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THE INTERACTION OF ELECTRON ACCEPTORS WITH BASES—XIX

THE INTERACTION OF 1,3,5-TRINITROBENZENE WITH SECONDARY AMINES IN ACETONE SOLUTION

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Abstract—Addition of diethylamine to acetone solutions of 1,3,5-trinitrobenzene very rapidly yields intensely coloured red solutions. The properties of such solutions slowly alter with time. The course of these slower reactions has been followed by NMR spectroscopy. Intermediates with σ-complex (Meisenheimer Compound) structures are involved. An end-product is N,N-diethyl-4-nitroaniline. Similar reactions are observed with other secondary amines.

MANY aromatic amines interact with 1,3,5-trinitrobenzene (TNB) in solution to form 1:1 electron-donor-acceptor complexes in which the two molecules are held together by a combination of charge-transfer and van der Waals forces.[1] These so-called "charge-transfer" complexes are generally characterized by a broad featureless absorption band in the visible or near UV region owing to an intermolecular charge-transfer transition.[1,2] Although the addition of aliphatic amines to solutions of TNB gives rise to intensely coloured solutions,[3–6] yet by contrast with the interaction of aromatic amines, this colour does not appear to be the result of charge-transfer complex formation. Evidence has been adduced[7,8] for the formation of charge-transfer complexes between TNB and aliphatic amines, but the absorption assigned to the transition is well below 400 mμ and cannot therefore contribute to the colour. A second distinguishing feature is the relative rate of reaction: the rate of formation of charge-transfer complexes appears to be nearly instantaneous even when low-temperature stopflow techniques are used.[6] Relaxation times of the order of 10^{-12} secs have been measured for such processes.[9] By contrast the rate of initial colouration and the subsequent development which occurs when TNB is mixed with aliphatic amines is many orders of magnitude slower. The course of these reactions appears to depend on the particular aliphatic amine and on the solvent. Miller and Wynne-Jones have shown[4] that TNB with several different aliphatic amines in a variety of protic solvents

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[1] R. S. Mulliken, *J. Amer. Chem. Soc.* **74,** 811 (1952); *J. Phys. Chem.* **56,** 801 (1952).

[2] G. Briegleb, *Electronen-Donator-Acceptor-Complexe.* Springer Verlag, Berlin (1961).

[3] G. N. Lewis and G. T. Seabourg, *J. Amer. Chem. Soc.* **62,** 2122 (1940).

[4] R. E. Miller and W. F. K. Wynne-Jones, *J. Chem. Soc.* 2375 (1959).

[5] R. Foster, *J. Chem. Soc.* 3508 (1959); R. Foster and R. K. Mackie, *Tetrahedron* **16,** 119 (1961).

[6] C. R. Allen, A. J. Brook and E. F. Caldin, *J. Chem. Soc.* 2171 (1961).

[7] W. Liptay and N. Tamberg, *Z. Electrochem.* **66,** 59 (1962); G. Briegleb, W. Liptay and M. Canter, *Z. Physik. Chem.* (*Frankfurt*) **26,** 55 (1960).

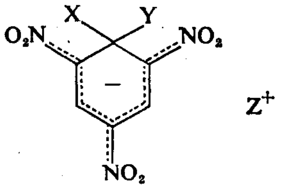
[8] R. Foster and R. K. Mackie, *J. Chem. Soc.* 3843 (1962).

[9] G. W. Noderbragt and J. Pelle, *Mol. Phys.* **1,** 97 (1957); J. E. Anderson and C. P. Smyth, *J. Amer. Chem. Soc.* **85,** 2904 (1963).

yields coloured solutions, the spectral characteristics of which alter with time. These workers have detected a weak e.s.r. signal in some solutions and have suggested that the colour results from the radical TNB^- formed by a single-electron transfer reaction.[10] Although other workers[11] have also detected e.s.r. signals in similar systems, the signal is so weak that it is difficult to argue that the major product is the radical TNB^-. Also the properties of TNB^-, generated electrolytically, show it to be sensitive to oxygen and to water,[12] neither of which has been completely excluded in the systems studied here.

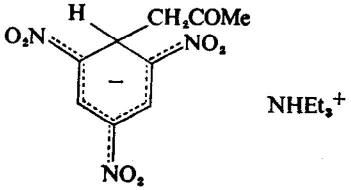
The solvent dependence of the processes is emphasized by the differences in stoicheiometry as measured by the intensity of the colours formed. In ethanolic solution[4] the stoicheiometry appears to be 1:1; in chloroform solutions[5] the ratio of amine to TNB is in many cases 3:1; and in acetone[6] the ratio is 2:1. In nearly every case the initial colour formation is complicated by further slow reactions.

Compounds with the general structure:



where X = H or alkoxy, Y = alkoxy and Z = alkali metal, were first described by Meisenheimer[13] and Lobry de Bruyn and van Leent.[14] From a detailed study, Briegleb, Liptay and their co-workers[7] have suggested a similar structure for the product formed by the addition of piperidine to an acetonitrile solution of TNB. A corresponding structure has been proposed[15] for the blue species formed when 1,3-dinitrobenzene is dissolved in liquid ammonia: in this case the attacking nucleophile appears[16] to be NH_2^-.

Recently it has been shown[17] that addition of triethylamine to TNB in acetone results in the formation of the salt:



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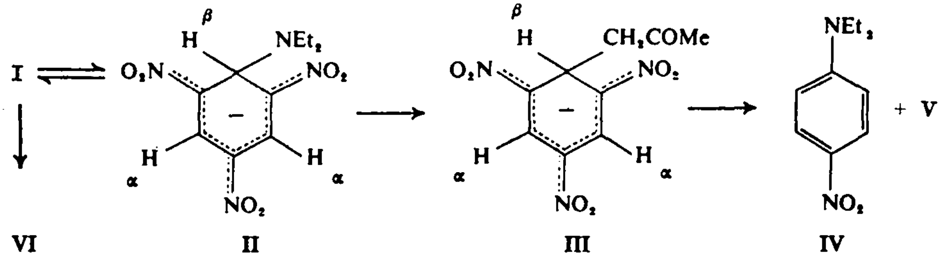
[10] R. E. Miller and W. F. K. Wynne-Jones, *Nature, Lond.* **186**, 149 (1960).
[11] D. Bijl, personal communication.
[12] R. L. Ward, *J. Amer. Chem. Soc.* **83**, 1296 (1961).
[13] J. Meisenheimer, *Liebigs. Ann.* **323**, 205 (1902).
[14] C. A. Lobry de Bruyn and F. W. van Leent, *Rec. Trav. Chim.* **14**, 150 (1895).
[15] J. D. Farr, C. C. Bard and G. W. Wheland, *J. Amer. Chem. Soc.* **71**, 2013 (1949).
[16] R. Foster and R. K. Mackie, *Tetrahedron* **18**, 161 (1962).
[17] R. Foster and C. A. Fyfe, *J. Chem. Soc.* (B), 53 (1966).

Attention is now concentrated on the system diethylamine, TNB in actone. The present paper describes the slower reactions of this system. The initial fast reactions are being studied at present by Caldin and Penkett.[18]

RESULTS AND DISCUSSION

The observations which have been made are discussed in relation to scheme 1. A study of the course of the reaction up to II is being made by Caldin and Penkett.[18]

$$\text{TNB} + 2\text{NHEt}_2 \rightleftharpoons \text{I}$$



Scheme 1

Most of the present study of the subsequent reactions has been made using NMR spectroscopy. Representative spectra are shown in Fig. 1. In the first few minutes after mixing an absorption occurs at $\delta = -8{\cdot}40$. If the ratio of amine to TNB is relatively low, say 1:1, then the absorption due to free TNB is also observed at $\delta = -9{\cdot}4$. Spectra showing these characteristics were first observed and correctly assigned by Penkett.[19] If only weak charge-transfer complexing had obtained, a single line would have been observed at some intermediate position resulting from the rapid exchange of TNB molecules between the free and complexed states.[20]

Recent work[19,21] has established that the protons attached to sp^2 hybridized carbon atoms (H_α in II) in such trinitropentadienate anion structures (Meisenheimer compounds) show a proton magnetic resonance absorption at ca. $\delta = -8{\cdot}40$. The absorption due to the proton attached to the "aliphatic" carbon (H_β in II) is not observed.

The absorption at $\delta = -8{\cdot}40$ gradually disappears as a second line develops close by at $\delta = -8{\cdot}48$ together with an absorption at $\delta = -5{\cdot}15$ (triplet, J = 6 c/s) due to H_α and H_β respectively in III (Fig. 1). Recently III has been obtained[17] by the action of a tertiary amine on TNB in acetone solution:

$$\begin{gathered}\text{NEt}_3 + \text{CH}_3\text{COCH}_3 \rightleftharpoons \text{NHEt}_3^+ + \text{CH}_3\text{COCH}_2^- \\ \text{CH}_3\text{COCH}_2^- + \text{TNB} \rightarrow \text{III}\end{gathered}$$

In that reaction the triethylammonium salt was isolated. The ion of III has also been

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[18] E. F. Caldin and S. A. Penkett, unpublished work.

[19] S. A. Penkett, Thesis, University of Leeds (1963).

[20] R. Foster and C. A. Fyfe, *Trans. Faraday Soc.* 61, 1626 (1965).

[21] M. R. Crampton and V. Gold, *J. Chem. Soc.* 4298 (1964).

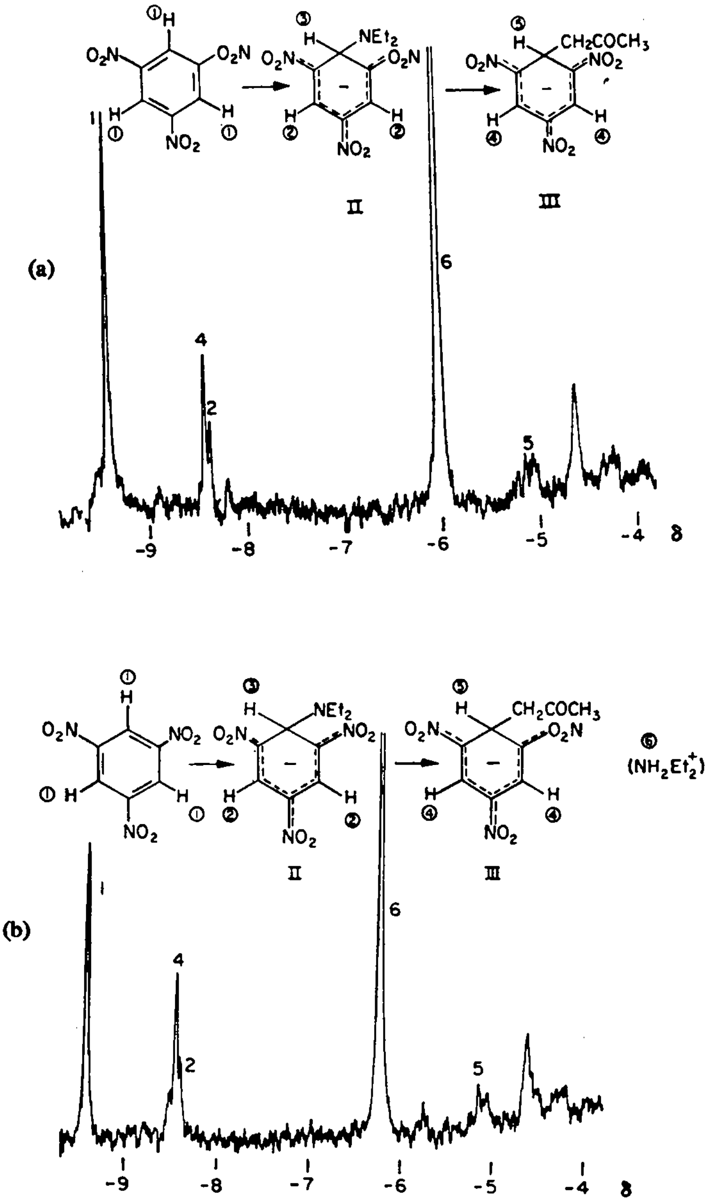
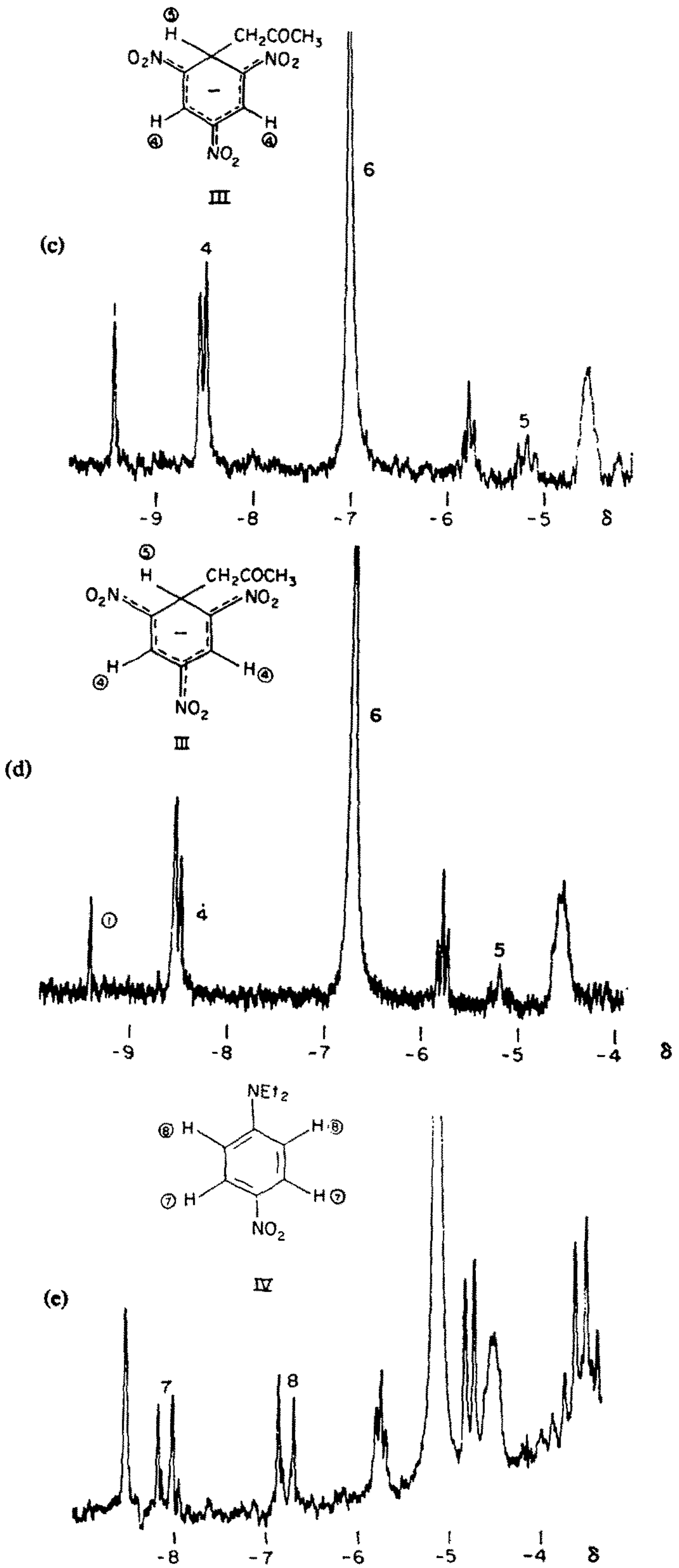
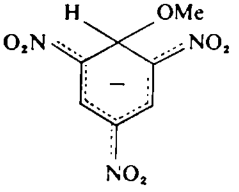


FIG. 1. PMR spectra of: (a) a 1:1 mixture of diethylamine + TNB in acetone after 10 min; (b) same after 30 min; (c) same after 2 hr; (d) same after 12 hr; (e) a 3:1 mixture of diethylamine + TNB in acetone after 60 hr.


(c)
CH₂COCH₃
O₂N
NO₂
NO₂
H
⑤
④
III
6
4
1
5
-9
-8
-7
-6
-5
δ
(d)
CH₂COCH₃
O₂N
NO₂
NO₂
H
⑤
④
III
6
①
4
5
-9
-8
-7
-6
-5
-4
δ
(e)
NEt₂
NO₂
H
⑧
⑦
IV
7
8
-8
-7
-6
-5
-4
δ

prepared[22] by the solvolysis of the Meisenheimer compound formed by the action of potassium methoxide on TNB.

$OMe^- + TNB$

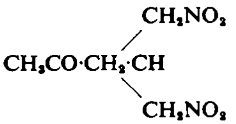


$+ CH_3COCH_3 \rightarrow III$

VII

The potassium salt of III was isolated.[22] The NMR spectrum of III obtained from either of these salts in acetone has absorptions at $\delta = -8{\cdot}4_8$ and $\delta = -5{\cdot}1_5$, identical with those obtained in the present work. Addition of large quantities of dry ether at this point precipitated a solid which after being dissolved in acetone, was shown by NMR spectroscopy to be a mixture of the diethylammonium salt of III and VI (see below).

As the diethylamine-TNB solution ages, the absorptions due to III gradually collapse, and are replaced by two doublets at $\delta = -8{\cdot}1_0$ and $\delta = -6{\cdot}7_8$ ($J = 10$ c/s). These are shown to result from the presence of N,N-diethyl-4-nitroaniline (IV) which was isolated from the reaction mixture as an ether–soluble material (experimental). A second ether–soluble product (V), separated from IV by its insolubility in aqueous acid, was obtained as an orange–yellow oil. The NMR spectrum of V, Fig. 2, shows a doublet at $\delta = -4{\cdot}6_8$ ($J = 6$ c/s, rel. intensity 4) a multiplet at $\delta = -3{\cdot}4_4$ (rel. intensity 1) a doublet at $\delta = -2{\cdot}7_7$ ($J = 6$ c/s, rel. intensity 2) and a singlet at $\delta = -2{\cdot}2_2$ (rel. intensity 3). It behaves as a primary aliphatic nitro compound. The infra-red indicates the presence of carbonyl and nitro groups. These observations and the elemental analysis are compatible with the structure:



$$CH_3CO{\cdot}CH_2{\cdot}CH\begin{cases}CH_2NO_2\\ CH_2NO_2\end{cases}$$

The mass spectrum of V shows no definite parent-ion. However the observed fragments of mass 43 (CH_3CO) and 30 (NO) give some support to the proposed structure. The various proton absorptions of IV and V are observable in the ethereal extract of the completed reaction. The relative intensities indicate that IV and V are formed in equimolar amounts.

Confirmation of the final step in the sequence is obtained from a study of the action of diethylamine on a solution of III in acetone. From observations of the NMR of a solution 0·5M with respect to III (as the potassium or triethylammonium salt) and M with respect to diethylamine at 33·5° over a period of several days, there is a 100% conversion of III into IV plus V. If the solvent is acetone-d_6, then N,N-diethyl-4-nitroaniline (2,6-d) is obtained.

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[22] R. Foster and C. A. Fyfe, *Tetrahedron* **21**, 3363 (1965).

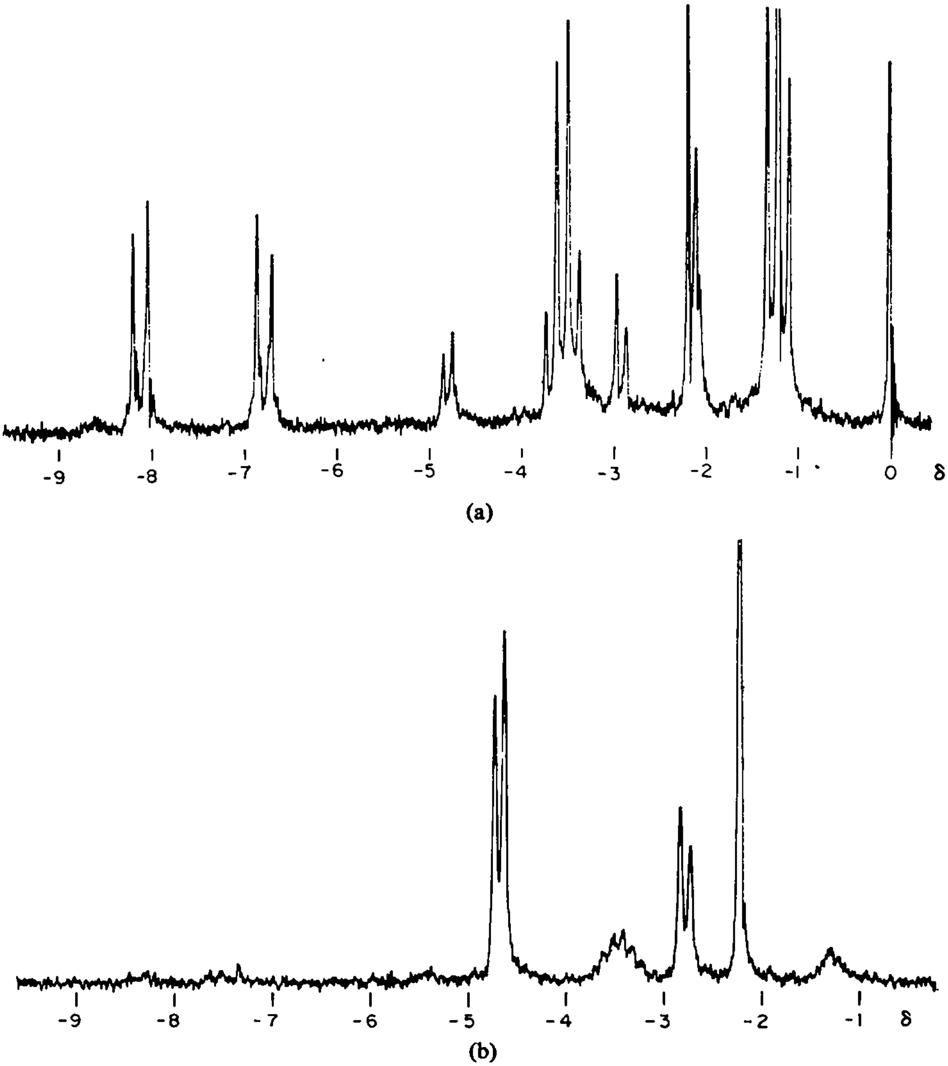

FIG. 2. PMR spectra in acetone-d_6 of: (a) the ether-soluble portion of the final reaction mixture from TNB + excess diethylamine + acetone (containing N,N-diethyl-4-nitroaniline + compound V); (b) the separated compound V.

The final mixture from the reaction of diethylamine with TNB in acetone not only contains the ether-soluble compounds IV and V but also a small amount of an ether-insoluble compound (VI). This substance accounts for other proton resonance lines which slowly build up in the NMR spectrum of the aging mixture. The NMR spectrum of the isolated material, dissolved in acetone-d_6 is shown in Fig. 3. The singlet at $\delta = -8{\cdot}5$ (rel. intensity 1) is observed at a very early stage in the reacting mixture (Fig. 1), (the absorptions at higher fields are obscured). This fact, combined with the observation already made that III is completely converted to IV, suggests that VI is formed by a side reaction from a stage in the sequence of the reactions prior to the formation of III. The broad line (Fig. 3) at $\delta = -7{\cdot}5$ (rel. intensity 2) intensifies

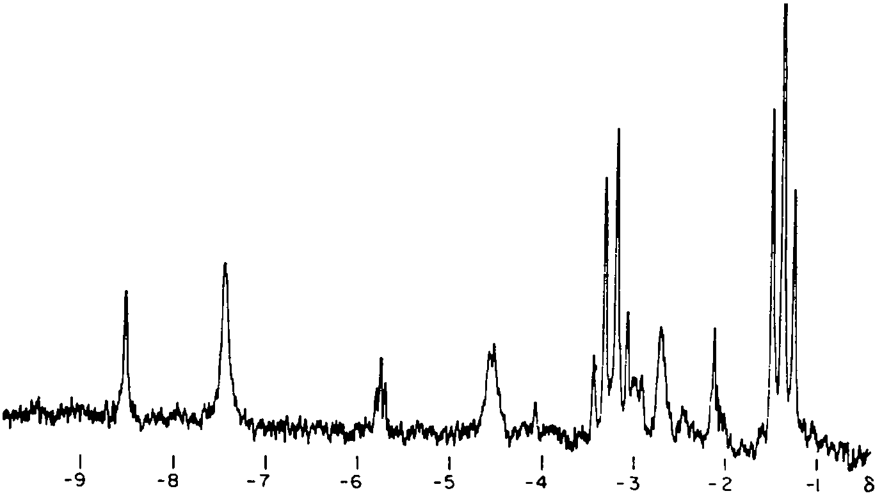

FIG. 3. PMR spectrum of compound VI in acetone-d_6.

and shifts to lower fields on the addition of diethylammonium chloride. This absorption is therefore due to protons directly attached to nitrogen in a diethylammonium ion. The intensities and positions of the quartet and triplet at higher fields are completely accounted for by the ethyl groups of this cation. Other absorptions are observed at $\delta = -5{\cdot}7_5$ (triplet, J = 3 c/s, rel. intensity 1) a broad, poorly-resolved doublet at $\delta = -4{\cdot}5$ ($J \approx 3$ c/s, rel. intensity 2) and a broad singlet at $\delta = -2{\cdot}7$ (rel. intensity 2). The weak absorption at $\delta = -2{\cdot}2$ is probably the result of contamination by free acetone, for which the compound appears to have a strong affinity. The intensity of this absorption is in excess of that which results from the proton impurity in the acetone-d_6 solvent. The IR spectrum of this compound indicates the presence of carbonyl and nitro groups. This spectrum is remarkably similar to that of the red product, described by Abe,[23] obtained by the addition of conc. aqueous ammonia solution to an acetone solution of TNB. The visible spectrum of this product and of VI are characterized by an absorption maximum at ca. 510 mμ which does not resemble the double-maxima spectrum typical of Meisenheimer compounds.[8,17] The structure of this compound remains unresolved.

Further evidence for the identity of II has been obtained from the NMR spectra sequence of solutions of the potassium salt of VII in dimethylsulphoxide to which an excess of diethylamine and then acetone was added (Fig. 4). Before the addition of amine there is an equilibrium between VII and a species assumed to result from the nucleophilic attack of dimethylsulphoxide on TNB.[22] In the presence of excess amine, only two singlets are observed at low fields: $\delta = -8{\cdot}4_2$ (rel. intensity 2) and $\delta = -5{\cdot}5_6$ (rel. intensity 1). These may be assigned to H_α and H_β respectively in structure II (there are some differences in chemical shifts consequent upon the different solvents). On addition of acetone to this mixture, the spectrum shows the appearance of III and its eventual disappearance and the final formation of IV, (Fig. 4). Absence in the final spectrum of absorptions which might be assigned to VI suggests that in the reaction of TNB with diethylamine in acetone originally discussed, VI is formed either directly from TNB or from I, rather than via II.

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[23] T. Abe, *Bull. Chem. Soc. Japan* **32**, 997 (1959).

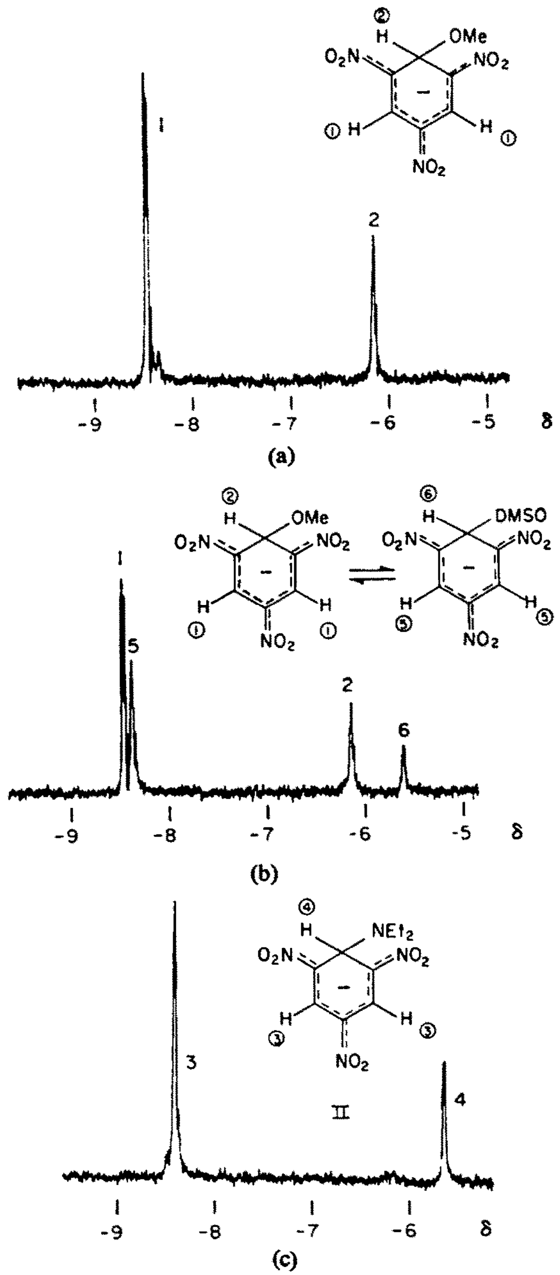
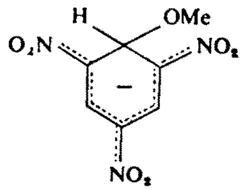
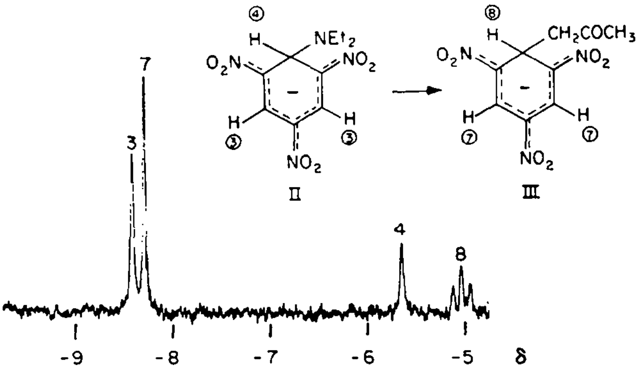


FIG. 4. PMR spectra of a solution of

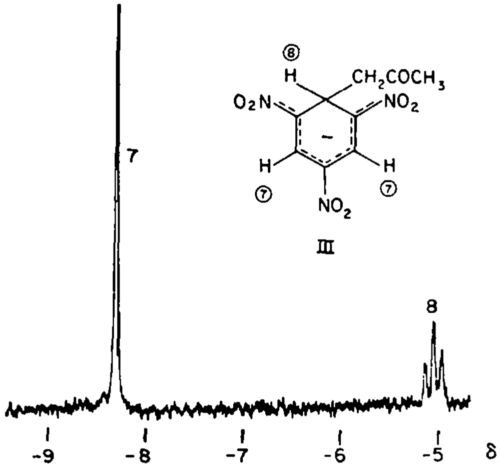


K^+ in dimethylsulphoxide:

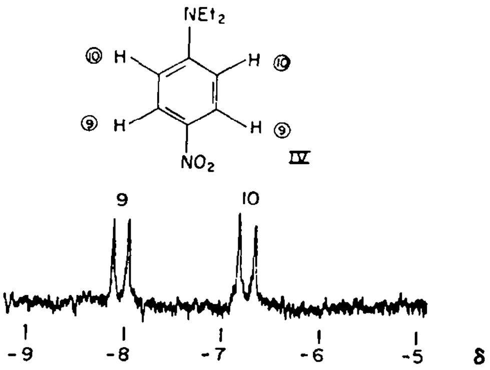
(a) immediately after dissolution; (b) same solution after 1 hr; (c) immediately after addition of excess diethylamine to either (a) or (b); (d) solution (c) after 1 hr; (e) solution (c) after 2 hr; (f) solution (c) after 12 hr.


④
H
NEt2
O2N
NO2
H
H
③
③
NO2
II
⑧
H
CH2COCH3
O2N
NO2
H
H
⑦
⑦
NO2
III
7
3
4
8
-9
-8
-7
-6
-5
δ

(d)


⑧
H
CH2COCH3
O2N
NO2
H
H
⑦
⑦
NO2
III
7
8
-9
-8
-7
-6
-5
δ

(e)


NEt2
⑩ H
H ⑩
⑨ H
H ⑨
NO2
IV
9
10
-9
-8
-7
-6
-5
δ

(f)

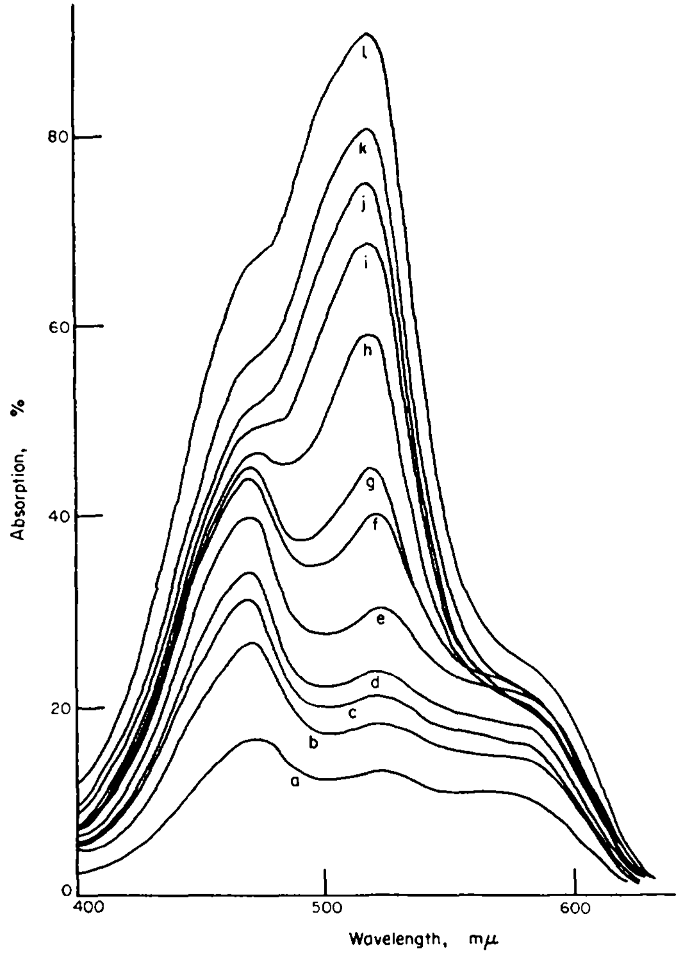


FIG. 5. Visible absorption spectra of an acetone solution 0·95 × 10^{-4} M with respect to 1,3,5-trinitrobenzene and 0·97 × 10^{-2} M with respect to diethylamine after (a) 1 min; (b) 4 min; (c) 7 min; (d) 11 min; (e) 23 min; (f) 43 min; (g) 54 min; (h) 96 min; (i) 131 min; (j) 161 min; (k) 181 min; (l) 265 min. All measured at 20°. No correction has been applied to compensate for the finite time of scanning (2 min).

The visible absorption spectra of very dilute solutions of diethylamine, TNB in acetone at room temp or below show an absorption similar to that of Meisenheimer compounds of established structure (Fig. 5). However it is the absorption due to VI which soon dominates the spectrum (Fig. 5) because of its relatively high extinction coefficient, ($\varepsilon = 1{\cdot}3 \times 10^4$ based on a m.w. = 358). Measurements of the visible absorption spectra of solutions at concentrations comparable with those used in the NMR measurements were not possible even with a short path-length cell because of the high optical absorptions of such mixtures.

EXPERIMENTAL

PMR spectra were measured using a Perkin–Elmer R.10 spectrometer operating at 60 Mc/s, 33·5°. Visible spectra were recorded using an Optica CF4DR spectrophotometer. All chemical shifts expressed as δ-values are measured in ppm from tetramethylsilane as an internal reference. Intensity measurements at maxima were measured using an Optica CF4 manually-operated spectrophotometer.

Reaction of TNB with diethylamine in acetone. In a typical determination TNB (1 g) and diethylamine (1.03 g) were dissolved in acetone (5 ml). The NMR spectrum was repeatedly scanned at frequent intervals over the first hr, thereafter becoming less frequent. After 90 hr the rate of change of the spectrum appeared to be very small. At this stage dry ether was added to the mixture when VI was precipitated as an amorphous red material. It was washed with ether and dried *in vacuo*. (Found: C, 46·86; H, 6·14; N, 15·77. $C_{10}H_{10}N_3O_7.C_4H_{12}N$ requires: C, 46·92; H, 6·19; N, 15·64%.) The solution remaining after the removal of VI was extracted with HCl aq, and the organic layer dried and the solvents removed *in vacuo* at 35–40°. The residual orange-yellow oil was dried over P_2O_5. (Found: C, 39·30; H, 5·56; N, 14·32. $C_6H_{10}N_2O_5$ requires: C, 37·89; H, 5·30; N, 14·73%.) Basification of the aqueous acid washings yielded IV (1·0 g; 11%), recrystallized from cyclohexane, m.p. 74·5°. (Found: C, 62·30; H, 7·38; N, 14·35. Calc. for $C_{10}H_{14}N_2O_2$: C, 61·83; H, 7·26; N, 14·42%.) The IR and NMR spectra were identical with those of an authentic specimen. Yields of IV, based on PMR intensities of the final reaction mixture spectra, of up to 40% were observed.

Reaction of TNB with piperidine in acetone. From similar reactions to the above, a compound corresponding to VI was obtained. Addition of piperidinium chloride to a solution of this compound enhanced the PMR absorption which may be assigned to the protons of this ion. The absorptions attributable to the anion are identical with those of the anion from the corresponding product from diethylamine. (Found: C, 48·43; H, 5·98; N, 15·08. $C_{10}H_{10}N_3O{\cdot}C_5H_{12}N$ requires: C, 48·64; H, 5·99; N, 15·13%.) From the ether-soluble portion of the final mixture of products 1-(4-nitrophenyl)-piperidine was obtained, yield 30%, recrystallized from cyclohexane, m.p. 102–103°. (Found: C, 63·97; H, 7·00; N, 13·39. Calc. for $C_{11}H_{14}N_2O_2$: C, 64·06; H, 6·84; N, 13·59%.) The IR and NMR spectra are identical with those of an authentic specimen.

Reaction of TNB with dimethylamine in acetone. From corresponding reactions with dimethylamine, only small amounts of ether-insoluble material were formed. The overall reaction was slower. From week-old solutions yields of 8–12% N,N-dimethyl-4-nitroaniline, recrystallized from cyclohexane, m.p. 163–164°, were obtained. (Found: C, 57·98; H, 6·16. Calc. for $C_8H_{10}N_2O_2$: C, 57·81; H, 6·07%.) The IR and NMR spectra are identical with those of an authentic specimen.

Acknowledgement—We wish to thank Dr. E. F. Caldin and Dr. S. A. Penkett for their cooperation, and the Royal Society for the provision of a variable path-length cell, also Dr. C. R. Falshawe and Dr. R. Alpin for mass spectra determinations.