Proton Nuclear Magnetic Resonance Studies of the Products formed by Polynitrobenzenes when dissolved in Liquid Ammonia

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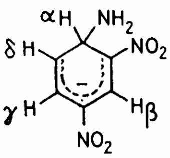
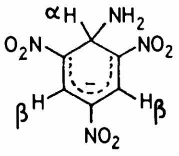
Proton n.m.r. spectra of the solutions formed by dissolving various polynitro- and substituted polynitro-benzenes in liquid ammonia have been measured. Products, with Meisenheimer-like structures, formed by nucleophilic attack of NH_2^- on the solutes have been identified. In a number of cases, attack by a second NH_2^- ion occurs. Some of the products show geometrical isomerism. With 2,4,6-trinitrotoluene there is no evidence for the formation of the carbanion formed by loss of a proton from the methyl group of 2,4,6-trinitrotoluene.

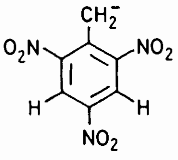
ALTHOUGH there have been many recent studies of the transient ions formed by the attack of nucleophiles on polynitroaromatic compounds in water, alcohols, dimethyl sulphoxide, and their mixtures,[1] relatively few studies have been made on the behaviour of such solutes in liquid ammonia. Early work showed such solutions usually have high electrical conductivity.[2-4] In 1949 Farr, Bard, and Wheland[5] proposed that the blue species formed when 1,3-dinitrobenzene is dissolved in liquid ammonia has structure (I). This structure is similar to that of the familiar 'Meisenheimer' or 'Jackson–Meisenheimer' compounds formed by the attack of alkoxides and other nucleophiles on 1,3,5-trinitrobenzene (TNB) and many substituted derivatives of TNB. In the formation of (I) it is reasonable to suppose that the substrate is attacked by the amide ion formed by the autoprotolysis of ammonia. This mechanism is substantiated by the intensification of the optical absorption when sodamide is added, and by the reverse effect when ammonium chloride is added.[6] Analogous structures for products formed by the attack of other nucleophiles on 1,3-dinitrobenzene (DNB) and on a range of 1-X-2,4-dinitrobenzenes in other ionising solvents have been made.[6]



(I)



(II)



(III)

The intense reddening which occurs when TNB is dissolved in liquid ammonia has similarly been accounted for in terms of the formation of a Meisenheimer-like compound (II).[6]

However, there has been no direct evidence for the structures (I) or (II). ^1H N.m.r. spectroscopy provides a possible means of substantiating such structures if they exist, and for clearly distinguishing between them and possible alternative ions such as the carbanion (III) in the case of reactions of 2,4,6-trinitrotoluene (TNT). In fact, it will be shown that for a number of substrates more than one reaction occurred.

EXPERIMENTAL

Commercial 1,3-dinitrobenzene was purified by recrystallisation, m.p. 89 °C (lit.,[7] m.p. 89.9 °C); likewise 1,3,5-trinitrobenzene, m.p. 123 °C (lit.,[8] m.p. 122.1—122.4 °C); 2,4,6-trinitrotoluene, m.p. 82 °C (lit.,[8] m.p. 81.1 °C). 2,4,6-Trinitroanisole was prepared by the nitration and subsequent decarboxylation of anisic acid, m.p. 68 °C (lit.,[9] m.p. 67—68 °C). 2,4,6-Trinitroethylbenzene was prepared by nitration of ethylbenzene, m.p. 37 °C (lit.,[10] m.p. 37 °C). Ethyl picrylacetoacetate, was prepared by the method of Kimura,[11] m.p. 96—98 °C (lit.,[11] m.p. 97.8 °C). Picrylacetone was obtained by the hydrolysis of ethyl picrylacetoacetate,[12] m.p. 89 °C (lit.,[12] m.p. 89 °C). Picramide, m.p. 192 °C (lit.,[13] m.p. 190—191 °C); *NN*-dimethylpicramide, m.p. 138 °C (lit.,[14] m.p. 138 °C); *NN*-diethylpicramide, m.p. 163 °C (lit.,[14] m.p. 163—164 °C); 2,4,6-trinitrothiophenetole, m.p. 44 °C (lit.,[15] m.p. 44—45 °C) were all prepared from picryl chloride. Liquid ammonia (I.C.I. anhydrous) was used without further purification.

Analytical.—Solutions were made up directly in 5-mm O.D. n.m.r. tubes. N.m.r. spectra were measured using a Bruker HX90 cw spectrometer fitted with a BST100—700 variable-temperature unit. Spectra are referenced to internal $SiMe_4$. Samples were run at temperatures varying between 210 and 235 K, the quoted positions being measured at 220 K. Because of the strong absorption by the solvent, no spectra could be measured beyond δ 2. For experiments with 1,3-dinitrobenzene and with ethyl picrylacetoacetate, the signals were weak and improved spectra were obtained by using a CAT.

Complex spectra were analysed using the Bruker BNC-28 ITRCAL line-fitting program which is based on LAOCN 3.

RESULTS AND DISCUSSION

1,3-*Dinitrobenzene.*—In liquid ammonia at 220 K, two sets of lines were observed in the n.m.r. spectrum: an approximately AM_2X system, attributable to free DNB on the basis of the similarity of the spectrum to that of DNB in non-interacting solvents such as carbon tetrachloride; the second set (Table) also appears to be a first-order system which could be directly assigned to structure (I). Of particular significance is the absorption at δ 4.66, corresponding to the proton H_α in (I), its high-field value reflecting the change from sp^2 to sp^3 hybridisation at this carbon on the formation of (I) from DNB. The pattern of the ^1H spectrum resembles closely that observed from the ion (IV) in acetone,[16] formed by the attack of $CH_3COCH_2^-$ on DNB in the presence of strong base in the Janovsky reaction.[17]

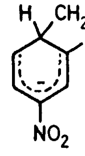
In liquid ammonia solutions of DNB, lowering the temperature intensifies the lines in the ^1H n.m.r. spectrum corresponding to the formation of (I) at the expense of

^{1}H N.m.r. spectra in liquid ammonia, δ in p.p.m. from $SiMe_4$; J/Hz

Structure [a]	δ of H_α [b]	δ of H_β [b]	δ of other protons [c]	J/Hz
(I)	4.66 (1 H, d)	8.32 (1 H, d)	6.80 (1 H, dd) H_γ	$J_{\alpha\delta} = 5$, $J_{\beta\gamma} = 1.5$
			5.61 (1 H, dd) H_δ	$J_{\gamma\delta} = 10$
(II)	5.50 (1 H, t)	8.37 (2 H, d)		$J_{\alpha\beta} = 1.0$
(V)	5.27 (2 H, d)	8.52 (1 H, t)		$J_{\alpha\beta} = 0.4$
(VI; R = Me)	5.36 (1 H, d)	8.31 (1 H, d)	2.23 (3 H, s) CH_3	$J_{\alpha\beta} = 1.2$
(VI; R = Et)	5.32 (1 H, d)	8.39 (1 H, d)	2.75 (2 H, q) CH_2	$J_{\alpha\beta} = 1.5$
(VI; R = OMe)	5.39 (1 H, d)	8.39 (1 H, d)	3.80 (3 H, s) CH_3O	$J_{\alpha\beta} = 1.5$
(VI; R = SEt)	5.42 (1 H, d)	8.22 (1 H, d)		$J_{\alpha\beta} = 1.5$
(VII; R = Me) (i) [d]	5.02 (2 H, d)	8.48 (2 H, d)	1.62 (9 H, s) CH_3	$J_{\alpha\beta} = 0.6$
(ii) [d]	4.90 (1 H, d)	8.44 (1 H, d)		$J_{\alpha\beta} = 0.8$
(VII; R = Et) (i) [d]	5.05 (2 H, d)	8.72 (2 H, d)	2.02 (10 H, q) CH_2CH_3	$J_{\alpha\beta} = 0.7$, $J(CH_2{-}CH_3) = 8$
(ii) [d]	5.03 (3 H, d)	8.74 (3 H, d)		$J_{\alpha\beta} = 0.6$
(VIII)		8.67 (1 H, d)	6.63 (1 H, s) H_γ	$J_{\beta\beta'} = 3$
		8.32 (1 H, d)		
(IX)	5.72 (1 H, s)	8.62 (1 H, s)	7.36 (1 H, s) H_δ	
(X)	5.28 (1 H, s)		7.60 (1 H, s) H_δ	
	5.32 (1 H, s)			
(XII)		8.77 (1 H, s)	3.85 (2 H, q)	$J_{CH_2-CH_3} = 7$
(XIII)	5.53 (1 H, s)	8.38 (1 H, s)		
(XIV; R = H)	5.38 (1 H, d)	8.44 (1 H, d)		$J_{\alpha\beta} = 1$
(XV; R = H) (a)	5.41 (3 H, s)			
	5.21 (1 H, s)			
(XV; R = Me)	5.45 (1 H, s)		2.89 (3 H, s)	
(XV; R = Et)	5.41 (1 H, s)		3.43 2.87 CH_2 [e]	$J_{CH_2} = 14$, $J_{CH_2-CH_3} = 7$
(XVI; R = OMe)	5.13 (2 H, s)		3.82 CH_3	
(XVI; R = SEt)	5.21 (2 H, s)		3.16 2.63 CH_2 [e]	$J_{CH_2} = 13$, $J_{CH_2-CH_3} = 8$

[a] Refers to structures in the text. [b] Most protons are identified in the structures: all α-H's are at ring sp^3 carbons; all β-H's are at ring sp^2 carbons in trinitro-substituted benzenes. [c] In 1,3-dinitrobenzene, the proton in a similar environment, namely at C(2) is similarly designated H_β. [d] Indicates two geometrical isomers; the relative integrals are compounded for the two isomers. [e] Non-equivalent methylene protons, see text.

the absorption due to DNB. The effect is reversible. Because of the uncertainty of the values of $[NH_2^-]$ in the solutions, we have not attempted to evaluate an equilibrium constant for the process:



(IV)

$$DNB + NH_2^- \rightleftharpoons (I)$$

SCHEME 1

but we have determined the quotient $Q = [(I)]/[DNB]$ at a number of temperatures from the relative integrals of the ^{1}H n.m.r. spectra. The linearity of the plot of $\log_{10}Q$ *vs.* T^{-1} suggests that $[NH_2^-]$ is effectively constant over the temperature range, and that the gradient of the line is a measure of the enthalpy change (−40 ± 10 kJ mol^{-1}) for the process (1). The fact that measurements for this plot were derived from more than one solution sample suggests that the equilibrium (1) is not sensitive to the precise amount of trace water which may be present in the liquid ammonia.

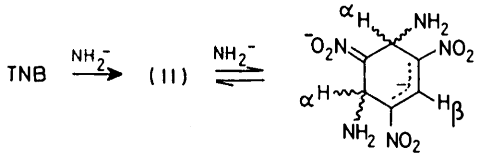
When the solvent from such solutions was allowed to boil off, pure DNB remained as a colourless residue, m.p. 89 °C.

1,3,5-*Trinitrobenzene*.—The red solution initially obtained by dissolving TNB in liquid ammonia shows only two ^{1}H absorptions, a low-field doublet (intensity 2) and a high-field triplet (intensity 1). These lines may be assigned to the two H_β's and H_α respectively in structure (II) (Table). The high-field position of this latter proton is typical of such structures and is well-established from studies of systems in other solvents.

With time this initial spectrum alters and another pair of lines appears, a low-field triplet (intensity 1) and a high-field doublet (intensity 2), at the expense of the original absorption (Table). The new spectrum may be assigned to a structure, or structures, represented by (V). Only one of the two possible geometrical isomers (*vide infra*) was positively observed. The n.m.r. spectrum could correspond to the *cis*- or the *trans*-isomer, with or without ring inversion. Changes in line shape over the limited temperature range possible (210—235 K) were not significant. The line positions of the absorptions due to the protons H_α and H_β are very close to those of the corresponding protons in (II), but of course now the relative intensities are reversed. Over and above the absorptions reported another weak line appears at $\delta = 4.99$. This may be due to the H_α protons of a second geometrical isomer of (V). We were not able to identify any proton corresponding to a H_β absorption for such an isomer. However, it would have had only half the intensity of the absorption at $\delta = 4.99$ and would possibly overlap with the absorption due to H_β of the isomer of (V) which was observed. If this signal is due to a second isomer of (V), the isomer ratio is estimated at *ca.* 20 : 1.

The initial set of lines never completely disappeared. At lower temperatures the second set of lines was enhanced at the expense of the set assigned to (II). The effect was reversible. At no stage was any absorption observed which could be assigned to free TNB. These observations are simply rationalised in Scheme 2.

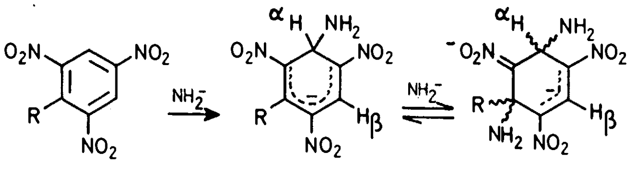
Removal of the ammonia from week-old solutions yielded red-brown residues. I.r. and n.m.r. spectroscopy indicated that these contained *ca.* 95% TNB.



(V)

SCHEME 2

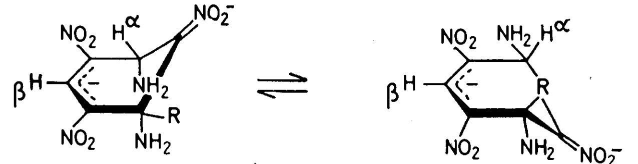
2,4,6-*Trinitrotoluene*.—Solutions of 2,4,6-trinitrotoluene (TNT) in liquid ammonia are dark red. Initially, two doublets of equal intensity, similar in position and coupling to the initial absorptions in the ^{1}H n.m.r. spectrum of solutions of TNB in liquid ammonia were observed (Table). These lines may be assigned to H_β and H_α in the ion (VI; R = Me). It was also possible to observe the absorption of the methyl protons (Table). Their relative intensity (3) confirms that the ion formed is not (III). From the n.m.r. spectra there is no evidence for free TNT in these solutions.



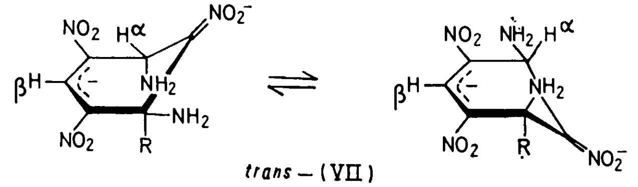
R = Me, Et (VI) (VII)

SCHEME 3

With time the spectrum corresponding to (VI; R = Me) decreases and two new sets of absorptions appear. Each set consists of a low-field doublet and a high-field doublet of equal intensity (Table), although the intensities of one set are about twice the intensities of the other set. This ratio is approximately constant over the temperature range 210—235 K. These two sets of absorptions are assigned to the ring protons in the two geometrical isomers represented by (VII; R = Me) (Table). The absorptions of the methyl groups in the two isomers coincide. However, the combined intensities of the appropriate absorptions for the two isomers indicate a ratio of 3 : 1 : 1 for the sets of protons Me : H_α : H_β as expected in structure (VII; R = Me). This type of geometrical isomerism has been reported separately by Crampton and Willison [18] and by Bernasconi and Bergstrom [19] for the 1 : 2 adduct formed from TNB and sulphite ion in aqueous solution. We may attempt to assign the sets of lines to the particular isomers of (VII; R = Me) which can be designated '*cis*' and '*trans*'. These isomers of (VII; R = Me) may be written as in Scheme 4. We assume that the energy barrier to ring-flexing is either low or else one of the two conformers in both *cis*-(VII) and *trans*-(VII) is energetically favoured, otherwise two more isomers would be observed. Of the conformers indicated in Scheme 3, it is only in *trans*-(VII) that there is a significant proximity between H_α and the amino-group on C(5). There is some evidence, for example in dihydrodeoxycodeine, for a long-range anisotropic deshielding effect along the *N*-atom–lone pair axis of an amino-group.[20] On the basis of this argument the H_α absorption corresponding to the *trans*-isomer (VII; R = Me) will be the absorption at 5.02 (the associated H_β absorption being at 8.48). These correspond to the preferred isomer, the lines having twice the intensity of the lines at 4.90 and 8.44 which we would assign to the *cis*-isomer (VII; R = Me).



cis-(VII)



trans-(VII)

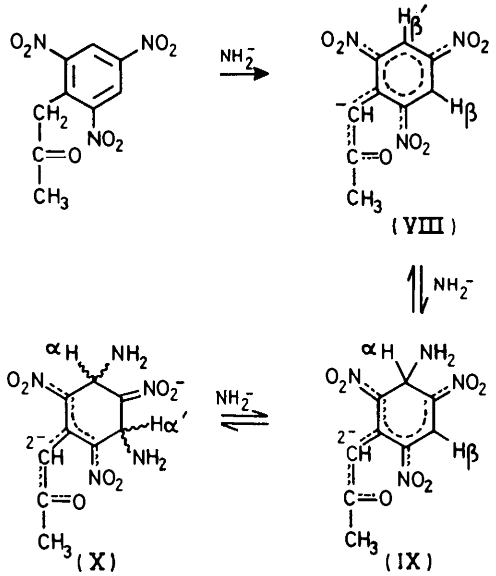
SCHEME 4

In solution the equilibrium between (VI; R = Me) and (VII; R = Me) was reversible with temperature. Removal of ammonia left a red residue which contained *ca.* 50% TNT.

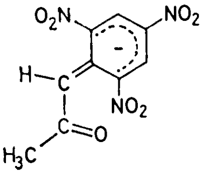
2,4,6-*Trinitroethylbenzene*.—The behaviour of 2,4,6-trinitroethylbenzene in liquid ammonia was similar to that of TNT, showing first the formation of (VI; R = Et) followed by (VII; R = Et) which again appeared to be the mixture of two isomers. The lines for corresponding protons in the two isomers were close together (Table) and were in the ratio 3 : 2. The less intense set of lines were rather broader than the other set. Crampton and Willison [18] in their study of the interaction of sulphite ion with TNB observed that the ^{1}H n.m.r. lines for one of the isomers TNB-3SO_3^{2-} were broader than the other. They suggested that the broadening was the result of ring inversion which in the case of the *cis*-isomer would be between two conformers with different environments for the ring nuclei, the sp^3 protons being either both pseudo-axial or both pseudo-equatorial; whereas for the *trans*-isomer the ring is probably much nearer to planar and any change is between equivalent conformers. If we apply Crampton and Willison's argument to our system we conclude that the *cis*-isomer, identified by the broader lines, is the less preferred isomer—as is the case both in their system and in the TNT-adduct described in the previous section. The lines corresponding to the ring-protons in (VI; R = Et) and (VII; R = Et) are very similar to those assigned to the corresponding protons in the TNT series (Table). The methylene protons of (VI; R = Et) and (VII; R = Et) are observable (Table). These have integrals of two relative to the ring-proton H_α and H_β, showing again that the observed ions are not carbanions formed by the loss of a proton attached to an exocyclic carbon atom.

The equilibrium between (VI; R = Et) and (VII; R = Et) is reversible with temperature. On evaporation a mixture of 2,4,6-trinitroethylbenzene and a red water-soluble compound which has not yet been identified was obtained.

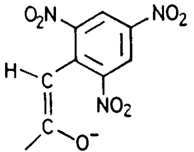
Picrylacetone (2,4,6-*Trinitrophenylpropan*-2-*one*).—Fresh solutions of picrylacetone in liquid ammonia show a low-field AB system (relative intensity 2) and a high-field singlet (relative intensity 1) (Table). These absorptions may be assigned to the carbanion (VIII). In a valence-bond description of (VIII) structures (VIIIa) and (VIIIb) will contribute significantly. These structures suggest that strong non-bonded interactions exist between one nitro-group and the acetonyl carbanionic group. Hence the non-equivalence of the ring protons (low field AB system) can be accounted for as a combination of the unsymmetrical nature of the substituent and the differential planarity of the two nitro-groups *ortho* to this substituent. We note that Fyfe and his co-workers [21] proposed a similar explanation for the non-equivalence of the two protons H(1) and H(2) in (XI) as observed in base solutions of TNT in methanol–dimethyl sulphoxide mixtures. An alternative explanation was considered by Fyfe for this product, namely, that steric hindrance by two *o*-nitro groups causes the CH$_2^-$ group to be rotated so that it is orthogonal to the ring. In such a case the two methylene protons would be non-equivalent since one would be *cis* and the other *trans* to the methoxy-group. The demand for delocalisation of the charge and hence the planarity of CH$_2^-$ with the ring in (XI) would seem to make this latter explanation of the non-equivalence of the two exocyclic protons unlikely. This possible basis for non-equivalence of these two protons has no analogue in the non-equivalence of H$_\beta$, H$_{\beta'}$ in (VIII).



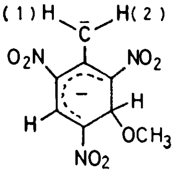
SCHEME 5



(VIIIa)



(VIIIb)

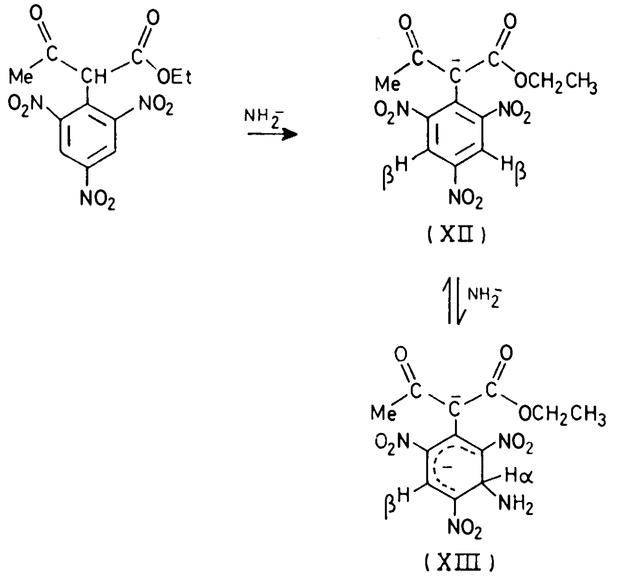


(XI)

With time the spectrum corresponding to (VIII) decreases and a new set of three lines develops (Table). This spectrum may be assigned to the di-anion (IX). The conversion of (VIII) into (IX) is reversible with temperature. At temperatures below *ca.* 225 K, yet another set of three lines appears. These we assign to (X) (Table). The protons marked H$_\alpha$, H$_{\alpha'}$ are not equivalent. This again would be the expected consequence of the carbanion moiety being coplanar with the ring. Changes in the spectra with temperature indicate that conversion of (IX) into (X) is also reversible.

On evaporation, a mixture of picrylacetone and an unidentified red compound is left.

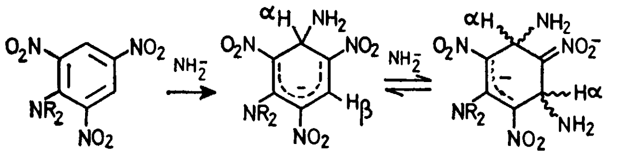
Ethyl Picrylacetoacetate.—A deep red solution is obtained by dissolving ethyl picrylacetoacetate in liquid ammonia. Two absorptions were observed, a singlet and a quartet in the ratio 1 : 1 (Table). This spectrum is assigned to (XII). In this case the carbanion moiety is too bulky to be coplanar with the ring. As a consequence the protons at the two unsubstituted positions in the ring are equivalent. With time two new absorp-



SCHEME 6

tions are observed to grow at the expense of the absorptions due to (XII). These are assigned to (XIII) (Table). The variation with temperature of these two sets of lines indicates that the equilibrium between (XII) and (XIII) is reversible.

Picramide.—On the addition of picramide to liquid ammonia a red solution is obtained which shows two doublets in the n.m.r. spectrum which can be assigned to (XIV; R = H) (Table). With time this spectrum diminishes and another spectrum consisting of two lines in the approximate ratio 3 : 1 develops. These are assigned to *cis*- and *trans*-isomers with the structure (XV; R = H) and correspond with the pair of isomers formed from TNB, having structure (VIIa) and (VIIb), with the difference that in the picramide case attack by the second amide-ion occurs at an unsubstituted position. In this case, we feel there is insufficient evidence to make the actual assignment of the lines at δ 5.21 and 5.41 with the particular isomer. Again, over the temperature range 210—240 K the equilibrium between (XIV) and (XV) is reversible. On evaporation pure picramide was left.

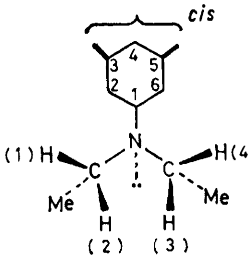


(XIV) (XV)

SCHEME 7

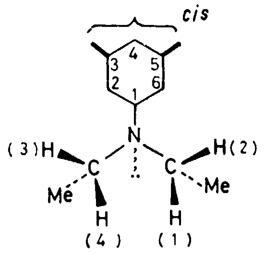
NN-*Dimethylpicramide*.—The red solution in liquid ammonia showed two lines in the ratio 3 : 1. These were assigned to the 2 : 1 adduct (XV; R = Me). The singlet at δ 5.45 suggests that only one of the possible isomers is formed. In the region of the methyl absorption, δ 2.89, there appeared to be the trace of another line which disappeared rapidly with time. This may be due to absorption by the methyl protons of the 1 : 1 adduct (XIV; R = Me). On evaporation of the solvent, pure *NN*-dimethylpicramide was left.

NN-*Diethylpicramide*.—Solutions of *NN*-diethylpicramide in liquid ammonia showed spectra commensurate with the 2 : 1 adduct (XV; R = Et) (Table). The methylene absorptions were complex, and analysed as non-equivalent. We suggest that this observation is consistent with the formation of the *trans*-isomer of (XV; R = Et). Consider first the *cis*-isomer, one conformer of which may be represented as:



cis—(XV)(a)

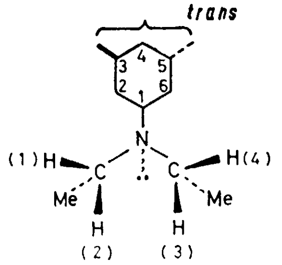
whence because of the C_2 plane through the N atom, H(1) ≡ H(4) and H(2) ≡ H(3). Inversion about N and rotation of the C(1)–N bond yields:



cis—(XV)(b)

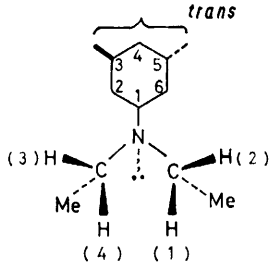
Now H(1) and H(4) occupy positions equivalent to those of H(3) and H(2) respectively in *cis*-(XV) (a). Hence all the protons H(1), H(2), H(3), H(4) are equivalent to one another.

For the *trans* isomer of (XV), we may represent one conformer as:



trans—(XV)(a)

For this structure, H(1) ≠ H(2) ≠ H(3) ≠ H(4). Inversion about N and rotation of the C(1)–N bond yields:

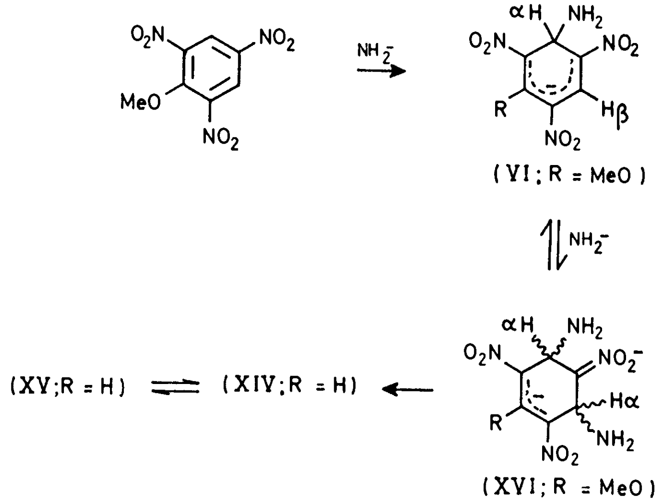


trans—(XV)(b)

Now H(1) occupies the position equivalent to H(3) in *trans*-(XV) (a) and likewise H(4) to H(2). Hence H(1) ≡ H(3) and H(2) ≡ H(4).

On evaporation of the solvent, pure *NN*-diethylpicramide was left.

2,4,6-*Trinitroanisole*.—Solutions of 2,4,6-trinitroanisole in liquid ammonia initially show two doublets and a singlet in the ratio 1 : 1 : 3. These may be assigned to the 1 : 1 adduct (VI; R = OMe) formed by nucleophilic attack by NH_2^- at the 3-position of 2,4,6-trinitroanisole (Table) (Scheme 8). With time several new absorptions appear at the expense of the initial spectrum. These include the absorptions by the picramide adducts (XIV; R = H) and (XV; R = H) identified from the spectra obtained from observations on solutions of picramide in liquid ammonia (see above). Two other lines, δ 3.83 and 5.13 may be assigned to (XVI; R = OMe) (Table). Although only one set of lines was observed for this structure, it is possible that another geometrical isomer is formed to some extent, yet not observed because of the absorptions of all the other species present, not least (XIV; R = H) and (XV; R = H). Changes in the intensities of the absorptions as the temperature is altered are consistent with the reactions in Scheme 8. An otherwise unassigned singlet at δ 3.03 is due to free methanol formed in the process (XVI; R = OMe) ⟶ (XIV; R = H). The assignment was confirmed by the addition of methanol. Eventually the absorptions due to (VI; R = OMe) and (XVI; R = OMe) disappear leaving only the picramide adducts and the methanol singlet. On evaporation pure picramide remains.



SCHEME 8

2,4,6-*Trinitrothiophenetole*.—The overall behaviour of solutions of 2,4,6-trinitrothiophenetole in liquid ammonia were similar but slower than those of 2,4,6-trinitroanisole, giving (VI; R = SEt) and (XVI; R = SEt) (Table), and eventually the adducts (XIV; R = H) and (XV; R = H) with the liberation of ethanethiol. The methylene protons of the ethyl group were not equivalent in either (VI; R = SEt) or (XVI; R = SEt). This would be expected for the former adduct. With respect to the latter, the observation suggests that a *trans*-type isomer has been formed, which would then account for the diastereotopic nature of the two protons concerned. It was not possible to resolve sufficiently the spectra for an analysis to be made in the case of the 1 : 1 adduct, but this was achieved for the 2 : 1 adduct (XVI; R = SEt) (Table).

When the solution finally was evaporated, pure picramide remained.

[8/1195 *Received*, 29*th June*, 1978]

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