_{cx} would lead to the best values and also show if any unique values existed. As the number of heteroatoms and groups is increased the problems become more difficult.

Reiger and Fraenkel[59] have determined the appropriate parameters for the nitro group and these values, together with those of Sioda and Koski[68] for the anhydride group, are largely those used in the calculations in the present study. The values used are shown in Table 15.

It is well known that M.O. parameters are sensitive to the precise experimental conditions[72] and the values used by Reiger and Fraenkel and by Koski and Sioda were based on electrolytic measurements in dimethylformamide solution. In our system a better correlation between the experimental and theoretical electron densities was obtained by increasing the value of K_{Cx}, the heteroatom parameter for the C-N bond, from 1.2 to 1.4 and by increasing the value of K_{CO}, the heteroatom parameter for the ring-anhydride bond, from 1.0 to 1.25.

In theory, the acenaphthene bridge system would not be expected to conjugate with the π -system. However it is well known that some degree of conjugation does occur and account must be taken of this interaction in the calculations. Coulson and Crawford[182] determined values of h_x and K_{cx} for the atoms and bonds of the methyl group when bonded to an aromatic system and although there was some arbitrariness in the choice, the values used reproduced the observed dipole moment of toluene and hence are unlikely to be seriously in error. The values used in this study for the acenaphthene bridge are very similar to the ones used for toluene, since to a first approximation the acenaphthene group may be considered as two independent methyl groups. The values which showed the best correlation between the observed and calculated electron densities are shown in Table 15. Thevalues used are within the ranges suggested by Streitwieser and Nair[183].

TABLE 15 Table of Constants, h_x and K_{xy}, for use in the Expressions for the Coulomb and Resonance Integrals of the Heteroatoms

Substituent	Atom X	h_x [a]	Bond X-Y	k_{xy} [a]
Nitro Group 	N O	2.2 1.4	N-O C-N	1.67 1.4 [b,d]
Acenaphthene Bridge 	H_2 C^1	-0.2 -0.1	C^1-H_2 $C-C^1$ C^1-C^{11}	1.5 1.0 0
Anhydride Group 	C* O^1 O^2	-0.4 2.0 1.2	C-C* $C^*=O^1$ C^*-O^2	1.25 [c] 1.6 1.0

a - For significance of these parameters see text.

b - Modified Reiger and Fraenkel value.

c - Modified Sioda and Koski value.

d - See section on 'Modification of Resonance Integral' for changes in this value.

The modification of resonance integrals for sterically hindered nitro groups

It has been shown by Geske and Ragle[184] that in nitrotoluene radical anions, when the nitro group is in the *ortho* position, the nitrogen coupling constant is larger and the ring proton coupling constants smaller than are observed in *meta* and *para*-nitrotoluene radical anions. Further evidence for this steric effect is observed in 1-nitro-2,6-dimethylbenzene where the increase in the nitrogen coupling constant is even more significant. A steric effect has also been observed in 1,8-dinitronaphthalene[185,186] and in 1,4,5,8-tetranitronaphthalene[187] resulting in higher nitrogen coupling constants and lower ring proton coupling constants then are observed in the isomeric dinitronaphthalenes and tetranitronaphthalenes where steric factors are not operative.

In all the radical anions being studied in this work, except that derived from 2,5-D.N.N.A., the interacting nitro groups are in structurally similar environments to those in 1,8-dinitronaphthalene. Hence, some allowance must be made in the calculations to account for these steric interactions which tend to twist the nitro groups occupying the *peri* positions out of the plane of the ring.

Reiger and Fraenkel[59] have shown that by altering the resonance integral for the C-N bond this twisting of the nitro groups out of the plane of the ring can be taken into account theoretically. The relationship

$$\beta_{CN}(\theta) = \beta_{CN}(0)\cos\theta \qquad (32)$$

has been used, where $\beta_{CN}(0)$ is the resonance integral for the nitro group planar with the ring and $\beta_{CN}(\theta)$ is the resonance integral when the nitro group is twisted θ degrees out of the plane of the ring.

In 4,5-D.N.N.A., Tri.N-1,8-N.A., T.N.A. and T.N.N.A. where both peri positions are occupied by nitro groups, the best correlation between the observed and calculated π -electron densities was obtained by assuming that the peri nitro groups were twisted 30° out of the plane of the ring (i.e. $\theta = 30^{\circ}$).

In 2,5-D.N.N.A., Tri.N-1,8-N.A. and T.N.N.A. where there is a nitro group ortho to the anhydride group, the best correlation between the experimentally observed electron densities and the calculated values was obtained by assuming that the nitro group ortho to the anhydride group was twisted 20° out of the plane of the ring (i.e. $\theta = 20^{\circ}$). This suggests an interaction between the carbonyl oxygen of the anhydride group and the oxygen of an adjacent nitro group which may not have been expected.

(ii) Radical anion spectra

(a) Estimation of π -electron densities

The analysis of the electron spin resonance spectrum of a radical anion yields the isotropic hyperfine coupling constants for those atoms in the molecule which have a non-zero magnetic moment. A relationship between the coupling constant and the π -electron spin density is required to allow a comparison of the experimental spin density with the value which is obtained by calculation.

For protons directly bonded to a carbon atom in the π -system of the molecule, it is assumed, following McConnell[179] that the coupling constant is given by:

$$a_i^H = Q_{CH}^H \rho_i^{\pi} \qquad (33)$$

where a_i^H is the proton hyperfine coupling constant in gauss and p_i^π, conventionally termed the π-electron spin density, is the atomic orbital spin polarisation on the carbon atom i to which the proton is bonded. The quantity Q^H_{CH}, called a sigma-pi interaction parameter, is assumed to be constant for all carbon atoms with equivalent sp^2 (120°) hybridisation and has a value of -23.7G. as determined theoretically by Karplus and Fraenkel[58]. The actual value of Q^H_{CH} for any system is expected to depend on the hybridisation of the carbon atom, the C-H bond length and may also depend on the net charge on the carbon atom in question[58,67].

A similar relationship may be used for a methyl group bonded to a carbon atom in the π-system[58,67,188,189]. In this case $Q^H_{CCH_3}$ has been assigned a value of +27.2G. This value has been used in calculating the experimental spin densities of the bridge protons in T.N.A. (Table 16).

The hyperfine coupling constants arising from the nitrogen nucleus of a nitro group can be formulated, according to the theory of Karplus and Fraenkel[58], as

$$a^N = (S^N + Q^N_{NC} + 2Q^N_{NO})p^\pi_N + Q^N_{CN}\,p^\pi_C + 2Q^N_{ON}\,p^\pi_O \qquad (34)$$

where p^π_N, p^π_O and p^π_C are, respectively, the pi-electron spin densities at the nitrogen and oxygen atoms and at the adjacent carbon atom, S^N represent the contribution to the coupling constant from the nitrogen 1^s electrons and the Q's account for the contribution of the 2^s electrons, where, for example, Q^N_{ON} is the sigma-pi interaction parameter for the nitrogen nucleus resulting from the interaction between the O-N bond and the spin density on the oxygen atom.

Unfortunately, no numerical estimates of any of the individual parameters in equation 34 are available. However, Reiger and Fraenkel[59], by applying McLachlan calculations to a series of nitro compounds and by applying the method of orthogonal vectors[58,190] have obtained the composite values

$$K_N = (S^N + Q_{NC}^N + 2Q_{NO}^N) = \pm (99 \pm 10.2)G \qquad (35a)$$

$$Q_{ON}^N = \mp (35.8 \pm 5.9)G \qquad (35b)$$

The value of Q_{CN}^N has been shown to make no significant contribution to the value of the nitrogen coupling constant. This arises in part from the small calculated spin density on the carbon atom adjacent to the nitro group and, also from experimental evidence which suggests that Q_{CN}^N is insignificant relative to the other parameters.

The values, derived by Reiger and Fraenkel[59], for the composite parameters in equation 34 are only meaningful for spin densities derived from McLachlan calculations. A complimentary set of values for use with spin densities derived from Huckel calculations have been obtained by Fischer and McDowell[186], and when substituted in equation 34 we have:

$$a_N = \pm 179\ p_N^{\pi} \pm 8.06\ p_C^{\pi} \mp 149.2 p_O^{\pi} \qquad (36)$$

The ratio of the constants and their relative signs in equation 36 compare well with those derived by Reiger and Fraenkel (equations 35a and 35b) and good agreement has been obtained for the isomeric dinitronaphthalenes[186] between the experimental nitrogen coupling constants and those derived from Huckel calculations, using equation 36.

(ii) Experimental spectra

The radical anions studied n this work were stored on formation in liquid nitrogen prior to recording their spectra on either a Varian E4 or E9 spectrometer. The samples were only allowed to warm up in the probe of the spectrometer where precise temperature control was available.

3,5,6,8-Tetranitroacenaphthene (T.N.A.)

The spectrum of the radical anion derived from T.N.A. recorded at -40°C consists of 80 distinct lines (figure 18) of linewidth 0.075G. The spectrum is arranged in 3 distinct groups of lines and has an overall width of 10.30G. Analysis of the spectrum leads to the coupling constants shown in Table 16. Although 375 lines would be expected from the T.N.A. radical anion if couplings from the two aromatic protons, the four aliphatic protons and the two sets of two equivalent nitrogen nuclei were observed, many of the lines would be of low intensity and considerable overlapping would be expected. The simulated spectrum, using the coupling constants in Table 16, matches very well with the experimentally observed spectrum.

2,4,5,7-Tetranitro-1,8-naphthalic anhydride (T.N.N.A.)

The spectrum of the radical anion derived from T.N.N.A., recorded at -40°C, consists of 45 distinct lines (Figure 19) of linewidth 0.05 G. The overall width of the spectrum os 5.25 G. If the couplings resulting from the two aromatic protons and the two sets of two equivalent nitrogen nuclei were observed a total of 75 lines would be expected but this number would be reduced through overlapping. Analysis of the spectrum leads to the coupling constants shown on Table 17, and the simulated spectrum computed from these coupling constants shows good agreement with the observed spectrum.

1,6,8-Trinitro-2,3-Naphthalic anhydride (Tri.N-2,3-N.A.)

The reduction of Tri.N-2,3-N.A. with sodium was attempted in several solvent systems (1,2-dimethoxyethane, tetrahydrofuran, dioxan) but in no case could the radical anion be detected. Also an unsuccessful attempt was made using potassium reduction. The failure to detect the radical anion was most probably due to the insolubility of this particular compound.

2,4,5-Trinitro-1,8-naphthalic anhydride (Tri.N-1,8-N.A.)

The spectrum of the radical anion derived from Tri.N-1,8-N.A. recorded at -40°C, consists of 30 distinct lines (Figure 20). The overall width of the spectrum os 5.78 G and the linewidth 0.05 G. Analysis of the spectrum leads to the coupling constants shown in Table 18. The simulated spectrum computed from these coupling constants agrees well with the experimentally observed spectrum in terms of line positions. However, the intensities of the lines in the experimental and simulated spectra compare less favourably.

4,5-Dinitro-1,8-naphthalic anhydride (4,5-D.N.N.A.)

The spectrum of the radical anion derived from 4,5-D.N.N.A., recorded at -40°C, consists of 9 distinct lines (Figure 21), of linewidth 0.1 G. The overall width of the spectrum is 6.80 G. The spectrum is readily interpreted assuming that the couplings arise from two sets of pairs of equivalent protons. The coupling constants are shown in Table 19, and the simulated spectrum computed from these couplings is in excellent agreement with the observed spectrum. There is no evidence for coupling due to the nitrogen nuclei.

2,5-Dinitro-1,8-naphthalic anhydride (2,5-D.N.N.A.)

The spectrum of the radical anion derived from 2,5-D.N.N.A., recorded at -40°C, consists of 30 distinct lines (Figure 22) of linewidth 0.05 G. The overall width of the spectrum is 9.26 G. Analysis of the spectrum leads to the coupling constants shown in Table 20. The simulated spectrum computed from these couplings is in excellent agreement with the observed spectrum.

In this spectrum the coupling constants derived from the nitrogen nuclei appear to be coincidently equivalent.

3,6-Dinitro-1,8-naphthalic anhydride (3,6-D.N.N.A.)

The reduction of 3,6-D.N.N.A. with sodium and potassium in various solvents (1,2-dimethoxyethane, tetrahydrofuran) was attempted and in each case a red colouration, normally indicative of anion formation, was observed. However, no resolved signal could be obtained from any of the samples. In each case a spectrum consisting of 9 broad lines was obtained which could, in some cases, be further resolved to show evidence of some fine structure.

A similar spectrum was observed from the radical anion of 4,5-D.N.N.A. after warming the sample up to room temperature and recooling. Hence it is likely that the spectrum observed in the case of the 3,6-D.N.N.A. radical anion is a product of decomposition.

The Tables 16 to 20 contain a summary of the experimental hyperfine coupling constants of the five radical anions studied. Complete unambiguous assignment of the coupling constants to the different nuclei is impossible from the experimental data and only in a few cases can one particular coupling be assigned to one particular nucleus.

By resorting to theoretical estimates of the spin density distribution further assignments can be made with a reasonable degree of confidence and the assignments given in the tables, when in doubt, are given on theoretical evidence.

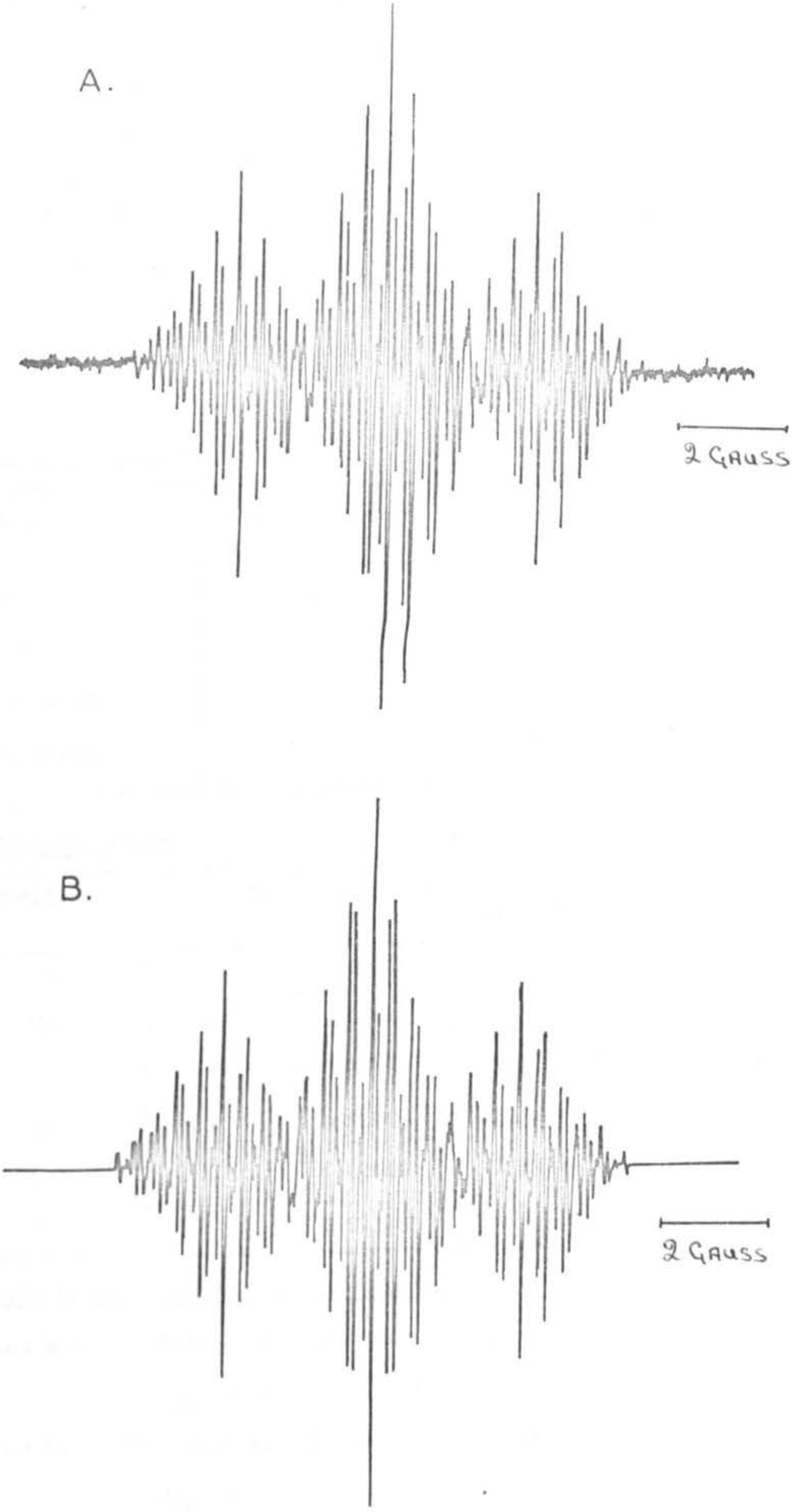
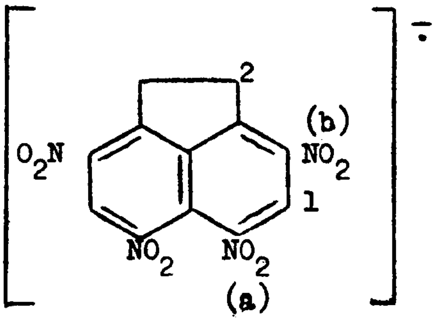


Figure 18 The electron spin resonance spectrum of the T.N.A. radical anio
(A) experimentally observed and (B) simulated

TABLE 16 The T.N.A. Radical Anion



Observed Spectrum - Figure 18

Experimental Conditions

Temperature -40°C

Counter Ion Sodium

Spectral Analysis

Nucleus	Assignment	Multiplicity	Coupling Constant (Gauss)
Proton	1	Triplet	2.74
Proton	2	Quintet	0.32
Nitrogen	*b	Quintet	0.44
Nitrogen	*a	Quintet	0.42

Spin Densities

Position	Ref. No.	Calculated Spin Density Huckel	Calculated Spin Density McLachlan	Experimental Spin Density
Oa		0.00649	0.00350	---
Na	a	0.00042	-0.00163	---
Ob		0.00054	-0.00819	---
Nb	b	0.00004	-0.00098	---
1	1	0.04066	0.10002	0.1157
2		0.01328	0.01313	0.0117

Calculated Nitrogen Coupling Constants

(a) Based on Huckel Spin Densities using equation 36

$J_{Na} = 0.41$ G $\qquad J_{Nb} = 0.06$ G

(b) Based on McLachlan Spin Densities using equations 34 and 35

$J_{Na} = 0.41$ G $\qquad J_{Nb} = 0.49$ G

* These coupling constants cannot be unambiguously assigned from the experimental or theoretical data.

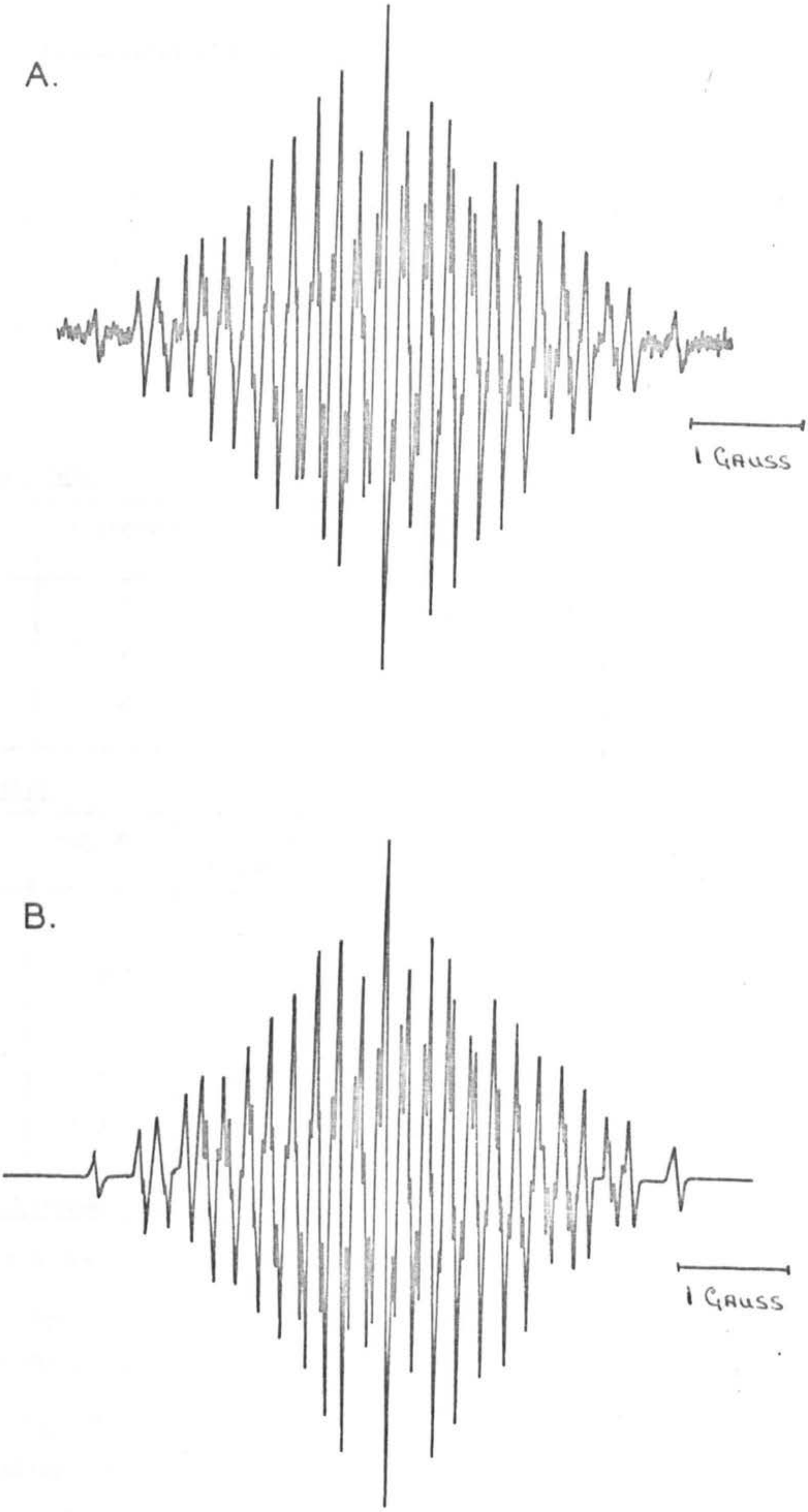
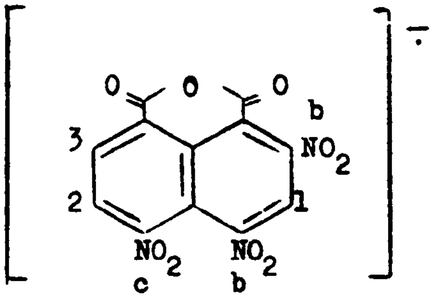


Figure 19 The electron spin resonance spectrum of the T.N.N.A. radical anion (A) experimentally observed and (B) simulated

TABLE 17 The T.N.N.A. Radical Anion



Observed Spectrum - Figure 19

Experimental Conditions

Temperature -40°C

Counter Ion Sodium

Spectral Analysis

Nucleus	Assignment	Multiplicity	Coupling Constant (Gauss)
Proton	1	Triplet	0.60
Nitrogen	*a	Quintet	0.35
Nitrogen	*b	Quintet	0.65

Spin Densities

Position	Ref. No.	Calculated Spin Density Huckel	McLachlan	Experimental Spin Density
O(a)		0.02866	0.02616	---
N(a)	c	0.01994	0.01639	---
O(b)		0.03400	0.03091	---
N(b)	d	0.02366	0002057	---
1	2	0.02823	0.02535	0.0253

Calculated Nitrogen Coupling Constants

(a) Based on Huckel Spin Densities using equation 36

$J_{Na} = 0.35$ G $\qquad J_{Nb} = 0.46$ G

(b) Based on McLachlan Spin Densities using equations 34 and 35

$J_{Na} = 0.25$ G $\qquad J_{Nb} = 0.18$ G

* These coupling constants cannot be unambiguously assigned from the experimental or theoretical data

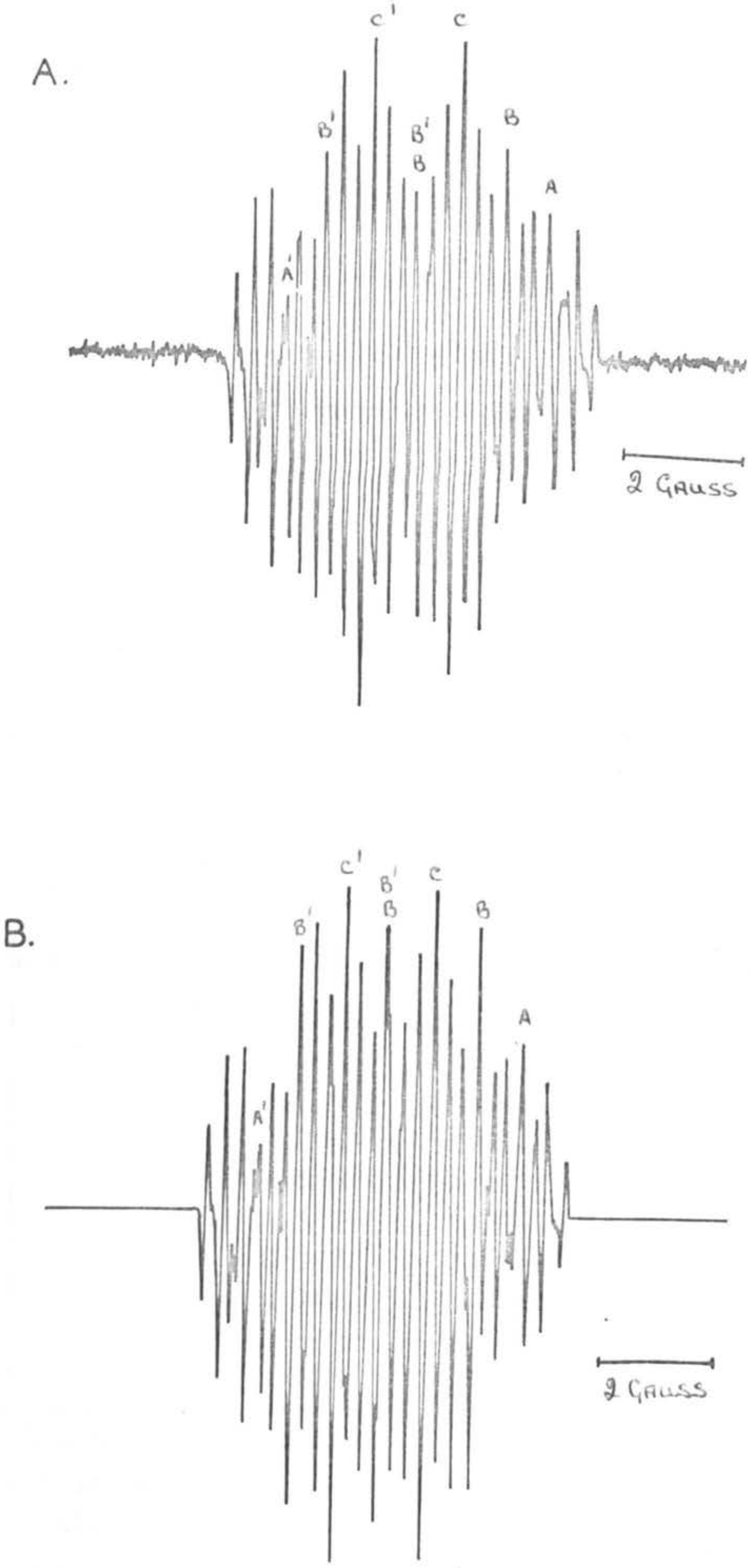
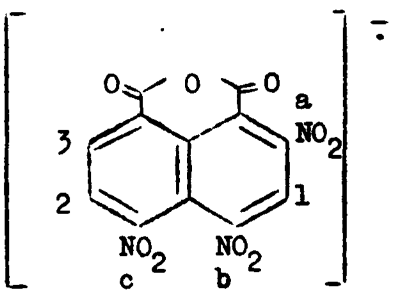


Figure 20 The electron spin resonance spectrum of the Tri.N.-1,8-N.A. radical anion (A) experimentally observed and (B) simulated

TABLE 18 The Tri.N-1.8-N.A. Radical Anion



Obsefved Spectrum - Figure 20

Experimental Conditions

Temperature -40°C

Counter Ion Sodium

Spectral Analysis

Nucleus	Assignment*	Multiplicity	Coupling Constant (Gauss)
Proton	1	Douolet	1.450
Nitrogen	Na, Nb	Quintet	0.730
Nitrogen	Nc	Triplet	0.460
Proton	2, 3	Triplet	0.250

Spin Densities

Position	Ref. No.	Calculated Spin Densities Huckel	McLachlan	Experimental Spin Densities
Oa		0.04739	0.04858	---
Na	e	0.03197	0.02819	---
Ob		0.03943	0.04041	---
Nb	f	0.02660	0.02270	---
Oc		0.03605	0.03585	---
Nc	g	0.02432	0.02072	---
1	3	0.10170	0.10122	0.0613
2	4	0.06785	0.07677	0.0105
3	5	0.06431	0.06888	0.0105

Calculated Nitrogen Coupling Constants

(a) Based on Huckel Spin Densities using equation 36

J_{Na} = 0.79 G J_{Nb} = 0.58 G J_{Nc} = 0.50 G

(b) Based on McLachlan Spin Densities using equation 34 and 35

J_{Na} = 0.69 G J_{Nb} = 0.65 G J_{Nc} = 0.51 G

* Assignments based largely on experimental evidence

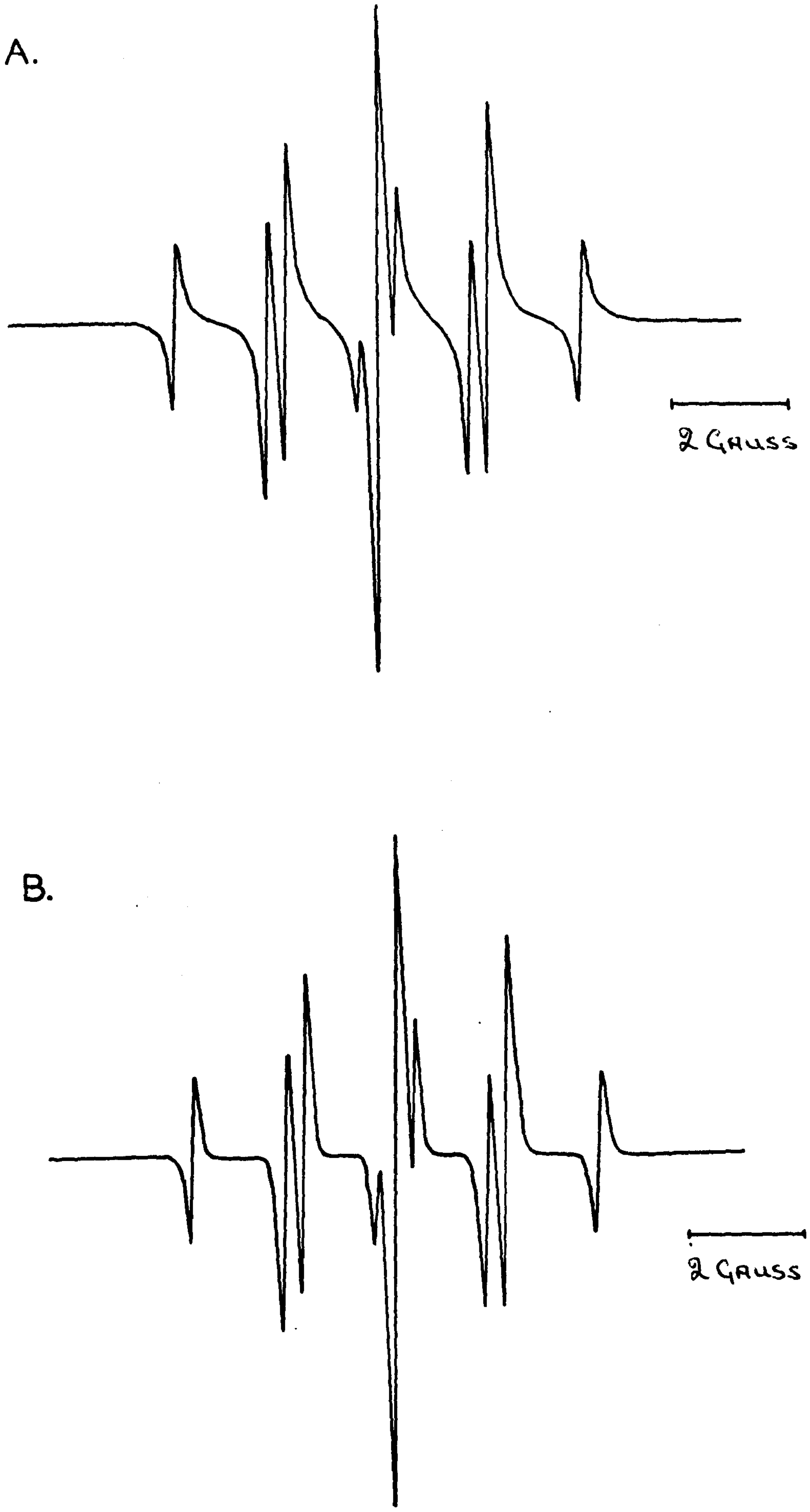
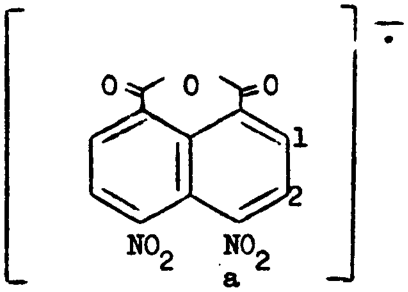


Figure 21 The electron spin resonance spectrum of the 4,5-D.N.N.A. radical anion (A) experimentally observed and (B) simulated

TABLE 19 The 4,5-D.N.N.A. Radical Anion



Observed Spectrum - Figure 21

Experimental Conditions

Temperature - 40°C

Counter Ion Sodium

Spectral Analysis

Nucleus	Assignment	Multiplicity	Coupling Constant (Gauss)
Proton	* 1	Triplet	1.86
Proton	* 2	Triplet	1.54
Nitrogen	a	Unobserved	

Spin Densities

Position	Ref, No.	Calculated Spin Density		Experimental Spin Density
		Huckel	McLachlan	
O(a)		0.05517	0.05713	----
N(a)	h	0.04100	0.03726	---
1	6	0.07074	0.07878	0.0785
2	7	0.06442	0.06492	0.0650

Calculated Nitrogen Coupling Constants

(a) Based on Huckel Spin Densities using equation 36

$$J_{Na} = 0.29 \text{ G}$$

(b) Based on McLachlan Spin Densities using equations 34 and 35

$$J_{Na} = 0.40 \text{ G}$$

* Assignments based on the calculated results.

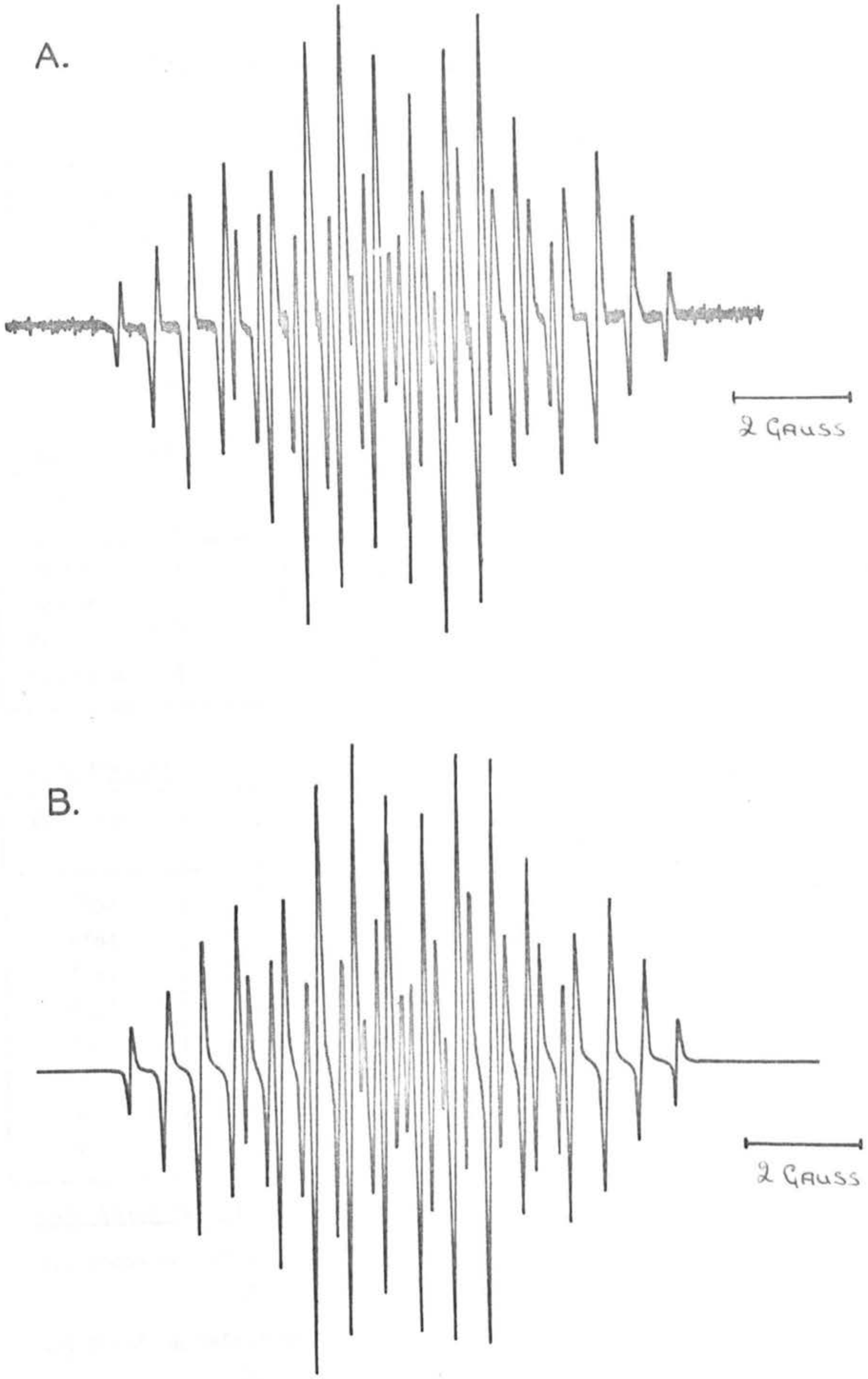
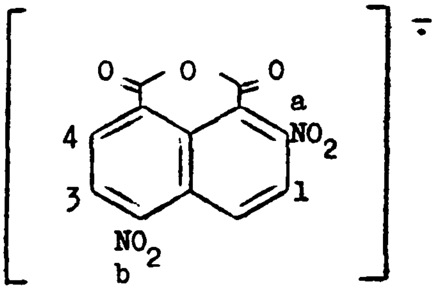


Figure 22 The electron spin resonance spectrum of the 2,5-D.N.N.A. radical anion (A) experimentally observed and (B) simulated

TABLE 20 The 2,5-D.N.N.A. Radical Anion



Observed Spectrum - Figure 22

Experimental Conditions

Temperature -40°C

Counter Ion Sodium

Spectral Analysis

Nucleus	Assignments*	Multiplicity	Coupling Constant (Gauss)
Proton	1	Doublet	0.64
Proton	2	Doublet	2.38
Proton	3, 4	Triplet	1.99
Nitrogen	a, b	Quintet	0.59

Spin Densities

Position	Ref. No.	Calculated Spin Density		Experimental Spin Density
		Huckel	McLachlan	
O(a)		0.05470	0.05802	---
N(a)	j	0.03885	0.03527	---
O(b)		0.06499	0.06726	---
N(b)	k	0.04616	0.04185	---
1	8	0.00028	0.03257	0.0272
2	9	0.07093	0.09600	0.1005
3	10	0.08291	0.09377	0.0841
4	11	0.07145	0.07559	0.0841

Calculated Nitrogen Coupling Constants

(a) Based on Huckel Spin Densities using equation 36

$J_{Na} = 0.64$ G $J_{Nb} = 0.74$ G

(b) Based on McLachlan Spin Densities using equations 34 and 35

$J_{Na} = 0.66$ G $J_{Nb} = 0.68$ G

* Assignments based on calculated results.

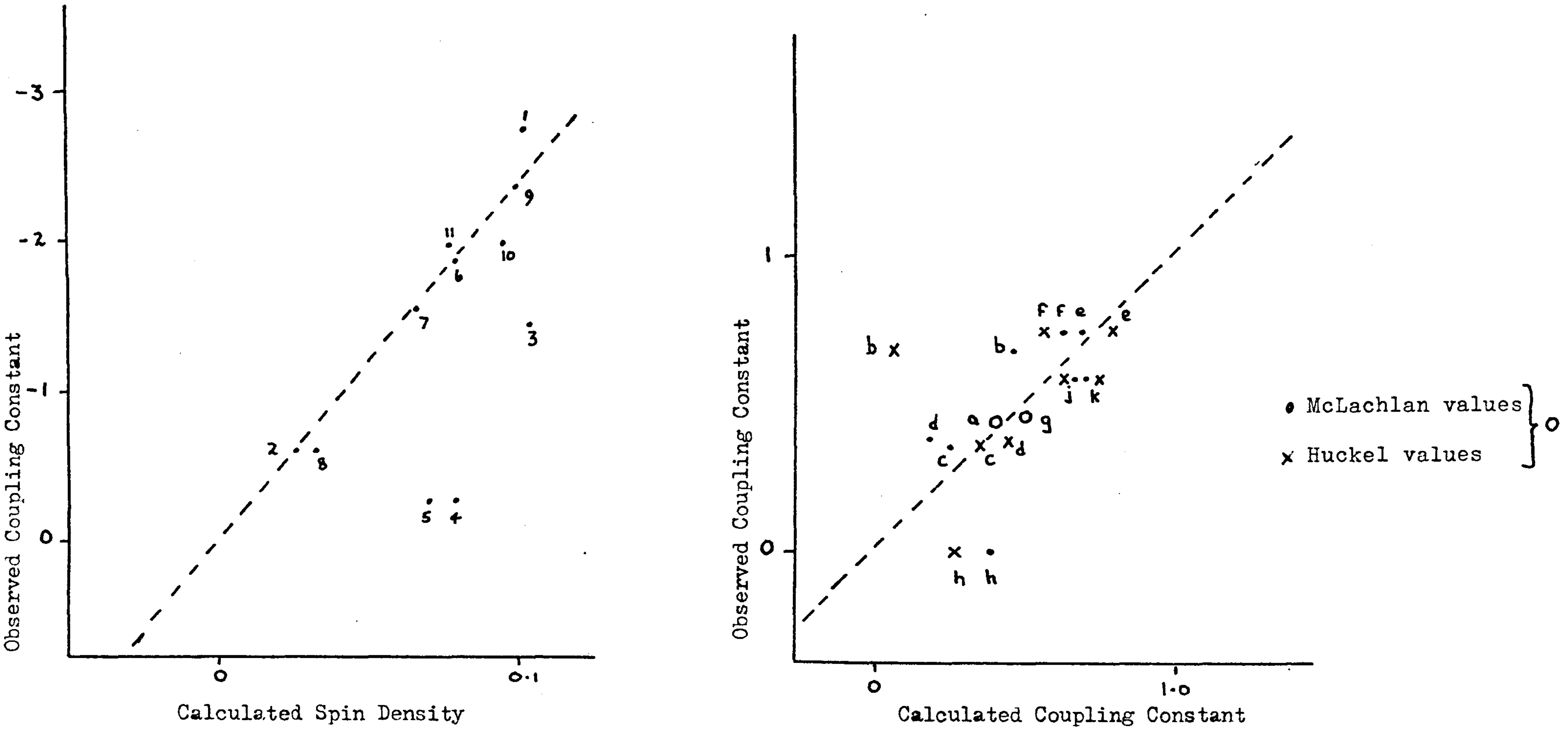
Certain assignments, to which reference is made in Tables 16 to 20, are not without some degree of ambiguity and isotopic labelling experiments would be required to fully justify the proposed assignment.

(c) Discussion

It can be seen from Tables 16 to 20 that the values of the calculated and experimentally determined π -electron densities are in reasonable agreement. In figure 23A the calculated electron densities obtained by the McLachlan method are plotted against the experimentally observed proton coupling constants, the signs of which have been chosen to agree with the calculated signs of p_i^{π} and the negative sign of Q_{CH}^{H}. The agreement is seen to be very satisfactory for most of the compounds studied. The straight line represents absolute correlation and corresponds to $Q_{CH}^{H} = -23.7$ G.

Relatively poor correlation is observed for points 3, 4 and 5 all derived from Tri.N-1,8-N.A. and this probably results from the effects of Alternating Line Width which will be discussed later.

In figure 23B the observed nitrogen coupling constants for the different nitrogen nuclei in the radical anions are plotted against the coupling constants calculated using both the Huckel and McLachlan methods. Apart from the points due to 4,5-D.N.N.A. where no nitrogen coupling constant was observed, although one was theoretically predicted, the correlation is very reasonable. This suggests that in the compounds studied there is little to choose between the two methods, particularly since it is almost certain that in such highly substituted aromatic



A. Proton Correlation Plot.

B. Nitrogen Correlation Plot.

The distinguishing letters and numbers correspond to the reference numbers in the tables 16 to 20.

Figure 23 Correlation diagrams of the theoretically calculated and experimentally observed results.

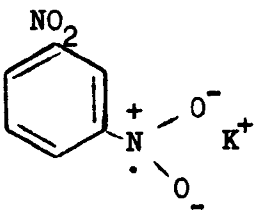
systems the relatively simple Huckel and McLachlan approaches do not result in a true picture of the spin distribution.

The results obtained from the radical anion of 4,5-D.N.N.A. are interesting because there is no evidence for the nitrogen hyperfine coupling. This is particularly remarkable since in the radical anion of 1,8-dinitronaphthalene the nitrogen coupling constant has a value of 3.03 G[196]. This value is the largest observed for the radical anions of the isomeric dinitronaphthalenes and is greater than the other values because of steric hindrance between the *peri* nitro groups. A similar value for the nitrogen coupling constant would be expected in the 4,5-D.N.N.A. radical anion where the steric factors involved are comparable. The reason for the complete absence of such a coupling is not entirely clear. The calculated spin densities for the ring protons in the 4,5-D.N.N.A. radical anion are in good agreement with the observed spin densities and the calculations for the nitrogen nuclei suggest a coupling constant of 0.4 G. If there were no anomalous effects in the 4,5-D.N.N.A. radical anion this nitrogen hyperfine coupling would be observable in the spectrum.

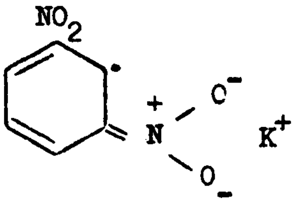
The failure to observe an expected nitrogen hyperfine coupling has been reported by Ward[138]. The radical anions of *meta* and *para* dinitrobenzene when produced by alkali metal reduction in dimethoxyethane solution exhibit only one nitrogen coupling constant.

The spectrum observed for the radical anion of *meta* dinitrobenzene can be accounted for in terms of the structures

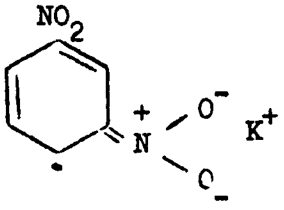
XV to XVIII below.



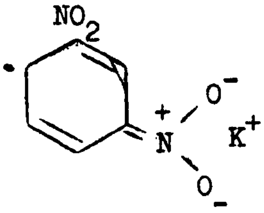
XV



XVI



XVII



XVIII

Structure XV will lead to a single nitrogen hyperfine coupling while structures XVI, XVII and XVIII will yield proton hyperfine couplings at the 2, 4, and 6 positions. It is not however possible to draw a cannonical form to represent the structure responsible for the observed hyperfine coupling at the 5-position. It can be theoretically shown that the product of the bond eigenfunctions of structures XVII and XVIII predicts some unpaired π-electron density at the 5-position and hence the observed coupling. Again the reasons for the complete lack of coupling from the second nitrogen nucleus is not entirely clear, but the structures where the odd electron resides on the uncomplexed nitro group must be of higher energy and apparently do not contribute.

The spectrum of the radical anion of *p*-dinitrobenzene is even more anomalous since in addition to the absence of coupling to one of the nitrogen nuclei the two protons *meta* to the interacting nitrogen nucleus do not exhibit coupling. This situation can be shown by drawing structures similar to those drawn for *m*-dinitrobenzene.

If the radical anions of *meta* and *para* dinitrobenzene are generated electrolytically, however, the spectra are as expected, and in *o*-dinitrobenzene and *sym* trinitrobenzene the spectra are as expected whether the anions are generated electrolytically or chemically.

In the radical anion of 4,5-D.N.N.A. the same structural features as in p-dinitrobenzene are observed, in that there is a nitro group para to an electron withdrawing substituent, in this case the anhydride. If the counter ion is associated with the anhydride group rather than with a nitro group, the structures where the odd electron residues on the nitro groups may be of too high energy to contribute to the observed spectrum, and hence the absence of the nitrogen coupling.

In the radical anion derived from 2,5-D.N.N.A., the nitrogen hyperfine coupling, although small, is apparent in the spectrum. An interesting feature is that the nitrogen couplings are coincidently equivalent. However since the nitro group in one ring is ortho to the anhydride group and the nitro group in the other ring para to the anhydride group, it is probably not too surprising that the nitrogen couplings are equivalent because with the anhydride group being ortho, para directing not much difference in the electron density at these sites would be expected. The coincidence in the coupling constants is reflected in the calculated spin densities at the nitrogen nuclei (see Table 20).

The calculated spin densities for the proton nuclei in the 2,5-D.N.N.A. radical anion are in good agreement with the experimental results. The calculations show that the two protons ortho to each other in the ring system (Table 20, protons 3 and 4) have similar spin densities and this fits well with the observation that these protons give rise to a triplet splitting pattern in the spectrum.

The spectra observed from the radical anions derived from the two tetranitro compounds are as expected and the comparison between the experimental results and the calculations are remarkably good, particularly for the proton couplings. The points of particular interest are the values of the nitrogen coupling constants ranging from 0.35 G to 0.65 G which are small for aromatic nitro compounds. The values of the nitrogen coupling constants for the electrolytically prepared radical anions derived from the isomeric dinitronaphthalenes ranged from 0.97 G to 3.03 G[166]. However, in contrast, the radical anion derived from 1,4,5,8-tetranitronaphthalene, prepared by sodium reduction in 1,2-dimethoxyethane solution, shows a nitrogen coupling constant of 0.25 G at -60°C which compares favourably with the present observations for the tetranitro-radical anions prepared by the same method.

Probably the most interesting system studied is the radical anion derived from Tri.N-1,8-N.A. Comparison of the observed and simulated spectra (Figure 20) reveals that although the line positions and the width of the overall spectra compare favourably, the intensities of the lines differ considerably. The complexity of the spectrum makes a complete analysis difficult. However, analysis of the nitrogen quintet (marked A.B.C.B.A) shows that the expected intensity ratio of 1:2:3:2:1 is not obeyed, and the lines marked B are less intense in the observed spectrum than expected. This effect, known as the Alternating Linewidth Effect, is well known in compounds with *meta* nitro groups and has been well reviewed by Hudson and Luckhurst[191]. The observation of this effect, together with the experimentally observed nitrogen quintet in the spectrum leads to the assignment

(Table 18) of the nitrogen nuclei a and b being equivalent. The alternating linewidth effect, however, could result from two nitro groups in <u>peri</u> positions oscillating out of phase with each other. Since this effect is not observed in the other systems studied it seems likely that the assignment given is correct.

Reiger and Fraenkel have shown[59] that in <u>meta</u>-dinitrobenzene where the alternating linewidth effect is in evidence, the correlation between the experimental and calculated spin densities is poor. This poor correlation is also observed in Tri.N-1,8-N.A. and this most likely results from the anomalies introduced into the electron distribution from the alternating linewidth effect.

The overall width of the spectra, recorded in the present study, vary from 5.28 G to 10.2 G. These widths are remarkably small, since the total width of the spectra derived from the radical anions of nitroaromatic compounds are generally between 20 G and 30 G. This observed small overall width largely reflects the small values observed for the nitrogen coupling constants. The value of the nitrogen coupling constants appear to be very dependent on the manner of preparation of the anion. Gerson and Adams[187] recorded the spectrum of the 1,8-dinitronaphthalene radical anion prepared by both electrolytic and chemical reduction and obtained values for the nitrogen coupling constant of 3.07 G and 7.5 G respectively, while the values of the proton hyperfine coupling constants remained unchanged. It appears that the preparation of radical anions by chemical reduction introduces anomalies into the spin density distribution at nitrogen, probably due to the complexing of the counter ion and it would be very interesting to repeat the present measurements using electrolytic reduction methods.

From a detailed crystallographic study[192,193] it has been shown that the nitro groups in 1,8-dinitronaphthalene are rotated 43° in one direction out of the plane of the ring. The distance between the nitrogen atoms increases from 2.42 Å to 2.93 Å and these atoms deviate +0.37 Å and -0.37 Å from the plane of the ring. The coplanarity of the rings is disturbed by the interaction of the nitro groups and the ring angles are deformed as much as 7°. It seems reasonable to assume that similar deformations would occur in other compounds with similar structural features and the value of 30°, calculated theoretically, for the angle of twist of the peri nitro groups in T.N.A., 4,5-D.N.N.A., Tri.N-1,8-N.A. and T.N.N.A. would seem to be a satisfactory value considering the limitations of the theoretical method when applied to systems of such complexity.

(2) Relative Electron Densities at the Proton Sites in 3,6-D.N.N.A.

It is unfortunate that it was not possible to obtain the electron spin resonance spectrum of the radical anion of 3,6-D.N.N.A. since this would have provided direct experimental evidence as to the electron densities at the proton sites in the molecule. These results could have been compared with the values calculated by the McLachlan method and provide information as to whether the theoretical values for the molecule were reasonable. The results obtained by calculation give the π-electron density at the 2- and 7-proton positions as 0.063 and at the 4- and 5-proton positions as 0.263. Since the calculated values indicate that the electron densities at the two different types of proton site are markedly different it would be expected that these electron deficient sites would complex to different extents with donor molecules capable of specific interaction with the protons at these sites. Thus by measuring the extent of the interaction at these sites for particular donor molecules an experimentally derived estimate of the relative electron densities at the proton sites may be obtained. Nuclear magnetic resonance spectroscopy provides a convenient method for measuring the extent of the interaction at particular sites since any alteration in the environment of the protons will result in a change in the chemical shift of these protons. A change in the environment of the protons may be produced simply by changing the solvent system. This environmental change is reflected by a change in the nuclear magnetic resonance spectrum.

The origins of the solvent effect in nuclear magnetic resonance spectroscopy have been much studied and the results reviewed in detail by Laszolo[194]. However, such detailed theory is outside the scope of the present investigation which takes the form of a semi-empirical study into the effects of several 'complexing solvents' on the nuclear magnetic resonance spectrum of 3,6-D.N.N.A. Dioxan, tetrahydrofuran, acetonitrile and dimethylsulphoxide were used as 'complexing' donor solvents for the study since (a) they are known electron donors, (b) they complex sufficiently strongly with 3,6-D.N.N.A. to give solutions concentrated enough for the observation of the proton resonances and (c) the chemical shifts of the proton resonances of 3,6-D.N.N.A. show considerable variation in these donor solvents.

(a) Experimental

Carbon tetrachloride was used as the 'inert' solvent and this and the donor solvents were distilled immediately prior to use.

A solution of 3,6-D.N.N.A. in each of the donor solvents was diluted gravimetrically using carbon tetrachloride. The mole fraction of carbon tetrachloride was slowly increased to the point at which the 3,6-D.N.N.A. began to precipitate. The nuclear magnetic resonance spectrum of each of the samples was obtained using a Perkin Elmer R.10 spectrometer operating at 60.004 MHz with a probe temperature of 33.5°C. The positions of the lines due to 3,6-D.N.N.A. were measured to an estimated accuracy of 0.5 Hz relative to an internal T.M.S. reference. Each shift was determined at least 3 times and the average value was taken.

(b) Results

The spectrum of 3,6-D.N.N.A. consists of a doublet of doublets showing *meta*-coupling of about 3 Hz. The position of the lines is dependent on the particular solvent.

Plots of the shift of the high field and low field doublet signals from 3,6-D.N.A.A. against the mole fraction of carbon tetrachloride in the sample were computed. A typical plot is shown in figure 24. From the plots, the position of the signal due to the 3,6-D.N.N.A. protons in pure carbon tetrachloride was obtained by extrapolation. The extrapolated positions in carbon tetrachloride were used as a standard for the determination of the association constants of the interactions calculated using the equation of Foster and Fyfe[36]. Plots of $\Delta / [D_o]$ against Δ were computed and a typical plot is shown in figure 25. The value of the association constant for each of the systems was obtained from the gradient of the appropriate plot. The results are summarised in Table 21.

(c) Discussion

It can be seen from Table 21 that the direction of the shift produced on the addition of carbon tetrachloride to solutions of 3,6-D.N.N.A. in dioxan, tetrahydrofuran and acetonitrile was upfield whereas that in dimethylsulphoxide was downfield. This suggests that a different type of interaction is taking place in the case of dimethylsulphoxide as against the other donor solvents. The direction of the shift in the case of dimethylsulphoxide solution suggests charge-transfer complex formation to be taking place. The fact that the association constants as derived from each of the proton resonances are, within experimental error, identical is a further indication that complex

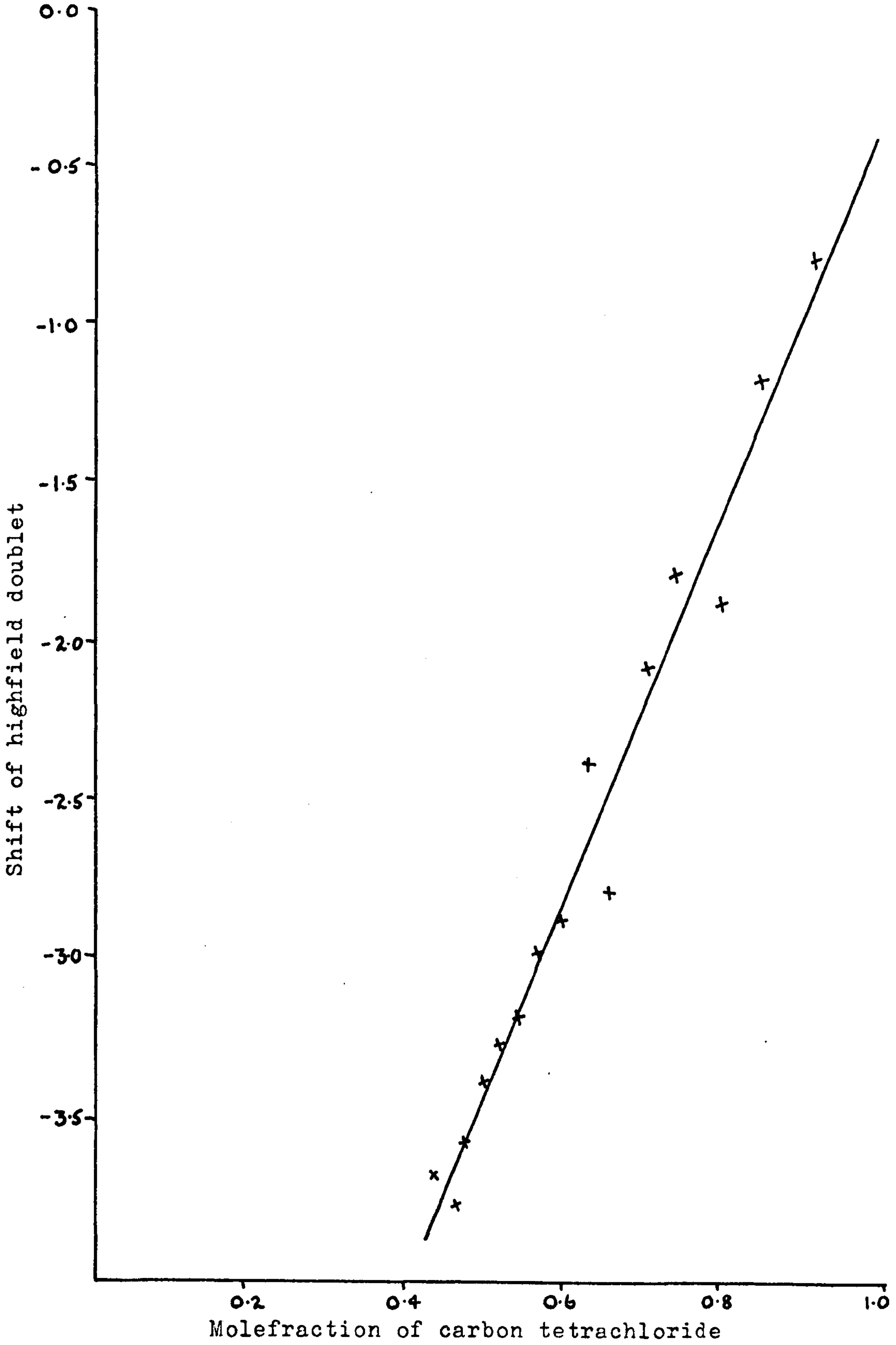
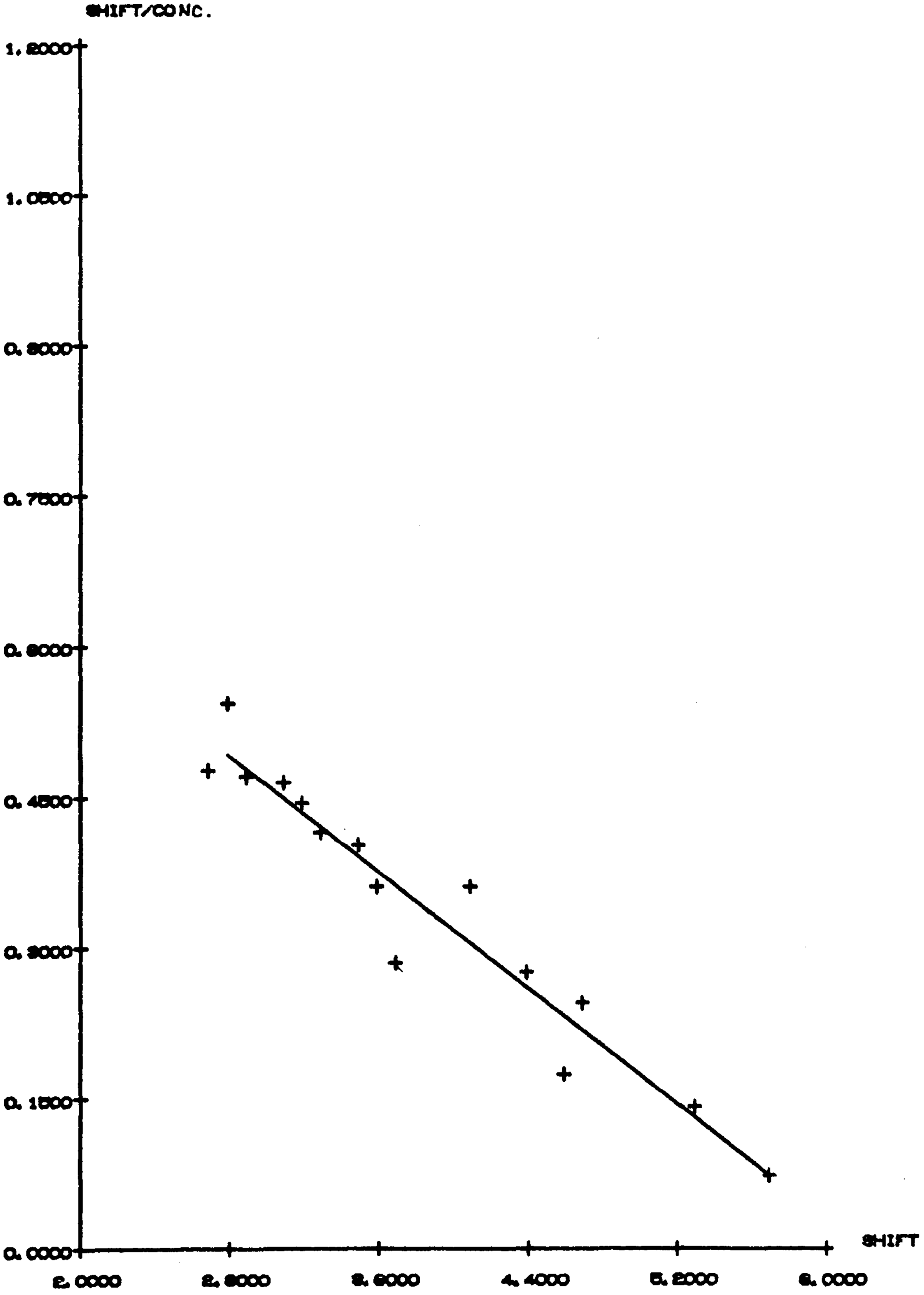


Figure 24 A plot of the shift of the highfield doublet of 3,6 - D.N.N.A. in tetrahydrofuran solution induced by the addition of carbon tetrachloride against the molefraction of carbon tetrachloride in the system.



<u>Figure 25</u> A plot of $\Delta/[D_o]$ against Δ for the shift (Δ) of the highfield doublet of 3,6 - D.N.N.A. using tetrahydrofuran as the donor and carbon tetrachloride as the inert solvent.

TABLE 21 The Direction of the Shift Produced in the Spectrum of 3,6-D.N.N.A. in various Solvents by the Addition of Carbon Tetrachloride, the Maximum Observed Shift and the Extrapolated position of the Resonance in Carbon Tetrachloride Solution together with the Association Constants for the Interaction at 33.5°C

Donor Solvent	Measurements from Lowfield Doublet				Measurements from Highfield Doublet			
	Direction of Shift	Maximum Observed Shift (Hz)	Extrapolated Position in CCl_4 (Hz)	Association Constant kgs/mole	Direction of Shift	Maximum Observed Shift (Hz)	Extrapolated Position in CCl_4 (Hz)	Association Constant kgs/mole
Dioxan	Up	4.8	575.8	0.10±0.03	Up	2.4	564.7	0.04±0.01
T.H.F.	Up	6.5	573.6	0.14±0.04	Up	1.6	562.8	0.06±0.01
D.M.S.O.	Down	4.9	574.7	1.3±0.1	Down	6.4	563.9	1.4±0.1
CH_3CN	Up	2.9	576.3	0.11±0.03	-	-	565.2	-

formation is via a charge-transfer interaction through the π-system of 3,6-D.N.N.A. rather than via an interaction at a specific molecular site. This type of behaviour is probably not unexpected since dimethylsulphoxide has been shown to be a strong electron donor and readily forms charge-transfer complexes with electron acceptors such as tetracyanoethylene and iodine[195].

The direction of the shift in the case of dioxan, tetrahydrofuran and acetonitrile suggests that these donor solvents are hydrogen-bonding to the electron deficient protons in the 3,6-D.N.N.A. molecule. The magnitude of the association constants for the interaction when measured from the shift of the lowfield doublet are very similar in each of the donor solvents and greater than the corresponding value of the association constants measured from the shift of the highfield doublet. These observations suggest that each of the solvents form hydrogen-bonds of similar strength and that stronger hydrogen-bonds are formed with 3,6-D.N.N.A. at the 2- and 7-positions than at the 4- and 5-positions. This would appear to correlate well with the expected results since the protons at the 2- and 7-positions are ortho to both the anhydride group and to a nitro group and the electron density at these sites has been shown by calculation to be lower than that at the 4- and 5-positions.

Although the experimental results are in qualitative agreement with the theoretical results it must be borne in mind that the association constants were derived on the assumption of a 1:1 complex being formed between the donor and the acceptor, and that it is possible that higher order complexes may have been formed especially as there are a total of four proton acceptor sites in the 3,6-D.N.N.A. molecule.

CHAPTER 4

REACTIONS WITH BASES

1. Introduction
2. Reactions with Alkoxides
3. Reactions with the Sulphite ion
4. Reactions with Amines
5. Discussion

1. Introduction

The reactions of bases with nitrobenzenoid compounds have been extensively studied and the results reviewed in detail[76,87,115]. A variety of different products have been isolated from such reactions and these are summarised in Chapter 1, section 4 of this thesis. It is to be expected that the nature of the product formed from the reactions of bases with an electron deficient π-system will depend upon both the strength of the reacting base and the degree of electron deficiency in the π-system.

In this chapter the reactions of T.N.A , 3,6-D.N.N.A. and 4,5-D.N.N.A. with bases are discussed. The compounds are taken as typical examples representative of the whole group of compounds at present under investigation. The bases used in the reactions, listed in order of decreasing basic strength, were the alkoxide ion, the sulphite ion and some amines. The products of these reactions are compared with the well established products resulting from the reactions of trinitrobenzene under similar conditions.

2. Reactions with alkoxides

(a) T.N.A.

The addition of a methanolic solution of sodium methoxide to a solution of T.N.A. in dichloromethane resulted in the immediate formation of a brown precipitate which was isolated and characterised. An analagous reaction was carried out with sodium ethoxide but the brown product from this reaction was found to detonate on touch. No further work with the ethoxide ion was therefore attempted.

(i) Experimental and Results

Dichloromethane was twice distilled from calcium hydride and the fraction boiling at 39° - 40°C was collected.

Methanol was purified by boiling under reflux with phosphoric acid followed by distillation from magnesium and iodine, the fraction boiling at 64°C was collected.

To a solution of T.N.A. (1 gm) in dichloromethane (100 ml) was added slowly an equimolar amount of sodium methoxide in methanol (10 ml). Dry nitrogen was bubbled through the mixture during the addition. A brown precipitate was formed and after cooling to 0°C the mixture was filtered under an atmosphere of dry nitrogen using a covered vacuum filter funnel. The solid was thoroughly washed with dry dichloromethane, dried under high vacuum and sealed in evacuated ampoules until required.

The compound was subjected to elemental analysis and was investigated by nuclear magnetic resonance, infrared and ultraviolet spectroscopy.

The nuclear magnetic resonance spectrum recorded in deuterodimethylsulphoxide solution, shown in figure 26, shows three single peaks at $3.8\,\tau$, $5.82\,\tau$ and $6.79\,\tau$. The relative intensity of the peaks is 1:2:3 respectively.

The ultraviolet spectrum of the product was completely featureless because the solution, being brown in colour, absorbed over the whole wavelength range.

The brown colour of the solid made it extremely difficult to obtain a reasonable infrared spectrum. However, a weak poorly resolved spectrum was obtained from a Nujol Mull.

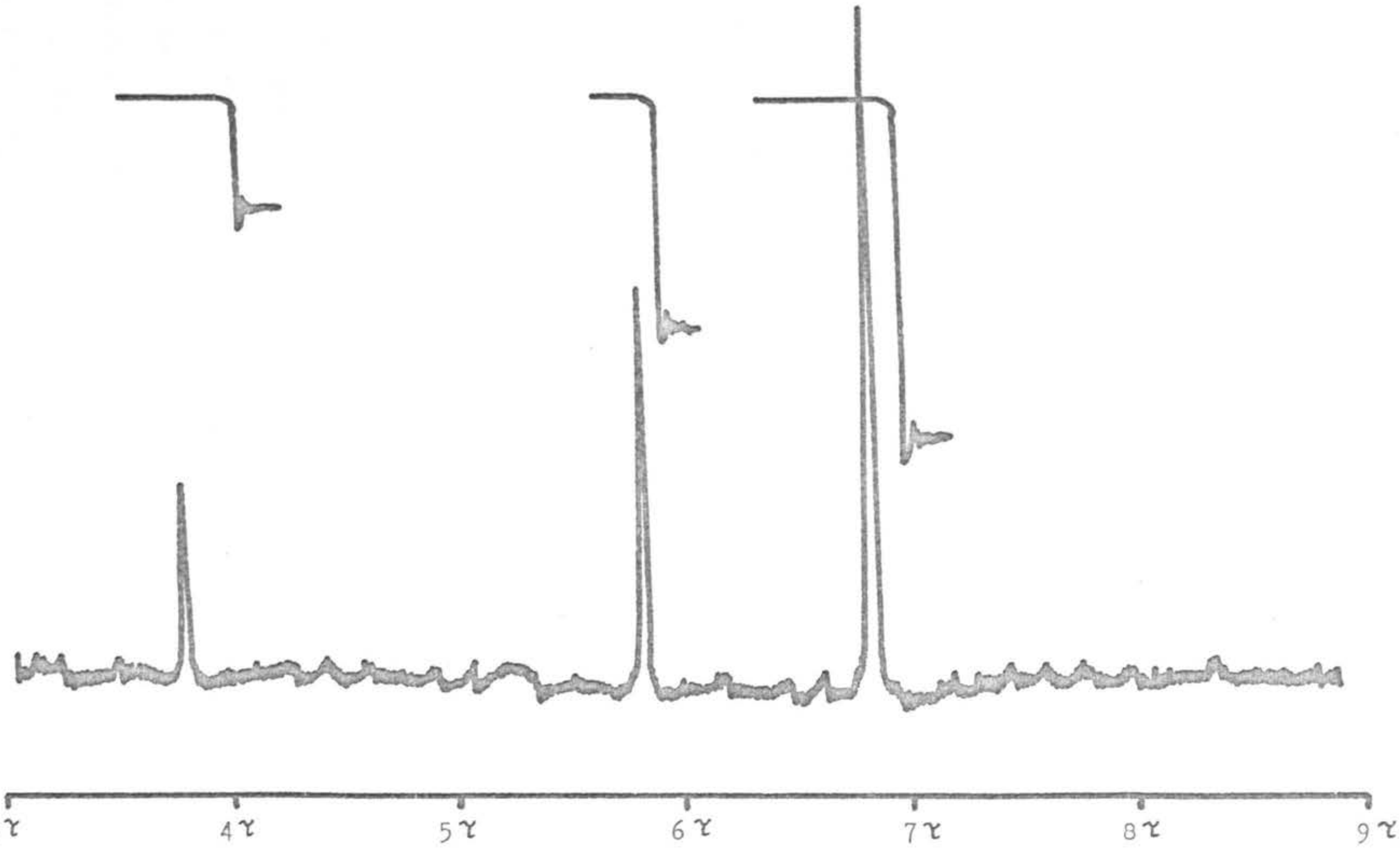


Figure 26 The spectrum of the product of the reaction of T.N.A. with the methoxide ion in deutero-dimethylsulphoxide solution.

The bands and their intensities are tabulated below:

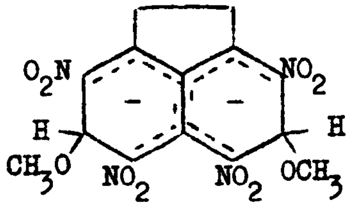
700 (vw)	721 (w)	735 (vw)	760 (vw)	795 (w)
830 (vw)	875 (m)	925 (w)	960 (m)	990 (m)
1022 (m)	1085 (m)	1143 (w)	1190 (m)	1240 (sh)
1262 (m)	1322 (w)	1500 (w)	1510 (w)	1520 (w)
1540 (w)	1560 (m)	1578 (w)	1640 (w)	

The results obtained from the elemental analysis were as follows:

C = 37.5%; H = 2.4%; N = 13.1%; Na = 10.6%

(ii) Discussion

The nuclear magnetic resonance spectrum indicates three different proton types in the molecule, and in view of the relative intensities of the peaks and the known reactions of the methoxide ion with trinitrobenzene, the most likely structure for the compound is as shown in structure XIX below.



$2Na^+$ XIX

The required analysis figures for this structure are:

C = 38.0%; H = 2.7%; N = 12.7%; Na = 10.4%

and these are in reasonable agreement with the experimentally observed figures.

The upfield shift of the aromatic proton resonance from 0.8 τ in T.N.A. to 3.8 τ in the complex is in keeping with the results obtained in the reaction of trinitrobenzene with the methoxide ion[80,81] and supports the proposed structure.

Although the infrared spectrum was poorly resolved, the presence of the bands at 1190 cm^{-1}, 1085 cm^{-1} and 1022 cm^{-1} all of medium intensity and not present in T.N.A. suggest that the compound is a sigma-complex[98] and not a charge-transfer complex.

No mass spectrum of the compound could be obtained and this is consistent with the product being a negative ion.

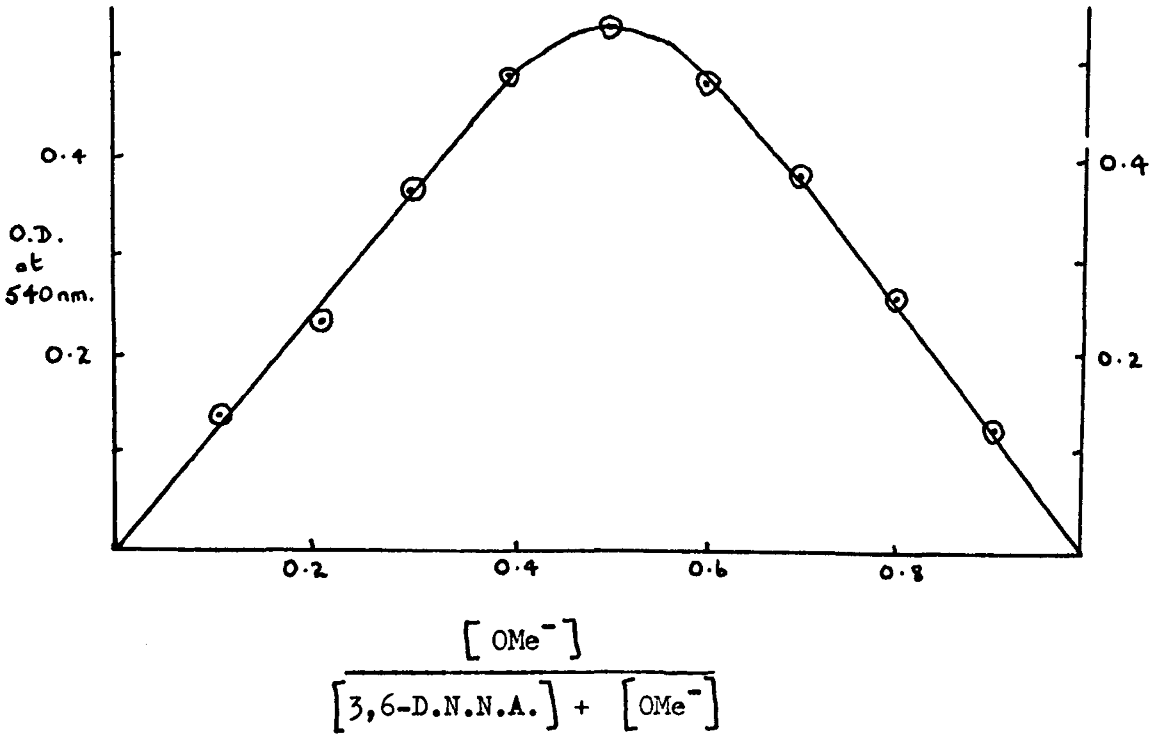
(b) 3,6-D.N.N.A. and 4,5-D.N.N.A.

(i) Experimental and Results

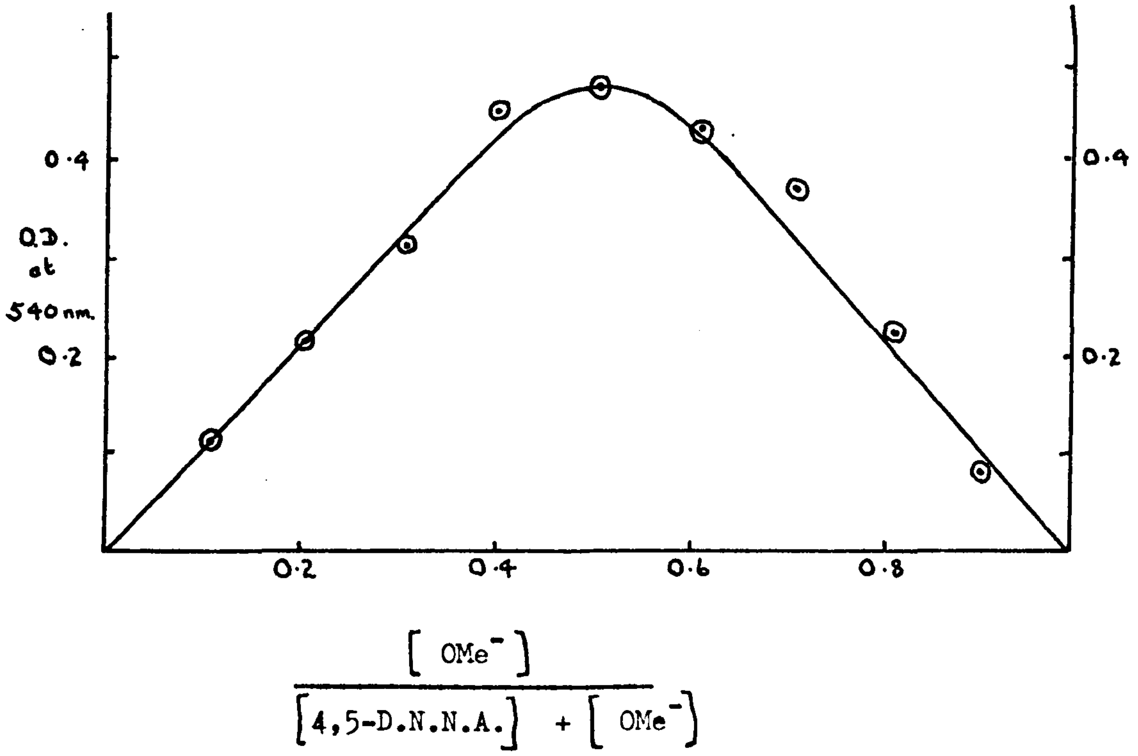
The addition of methanolic sodium methoxide to 3,6-D.N.N.A. and 4,5-D.N.N.A. in each case gave a bright red solution characteristic of the formation of a complex between the alkoxide ion and the nitroaromatic compounds. The stoichiometry of the complexes was investigated by the method of continuous variations[137]. This was achieved by mixing solutions of 3,6-D.N.N.A. and 4,5-D.N.N.A. in sulpholane with solutions of sodium methoxide in methanol in known molar ratios and keeping the total molar concentration constant. The absorbance of the solutions was measured at a wavelength of 540 nm. using a Unicam SP 600 spectrophotometer. The optical density of the solutions decreased markedly with time and measurements taken at 30 second intervals and extrapolated back to zero time gave the optical density of the solution at the time of mixing. The Job plots of the results for the isomeric D.N.N.A. - methoxide ion systems are shown in figure 27.

The reaction between methanolic sodium methoxide and 3,6-D.N.N.A. in sulpholane was followed by nuclear magnetic resonance spectroscopy. Equimolar quantities of the reactants were mixed and the nuclear magnetic resonance spectrum was

A. Total concentration of 3,6 - D.N.N.A. plus methoxide ion $= 2.85 \times 10^{-4}$M.



B. Total concentration of 4,5 - D.N.N.A. plus methoxide ion $= 4.37 \times 10^{-4}$M.



<u>Figure 27</u> Job plots for the D.N.N.A. - methoxide ion systems

recorded (A) immediately after mixing, (b) 20 minutes after mixing, (C) 40 minutes after mixing, (D) 1 hour after mixing, (E) 2 hours after mixing and (F) 20 hours after mixing. The spectra are shown in figure 28.

The reactions of 3,6-D.N.N.A. and 4,5-D.N.N.A. with the methoxide ion were studied on a preparative scale. The dinitronaphthalic anhydride (1 gm) was dissolved in dimethylsulphoxide (50 ml) and an equimolar quantity of sodium methoxide in methanol (10 ml) was added. Dry nitrogen was bubbled through the system during the addition. The solution became bright red and after one hour dry ether (50 ml) was added to the system. A pale yellow solid was precipitated which was removed by filtration, dried under high vacuum and sealed in ampoules until required. The dimethylsulphoxide used in the preparation was dried over 4A molecular sieve for one month and then distilled under reduced pressure from calcium hydride. The dried material was redistilled under reduced pressure (~ 12 torr) and the fraction boiling between 75° and 76°C was used.

The products of the reaction were analysed and the nuclear magnetic resonance, infrared and the mass spectra of the products recorded.

The electron spin resonance spectrum of a solution of a mixture of 3,6-D.N.N.A. and sodium methoxide in methanol was recorded. The spectrum which is shown in figure 29 was recorded immediately after mixing and on standing the intensity of the signal diminished.

(ii) Discussion

The plots shown in figure 27 suggest that initially, at least, a 1:1 complex is formed between the isomers 3,6-D.N.N.A., 4,5-D.N.N.A. and the methoxide ion under the reaction conditions

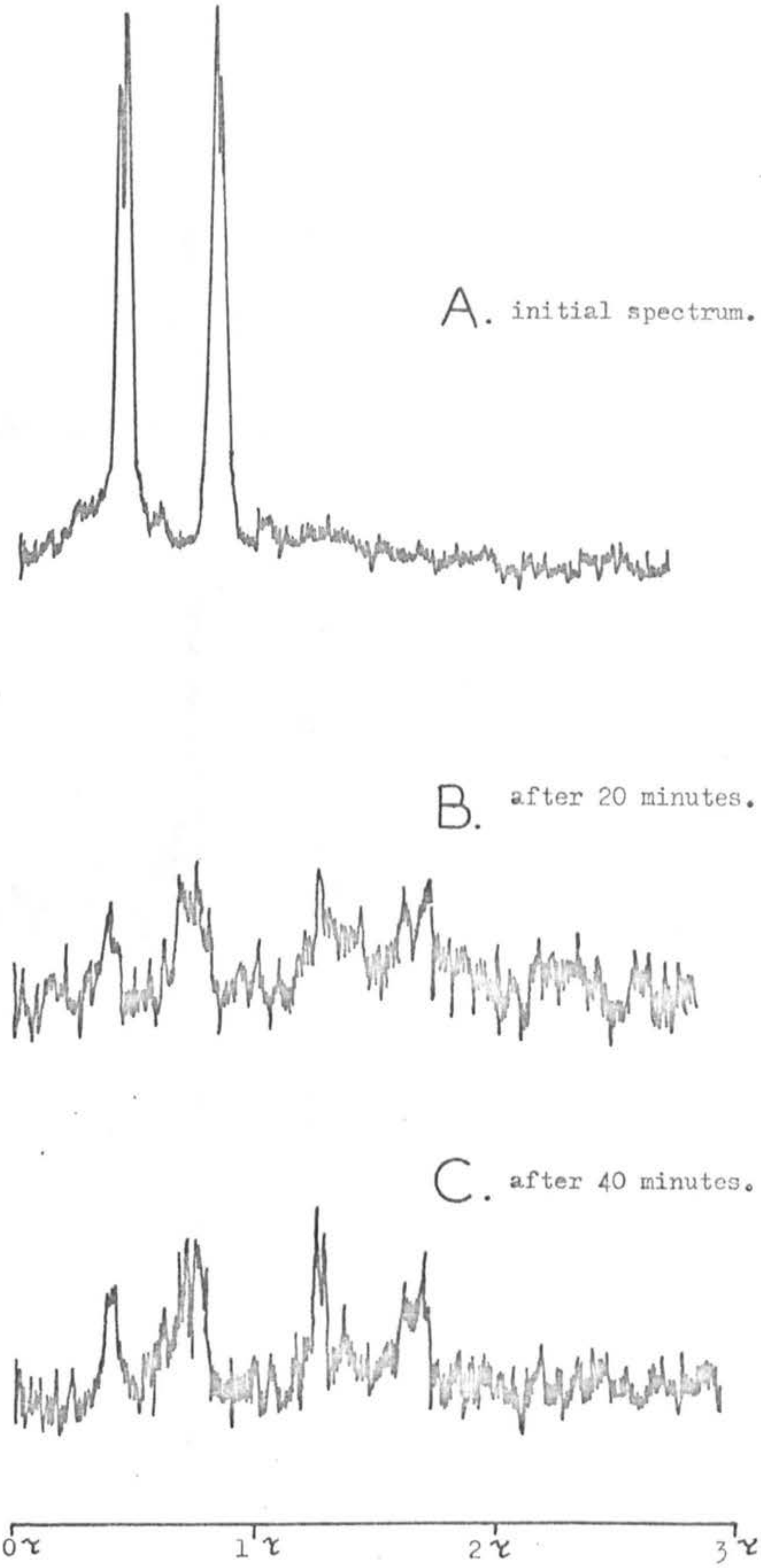
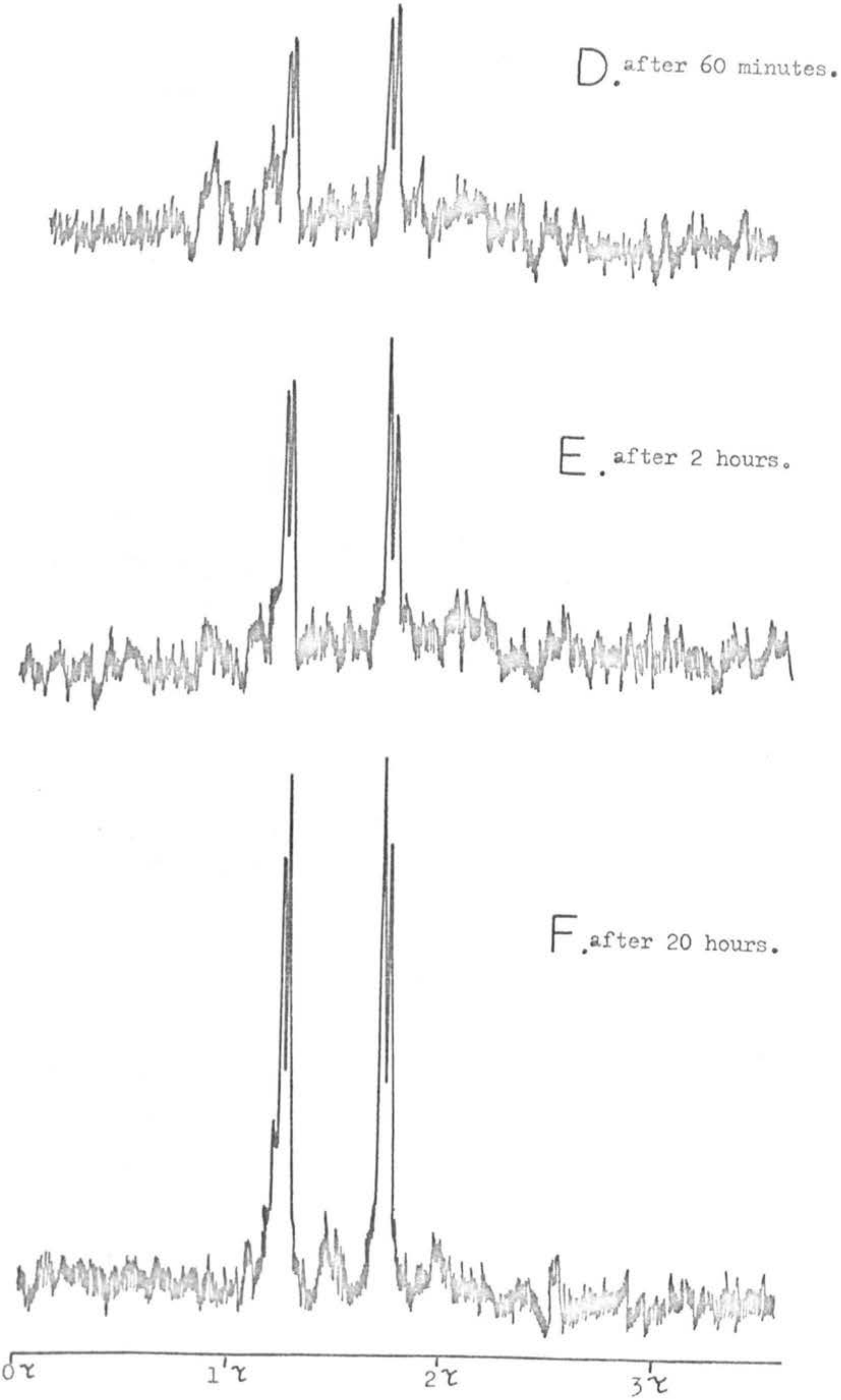
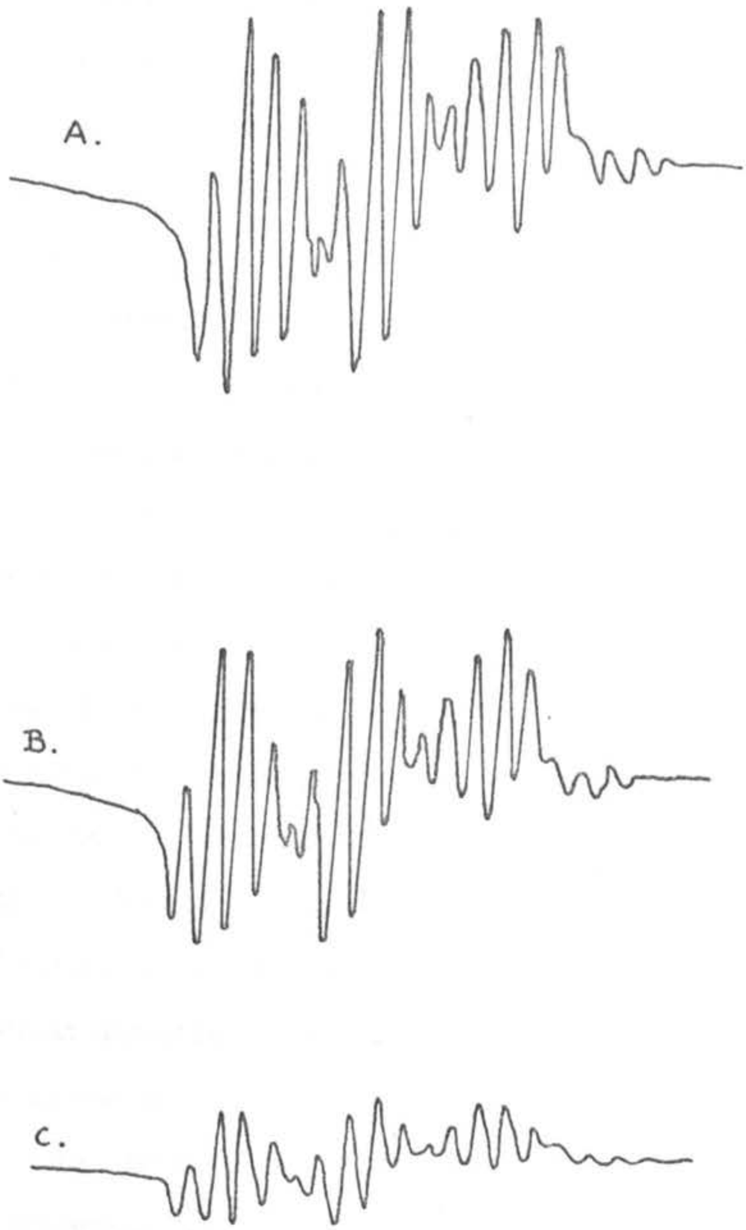


Figure 28 The spectra recorded at various times during the reaction of 3,6 - D.N.N.A. with the methoxide ion in sulpholane solution.

Figure 28 - Continued.





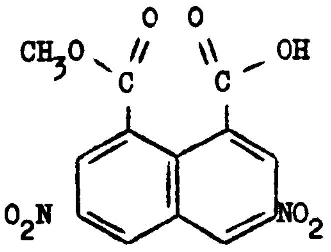
<u>Figure 29</u> The electron spin resonance spectrum of a mixture of 3,6 - D.N.N.A. and sodium methoxide in methanol solution recorded (A) immediately after mixing (B) 10 minutes after mixing and (6) 20 minutes after mixing.

used. The nuclear magnetic resonance spectrum of this complex could not be obtained and although the disappearance with time of the signals due to 3,6-D.N.N.A. could be followed (see figure 28) no signals appeared which could be assigned to the presence of the complex. This can be explained by the electron spin resonance results since it is apparent from figure 29 that in the early stages of the reaction a paramagnetic species is involved, and if this paramagnetic species were the complex then no nuclear magnetic resonance spectrum for the complex would be expected. Examination of the electron spin resonance spectrum shows a basic triplet due to nitrogen of intensity 1:1:1 split into a quartet of intensity 1:3:3:1 and further small couplings. This suggests that the major pattern is derived from the interaction of an unpaired electron with a nitrogen atom and the 3 protons of the methoxide group. The minor splittings may be due to interaction with the ring proton at the site of attack of the methoxide ion.

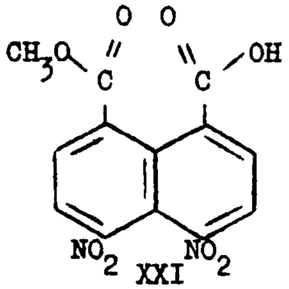
The nuclear magnetic resonance results are very similar to those of Foster and Foreman[117] who observed that in the reaction of the ethyl ester of 2,4-dinitrobenzoic acid and of 1-iodo-2,4-dinitrobenzene with the methoxide ion the initial nuclear magnetic resonance absorptions collapsed and reappeared on standing. In the present case, although the signal which reappears has the same pattern as the original signal, suggesting two sets of meta coupled protons, the signal has shifted to higher field. This probably implies that the anhydride group has been converted into methyl carboxylate groups or acid groups which do not withdraw electrons from the ring to the same extent as does the anhydride group.

The nuclear magnetic resonance spectrum of the solid product isolated from the reaction of 3,6-D.N.N.A. with the methoxide ion in sulpholane solution shows an aromatic region identical to that shown in figure 28F together with a single peak at 7.1 τ. The aromatic region consists of a doublet of doublets showing a meta coupling of 3Hz. The doublets are centred at 1.25 τ and 1.72 τ. The relative intensity of the aromatic peaks and the aliphatic peak is 4:3.

The nuclear magnetic resonance spectrum of the product derived from the reaction of 4,5-D.N.N.A. with the methoxide ion in sulpholane solution shows a doublet of doublets showing an ortho coupling of 6Hz and centred at 1.13 τ and 1.52 τ and a single peak at 6.95 τ. The pattern of the aromatic resonances is very similar to that observed in the spectrum of 4,5-D.N.N.A. in sulpholane, see figure 42B, except the signal from the reaction product are shifted upfield. The relative intensity of the aromatic peaks to the aliphatic peak is again 4:3. These nuclear magnetic resonance results suggest the product of the reactions to be the half esters shown in structures XX and XXI.



XX



XXI

There is no evidence in the nuclear magnetic resonance spectra for any peaks due to the acid proton.

The elemental analyses are consistent with the proposed structures:-

Product from 3,6-D.N.N.A.

Found C = 49.1%; H = 2.9%; N = 8.5%;

Product from 4,5-D.N.N.A.

Found C = 48.9%; H = 2.8%; N = 8.8%;

For both isomers the required analysis figures are:

C = 48.8%; H = 2.5%; N = 8.7%;

The important features in the infrared spectra of the products are:-

(a) The disappearance of the two carbonyl bands which are replaced in the case of the product derived from 3,6-D.N.N.A. by a single strong band at 1710 cm^{-1} and in the case of the product derived from 4,5-D.N.N.A. by a single strong band at 1717 cm^{-1}. These new bands will be due to the carbonyl stretching vibration in structures XX and XXI.

(b) The appearance of a strong band at 1290 cm^{-1} in the product from the reaction of 3,6-D.N.N.A. with the methoxide ion and at 1295 cm^{-1} in the product derived from 4,5-D.N.N.A. Both these bands will be due to the C-O stretching vibration of the ester group[196] in the structures XX and XXI.

The infrared spectrum of the product derived from the reaction of 3,6-D.N.N.A. with the methoxide ion is shown in figure 30 and that derived from 4,5-D.N.N.A. in figure 31.

3. Reactions with the Sulphite Ion

(a) 3,6-D.N.N.A. and 4,5-D.N.N.A.

(i) Experimental and Results

The addition of aqueous sodium sulphite to 3,6-D.N.N.A. and 4,5-D.N.N.A. in each case gave initially a red solution which darkened on standing to produce a brown solution. The

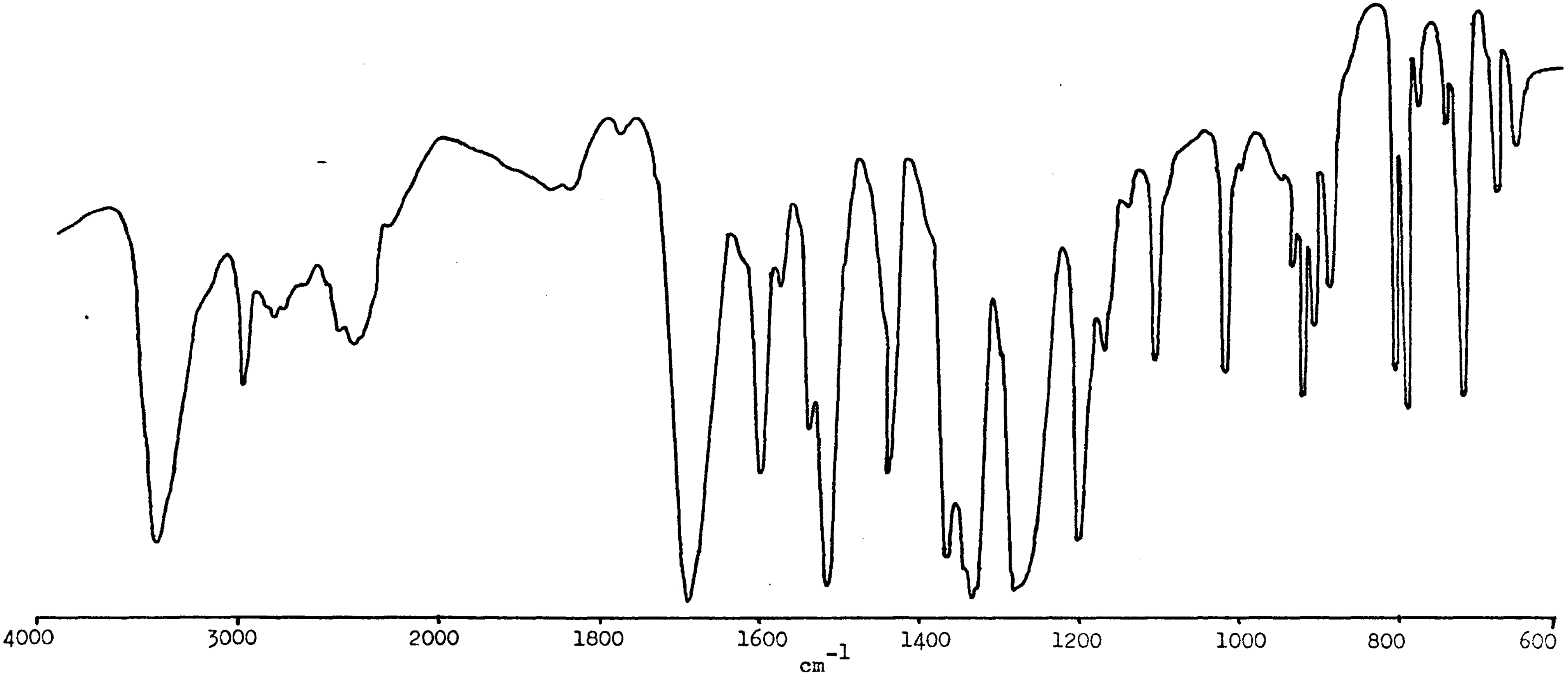


Figure 30 The infra red spectrum of the product of the reaction of 3,6 - D.N.N.A. with the methoxide ion.

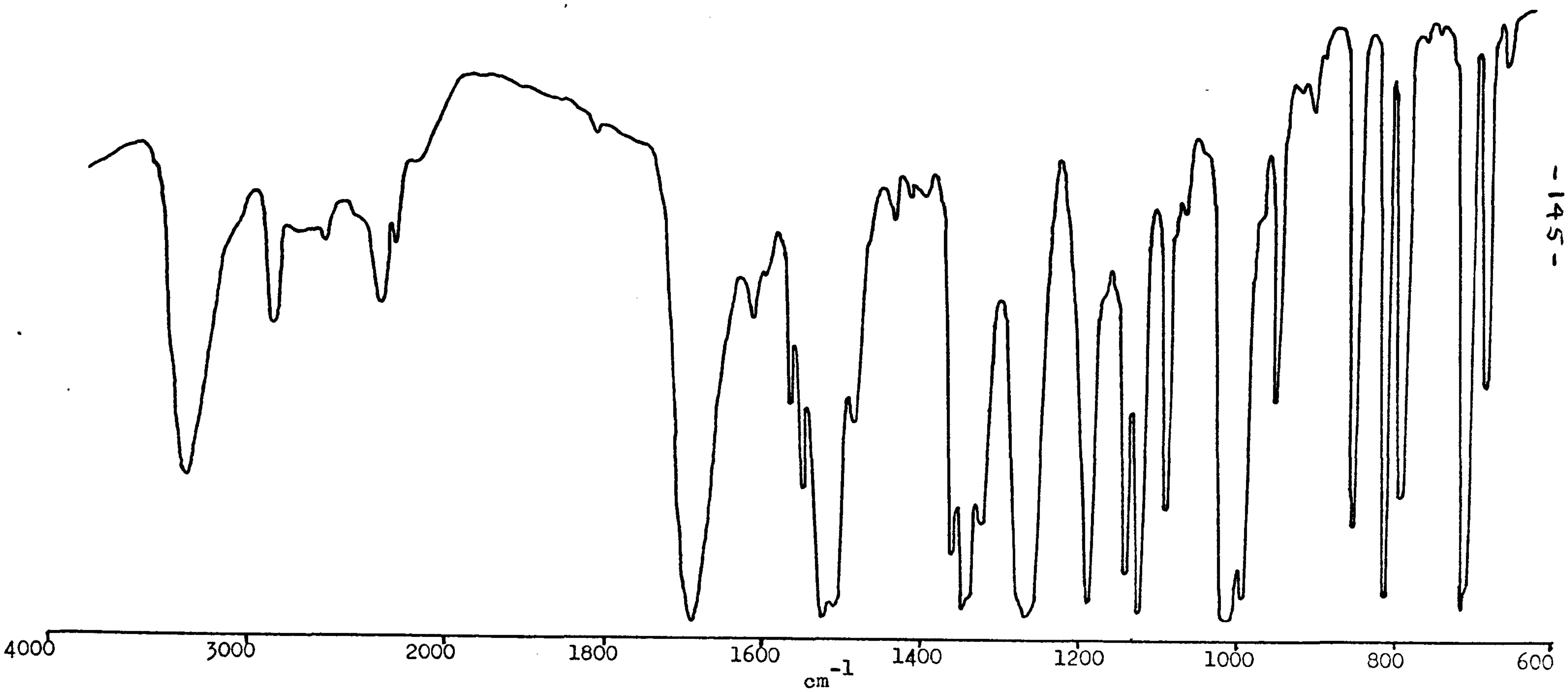


Figure 31 The infrared spectrum of the product of the reaction of 4,5 - D.N.N.A. with the methoxide ion.

stoichiometry of the complexes intially formed was investigated by the method of continuous variations[137]. This was achieved by mixing solutions of 3,6-D.N.N.A. and 4,5-D.N.N.A. in dimethylsulphoxide with aqueous solutions of sodium sulphite in known molar ratios and keeping the total molar concentration constant. The absorbance of the solutions was measured at a wavelength of 540 nm using a Unicam SP 600 spectrophotometer. The absorbance of the solutions was observed to decrease markedly with time and measurements taken at 30 second intervals were extrapolated back to zero time to give the value of the absorbance at the time of mixing. The Job plots for the results from the two systems are shown in figure 32.

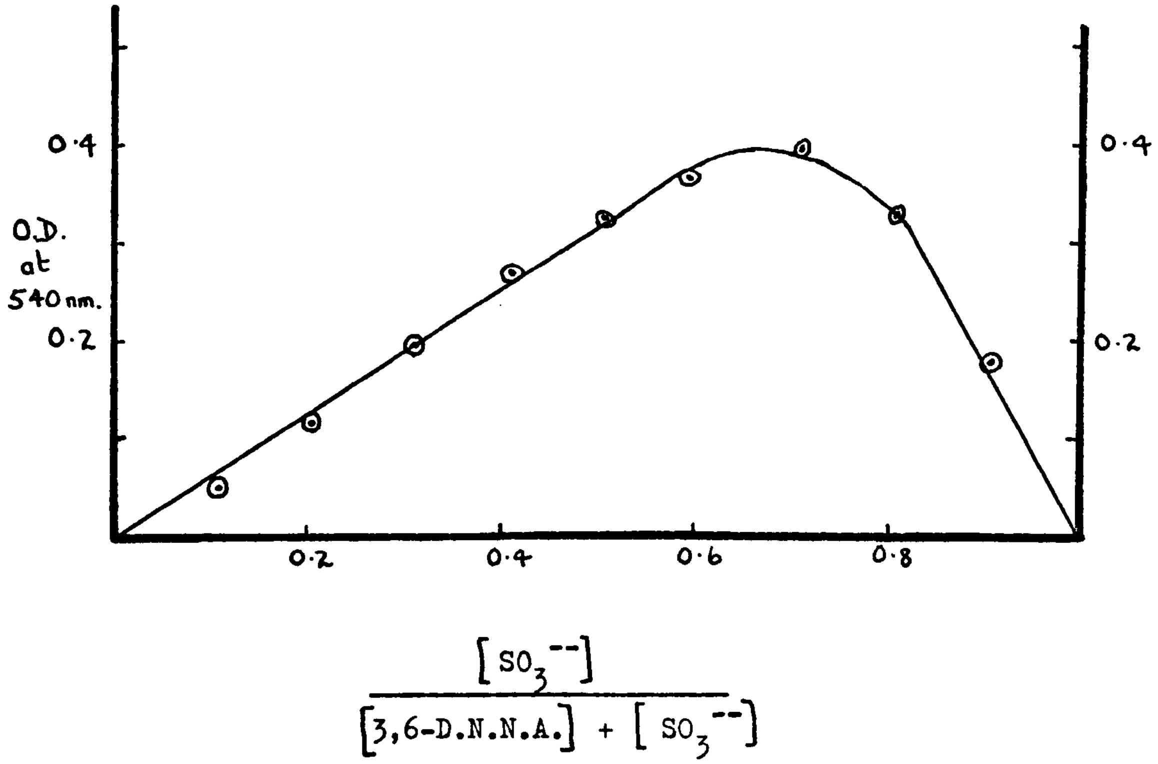
The Benesi-Hilderbrand method[32] for the determination of the association constant of the interaction was also applied to each of the systems but the results led to curved plots.

The reaction between aqueous sodium sulphite and 3,6-D.N.N.A. in dimethylsulphoxide in equimolar quantities was followed by nuclear magnetic resonance spectroscopy. The spectrum was recorded immediately after mixing, after 10 minutes, after 35 minutes, after 1 hour, after 3 hours and after 24 hours. The observed spectra were very similar to those shown in figure 28 for the 3,6-D.N.N.A.-methoxide reaction.

An attempt was made to record the electron spin resonance spectrum of a mixture of 3,6-D.N.N.A. in dimethylsulphoxide solution and sodium sulphite in aqueous solution. However, the dielectric constant of the solvent mixture was too high to allow the instrument to be tuned.

The reactions of 3,6-D.N.N.A. and 4,5-D.N.N.A. with the sulphite ion were studied on the preparative scale. The dinitronaphthalic anhydride (2 gm) was dissolved in dimethyl-

A. Total concentration of 3,6 - D.N.N.A. plus sodium sulphite $= 1.575 \times 10^{-4}$M.



B. Total concentration of 4,5 - D.N.N.A. plus sodium sulphite $= 4.372 \times 10^{-4}$M.

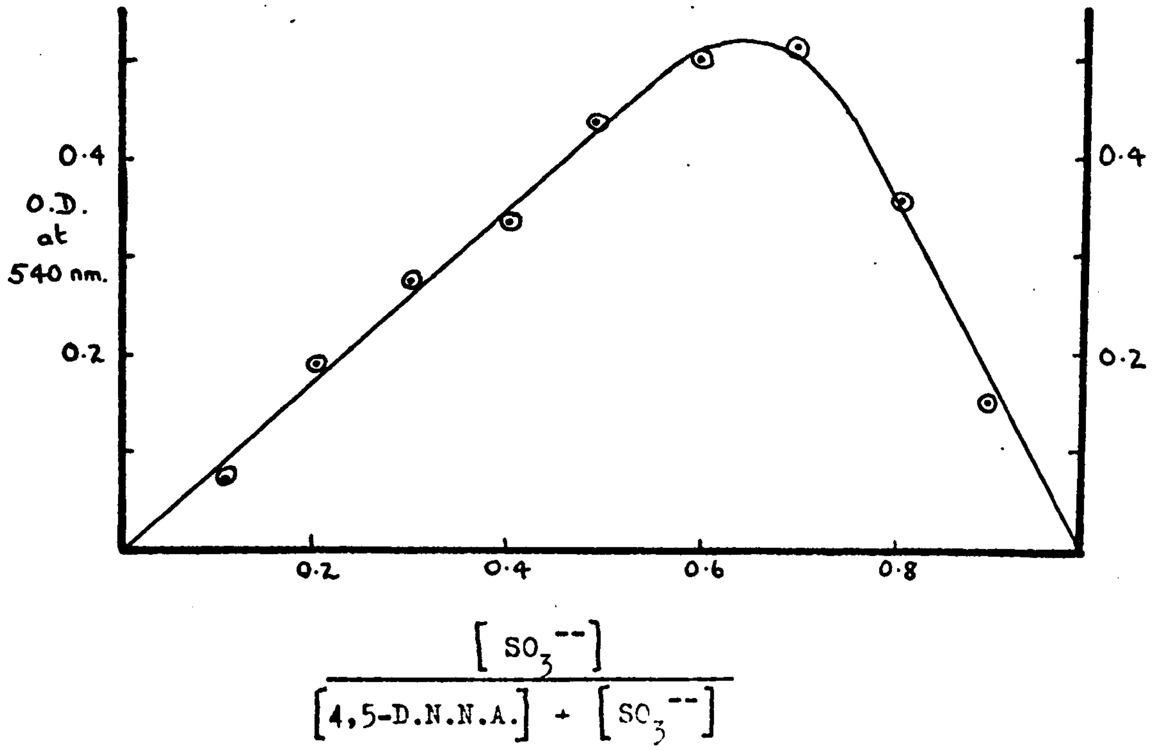


Figure 32 Job plots for the D.N.N.A. - sulphite ion system.

sulphoxide and an equimolar quantity of sodium sulphite in aqueous solution was added. The mixture became bright red in colour and on standing the colour slowly diminished and the mixture became brown and after 3 days a solid was precipitated. The solid was filtered off, washed with water, ethanol and ether and dried under vacuum.

The solid products obtained were analysed and the nuclear magnetic resonance, infrared and mass spectra recorded.

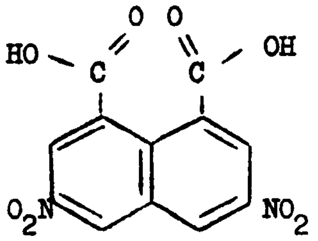
(ii)Discussion

The plots shown in figure 32 suggest that initially, at least, 1:2 (D.N.N.A. : SO_3^{--}) complex formation occurs under the conditions of the reaction. In the knowledge that 1:2 complex formation occurs it is not unexpected that the results from the Benesi-Hilderbrand method give a curve since the theory of the method is based on 1:1 complex formation.

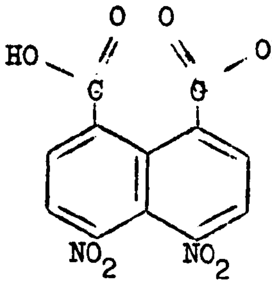
The nuclear magnetic resonance spectrum of the complex could not be obtained and although the signals due to 3,6-D.N.N.A. could be observed to disappear with time no signals appeared which could be assigned to the complex. Since the presence of water in the system made it impossible to obtain an electron spin resonance spectrum it cannot be stated categorically that a paramagnetic intermediate is formed in the reaction. However, by analogy with the reaction of 3,6-D.N.N.A. with the methoxide ion under similar conditions a paramagnetic intermediate would seem likely.

The nuclear magnetic resonance spectrum of the solid product isolated from the reaction of 3,6-D.N.N.A. with the sulphite ion in dimethylsulphoxide solution showed a doublet of doublets centred at 0.8 τ and 1.2 τ showing a <u>meta</u> coupling of 3Hz. The spectrum of the corresponding product insolated from the 4,5-D.N.N.A. reaction with the sulphite ion in dimethylsulphoxide solution showed a doublet of doublets centred at 0.91 τ and 1.31 τ , the doublets showed an ortho coupling of 6Hz.

These results suggest that the products of the reactions were the diacids, of structures XXII and XXIII, and that complex formation, which was shown by the method of continuous variations to initially occur, must involve a paramagnetic species which was not observed in the nuclear magnetic resonance spectrum.



XXII



XXIII

The solid products isolated in the reactions had analysis figures consistent with the proposed structure:-

<u>Product from 3,6-D.N.N.A.</u>

<u>Found</u> C = 47.6%; H = 2.3%; N = 9.3%

<u>Product from 4,5-D.N.N.A.</u>

<u>Found</u> C = 47.4%; H = 2.5%; N = 9.4%

For both isomers the required analysis fitures are:

C = 47.1%; H = 1.9%; N = 9.1%

The mass spectrum of each of the isomers showed a parent peak at a value of m/e = 288. This suggests the product of the reactions to be the unchanged anhydride, but it is likely that the diacid is unstable in the mass spectrometer and that loss of water from the acid groups leads to the production of the anhydride.

The infrared spectra of the solid reaction products are consistant with them being the diacids. The spectrum of the product derived from 3,6-D.N.N.A. is shown in figure 33 and the spectrum of the product derived from 4,5-D.N.N.A. is shown in figure 34. The important features to note from both the spectra which were recorded as Nujol Mulls are:

(a) The presence of the peaks due to the O-H stretching vibration at 3120 cm^{-1} in the case of the product derived from 3,6-D.N.N.A. and at 3180 cm^{-1} in the case of the product derived from 4,5-D.N.N.A.

(b) The disappearance of the double carbonyl band, characteristic of the anhydride, which is replaced in the 3,6-isomer by a single strong band at 1695 cm^{-1} and in the 4,5-isomer by a single strong band at 1705 cm^{-1}. These bands are characteristic of aromatic dicarboxylic acids[196].

(b) T.N.A.

The results of similar experiments, to these described above, carried out on T.N.A. suggested that the course of the reaction is more complicated. The red colouration, characteristic of complex formation, was only visible momentarily on mixing the reactants making any visible spectroscopic study impossible. The final product of the reaction was dark brown in colour and only very sparingly soluble in most solvents. Solubility precluded the observation of the nuclear magnetic resonance spectrum of

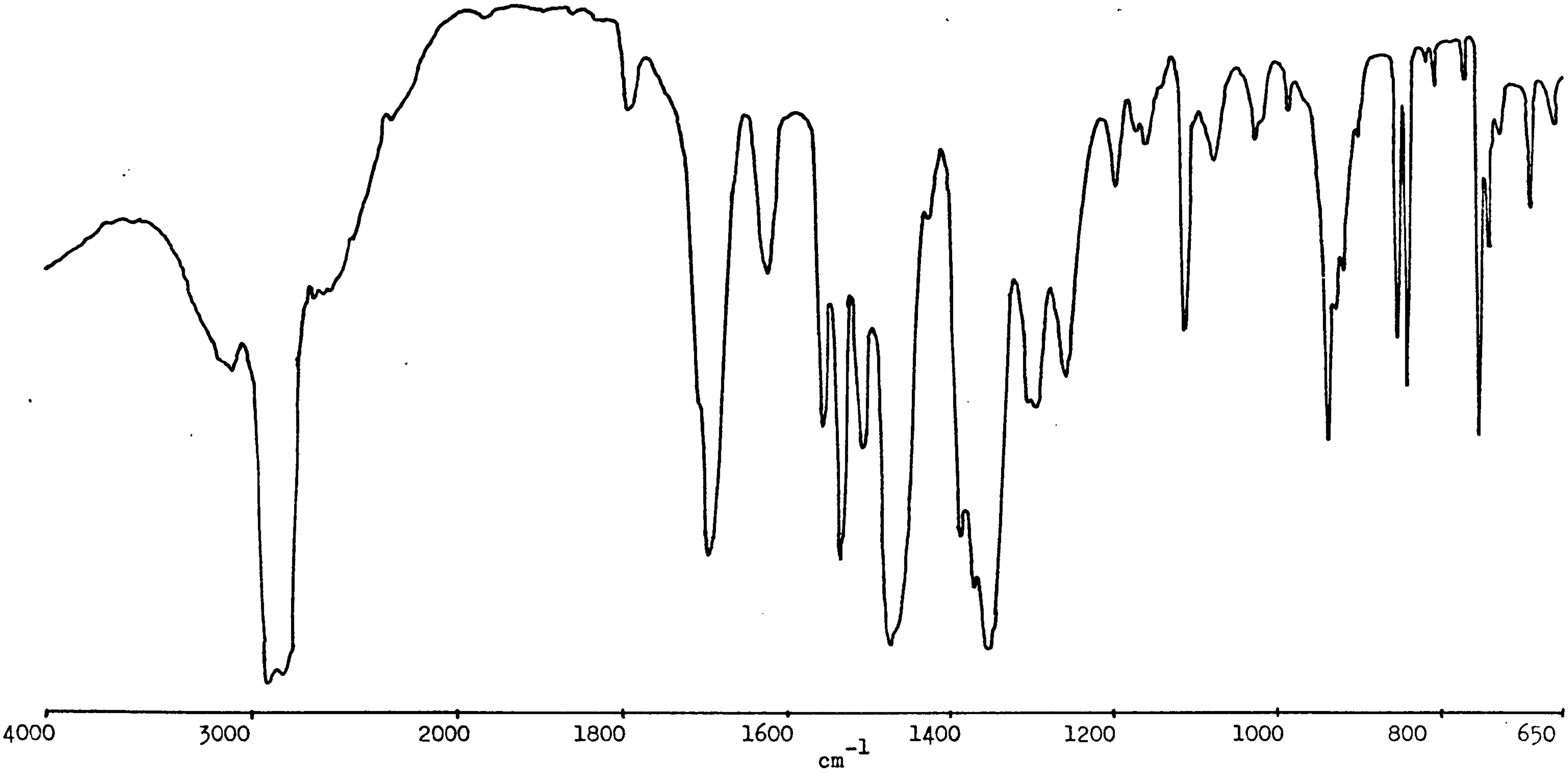


Figure 33 The infrared spectrum of the product of the reaction of 3,6 - D.N.N.A. with the sulphite ion.

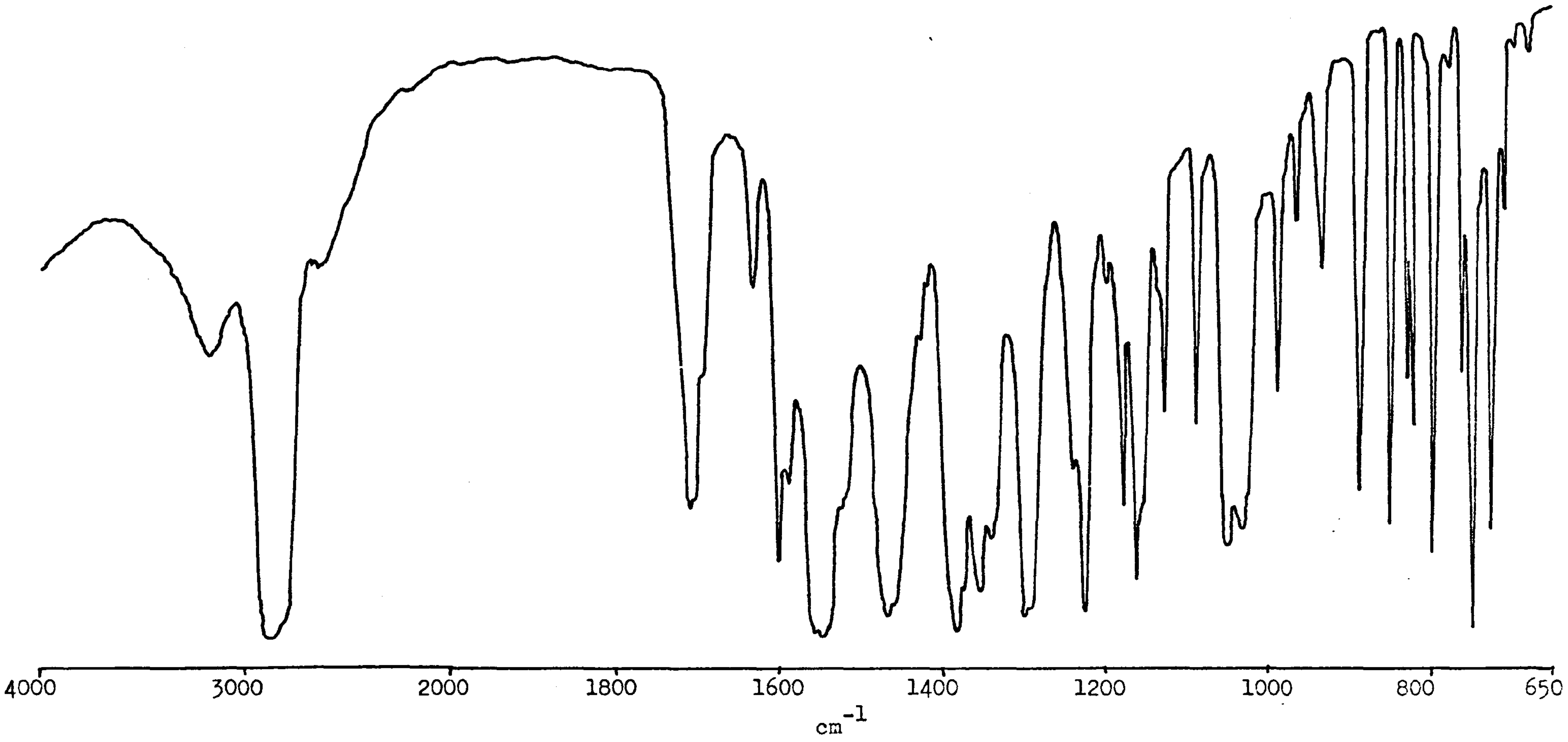


Figure 34 The infrared spectrum of the product of the reaction of 4,5 - D.N.N.A. with the sulphite ion.

the product and the colour of the product made it impossible to observe the infrared spectrum. No final conclusions on the nature of this product were obtained.

4. Reactions with Amines

The reactions of amines with T.N.A. and 3,6-D.N.N.A. were studied in two types of solvent - ketonic and non-ketonic. In non-ketonic solvents any reaction is liable to involve the amine as the base, whereas in a ketonic solvent, such as acetone, bases such as $^{-}CH_2COCH_3$ will be formed, and the possibility of reaction with this type of base will exist. The present investigation was carried out with a number of amines covering a wide range of basic strength.

(a) Experimental

The addition of a solution of an amine in either a ketonic or a non-ketonic solvent to a solution of the nitroaromatic compound in the same solvent resulted in the immediate precipitation of a coloured solid. The method of preparation of the solids is described below:

The nitroaromatic compound (0.5 gm) was dissolved in the required solvent at about 40°C. An equimolar quantity of the amine in the same solvent was added with stirring. The resulting solution immediately became dark blue and on cooling a solid was precipitated. The solid was filtered off, washed with ether and dried under vacuum. The elemental analysis of the product was obtained.

The ultraviolet - visible, nuclear magnetic resonance and mass spectra of a selection of the complexes were recorded.

(b) Results and Discussion of Products

The solid products obtained from the reaction in dichloromethane of a number of amines with T.N.A. were only very slightly soluble in most solvents and no recrystallisation procedure was possible. However results from the elemental analysis suggest that 1:1 complex formation has occured in the reaction. The results are summarised in the table below:

T.N.A. Complex with		% Carbon	% Hydrogen	% Nitrogen	% Oxygen
Triethylamine	Found	50.4	4.32	15.8	29.5
	Required	49.8	4.83	16.1	29.4
Pyridine	Found	49.8	2.74	16.2	31.0
	Required	49.4	2.66	16.5	31.0
T.M.P.D.(i)	Found	53.3	4.10	15.2	28.2
	Required	53.0	4.41	16.8	25.7
T.M.E.(ii)	Found	47.1	4.72	17.8	27.9
	Required	47.9	4.89	18.7	28.4
T.E.E.(iii)	Found	52.7	5.36	16.3	26.1
	Required	52.1	5.93	16.7	25.3
α-Picoline	Found	49.8	2.65	15.8	30.8
	Required	50.5	3.04	16.4	30.0
Tri-n-propylamine	Found	53.4	4.92	15.4	27.1
	Required	52.8	5.65	14.7	26.9
Tri-n-butylamine	Found	55.3	5.62	13.7	24.5
	Required	55.5	6.35	13.5	24.6

(i) T.M.P.D. ≡ N,N,N',N' - Tetramethyl-p-phenylene diamine

(ii) T.M.E. ≡ N,N,N',N' - Tetramethyl-ethylene diamine

(iii) T.E.E. ≡ N,N,N',N' - Tetraethyl-ethylene diamine

Solid products were obtained from the reaction of triethylamine with T.N.A. and 3,6-D.N.N.A. in acetone, ethyl-methyl ketone and acetylacetone. The results of elemental analysis of the solid products are given in the table below together with comparable results obtained in dichloromethane solution.

Solvent		% Carbon	% Hydrogen	% Nitrogen	% Oxygen
	T.N.A. Complexes				
Dichloro- Methane	Found Required (i)	50.4 49.7	4.3 4.8	29.5 29.4	15.8 16.1
Acetone	Found Required (ii)	50.4 51.1	4.6 5.5	28.5 29.2	16.0 14.2
Ethyl-Methyl Ketone	Found Required (ii)	50.2 52.1	4.5 5.7	29.3 28.4	16.2 13.8
Acetylacetone	Found Required (ii)	50.3 51.6	4.6 5.4	28.9 29.9	15.9 13.1
	3,6-D.N.N.A. Complexes				
Dichloro Methane	Found Required (i)	55.8 55.5	4.5 4.9	29.1 28.8	10.5 10.8
Acetone	Found Required (ii)	55.3 56.4	4.8 5.6	29.0 28.6	10.3 9.4
Ethyl-methyl Ketone	Found Required (ii)	55.7 57.3	4.3 5.6	28.4 27.8	10.6 9.1
Acetylacetone	Found Required (ii)	55.7 56.4	4.9 5.5	28.7 29.5	10.9 8.6

Required (i) $\equiv$ 1:1 complex formation

Required (ii) $\equiv$ Sigma complex formation <u>via</u> ketone anion

The results of the analyses remained, within experimental error, constant and independent of the solvent and this suggests that the solvent does not participate in the reaction and that 1:1 charge-transfer complex formation has occured in each case.

The insolubility of the solid products made it difficult to obtain a nuclear magnetic resonance spectrum. However spectra were obtained in a few of the systems and the observed spectra were a composite of the spectra of the individual components added to the solution from which the solid was isolated. The resonances derived from the nitroaromatic compound were in each case shifted to higher field and the resonances from the amine to lower field than observed in the individual free components. In no case was there any evidence for peaks resulting from Meisenheimer complex formation and it is suggested that the products are charge-transfer complexes formed between the amine and the nitroaromatic compound. The spectra of 3,6-D.N.N.A., triethylamine and the 3,6-D.N.N.A.-triethylamine complex all in acetone-d_6 solution are shown in figure 35.

The mass spectrum of the adduct formed between triethylamine and T.N.A. derived from the reaction both in dichloromethane and acetone was recorded. Also the mass spectra of the comparable 3,6-D.N.N.A. adducts were recorded. In each case the parent ion appeared at a value of m/e = 101 which is characteristic of triethylamine and not the ion $^{+}NH(C_2H_5)_3$ which would be expected if the ketone anion had participated in the reaction. This latter ion would have a parent peak at m/e = 102. The mass spectra are shown in figures 36 and 36A.

The visible spectrum of each of the complexes was recorded and each showed a broad band in the region 490 - 530 nm irrespective of the solvent used in the preparation. The spectra obtained from the complex between T.N.A. and triethylamine prepared in different solvent systems are shown in figure 37. The spectra obtained by dissolving the solid complex in acetone remained constant with time. If, however, a dilute solution of the amine in acetone was added to a dilute solution of the nitroaromatic

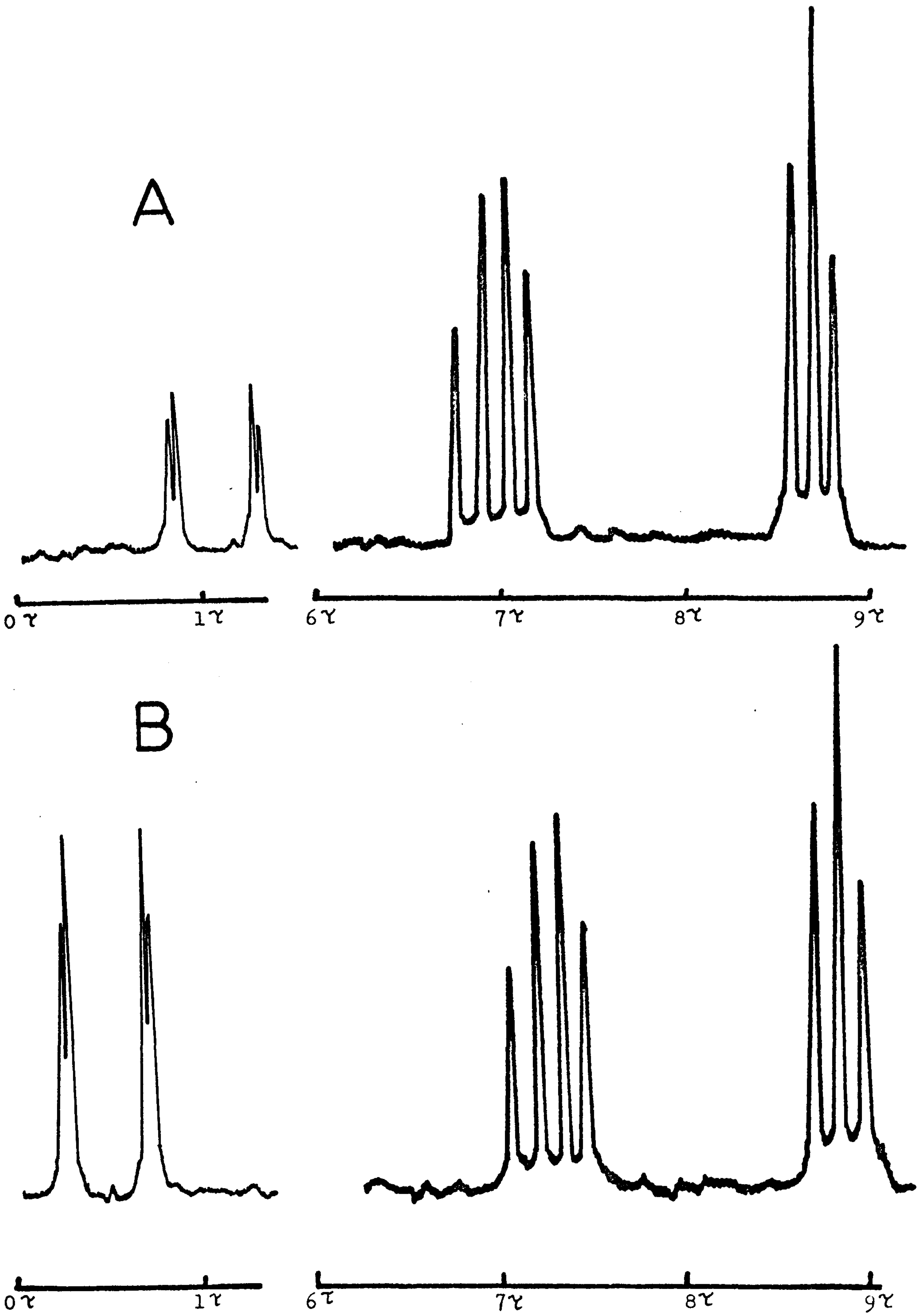


Figure 35 The positions of the resonances (A) from the 3,6 - D.N.N.A.-triethylamine complex and (B) from free 3,6 - D.N.N.A. and free triethylamine all in acetone solution.

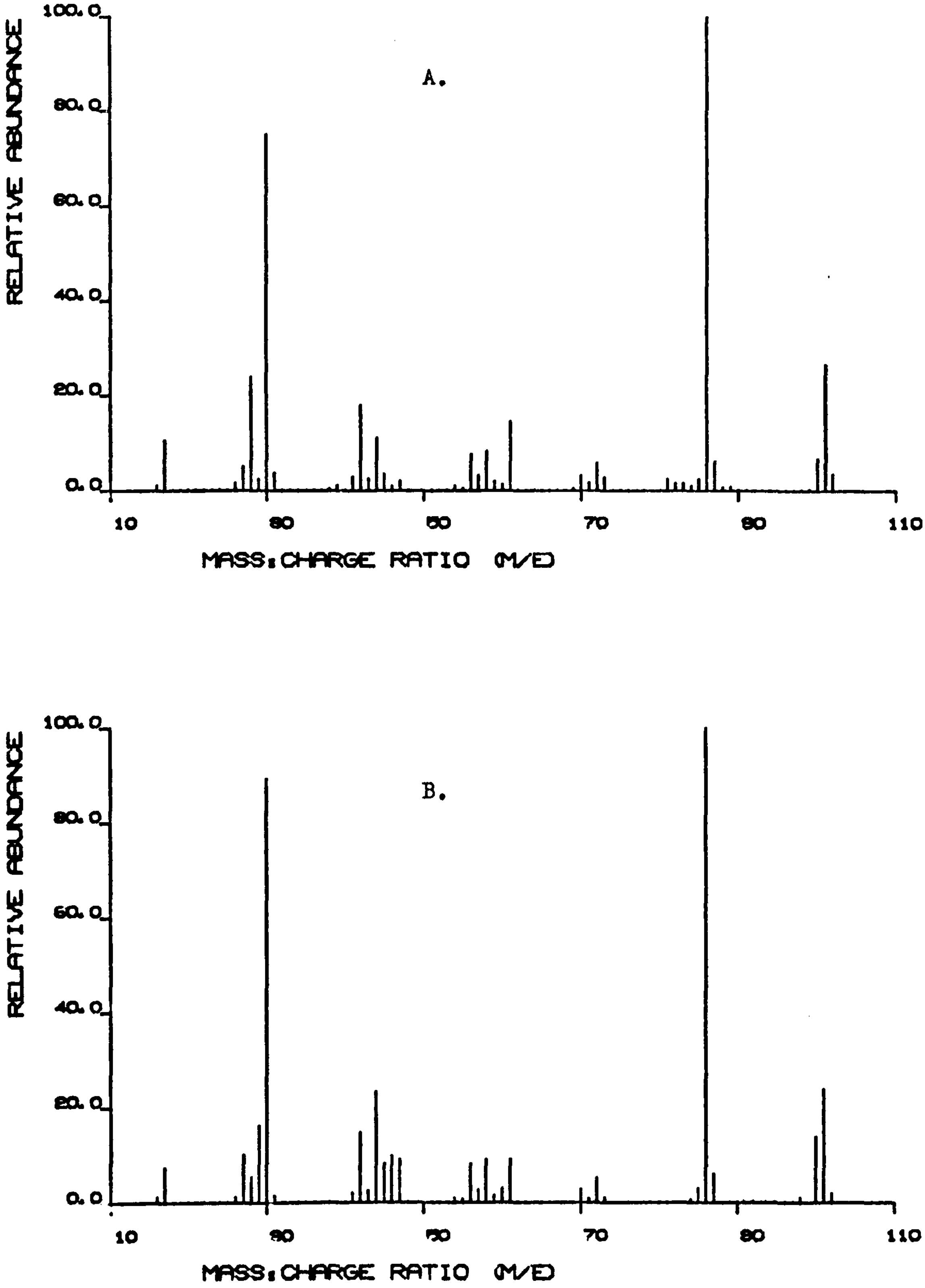


Figure 36 The mass spectra (A) of the T.N.A. - triethylamine complex prepared from dichloromethane solution and (B) of the T.N.A. - triethylamine complex prepared from acetone solution.

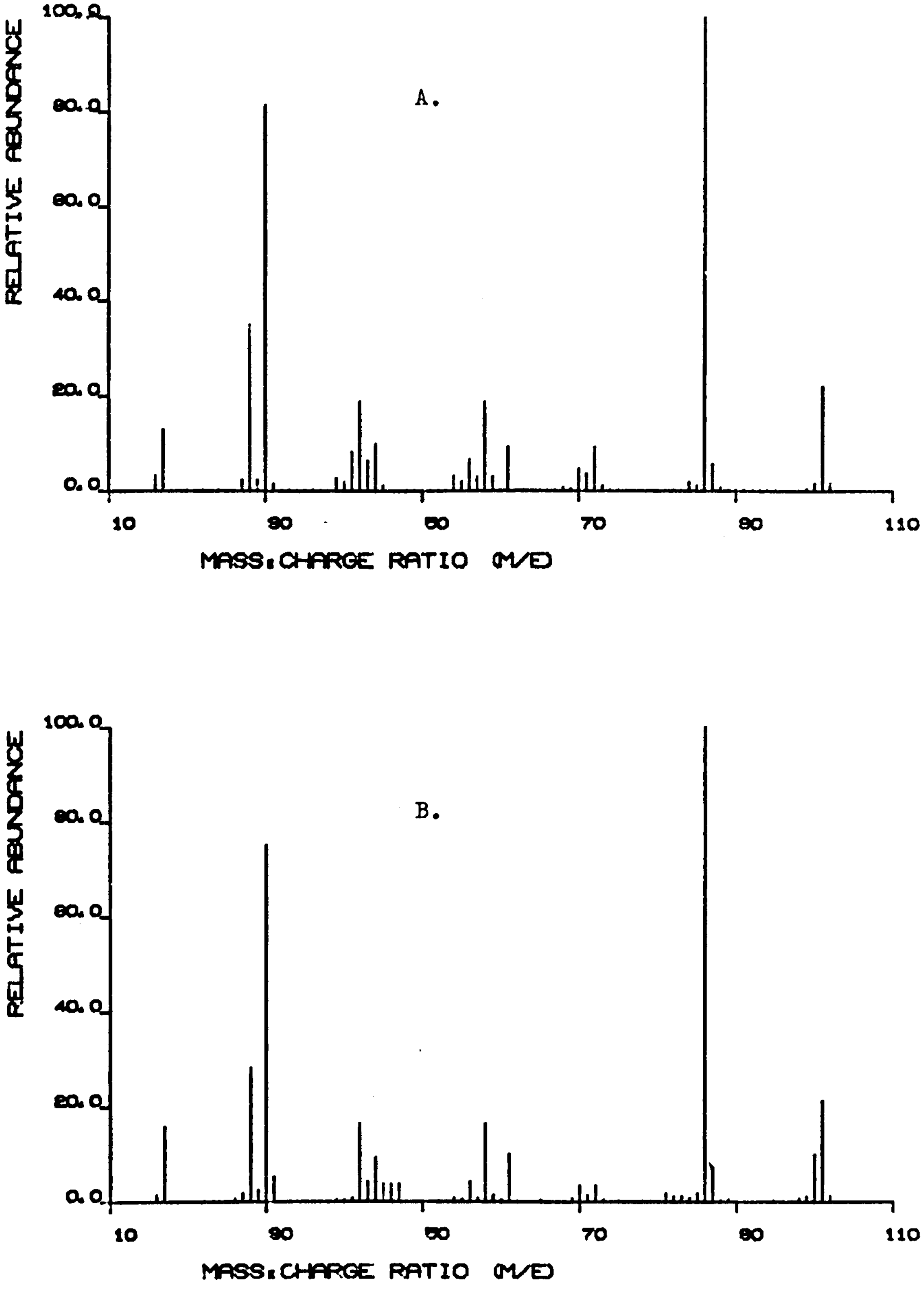


Figure 36A The mass spectra (A) of the 3,6 - D.N.N.A. - triethylamine complex prepared from dichloro - methane solution and (B) of the 3,6 - D.N.N.A. - triethylamine complex prepared from acetone solution.

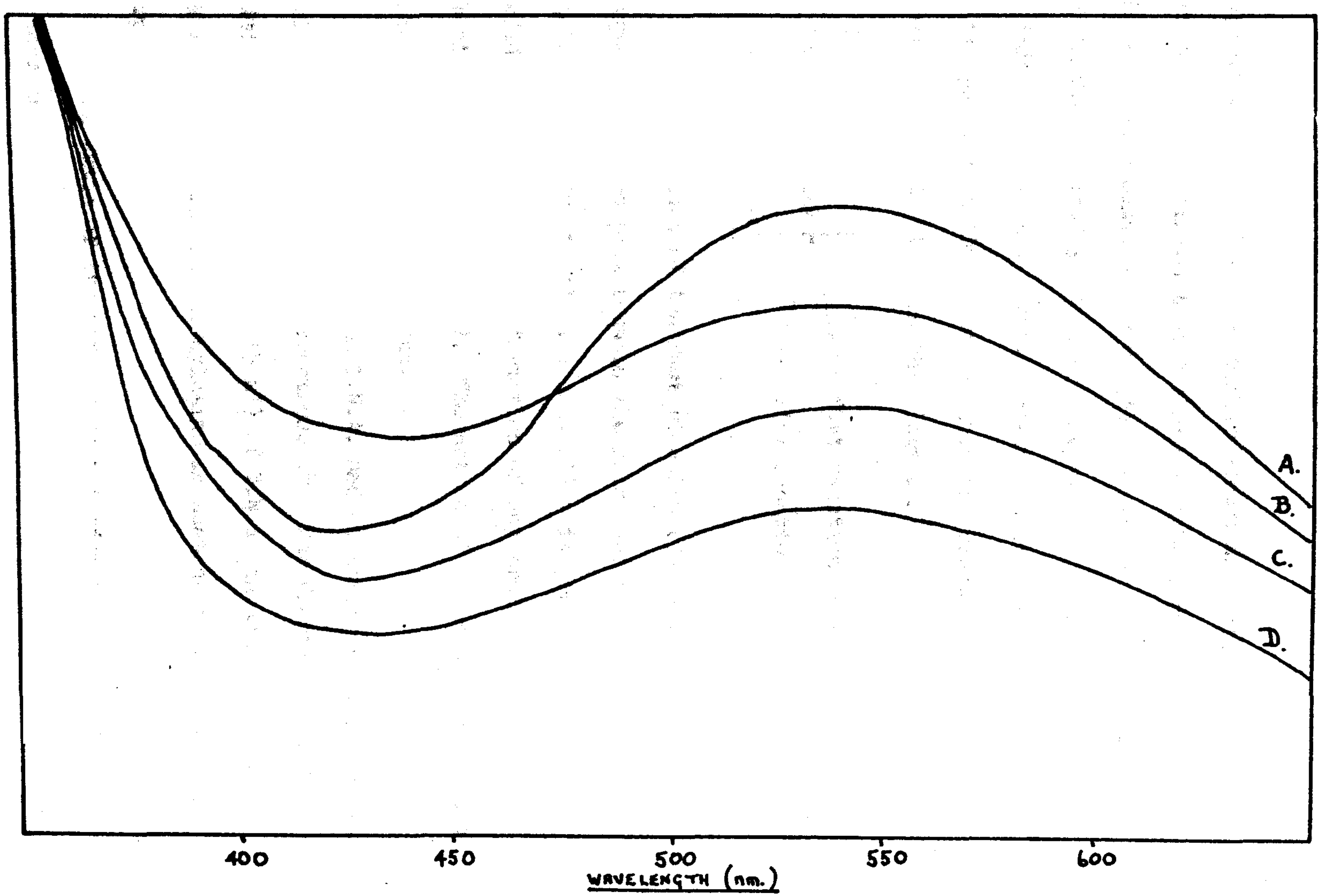
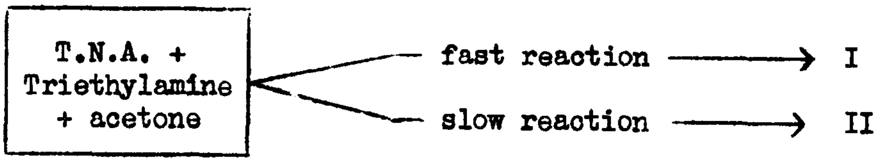


Figure 37 The visible spectrum of the T.N.A. - Triethylamine complex when derived from (A) dichloromethane (B) acetone (C) acetylacetone and (D) ethyl methyl ketone solution

compound in acetone and the visible spectrum of the resulting mixture recorded immediately the above broad band is observed. This spectrum changes rapidly with time as is shown in figure 38 for the T.N.A.-triethylamine-acetone system. The explanation for this change is not entirely clear but it appears that there are two possible pathways involved in the reaction. A possible reaction scheme is shown in the diagram.



The product of the fast reaction (I) is an n → π charge-transfer complex between the amine and the nitroaromatic compound, which due to its low solubility is precipitated. This precipitation inhibits the formation of any products derived from the slow reaction, (II). The nature of the products of this reaction were not investigated.

The reaction between T.N.A. and diethylamine was studied by electron spin resonance spectroscopy. The spectrum from the addition of a 1.5M solution (5 ml) of T.N.A. in acetone to a 1.5M solution (5 ml) of diethylamine in acetone showed a single sharp line.

The ratio of the amine concentration to that of T.N.A. was increased to 10:1 and the spectrum was recorded and showed a single line with a shoulder of greater linewidth than the original line. The ratio of the amine concentration to that of T.N.A. was increased further to 30:1 and then to 60:1 and the spectrum recorded. It was observed that the shoulder increased in intensity at the expense of the initial line as the ratio of the

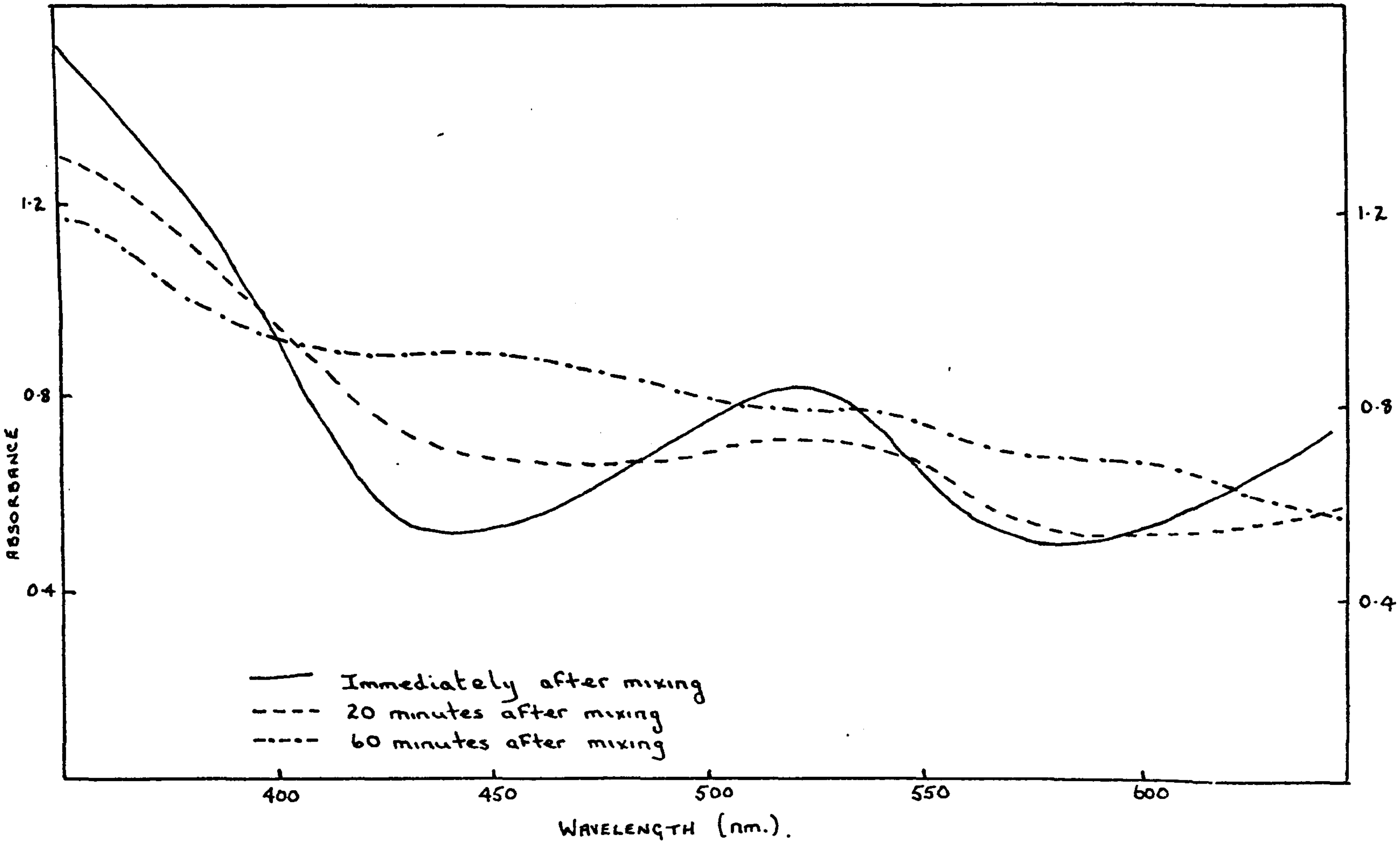


Figure 38 The variation of the visible spectrum of the T.N.A. - Triethylamine complex in dilute acetone solution.

amine concentration was increased. The ratio was finally increased to 100:1 and the spectrum showed a single line of greater linewidth than the initially observed line. The sequence of spectral changes is shown in figure 39.

The results suggest that as the amine concentration is increased a second species is produced in the reaction. The species builds up with increasing amine concentration until at a ratio of 100;1 it is the only observable species remaining. It is very likely that the observed signals result initially from the 1:1 complex and subsequently from the 2:1 (amine : T.N.A.) complex.

5. Discussion

(a) T.N.A.

The product of the reaction of T.N.A. with a strong base such as the alkoxide ion is analagous to the Meisenheimer complexes formed with polynitrobenzenoid compounds. However the product has a 2:1 ($^-$OMe : T.N.A.) stoichiometry owing to the fact that it has two identical sites fairly well removed from each other. It is possible to observe 2:1 stoichiometry in the benzenoid systems but a large excess of the alkoxide ion is required in this situation[81].

There is no apparent attack of the alkoxide ion at the acenaphthene bridge in T.N.A. and products resulting from hydrogen abstraction at the bridge are not observed. It has been reported that the reaction of the alkoxide ion with <u>sym</u>-trinitrotoluene results in proton abstraction at the methyl group[122] although this has been disputed[97] and the precise nature of the reaction is undecided.

The nature of the reaction with the sulphite ion, a base of intermediate strength is not known.

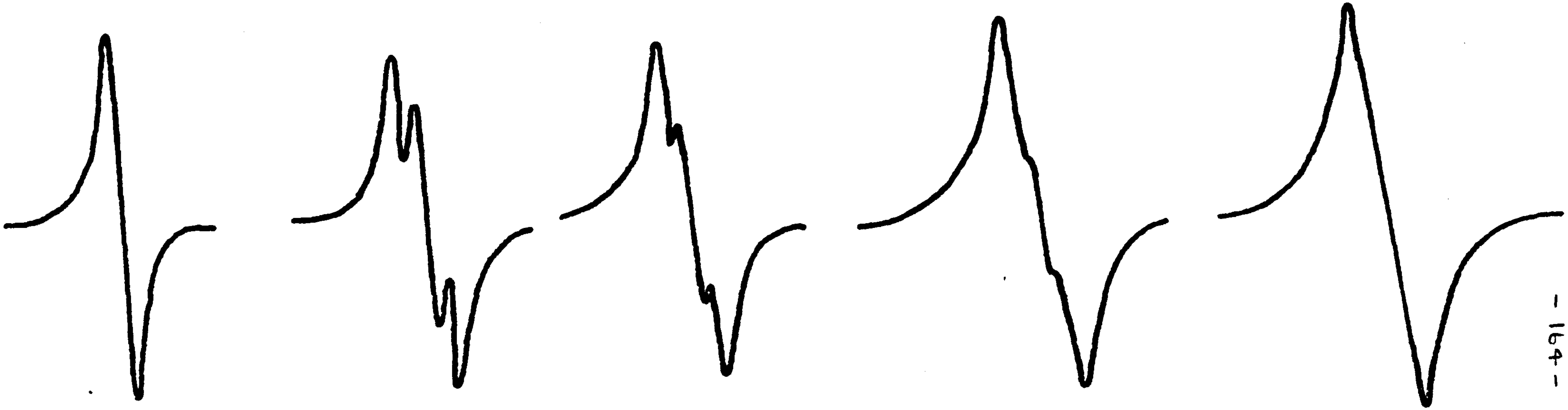
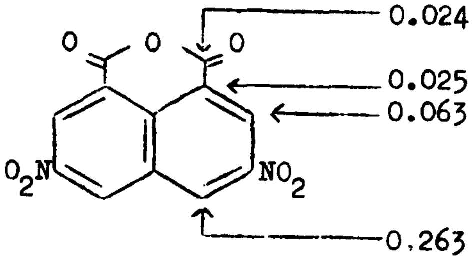


Figure 39 The e.s.r. spectra observed from a mixture of T.N.A. plus diethylamine in acetone solution when the amine concentration is increased.

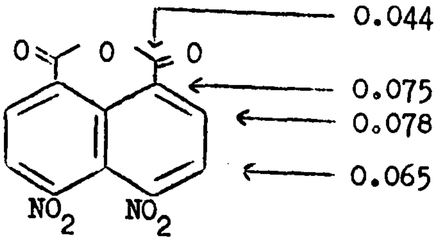
With weak bases such as the amines there is no evidence for the formation of a sigma complex with T.N.A. which is unlike observations made on trinitrobenzene. The reasons for this difference are not entirely clear since these two nitroaromatic compounds have been shown to be similar in acceptor strength. Although various amines of differing electron donor power and various ketonic solvents have been used, the n → π charge-transfer complex formed in the initial fast reaction is in all cases very insoluble and is precipitated. This precipitation inhibits the slow reaction to such an extent that the products of the reaction are not formed to any measurable extent.

(b) 3,6-D.N.N.A. and 4,5-D.N.N.A.

The product of the reaction with the alkoxide ion is shown by the Job plots (figure 27) initially, at least, to be a 1:1 complex. The nuclear magnetic resonance spectrum of the complex could not be seen although the collapse of the signal due to the nitroaromatic was observed. This lack of a nuclear magnetic resonance signal is explained since the intermediate is shown by electron spin resonance spectroscopy to be paramagnetic and the intermediate probably involves the sigma-complex. The final product of the reaction is shown to have the half-ester structure (XX and XXI). A probable explanation of this result may be seen by comparing the π -electron densities at various positions round the ring systems of 3,6-D.N.N.A. and 4,5-D.N.N.A. These results, obtained by McLachlan type calculations, are inserted at the appropriate points on structures XXIV and XXV.



XXIV

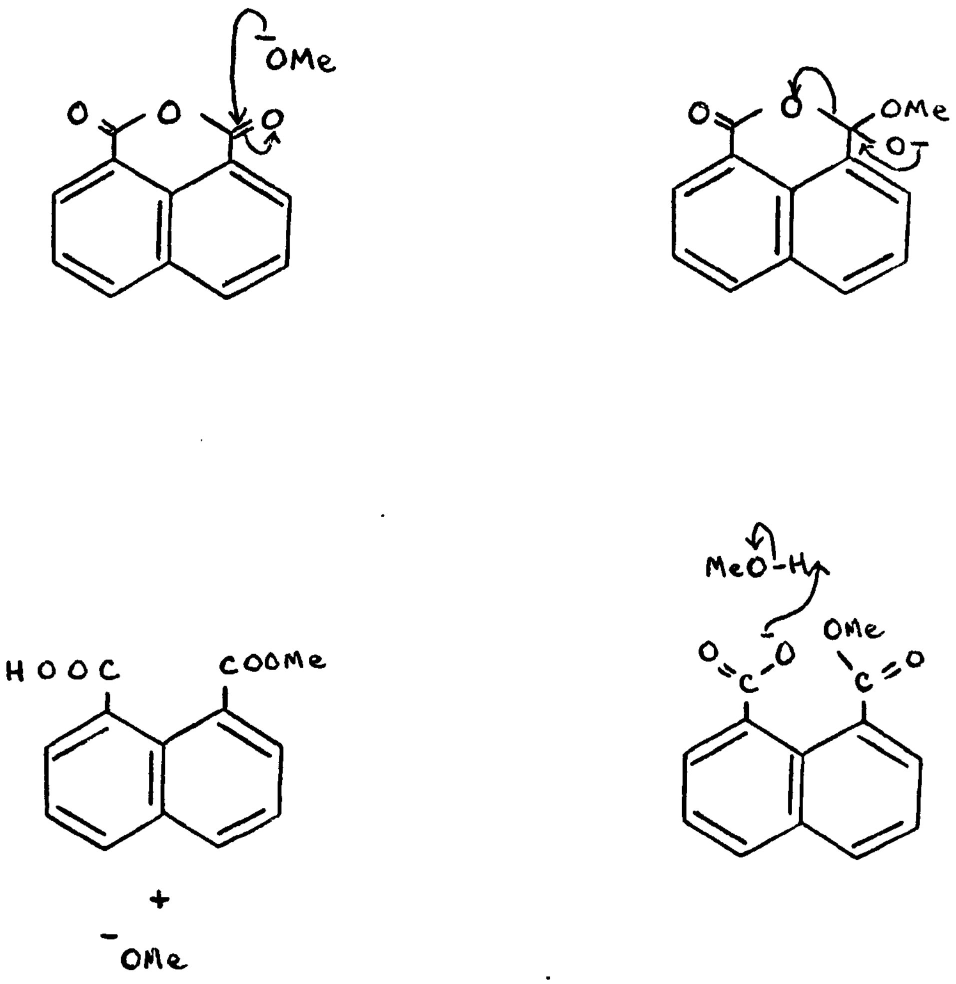


XXV

It can be seen that in both cases the electron density at the carbonyl carbon atom is the lowest of all the probable sites of attack and hence attack of the base at this site will be favoured. The initial attack of the base may possibly be at the ring proton site, however, once the ester is formed by attack at the carbonyl group the electron density at the proton sites will be increased and further attack at these sites will be inhibited.

The reaction with the sulphite ion, a weaker base, is very similar to the above. Job plots (figure 32) show that initially at least 2:1 (SO_3^{--} : D.N.N.A.) complex formation occurs but the final product is shown to be the diacid. The explanation for this product and not a sigma-complex being formed in the reaction is probably similar to the above case and the facile attack of the base at the carbonyl carbon atom is favoured.

Any suggested mechanism at this stage would be conjecture due to the lack of direct evidence, but it is possible that the mechanism for the reaction of 3,6-D.N.N.A. with the methoxide ion is as shown in figure 40. A similar mechanism may be expected in the reaction with the sulphite ion, the initial attack being by the sulphite ion which is subsequently hydrolysed off in aqueous solution.



$OMe \equiv OCH_3$

Figure 40 The proposed mechanism for the reaction of 3,6 - D.N.N.A. with the methoxide ion.

With weak bases such as amines there is no evidence for sigma-complex formation with 3,6-D.N.N.A. and 4,5-D.N.N.A. which is unlike observations made on trinitrobenzene[139]. As in the case of T.N.A. the reason for the difference seems to be a result of the insolubility of the complex. However, it has been shown[197] that in the case of phthalic anhydride and tetrachlorophthalic anhydride that the initial product of the reaction with triethylamine is an $n \rightarrow \pi$ charge-transfer complex which reacts further in a subsequent slow reaction.

CHAPTER 5

PHYSICAL AND SPECTRAL PROPERTIES

(a) Introduction

The compounds which form the basis of this study are listed at the beginning of chapter 2 (see pages 45 and 46). In this chapter their preparation and spectral properties are outlined.

The compounds 2,5-D.N.N.A., Tri.N-1,8-N.A., Tri.N-2,3-N.A. and T.N.N.A. are new compounds prepared during the course of this study. T.N.A. and the intermediate 3,6-dinitroacenaphthene were prepared by modifications of existing methods whilst 3,6-D.N.N.A., 4,5-D.N.N.A. and the intermediates 5-nitroacenaphthene, 3-nitroacenaphthene and 5,6-dinitroacenaphthene were prepared by methods obtained from the literature.

The infrared spectrum of each of the compounds was recorded as a Nujol Mull on a Perkin Elmer 457 spectrometer.

The nuclear magnetic resonance spectrum of each of the compounds was recorded on a Perkin Elmer R.10 spectrometer in deutero-dimethylsulphoxide solution (D.M.S.O.-d_6).

The mass spectrum of each of the compounds was recorded on an MS.9 double beam mass spectrometer operating at 70 eV and with a probe temperature of 200°C.

The elemental analyses were carried out by the 'Beller Microanalytical Laboratory' in West Germany.

(b) Tetranitroacenaphthene (T.N.A.)

5-nitroacenaphthene was prepared by the method of Cava, Herkel and Schlessinger[198] and was used in the preparation of tetranitroacenaphthene using a modification of the method of Vernon and Wilson[199].

5-nitroacenaphthene (20 gms) was added slowly with stirring to a 1:1 mixture of concentrated sulphuric acid (S.G. = 1.84, 500 mls) and concentrated nitric acid

(S.G. = 1.42, 500 mls). After standing for seven days the mixture was poured into iced water (5 litres), when the crude product was precipitated. The product was five times recrystallised from nitromethane yielding white needles of tetranitroacenaphthene which were dried at 40°C under reduced pressure.

Melting Point = 216°C (lit = 212°C)[199]

Yield = 10.3 gm

Percentage theoretical yield = 30%

Elemental Analysis

Found C = 42.6%; H = 1.76%; N = 16.5%; O = 38.3%

Required C = 43.2%; H = 1.81%; N = 16.7%; O = 38.3%

Infrared Spectral Bands

358 (w), 373 (w), 489 (w), 510 (w), 580 (w),
682 (m), 708 (w), 737 (m), 746 (m), 778 (w),
809 (s), 828 (m), 870 (s), 891 (m), 930 (m),
960 (w), 972 (w), 1081 (w), 1096 (vw), 1105 (vw),
1139 (w), 1165 (m), 1192 (w), 1242 (w), 1262 (vw),
1289 (w), 1350 (vs), 1422 (w), 1538 (vs), 1617 (vs),
1850 (w), 2864 (vw), 2890 (vw), 2930 (sh), 2946 (w),
2975 (w), 3070 (m), 3108 (w);

Abbreviations used throughout

vw = very weak. w = weak
sh = shoulder m = medium
s = strong vs = very strong

Mass Spectral Analysis

The mass spectrum shows a parent ion peak at a value of m/e = 334 and also an intense peak at m/e = 332. This strong M-2 peak is not unexpected since it is apparent in the spectrum of acenaphthene, the parent hydrocarbon[200]. The base peak in the spectrum is at m/e = 286 which corresponds to the loss of the

$NO_2^{\cdot}$ fragment from the M-2 fragment. The strong peak at m/e = 317 and the metastable peak, m* = 300.86, suggest the loss of a fragment with a value of m/e = 17. This is probably the $^{\cdot}OH$ fragment since this loss is well known in compounds with <u>meta</u> nitro groups[201]. The mass spectrum is shown in figure 41.

<u>Nuclear Magnetic Resonance Spectrum</u>

The nuclear magnetic resonance spectrum of T.N.A. in D.M.S.O. $-d_6$ shows a peak at 0.8 τ and a peak at 5.83 τ. The relative intensity of the peaks is in the ratio of 1:2 respectively.

(c) <u>3,6- and 4,5-dinitronaphthalic anhydride (3,6-D.N.N.A. and 4,5-D.N.N.A.)</u>

The dinitronaphthalic anhydride isomers were prepared by Bell's[202] modification of the method of Hodgson and Ward[203].

3,6-D.N.N.A.: Melting Point = 216 - 217°C (lit = 216°C)[202]

4,5-D.N.N.A.: Melting Point = 320 - 322°C (lit = 322°C)[202]

<u>Elemental Analysis</u>

<u>3,6-D.N.N.A.</u>

<u>Found</u> C = 49.6%; H = 1.56%; N = 9.8%; O = 38.6%;

<u>Required</u> C = 50.0%; H = 1.38%; N = 9.7%; O = 38.9%;

<u>4,5-D.N.N.A.</u>

<u>Found</u> C = 49.8%; H = 1.53%; N = 9.7%; O = 38.5%;

<u>Required</u> C = 50.0%; H = 1.38%; N = 9.7%; O = 38.9%;

<u>Infrared Spectral Bands</u>

<u>3,6-D.N.N.A.</u>

670 (w), 695 (s), 718 (s), 730 (sh), 738 (w),
755 (s), 768 (sh), 810 (sh), 818 (s), 835 (s),
852 (m), 885 (m), 898 (vw), 932 (m), 942 (sh),
950 (m), 1002 (sh), 1028 (s), 1053 (w), 1078 (s),

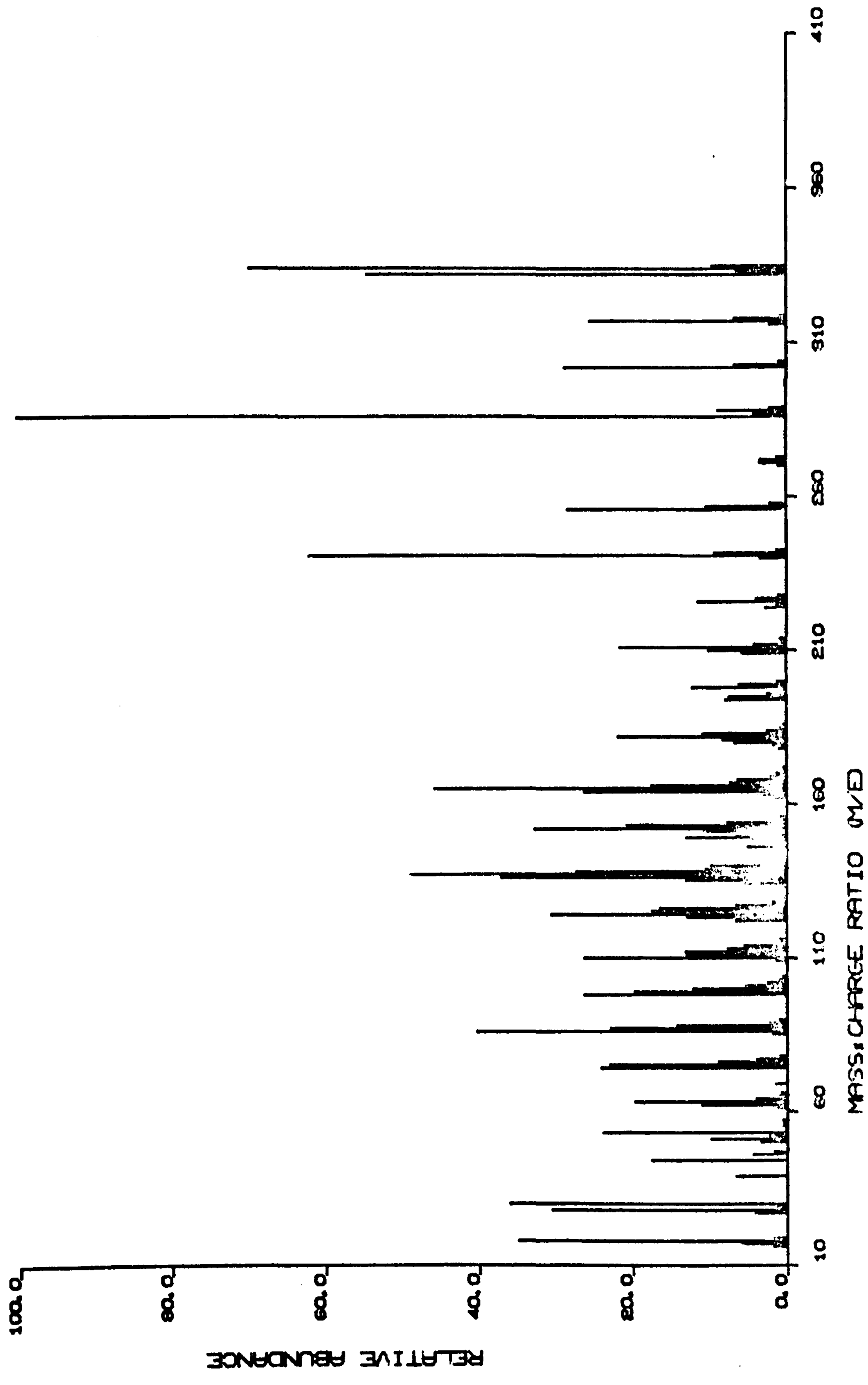


Figure 41 The mass spectrum of T.N.A.

1118 (vw), 1138 (m), 1155 (sh), 1168 (s), 1238 (m),
1280 (s), 1342 (s), 1385 (w), 1415 (m), 1435 (w),
1460 (sh), 1472 (m), 1490 (sh), 1503 (sh), 1510 (sh),
1540 (s), 1555 (sh), 1602 (sh), 1612 (s), 1632 (m),
1662 (sh), 1680 (sh), 1690 (sh), 1710 (sh), 1738 (s),
1780 (s), 1825 (m), 1858 (w), 1900 (w), 3050 (m);

4,5-D.N.N.A.

662 (w), 680 (w), 698 (w), 710 (m), 725 (s),
745 (s), 762 (s), 778 (s), 812 (m), 822 (s),
830 (m), 850 (s), 885 (s), 890 (m), 933 (m),
941 (w), 965 (w), 988 (m), 1005 (sh), 1030 (s),
1050 (w), 1088 (m), 1118 (sh), 1127 (m), 1138 (w),
1155 (sh), 1160 (s), 1178 (m), 1190 (sh), 1198 (w),
1222 (s), 1295 (s), 1330 (s), 1400 (s), 1418 (w),
1428 (w), 1470 (s), 1520 (sh), 1550 (s), 1588 (w),
1602 (s), 1632 (m), 1693 (sh), 1755 (s), 1790 (s),
1860 (w), 1880 (w), 1910 (w), 1960 (w), 3050 (m);

Mass Spectral Analysis

The mass spectrum of each of the isomers show a parent ion peak at a value m/e = 288. For a detailed analysis see section (i) of this chapter.

Nuclear Magnetic Resonance Spectrum

3,6-D.N.N.A.

The nuclear magnetic resonance spectrum consists of a doublet of doublets centred at 0.5 τ and 0.7 τ . The coupling constant is consistent with the expected *meta* coupling and has a value of 3Hz. The spectrum is shown in figure 42A.

4,5-D.N.N.A.

The nuclear magnetic resonance spectrum in dimethylsulphoxide solution consists of a single line at 0.65 τ . Hence in dimethyl sulphoxide solution the protons appear coincidentally equivalent. The addition of benzene to the system causes the single line to show some splitting. The spectrum observed in sulpholane solution is as expected, showing a doublet of doublets centred at 0.85 τ and 1.25 τ . The coupling constant has a value of 6Hz which is consistent with ortho coupling. The spectrum is shown in figure 42B.

(d) 2,5-dinitronaphthalic anhydride (2,5-D.N.N.A.)

The intermediate 3-nitroacenaphthene was prepared by the method of Morgan and Harrison[204] and was used in the preparation of 3,6-dinitroacenaphthene by a modification[205] of the method of Dashevskii and Malevannaya[206].

3-nitroacenaphthene (5 gm) was dissolved in a stirred solution of nitromethane (50 mls) and concentrated nitric acid (SG = 1.42, 10 mls). The 3,6-dinitroacenaphthene began precipitating almost as soon as dissolution was complete. The mixture was allowed to stand for one hour whence it was cooled to 0°C and the crude product was obtained by filtration. The crude product was recrystallised from hot nitromethane and was dried at 90°C under reduced pressure.

Melting Point = 206 - 207°C (lit = 209 - 210°C)[206]
Yield = 3.8 gm
Percentage Theoretical Yield = 60%

The 3,6-dinitroacenaphthene was converted to 2,5-dinitronaphthalene-1,8-dicarboxylic acid by chromic acid oxidation and then by treatment with thionyl chloride the acid was converted to 2,5-D.N.N.A. The method was as follows:

Finely ground sodium dichromate (7.2 gms) was added very slowly over a period of 1 hour with constant vigorous stirring to a solution of 3,6-dinitroacenaphthene (2 gm) in a mixture of fuming nitric acid (SG = 1.5, 9 mls) and oleum (SG = 1.92, 1.8 mls) the mixture being kept between -10°C and -5°C using an ice-salt mixture. When the addition was complete the mixture was stirred for a further 2 hours at 0°C. The mixture was then poured onto crushed ice (5 gms) and stirred vigorously. The mixture was filtered and the crude product dried at 60°C under reduced pressure. The pale yellow solid was dissolved in thionyl chloride (10 mls) and the mixture was heated under reflux for 2 hours. Carbon tetrachloride was added to the solution and the solid 2,5-D.N.N.A. was precipitated. The mixture was filtered, washed with carbon tetrachloride and dried at 60°C under reduced pressure.

Melting Point = 232 - 235°C
Yield = 0.7 gm
Percentage Theoretical Yield = 11%

Elemental Analysis

Found C = 50.3%; H = 1.54%; N = 9.3%; O = 39.1%
Required C = 50.0%; H = 1.38%; N = 9.7%; O = 38.9%

Infrared Spectral Bands

670 (w), 700 (s), 733 (m), 742 (m), 780 (w),
815 (s), 827 (m), 840 (m), 856 (w), 863 (w),
885 (m), 900 (sh), 930 (w), 990 (sh), 1018 (sh),
1055 (s), 1100 (sh), 1110 (sh), 1122 (m), 1175 (s),
1198 (sh), 1218 (sh), 1278 (s), 1300 (sh), 1342 (s),
1365 (sh), 1375 (s), 1385 (sh), 1425 (w), 1465 (sh),
1473 (sh), 1515 (sh), 1550 (s), 1588 (m), 1602 (m),
1690 (sh), 1710 (sh), 1745 (s), 1780 (s), 1870 (w)
1895 (w), 3040 (m),

Mass Spectral Analysis

The mass spectrum showed a parent ion peak at a value of m/e = 288. For a more detailed analysis see section (i) of this chapter.

Nuclear Magnetic Resonance Spectrum

The spectrum is as shown in figure 42C. The apparent triplet centred at 1.09 τ has resulted from the accidental equivalence of a pair of lines in two of the doublets. The expected spectrum would be two doublets of doublets each showing ortho coupling. The observed coupling constant of 6Hz is consistent with ortho coupling.

(e) 1,6,8-Trinitro-2,3-naphthalic anhydride (Tri.N-2,3-N.A.)

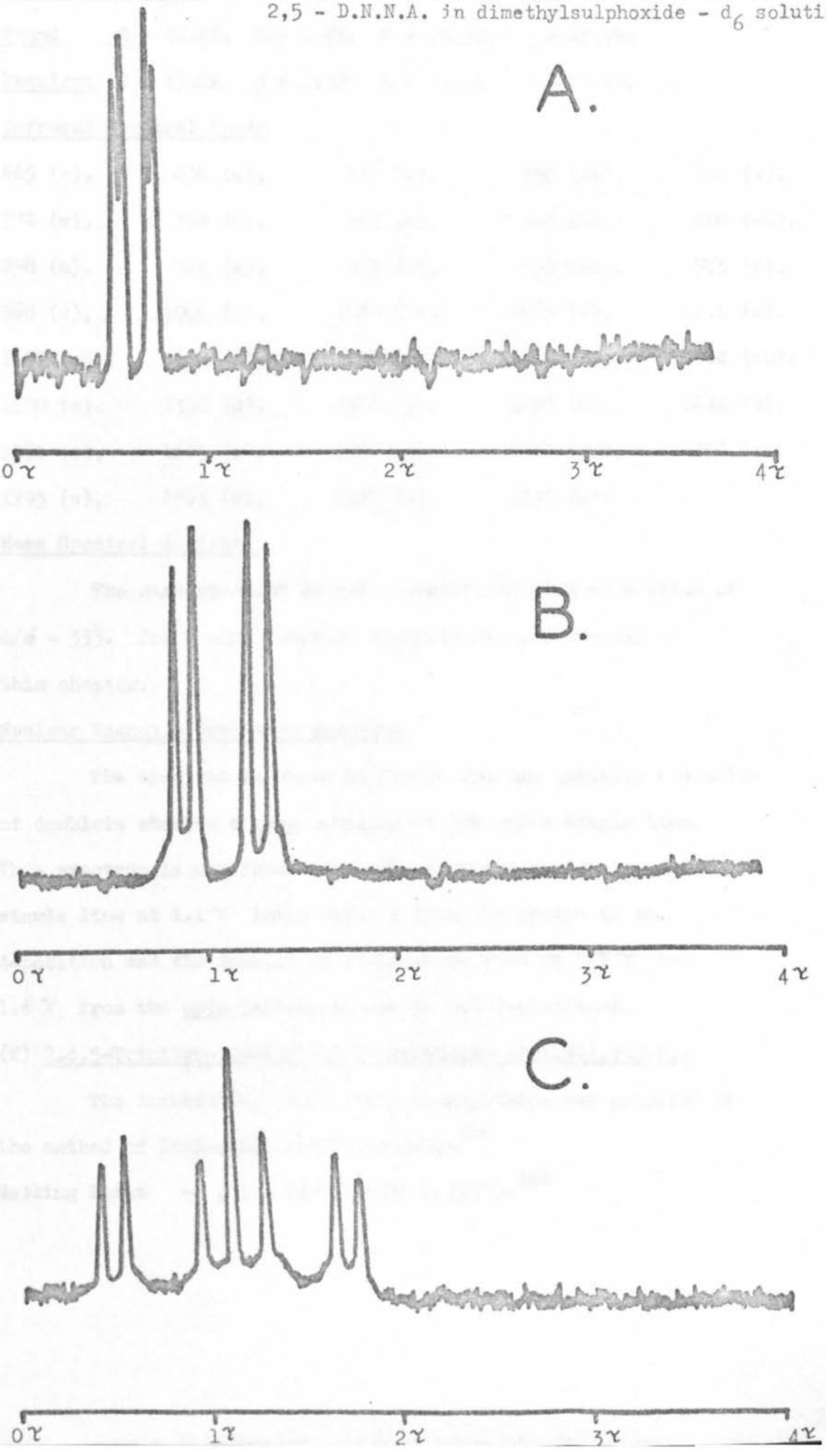
Naphthalene-2,3-dicarboxylic acid was converted into the anhydride by boiling under reflux with thionyl chloride.

Melting Point = 244 - 245°C (lit = 246°C)[207]

The 2,3-naphthalic anhydride (5 gm) was dissolved in a mixture of oleum (SG = 1.92, 25 mls) and fuming nitric acid (SG = 1.5, 20 mls) and was stirred for 24 hours at room temperature. The mixture was then poured onto crushed ice (25 gms) and stirred vigorously when the white trinitronaphthalic anhydride was precipitated. The crude product was removed by filtration, washed with ice cold water and dried at 90°C under reduced pressure. The crude product was recrystallised from hot acetic anhydride and redried.

Melting Point = 254 - 256°C
Yield = 5 gms
Percentage Theoretical Yield = 60%

Figure 42 The n.m.r. spectra of the isomeric dinitronaphthalic anhydrides -- (A) 3,6 - D.N.N.A. in dimethylsulphoxide - d_6 solution (B) 4,5 - D.N.N.A. in sulpholane solution and (C) 2,5 - D.N.N.A. in dimethylsulphoxide - d_6 solution.



Elemental Analysis

Found C = 42.9%; H = 1.5%; N = 12.3%; O = 43.7%;

Required C = 43.2%; H = 0.9%; N = 12.6%; O = 43.2%;

Infrared Spectral Bands

665 (m), 690 (w), 711 (m), 730 (sh), 760 (w),
778 (w), 798 (m), 815 (m), 824 (s), 880 (vw),
898 (m), 918 (w), 927 (m), 933 (sh), 955 (m),
968 (w), 1006 (w), 1020 (vw), 1063 (w), 1118 (m),
1155 (sh), 1180 (s), 1198 (w), 1220 (sh), 1264 (sh),
1300 (s), 1350 (s), 1400 (m), 1498 (sh), 1513 (s),
1578 (s), 1605 (w), 1660 (w), 1710 (sh), 1750 (s),
1793 (s), 1863 (w), 1890 (w) 3040 (m);

Mass Spectral Analysis

The mass spectrum showed a parent ion peak at a value of m/e = 333. For a more detailed analysis see section (i) of this chapter.

Nuclear Magnetic Resonance Spectrum

The spectrum is shown in figure 43A and exhibits a doublet of doublets showing a meta coupling of 3Hz and a single line. This spectrum is consistent with the proposed structure, the single line at 1.1 τ being derived from the proton in the 4-position and the doublet of doublets centred at 0.7 τ and 1.6 τ from the meta protons in the 5- and 7-positions.

(f) 2,4,5-Trinitro-1,8-naphthalic anhydride (Tri.N-1,8-N.A.)

The intermediate 5,6-dinitroacenaphthene was prepared by the method of Dashevskii and Malevannaya[206].

Melting Point = 213 - 214°C (lit = 215°C)[206]

The 5,6-dinitroacenaphthene (24 gms) was added with stirring to a 1:1 mixture of fuming nitric acid (SG = 1.5, 10 mls) and nitromethane (10 mls). The mixture was stirred for five days at room temperature when ice cold water (25 mls) was added and the solution was stirred until precipitation was complete. The crude trinitroacenaphthene[205] was removed by filtration, recrystallised from a 1:1 mixture of acetic acid and nitromethane and dried at 90°C under reduced pressure. The trinitroacenaphthene (10 gms) was converted into 2,4,5-trinitronaphthalic anhydride using chromic acid oxidation followed by reaction with thionyl chloride in a manner analagous to that used in the preparation of 2,5-dinitronaphthalic anhydride (see page 115).

Melting Point = 244 - 245°C with decomposition
Yield = 6.5 gms
Percentage Theoretical Yield = 56%

Elemental Analysis

Found C = 43.6%; H = 1.4%; N = 12.1%; O = 43.4%;
Required C = 43.2%; H = 0.9%; N = 12.6%; O = 43.2%;

Infrared Spectral Bands

663 (m), 678 (w), 700 (w), 720 (m), 745 (m),
782 (m), 815 (m), 825 (w), 854 (s), 886 (w),
910 (m), 920 (sh), 964 (sh), 990 (sh), 1022 (sh),
1043 (m), 1068 (s), 1120 (w), 1155 (m), 1174 (s),
1210 (sh), 1219 (s), 1260 (sh), 1290 (s), 1320 (w),
1355 (s), 1393 (sh), 1410 (w), 1550 (s), 1585 (s),
1600 (sh), 1625 (w), 1673 (sh), 1690 (sh), 1745 (s),
1790 (s), 1860 (w), 1890 (w), 3040 (m);

Mass Spectral Analysis

The mass spectrum showed a parent ion peak at a value of $m/e = 333$. For a more detailed analysis see section (i) of this chapter.

Nuclear Magnetic Resonance Spectrum

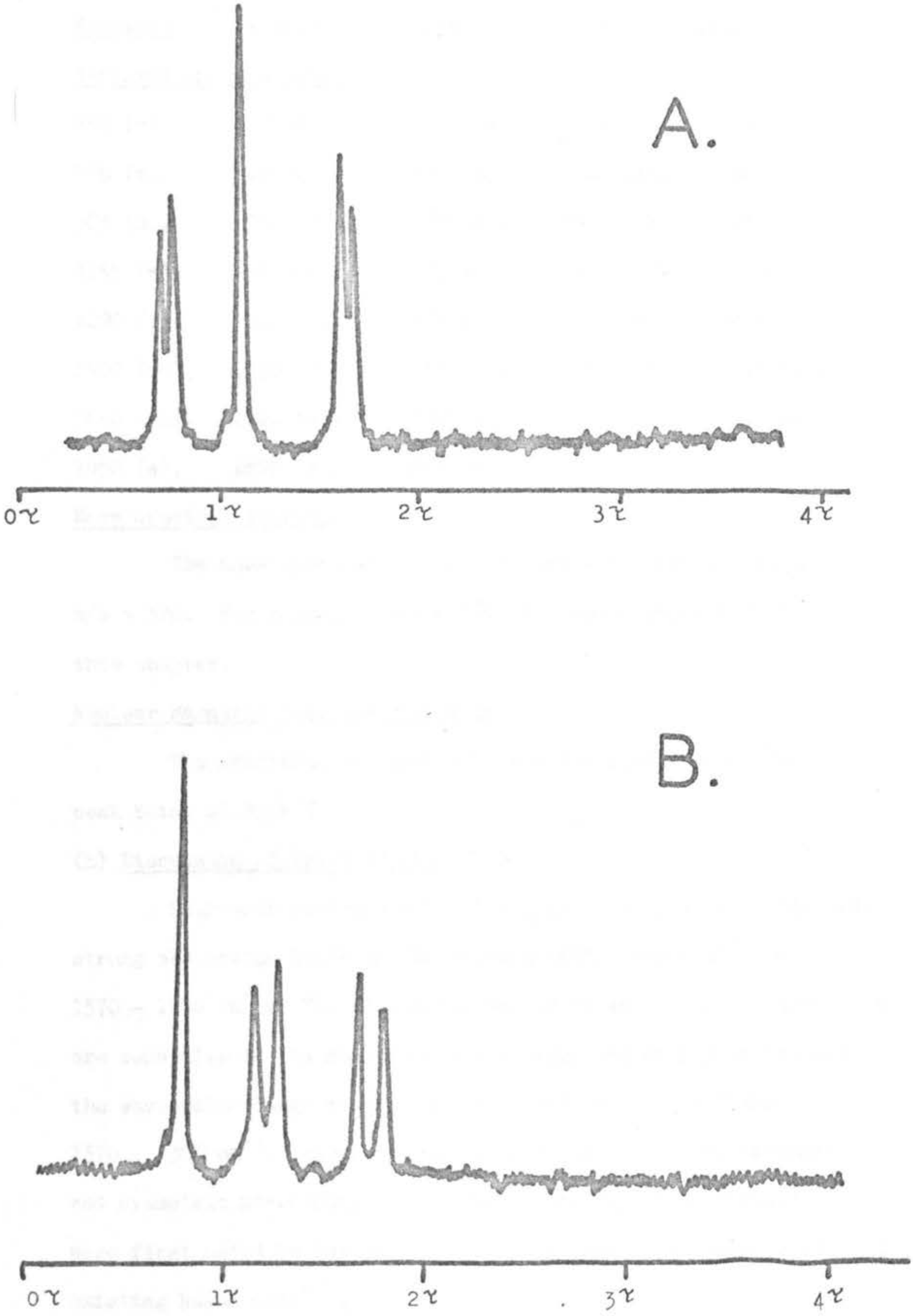
The spectrum shown in figure 43B consists of a doublet of doublets and a single line. The spectrum is consistent with the proposed structure, the single line at 0.8 τ being derived from the proton at the 3-position and the doublet of doublets centred at 1.21 τ and 1.76 τ from the *ortho* protons in the 6- and 7-positions. The coupling constant is 6Hz.

(g) 2,4,5,7-Tetranitronaphthalic anhydride (T.N.N.A.)[205]

Finely ground sodium dichromate (72 gms) was added, with stirring, over a period of 45 minutes to a solution of T.N.A. (20 gms) in a mixture of fuming nitric acid (SG = 1.5, 90 mls) and oleum (SG = 1.92, 18 mls) and the whole mixture was kept at 0°C. When the addition was complete the temperature was allowed to rise to 20°C and the mixture was stirred for 72 hours. The mixture was poured onto crushed ice (100 gms) and stirred vigorously and a white precipitate was formed. The crude product was removed by filtration and dried at 65°C under reduced pressure. The tetranitronaphthalene dicarboxylic acid was converted to the anhydride by refluxing with thionyl chloride using the procedure described earlier (see preparation of Tri.N-2,3-N.A.). The product obtained was recrystallised from hot acetic anhydride and dried at 90°C under reduced pressure.

Melting Point	= 292 - 295°C with decomposition
Yield	= 6.1 gms
Percentage Theoretical Yield	= 27%

Figure 43 The n.m.r. spectra of the trinitronaphthalic anhydrides (A) Tri.N. -2,3- N.A. and (B) Tri.N. -1,8- N.A. both in dimethylsulphoxide -d_6 solution.



Elemental Analysis

Found C = 37.6%; H = 1.1%; N = 15.0%; O = 46.2%;

Required C = 38.1%; H = 0.5%; N = 14.8%; O = 46.6%;

Infrared Spectral Bands

660 (m), 682 (w), 700 (m), 738 (m), 755 (w),
808 (m), 818 (s), 837 (s), 850 (sh), 862 (m),
903 (m), 910 (sh), 975 (w), 1060 (s), 1135 (m),
1155 (w), 1182 (s), 1195 (sh), 1221 (sh), 1262 (sh),
1290 (s), 1345 (s), 1372 (sh), 1385 (sh), 1400 (sh),
1500 (sh), 1510 (sh), 1550 (s), 1583 (s), 1615 (m),
1640 (sh), 1700 (sh), 1742 (s), 1787 (s), 1840 (w),
1860 (w), 1880 (w), 3060 (w);

Mass Spectral Analysis

The mass spectrum showed a parent ion peak at a value of m/e = 378. For a more detailed analysis see section (i) of this chapter.

Nuclear Magnetic Resonance Spectrum

The spectrum, as expected, showed a single peak, the peak being at 0.56 τ.

(h) Discussion of Infrared Data

Compounds containing the $R-NO_2$ group exhibit two extremely strong absorption bands in the regions 1650 - 1500 cm^{-1} and 1370 - 1250 cm^{-1}. The wavenumber values at which these bands occur are sensitive to the nature of the R group and when R is aromatic the wavenumber range is contracted to 1570 - 1500 cm^{-1} and 1370 - 1300 cm^{-1}. These strong absorptions due to the asymmetric and symmetric stretching vibrations of the NO_2 group respectively were first noted by Barnes[208] in 1944 and this assignment confirmed existing Raman data[209].

No detailed systematic study of absorptions due to the anhydride group has been carried out. However all anhydrides show two strong carbonyl absorption bands. The position, separation and intensity of these bands are dependent on the precise nature of the molecule[196]. The two absorptions are due to the symmetric and asymmetric stretching vibrations of the two carbonyl groups. In addition to the carbonyl absorptions, anhydrides also show a strong band due to the C-O-C stretching vibration and in aromatic anhydrides this vibration usually occurs in the range 1310 - 1210 cm^{-1} depending on the amount of ring strain[210].

The other characteristic absorption band of the compounds at present under investigation is that due to the aromatic C-H bond normally occuring around 3030 cm^{-1} [211].

In the table the major bands are listed for comparison.

The positions of the nitro group stretching frequencies fall comfortably within the expected range and show only little variation within the group of compounds. Similarly the position of the C-O-C stretching frequency of the anhydride group is fairly consistant and within the literature range.

The position of the aromatic C-H stretching frequency is slightly higher than expected in all the compounds and this may be a result of the considerable ring strain in the systems.

The range of values for the carbonyl stretching frequencies of anhydrides is less well documented but typical values for simple anhydrides seem to be around 1840 cm^{-1} and 1780 cm^{-1}. In the case of 6-membered ring anhydrides attached to polycyclic aromatic systems, however, it has been shown[212] that the bands occur at rather lower frequencies than in the

Compound	Wavenumber Values for the Nitro Group		Aromatic C-H cm^{-1}	Wavenumber Values for the Anhydride Group		Anhydrid C-O-C Stretch cm^{-1}
	Asymmetric Stretch cm^{-1}	Symmetric Stretch cm^{-1}		Asymmetric Stretch cm^{-1}	Symmetric Stretch cm^{-1}	
T.N.A.	1538	1350	3070	-	-	-
2,5-D.N.N.A.	1550	1342	3040	1780	1745	1278
3,6-D.N.N.A.	1540	1342	3050	1780	1738	1280
4,5-D.N.N.A.	1550	1330	3050	1790	1755	1295
Tri.N-2,3-N.A.	1543	1350	3040	1793	1750	1300
Tri.N-1,8-N.A.	1550	1355	3040	1790	1749	1290
T.N.N.A.	1550	1345	3060	1787	1742	1290

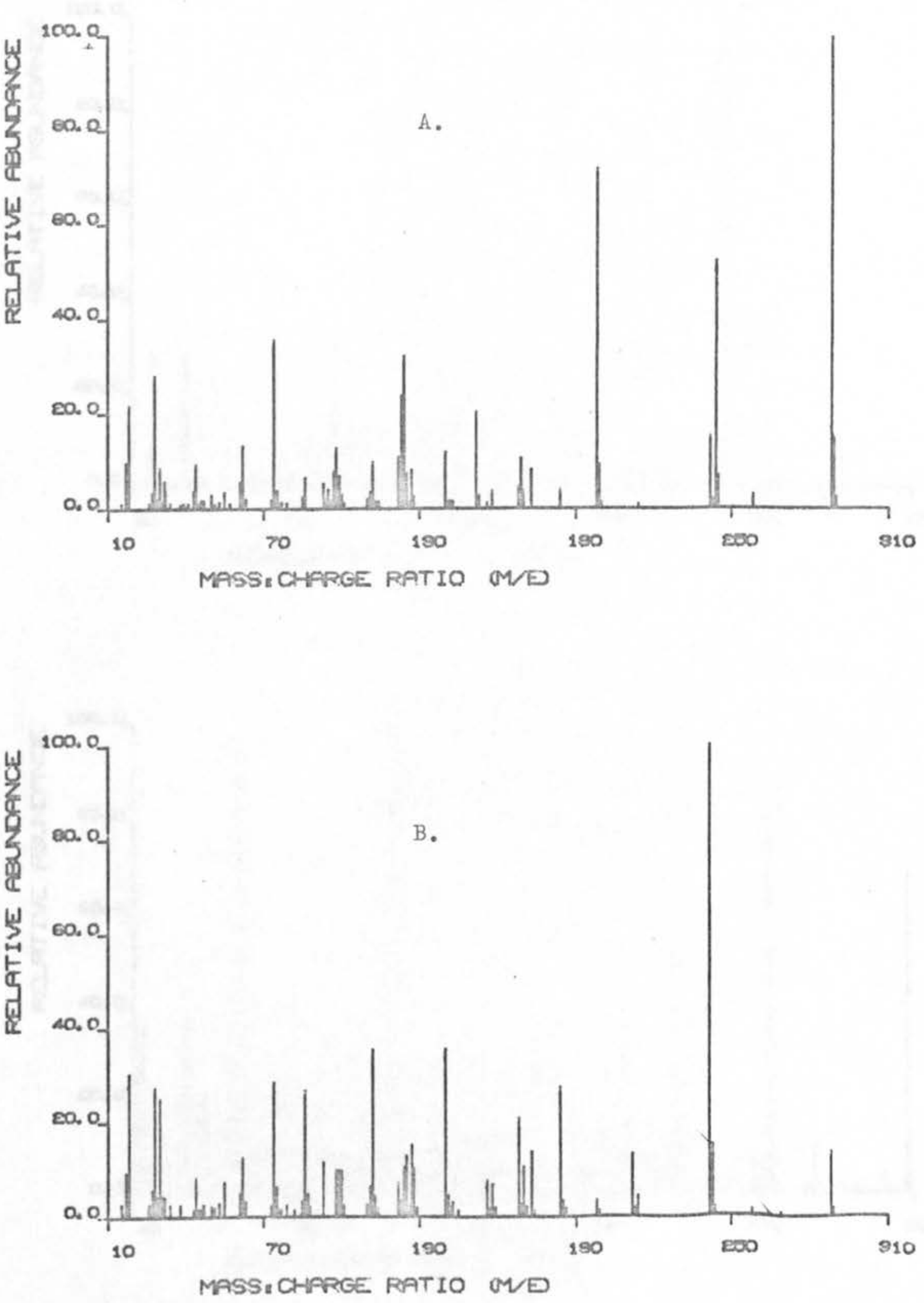
simple systems, (1770 cm^{-1} and 1735 cm^{-1}) and have a smaller separation. In the systems studied it appears that a similar effect is being observed.

(i) Discussion of Mass Spectral Data

In this section the mass spectra of the six nitroaromatic anhydrides at present under investigation are discussed. The results are correlated with the number of nitro groups on the naphthalene skeleton and with the positions of the nitro groups with respect to each other and with respect to the anhydride group.

The mass spectra of the compounds were computed and are presented as bar diagrams in figures 44, 45 and 46. The fragmentation pathways proposed for the systems, resulting from an analysis of the spectra together with a consideration of the metastable transitions, are shown in figures 47 to 52.

The mass spectra of nitroaromatic compounds have been extensively studied[201,213-215] and the various fragments derived from the nitrogroup have been well characterised. The fragmentation mechanism of the anhydride group in aromatic anhydrides has also been well characterised[216].



<u>Figure 44</u> The mass spectra of (A) 3,6 - D.N.N.A. and (B) 4,5 - D.N.N.A..

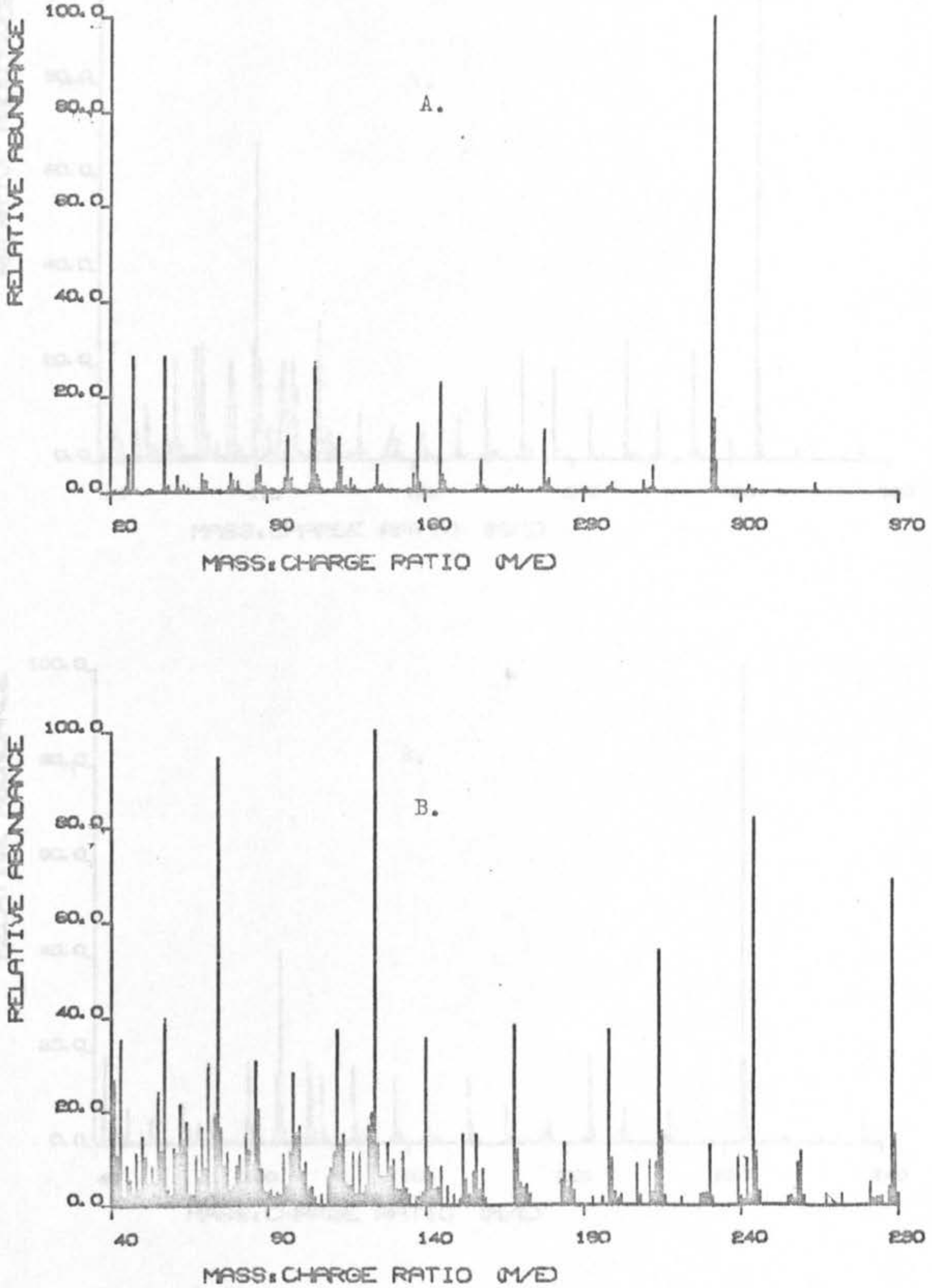
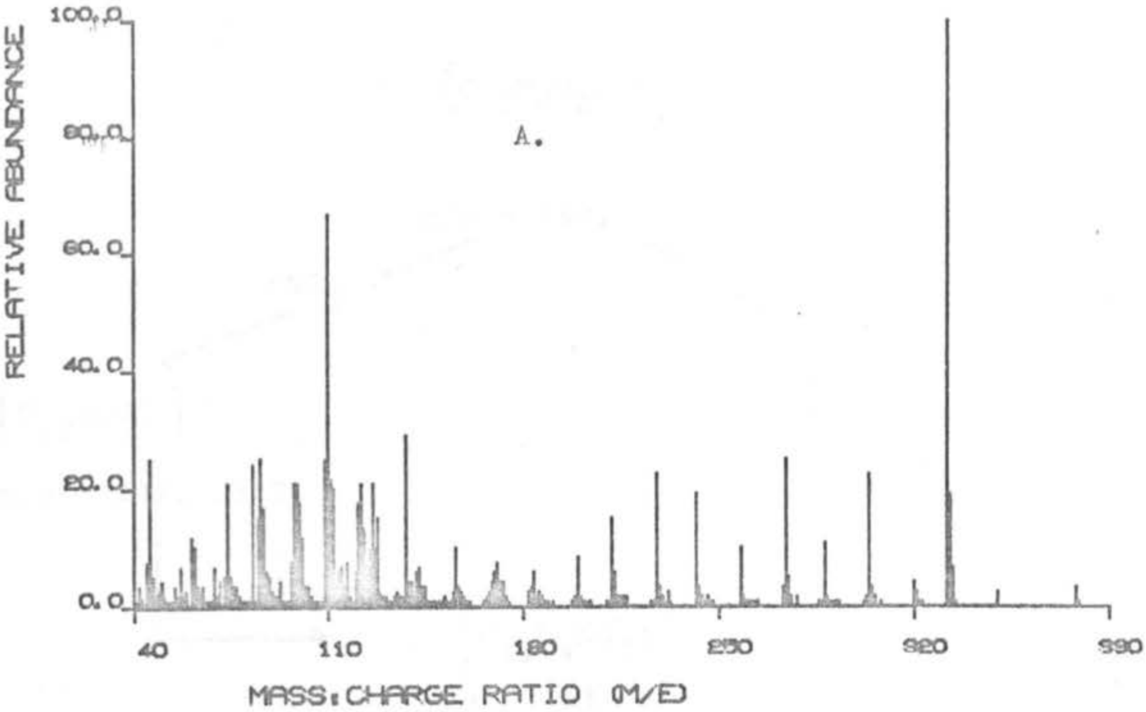


Figure 45 The mass spectra of (A) Tri.N. -2,3- N.A. and (B) 2,5 - D.N.N.A.



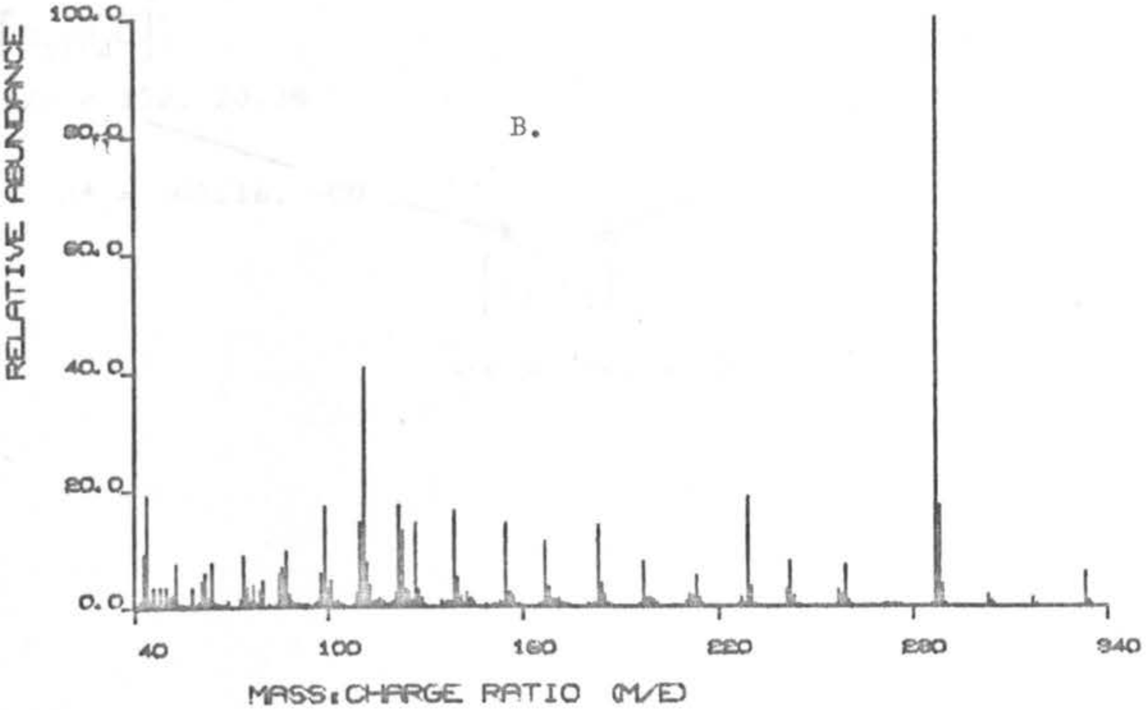


Figure 46 The mass spectra of (A) T.N.N.A. and (B) Tri.N. -1,8- N.A..

FIGURE 47 Proposed Fragmentation Pathway of 3,6-D.N.N.A.

$$\begin{tikzcd}[column sep=small]
 & \begin{array}{c}\left[C_{12}H_4N_2O_7\right]^{+\cdot} \\ m/e = 288,\ 100\% \end{array} \arrow[dl, "-NO_2^{\cdot}"'] \arrow[dr, "-CO_2\ m^* = 206.72"] & \\
\begin{array}{c}\left[C_{12}H_4NO_5\right]^{+} \\ m/e = 242,\ 15.2\% \end{array} \arrow[dr, "-CO_2"] & & \begin{array}{c}\left[C_{11}H_4N_2O_5\right]^{+\cdot} \\ m/e = 244,\ 52.5\% \end{array} \arrow[dl, "-NO_2^{\cdot}"', "m^* = 160.67"] \\
 & \begin{array}{c}\left[C_{11}H_4NO_3\right]^{+} \\ m/e = 198,\ 72.0\% \end{array} \arrow[dl, "m^* = 116.69\ -NO_2^{\cdot}"'] \arrow[dr, "-CO\ m^* = 145.69"] & \\
\begin{array}{c}\left[C_{11}H_4O\right]^{+\cdot} \\ m/e = 152,\ 20.3\% \end{array} \arrow[dr, "m^* = 101.16,\ -CO"'] & & \begin{array}{c}\left[C_{10}H_4NO_2\right]^{+} \\ m/e = 170,\ 3.8\% \end{array} \arrow[dl, "-NO_2^{\cdot}"] \\
 & \begin{array}{c}\left[C_{10}H_4\right]^{+\cdot} \\ m/e = 124,\ 32.2\% \end{array} &
\end{tikzcd}$$

FIGURE 48 Proposed Fragmentation Pathway of 4,5-D.N.N.A.

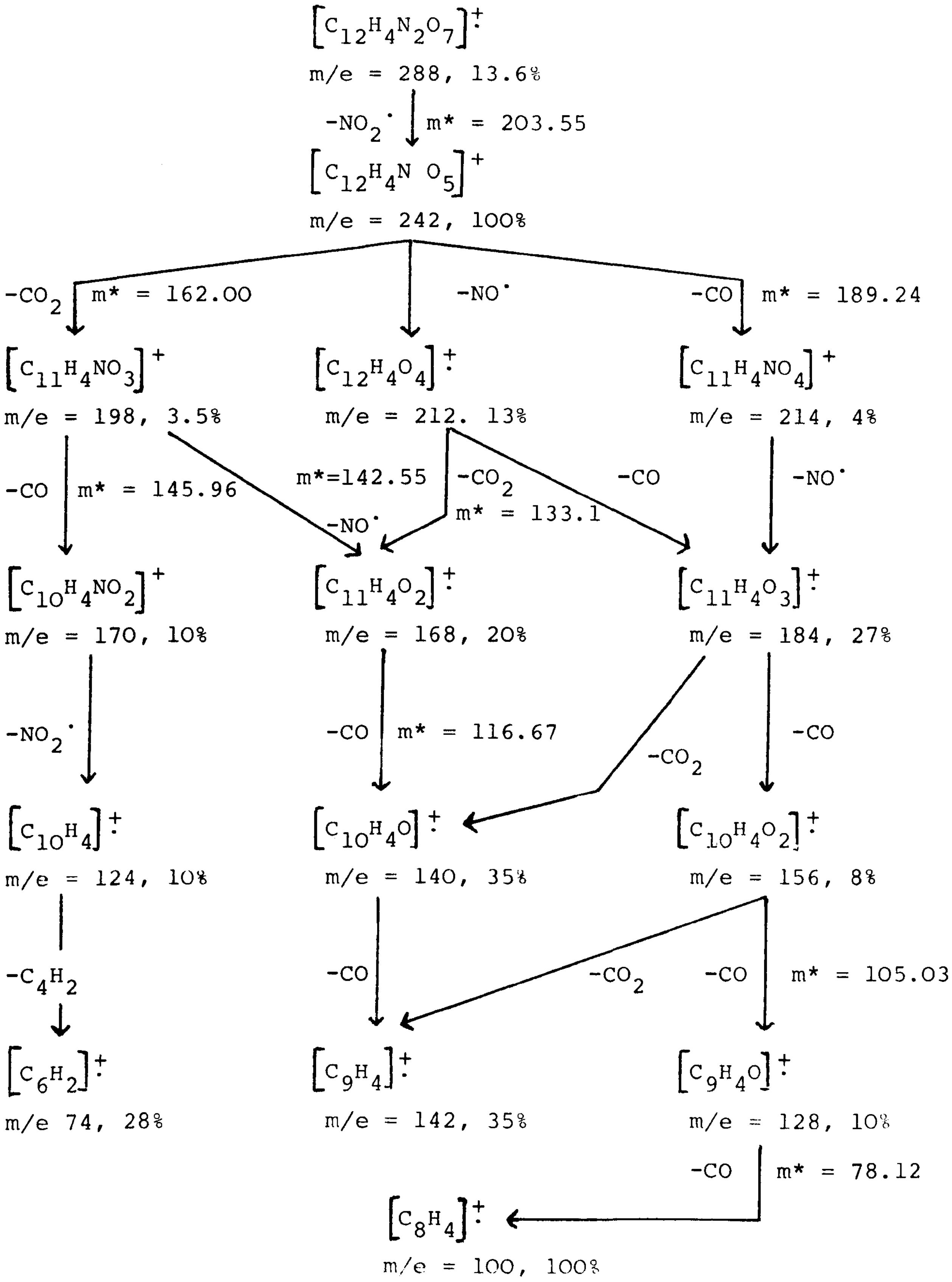


FIGURE 49 Proposed Fragmentation Pathway of 2,5-D.N.N.A.

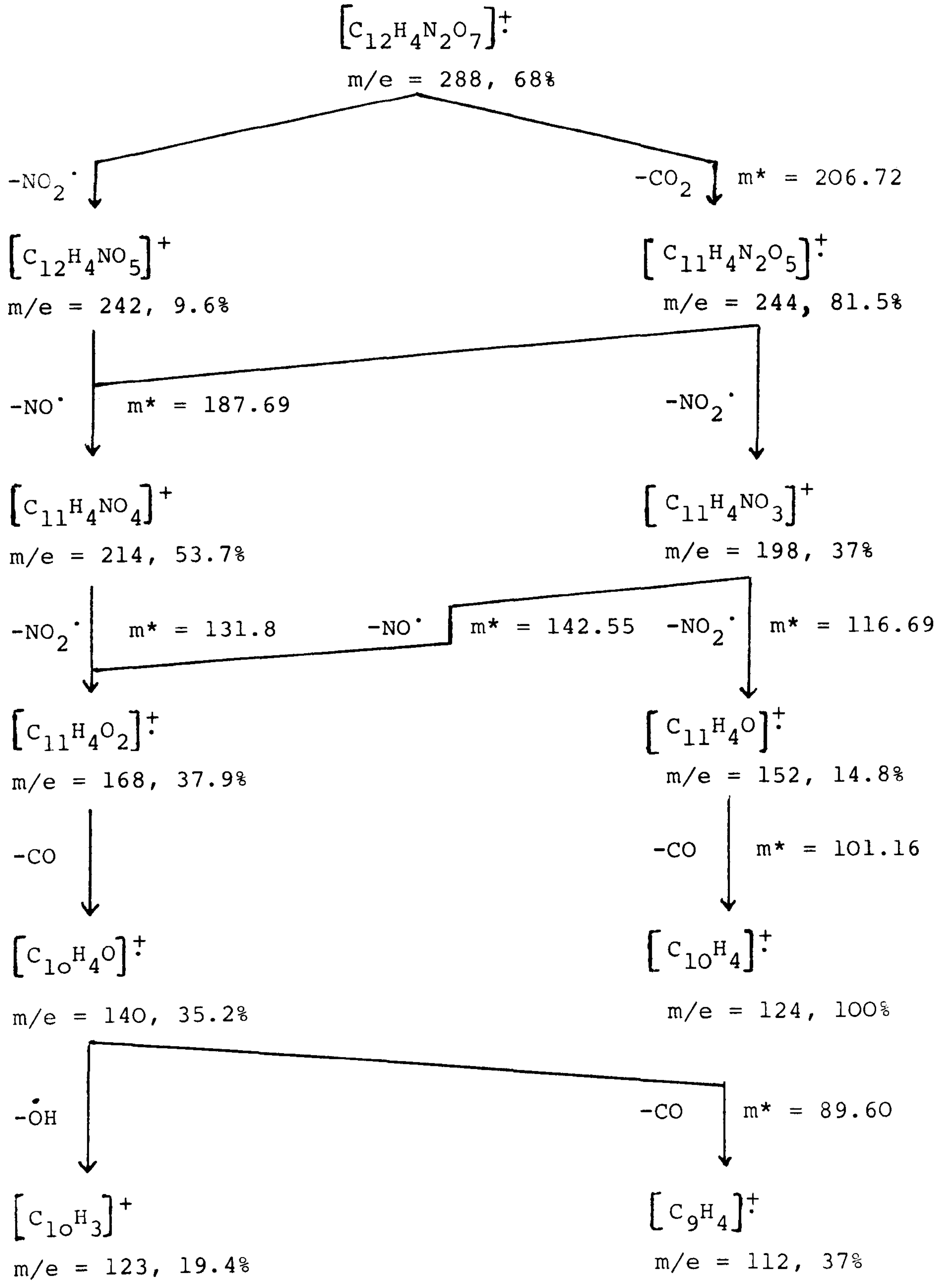


FIGURE 50 Proposed Fragmentation Pathway of Tri.N-2,3-N.A.

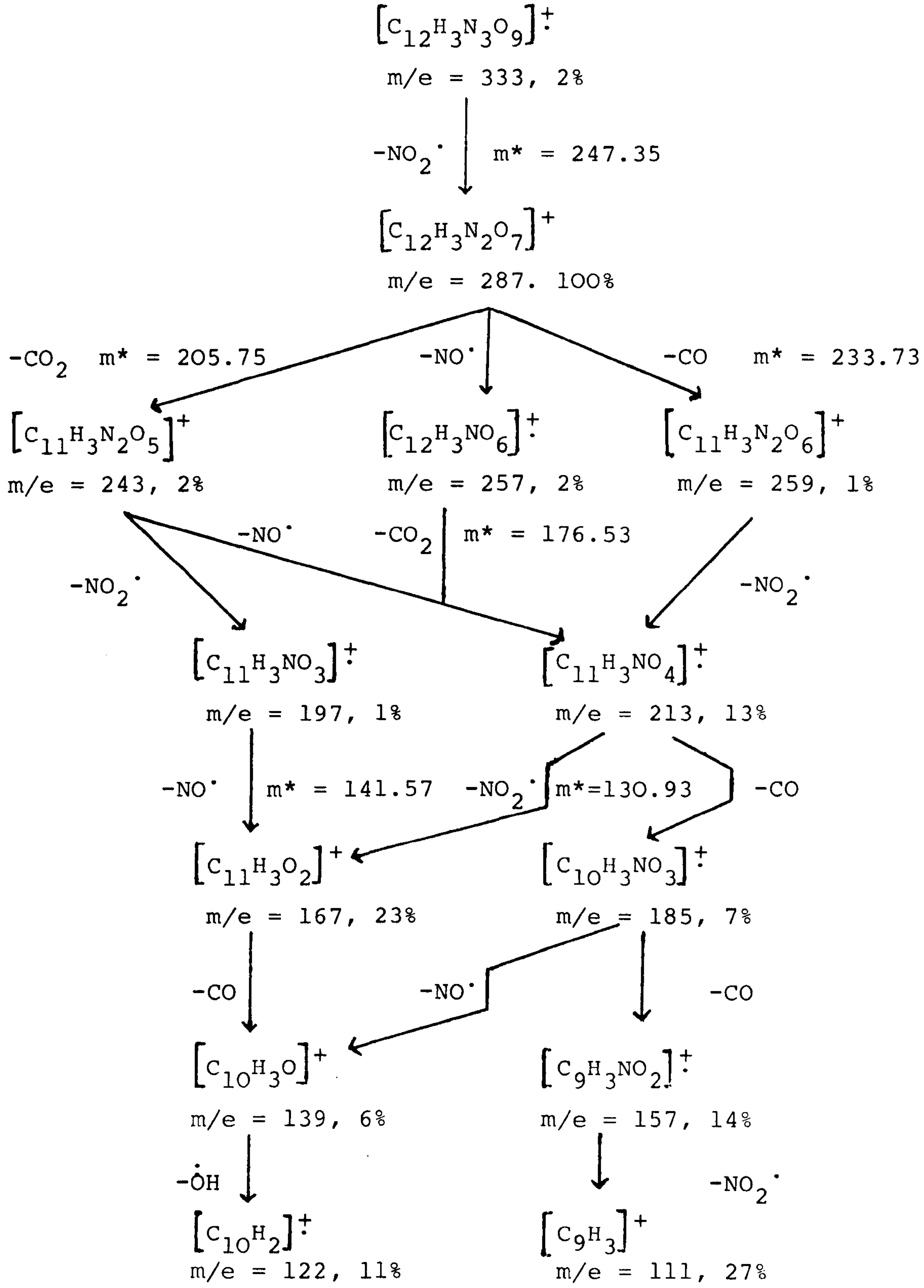


FIGURE 51 Proposed Fragmentation Pathway of Tri.N-1,8-N.A.

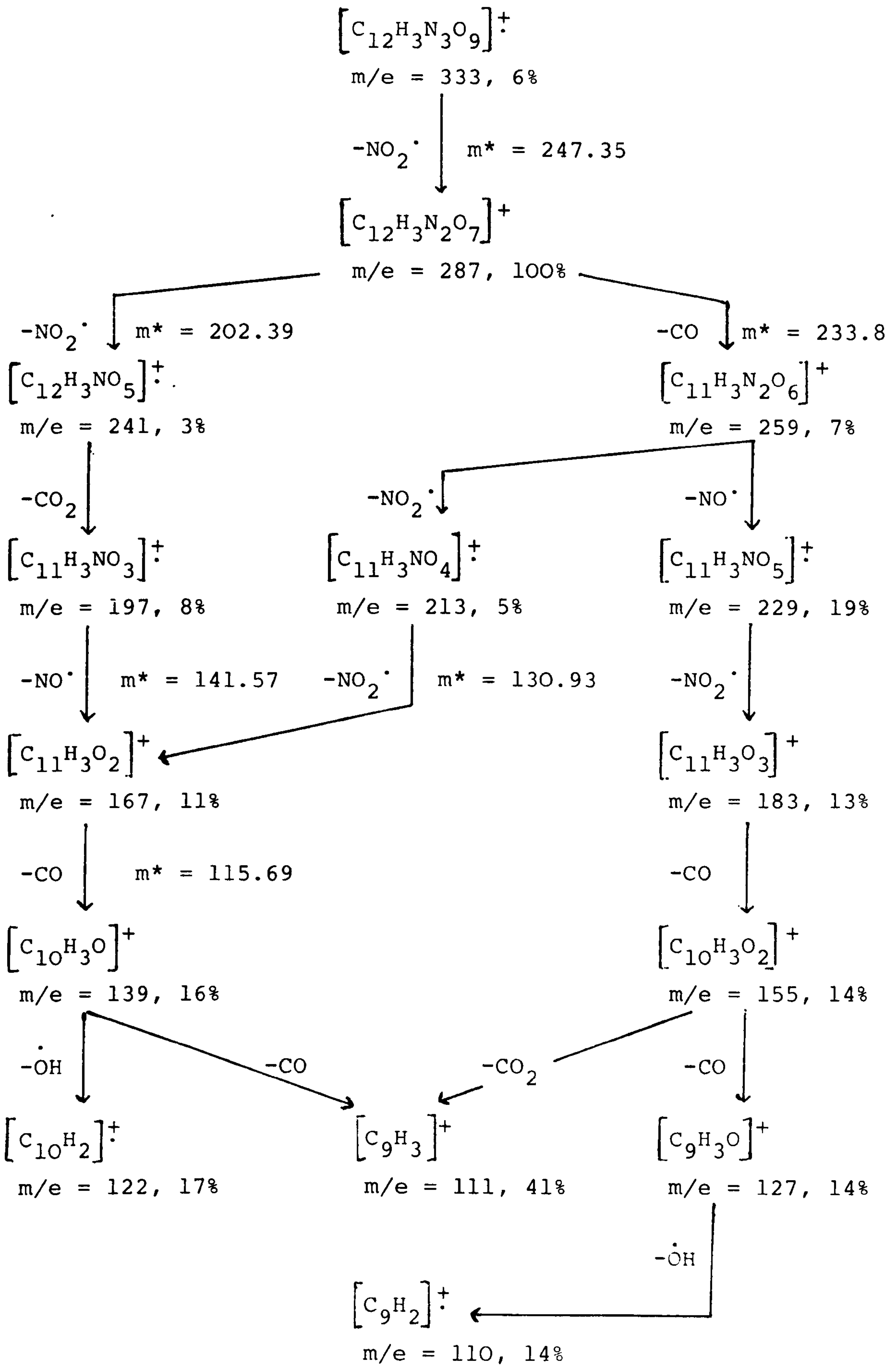
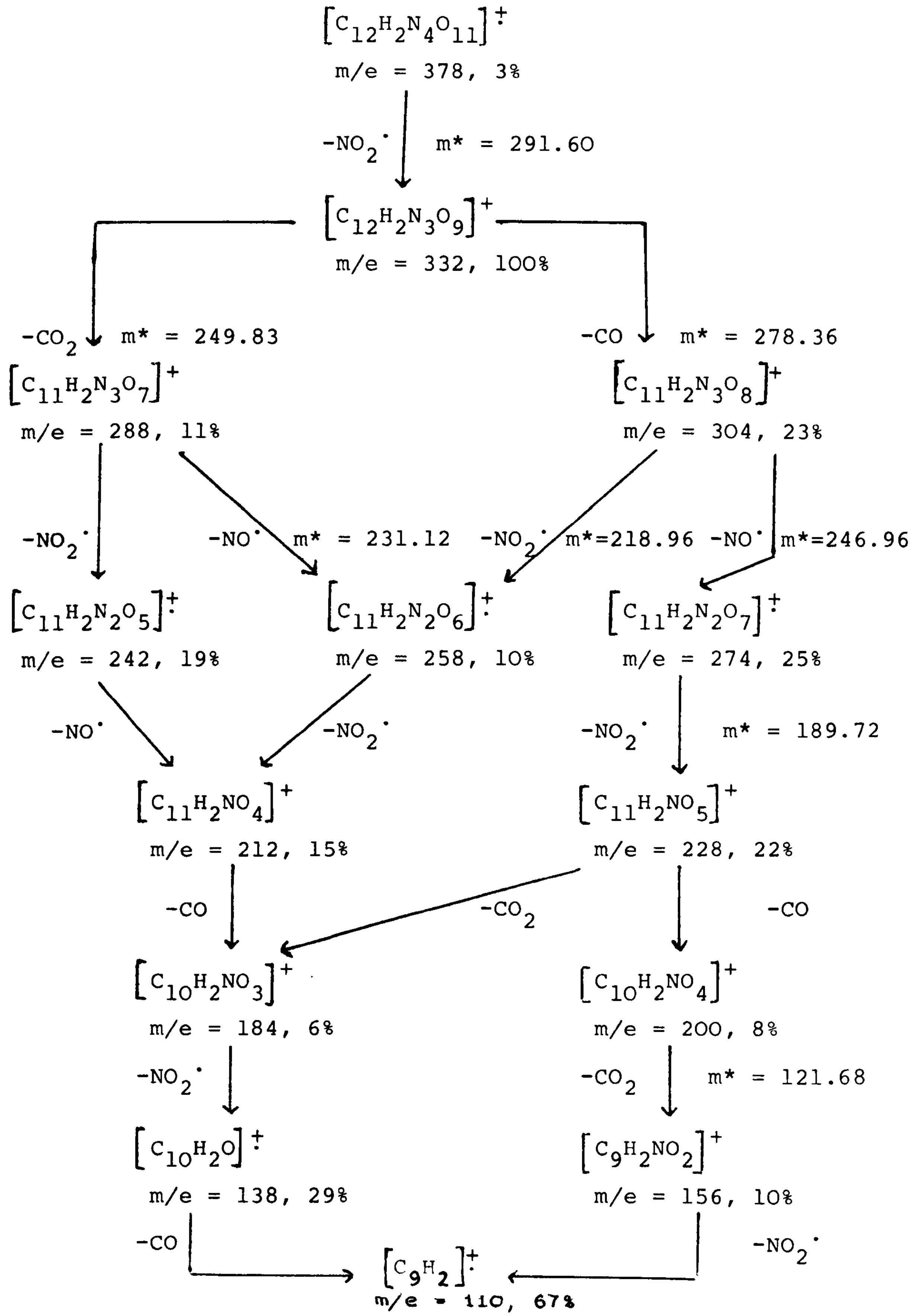


FIGURE 52 Proposed Fragmentation Pathway of T.N.N.A.



In the compounds studied the initial fragmentation from the molecular ion was either loss of the $NO_2\cdot$ fragment or simultaneous loss of the $NO_2\cdot$ and CO_2 fragments. In 4,5-D.N.N.A., Tri.N-1,8-N.A., Tri.N-2,3-N.A. and T.N.N.A. the molecular ions at values of m/e = 288, m/e = 333, m/e = 333 and m/e = 378 respectively are very unstable and in each case loss of the $NO_2\cdot$ fragment gives rise to the base peak in the spectrum. Each of these fragmentations have associated metastable transitions at m* = 203.55, m* = 247.35, m* = 247.35 and m* = 291.60 respectively. In each of these compounds both of the <u>peri</u> positions are occupied by nitro groups and the system, in this respect, is analagous to 1,8-dinitronaphthalene where loss of a nitro group from the molecular ion leads to the base peak in the spectrum[201]. The instability of the molecular ion appears to be the result of an interaction between the nitro groups in the <u>peri</u> positions where considerable overlap of the electron clouds associated with the oxygen atoms in the different nitro groups would be expected.

The nitro groups in 2,5-D.N.N.A. and 3,6-D.N.N.A. are sterically unhindered and this leads to a considerable enhancement of the stability of the molecular ion. These systems differ also from the above mentioned systems in that the preferential loss from the molecular ion is CO_2 ($M-CO_2$, 81% and 53% respectively) and not $NO_2\cdot$ ($M-NO_2\cdot$, 10% and 15% respectively). Thus it would appear that there are two competing processes for the initial fragmentation of the molecular ion, namely loss of CO_2 and $NO_2\cdot$. In those molecules where there is an interaction between nitro groups in the <u>peri</u> positions the loss of $NO_2\cdot$ is an energetically more favoured route and occurs to the exclusion of the alternative route. The loss of the CO_2

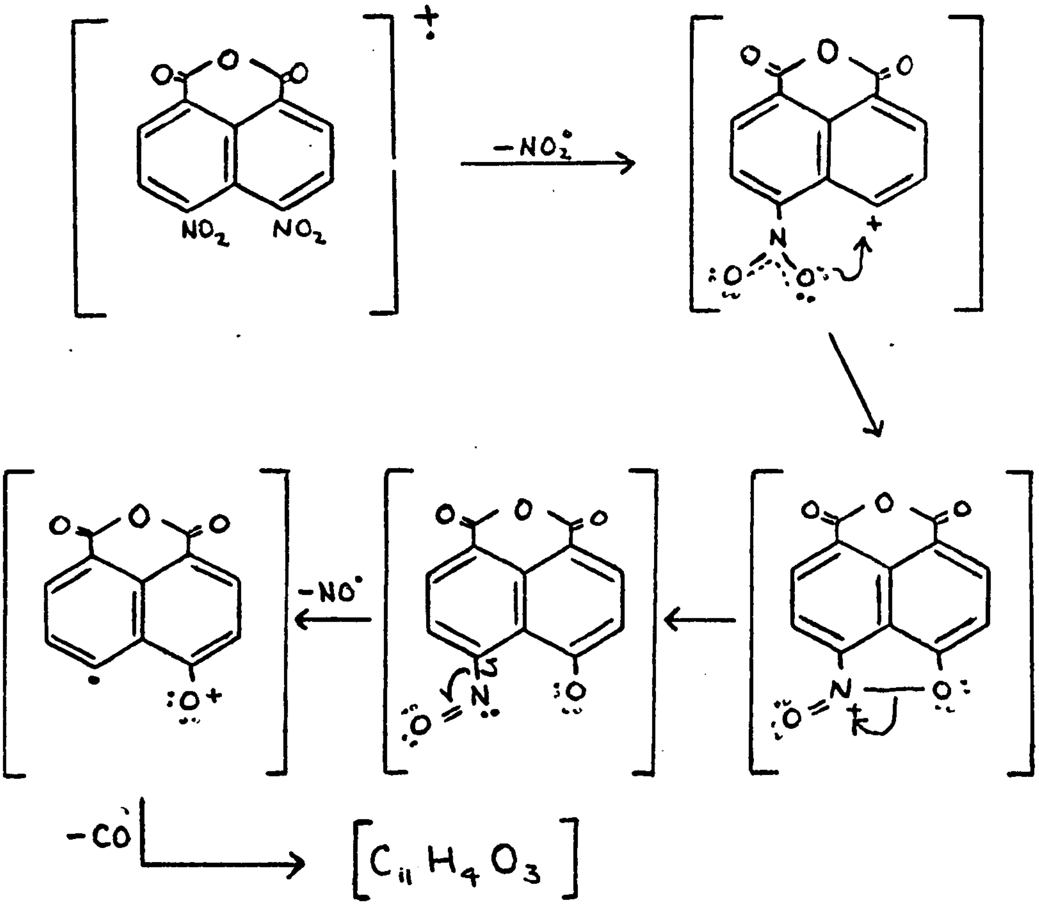
fragment from the molecular ion in 2,5-D.N.N.A. causes an increase in relative intensity of the fragment from 68% to 82% also the M-CO_2 fragment is more stable in 2,5-D.N.N.A. (81%) than in 3,6-D.N.N.A.(53%). These observations may be indicative of an interaction between the electron clouds associated with the oxygen atoms of the nitro group in the 2-position and the oxygen atom of the anhydride carbonyl group at the 1-position.

In systems where there is steric interaction at the peri positions or where one of the peri positions is occupied there is considerable evidence for fragments which must be derived from rearrangement processes. In all the compounds, apart from 3,6-D.N.N.A., the NO° fragment is observed and the CO fragment is apparent to a greater extent than would be expected simply from the anhydride group. Both these fragmentations are supported by metastable evidence.

A mechanism has been suggested[201] for the loss of NO° and CO fragments from dinitronaphthalenes where the nitro groups occupy the peri positions and it seems reasonable to assume that the mechanism still applies in the case of the nitroaromatic anhydrides which show similar structural features (see Figure 53, scheme A).

The loss of the CO fragment from dinitronaphthalenes in which there is no steric interaction between the nitro groups has been suggested[216] to arise by two mechanisms. The initial stages as applied to 2,5-D.N.N.A. are shown in figure 53B. Since there is no evidence for the loss of ȮH or HONO from the molecular ion of 2,5-D.N.N.A. it appears that route I is prefered in this system. Since fragmentation by route II requires a high electron density at the unoccupied peri position[216] it seems reasonable to

A. Loss of NO˙ and CO fragments



B. Loss of ˙OH and HONO fragments

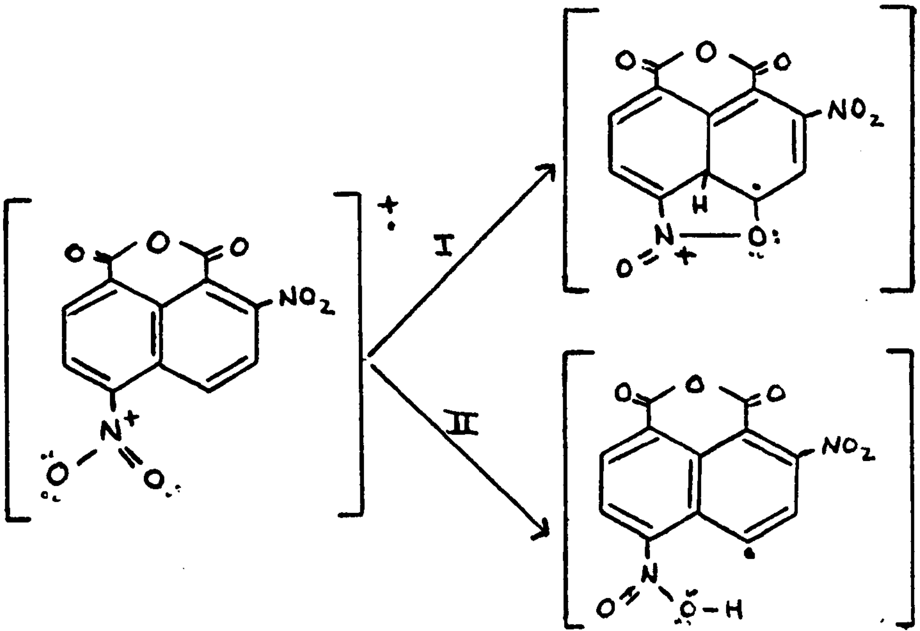


Figure 53 The rearrangement processes suggested to account for the observed fragmentations in nitroaromatic anhydrides.

assume that route II would be even less favoured in the nitroaromatic anhydrides than in the dinitronaphthalenes[201] because of the extra electron withdrawing effect of the anhydride group.

It appears that, overall, steric factors are the major contributors to the fragmentation pathways shown by the nitroaromatic anhydrides. The initial fragmentations of the molecular ion are well characterised but it is not possible to obtain a meaningful comparison between the spectra since there are a large number of possible fragmentation pathways for the formation of ions with relatively low m/e values.

CHAPTER 6

GENERAL CONCLUSIONS

General Conclusions

The introduction of electron withdrawing substituents into aromatic molecules leads to an electron deficiency in the π-system of the molecule. The extent of this electron deficiency as measured by the overall electron acceptor properties are, for a particular π-system, dependent upon the number of substituents and often their relative positioning within the system. In this work the relative electron deficiency of the π-systems based on the naphthalene moiety have been measured in compounds where the electron withdrawing substituents are nitro and anhydride groups.

Estimates of the electron affinity (Tables 8 and 9) and of the energy of the lowest vacant molecular orbital (Tables 3 and 4) of the acceptor molecules under investigation suggest that the electron deficiency in the π-systems increase in the order T.N.A. < 2,5-D.N.N.A. ~ 3,6-D.N.N.A. ~ 4,5-D.N.N.A. < Tri.N-2,3-N.A. ~ Tri. N-1,8-N.A. Although no values were obtained for T.N.N.A. due to the instability of the solid state complexes and the insolubility of T.N.N.A., it seems reasonable to assume that this compound would have the most electron deficient π-system of the compounds under investigation.

There is a marked decrease in the energy of the lowest vacant molecular orbital and a marked increase in the electron affinity of the acceptors in the anhydride series as the number of nitro groups is increased from one to two to three and a similar trend is expected on the addition of the fourth nitro group. However, it appears that to the accuracy of the present measurements the relative positioning of the nitro groups has very little effect either on the energy of the lowest vacant molecular orbital or the electron affinity of the acceptor. This is somewhat unexpected since it has been shown[5] that in the isomeric dinitronaphthalenes the acceptor strength is dependent on the relative positions of the nitro groups. However if, in the present study the solubility of the compounds had permitted measurements of the association constants for complex formation, some positional effects may have been observed.

It is of interest to note that the isomeric D.N.N.A. molecules are considerably stronger acceptors than T.N.A. This suggests that the anhydride group is at least equivalent in acceptor strength to two nitro groups since two nitro groups combined with the weakly electron donating acenaphthene bridge is a considerably less powerful electron accepting system in T.N.A. than is the anhydride group itself in any of the D.N.N.A. molecules.

The observation that T.N.A. is the least powerful of the acceptors at present under investigation is borne out by the results of the electron spin resonance study of the complexes formed with T.M.P.D. Only in the case of the T.N.A. complex was the spectrum of the T.M.P.D.$^{+}$ radical cation not observed and this suggests a lesser degree of electron transfer in the case of the T.N.A. complex than in the complexes formed with the anhydrides.

Measurements of the association constants and heats of formation for complex formation in selected complexes formed with aromatic hydrocarbons as donors show that the electron deficiency is similar in extent in the compounds under study to other well characterised electron acceptor compounds.

The results derived from the determination of the association constants for the complexes of T.N.A. with some methyl benzenes give an insight into the structure of the complexes.

The determined value of the chemical shift of the pure complex, Δ_0, suggests that the donor molecule is positioned over the aliphatic bridge of T.N.A. in the complexes. This implies that the aliphatic bridge in T.N.A. is the site of lowest electron density and this implication is corroborated both experimentally and theoretically in the investigation of the T.N.A. radical anion. When the aliphatic bridge is oxidised to the electron withdrawing anhydride function, the area of lowest electron density would be expected to be nearer to the centre of the aromatic ring system. Under these conditions if the donor molecule is large, a considerable steric influence will be exerted on the donor molecule by the nitro groups in the <u>peri</u> positions since these are twisted and of the plane of the ring. In such compounds as T.N.N.A., 4,5-D.N.N.A. and Tri.N-1,8-N.A. this interaction probably results in the observed instability of some of the solid complexes (see Table 1). In the case of Tri.N-2,3-N.A. although the 1- and 8- <u>peri</u> positions are occupied, the 4- and 5- <u>peri</u> positions are free and it is likely that the donor molecules are sited preferentially over the 4- and 5- positions. This will keep the steric interaction to a minimum and the complexes thus show a greater stability in the solid state. This situation might be expected since the results calculated for the π -electron densities show that the lowest electron densities occur at the 4- and 5- positions.

The positioning of the nitro groups in the π -systems is of importance in relation to the electron densities at the proton sites in the molecules. Consider, for example, the isomeric D.N.N.A. compounds. In the symmetrical 4,5-D.N.N.A. the electron densities at the proton sites are very similar (see Table 19) and both the experimental and calculated results suggest that the electron density at the proton sites ortho to the anhydride group is greater than at the sites ortho to the nitro groups. This observation further suggests the anhydride group to be a stronger electron acceptor than 2 nitro groups in the peri positions. In 3,6-D.N.N.A. and 2,5-D.N.N.A. the electron densities at the proton sites around the ring vary significantly and show well the dependence of the electron density on the position of the nitro groups.

It is interesting to compare, where possible, the experimentally observed electron density at a corresponding position in each of the compounds. The position chosen in each case is meta to the anhydride group, or in the case of T.N.A. meta to the acenaphthene bridge. The experimentally derived electron densities at these positions are given in the table.

Acceptor	Position	Experimental Electron Density
T.N.N.A.	3	0.0253
Tri.N-1,8-N.A.	6	0.0613
4,5-D.N.N.A.	3	0.0650
2,5-D.N.N.A.	3	0.0841
T.N.A.	3	0.1157

It is significant that the observed decrease in electron density at the proton site correlates with the order of electron acceptor ability of the compounds as determined from the results of the visible spectroscopic study. This method may be useful in the determination of relative electron acceptor abilities in structurally related compounds at times when other, more conventional, methods cannot be used.

Although the positioning of the nitro groups appears to have little effect on the overall electron deficiency of the systems under investigation, the relative stability of the molecules under electron impact shows a marked dependence on the positioning of the groups. Calculation has shown that in situations where electron withdrawing groups are ortho to each other, namely the anhydride group ortho to a nitro group or two nitro groups in the peri positions, that the nitro groups are no longer planar with the ring. In such cases it is found that the molecule readily fragments under electron impact and a fragment is lost such that any steric strain is reduced to a minimum. This steric effect causes the mass spectra of the isomers to exhibit significant differences in the intensities of corresponding peaks.

It might be expected that the position of the band due to the C-H stretching vibration in the infrared spectrum would vary as the number of nitro groups is increased. However, apart from a diminution in intensity there appears to be no systematic change in the position of the band.

The reactions of the anhydrides with bases cannot be compared with other systems since it has been shown that the final product of the reaction results from attack at the carbonyl group and not at a ring proton site. The carbonyl carbon atom has been shown, by calculation, to be the most likely site of attack by a base and a mechanism for the reaction has been proposed (see figure 40).

T.N.A. reacts with strong bases to form a Meisenheimer complex. However the only isolated product of the reaction results from the attack of two alkoxide groups and such a species is normally only observed in other well characterised acceptor molecules in the presence of an excess of the base[81]. It has been reported[122] that strong bases react with sym-trinitrotoluene and that abstraction of a hydrogen from the methyl group occurs. There is no evidence, however, for similar attack at the aliphatic bridge in T.N.A.

In the reaction of T.N.A. with weaker bases, such as amines, there is only evidence for charge-transfer complex formation. This however may well be the result of the insolubility of the complex which when precipitated inhibits further reaction. A similar situation is observed in the anhydrides where the complex is precipitated on formation. The initial formation of a charge-transfer complex in the reaction of anhydrides with amines is, however, consistent with previously reported results[197].

CHAPTER 7

APPENDICES

1. Some properties of π -electron systems

2. Computer programs used in this study

3. Courses attended during 1967 - 1970 in fulfilment of C.N.A.A. regulations

1. SOME PROPERTIES OF π -ELECTRON SYSTEMS

Conjugated molecules consist of a sigma-bonded network composed of sp^2 hybridised bonds which are localised and only overlap the nearest neighbour. The π -orbitals are assumed to be formed from the $2p_z$ atomic orbitals which give a delocalised π -system. In most theories of π -bonding the effect of the sigma-bonded network is ignored, this is justified on the grounds that there is a symmetry difference and an energy difference between the π -orbitals and the sigma orbitals and hence, to a first approximation, they do not interact.

In π -bonding theory the π -molecular orbitals are expressed as Linear Combinations of the π - Atomic Orbitals such that

$$\Psi_{MO} = \sum_i c_i \phi_{i\,AO}$$

By application of the Variation Theorem, it can be shown that there exist a set of secular equations such that:

$$\sum_i C_i(H_{ik} - ES_{ik}) = 0 \quad \text{where } k = 1,2,3......n$$

and where E is the orbital energy and the terms H_{ik} and S_{ik} will be defined later in the text.

These equations will have a non-trivial solution only if the determinant of the coefficients is equal to zero

i.e. $/H_{ik} - ES_{ik}/ = 0$

Thus given the values of H_{ik} and S_{ik}, the values of the orbital energies E and the coefficients may be determined by finding the latent roots and corresponding eigenvectors respectively of the matrix $\left[H_{ik} - S_{ik}\right]$.

The simplest method of solution is to use the assumptions of the Huckel Theory which may be summarised as follows:

(a) $H_{ii} = \alpha$ The terms H_{ii} are called Coulomb integrals. From the definition $H_{ii} = \psi_i H \psi_i \, d\tau$, the Coulomb integral represents approximately the energy of an electron in a carbon 2p - orbital. This is only an approximation since perturbations from other atoms are ignored.

(b) $H_{ij} = 0$ except when atoms i and j are bonded then $H_{ij} = \beta$ The terms H_{ij} are called resonance integrals. From the definition $H_{ij} = \psi_i H \psi_j \, d\tau$, these integrals represent the energy of interaction of two atomic orbitals. Since H_{ij} has only a finite value when atoms i and j are bonded the approximation implies that only nearest neighbour interactions are important in the Huckel theory.

(c) $S_{ii} = 1$ This is the Overlap integral and equivalent to treating the constituent atomic orbitals as orthogonal since in the Huckel theory S_{ij} is given the value of zero. This assumption greatly simplifies the mathematics but is rather drastic since it has been shown that S_{ij} has a value of around 0.25.

The π-electron theory also provides a method of calculating the charge density, q_i, on any atom, i, in the π-system. The general expression for the charge density is given by

$$q_i = \sum_j n_j C_{ij}^2$$

where n_j is the number of electrons in the molecular orbital ψ_j, C_{ij} is the coefficient of the atom i in the molecular orbital ψ_j, and the summation is over the occupied orbitals.

In electron spin resonance spectroscopy only the unpaired electron spin density is of importance and hence the expression is simplified to

$$q_i = C_{ij}^2$$

where C_{ij} is the coefficient of the atom i in the molecular orbital, ψ_j, which contains the unpaired electron.

The relatively simple Huckel theory of π -electron systems has proved remarkably successful in the prediction of resonance energies, polarographic reduction potentials, some electronic absorption bands and the spectral splittings derived from electron spin resonance spectroscopy. However, in general it is not a good theory for the prediction of the position of electronic absorption bands and it cannot deal with the details of electron spin resonance spectroscopy, for example negative spin densities.

There are several other theoretical approaches to π -electron systems and the one which is usually applied to predict the results of electron spin resonance spectroscopy is the method of McLachlan.

The occurrence of negative spin densities may be thought of as arising through the correlation of electrons of opposite spin which is neglected in the simple Huckel theory and even in restricted Self Consistant Field methods. McLachlan introduced some configuration interaction into the simple Huckel theory to allow for negative spin densities. It involves introducing a perturbation into the Huckel spin densities such that

$$q_i = C_{ij}^2 - \lambda \sum_s \pi_{is} C_{js}$$

where C_{ij} is the coefficient of the molecular orbital, ψ_j, which contains the unpaired electron, C_{js} is the coefficient of the first excited molecular orbital and λ is an empirical constant and normally takes the value 1.2β. The value of the atom-atom polarisability, π_{is}, is required and is derived from the simple Huckel theory using the equation

$$\pi_{is} = -4 \sum_{q} \sum_{j} (C_{qi}C_{js}C_{qs}C_{ji})/(e_q - e_j)$$

where the index q runs over the occupied molecular orbitals of the neutral molecule in the ground state and the index j refers to the vacant orbitals, the C_{qi}, C_{js}, C_{qs} and C_{ji} are orbital coefficients and e_q and e_j orbital energies in units of the carbon-carbon resonance integral

When there is easy access to a computer the theory is ideally suited to solution by this means and the program for such a solution is shown in this chapter in section 2(a).

2. COMPUTER PROGRAMS

Several computer programs have been written in the ALGOL 60 computing language suitable for use on the Elliott 4120 computer with line printer, digital plotter and magnetic tape peripheral devices. Certain procedures used in these programs were provided by the computer unit staff at Kingston Polytechnic, these being JACOBI, KEY and AXESON. The version of the program SIMUL was written in collaboration with Dr. A.J. Bowles, formerly of Kingston Polytechnic, who also wrote the procedure ALSAXES.

The programs which will be discussed are:

(a) MCLACHLAN - A program for molecular orbital calculations

(b) SIMUL - An electron spin resonance simulator

(c) ROVERS - A comprehensive program for calculating association constants from nuclear magnetic resonance data

(d) MSPEC - A general purpose mass spectrometry program

(e) THESISPLOTER - A simple linear plotting program

(a) MCLACHLAN

A program, translated from fortran and modified for use in the present study, for the solution of McLachlan type molecular orbital calculations. The output consists of the unpaired π -electron spin densities calculated using both the Huckel and McLachlan methods together with the orbital energies, and if required the orbital coefficients, the mutual polarisabilities of the atoms and the bond orders all of which are derived in the course of the calculation.

The input data is as follows:

(i) The number of atoms in the molecule

(ii) The name of the compound

(iii) The non-zero elements of the secular determinant, each element being preceeded by its row and column number. The list must be terminated by the value of the element in the nth row and nth column even if it has a value of zero

(iv) The number of occupied orbitals

(v) An index number, usually 1 for odd electron systems

(vi) The value of lambda, normally 1.2β.

```
MCLACHLAN
"BEGIN"
"INTEGER"NCOMP,NATOMS,I,J,KKK,NOCC,IND;
"REAL"RHO
"READ"NATOMS;
"BEGIN"
"REAL""ARRAY"H,Q[1:NATOMS,1:NATOMS];
"INTEGER""ARRAY"T[1:20];


"BOOLEAN" "PROCEDURE" KEY(I);
   "VALUE" I;  "INTEGER" I;
"BEGIN"
"CODE"
 $  $  $ LDR $ I
 $  $  $ ID:L $ 1
 $  $  $ SUBR:L $ 1
 $  $  $ JZ $ ZERO
 $  $  $ RTOK
 $  $  $ SML
 $  $ ZERO $ ST $ I
 $  $  $ CTUM
 $  $  $ AND $ I
 $  $  $ ST $ I
;
KEY:=I"NE"O
"END" KEY;

"PROCFDURE" JACOBI(A,S,N,RHO);
   "VALUE" N,RHO
   "INTEGER" N;
   "REAL" RHO
   "REAL" "ARRAY" A,S;
"BEGIN""COMMENT" SEGMENT ONE;
 "REAL" NORM1,NORM2,THR,MU,OMEGA,SINT,COST,INT1,V1,V2,V3;
         "INTEGER" I,J,P,Q,IND;

        "FOR" I:=1 "STEP" 1 "UNTIL" N "DO"
        "FOR" J:=1 "STEP" 1 "UNTIL" I "DO"
        "IF" I=J "THEN" S[I,J]:=1.0
        "ELSE" S[I,J]:=S[J,I]:=0.0;

        INT1:=0.0;
        "FOR" I:=2 "STEP" 1 "UNTIL" N "DO"
        "FOR" J:=1 "STEP" 1 "UNTIL" I-1 "DO"
        INT1:=INT1+2.0*A[I,J]↑2;
        NORM1:=SQRT(INT1);  NORM2:=(RHO/N)*NORM1;
        THR:=NORM1;  IND:=0;

MAIN:   THR:=THR/N;

MAIN1:  "FOR" Q:=2 "STEP" 1 "UNTIL" N "DO"
        "FOR" P:=1 "STEP" 1 "UNTIL" Q-1 "DO"
        "IF" ABS(A[P,Q])"GE"THR "THEN"
```

```
          "BEGIN" IND:=1;  V1:=A[P,P];  V2:=A[P,Q];
                 V3:=A[Q,Q];  MU:=0.5*(V1-V3);
                 OMEGA:="IF" MU=0.0 "THEN" -1.0
                         "ELSE"
  -SIGN(MU)*V2/SQRT(V2↑2+MU↑2);

SINT:=OMEGA/SQRT(2.0*(1.0+SQRT(1.0-OMEGA↑2)));
                  COST:=SQRT(1.0-SINT↑2);
                 "FOR" I:=1 "STEP" 1 "UNTIL" N "DO"
                 "BEGIN" "IF" I"NE"P "AND" I"NE"Q "THEN"
                         "BEGIN" INT1:=A[I,P];  MU:=A[I,Q];

A[Q,I]:=A[I,Q]:=INT1*SINT+MU*COST;

A[P,I]:=A[I,P]:=INT1*COST-MU*SINT
                          "END";
                         INT1:=S[I,P];  MU:=S[I,Q];
                         S[I,Q]:=INT1*SINT+MU*COST;
                         S[I,P]:=INT1*COST-MU*SINT
                 "END";
                 A[P,P]:=V1*COST↑2+V3*SINT↑2-2*V2*SINT*COST;

A[Q,Q]:=V1*SINT↑2+V3*COST↑2+2.0*V2*SINT*COST;

A[P,Q]:=A[Q,P]:=(V1-V3)*SINT*COST+V2*(COST↑2-SINT↑2)
          "END";

         "IF" IND=1 "THEN"
         "BEGIN" IND:=0;  "GOTO" MAIN1
         "END"
         "ELSE" "IF" THR>NORM2 "THEN" "GOTO" MAIN

"END" JACOBI;

"PROCEDURE" SECDET(DET,SIZE);
"VALUE" SIZE;        "INTEGER"SIZE;
"ARRAY" DET;
"BEGIN""COMMENT" SEGMENT TWO;
"INTEGER"I,J,X,Y;
"REAL"Z;
   "FOR"I:=1"STEP"1"UNTIL"SIZE"DO"
    "FOR"J:=1"STEP"1"UNTIL"SIZE"DO"
     "BEGIN"
         DET[I,J]:=0.0;
     "END";
START:
      "READ"X,Y,Z;
      DET[X,Y]:=Z;
      "IF" X=SIZE "AND" Y=SIZE "THEN" "GOTO" OUT
      "ELSE" "GOTO" START;
OUT:
"END" OF SECDET;

"PROCEDURE"WRITE(C,NS);
"VALUE"NS;           "INTEGER"NS;
"ARRAY"C;
"BEGIN"
"INTEGER"I,J,M,N;
```

```
        M:=0;
L50:    N:=M+1;
        "IF" KEY(1) "THEN" M:=M+5 "ELSE" M:=M+8;
        "IF" (NS-M) "LE" 0 "THEN" "GOTO" L100;
        "FOR" I:=1 "STEP" 1 "UNTIL" NS "DO"
        "BEGIN"
               "PRINT" ''L'';
        "FOR" J:=N "STEP" 1 "UNTIL" M "DO"
        "BEGIN"
              "PRINT" ''S2'',  ALIGNED(5,6),SAMELINE,Q[I,J];
        "END";
        "END";
              "PRINT" ''L''
              "GOTO" L50;
L100:
        "FOR" I:=1 "STEP" 1 "UNTIL"NS "DO"
        "BEGIN"
              "PRINT" ''L'';
        "FOR" J:=N "STEP"1 "UNTIL" NS "DO"
        "BEGIN"
               "PRINT" ''S2'', ALIGNED(5,6),SAMELINE,Q[I,J];
        "END";
        "END";
               "PRINT" ''L'';
"END" OF WRITE;
"PROCEDURE"  ORDER(H, Q, NATOMS);
"VALUE" NATOMS;      "INTEGER"NATOMS;
"ARRAY" H,Q;

 "BEGIN""COMMENT" SEGMENT THREE;
  "INTEGER" I, J, JJ, K;
  "REAL"    A, B, D;
  "FOR" I:=1 "STEP" 1 "UNTIL" NATOMS "DO"

   "BEGIN"
    A:=H[I,I];
    JJ:=I;
    "FOR" J:=I "STEP" 1 "UNTIL" NATOMS "DO"

     "BEGIN"
      "IF" A-H[J,J]>0.0 "THEN" "GOTO" LL1;
      "IF" A-H[J,J]=0.0 "THEN" "GOTO" LL1;
      JJ:=J;
      A:=H[J,J];
LL1: "END";
    B:=H[I,I];
    H[I,I]:=H[JJ,JJ];
    H[JJ,JJ]:=B;
    "FOR" K:=1 "STEP" 1 "UNTIL" NATOMS "DO"

     "BEGIN"
      D:=Q[K,I];
      Q[K,I]:=Q[K,JJ];
      Q[K,JJ]:=D;
     "END";
```

```
    "END";
  "END" OF ORDER;

"PROCEDURE" SPINDENSITY(Q,PI,NATOMS,NOCC);
"VALUE"NATOMS,NOCC;        "INTEGER"NATOMS,NOCC;
"ARRAY"Q,PI;
"BEGIN"
"REAL""ARRAY" RHOR[1:NATOMS]:
"INTEGER"I,J;
"REAL"GAMMA,SUM;
"READ" GAMMA;
      "PRINT"´´LS5``,´SPIN DENSITIES`;
      "FOR" I:=1 "STEP" 1 "UNTIL" NATOMS "DO"
      "BEGIN"
              SUM:=0.0;
       "FOR" J:=1 "STEP" 1 "UNTIL" NATOMS "DO"
       "BEGIN"
           SUM:=SUM+PI[I,J]*Q[J,NOCC]*Q[J,NOCC];
       "END";
           RHOR[I]:=Q[I,NOCC]*Q[I,NOCC]-(GAMMA*SUM);
           "PRINT" ´´LS5``,SAMELINE,DIGITS(2),I,´´S5``,
                                                SAMELINE,
                  ALIGNED(3,5), RHOR[I];
      "END";
"END" OF SPIN DENSITY;

"PROCEDURE" POLAR(H,Q,NATOMS,NOCC);
"VALUE"NATOMS,NOCC;        "INTEGER"NATOMS,NOCC;
"ARRAY"H,Q;
"BEGIN""COMMENT" SEGMENT FOUR;
"REAL""ARRAY"PI,BOOT[1:NATOMS,1:NATOMS];
"INTEGER"R,S,I,J,N,M;
"REAL"SUM;
   "FOR" R:=1 "STEP" 1 "UNTIL" NATOMS "DO"
   "BEGIN""IF" KEY(6) "THEN" "PRINT" PUNCH(3),DIGITS(2),R;
    "FOR" S:=R "STEP" 1 "UNTIL" NATOMS "DO"
    "BEGIN" "IF" KEY(5) "THEN" MTDUMP;
     "FOR" I:=1 "STEP" 1 "UNTIL" NOCC-1 "DO"
     "BEGIN"
      "FOR" J:=NOCC "STEP" 1 "UNTIL" NATOMS"DO"
      "BEGIN"
          "IF" H[J,J]-H[I,I] = 0.0 "THEN" "GOTO" L12;

BOOT[I,J]:=4*Q[R,I]*Q[S,J]*Q[S,I]*Q[R,J]/(H[J,J]-H[I,I]);
 L12:
       "END";
      "END";
      SUM:=0.0;
      "FOR" N:=1 "STEP" 1 "UNTIL" NOCC-1 "DO"
      "BEGIN"
       "FOR" M:=NOCC "STEP" 1 "UNTIL" NATOMS "DO"
       "BEGIN"
           SUM:=SUM+BOOT[N,M];
       "END";
      "END";
              PI[R,S]:=SUM;
```

```
                 PI[S,R]:=SUM;
 "END";
"END";
   "IF" KEY(4) "THEN" "GOTO" Q33;
   "PRINT" ''LS40``,'MUTUAL POLARIZABILITY `
          WRITE(PI,NATOMS);
   Q33;
          SPINDENSITY(Q,PI,NATOMS,NOCC);
   "END" OF POLAR;

"PROCEDURE" BONDORDER(Q,NATOMS,NOCC,IND);
"VALUE"NATOMS,NOCC,IND;
"INTEGER"NATOMS,NOCC,IND;
"ARRAY"Q;
"BEGIN""COMMENT" SEGMENT FIVE;
"REAL""ARRAY" P[1:NATOMS,1:NATOMS];
"REAL" SUM;
"INTEGER"I,J,K;
   "FOR" I:=1 "STEP" 1 "UNTIL" NATOMS "DO"
   "BEGIN"
    "FOR" J:=1 "STEP" 1 "UNTIL" NATOMS "DO"
    "BEGIN"
          SUM:=0.0;
     "FOR" K:=1 "STEP" 1 "UNTIL" NOCC "DO"
     "BEGIN"
          "IF" (NOCC-K) > 0 "THEN" "GOTO" L30;
          "IF" IND -1 < 0 "THEN" "GOTO" L30;
          "IF" IND -1 = 0 "THEN " "GOTO" L31;
L30:
      SUM:=SUM + 2*Q[I,K]*Q[J,K];
      "GOTO" L22;
L31:
      SUM:=SUM + Q[I,K]*Q[J,K];
L22:
     "END";
      P[I,J]:=SUM;
          P[J,I]:=P[I,J];
     "END";
    "END";
         "IF" KEY(4) "THEN" "GOTO" Q44;
          "PRINT" ''LS40``,'    BOND ORDERS    `;
          WRITE(P,NATOMS);
Q44:
"END" OF BONDORDER;

"PROCEDURE" ANDY(Q, NATOMS, NOCC);
 "VALUE" NATOMS,NOCC;            "INTEGER" NATOMS, NOCC;
 "ARRAY" Q;

  "BEGIN""COMMENT" SEGMENT SIX;
 "REAL" "ARRAY" P[1:NATOMS,1:NATOMS];
          "INTEGER" I, J;
   "FOR" I:=1 "STEP" 1 "UNTIL" NATOMS "DO"

    "BEGIN"
     "FOR" J:=1 "STEP" 1 "UNTIL" NATOMS "DO"
```

```
        "BEGIN"
         P[I,J]:=Q[I,NOCC]*Q[J,NOCC];
         P[J,I]:=P[I,J];
        "END";
      "END";
"IF" KEY(4) "THEN" "GOTO" Q99;

   "PRINT"''L``,''S30``,'HUCKEL SPIN DENSITY MATRIX`

   WRITE(P,NATOMS);
Q99:    "PRINT" ''LS5``,'HUCKEL SPIN DENSITIES`;
        "FOR" J:=1 "STEP" 1 "UNTIL" NATOMS "DO"
        "PRINT" ''LS5``,SAMELINE,DIGITS(2),J,''S5``,
                SAMELINE,ALIGNED(3,5),P[J,J];
 "END" OF ANDY;
   "PRINT" PUNCH(3),''L``,' PLEASE SEE THAT ALL KEYS ARE
                                                          OFF
UNLESS OTHERWISE INSTRUCTED THANKS `;
WAIT;

"IF" KEY(1) "THEN" PUNCH(1) "ELSE" PUNCH(4);
"BEGIN"
   I:=1;     INSTRING(T,I);
   I:=1;     OUTSTRING(T,I);
             SECDET(H,NATOMS);
              "IF" KEY(4) "THEN" "GOTO" Q55;
             "PRINT" ''LS40``,'HAMILTONIAN`;
             WRITE(H,NATOMS);
              Q55:
         RHO:=0.0000001;
             JACOBI(H,Q,NATOMS,RHO);
             ORDER(H,Q,NATOMS);
             "PRINT" ''LS5``,'EIGENVALUES`;
         "FOR" I:=1 "STEP" 1 "UNTIL" NATOMS "DO"

         "BEGIN"
                 "PRINT" ALIGNED(3,5),H[I,I];
         "END";
              "IF" KEY(4) "THEN" "GOTO" Q66;
             "PRINT" ''LS40``,'EIGENVECTORS`;
             WRITE(Q,NATOMS);
              Q66:
             "READ" NOCC, IND;
             POLAR(H,Q,NATOMS,NOCC);
             BONDORDER(Q,NATOMS,NOCC,IND);
             ANDY(Q,NATOMS,NOCC);
"END";
"END";
"END" OF MCLACHLAN;
```

(b) SIMUL

A program to simulate an electron spin resonance spectrum, and if required the position of each spectral line may be printed by operation of key 1. The program can deal with up to 5 couplings and spin quantum numbers of ½ and 1 only.

The input data is:

(i) Title of spectrum

(ii) Multiplicity of each splitting (5 values required)

(iii) The corresponding coupling constants (5 values required)

(iv) The corresponding spin quantum numbers (5 values required)

(v) Size of X axis (in cms)

(vi) Size of Y axis (in cms)

(vii) The number of increments in the spectral trace, the value usually taken is 1000.

```
SIMUL;
"BEGIN"
"REAL"ZERO,SCX,SCY,GAUSS,LIMIT,Y,YY,P,J1,J2,J3,J4,J5,B,Z,
                                DH,MIN,TOT,AA,XNEW,XAXIS,YAXIS;
"INTEGER"TT,G,K,L,M,N,O,S,T,U,V,W,D,E,CON,SIZE,AAA;
"INTEGER""ARRAY" NAME[1:30];
K:=1;      INSTRING(NAME,K);
"READ"S,T,U,V,W,J1,J2,J3,J4,J5;
Y:=S*T*U*V*W;
YY:=Y/W;
TOT:=0.0;       AAA:=1;
"BEGIN"
"REAL" "ARRAY"A1,X1[1:10],I,SPIN,CPL[1:5],A5,X5[1:Y],A2,
                                        X2[1:YY],X,TOTA[1:100];
   CPL[1]:=J1;
   CPL[2]:=J2;
   CPL[3]:=J3;
   CPL[4]:=J4;
   CPL[5]:=J5;
   CON:=0;
   "FOR" K:=1 "STEP" 1 "UNTIL" 5 "DO"
   "BEGIN"
         "IF" CPL[K] > 0.0 "THEN" CON:=CON+1;
   "END";
"BEGIN"

"BOOLEAN" "PROCEDURE" KEY(I);
   "VALUE" I;  "INTEGER" I
"BEGIN"
"CODE"
 $  $  $ LDR $ I
 $  $  $ LD:L $ 1
 $  $  $ SUBR:L $ 1
 $  $  $ JZ $ ZERO
 $  $  $ RTCK
 $  $  $ SML
 $  $ ZERO $ ST $ I
 $  $  $ CTOM
 $  $  $ AND $ I
 $  $  $ ST $ I
;
KEY:=I"NE"0
"END" KEY;
"INTEGER"
"PROCEDURE"NCR(N,R);
"VALUE"N,R;
"INTEGER"N,R;
"BEGIN"
"INTEGER"I,T,B;
T:=B:=1;
N:=N-1;
R:=R-1;
```

```
"FOR"I:=1"STEP"1"UNTIL"R"DO"
"BEGIN"
T:=T*N
B:=B*I;
N:=N-1;
"END";
NCR:=T/B;
"END";
"REAL""PROCEDURE"HOWBIG(Z,F,I,H);
"VALUE"F,I,H;
"REAL"I;
"INTEGER"F,H;
"ARRAY"Z;
"BEGIN"
"INTEGER"ANY;
"BEGIN"ANY:=(H+1)"DIV"2;
"IF"I=0.5
"THEN"
"BEGIN"
"IF"F=1"THEN"Z[F]:=1
"ELSE"Z[F]:=NCR(H,F)
"END"
"ELSE"
"BEGIN"
"IF"I=0.0"THEN"Z[F]:=1
"ELSE"
"BEGIN"
"IF"H=2*I+1
"THEN"Z[F]:=1
"ELSE"
"BEGIN"
"IF"H=4*I+1
"THEN"Z[F]:=ANY-ABS(ANY-F)
"ELSE"
"BEGIN"
"PRINT"PUNCH(3),'REQUIRE INFORMATION';
"READ"READER(3),Z[F];
 "END";
"END";
"END";
"END";
"END";
"END";


"PROCEDURE" QUICKERSORT(A,X,J);
  "VALUE" J; "INTEGER" J; "ARRAY" A,X;
  "BEGIN""COMMENT" SEGMENT TWO;
 "INTEGER" I,K,Q,M,P; "REAL" T,XY,TX,XX; "INTEGER""ARRAY"
                                                          UT,
    LT[1:LN(ABS(J)+2)/LN(2)+0.01];
    I:=M:=1;
N:  "IF" J-I>1 "THEN"
```

```
    "BEGIN" P:=(J+I) "DIV" 2; T:=A[P]; A[P]:=A[I];
      TX:=X[P];X[P]:=X[I];
         Q:=J;
      "FOR" K:=I+1 "STEP" 1 "UNTIL" Q "DO"
      "BEGIN" "IF" A[K]>T "THEN"
        "BEGIN" "FOR" Q:=Q "STEP" -1 "UNTIL" K "DO"
          "BEGIN""IF" A[Q]<T "THEN"
            "BEGIN" XY:=A[K];XX:=X[K]; A[K]:=A[Q];
                X[K]:=X[Q]; A[Q]:=XY; X[Q]:=XX; Q:=Q-1;
                                                "GOTO" L
            "END"
          "END" FORQ;
          Q:=K-1;  "GOTO" MM
        "END";
L:    "END" FOR K;
MM:     A[I]:=A[Q]; X[I]:=X[Q];
       A[Q]:=T;
     X[Q]:=TX;

      "IF" 2*Q>I+J "THEN"
      "BEGIN" LT[M]:=I; UT[M]:=Q-1; I:=Q+1
      "END" "ELSE"
      "BEGIN" LT[M]:=Q+1; UT[M]:=J; J:=Q-1
      "END";
      M:=M+1; "GOTO" N
    "END"
    "ELSE" "IF" I "GE" J "THEN"
    "GOTO" PP
    "ELSE"
    "BEGIN"
      "IF" A[I]>A[J] "THEN"
      "BEGIN" XY:=A[I];XX:=X[I]; A[I]:=A[J];X[I]:=X[J];
        A[J]:=XY;
        X[J]:=XX;
         "END";
PP:    M:=M-1;
      "IF" M>0 "THEN"
      "BEGIN" I:=LT[M]; J:=UT[M]; "GOTO" N
      "END"
    "END"
  "END" QUICKERSORT;
"PROCEDURE"TITLE(AAA,CON,XAXIS,YAXIS,SPIN,CPL,STRING);
"VALUE"AAA,CON,XAXIS,YAXIS;
"INTEGER"AAA,CON,XAXIS,YAXIS;
"ARRAY"SPIN,CPL;
"INTEGER""ARRAY"STRING;
"BEGIN""COMMENT" SEGMENT THREE;
"INTEGER"K;
WAY(0,4);
MOVEPEN((-XAXIS/2)*40,(YAXIS-5)*60);
"IF" AAA=1 "THEN"
"PRINT"PUNCH(5),´THEORETICAL E.S.R. LINE POSITIONS IN `
"ELSE"
```

```
"PRINT"PUNCH(5),´SIMULATED E.S.R. SPECTRUM OF `;
   PUNCH(5);
   K:=1;   OUTSTRING(STRING,K);
   "FOR" K:=1 "STEP" 1 "UNTIL" CON "DO"
   "BEGIN"
WAY(0,4);
         MOVEPEN((XAXIS/2)*40,(((YAXIS-7)*60)-(50*K)));
         "PRINT" PUNCH(5), ´ J `
         WAY(0,4);
         "IF" SPIN[K] = 0.5 "THEN"
         "PRINT"PUNCH(5), ´HYDROGEN`
         "IF" SPIN[K] = 1.0 "THEN"
         "PRINT"PUNCH(5), ´NITROGEN`;
"IF" SPIN[K] "NE" 0.5 "AND" SPIN[K] "NE" 1.0 "THEN" "GOTO"
                                                       OUT;
         WAY(0,4);
         "PRINT" PUNCH(5), ´ = `,ALIGNED(2,3),CPL[K];
"END";
   OUT:
   "END" OF TITLE;
"PROCEDURE"LINEFUNCTION(X,TOT,AC,TC,Z,DH,MIN,KY,TOTA,SIZE,
                                                      BIG);
"VALUE"KY,SIZE;
"INTEGER"SIZE,KY;
"REAL"BIG,TOT,Z,DH,MIN;
"ARRAY"AC,TC,TOTA,X;
"BEGIN""COMMENT" SEGMENT FIVE;
"INTEGER"J,K,T;
"REAL"XMIN,R;
T:=0;     XMIN:=X[1]-Z;
"FOR"J:=1"STEP"1"UNTIL"SIZE"DO"
"BEGIN"
    "IF" KEY(6) "THEN" MTDUMP
    "IF" KEY(5) "THEN" "PRINT" PUNCH(3),DIGITS(4),J;
T:=T+1;
    X[T]:=XMIN+Z;
    XMIN:=X[T];
     TOT:=0.0;
  TOTA[T]:=0.0;
"FOR"K:=1"STEP"1"UNTIL"KY"DO"
"BEGIN"
    R:=2*(X[T]-AC[K])/DH;
   "IF" (ABS(R)-MIN)<0.0 "THEN"
   TOT:=TOT+TC[K]*R/((3.0+R*R)*(3.0+R*R));
"END";
     TOTA[T]:=TOTA[T]+TOT;
    "IF" J=1 "THEN" BIG:= TOTA[1]
    "ELSE"
    "BEGIN"
           "IF" TOTA[T] >  BIG
           "THEN"
           BIG:=TOTA[T];
    "END";
    "IF" T=100 "OR" J=SIZE "THEN"
    "BEGIN"
           MTWRITE(2,X,1,100); T:=0;
           MTWRITE(2,TOTA,1,100);
    "END";
```

```
"END";
"END" OF LINEFUNCTION;
"PROCEDURE"DELETE(AA);
"VALUE"AA;
"REAL"AA;
"BEGIN""COMMENT" SEGMENT SIX;
WAY(0,4);
   MOVEPEN(10*158,0);
   CENCHAR(3);
   MOVEPEN(10*158+25,0);
   "PRINT" PUNCH(5),ALIGNED(2,2),AA,'  GAUSS`;
   MOVEPEN(-10*158,0);
   CENCHAR(3);
   MOVEPEN(-10*158-150,0);
   "PRINT" PUNCH(5),ALIGNED(2,2),-AA;
"END" OF DELETE;

   REQUIRES PROCEDURE AXESON.

"IF" KEY(4) "THEN" "GOTO" FIND;
   "IF" KEY(2) "THEN" PUNCH(1)
   "ELSE" PUNCH(4);
"IF" KEY(1) "THEN" "BEGIN"
K:=1;     OUTSTRING(NAME,K);
"END";

"FOR"K:=1"STEP"1"UNTIL"5"DO"
"BEGIN"
"READ"I[K];
SPIN[K]:=I[K];
"END";
"READ"XAXIS,YAXIS,SIZE;
"BEGIN"
G:=1;  D:=3;  E:=3;  GAUSS:=1;  P:=0.01;
ZERO:=0.0;
"FOR"K:=1"STEP"1"UNTIL"S"DO"
"BEGIN"
A1[K]:=ZERO-(S+1)*J1/2+J1*K;
HOWBIG(X1,K,I[G],S);
"END";
G:=G+1;
"FOR"K:=1"STEP"1"UNTIL"S"DO"
"BEGIN"
"FOR"L:=1"STEP"1"UNTIL"T"DO"
"BEGIN"
A2[L+T*(K-1)]:=A1[K]-(T+1)*J2/2+J2*L;
X2[L+T*(K-1)]:=X1[K]
"END";
"END";
"FOR"K:=1"STEP"1"UNTIL"S"DO"
"BEGIN"
"FOR"L:=1"STEP"1"UNTIL"T"DO"
"BEGIN"
HOWBIG(X1,L,I[G],T);
 X2[L+T*(K-1)]:=X2[L+T*(K-1)]*X1[L];
"END";
"END";
```

```
G:=G+1;
"FOR"K:=1"STEP"1"UNTIL"S"DO"
"BEGIN"
"FOR"L:=1"STEP"1"UNTIL"T"DO"
"BEGIN"
"FOR"M:=1"STEP"1"UNTIL"U"DO"
"BEGIN"
A5[M+U*(L-1+T*(K-1))]:=A2[L+T*(K-1)]-(U+1)*J3/2+J3*M;
X5[M+U*(L-1+T*(K-1))]:=X2[L+T*(K-1)];
HOWBIG(X1,M,I[G],U);
X5[M+U*(L-1+T*(K-1))]:=X5[M+U*(L-1+T*(K-1))]*X1[M];
"IF" KEY(1) "AND"V<1.5"THEN"
"BEGIN"
"PRINT"ALIGNED(D,E),A5[M+U*(L-1+T*(K-1))],
                              ALIGNED(3,1),X5[M+U*(L-1+T*(K-1))];

"END";
"END";
"END";
"END";

G:=G+1;
"IF"V>1.5"THEN"
"BEGIN"
"FOR"K:=1"STEP"1"UNTIL"S"DO"
"BEGIN"
"FOR"L:=1"STEP"1"UNTIL"T"DO"
"BEGIN"
"FOR"M:=1"STEP"1"UNTIL"U"DO"
"BEGIN"
"FOR"N:=1"STEP"1"UNTIL"V"DO"
"BEGIN"
A2[N+V*(M-1+U*(L-1+T*(K-1)))]
:=A5[M+U*(L-1+T*(K-1))]-(V+1)*J4/2+J4*N;
X2[N+V*(M-1+U*(L-1+T*(K-1)))]:=X5[M+U*(L-1+T*(K-1))];
HOWBIG(X1,N,I[G],V);
X2[N+V*(M-1+U*(L-1+T*(K-1)))]:=
X2[N+V*(M-1+U*(L-1+T*(K-1)))]*X1[N];
"IF" KEY(1) "AND"W<1.5"THEN"" PRINT"ALIGNED(D,E),
                        A2[N+V*(M-1+U*(L-1+T*(K-1)))],
  ALIGNED(3,1),X2[N+V*(M-1+U*(L-1+T*(K-1)))]
"END";
"END";
"END";
"END";
"END";
G:=G+1;
"IF"W>1.5"THEN"
"FOR"K:=1"STEP"1"UNTIL"S"DO"
"BEGIN"
"FOR"L:=1"STEP"1"UNTIL"T"DO"
"BEGIN"
"FOR"M:=1"STEP"1"UNTIL"U"DO"
"BEGIN"
"FOR"N:=1"STEP"1"UNTIL"V"DO"
"BEGIN"
```

```
"FOR"O:=1"STEP"1"UNTIL'W'DO"
"BEGIN"
A5[O+W*(N-1+V*(M-1+U*(L-1+T*(K-1))))]:=
            A2[N+V*(M-1+U*(L-1+T*(K-1)))]
-(W+1)*J5/2+J5*O;
X5[O+W*(N-1+V*(M-1+U*(L-1+T*(K-1))))]:=
           X2[N+V*(M-1+U*(L-1+T*(K-1)))];
HOWBIG(X1,O,I[G],W);
X5[O+W*(N-1+V*(M-1+U*(L-1+T*(K-1))))]:=
X5[O+W*(N-1+V*(M-1+U*(L-1+T*(K-1))))]*X1[O];
"IF" KEY(1)"THEN"
      "PRINT" ALIGNED(D,E),
A5[O+W*(N-1+V*(M-1+U*(L-1+T*(K-1))))],
               ALIGNED(4,1),
X5[O+W*(N-1+V*(M-1+U*(L-1+T*(K-1))))];
   "END";
"END";
"END";
"END";
"END";
"IF" W=1"AND"V"NE"1"THEN"
"BEGIN"
"FOR"K:=1"STEP"1"UNTIL"Y"DO"
"BEGIN"A5[K]:=A2[K];
X5[K]:=X2[K]
"END";
"END";
QUICKERSORT(A5,X5,Y);
MTDEST(2,´MOLE`,"FALSE");
"IF" GAUSS = 1 "THEN"
"BEGIN"
"PRINT"PUNCH(3),´´L`   LIMITING VALUE OF X AXIS = `
"READ" READER(3),AA;
    X[1]:=-AA;
    Z:=(2*AA)/SIZE;
    MIN:=20;
    AAA:=0;
    "READ"DH;
LINEFUNCTION(X,TOT,A5,X5,Z,DH,MIN,Y,TOTA,SIZE,B);
     MTMARK(2);
     MTMARK(2);
FIND:
"PRINT"PUNCH(3),´´L``,´SWITCH ON PLOTTER`;
WAIT;
AXESON(AAA,AA,-AA,B,-B,SCX,SCY,´GAUSS`,XAXIS,YAXIS);
DELETE(AA);
WAY(1,3);
MTREWIND(2);
MTSEEK(2);
    TT:=0;
    "FOR" K:=1 "STEP" 1 "UNTIL" SIZE "DO"
    "BEGIN"
             TT:=TT+1;
             "IF" TT=1 "THEN"
             "BEGIN"
```

```
                MTREAD(2,X,1,100);
                MTREAD(2,TUTA,1,100);
          "END";
          "IF" K=1 "THEN"
          MOVEPEN(X[1]*SCX,TUTA[1]*SCY);
          DRAWLINE(X[TT]*SCX,TUTA[TT]*SCY);
          "IF" TT=100 "THEN" TT:=0;
   "END";
"IF" KEY(3) "THEN" "GOTO" FIN;
TITLE(AAA,CON,XAXIS,YAXIS,SPIN,CPL,NAME);
FIN:
"END";
"END";
"END";
"END";
"END";
```

(c) ROVERS

A program to determine the association constants from nuclear magnetic resonance measurements normally using the equation of Foster and Fyfe[36] but by operation of key 3 the Hanna and Ashbaugh[35] equation may be used. The output consists of a plot appropriate to the equation used together with the association constant, its associated error and the value of Δ_0. The program normally uses the shift of the acceptor protons but by operation of key 2 it is converted to deal with the shift of donor protons. If it is required to analyse the results from the shift of more than one proton in the same molecule key 1 must be operated.

The input data is as follows:

(i) The number of proton shifts being studied
(ii) The number of measurements taken
(iii) The molecular weight of the donor (or acceptor)
(iv)

Wt. of empty n.m.r. tube	Wt. of tube, + donor	Wt. of tube + donor + acceptor solution
-	-	-
-	-	-
-	-	-
-	-	-
-	-	-

A.

(v) Title for graph
(vi) Shift of pure acceptor (or donor) proton
(vii) Shift of complexed acceptor (or donor) proton
-
-
-
-
-

B.

If the number of proton shifts studied is greater than unity, then if the protons are within the same molecule data B is repeated for each subsequent proton. If the protons are from a different system data A is repeated for each subsequent system.

```
ROVERS;
"BEGIN"


"REAL"W,A,XX,YY,XHIGH,XLOW,YHIGH,SCX,SCY,YLOW,
SM1,SM2,BG1,BG2,X1,X2,Y1,Y2,
 MM,MMM,STDV,SX,SXY,SXX,SV,SY,SXA,CC;

"INTEGER"N,J,R,F;
"READ"R;
"BEGIN"
"REAL""ARRAY"X,Y,Z,C,H,I,K,V,XA,XNEW,YNEW[1:N],Q[1:3];
"INTEGER""ARRAY"S1,S2[1:70];



"BOOLEAN" "PROCEDURE" KEY(I);
   "VALUE" I   "INTEGER" I;
"BEGIN"
"CODE"
 $  $   $ LDR $ I
 $  $   $ LD:L $ 1
 $  $   $ SUBR:L $ 1
 $  $   $ JZ $ ZERO
 $  $   $ RTOK
 $  $   $ SML
 $  $ ZERO $ ST $ I
 $  $   $ CTOM
 $  $   $ AND $ I
 $  $   $ ST $ I
;
KEY:=I"NE"0
"END" KEY;
 "PROCEDURE"SCAN(A,BIG,LITTLE,N);
      "VALUE"N;    "REAL" BIG,LITTLE;
      "INTEGER"N;
      "ARRAY"A;
      "BEGIN"
             "INTEGER"J;
             J:=1;
                  BIG:=LITTLE:=A[J];
             "FOR"J:=2"STEP"1"UNTIL"N"DO"
             "BEGIN"
                    "IF"A[J]>BIG"THEN"BIG:=A[J];
                    "IF"A[J]<LITTLE"THEN"LITTLE:=A[J];
             "END";
"END" OF SCAN;

   REQUIRES PROCEDURE ALSAXES.

QQQ:
"BEGIN"
```

```
 "READ"N,W;
   "IF" KEY(3) "THEN" "GOTO" HANNA;
   "IF" KEY(2) "THEN"
   "PRINT" PUNCH(1),´CONC OF ACCEPTOR´L2``
   "ELSE"
   "PRINT" PUNCH(1), ´CONC OF DONOR´L2``;

"FOR"J:=1"STEP"1"UNTIL"N"DO"
"BEGIN"
"READ"X[J],Y[J],Z[J];
H[J]:=((Y[J]-X[J])*1000.0)/(W*(Z[J]-Y[J]));
"PRINT"ALIGNED(2,3),H[J];
"END",
 Q:
F:=1;INSTRING(S1,F);
F:=1;INSTRING(S2,F);
"READ"A;
"PRINT" PUNCH(1),´´L`SHIFT´S4`SHIFT/CONC´L2``

"FOR"J:=1"STEP"1"UNTIL"N"DO"
"BEGIN"
"READ"C[J];
    "IF"KEY(2)"THEN"I[J]:=(C[J]-A)"ELSE"
    I[J]:=(A-C[J]);
    K[J]:=I[J]/H[J];
"PRINT" PUNCH(1),ALIGNED(2,3),I[J],SAMELINE,K[J];
X[J]:=I[J];
Y[J]:=K[J];
"END";
    SCAN(I,BG1,SM1,N);
    SCAN(K,BG2,SM2,N);


XX:=XLOW:=ENTIER(SM1-1);
YHIGH:=BG2+1;
YY:=YLOW:=ENTIER(SM2-1);
XHIGH:=BG1+1;
HANNA:  ;  "COMMENT" THIS BLOCK USES THE HANNA AND
                            ASHBAUGH METHOD
                OF DETERMINING K  TO ENTER IT SWITCH
                                        KEY 3 ;
     "IF" KEY(3) "THEN"
     "BEGIN"    "READ"N,W;
        "IF" KEY(2) "THEN"
        "PRINT"PUNCH(1),´´L` CONC. OF ACCEPTOR ´S10`
                                    SHIFT´L2``
        "ELSE"
        "PRINT"PUNCH(1),´´L` CONC.OF DONOR ´S13`
                                SHIFT´L2``;
        "FOR"J:=1"STEP"1"UNTIL"N"DO"
        "BEGIN"
            "READ"X[J],Y[J],Z[J],
            H[J]:=((Y[J]-X[J])*1000.0)/(W*(Z[J]-Y[J]));
```

```
          "END";
ASHBAUGH:  F:=1; INSTRING(S1,F); F:=1; INSTRING(S2,F);
          "READ"A;
             "FOR"J:=1"STEP"1"UNTIL"N"DO"
              "BEGIN"
                   "READ"C[J];
                   "IF" KEY(2) "THEN"
                   I[J]:=(C[J]-A)
                   "ELSE"
                   I[J]:=(A-C[J]);
                   "PRINT"PUNCH(1),ALIGNED(2,3),´´LS5``,
                                             SAMELINE,
          H[J],SAMELINE,´´S14``,I[J];
                   X[J]:=1/H[J];
                   Y[J]:=1/I[J];
              "END";
        SCAN(X,BG1,SM1,N);
        SCAN(Y,BG2,SM2,N);
        XX:=XLOW:=ENTIER(SM1-1);
        YHIGH:=BG2+1;
        YY:=YLOW:=ENTIER(SM2-1);
        XHIGH:=BG1+1;
       "END";
 "BEGIN"
"FOR"J:=1"STEP"1"UNTIL"N"DO"
   "BEGIN"
    XNEW[J]:=X[J]-XX;
    YNEW[J]:=Y[J]-YY;
   "END";
  SX:=SXY:=SXX:=SY:=SV:=SXA:=0.0;
  "FOR"J:=1"STEP"1"UNTIL"N"DO"
   "BEGIN"
   SX:=SX+X[J];SXY:=SXY+X[J]*Y[J];
   SXX:=SXX+X[J]*X[J];SY:=SY+Y[J];
   "END";
  MM:=(N*SXY-SX*SY)/(N*SXX-SX*SX);
  CC:=(SX*SXY-SY*SXX)/(SX*SX-N*SXX);
  "FOR"J:=1"STEP"1"UNTIL"N"DO"
   "BEGIN"
   V[J]:=Y[J]-MM*X[J]-CC;
   V[J]:=V[J]*V[J];
   SV:=SV+V[J];
   XA[J]:=X[J]-SX/N;XA[J]:=XA[J]*XA[J];
   SXA:=SXA+XA[J]
   "END";
  STDV:=SQRT(SV/(SXA*(N-2)));
"IF" KEY(3) "THEN"
"BEGIN"
"PRINT"PUNCH(1),´´L`SLOPE= `,SAMELINE,MM,´+OR-`,SAMELINE,
                                                STDV,
               ´´L`INTERCEPT= `,SAMELINE,CC;
MMM:=MM-STDV;
"FOR"J:=1"STEP"1"UNTIL"3"DO"
```

```
"BEGIN"
        Q[J]:=CC/MMM;
        MMM:=MMM+STDV;
"END";
"PRINT"PUNCH(1),´´L` K= `,SAMELINE,ALIGNED(3,3),Q[2],
                                                      ´+CR-`,
SAMELINE,(Q[1]-Q[3])/2,´´L` MAX. SHIFT= `, 1/CC,´´R100``;
"END"
"ELSE"
"BEGIN"
  "PRINT"PUNCH(1),´´L` K = `,SAMELINE,ABS(MM),´ CR-`,
                                          SAMELINE,STDV;
  MMM:=ABS(MM)-STDV;
"FOR"J:=1"STEP"1"UNTIL"3"DO"
"BEGIN"
Q[J]:=CC/MMM;
MMM:=MMM+STDV
"END";
"PRINT"PUNCH(1),´´L` MAX. SHIFT = `,SAMELINE,ALIGNED(3,3),
             Q[2],´ CR-`,SAMELINE,(Q[1]-Q[3])/2,´´L5R100``
"END";

  X1:=XLOW;
  Y1:=MM*X1+CC;
  X2:=XHIGH;
  Y2:=MM*X2+CC;

X1:=X1-XX;
Y1:=Y1-YY;
X2:=X2-XX;
Y2:=Y2-YY;
XHIGH:=XHIGH-XX;
XLOW:=XLOW-XX;
YHIGH:=YHIGH-YY;
YLOW:=YLOW-YY;
   "IF" KEY(3) "THEN"
   ALS AXES (XHIGH,XLOW,YHIGH,YLOW,SCX,SCY,´1/C`,´1/D`)
   "ELSE"
ALS AXES (XHIGH,XLOW,YHIGH,YLOW,SCX,SCY,´ D `,´D/C`);
"FOR"J:=1"STEP"1"UNTIL"N"DO"
"BEGIN"
MOVEPEN(XNEW[J]*SCX,YNEW[J]*SCY);
CENCHAR(3);
"END";
"IF" KEY(4) "THEN" "GOTO" TERM;

MOVEPEN(X1*SCX,Y1*SCY);
DRAWLINE(X2*SCX,Y2*SCY);
   "IF" KEY(3) "THEN"
   "BEGIN"
      MOVEPEN(500,1600);
      "PRINT"PUNCH(5), ´SLOPE= `,ALIGNED(4,3),MM,´+CR-`,
                              ALIGNED(2,4),STDV;
```

```
        MOVEPEN(500,1550);
        "PRINT"PUNCH(5),' INTERCEPT = `,ALIGNED(2,4),CC;
     "END"
     "ELSE"
     "BEGIN"

  MOVEPEN(500,1600);
 "PRINT"PUNCH(5),'SLOPE K = `,ALIGNED(4,3),ABS(MM),'+OR-`,
 ALIGNED(1,4),STDV;
 "END";
 TERM:
       MOVEPEN(200,1900);
       PUNCH(5);F:=1; OUTSTRING(S1,F);
       MOVEPEN(200,1850);
       F:=1; OUTSTRING(S2,F);
       MOVEPEN(0,2400);

R:=R-1;
     "IF" R>0.5 "THEN"
     "BEGIN"
   "IF" KEY(3) "THEN"
   "BEGIN"
      "IF" KEY(1) "THEN" "GOTO"ASHBAUGH
                  "ELSE" "GOTO"HANNA;
   "END";
          "IF" KEY(1) "THEN"
          "GOTO" QQ
          "ELSE"
          "GOTO" QQ;
          "END";
"END";
"END";
"END";
"END";
```

(d) MSPEC

A program designed for the analysis of mass spectral data. The program draws out the spectrum in the form of a bar diagram to a size chosen by the user, the intensity data is tabulated and if required a new data tape can be produced for use in a program to analyse metastable transitions.

The input data is as follows:

(i) The number of sets of data to be processed

(ii) The title of the spectrum

(iii) The size, denoted by 1, 2 or 3

(iv) A character, normally unity but may be 2 if m/2e peaks are being considered

(v) The number of peaks in the spectrum

(vi) The height of the base peak

(vii) The m/e value of the first peak

(viii) A list of heights of each of the peaks, if there is a sequence of n peaks of zero intensity this may be represented as -n on the data tape.

For subsequent sets of data items (ii) to (viii) are repeated, each set being terminated with the character E. This character is used in a data check and any errors in the data are reported to the operator.

```
MSPEC;

"BEGIN"
 "INTEGER" I,J,N,M,S,T,X,NN,Z,C,E,CC;
 "REAL" B,D,F,K,L,U,V,SUM,SIZE,G,H,GG,YY,LL,LIMIT;

"BOOLEAN" "PROCEDURE" KEY(I);
   "VALUE" I;  "INTEGER" I;
"BEGIN"
"CODE"
 $  $  $ LDR $ I
 $  $  $ LD;L $ 1
 $  $  $ SUBR:L $ 1
 $  $  $ JZ $ ZERO
 $  $  $ RTOK
 $  $  $ SML
 $  $ ZERO $ ST $ I
 $  $  $ CTOM
 $  $  $ AND $ I
 $  $  $ ST $ I
;
KEY:=I"NE"0
"END" KEY;

"INTEGER""ARRAY" A[0:50];
"READ"E;
"IF" E "GE" 0.5 "THEN"
"PRINT" PUNCH(3),´´L` SET KEYS -- IF NO INSTRUCTION GIVEN
SEE THAT ALL THE KEYS ARE UP -- THANK YOU ´L``;
WAIT;
CC:=0;
C:=E;
LLL:
I:=0; INSTRING(A,I);
"IF"KEY(1)"THEN"PUNCH(1)
"ELSE"
PUNCH(4);


"READ"SIZE, U,X,B,K;
"BEGIN"
"REAL""ARRAY" P[1:X+25],Q[1:X+25],R[1:X+25];
N:=0;T:=0;F:=K-U;V:=0;SUM:=0;YY:=0;
STEP A: F:=F+U; N:=N+1;P[N]:=F
"IF" N<X "THEN" "GO TO" STEP A;
STEP B: NN:=0;
        ADVANCE(1);
        LL:=DECODE(1);
        "IF" LL=37 "THEN" "GOTO" STEP B1A;
        "IF" LL=11 "OR" LL =13 "OR" LL=14 "OR" LL>15
        "AND" LL<26 "OR" LL=31
"THEN"
```

```
"BEGIN"
"READ"L;
"IF"L"GE"0.0"THEN""GOTO"LOOP1
"ELSE"
"GOTO"LOOP2;
LOOP1:
        T:=T+1;
        Q[T]:=L;
        R[T]:=L*100/B;
        SUM:=SUM+L;
        "GOTO"STEP B;
LOOP2:
        T:=T+1;
        NN:=NN+1;
        Q[T]:=0.0;
        R[T]:=0.0*100/B;
        SUM:=SUM+0.0;
        "IF"NN<ABS(L)"THEN""GOTO"LOOP2
        "ELSE"
        "GOTO"STEP B;
"END"
"ELSE"
"BEGIN"
            "GOTO" STEP B;
"END";
STEP B1A:       "IF" T=X "THEN"
                "BEGIN"
                "IF"KEY(2)"THEN"
                "BEGIN"
                T:=0;
                "GOTO" STEP C;
                "END"
                "ELSE"
                "BEGIN"
                T:=0;
                "GOTO" STEP B2;
                "END"
                "END"
                "ELSE"
                "BEGIN"
                "PRINT"PUNCH(3),´´L` DATA INCORRECT ON RUN`,
                                                            E-C+1,
T,´PEAKS GIVEN NOT`,X,´AS DECLARED--PROGRAM PROCEEDING´L``;

                "GOTO" FIN;
                "END";
STEP B2: "PRINT"´´L4``; I:=0; OUTSTRING(A,I);
"PRINT" PREFIX(´,`),
´´L`     M/E  , INTENSITY ,  REL INT  ,  100I/SIGMA I `
LOOP 4: T:=T+1;
        "IF" R[T]>V "THEN" V:=R[T];"IF" R[T]>0.1 "THEN"
        "PRINT" ALIGNED(5,2),
        P[T],PREFIX(´ ,`),ALIGNED(7,1), Q[T],
```

```
         ALIGNED(5,2), R[T],ALIGNED(5,2), Q[T]*100/SUM;
         "IF"T<X "THEN" "GO TO" LOOP 4;
"PRINT"''L4`SIGMA I = `,SAMELINE,ALIGNED(6,4),SUM,''F``;
"IF" KEY(5) "THEN"
"BEGIN"
       "PRINT"PUNCH(3),''L` METASTABLE LIMIT = `
       "READ" READER(3),LIMIT;
       "PRINT"PUNCH(1),''R100``;
       "FOR"T:=1 "STEP"1"UNTIL"X"DO"
       "BEGIN"
             "IF" R[T]>0.1 "AND"  P[T] "GE" LIMIT "THEN"
            "PRINT"PUNCH(1),ALIGNED(5,0),P[T];
       "END";
       "PRINT"PUNCH(1),''LR50HR50``;
       T:=0;
"END";
         V:=(ENTIER((V+9)/10))*10;
         S:=(ENTIER(P[1]/10))*10;
         D:=(ENTIER((P[X]+9)/10))*10;
         "GOTO"STEP D;

STEP C:
          LOOP 5:  T:=T+1;
                   "IF" R[T]>V "THEN" V:=R[T];
                   "IF" T<X "THEN" "GOTO" LOOP 5;
                   V:=(ENTIER((V+9)/10))*10;
                   S:=(ENTIER(P[1]/10))*10;
                   D:=(ENTIER((P[X]+9)/10))*10;
                   "GOTO"STEP D;
STEP D:"IF" KEY(3) "THEN" "GOTO" FIN;
        "IF"C"NE"E"THEN""BEGIN"
"PRINT"PUNCH(3),''L` NEW SPECTRUM ABOUT TO BE DRAWN
PEN CORRECTLY SET TYPE F/STOP TO PROCEED`
WAIT;"END"
"ELSE"
"BEGIN"
"PRINT"PUNCH(3),''L` SET PEN ONE INCH FROM EDGE OF PAPER`;
WAIT;
"END";
"IF"SIZE=1"THEN"
"BEGIN"
         G:=120;  GG:=5;   H:=800;  CC:=CC+1;
"END"
"ELSE"
"IF"SIZE=2"THEN"
"BEGIN"
         G:=200;   GG:=8;   H:=500;
"IF" CC "DIV" 2*2 "NE" CC
"THEN"
      "BEGIN"
      MOVEPEN(0,(G*6));
      CC:=0;
      "END"
```

```
      "ELSE"
          CC:=0;
"END"
"ELSE"
"IF"SIZE=3"THEN"
"BEGIN"
      G:=240;    GG:=10;    H:=300;
"IF" CC "DIV" 2*2 "NE" CC
"THEN"
     "BEGIN"
     MOVEPEN(0,(G*6)-40);
     CC:=0;
     "END"
     "ELSE"
         CC:=0;
"END";

 SET ORIGIN(H,0) ;WAY(0,3);
"FOR"J:=0 "STEP"1"UNTIL" 5 "DO"
 "BEGIN"
 DRAWLINE (0,G*J);
DRAWLINE (-12,G*J);
MOVEPEN(-130,G*J);
 "PRINT" PUNCH(5),DIGITS(2),ALIGNED(5,1),V*J/5;
MOVEPEN (0,G*J);
 "END";
MOVEPEN (-110,2*G),WAY(1,4);
"PRINT" PUNCH(5),'RELATIVE ABUNDANCE'
MOVEPEN (G,(5*G)-50), WAY(0,4);
PUNCH(5);
I:=0;OUTSTRING(A,I) PUNCH(1);
MOVEPEN (0,0);
"FOR" M:=0 "STEP"1"UNTIL"GG"DO"
"BEGIN"
 DRAWLINE(200*M,0);
DRAWLINE (200*M,-12);

MOVEPEN(200*M-100,-50);
WAY(0,3);
"PRINT" PUNCH(5),
ALIGNED(5,1),(S+(ENTIER((D-S+((GG*10)-1))/(GG*10)))*10*M);

MOVEPEN(200*M,0);
"END";

MOVEPEN(G,-100) WAY(0,4);
"PRINT"PUNCH(5),
'MASS:CHARGE RATIO (M/E)'

    YY:=((S+(ENTIER((D-S+((GG*10)-1))/(GG*10)))*10*GG)-S);

    YY:=(200*GG)/YY;
```

```
"FOR"Z:=1"STEP"1"UNTIL" X"DO"
"BEGIN"
"IF"Z"DIV"2*2"NE"Z"THEN"
"BEGIN"

MOVEPEN((P[1]-S-U)*YY+(Z*YY*U),0)
DRAWLINE((P[1]-S-U)*YY+(Z*YY*U),R[Z]*(G*5)/V);
"END"
"ELSE"
"BEGIN"
MOVEPEN((P[1]-S-U)*YY+(Z*YY*U),R[Z]*(G*5)/V);
DRAWLINE((P[1]-S-U)*YY+(Z*YY*U),0);
"END";
"END";
"IF" SIZE=1 "THEN"
"BEGIN"
          "IF" KEY(4) "THEN"
          MOVEPEN(0,(G*16))
          "ELSE"
          "BEGIN"
          "IF" CC "DIV"2*2 "NE" CC
          "THEN"
          MOVEPEN(0,(G*5)+300)
          "ELSE"
          MOVEPEN(0,(G*16))
          "END";
"END";
"IF" SIZE=2 "THEN"
MOVEPEN(0,(G*11))
"ELSE"
"IF" SIZE=3 "THEN"
MOVEPEN(0,(G*10));
"END";
FIN:    C:=C-1;
"IF"C"GE"0.5"THEN""GOTO"LLL;
"END";
```

(e) THESISPLOTER

A general purpose program for plotting straight line graphs on cartesian axes of suitable size for presentation in a thesis. The input data is as follows:

(i) Title of X axis

(ii) Title of Y axis

(iii) Number of graphs to be drawn on axes

(iv) Low limits of X and Y axes

(v) Upper limits of X and Y axes

(vi) The data sets for each graph consisting of the number of points and the coordinates of each point.

The output from the program is the graph together with the gradient of each line, its associated standard deviation and intercept.

```
THESISPLOTER;
"BEGIN"
"REAL"XX,YY,XHIGH,XLOW,YHIGH,SCX,SCY,YLOW,X1,X2,Y1,Y2,M,
STDV,SX,SXY,SXX,SV,SY,SXA,C;
"INTEGER"J,N,KK,NN;
"INTEGER" "ARRAY" INTA,INTB[1:20];

   REQUIRES PROCEDURES ALSAXES AND INATOS.


"PROCEDURE" ALSOUT(S1,S2,A,B);
   "STRING" S1,S2;
   "INTEGER" "ARRAY" A,B;
"BEGIN" "INTEGER" I;
          I:=1;   INATOS(A,I,S1);
          I:=1;   INATOS(B,I,S2);
          ALS AXES(XHIGH,XLOW,YHIGH,YLOW,SCX,SCY,S1,S2)
"END";

          J:=1;   INSTRING(INTA,J);
          J:=1;   INSTRING(INTB,J);
"READ"NN,XX,YY,XHIGH,YHIGH
     XLOW:=XX;         YLOW:=YY;
"FOR" KK:=1 "STEP" 1"UNTIL" NN "DO"
"BEGIN"
"READ" N
"BEGIN"
"REAL""ARRAY"X,Y,V,XA,XNEW,YNEW[1:N];


"FOR"J:=1"STEP"1"UNTIL"N"DO"
"BEGIN"
"READ"X[J],Y[J];
XNEW[J]:=X[J]-XX;
YNEW[J]:=Y[J]-YY;
"END";
SX:=SXY:=SXX:=SY:=SV:=SXA:=0.0;
"FOR"J:=1"STEP"1"UNTIL"N"DO"
"BEGIN"
SX:=SX+X[J] SXY:=SXY+X[J]*Y[J]
SXX:=SXX+X[J]*X[J] SY:=SY+Y[J];
"END";
M:=(N*SXY-SX*SY)/(N*SXX-SX*SX);
C:=(SX*SXY-SY*SXX)/(SX*SX-N*SXX);
"FOR"J:=1"STEP"1"UNTIL"N"DO"
"BEGIN"
V[J]:=Y[J]-M*X[J]-C
V[J]:=V[J]*V[J];
SV:=SV+V[J];
XA[J]:=X[J]-SX/N; XA[J]:=XA[J]*XA[J];
SXA:=SXA XA[J]
"END";
```

```
STDV:=SQRT(SV/(SXA*(N-2)));
"PRINT"PUNCH(4),´´L2S10``,´LINE `,SAMELINE,DIGITS(2),KK,
                                                                ´´L2``,
SAMELINE,M,´ OR-`,STDV,
,
Y=`,M,´X `,C,´´L2``;
    X1:=X[N];
    Y1:=M*X[N] C;
    X2:=X[1];
    Y2:=M*X[1] C;

X1:=X1-XX;
Y1:=Y1-YY;
X2:=X2-XX,
Y2:=Y2-YY;
XHIGH:=XHIGH-XX;
XLOW:=XLOW-XX;
YHIGH:=YHIGH-YY;
YLOW:=YLOW-YY;
"IF" KK=1 "THEN"
 ALS OUT(´



          INTA,INTB);
"FOR"J:=1"STEP"1"UNTIL"N"DO"
"BEGIN"
MOVEPEN(XNEW[J]*SCX,YNEW[J,*SCY);
CENCHAR(KK);
"END";

MOVEPEN(X1*SCX,Y1*SCY);
DRAWLINE(X2*SCX,Y2*SCY);

MOVEPEN(500,1600);
"END";
"END";
"END";
```

3. Short courses attended during the period 1967 - 1970 in fulfilment of C.N.A.A. regulations

1967 - 1968

Applications of Mass Spectrometry (6 lectures)

Interpretation of n.m.r. spectra (6 lectures)

Spectroscopic methods of trace analysis (6 lectures)

1968 - 1969

Algol programming (6 lectures)

The following sections of the M.Sc. course in Molecular Spectroscopy held at Kingston Polytechnic.

Microwave spectroscopy (3 lectures)

Vibrational spectroscopy (36 lectures)

Wave mechanics and electronic spectroscopy (10 lectures)

Meetings at Kingston Polytechnic

Spectroscopic methods in organometallic chemistry (2 days)

Infrared discussion group meeting on organometallics (1 day)

1969 - 1970

Symposia

Recent advances in gas-liquid chromatography

Kingston Polytechnic (1 day)

Mass Spectrometry Kingston Polytechnic (1 day)

Meeting of the photoelectron spectroscopy discussion group

Imperial College, London (½ day)

During the course at Kingston Polytechnic I have given a research colloquium and attended various research colloquia given by internal and external lecturers on research or topics of general chemical interest.

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