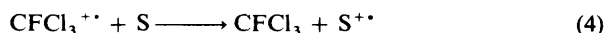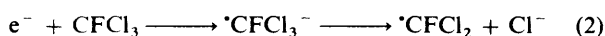# Amine Radical Cations: an Electron Spin Resonance Study of Cations generated by Radiolysis

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Amine radical cations have been generated by exposing dilute solutions of amines to $^{60}$Co γ-rays at 77 K. They are well characterised by their e.s.r. spectra, the method and interpretation being established by showing that the e.s.r. data for $Me_3\dot{N}+$ cations are identical with literature values. Results for the triethylammonium cation show that the β-protons do not occupy the most favourable sites for maximum hyperconjugation, in contrast with other radical cations. This is explained in terms of steric factors, and an equilibrium between two preferred conformations. 1,1-Diamines, $R_2NCH_2NR_2$, give cations having localised structures, $R_2\dot{N}CH_2NR_2$, rather than the delocalised structure adopted by acetal cations. Possible evidence for weak N–N bonding and delocalisation is adduced for NN'-dimethylpiperazine cations, but we confirm that the cation of triethylenediamine has a truly delocalised σ* structure. There is no tendency for $R_3N^{+\cdot}$ cations to react with neutral amines to give $(R_3N\dot{-}NR_3)^+$ dimer cations, in marked contrast with results for corresponding trialkylphosphine systems.

Because of their low ionization potentials, amines are good electron donors and, in contrast with most simple organic derivatives, their radical cations had been extensively studied by e.s.r. spectroscopy prior to the introduction of the use of Freon (CFCl₃) and related solvents for the radiolytic preparation of such cations. In particular, both the parent cation, $\dot{N}\overset{+}{H}_3$, and the trimethylamine cation, $(CH_3)_3N^{+\cdot}$, have been studied in a variety of matrices by e.s.r. spectroscopy.[1-6] The results show that these cations are effectively planar at nitrogen, and that hyperconjugation (σ–π delocalisation) for β-C–H bonds is of greater importance than for corresponding isoelectronic alkyl radicals.

In many other studies, amine cations are one of several paramagnetic products and the resulting e.s.r. spectra are consequently often difficult to interpret. We have recently helped develop an important new method for preparing radical cations in conditions suitable for e.s.r. study, such that only the cations contribute significantly to the e.s.r. spectra. This method[7-10] involves irradiating dilute solutions of the substrate in Freon or other related halogenated solvents at low temperatures (usually 77 K). Under these conditions ejected electrons react efficiently with solvent molecules, whilst solvent cations are mobile via electron-transfer, and react with solute molecules (S) provided that their ionization potentials are less than ca. 11.8 eV. These reactions are summarized in equations (1)—(4).

$$CFCl_3 \longrightarrow CFCl_3^{+\cdot} + e^- \qquad (1)$$

$$e^- + CFCl_3 \longrightarrow {}^\cdot CFCl_3^- \longrightarrow {}^\cdot CFCl_2 + Cl^- \qquad (2)$$

$$CFCl_3^{+\cdot} + CFCl_3 \longrightarrow CFCl_3 + CFCl_3^{+\cdot} \qquad (3)$$

$$CFCl_3^{+\cdot} + S \longrightarrow CFCl_3 + S^{+\cdot} \qquad (4)$$

The aim of the present study was to check that this is a suitable method for making amine cations, and then to study various diamine cations to discover any tendency for delocalisation between adjacent nitrogen atoms. We include details of our results for the cation of triethylenediamine (TED),[11] which is remarkably long lived in the liquid phase.[12] The results make an interesting comparison with those for certain ether cations.[13,14]

## Experimental

NN'-Dimethylimidazolidine was prepared by condensing form-aldehyde with sym-dimethylethylenediamine, according to the method of Riddel.[15] All other chemicals used in these studies were of the highest grade commercially available. They were generally used as supplied but purifications were carried out when required. Solutions were prepared by dissolving the amine in trichlorofluoromethane, usually in the ratio of 1 : 1000 (w/w), and were frozen in liquid nitrogen. They were exposed to γ-rays in a $^{60}$Co Vickrad cell with doses of ca. 1 Mrad.

E.s.r. spectra were obtained on a Varian E-109 spectrometer calibrated with a Hewlett–Packard 5246L frequency counter and a Bruker B-H 12E field probe, standardised with diphenylpicrylhydrazyl. Samples were annealed using a Varian variable-temperature accessory or by decanting the liquid nitrogen from the insert Dewar and re-cooling to 77 K whenever significant changes were observed in the spectra.

## Results and Discussion

Our results for $Me_3N^{+\cdot}$ cations (Table) are in good agreement with those of others, thereby confirming the utility of the method. It is interesting that even at 77 K the nine protons are equivalent. In many studies of organic radical cations prepared by this technique, methyl groups have been found to be held in a well defined conformation rather than rotating freely. The e.s.r. spectrum is dominated by central features split by proton hyperfine coupling but no $^{14}N$ coupling. These are features having $M_I(^{14}N) = 0$. They are intense because the g anisotropy is small. The $M_I(^{14}N) = \pm 1$ features are much less intense because of the large $^{14}N$ hyperfine anisotropy. The parallel ($z$) features appear as weak shoulders in the wings of the spectra, but the perpendicular ($x,y$) features are hidden beneath the $|0>$ lines because $A_\perp$ ($^{14}N$) is close to zero. Similar considerations have governed our interpretations of the spectra of other amine cations obtained in this study. These results clearly establish the planarity of these cations at nitrogen, the SOMO (semi-occupied molecular orbital) being strongly confined to the $2p_z$ orbital on nitrogen. Thus, for example, for $Me_3N^{+\cdot}$, we have $A_{iso} = 16 \pm 2$ G, $2B = 31 \pm 2$ G, whence, by comparison with estimated atomic data in the usual way,[16] we find $a_s^2$ ca. 3% and $a_p^2$ ca. 94%. The 2 s population is close to that expected for spin polarisation of the σ-bonding electrons. Since from liquid-phase studies the $^{14}N$ coupling is expected to be ca. 19 G we favour the extreme of $A_\perp = +4$ G. This gives ca. 85% for the spin density on N.

*Triethylamine.*—At 77 K, the perpendicular $|0>$ features comprise a broad quartet (ca. 1 : 3 : 3 : 1) with $A$ ($^1H$) 38 G (Figure
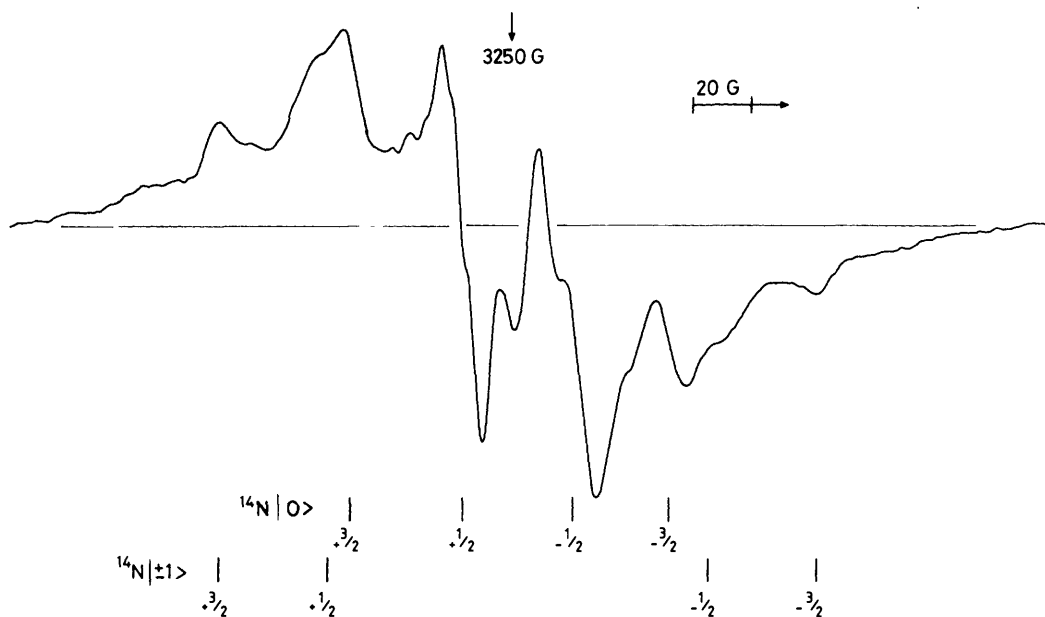
**Figure 1.** First-derivative e.s.r. spectrum for triethylamine in trichlorofluoromethane after exposure to $^{60}$Co γ-rays at 77 K, showing features assigned to the $Et_3N^{+\cdot}$ cations

Hyperfine coupling constants for certain amine radical-cations

| | | | $A(^{14}N)/G^a$ | | | |
|---|---|---|---|---|---|---|
| Cation | $T/K$ | $A_{iso}(^1H)/G^a$ | $A_{\parallel}$ | $A_\perp$ | $A_{iso}$ | $2B$ |
| $\cdot NMe_3^+$ | 77 | 28.2 | 47 | $0 \pm 4$ | $16 \pm 2$ | $31 \pm 2^c$ |
| $\cdot NEt_3^+$ | 77 | 38 (3 H) | 48 | $0 \pm 4$ | $16 \pm 2$ | $32 \pm 2$ |
| | 140$^+$ | 19 (6 H) | | | | |
| (pyrrolidine) Me | 120 | 28 (CH$_3$) 28 (2 H) 57 (2 H) | 48 | $0 \pm 4$ | $16 \pm 2$ | $32 \pm 2$ |
| (piperidine) Me | | 29 (CH$_3$) 38 (2 H) | 48 | $0 \pm 4$ | $16 \pm 2$ | $32 \pm 2$ |
| $Me_2\overset{\cdot+}{N}CH_2NMe_2$ | | 27 (2 CH$_3$) 18 (2 H) | $^b$ | $0 \pm 4$ | | |
| $Me\overset{\cdot}{N} \quad NMe$ | | 27.5 (4 H) 36 (1 H) 56 (1 H) 64 (1 H) | 44 | $0 \pm 4$ | $15 \pm 2$ | $29 \pm 2$ |
| $Me\overset{\cdot+}{N} \quad NMe$ | | 9 (ca. 10 H)$^d$ | $^b$ | $0 \pm 4$ | | |
| $\overset{\cdot+}{N}—CH_2N$ | | 20 (2 H)$^d$ 40 (2 H) | $^b$ | $0 \pm 4$ | | |
| (bipyridine) | | $^e$24 7.3 (12 H) or 28$^e$ | 13.5 or 22$^e$ | 17 | 7 or 11$^e$ | |

$^a$ $G = 10^{-4}$ T. $^b$ $\parallel$ Features not defined. $^c$ We favour $A_\perp$ ca. 4 G giving $A_{iso}$ 18 G and $2B$ 29 G. $^d$ Uncertain—see text. $^e$ Two equivalent $^{14}$N.



(I) ⇌ (II)
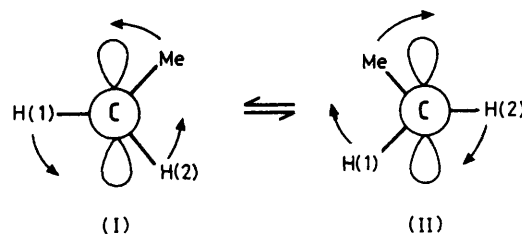
1). On annealing to ca. 140 K this changes reversibly into a 19 G septet. Outer parallel features can be detected in the wings, but are poorly defined ($A_{\parallel}$ $^{14}$N ca. 48 G). It is noteworthy that Trifunac and his co-workers have recently obtained a proton splitting of ca. 19 G for six equivalent protons for $Et_3N^{+\cdot}$ at room temperature.[17] This suggests that the coupling is not very temperature sensitive, apart from the averaging process observed at high temperatures. We interpret these results in terms of the preferred conformations (I) and (II), which undergo slow exchange at 77 K, but rapid exchange above ca. 140 K. [Only one of the methyl groups is depicted in (I) and (II): we envisage a synchronous motion for all three groups.] From the average proton coupling of 28 G observed for $Me_3N^{+\cdot}$, we calculate a coupling of ca. 42 G for (I) or (II) if the limiting structure, with one C–H bond in the plane, is adopted. This is quite close to the observed coupling of 38 G. There must be a remarkably strong preference for these conformations since, even at room temperature, the coupling has not moved towards the overall average coupling of ca. 28 G.

It is interesting that the same situation is found for the triethylmethyl radical, $Et_3C^{\cdot}$.[18] Structures similar to (I) and (II) in rapid equilibrium should give a coupling of 33.6/2 = 16.8, in good agreement with the observed value. We therefore postulate that this equilibrium governs the behaviour of the triethylmethyl cation. One controlling factor for this equilibrium must be the large steric barrier constraining the three methyl groups close to the radical plane. This would be an interesting problem to study by molecular dynamics.

*N-Methylpyrrolidine Cations.*—These were studied to provide a comparison with recent results for tetrahydrofuran cat-
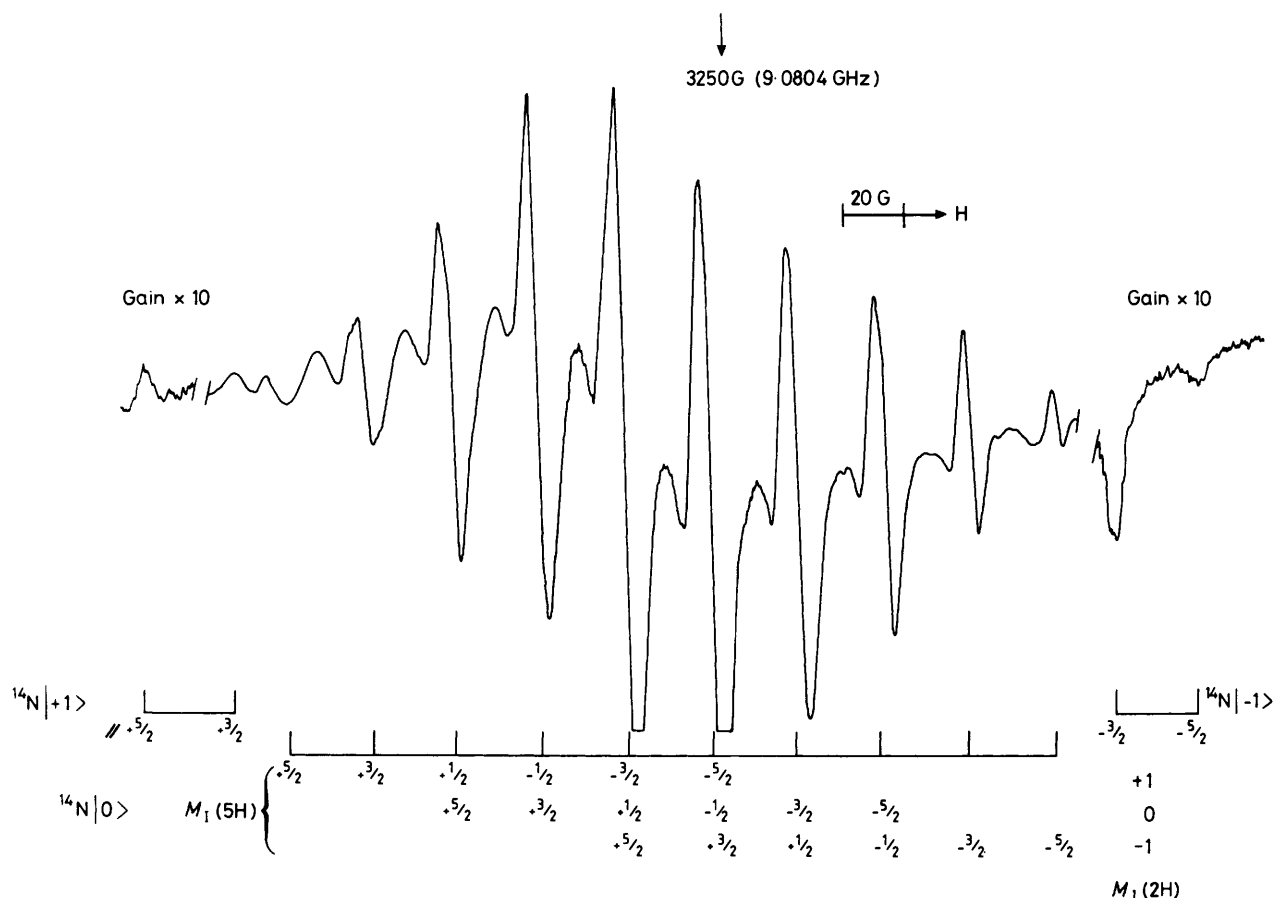
**Figure 2.** First-derivative e.s.r. spectrum for $N$-methylpyrrolidine in trichlorofluoromethane after exposure to $^{60}$Co $\gamma$-rays at 77 K, showing features

ions,[19,20] and to provide a gauge against which the results for the 1,3-diamine derivative could be tested (see below). The spectrum is well resolved (Figure 2) relative to that for the triethyl derivative, and proved an invaluable aid in the interpretation of the diamine spectrum.

As with the tetrahydrofuran cations, there are two strongly coupled ring protons (57 G) and two more weakly coupled ring protons (28 G), the latter being close to the average value. The corresponding data for the ether are ca. 89 and 40 G, the latter also being close to the average derived from the $Me_2O^{+\cdot}$ cations (43 G). For the ether cations, rapid inversion set in at ca. 150 K, making the four $\beta$-protons equivalent on the e.s.r. time-scale. The activation energy ($\Delta H$) for ring puckering was estimated at ca. 1.65 kcal mol$^{-1}$ from the linewidth alternation.[19] However, for the amine, no clear change in the e.s.r. spectrum was detected below the normal decomposition temperature (ca. 160 K), so the inversion barrier must be > ca. 4 kcal mol$^{-1}$. Presumably the need to move the methyl group relative to the ring fairly extensively greatly increases this barrier.

$N$-*Methylpiperidine.*—In our study of ether cations,[20] we found a remarkable difference between the axial and equatorial $\beta$-proton hyperfine coupling for the cations of tetrahydrofuran and tetrahydropyran. The former, discussed above, had coupling constants much greater than those for the latter. This was explained in terms of a major change in conformation such that, for the latter cations, two $\beta$-protons (equatorial) lie quite close to the nodal plane, giving a small coupling (14 G) while the other two give a coupling of ca. 34.5 G. If this is correct, we

expect to find greatly reduced splittings for the $N$-methyl-piperidine cation when compared with those for the $N$-methylpyrrolidine cation. This is indeed the case. The spectral features (Figure 3) cover a far smaller range of field, and apart from the methyl protons, there are only two strongly coupled protons [$A(^1H)$ ca. 38 G]. Thus, in this case, the equatorial protons must be very close to the nodal plane, while the other two are close to the $\theta = 30°$ site for which a splitting of ca. 40 G is expected.

*Tetramethyldiaminomethane.*—The e.s.r. spectra obtained for solutions of $Me_2NCH_2NMe_2$ after irradiation are noteworthy in that there is no evidence for two strongly coupled protons. Corresponding acetal cations, $(ROCH_2OR)^{+\cdot}$, have e.s.r. spectra dominated by very large splittings from the two methylene protons.[13,14] This is good evidence for $\pi$-delocalisation via the $CH_2$ groups for the acetal, as in (III). In principle, we see no reason why a similar structure (IV) should not be adopted for the diamine. The $CH_2$ proton splitting would be less than that for the acetal (ca. 100 G by comparison between amino and ether cations) but would surely be clearly resolved in the e.s.r. spectra. We conclude that the SOMO remains localised on one $R_2\dot{N}$ moiety. However, the spectrum was broad and poorly resolved, so that only the proton coupling constants could be derived (Table). The methylene proton coupling is close to that for the triethylamine cation. We therefore prepared a cyclic diamino cation in the expectation that the spectrum would be better resolved. This proved to be the case.

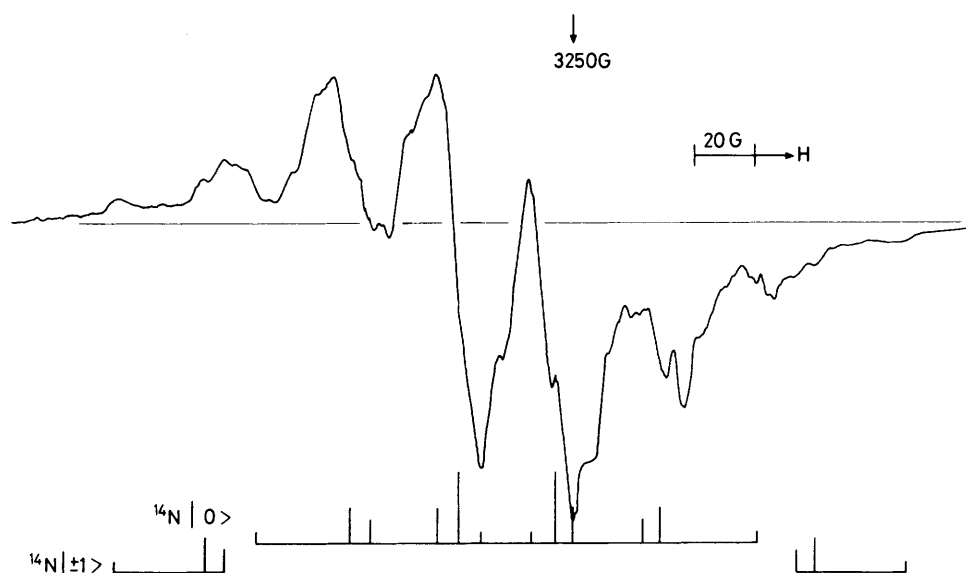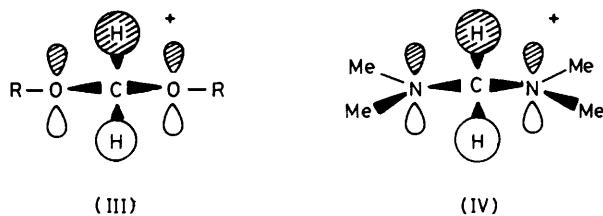N$N$-*Dimethylimidazolidine.*—As with the open-chain di-

**Figure 3.** First-derivative e.s.r. spectrum for $N$-methylpiperidine in trichlorofluoromethane after exposure to $^{60}$Co $\gamma$-rays at 77 K, showing features assigned to its radical cation



amine, the results again gave no evidence for large hyperfine coupling to two protons (Figure 4). Instead, our analysis gives parameters in good accord with expectation for a completely localised cation. The spectrum is remarkably similar to that for the $N$-methylpyrrolidine cation (Figure 2), which strongly supports our analysis.

Thus, the major barrier to $\pi$-delocalisation *via* the methylene group is not steric repulsion. Instead, we envisage the major barrier arising from the pyramidal nature of the neutral amine at nitrogen. Even for simple charge-transfer between the groups near-planarity of both centres is necessary. It seems that it is energetically more favourable for the SOMO to be confined largely to one planar nitrogen centre, the other remaining fully pyramidal, rather than for both to attain near-planarity, despite the gain in delocalisation energy that would ensue.

*Bipiperidylmethane.*—In the light of the above results, the cation of bipiperidylmethane should closely resemble that of $N$-methylpiperidine rather than having a delocalised structure. This was indeed the case, although the features were poorly defined, making interpretation difficult (Figure 5a). There appears to be a major quintet for the |0> features, with a basic splitting of *ca.* 20 G. However, there are outer lines, separated also by 20 G for the quintet features, which may also be part of the |0> set, or may be parallel features. Other parallel features are poorly defined. If the former analysis is correct, we need two protons with coupling close to 40 G and two others at *ca.* 20 G each. For steric reasons the methylene proton coupling constants are expected to be less than average, so we assign the 20 G splitting to the two $CH_2$ protons and the 40 G splitting to the two axial ring protons. These values are quite satisfactory, the only problem being that the intensity of the outermost |0>

lines is low. The other alternative requires one proton giving *ca.* 40 G and three equatorial protons at *ca.* 20 G. The unique proton must be a $CH_2$ proton, so that the ring protons give only 20 G splitting. A conformation similar to that for the $Et_3N^{+\cdot}$ cation would explain the 40 G splitting satisfactorily, but 20 G for the two axial protons is extremely small. Hence, we are inclined to favour the former analysis.

*NN'-Dimethylpiperazine.*—The total proton coupling for this cation is greatly reduced relative to that for the cation of $N$-methylpiperidine (*cf.* Figures 5b and 3). We can interpret the central region in terms of eight or ten nearly equivalent protons with $A$ *ca.* 9 G, but the parallel lines are too poorly defined for definitive interpretation. It is difficult to understand this dramatic reduction in proton hyperfine coupling if the SOMO remains largely localised on one nitrogen atom. However, we note that the structurally similar cation of $p$-dioxane also exhibits a greatly reduced proton coupling.[20] We tentatively interpreted this reduction in terms of a boat conformation with weak $\sigma$-bonding between the two oxygen atoms, giving a $\sigma^*$ SOMO. The same situation may be occurring for the pyrazine derivative.

We conclude that there probably is delocalisation, but fail to understand why it occurs for this structure. However, for the cation of triethylenediamine, delocalisation is unambiguous.

*Triethylenediamine (TED) Cation.*—The original liquid-phase study of (TED)$^+$ cations by McKinney and Geske[12] showed that the two nitrogen atoms and all 12 hydrogen atoms are equivalent on an e.s.r. time-scale. We feel, however, that in light of our present results, this might possibly arise from a rapid electron-transfer from one nitrogen to the other, as in (VI), rather than implying the formation of an N–N bond, as in (VII).[11]

We have studied TED$^+$ cations in rigid media, prepared by freezing solutions of the ion generated chemically or electrochemically in various solvents, and prepared by radiolysis in Freon. The resulting spectra are essentially identical (a spectrum for TED$^+$ produced in Freon is given in Figure 6). Furthermore, the 12 protons remain identically·coupled ($A_{iso} = 7.3$ G), and the two nitrogen atoms remain equivalent. This is clear, even though we are not certain about the identity of the outermost parallel lines. If we assume that we detected all the proton
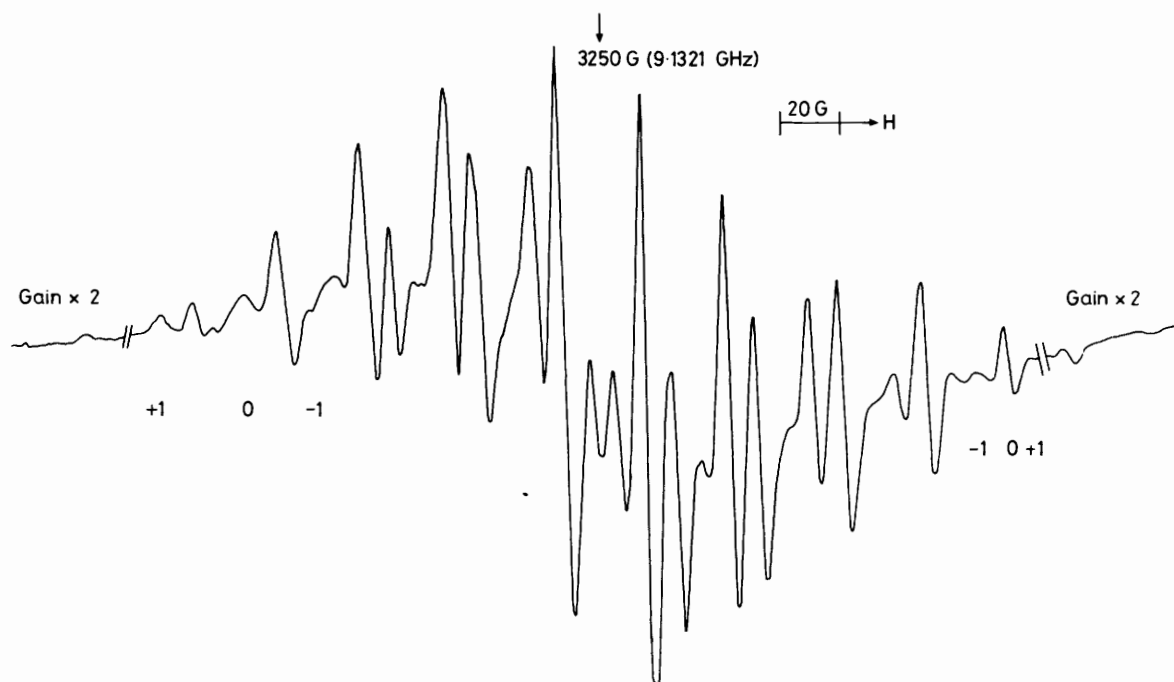
**Figure 4.** First-derivative e.s.r. spectrum for $NN$-dimethylimidazolidine in trichlorofluoromethane after exposure to $^{60}$Co γ-rays at 77 K, showing features assigned to its radical cation
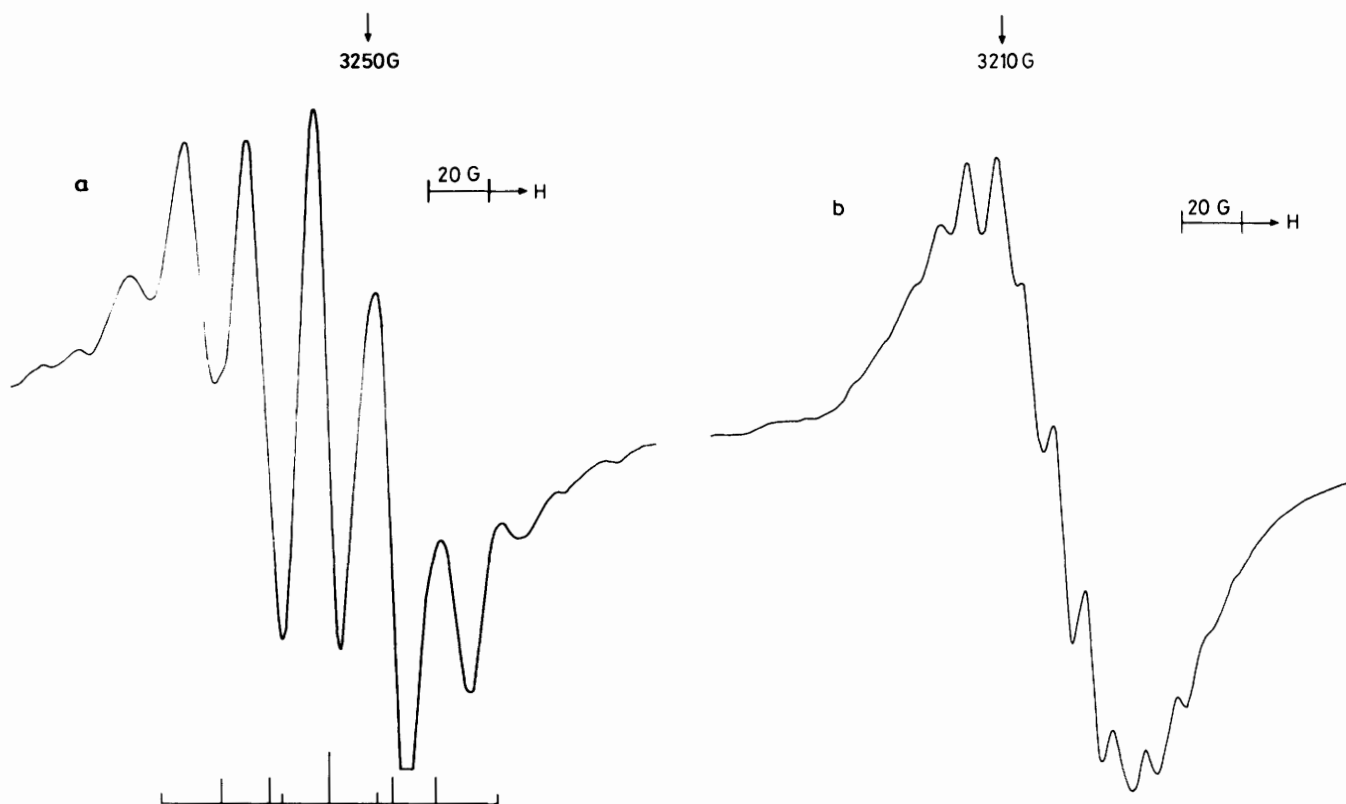


**Figure 5.** a, First-derivative e.s.r. spectrum for bipiperidylmethane in trichlorofluoromethane after exposure to $^{60}$Co γ-rays at 77 K, showing features assigned to its radical cation. b, First-derivative e.s.r. spectrum for $NN'$-dimethylpiperazine in trichlorofluoromethane after exposure to $^{60}$Co γ-rays at 77 K, showing features assigned to its radical cation

features, then $A_{\parallel}(^{14}N) = 28$ G. If the outermost features are missing then $A_{\parallel}(^{14}N) = 24$ G. Using those values and $A_{iso} = 17$ G, we find $A_{\perp} = 13.5$ or 22 G. From the form of the spectrum we require $A_{\perp}$ $ca.$ $n \times 7.3$, so both of these results are reasonable. Then, given $2B = 7$ or 11 G, we obtain approximate spin densities of 21 or 33%, respectively, on each nitrogen atom.
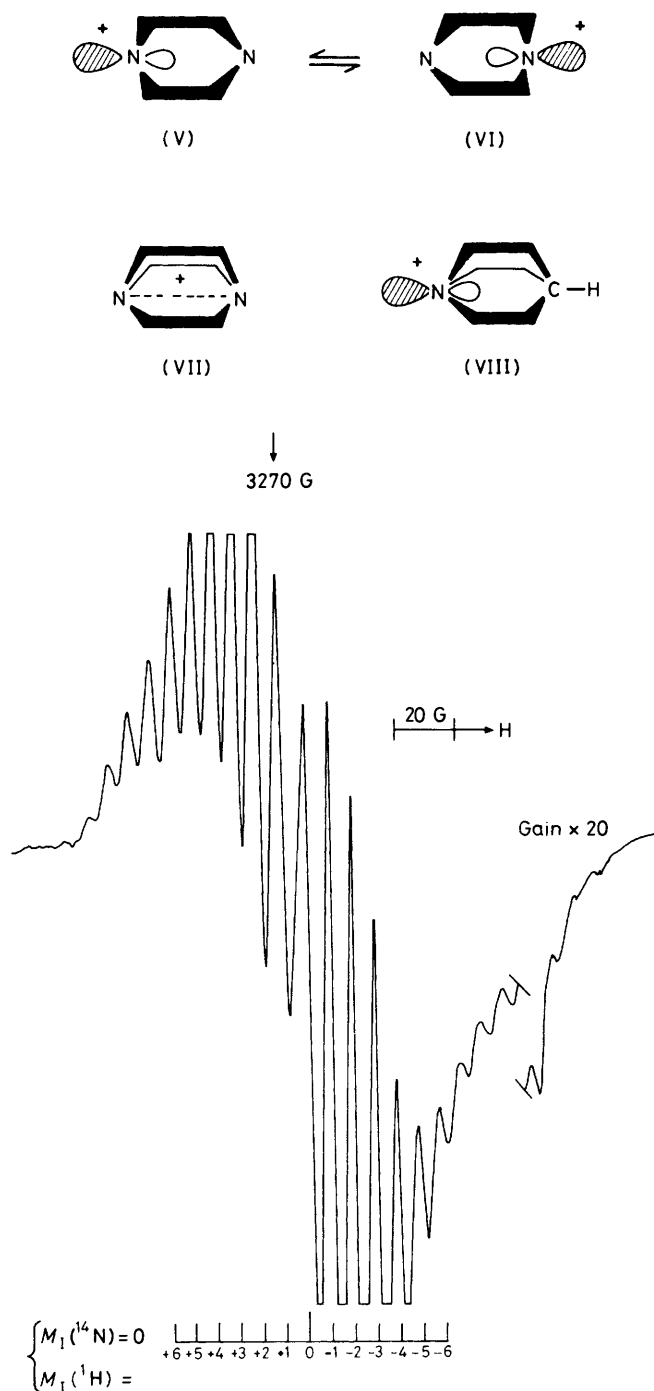
(V)   (VI)

(VII)   (VIII)

↓
3270 G



20 G
├────────┤──►H

Gain × 20

$\begin{cases} M_I(^{14}N) = 0 \\ M_I(^1H) = \end{cases}$

+6 +5 +4 +3 +2 +1  0 -1 -2 -3 -4 -5 -6

**Figure 6.** First-derivative e.s.r. spectrum for triethylenediamine in tri-chlorofluoromethane after exposure to $^{60}Co$ γ-rays at 77 K, showing features assigned to its radical cation

We conclude rather firmly that, as predicted theoretically, there is true static delocalisation, rather than rapid equilibration by a fast electron-transfer. Also there is extensive delocalisation from nitrogen into the ring (ca. 44—58%).

We note that the value for $A_{iso}(^{14}N)$ of 17 G is large compared with 50% of the normal value (ca. 9.5 G) for planar, localised amine cations. This strongly supports the idea of pyramidality at nitrogen required by the rather rigid bicyclic structure, although the 2s-character, calculated to be ca. 3%, requires considerable flattening, the $p:s$ ratios being either ca. 5
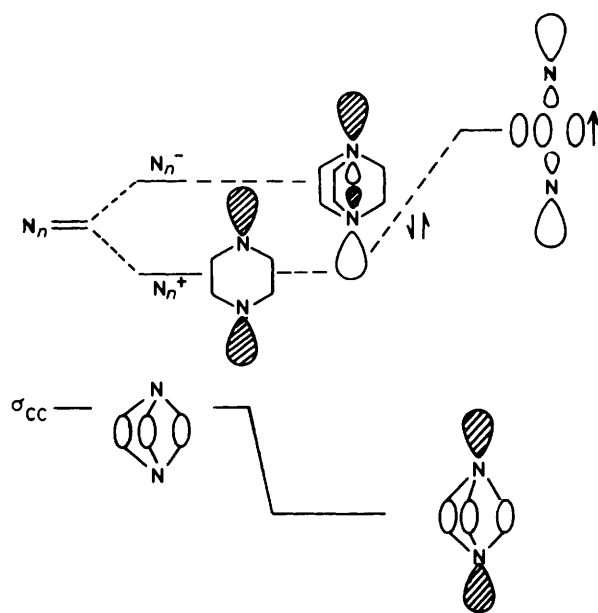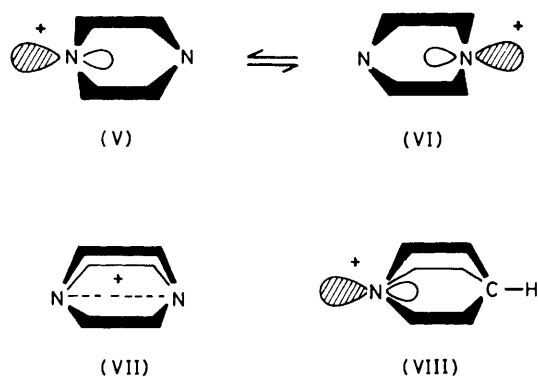


**Figure 7.** Construction of molecular orbitals for triethylenediamine, according to Bock and Ramsey[25]

or ca. 7. This, of course, presupposes approximate orbital following, which is not a necessary requirement,[21] even though, in our view, it is commonly found for simple radicals.[22]

It is interesting to compare these results with those for the mononitrogen derivative (VIII).[23] The most striking feature is the very large δ-proton coupling of 14.3 G, which establishes considerable delocalisation onto this site. The isotropic $^{14}N$ coupling is, however, remarkably small, implying even greater planarity at nitrogen or very extensive delocalisation. The value of the β-proton coupling does not accord with greater planarity, so it seems that delocalisation may indeed be extensive.

There are two alternative, extreme descriptions of this delocalisation; one being a through-space overlap of the σ-orbitals on nitrogen, or the nitrogen σ and C–H σ orbitals, and the other, generally favoured, being delocalisation via the C–C σ orbitals of the rings. Probably both processes contribute.

Finally, we draw attention to a description of the SOMO for this radical which differs markedly from the simple σ* description normally used at a qualitative level. The latter depicts the SOMO as the out-of-plane combination of the 'lone-pair' orbitals, $(n-;a_2'')$, the first filled level being the in-phase combination $(n+;a_1')$. Indeed, INDO calculations also suggest this order, the optical band at 470 nm being assigned to the transition $a_1'(n+) \longrightarrow a_2''(n-)$.[23,24] The novel description proposed by Bock and Ramsey[25] is summarized in Figure 7. The key point is that the normal σ, σ* order for the nitrogen 'lone-pair' orbitals is inverted by strong coupling to the three C–C orbitals, which mix strongly with the in-phase lone-pair combination $(N_n^+)$ but not with the out-of-phase combination $(N_n^-)$. This pushes the in-phase orbital above the $N_n^-$ orbital so that this becomes the SOMO. Unfortunately, our present results are still not enough to probe this novel suggestion.

*Conclusions.*—We conclude that amine radical cations can readily be prepared by our procedure and trapped indefinitely. They show no tendency to undergo unimolecular reactions, nor do they lose protons to give neutral α-aminoalkyl radicals. Because of recent interest in such deprotonation, we incorporated some ethanol in the trimethylamine–Freon system. However, the e.s.r. spectrum for $Me_3N^{+\cdot}$ cation was unaltered, and $H_2\dot{C}NMe_2$ radicals were not trapped on annealing to 160 K.

In general, $R_3N^{+\cdot}$ radicals do not react with $R_3N$ molecules to give $(R_3N\dot{\underline{\phantom{}}}NR_3)^+$ $\sigma^*$ radicals. However, possible evidence for weak N $\cdots$ N bonding was obtained from $NN'$-dimethylpiperazine and the cation of TED clearly has a fully delocalised SOMO.

## Acknowledgments

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