

^{13}C Nuclear Magnetic Resonance of Jackson–Meisenheimer (σ -Anionic)-type Products formed when 1,3,5-Trinitrobenzene, and when 2,4,6-Trinitrotoluene, are dissolved in Liquid Ammonia

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1:1 and 2:1 products formed by nucleophilic attack of ammonia in liquid ammonia solutions of 1,3,5-trinitrobenzene and of 2,4,6-trinitrotoluene have been observed by ^{13}C n.m.r. spectroscopy. In the latter reaction three 2:1 products are observed: two geometrical isomers formed by attack at the 1- and 3-position of 2,4,6-trinitrotoluene and a structural isomer formed by attack at the 3- and 5-position.

Ammonia behaves as a nucleophile towards π -electron-deficient molecules such as 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT) especially when these molecules are dissolved in the effective ionising solvent liquid ammonia. There is extensive evidence¹ that, at least in the case of TNB, the initial step is the formation of the zwitterion (1) followed by deprotonation by a second molecule of ammonia to form the anionic species (2) (Scheme). The product is a typical Jackson–Meisenheimer³ (σ -anionic) compound.^{4–9} An earlier ^1H n.m.r. study¹⁰ of the TNB–liquid ammonia system had shown that, at 220 K, the initial formation of (2) was rapidly followed by almost complete conversion into (3). Only one of the two possible geometrical isomers represented by (3) was observed. From the ^1H n.m.r. absorption spectra, it was apparent that the formation of (3) from (2) was reversible, although at 240 K the equilibrium was still in favour of (3). No free TNB was observed.

A corresponding ^1H n.m.r. study¹⁰ of the products formed by dissolving TNT in liquid ammonia produced rather similar results. However, the general Scheme, with the formation of (4) and (5), both geometrical isomers of (6), was observed. In those experiments the structural isomer (7) was not detected.

We have now restudied both systems using ^{13}C n.m.r. spectroscopy.

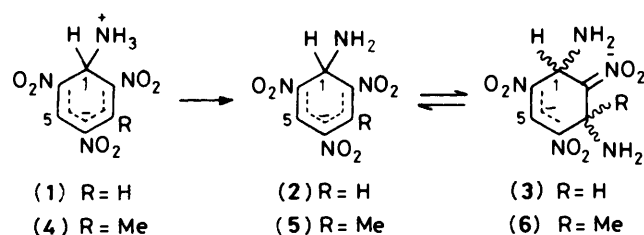
Experimental

Materials.—1,3,5-Trinitrobenzene (B.D.H.) was recrystallised twice from ethanol and once from chloroform, m.p. 123 °C (lit.,¹¹ 123 °C). 2,4,6-Trinitrotoluene (Eastman) was recrystallised twice from ethanol, m.p. 82 °C (lit.,¹² 81.1 °C). Ammonia (B.O.C.) was used without further purification.

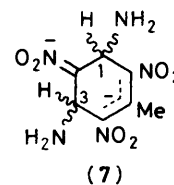
Analytical.— ^{13}C N.m.r. spectra were measured at 15.08 MHz and ^1H n.m.r. spectra at 60 MHz, both on a Bruker WP60 fourier transform spectrometer fitted with a variable-temperature unit (Bruker B-VT 1000). Samples were prepared directly in n.m.r. tubes: 10 mm (^{13}C); 5 mm (^1H). An external $(\text{CD}_3)_2\text{CO}$ lock was used and the spectra were referenced to external tetramethylsilane. Off-resonance ^1H decoupling was used where appropriate to confirm the ^{13}C assignments.

Results and Discussion

1,3,5-Trinitrobenzene.—At 220 K the solution formed by dissolving TNB in liquid ammonia shows four lines in the ^{13}C spectrum. Of the three lowfield lines those at δ_{C} 131.0 and 129.7 p.p.m. are of about equal intensity and are about twice as intense as the next lowest field line, δ_{C} 119.8 p.p.m. Off-resonance decoupling shows that, of this group, only δ_{C} 131.0



Scheme.†



p.p.m. splits into a doublet. We therefore assign the more intense of the remaining two lines (δ_{C} 129.7 p.p.m.) to C(4,6) in (3), with C(2) at δ_{C} 119.8 p.p.m. The remaining line at δ_{C} 46.8 p.p.m. corresponds in shift to an sp^3 carbon and is assigned to C(1,3). Off-resonance decoupling confirms that these are methine C atoms (results summarised in the Table). As in the earlier ^1H n.m.r. study,¹⁰ no evidence for a second geometrical isomer of (3) was observed.

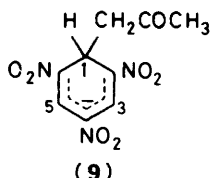
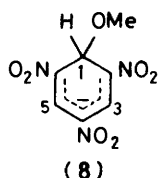
On warming to 240 K, four new lines develop in the ^{13}C n.m.r. spectrum. These grow at the expense of the original lines attributed above to (3); the original lines, however, remained dominant. The new lines may be assigned unambiguously to (2) (Table) by comparison with ^{13}C n.m.r. spectra of (8) and (9) in $(\text{CD}_3)_2\text{SO}$ determined recently by Macháček and his co-workers¹³ (see Table). Off-resonance decoupled spectra confirmed that the lines at δ_{C} 126.4 and 46.4 p.p.m. corresponded to methine C atoms. Thus the warming process corresponds to the formation of (2) from (3). Because of the time taken to accumulate spectra (2 h), it was not possible to observe (2) alone in the absence of (3) at an early stage in the reaction. However, since the processes described above are reversed by recoiling to 220 K, our earlier conclusions in terms of the Scheme (R = H), based on ^1H n.m.r., are amply confirmed by our present observations using ^{13}C n.m.r. spectroscopy.

† The numbering of the C atoms in (2) and (5) follows that adopted in ref. 9. The numbering in the subsequent structures (3), (6), and (7) is a simple extension of this principle.

Table. ^{13}C N.m.r. spectra in liquid ammonia^a

Structure	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	R = Me	
(2)	46.4	132.1	126.4	119.6	126.4	132.1		} monoadducts
(5)	49.1	138.0	141.3	124.8	129.3	134.6	20.0	
(8) ^b	69.14	132.40	126.35	121.72	126.35	132.40		
(9) ^b	34.03	133.50	127.71	121.02	127.71	133.50		
(3)	46.8	119.8	46.8	129.7	131.0	129.7		} diadducts
(6) {	major 47.8	122.8	54.3	133.0	131.4	128.7	24.2	
minor 47.4	122.0	54.3 ^c	133.0 ^c	131.4 ^c	128.4	24.8		
(7)	49.8	121.5	49.8	133.1	145.9	133.1	20.0	

^a Measured at 15.08 MHz, shifts expressed in p.p.m.; external Me_4Si standard. ^b In $(\text{CD}_3)_2\text{SO}$, from ref. 13. ^c Assumed to coincide with line in major geometrical isomer.



2,4,6-Trinitrotoluene.—At 240 K fresh solutions formed by dissolving TNT in liquid ammonia have ^{13}C spectra which are dominated by a set of seven lines. These can readily be assigned to (5) (Table). As with (2) above, this assignment can be made by comparison with the ^{13}C spectra of (8) and (9) obtained by Macháček and his co-workers¹³ (Table), combined with the off-resonance ^{13}C n.m.r. spectrum which indicates that the line at δ_{C} 129.3 p.p.m. is the only line in the sp^2 region which corresponds to a methine carbon. The high-field line at δ_{C} 49.1 p.p.m. was likewise shown to be a methine carbon.

With time (ca. 4 h at 230 K) other lines appear. The eventual dominant set is a new seven-line spectrum, with three of the lines showing weaker, very close, neighbours. These observations are consistent with the earlier observation, based on ^1H n.m.r., that both geometric isomers of (6) are formed. By analogy with (3) and from off-resonance experiments, which show that the lines at δ_{C} 47.8 (major), 47.4 (minor), and 131.4 p.p.m. correspond to methine carbons, the assignments for the various lines can be made (Table). Because of the very small differences in δ_{C} for equivalent atoms in the two isomers, it is not possible to provide an argument, independent of that already given, based on ^1H n.m.r., that the dominant isomer is *trans*.

Over and above these absorptions, other lines are observed when fresh solutions are left to accumulate for several hours at temperatures below 220 K, namely δ_{C} 145.9, 133.1, 121.5, 49.8, and 20.0 p.p.m. These we assign to the hitherto unobserved ion (7) which is structurally isomeric with (6). All three lowfield (sp^2) lines remain as singlets with ^1H off-resonance decoupling, whereas the two highfield lines split, indicating methine and methyl carbons as assigned in the Table. Confirmation of (7) has now been obtained from a ^1H n.m.r. spectrum recorded under conditions identical with those used above for the ^{13}C n.m.r. spectrum. Two hitherto unreported lines are observed at δ_{H} 5.0 and 2.4 (intensities 2:3), corresponding to the equivalent protons on C(1,3) and the methyl protons respectively in (7). On raising the temperature above 220 K, (7) disappears quickly, the concentration of (6) falls and that of (5) increases. Subsequent lowering of the temperature causes the re-formation of (7) along

with (6), although (7) is never a major product. With time the signals due to (7) disappear at the expense of (6). There is some analogy in the behaviour of the dianion products (6) and (7) with the observations by Servis¹⁴ on the mono-additions of OMe^- to 2,4,6-trinitroanisole (TNA) in $(\text{CD}_3)_2\text{SO}$. This addition occurs initially in the 3-position of TNA (kinetic control) although the final product arises from addition at the 1-position of TNA. Structure (7) is of interest also in that it corresponds to the diadduct formed by the addition of sulphite ion to TNT.^{15,16} No disulphite adduct of TNT corresponding to structure (6), described above, has been reported.

Acknowledgements

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