Electron Spin Resonance Study of Azoalkane and Imine Radical Cations

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Radical cations of azoalkanes have been observed for the first time in a lowtemperature matrix by e.s.r. spectroscopy. The e.s.r. data show that they are π -cations despite photoelectron studies which indicate the HOMO for an azoalkane to be the σ (n) orbital. Interestingly, these species appear to be stable, at least up to ca. 160 K, and show no tendency to fragment to form alkyl radicals. This contrasts with the solution-phase behaviour of these species, which are intermediates in the oxidation of azoalkanes, and give rise to carbocations and alkyl radicals. Imines form similar π -radical cations which show a greater tendency to decompose. The structures and stabilities of these cations are discussed. Attempts to observe the corresponding azoalkane anions in solid matrices resulted only in the formation of alkyl radicals, and so we conclude that the anions decompose by fragmentation, although they have been studied in solution under steady-state conditions. Previously derived coupling parameters predict isotropic ¹⁴N hyperfine couplings for these species which are larger than those observed. Therefore, new values are calculated, and these fit well with the observed couplings. In this way, spin polarisation parameters are obtained for individual contributions to the couplings, as opposed to previous approaches which treat them collectively.

Considerable attention has been focused on radical cation intermediates, particularly in recent years. Direct information regarding the nature of these species has been obtained from electronic,¹ CIDNP² and e.s.r.³⁻⁵ spectroscopies. E.s.r. may be used to study relatively stable radical cations in the liquid phase,⁶ but in order to obtain e.s.r. data for more reactive species matrix-isolation techniques must be used. Matrix methods have tended to fall into two categories: (1) isolation of the cation in an inert-gas matrix by co-deposition, following photoionisation of its precursor, which has been used mainly for small molecules;³ and (2), by far the most widely used method, exposure of dilute frozen solutions of cation substrates in various freons to ionising radiation at low temperatures. This approach has proved extremely successful in the study of cations of larger organic and organometallic molecules,^{4,5} and is used in the present work.

Azoalkanes are well known as thermal or photochemical sources of alkyl radicals, perhaps the most familiar compound of this type being the radical initiator AIBN $[Me_2C(CN)-N=N-C(CN)Me_2]$. In terms of free-radical chemistry of the -N=N bond, a recent example is the study of muonated hydrazyl radicals, R-N-N(Mu)R, observed during the irradiation of a series of azo-compounds with positive muons.⁷ Our present interest in azoalkanes and imines stemmed from our expectation that they would readily form their radical cations on irradiation in CFCl₃. These cations are interesting since they could potentially exist in either σ or π -states, and it is possible that the π -states might adopt twisted structures, as proposed for some alkene cations.⁵

We are not aware of any previous e.s.r. work on these species other than our own

radical	coupling constants/G ^a	T/K
$Pr^{i} \rightarrow N = N - Pr^{i(\cdot +)}$	$(2H) 20, ({}^{14}N_{\parallel}) 24, ({}^{14}N_{\perp}) 0$	77
	(2H) 16.0, (¹⁴ N _a) 19	150
$Pr^n - N = N - Pr^{n(\cdot +)}$	$(4H)$ 21, $(^{14}N_{\parallel})$ 24, $(^{14}N_{\parallel})$ 0	77
	(4H) 17.6	150
$Et - N = N - Et^{+}$	$(4H)$ 21, $({}^{14}N_{\parallel})$ 24, $({}^{14}N_{\perp})$ 0	77
	(4H) 17.8	150
PhCH=NBu ⁿ⁽⁺⁾	(1H) 9, (2H) 21, (¹⁴ N ₁) 30,	77
	$(^{14}N_{\perp})0$	
MeCH=NBu ⁿ⁽⁺⁾	(4H) ¹ 12, (2H) 22, (¹⁴ N ₁) 32,	77
	$(^{14}N_{\perp})0$	
Et-N=N-Et'-	(4H) 12.8, (¹⁴ N ₁₅₀) 7.75 ^b	
$Pr^{i} - N = N - Pr^{i(\cdot -)}$	$(2H)$ 9.73, $({}^{14}N_{150})$ 8.0 ^b	
Et'	(3H) 27, (2H) 22	77
Pr ⁱ	(6H) 24, (1H) 22	77
Pr ⁿ '	(2H) 35, (2H) 22	77
Bu ⁿ .	(2H) 36, (2H) 22	77

 Table 1. E.s.r. data for azoalkane and imine radical cations and related radicals

^a 1 G = 10^{-4} T. ^b From ref. (19). All other data are from this work.

preliminary report of azoalkane cations,⁸ although studies have been made of reactions believed to involve azoalkane and imine radical cations,^{9,10} and well defined photoelectron spectra have been obtained from both azoalkanes¹¹ and imines.¹²

Experimental

The azoalkanes and imines were kindly provided by Dr P. W. F. Louwrier (Amsterdam). Dilute solutions (*ca.* 0.1% by wt) of these compounds were prepared in $CFCl_3$, and reduced to powders by pipetting into liquid nitrogen. The powders were γ -irradiated to a dose of *ca.* 1 Mrad at 77 K and the e.s.r. spectra were recorded using a Varian E109 spectrometer. The samples were annealed either by decanting the liquid nitrogen from the insert Dewar and allowing the sample to warm; refreezing when significant spectral changes occurred, or using a Varian variable-temperature device when specific temperatures were required.

Results and Discussion

The e.s.r. data for azoalkane and imine radical cations are summarised in table 1; for comparison, data for related radicals, taken from the literature, are also included.

Azoalkane Cations

The radical cations of azoethane, azo-n-propane and azo-isopropane all show parallel ¹⁴N couplings of 24 G to two equivalent nitrogen nuclei at 77 K. Typical spectra are shown in fig. 1 and 2. This implies a 2*B* term¹³ of *ca*. 16 G, and so the p-orbital spin density on each nitrogen atom is *ca*. 0.5. We therefore assign the SOMO as being the N—N π -bonding orbital (a_u). The appearance of the spectra shows that the two ¹⁴N hyperfine tensors are parallel and so the cations are planar rather than twisted, in contrast with certain alkene cations.⁵ For significant twisting a more complex ('*x*, *y*, *z*') pattern would be expected.

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Fig. 1. E.s.r. spectrum of $Et-N=N-Et^{++}$ radical cations recorded following γ -irradiation of the parent azoalkane in a CFCl₃ matrix at 77 K.



Fig. 2. E.s.r. spectrum of Pr^{i} —N=N— $Pr^{i(\cdot+)}$ radical cations at 77 K.

In both $Et-N=N-Et^+$ and $Pr^n-N=N-Pr^{n(++)}$ cations, a(H) couplings of 21 G to four equivalent protons were observed at 77 K; however, on annealing to 150 K, the couplings decreased to 18 G. This indicates a preferred conformation of the alkyl groups, as in (I), similar to that found for primary alkyl radicals,¹⁴ which maximises $\sigma-\pi$ conjugation, since this is believed to be more effective for C-H bonds than for C--C bonds.¹⁵ The rotational barriers must be low, since these changes in coupling constants over a range of *ca*. 70 K are fairly large.

Interestingly, the conformation (I) was not adopted by the ethyl groups in the Et_3N^{+} radical cation,¹⁶ but this is probably because of steric interactions between the alkyl groups, as is believed to be the case in tertiary alkyl radicals.¹⁴ The proton coupling is lower in the isopropyl derivative, most likely as a result of a steric effect which



Fig. 3. E.s.r. spectrum showing features assigned to PhCH=NBuⁿ⁽⁺⁾ radical cations recorded following γ -irradiation of the parent imine in a CFCl_a matrix at 77 K.

disfavours conformations such as (I). The actual conformation (on average) appears to be a compromise which maximises hyperconjugation and minimises steric repulsion. This average conformation is still that with a dihedral angle between the C—H bond and the density axis of the SOMO of less than 45° , since the coupling is reduced by raising the temperature.



In all cases, a decrease in the ${}^{14}N_{\parallel}$ coupling was observed during annealing as a result of increased librational motion of the cations. This would also account for the improved resolution obtained at higher temperatures, particularly for the n-propyl derivative.

Imine Cations

From the ¹⁴N_µ couplings in MeCH=NBuⁿ⁽⁺⁺⁾ and PhCH=NBuⁿ⁽⁺⁺⁾ cations, we calculate 2p spin densities on nitrogen of 0.64 and 0.60, respectively. The spectrum of the latter cation is shown in fig. 3. Since the perpendicular features show zero splitting, the isotropic coupling must be low (*ca.* 10 G) giving an N 2s contribution of *ca.* 2%, and so the p/s ratio is *ca.* 30, showing that these are also π -cations. The results show that a high proportion of the spin resides on the exocyclic group in the PhCH=NBuⁿ⁽⁺⁺⁾ cation, by comparison with the data for other benzene cations with unsaturated substituents.¹⁷ If the 9 G (1H) coupling is due to the *para*-proton, then the SOMO is still essentially the styrene-type π_4 orbital (II), but with some distortion which increases the coefficient on nitrogen. However, since the spin density on nitrogen is so large, and is very similar to that in the MeCH=NBuⁿ⁽⁺⁾ cation, it is possible that the 9 G coupling is due to the α -proton and so essentially all the spin is on the C=N group; however, such a small degree of delocalisation onto the phenyl ring would appear surprising, and so we favour the former assignment. As with the azoalkane cations, there is no evidence that these cations are significantly twisted.

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Cation Stabilities

Photoelectron spectra of azoalkanes¹¹ show that the non-bonding (a_g) orbitals on nitrogen are of higher energy than the π -orbitals (a_u) , yet it is clearly the π -cations that are observed under the present conditions. Our suggestion is that the initial electron loss is from the (a_g) orbital, giving a σ -cation which then converts to the π -state, since this will be stabilised by hyperconjugation (enhanced by the positive charge).

We can argue similarly for the imines, since photoelectron studies¹² also indicate that the initial state should be σ , although the σ - π energy difference is less than that for azoalkanes. Studies of the behaviour of azoalkanes with single-electron oxidants in solution^{9, 10} indicate a facile fragmentation of the azoalkane radical cation

$$\mathbf{R} - \mathbf{N} = \mathbf{N} - \mathbf{R}^{+} \rightarrow \mathbf{R}^{+} + \mathbf{N}_{2} + \mathbf{R}^{+} \tag{1}$$

followed by a rapid oxidation of the alkyl radical, giving products compatible with predominant carbocation chemistry. Under our conditions, the azoalkane cations were stable; even on annealing to the melting point of the matrix (ca. 160 K) we were unable to detect the presence of alkyl radicals. Probably, attack on the cation by solvent molecules is required to induce the decomposition, although we note that unimolecular fragmentation of other organic cations has been observed previously in a freon matrix.¹⁸

The imine radical cations appeared to be less stable. Following irradiation of $Pr^{n}CH=NPr^{i}$ in CFCl₃ only alkyl radicals were observed: the spectrum could be ascribed mainly to isopropyl radicals, but features were also present which indicated the formation of lesser amounts of n-propyl radicals. The PhCH=NBuⁿ⁽⁺⁺⁾ and MeCH=NBuⁿ⁽⁺⁺⁾ cations were stable at 77 K, but, on annealing, features assigned to n-butyl radicals were observed. We suggest the fragmentation

$$\mathbf{R}'\mathbf{C}\mathbf{H} = \mathbf{N} - \mathbf{R}^{+} \to \mathbf{R}'\mathbf{C} \equiv \mathbf{N}\mathbf{H}^{+} + \mathbf{R}^{-}$$
(2)

to account for this, in which the relatively stable protonated nitriles are formed. The greater stability of the isopropyl radical probably accounts for the greater tendency of $Pr^nCH=NPr^{i(+)}$ to fragment. We suggest that the reaction

$$Pr^{n}CH = NPr^{i(*+)} \rightarrow Pr^{n} + HC \equiv NPr^{i}$$
(3)

also occurs to a lesser extent.

Azoalkane Radical Anions

Azoalkane radical anions have recently been observed by e.s.r. during continuous photolysis of THF solutions containing the azoalkanes and crotylpotassium;¹⁹ however,



Fig. 4. E.s.r. spectrum assigned to ethyl radicals formed by γ -irradiation of pure azoethane at 77 K.

we have been unable to observe these species in the solid state. γ -Irradiation of pure materials of relatively high electron affinities at low temperatures often gives rise to the corresponding radical anions; however, on irradiating the pure azoalkanes, we observed well defined spectra of only the substituent alkyl radicals (fig. 4). Since we know that the cations are stable at 77 K [even concentrated solutions (*ca.* 20% in CFCl₃) show only the parent cations, so these do not react with neutral R—N=N—R molecules at 77 K] we suggest that the alkyl radicals may be formed partly *via* dissociation of the radical anions:

$$R - N = N - R^{-} \rightarrow R^{+} + R - N_{2}^{-}$$
(4)

although high-energy electron return to a cation in the pure solid could also give alkyl radicals, via an excited state of R-N=N-R. Irradiation of dilute solutions of the azoalkanes in CD_3OD , which is a good radiolytic source of electrons in which only anions or anion-derived radicals are formed, gave rise to spectra with wing features assignable to the same alkyl radicals. Simulations obtained by taking Sustmann's isotropic values¹⁹ and estimating the anisotropic ¹⁴N hyperfine couplings did not fit the observed features. This supports our conclusion that anion fragmentation takes place.

The proton couplings in the azoalkane anions in solution are markedly lower than those in the corresponding cations; this may be due partly to the higher temperatures at which the anion spectra were recorded, resulting in an increased weighting of conformations with low couplings, but mainly to the expectedly weaker hyperconjugation compared with the cations.

We were unable to obtain well defined spectra assignable to imine radical anions.

Coupling Parameters for ¹⁴N

A quantitative theoretical treatment was made by Karplus and Fraenkel²⁰ for carboncentred π -radicals which evaluated the various contributions to the isotropic ¹³C hyperfine couplings; these are symbolised by the S and Q parameters in the equation

$$a^{\rm C} = (S^{\rm C} + \sum_{\rm X} Q^{\rm C}_{\rm C-X}) \rho^{\pi}_{\rm C} + \sum_{\rm X} Q^{\rm X}_{\rm X-C} \rho^{\pi}_{\rm X}$$
(5)

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nitrogen ^b		carbon ^c	
$Q_{\rm N-R(H)}^{\rm N}$	7.2	Q_{C-H}^{c}	19.5
S_{1s}^{N}	-2.1	$U^{\circ}_{\mathrm{C}-\mathrm{C}'}$ S°_{1s}	-12.7
S_{1p}^{N} $O_{N-N'}^{N}$	2.9 8.0	<i>O</i> ^{c′} _{c−c′} –	- 14.4
$\tilde{Q}^{\rm N+}_{\rm N'-N}$	2.7	$ ilde{\mathcal{Q}}_{\mathrm{c'-c}}^{\mathrm{c}-\mathrm{c}}$	-13.9

Table 2. Coupling parameters $(G)^a$ for ¹⁴N and ¹³C

^{*a*} 1 G = 10^{-4} T. ^{*b*} This work. ^{*c*} Ref. (20).

where a^{c} is the isotropic ¹³C coupling, Q_{C-x}^{c} reflects the polarisation of the C-X bonding electrons by π -spin density on the carbon atom (ρ_{C}^{π}) , Q_{X-c}^{x} reflects the polarisation of the C-X bond by π -spin density (ρ_{X}^{π}) on the substituents X, and S^{c} represents the exchange polarisation of the carbon 1s² core electrons. This approach has predicted very successfully the ¹³C couplings in a variety of carbon-centred π -radicals. Similar expressions such as

$$a^{N} = (S^{N} + \sum_{X} Q^{N}_{N-X})\rho^{\pi}_{N} + Q^{X}_{X-N} \sum_{X} \rho^{\pi}_{X}$$
(6)

have been proposed to account for ¹⁴N couplings.^{21, 22} The parameters have usually been empirically derived owing to the necessary exchange integrals not being available for all the polarisations. In eqn (6), S^N contains both the 1s² and lone-pair terms. From the data for a series of heteroaromatic radical ions it was not possible to achieve a separation of the S^N and Q_{N-x}^N terms²² and so one parameter Q^N was used which reflects all contributions to the coupling from π -spin density on the nitrogen atom itself, leading to the simplified expression:

$$a^{N} = Q^{N} \rho_{N}^{\pi} + Q_{X-N}^{X} \sum_{X} \rho_{X}^{\pi}.$$
 (7)

Expressions of this form have been applied successfully to a number of aromatic radical anions^{21, 22} and, more recently, to neutral nitrogen-containing radicals.²³ However, the parameters derived from various systems to fit eqn (7) predict ¹⁴N couplings for R-N=N-R radical anions and cations which are 60–80% larger than those observed. This, and the conceptual desirability of separating out the individual contributions to the ¹⁴N couplings, prompted us to try to obtain values for all the coupling parameters in the fuller equation,

$$a^{N} = (S_{1s}^{N} + S_{1p}^{N} + \sum_{X} Q_{N-X}^{N}) \rho_{N}^{\pi} + \sum_{X} Q_{X-N}^{X} \rho_{X}^{\pi}$$
(8)

where S_{1s}^{N} reflects the 1s² core polarisation and S_{1p}^{N} reflects polarisation of the lone pair.

By a consideration of the isotropic couplings for nitrogen atoms,²⁴ $\dot{N}H_2^{25}$ and $\dot{N}H_3^{26}$ radicals, with different numbers of lone pairs and bonds, and Sustmann's value for the ¹⁴N coupling in R—N=N—R⁻ radical anions,¹⁹ we obtained the parameters in table 2. From eqn (8) and our derived parameters (taking $Q_{X-N}^x = 0$) we predict an isotropic coupling of 10.15 G for the hydrazine radical cation H_2N —N H_2^{+} . This compares very well with the experimental value of 11.5 G;²⁷ however, it has been shown that in the case of 1,4-dihydropyrazine cations²⁸ there is a small positive Q_{X-N}^x term of 2.62 G. We can

therefore calculate a nearly equal value of 2.7 G for the hydrazine cation. From our data, we calculate ¹⁴N couplings of 9.3 G in R—N=N—R⁺ cations. This is close to the experimental values of 8 G, although the broad e.s.r. lines put an error of ± 2 G on these. The derived S and Q values show clearly that the difference in the isotropic couplings for the hydrazine and azoalkane radical cations is due to the smaller contribution resulting from polarisation of the lone pair than of the N—H bonding electrons. We note that the term due to polarisation of the 1s² core is negative, as in the case of ¹³C, although it is much smaller. In contrast with the (Q_{X-C}^{x}) parameter for carbon, which is negative, the $Q_{N'-N}^{N+}$ parameter for nitrogen is positive and cannot therefore be due to the bond excitation $\sigma_{N-N} \rightarrow \sigma_{N-N}^{*}$. Similar conclusions were drawn previously from work on aromatic nitrogen-containing anions.²¹

From the anisotropic ¹⁴N coupling in the imine cation, MeCH=NBuⁿ⁽⁺⁺⁾, we obtain a 2p orbital density on nitrogen of 0.64. From eqn (8), we predict an isotropic coupling of 10.7 G, which compares excellently with the experimental value of 10.7 G obtained by taking $A_{N_{\perp}} = 0$. This suggests that the derived S and Q parameters are also applicable to imine cations.

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References

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- 1 T. Shida and S. Iwata, J. Am. Chem. Soc., 1973, 95, 3473.
- 2 H. D. Roth, Acc. Chem. Res., 1987, 20, 343.
- 3 L. B. Knight, B. W. Gregory, S. T. Cobranchi, F. Williams and X-Z. Qin, J. Am. Chem. Soc., 1988, 110, 327, and references therein.
- 4 M. C. R. Symons, Chem. Soc. Rev., 1984, 13, 393.
- 5 M. Shiotani, Magn. Reson. Rev., 1987, 12, 333.
- 6 H. Bock and W. Kaim, Acc. Chem. Res., 1982, 15, 9.
- 7 P. W. F. Louwrier, G. A. Brinkmann, C. N. M. Bakker and E. Roduner, Hyperfine Int., 1986, 32, 753.
- 8 C. J. Rhodes and P. W. F. Louwrier, J. Chem. Res. (S), 1988, 38.
- 9 D. H. Bae, P. S. Engel, A. K. M. Mansural Hoque, D. E. Keys, W-K. Lee, R. W. Shaw and H. J. Shine, J. Am. Chem. Soc., 1985, 107, 2561.
- 10 W. Adam and M. Dorr, J. Am. Chem. Soc., 1987, 109, 1570.
- 11 K. N. Houk, Y-M. Chang and P. S. Engel, J. Am. Chem. Soc., 1975, 97, 1824.
- 12 C. Sandorfy, J. Photochem., 1981, 17, 297.
- 13 M. C. R. Symons, Chemical and Biochemical Aspects of Electron Spin-Resonance Spectroscopy (Van Nostrand Reinhold, New York, 1978).
- 14 J. K. Kochi, Adv. Free-Radical Chem., 1975, 5, 189.
- 15 D. D. M. Wayner and D. R. Arnold, Can. J. Chem., 1985, 63, 2378.
- 16 G. W. Eastland, D. N. Ramakrishna-Rao and M. C. R. Symons, J. Chem. Soc., Perkin Trans. 2, 1984, 1551.
- 17 D. N. Ramakrishna-Rao and M. C. R. Symons, J. Chem. Soc., Perkin Trans. 2, 1985, 991.
- 18 C. J. Rhodes and M. C. R. Symons, J. Chem. Soc., Chem. Commun., 1987, 258.
- 19 R. Sustmann and R. Sauer, J. Chem. Soc., Chem. Commun., 1985, 1248.
- 20 M. Karplus and G. K. Fraenkel, J. Chem. Phys., 1961, 35, 1312.
- 21 J. C. M. Henning, J. Chem. Phys., 1966, 44, 2139, and references therein.
- 22 C. L. Talcott and R. L. Myers, Mol. Phys., 1967, 12, 549, and references therein.
- 23 R. A. Jackson and C. J. Rhodes, J. Chem. Soc., Perkin Trans. 2, 1985, 121.
- 24 P. W. Atkins and M. C. R. Symons, The Structure of Inorganic Radicals (Elsevier, Amsterdam, 1967).
- 25 D. W. Pratt, J. J. Dillon, R. V. Lloyd and D. E. Wood, J. Phys. Chem., 1971, 75, 3486.
- 26 T. Cole, J. Chem. Phys., 1961, 35, 1169.
- 27 J. Q. Adams and J. R. Thomas, J. Chem. Phys., 1963, 39, 1904.
- 28 B. L. Barton and G. K. Fraenkel, J. Chem. Phys., 1964, 41, 1455.

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