Proton Magnetic Resonance Studies of Products formed by Cyanobenzenes and Nitrocyanobenzenes when dissolved in Liquid Ammonia

By **John A. Chudek** and **Roy Foster**,* Chemistry Department, University of Dundee, Dundee DD1 4HN

Meisenheimer-like anionic σ-complexes have been identified by ^1H n.m.r. spectroscopy in liquid ammonia solutions of 1,3,5-tricyanobenzene, of 1,2,4,5-tetracyanobenzene (pyromellitonitrile), and of 3,5-dinitrobenzonitrile.

From the initial experiments of Meisenheimer[1] and Jackson[2] and from more recent studies,[3] the formation of anionic σ-complexes [so-called Meisenheimer(–Jackson) complexes] by the attack of nucleophiles on polynitrobenzenes is well established. Hitherto attempts to form corresponding products from polycyanobenzenes have been unsuccessful. In aqueous or alcoholic solution the cyano-groups hydrolyse fairly rapidly in the presence of bases such as alkoxide or hydroxide when used as the nucleophile. The recent demonstration[4] that σ-complexes can be formed by the dissolution of polynitrobenzenes in liquid ammonia has led us to study the behaviour of some cyanobenzenes under similar conditions.

EXPERIMENTAL

Dicyanobenzenes.—These were prepared by Kirsanov and Abrazhanova's method.[5] The 1,2-isomer was recrystallised thrice from water, m.p. 139 °C (lit.,[6] 141 °C). The 1,3-isomer was recrystallised twice from water, m.p. 161° C (lit.,[6] 161.5—162 °C). The 1,4-isomer was recrystallised twice from benzene, m.p. 222 °C (lit.,[6] 222 °C).

1,3,5-*Tricyanobenzene.*—This was prepared by the dehydration of trimesamide by thionyl chloride in dimethylformamide at 60 °C as described in Lawton and McRitchie[7] for the preparation of 1,2,4,5-tetracyanobenzene. This was recrystallised thrice from methanol, m.p. 261—262 °C (lit.,[8] 261—263 °C).

1,2,4,5-*Tetracyanobenzene.*—This was prepared by Lawton and McRitchie's method[7] and recrystallised twice from ethanol, m.p. 270—271 °C (lit.,[7] 258 °C; lit.,[9] 270—272 °C).

3-*Nitrobenzonitrile.*—This was a commercial sample, recrystallised from water, m.p. 117° C (lit.,[6] 117—118 °C).

3,5-*Dinitrobenzonitrile.*—This was a commercial sample, recrystallised twice from ethanol, m.p. 127—128 °C (lit.,[8] 127 °C).

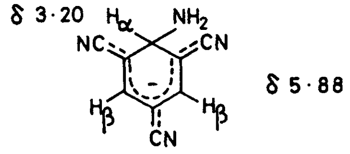
Liquid ammonia (I.C.I. anhydrous) was used without further purification.

Analytical.—Solutions were made up directly in standard 5 mm n.m.r. tubes. N.m.r. spectra were measured using a Bruker WP60 Fourier transform spectrometer fitted with a BST 100-700 variable-temperature unit. A capillary of $[^2H_6]$acetone was used as an external lock and spectra were referenced to internal tetramethylsilane. Samples were run at temperatures between 210 and 235 K. A pulse angle of 60° was used and *ca.* 250 scans were averaged for each spectrum. The ammonia signal was removed by saturation using gated homonuclear double irradiation.

RESULTS AND DISCUSSION

Dicyanobenzenes; 3-*Nitrobenzonitrile.*—When each of these compounds was added to liquid ammonia no colour developed and no absorptions were observed by n.m.r. spectroscopy. These negative observations are consistent with the known[4] behaviour of dinitrobenzenes in liquid ammonia in that, with the more strongly activating nitro-groups, only the *m*-isomer was observed to react and even there the σ complex is in equilibrium with a significant concentration of uncomplexed reactant.

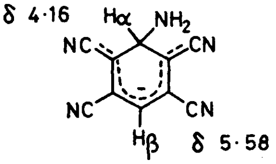
1,3,5-*Tricyanobenzene.*—A reddish brown solution with a green fluorescence is formed by dissolution in liquid ammonia. The colour slowly intensifies. Initially the ^1H n.m.r. spectrum shows a singlet, δ 8.33, which may be assigned to free tricyanobenzene. With time two lines, δ 5.88 and 3.20 (relative intensity 2 : 1), develop at the expense of the original singlet. These observations are consistent with the formation of (I) by the attack of the amide ion at the 2-position of 1,3,5-tricyanobenzene. No coupling was observed between H_α and H_β. [In (I) and subsequent structures, protons attached to the sp^3-hybridised carbon at which nucleophilic attack has occurred are labelled α. Protons at sp^2-hybridised ring carbons are labelled β and γ.] Based on the relative line intensities, at 220 K there is *ca.* 50% conversion into (I) at equilibrium. On lowering the temperature, (I) is favoured. The equilibrium can be reversed an indefinite number of times by altering the temperature. No absorptions corresponding to a 2 : 1 adduct were observed. When ammonia was removed, pure 1,3,5-tricyanobenzene was recovered.



(I)

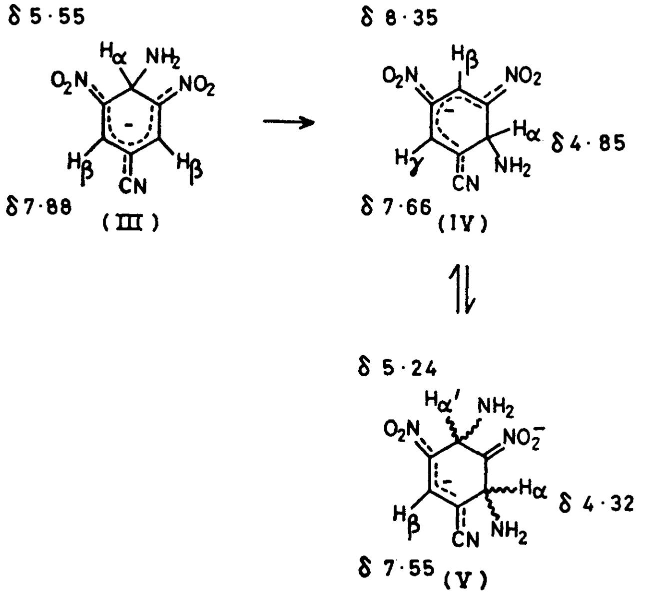
1,2,4,5-*Tetracyanobenzene.*—In liquid ammonia a pinkish red colouration develops. In the ^1H n.m.r. spectrum a singlet at δ 9.60, assigned to free tetracyanobenzene, slowly decreases as two singlets, δ 5.58 and 4.16, of equal intensity, develop. These latter absorptions may be assigned to the σ-complex (II). At 220 K the conversion into (II) is *ca.* 80% after 30 min. Reduction of the temperature favours (II). The equilibrium is reversible. There is no evidence for attack by a second amide ion at the 6-position. On evaporation of the ammonia, pure 1,2,4,5-tetracyanobenzene is recovered.

3,5-*Dinitrobenzonitrile.*—On dissolving in liquid ammonia a purple solution is obtained. Measurements on a fresh solution (<10 min) show two absorptions, δ 7.88 (d) and δ 5.55 (t, *J* 1 Hz) (relative intensity 2 : 1). This set of absorptions may be assigned to (III) by the attack of amide ion at the 4-position of the substrate.



(II)

With time (45—60 min at 240 K, hours at 220 K) these lines disappear at the expense of absorptions at δ 8.35 (dd), 7.66 (d), and 4.85 (d), all of equal intensity. These may be assigned to the ion (IV). It is suggested that the signal at lowest field is due to the proton H_β, the result of the high anisotropy of the two *ortho*-nitro-groups. It corresponds closely to the line positions of similarly situated protons in the corresponding σ-complexes of 1,3-dinitrobenzene (δ 8.32) and of 1,3,5-trinitrobenzene (δ 8.37).[4] The absorption of the proton, H_γ, between a cyano- and a nitro-group in (IV) (δ 7.66) corresponds well with the similarly situated H_β in (III) (δ 7.88). Coupling is observed between H_α and H_β (*J* 1 Hz), *i.e.* between the proton (H_α) attached to the sp^3-carbon and the proton (H_β) attached to an sp^2-carbon separated by a C-NO_2, but with no coupling between H_α and the proton H_γ attached to an sp^2-carbon separated by a C-CN. This corresponds with the coupling between H_α and H_β in (III) and with the absence of coupling between H_α and H_β in (I). In (IV), coupling is also observed between H_β and H_γ (*J* 2.2 Hz). The formation of (III) under kinetic control followed by the gradual replacement by the thermodynamically more stable (IV) corresponds exactly with previous observations made on the reaction between methoxide ion and 3,5-dinitrobenzonitrile in DMSO[10] and DMSO–methanol mixtures.[11]



At 220 K a further set of lines slowly appears. Their intensity is weak. Their development corresponds to a diminution of the lines corresponding to (IV) although these latter do not entirely disappear. The new set, δ 7.55 (dd), 5.24 (d), and 4.32 (d), (relative intensities 1 : 1 : 1), may be attributed to structure (V) which could be formed from (IV) by the attack of a second amide ion. By analogy with structures (III) and (IV) H_α [on sp^3-carbon between C-NO_2 and C-CN, *cf.* H_α in (IV), δ 4.85] is assigned to the higher-field doublet at δ 4.32 whilst $H_{\alpha'}$ [on sp^3-carbon between C-NO_2 and C-NO_2, *cf.* H_α in (III), δ 5.55] is assigned to the lower-field doublet at δ 5.24. However, this implies a significant coupling (*J* 1.5 Hz) between H_α and H_β (separated by C-CN) not observed in corresponding situations in structure (I) or (IV). By contrast, the coupling between $H_{\alpha'}$ and H_β (*J* 0.8 Hz) is consistent with corresponding couplings in other ions, for example (III). H_β at δ 7.55 is not dissimilar in position from H_γ in (IV) (δ 7.66).

The present spectra give no indication that more than a single isomer of (V) is present nor is it possible to determine from the data whether (V) is the *cis*- or *trans*-isomer.

On evaporation of solutions in which (III)—(V) had been detected, pure 1,3-dinitrobenzonitrile was recovered.

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