Electron Paramagnetic Resonance Study of Imine Radical Cations in Low-temperature Solid Matrices

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A series of imine radical cations has been studied by EPR spectroscopy, generated in low-temperature halogenocarbon matrices by γ -radiolysis. Radicals of the type ArCH=NR⁺⁺ [Ar = Ph or *p*-Me-C₆H₄⁻] tend to be formed in the ²A' state, corresponding to ionisation of the in-plane (mainly the nitrogen lone-pair) a' orbital (I). These are isostructural with the corresponding vinyl radicals and show angular geometries at the radical centres and large couplings (*ca.* 85 G) to the proton *trans* to the nominally nitrogen-localised SOMO (I). When R = Bu^t, a 12 G long-range coupling is observed to a single proton from the Bu^t group, arising *via* the W-configuration (II). This coupling was found to persist in the CFCl₃ matrix up to its melting point (*ca.* 160 K), but was lost reversibly in the higher melting CCl₄ matrix at *ca.* 200 K.

When R = phenyl, the radical centre is rendered linear, because of the partial π -bonding between the aromatic ring and the nitrogen atom due to delocalisation of the unpaired electron, as shown by a fall in the parallel (¹⁴N) coupling with a concomitant increase in the nitrogen 2p/2s ratio, and by the observation of couplings to the *ortho* and *para* phenyl protons.

For imines derived from benzophenone (Ph₂C=NR) the tendency is for ionisation to occur from the π -orbital (III) which has large spin densities on the *para* carbon atoms.

Benzophenone imine ($Ph_2C=NH$), in addition to forming the π -state (**III**), was found to deprotonate, giving rise to the $Ph_2C=N^*$ radical. Similar behaviour was shown by benzophenone oxime, which gave only the corresponding iminoxyl radical ($Ph_2C=N-O^*$), and we propose that this is due to the dissolution of the latter two materials in the form of hydrogen-bonded molecular clusters in the non-polar freon solvent, thus facilitating deprotonation of the primary cations.

Despite the involvement of imine radical cations in some chemical reactions^{1,2} and in mass spectrometry of organic nitrogen compounds,³ there is little direct experimental evidence for their structural nature, although there have been theoretical studies^{4,5} and photoelectron (PES) measurements made on the parent compounds.^{6,7} An imine radical cation $[R_2C=N-R^{++}]$ is isoelectronic with the corresponding vinyl radical $[R_2C=C-R]$ and so structural parallels might be expected between the two. PES studies indicate that σ -cations, which are isostructural with vinyl radicals, are formed from simple imines,⁶ by the lowest-energy ionisation of the in-plane a' orbital (I) corresponding mainly to the nitrogen lone pair; this is supported by theoretical calculations at both MNDO⁵ and *ab initio*⁴ levels which predict ²A' geometries.

The situation is different for conjugated imines, where the π -level is brought into close energetic proximity with the a' level,⁶ and so the formation of an alternative π -structure is a real possibility: indeed, for the phenyl-substituted imines, PhCH=NMe and Ph₂C=NMe, PES⁷ shows that the lowest energy bands are due to ionisation from π -levels. Our pre-liminary EPR work on a limited number of imines⁸ indicated that π states were formed, and did not provide evidence for the expected ²A' cations; thus, the question of whether a ²A' or a π ground state is appropriate for imine radical cations seemed worthy of a more detailed investigation using a wider range of compounds.

Experimental

The imines were prepared by condensation of the appropriate aldehyde or ketone with the corresponding amine. The products were purified by distillation or by crystallization and purities (>97% in all cases) were determined by GC and ¹H

NMR spectroscopy. Samples of benzophenone imine and benzophenone oxime were obtained from Aldrich and were used as supplied.

Dilute solutions of each compound (0.05-1.0%) were prepared in CFCl₃ or CCl₄ solvents (both obtained in the highest available grade of purity from Aldrich, and further purified by filtering through activated alumina) and were frozen in liquid nitrogen prior to exposure to ⁶⁰Co γ -rays to a dose of *ca.* 1 Mrad. The EPR spectra were recorded with a Bruker ER 200D spectrometer, usually at 77 K using a liquid-nitrogen sample finger Dewar supported in the microwave cavity, or using a Bruker variable-temperature device when specific temperatures (referred to in the text) were required.

Results and Discussion

p-MeC₆H₄CH=NBu^{t·+}, PhCH=NBu^{t·+} and *p*-MeC₆H₄CH=NMe^{·+} Radical Cations

The radical cation of p-MeC₆H₄CH=NBu^t in CFCl₃ at 77 K exhibits an anisotropic coupling to ¹⁴N and a large doublet coupling to a single proton of *ca*. 80 G. (A typical spectrum is shown in fig. 1.) We therefore assign this to the ²A' state of the parent cation (I). The other potential candidate for this species, which would also be expected to show a large proton coupling in the region of 80 G, is the neutral radical, p-MeC₆H₄CH=N', formed by elimination of a Me₃C⁺ carbenium ion; however, the value for $A_{||}$ (¹⁴N) (50 G) is much larger than is normally observed for (π) RCH=N' radicals^{9,10} (*ca*. 35 G, see later section) and the resolution of perpendicular (¹⁴N) components (13 G) clearly discloses the σ nature of the SOMO. Interestingly, there is an additional isotropic doublet splitting (12 G) of all the features, and one possible explanation is that this is due to superhyperfine



Fig. 1. X-Band EPR spectrum recorded following γ -irradiation of p-MeC₆H₄CH=NBu⁴ in CFCl₃ at 77 K, and assigned to the ²A' radical cation.

coupling to a single solvent ¹⁹F nucleus, as has been documented previously for other organic radical cations in solid $CFCl_3$.^{11,12} In order to test for this, we repeated the experiment using solid CCl_4 as the matrix, where no such ¹⁹F coupling is possible, but obtained the spectrum in fig. 2(*a*) in which the doublet splitting is still present.

It is clear then, that the 12 G splitting must be due to coupling with a single proton: this is presumably from the Bu' group, since no such splitting was observed in the analogous $p-\text{MeC}_6\text{H}_4\text{CH}=\text{N}-\text{Me}^{++}$ radical cation. We propose that a W-configuration of the Bu' group is adopted (II) at low temperatures, that can transmit spin density through the C-C σ system to the single proton shown.



Fig. 2. (a) EPR spectrum showing features from the ${}^{2}A'$ p-MeC₆H₄CH-NBu^{"+} radical cation at 77 K in CCl₄; (b) sample from (a), recorded at ca. 200 K, showing loss of the doublet substructure. Feature marked a is from CCl₃ radicals.

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Although (II) must be stable on the EPR timescale at 77 K, it is expected that, on raising the temperature, the increased weighting of torsional states, with negligible proton coupling, will result in the reversible loss of the 12 G splitting. No change was observed in the spectrum when using the CFCl₃ matrix, even on annealing up to the melting point (*ca.* 160 K); however, in the higher-melting solid CCl₄, the doublet was lost at *ca.* 200 K, where the matrix was still rigid [fig. 2(*b*)], but was restored on subsequent recooling to 77 K. We note that the features are much better resolved in CCl₄ [fig. 2(*a*)] than in CFCl₃ (fig. 1) because the linewidth is smaller in the former medium, and may be due to a weak but unresolved ¹⁹F coupling in the CFCl₃ matrix.

The spectrum in fig. 3(a) was recorded following γ -radiolysis of PhCH=NBu^t in CFCl₃, from which ¹⁴N and ¹H couplings are obtained (table 1) that are very similar to those mea-



Fig. 3. (a) EPR spectrum from PhCH=NBu¹ following γ -radiolysis in CFCl₃, assigned to the ²A' cation, showing additional ¹⁹F superhyperfine coupling (see text); (b) from PhCH=NBu¹ in a CCl₄ matrix, showing loss of ¹⁹F coupling. Feature marked *a* is from CCl₃ radicals.

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Table 1. Hyperfine couplings for imine radical cations and related radicals

radical	coupling/G ⁴	T/K
p-MeC _c H ₄ CH=NBu ^{t*+} /CFCl ₂	80(1H), 12(1H), 50(A_{\parallel}^{-14} N), 13(A_{\perp}^{-14} N), 25.3(A_{ieo}^{-14} N)	77
$p-MeC_{\epsilon}H_{\epsilon}CH=NBu^{\iota+}/CCl_{\epsilon}$	84(1H), 13(1H), 51($A_{\parallel}^{\parallel 14}$ N), 14($A_{\perp}^{\perp 14}$ N), 26.3($A_{iso}^{\perp 14}$ N)	77
$p-MeC_{H}CH=NBu^{i++}/CCL$	85(1H)	200
PhCH=NBu ^{''+} /CFCl,	$84(1H)$, 12(1H), 50($A_{\parallel}^{14}N$), 12($A_{\perp}^{14}N$), 24.7($A_{ieo}^{14}N$), 8(¹⁹ F)	77
$PhCH = NBu^{t+}/CCL$	86(1H), 12(1H), 48($A_{\parallel}^{\parallel 14}$ N), 11($A_{\perp}^{\perp 14}$ N), 23.7($A_{\perp 0}^{\parallel 14}$ N)	77
PhCH=NBu ^{te+} /CCl	86(1H)	200
p-MeC, H, CH=NMe' +/CFCl,	$85(1H)$, 33(3H), 49($A_{\parallel}^{-14}N$), 13($A_{\perp}^{-14}N$), 25.0($A_{\perp}^{-14}N$)	77
$Ph_2C = NPh^{+}/CFCl_2$	$6(2H), 8(2H), 28(A_{\parallel}^{-14}N)$	77
$PhCH = NPh'^+/CFCl_2$	$33(1H), 6(2H), 8(1H), 26(A_{\parallel}^{14}N)$	77
$Ph_{c}C = NMe^{+}/CFCl_{2}$	$30(3H)$, $53(A_{\parallel}^{14}N)$, $18(A_{\perp}^{14}N)$, $29.7(A_{in}^{14}N)$	77
$Ph_2C = NBu^{t+}/CFCl_2$	$9.2[A_{\parallel}(2H)], 5.2[A_{\parallel}(2H)], 6.5[A_{\mu}(2H)]$	77
$Ph_{2}C = NBu^{n^{*}+}/CFCl_{2}$ (π)	$8.8[A_{1}](2H), 5.2[A_{1}](2H), 6.4[A_{10}](2H)]$	77
$Ph_{2}C = NBu^{n^{+}}/CFCl_{2}$ (σ)	$15(\bar{1}H), 51(A_{\parallel}^{14}N), 22(A_{\parallel}^{14}N), 31.7(A_{\mu}^{14}N)$	
$Ph_2C = NH'^+/CFCl_2$ (π)	7(2H)	77
$Ph_2C=N$	$37.5(A_{\parallel}^{-14}N)$	77
$Ph_2^2C=N-O^*$	$27(A_x)^{\mu} 26(A_y), 43(A_z), 32.3(A_{iso})$	77

 $a = 1 G = 10^{-4} T.$

sured from p-MeC₆H₄CH=NBu^t in this medium: this shows that the ²A' cation is again formed, but here, the substructure is more complex. In CCl₄ [fig. 3(b)] the simple 12 G doublet splitting is again apparent, suggesting that there is a similar preferred W-conformation of the Bu^t group (II). Careful comparison of the two spectra [fig. 3(a) and (b)] reveals that the additional substructure in solid CFCl₃ is due to an additional (8 G) doublet coupling, almost certainly from a single solvent ¹⁹F nucleus. As before, annealing the CCl₄ matrix to *ca*. 200 K resulted in loss of the ¹H doublet splitting, which was restored on cooling again to 77 K.

The central region of the spectrum recorded from $p-MeC_6H_4CH=NMe$ in CFCl₃ (fig. 4) is partially obscured by features from a second radical, the origin of which is as yet unclear to us. The remaining features, however, establish the presence of the ²A' cation (I). The spectum shows no evidence of superhyperfine coupling to a solvent nucleus and the long-range coupling observed for the t-butyl analogue is absent, thus supporting our assignment of its origin in the previous two examples.

The results from these radicals confirm their close structural analogy with (bent) vinyl radicals,¹³ and enable us to determine the distribution of the a' SOMO (I). The total spin density on the nitrogen atom is *ca.* 0.79 with significant density in the *trans* hydrogen 1s orbital. From the anisotropic ¹⁴N couplings, p/s ratios of *ca.* 16 are derived which lead to C=N-R bond angles of *ca.* 153° (table 2) using Coulson's equation for C_{2v} symmetry.¹⁴ This compares favourably with the value of 156.1° obtained from an *ab initio* calculation on the H₂C=N-Me'⁺ radical cation.⁴ However, the standard treatment for deriving bond angles from EPR data assumes that all of the s-orbital component arises from the s-p hybridisation of the singly occupied orbital.¹⁵ Since some of this actually stems from spin-polarisation of the other selectrons on the nitrogen atom,¹⁶ the p/s ratios will be somewhat smaller than that corresponding to the true hybridisation of the SOMO, leading to apparently reduced bond angles. We therefore adopted our previous treatment and parametrisation for spin-polarisation in nitrogen-containing radicals⁸ to estimate this indirect s contribution using the measured 2p spin densities. Correction of the measured s-orbital spin density for this induced component leads to an s contribution of 0.029 from hybridisation of the SOMO and a true p/s ratio of ca. 26. The C=N-R angle thus becomes ca. 158°, which is marginally closer to, but now



Fig. 4. EPR spectrum recorded from $p-MeC_6H_4CH=NMe$ in CFCl₃ at 77 K, following γ -radiolysis. Parallel and perpendicular ¹⁴N features are marked that are readily assigned to the ²A' cation; the central region is partially obscured by features from a secondary radical (d).

Table 2. Orbital spin densities and derived C=N-R bond angles for σ imine radical cations

radical	N(2p)	N(2s)	p/s	$C = N - R^{a}$	C=N-R ^b	$\sum_{N} p + s$
PhCH=NBu ⁱ +	0.744	0.046	16.2	152.9	158.0	0.790
$p-MeC_6H_4CH=NBu^{t+1}$	0.744	0.046	16.3	153.0	158.4	0.790
$p-MeC_{6}H_{4}CH=NMe^{+}$	0.724	0.045	16.1	152.8	157.8	0.769
Ph ₂ C=NMe ⁺	0.704	0.053	13.3	150.4	154.5	0.757
Ph ₂ C=NBu ^{n·+}	0.744	0.051	14.6	151.6	154.4	0.795

^a Calculated from p/s ratio using the appropriate equation from ref. (14). ^b Calculated from correcting for the spin-polarisation contribution to the isotropic coupling.

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larger than, the *ab initio* result.⁴ We note that although this type of procedure should lead to an improvement in the accuracy of bond angles calculated from EPR data, the uncertainty regarding the degree of bent bonding (incomplete orbital following) that exists in radicals¹⁷ remains a potential source of error.

A C=C-H bond angle of 151° was calculated by Fessenden¹³ for the vinyl radical, $H_2C=\dot{C}-H$, from the isotropic ¹³C coupling, presumably on the basis that the occupancy of the singly occupied hybrid s-p orbital was unity, after correcting for the spin-polarisation contribution. However, the large β -proton couplings in vinyl show that there is an appreciable delocalisation of spin density into the hydrogen 1s orbitals, and by allowing for this, we obtain a revised value of 148° for vinyl, which is only marginally different from that above, but indicates that the imine cations are apparently more linear than their isoelectronic, carboncentred, counterparts by ca. 10°. Alternatively, if we derive the C=N-R bond angles from the isotropic ¹⁴N couplings, correct for spin-polarisation (see above) and make the same assumption of unit occupancy as was made for vinyl, we obtain an angle of 161°, which is again 10° greater than that obtained for vinyl by a similar treatment, and so both models lead to the same conclusion regarding the relative configurations of these two systems.

Ph₂C=N-Ph⁺ and PhCH=N-Ph⁺⁺ Radical Cations

In the spectrum of the $Ph_2C=N-Ph'^+$ radical cation, well defined parallel components are resolved (fig. 5) which again show that ionisation has occurred from the a' orbital (I); however, the perpendicular components are not resolved and are taken to be within the linewidth [$\therefore A_{\perp}(^{14}N) = 0 \pm 2$ G]. This leads to a p/s ratio of >27, which is within the typical range found for π radicals and establishes a linear geometry at the nitrogen atom. We attribute this change in structure to partial π -bonding between the aromatic ring and the nitrogen atom. This is supported by the observed reduction in the N 2p spin density to 0.56, assuming that $A_{\perp}(^{14}N) = 0$, and by the observation of couplings to the ortho and para ring protons that are of similar magnitude to those reported for the Me_2NPh^{+} radical cation¹⁸ and for the anilino radical, PhNH¹⁹

A similar effect was found to operate in vinyl radicals with α -phenyl substituents, which have been shown to possess a linear configuration of the radical centre by both EPR²⁰ and μ SR^{21,22} methods. We have estimated²² that the spin density at the radical centre in the H₂C=C-Ph radical is 0.65, and so, given the spin density (2p) at the nitrogen atom in the $Ph_2C=N-Ph^{+}$ radical of 0.56, we conclude that spin delocalisation by a phenyl substituent from a nitrogen radical centre is more effective than that from a carbon radical centre.

The PhCH=NPh'⁺ radical cation has a very similar structure and spin distribution, the main difference being the additional doublet splitting of 33 G from the β -proton. Since the 2p spin density at the nitrogen atom is 0.52, a β -proton coupling of 63 G may be predicted for a hypothetical localised linear imine radical cation. This is to be compared with the nearly identical value obtained for a similar (hypothetical) localised linear vinyl radical (63.8 G).²² In view of the well established enhancement of hyperconjugation in radical cations compared with that in neutral radicals,²³ this value might appear somewhat low.

Radicals derived from Ph2C=NBu^t, Ph2C=NBuⁿ and Ph₂C=NMe

The spectrum recorded from Ph₂C=NBu^t in CFCl₃ at 77 K (fig. 6) is quite different from those discussed so far, and the absence of coupling to the ¹⁴N nucleus excludes a ²A' structure. In fact, the spectrum may be readily analysed as an anisotropic two-proton triplet pattern $[A_{\parallel} = 9.2 \text{ G}; A_{\perp} =$ 5.2 G] which we ascribe to the formation of the π structure with the SOMO of the form (III): this is the form of the Huckel HOMO for the related 1,1-diphenylethene.²⁴



The spectrum from the n-butyl derivative, Ph₂C=NBuⁿ (fig. 7), shows intense central features with identical parallel and perpendicular coupling constants (table 1) owing to the formation of a cation with a similar π -SOMO (III); however, this pattern is flanked by weaker features which we tentatively assign to the simultaneous formation of the ²A' state. This phenomenon has been documented for other systems²⁵ and shows that the σ (a') and π (III) levels are of similar energy. In support of this interpretation we note that the derived orbital populations are in good accord with those for the other ${}^{2}A'$ cations given in the table 2.





10 G

Fig. 6. EPR spectrum recorded from Ph₂C=NBu^t in CFCl₃ at 77 K, after radiolysis, showing only the alternative π radical cation (III).

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Fig. 7. EPR spectrum from $Ph_2C=NBu^n$ in CFCl₃ at 77 K, after radiolysis, showing features from both $\pi(e)$ and ²A' radical cations.

The other extreme of behaviour is shown by the methyl derivative, $Ph_2C=NMe$, from which a spectrum was recorded (fig. 8) showing only the formation of the ²A' radical cation, although the presence of minor amounts of the alternative π state cannot be excluded. Collectively, these results indicate that the π and a' orbitals in imines of the type $Ph_2C=NR$ are very close together in energy, and so the subtle choice between them regarding ionisation can be influenced by the nature of the group R. PES data⁷ for $Ph_2C=NMe$ shows that the lowest-energy ionisation corresponds to a π -orbital, in contrast with the EPR results, but whereas PES results can be thought of as relating to cations formed by essentially vertical ionisations, the EPR results refer to the fully relaxed cations, which may partly account for the difference.

Radicals derived from Benzophenone Imine, Ph₂C=NH

Ph₂C=NH also exhibits features (fig. 9) from a mixture of two radicals: (i) a central triplet (c), with an average spacing of *ca*. 7 G, similar to that observed from the π states of Ph₂C=NBu^{*+} and Ph₂C=NBu^{*+} radical cations, discussed above, and (ii) a pair of parallel features separated by 75 G, which we assign to the $|\pm 1\rangle$ components of a ¹⁴N triplet, the central $|0\rangle$ feature being coincident with the central line of the (2H) triplet pattern (I). This leads to a



Fig. 8. EPR spectrum from $Ph_2C=NMe$ in CFCl₃ at 77 K, after γ -radiolysis, showing only the presence of the ²A' cation.



Fig. 9. EPR spectrum recorded from benzophenone imine after radiolysis in $CFCl_3$, showing features from the π cation (f) and from $Ph_2C=N^2$.

parallel (¹⁴N) coupling of 37.5 G which we ascribe to the neutral $Ph_2C=N^*$ radical, formed by deprotonation of the parent $Ph_2C=NH^{*+}$ cation. Since we were unable to prevent the formation of this species, even on dilution of the freon solution to a substrate concentration of 1:2000, and thus obtain the spectrum of the parent radical cation, we propose that $Ph_2C=NH$ does not dissolve in freon to give isolated single molecules, but associates through hydrogen bonding to give dimeric (or higher) clusters, wherein deprotonation may readily occur (scheme 1). Similar reactions within clusters have been observed previously with relatively polar substrates in CFCl₃, leading to the formation of neutral radicals.²⁶



The parallel ¹⁴N coupling in the $Ph_2C=N$ radical (37.5 G) is significantly larger than that in the $H_2C=N$ radical $(34.4 \text{ G})^9$ and is of relevance to the question of the relative magnitude of hyperconjugation, involving C-H or C-C bonding pairs, in radicals. It is reasonable that the difference in A_{\parallel} (¹⁴N) is to be found in the smaller degree of spindelocalisation from the nitrogen atom in the $Ph_2C=N$ than that in $H_2C=N$, and we can scale up the isotropic value for the nitrogen coupling in $H_2C=N^*$ (9.5 G)⁹ by (37.5/34.4) to give an estimated value of $A_{iso} = 10.4$ G for Ph₂C=N^{*}, which on subtraction from A_{\parallel} yields a nitrogen 2p spin density of 0.819: therefore, each phenyl group has delocalised 0.091 of the total spin density. This compares with a value of 0.124 per hydrogen atom in $H_2C=N'$, and so the relationship $(\Delta_{\rm C} = 0.731 \Delta_{\rm H})$ is obtained, in accord with the view that hyperconjugation involving a C-H bond pair is more effective than that involving a C-C bond pair;²⁷ however, it is important to note that C-C hyperconjugation is by no means negligible. It is noteworthy that a delocalisation of 0.124 into a hydrogen 1s orbital implies a coupling of only 62 G, in contrast with that observed (91.2 G);⁹ therefore, we attribute the further enhancement of the coupling to the indirect $[C-H \rightarrow C-H^*]$ spin-polarisation mechanism.²⁸ This

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Fig. 10. EPR spectrum recorded from benzophenone oxime after radiolysis in $CFCl_3$, showing features from the iminoxyl radical, $Ph_2C=N-O$.

must provide an additional H (1s) spin density of 0.059, and so we obtain the result that the contributions to the β -proton coupling are 68% from the direct (hyperconjugative) and 32% from the indirect (spin-polarisation) mechanisms.



Radiolysis of Ph₂C=NOH in CFCl₃

Fig. 10 shows a typical spectrum obtained following γ -radiolysis of benzophenone oxime in CFCl₃. The parameters obtained (table 1) are extremely similar to those previously reported from γ -irradiation of the pure material²⁹ and assigned to the iminoxyl radical, Ph₂C=N-O', and no additional proton coupling is observed. The spectrum was found not to change appreciably on further dilution of the solution and so we propose that the oxime is not present in 'monomeric' form in freon solution (*cf.* results for Ph₂C=NH, discussed above) and that deprotonation of the Ph₂C=NOH' + radical cation occurs within an associated state (scheme 2).

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