Radical Cations from *N*-Alkyl Substituted Imines: an EPR Study

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Following γ-radiolysis of dilute solutions of imines in trichlorofluoromethane at 77 K, EPR spectra of the corresponding radical cations were recorded. For PhCH=NEt and $PhCH{=}NCHMe_2$ the primary $^2A'$ cations were formed, but in each case as a mixture of cations with different conformations of the alkyl group. The complex spectra were assigned with the aid of those for the deuteriated analogues PhCD=NEt and $PhCD{=}NCHMe_2$. For $Ph_2C{=}NEt$, two cations differing by the conformation of the ethyl group were observed; for $Ph_2C{=}NCHMe_2$, only a single conformer was evident. In an attempt to induce a σ/π 'crossover', the compounds p-Cl–$C_6H_4CH{=}NBu^t$ and p-MeO–$C_6H_4CH{=}NBu^t$ were studied: the latter did indeed form a π-cation, while the former gave the normal $^2A'$ cation. The neopentyl derivatives $PhCH{=}NCH_2Bu^t$ and $Ph_2C{=}NCH_2Bu^t$ gave only the distonic radical cations $PhCH{=}\overset{+}{N}H{-}CH_2C(Me_2)CH_2^{\bullet}$ and $Ph_2C{=}\overset{+}{N}H{-}CH_2C(Me_2)CH_2^{\bullet}$, formed by an intramolecular hydrogen atom transfer. By studying the series of deuteriated compounds, $PhCD{=}NCH_2CH_2CH_2CH_3$, $PhCD{=}NCD_2CH_2CH_2CH_3$ and $PhCH{=}NCD_2CH_2CH_2CH_3$, it is shown that, on radiolytically-induced single electron oxidation, PhCH=NBu gives the distonic radical cation $PhCH{=}\overset{+}{N}HCH_2CH_2\dot{C}HCH_3$.

Imine radical cations have been implicated as intermediates in chemical reactions[1,2] and in mass spectrometry of organic nitrogen containing compounds.[3] That these cations should readily perform hydrogen atom abstractions[1,2] suggests a σ-electronic structure, analogous to that of vinyl radicals: this was confirmed by our previous EPR study[4] which showed that they exist in $^2A'$ states, unless the π-system is extensively conjugated in which case a π-structure may be formed. These conclusions are broadly in accord with photoelectron studies.[5]

Since they are σ-type radicals, imine radical cations are of particular interest in terms of the coupling that is shown by β-protons from *N*-alkyl substituents R ($C{=}\overset{+\bullet}{N}{-}R$), because the sp hybridisation of the singly-occupied orbital lowers the symmetry of the hyperfine interaction from that present in a π-radical, such that two inequivalent maxima are present, corresponding to the eclipsing by the C–H bond of either the large or small lobe of the nominally localised singly occupied molecular orbital (SOMO); the latter corresponding to the greater maximum.[6–8]

Under cryogenic conditions, specific conformations arising through the influence of steric and electronic control might be expected to be 'frozen-out', thus giving information about conformations close to energy minima. With this in view, we undertook the present study, in which the nature of the alkyl group R is varied through two series of radicals: PhCH=N–R and $Ph_2C{=}N{-}R$.

Experimental

Procedure for Generating Radical Cations.—Dilute (*ca.* 0.1–1.0 mol) solutions of each imine were prepared in trichlorofluoromethane and were frozen to small polycrystalline beads in liquid nitrogen, prior to irradiation with a ^{60}Co source to a dose of *ca.* 1.5 Mrad.‡ EPR spectra were recorded, also at 77 K, using a Bruker ER 200D spectrometer.

Preparation of Compounds.—All the required starting materials were purchased from Aldrich.

$PhCD{=}NCHMe_2$, PhCD=NEt *and* $PhCD{=}NBu^n$. $PhCD_2OH$ was prepared by the reaction of freshly-distilled benzoyl chloride with $LiAlD_4$ in diethyl ether. Oxidation of the alcohol with CrO_3–pyridine[9] yielded PhCDO. This was used for the preparation of the imines titled above, *via* dropwise addition of a 50% excess of the appropriate amine (70% $EtNH_2$–H_2O) to a stirred solution of the benzaldehyde in diethyl ether. The stirring was continued for 1 h, after which the mixture was dried ($MgSO_4$), then the solvent was evaporated to yield the product imine.

$PhCD{=}NCHMe_2$. $\delta_H(CDCl_3)$ 7.68 (2 H, m, Ar), 7.39 (3 H, m, Ar), 3.59 (1 H, septet, CH) and 1.24 (6 H, d, Me).

PhCD=NEt. $\delta_H(CDCl_3)$ 7.70 (2 H, m, Ar), 7.42 (3 H, m, Ar), 3.71 (2 H, q, CH_2) and 1.22 (3 H, t, Me).

$PhCD{=}NBu^n$. $\delta_H(CDCl_3)$ 7.69 (2 H, m, Ar), 7.41 (3 H, m, Ar), 3.68 (2 H, t, CH_2), 1.61 (4 H, m, CH_2CH_2) and 1.04 (3 H, t, Me).

$PhCD{=}NCD_2CH_2CH_2CH_3$ *and analogues.* $CH_3CH_2CH_2CN$ was reduced to $CH_3CH_2CH_2CD_2NH_2$ with $LiAlD_4$.[10] An ether solution of this amine was treated with PhCDO as above, to afford the product imine. $\delta_H(CDCl_3)$ 7.69 (2 H, m, Ar), 7.41 (3 H, m, Ar), 1.58 (4 H, m, CH_2CH_2) and 1.05 (3 H, t, Me).

Similarly prepared were $PhCH{=}NCD_2CH_2CH_2CH_3$, $\delta_H(CDCl_3)$ 8.25 (1 H, s, CH=N); and $PhCD{=}NCH_2CH_2CH_2CH_3$, $\delta_H(CDCl_3)$ 3.62 (2 H, t, NCH_2).

p-MeO–$C_6H_4CH{=}NBu^t$. This compound was prepared by adding a 50% excess of *tert*-butylamine in diethyl ether to an ether solution of 4-methoxybenzaldehyde, followed by stirring for 3 days at room temperature. The solution was dried ($MgSO_4$) and solvent evaporated to yield the product. $\delta_H(CDCl_3)$ 8.11 (1 H, s, CH), 7.65 (2 H, d, Ar), 6.82 (2 H, d, Ar), 3.74 (3 H, s, CH_3O) and 1.24 (9 H, s, Bu^t).

p-Cl–$C_6H_4CH{=}NBu^t$. This compound was prepared as for p-MeO–$C_6H_4CH{=}NBu^t$ from p-chlorobenzaldehyde with stirring overnight. $\delta_H(CDCl_3)$ 8.13 (1 H, s, CH=N), 7.68 (2 H, d, Ar), 7.23 (2 H, d, Ar) and 1.24 (9 H, s, Bu^t).

$Ph_2C{=}NCHMe_2$ *and* $Ph_2C{=}NCH_2Bu^t$. These compounds were prepared by condensation of benzophenone with the corresponding amine in the presence of titanium(IV) chloride.[11]

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‡ 1 rad = 0.01 Gy.

Table 1 Hyperfine couplings measured for imine radical cations in a solid $CFCl_3$ matrix at 77 K

Radical	Coupling constant/G
$Ph_2C{=}NEt^{\bullet +}$ A	(1 H) 90.1, $(^{14}N)_{\parallel}$ 50.7, $(^{14})N_{\perp}$ 14.1
B	(1 H) 40.8, $(^{14}N)_{\parallel}$ 53.5, $(^{14})N_{\perp}$ 14.8
$PhCD{=}NEt^{\bullet +}$	(1 D) 12.7, (1 H) 90.1, $(^{14}N)_{\parallel}$ 51.8, $(^{14}N)_{\perp}$ 12.0
$PhCH{=}NEt^{\bullet +}$ C	(1 H) 83.5, (1 H) 91.3, $(^{14}N)_{\parallel}$ 52.1, $(^{14}N)_{\perp}$ 12.0
D	(1 H) 82.0, (1 H) 70.0, $(^{14}N)_{\parallel}$ 52.5, $(^{14}N)_{\perp}$ *ca.* 12
E	(1 H) 81.7, (1 H) 53.8, $(^{14}N)_{\parallel}$ 52.8, $(^{14}N)_{\perp}$ *ca.* 12
$Ph_2C{=}NCHMe_2^{\bullet +}$	(1 H) 40.8, $(^{14}N)_{\parallel}$ 50.7, $(^{14}N)_{\perp}$ 11.3
$PhCD{=}NCHMe_2^{\bullet +}$	(1 D) 13.2, (1 H) 69.0, $(^{14}N)_{\parallel}$ 52.1, $(^{14}N)_{\perp}$ 10.6
$PhCH{=}NCHMe_2^{\bullet +}$ F	(1 H) 85.9, (1 H) 69.7, $(^{14}N)_{\parallel}$ 52.1, $(^{14}N)_{\perp}$ 10.6
G[a]	(1 H) 85.9, (1 H) 23.2
$PhCH{=}NCHMe_2^{\bullet +}/CCl_4$	Σ(1 H) = 115.5, $(^{14}N)_{\parallel}$ 51.4, $(^{14}N)_{\perp}$ 12.1
$p\text{-}ClC_6H_4CH{=}NBu^{t\bullet +}$	(1 H) 80.3, (1 H) 13.4, $(^{14}N)_{\parallel}$ 52.0, $(^{14}N)_{\perp}$ 15.5
$p\text{-}MeOC_6H_4CH{=}NBu^{t\bullet +}$[b]	<5
$Ph_2C{=}\overset{+}{N}H{-}CH_2CMe_2CH_2^{\bullet}$	(2 H) 22.5
$PhCH{=}\overset{+}{N}H{-}CH_2CMe_2CH_2^{\bullet}$	(2 H) 22.5
$PhCH{=}\overset{+}{N}H{-}CH_2CH_2\dot{C}HCH_3$	(3 H) 26.0, (1 H) 22.0, (1 H) 17.2, (1 H) 9.2

[a] ^{14}N couplings not clearly resolved. [b] π-cation.

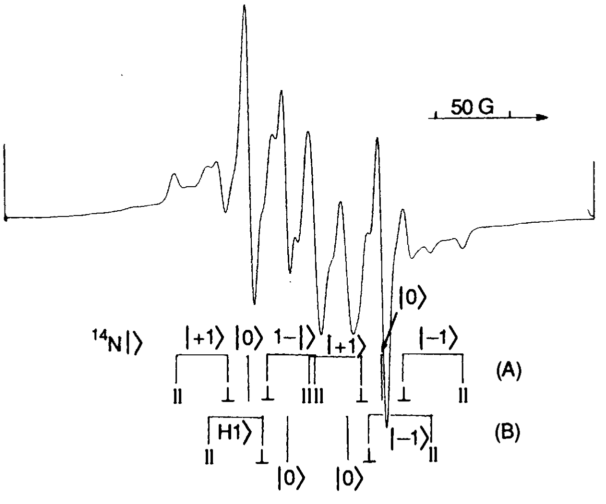

Fig. 1 EPR spectrum recorded at 77 K, showing features from $PH_2C{=}NEt^{\bullet +}$ radical cations, existing in the two conformations **I** and **II**, marked (A) and (B)

$Ph_2C{=}NCHMe_2$. $\delta_H(CDCl_3)$ 7.05 (10 H, m, Ar), 3.15 (1 H, septet, CH) and 0.88 (6 H, d, Me).

$Ph_2C{=}NCH_2Bu^t$. $\delta_H(CDCl_3)$ 7.33 (10 H, m, Ar), 3.15 (2 H, s, CH_2) and 0.95 (9 H, s, Bu^t).

$Ph_2C{=}NEt$. This compound was prepared by dropwise addition of 70% aqueous $EtNH_2$ to a stirred solution of Ph_2CCl_2 in ether. After being stirred overnight, the ether layer was dried ($MgSO_4$) and evaporated. $\delta_H(CDCl_3)$ 7.34 (10 H, m, Ar), 3.44 (2 H, q, CH_2) and 1.25 (3 H, t, Me).

Results and Discussion

The hyperfine coupling data measured for imine radical cations are presented in Table 1, and illustrate the overall view of these radicals as σ-species formed by ionisation from the a′ orbital. We now consider results for particular examples.

$Ph_2C{=}NEt$.—The spectrum shown in Fig. 1 was recorded from a sample of $Ph_2C{=}NEt$ in $CFCl_3$ at 77 K. The principal species present is the nitrogen-centred $^2A'$ cation, showing very similar ^{14}N hyperfine couplings to those reported for the $Ph_2C{=}NMe^{\bullet +}$ radical cation.[4] In the present case, the very large doublet splitting of 90.1 G* shows that the ethyl group is oriented so that one of the β-C–H bonds eclipses the small lobe of the SOMO; the position of maximum coupling **I**. We can be quite certain that this is so since this coupling is close to that (*ca.* 85 G) observed to the imine (CH=N) proton, where the geometry of the C=N double bond forces the imine C–H bond to eclipse the smaller lobe of the SOMO. Inspection of the coupling *vs.* conformation curve (see later section) indicates that for conformation **I** the second β-proton should have a very small coupling and indeed is not resolved in the experimental spectrum. Additional features present in the spectrum are assigned to a second $^2A'$ cation, formed in lower abundance and differing in the conformation adopted by the ethyl group so that a coupling of 40.8 G to a single β-proton is observed. The magnitude of this coupling suggests the conformation **II** where H_a is the more strongly coupled proton (θ = 130°) and, in agreement with the coupling/θ curve (Fig. 2), H_b shows no resolvable coupling since it occupies a position close to the coupling minimum (θ = 250°). Thus, **I** maximises the electronic effect of hyperconjugation while **II** largely minimises steric repulsions.

We also considered an alternative interpretation, that all the features of the spectrum in Fig. 1 arise from a single radical species with the $|0\rangle$ features comprising a doublet (65 G) of doublets (25 G), which can indeed be accommodated on the curve (Fig. 2) so that the conformation **III** is adopted. However, the inner two lines are of much lower intensity than their outer counterparts and there is a clear difference between the measured parallel ^{14}N coupling for the two sets of lines. We therefore favour the assignment of the spectrum as a mixture of two radicals.

$PhCH{=}NEt$.—The spectrum recorded from this compound is shown in Fig. 3(*a*) and is obviously extremely complex. To simplify the situation, we studied the deuteriated analogue $PhCD{=}NEt$ and obtained the spectrum shown in Fig. 3(*b*). This shows a pattern of the $|0\rangle$ features comprising a 90.1 G doublet of 12.7 G (deuterium) triplets; multiplication by the ratio of proton/deuteron magnetogyric ratios yields an equivalent coupling of 83 G. This pattern may be readily recognised in

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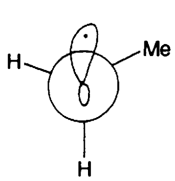
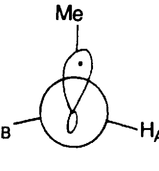
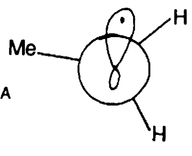
* 1 G = 10^{-4} T.



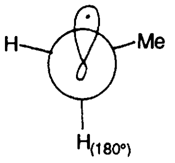
I



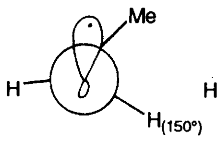
II



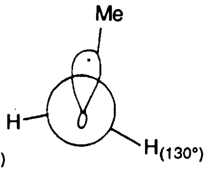
III



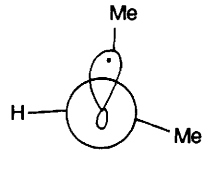
IV(C)



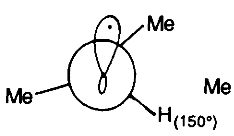
V(D)



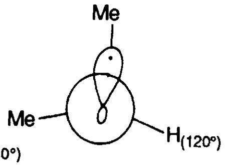
VI(E)



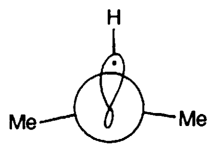
VII



VIII



IX



X

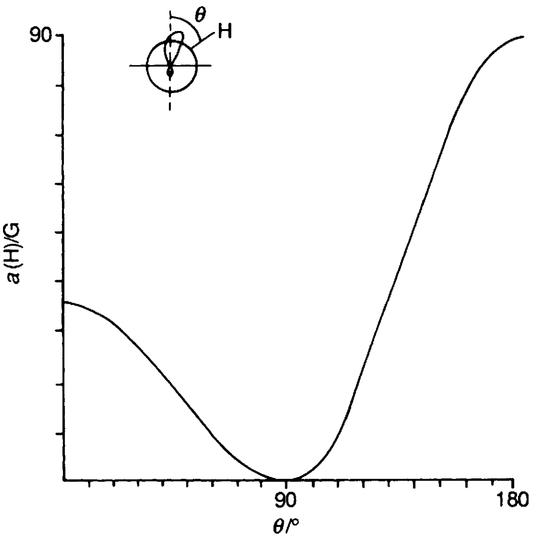


Fig. 2 Curve showing the dependence of the β-proton coupling in an imine radical cation, $C{=}\overset{+\bullet}{N}{-}C$, on its conformation (see the text)

the spectrum in Fig. 3(*a*) along with a set of parallel and perpendicular ^{14}N couplings (marked C). It is clear, however, that there are many additional features present, which we assign to the presence of two other radical cations (D, E), again differing in the precise orientation of their ethyl groups; the ^{14}N couplings are very similar for all three radicals.

The structure of the outer features of the spectrum was essentially unchanged when CCl_4 was used as a matrix which rules out the contribution of ^{19}F superhyperfine coupling[4] to the spectral complexity. The features assigned to the |0⟩ components of the species marked D overlap the perpendicular features of C and E but are genuinely from a third radical since they are matched by parallel features, as are the |0⟩ components of C and E. Consultation of the coupling/θ curve (Fig. 2) reveals that for all three conformers the coupling to the second β-proton should be only small, and accounts for the fact that only a single β-proton coupling is observed in C, D and E. The conformers are thus assigned, respectively, as **IV–VI**.

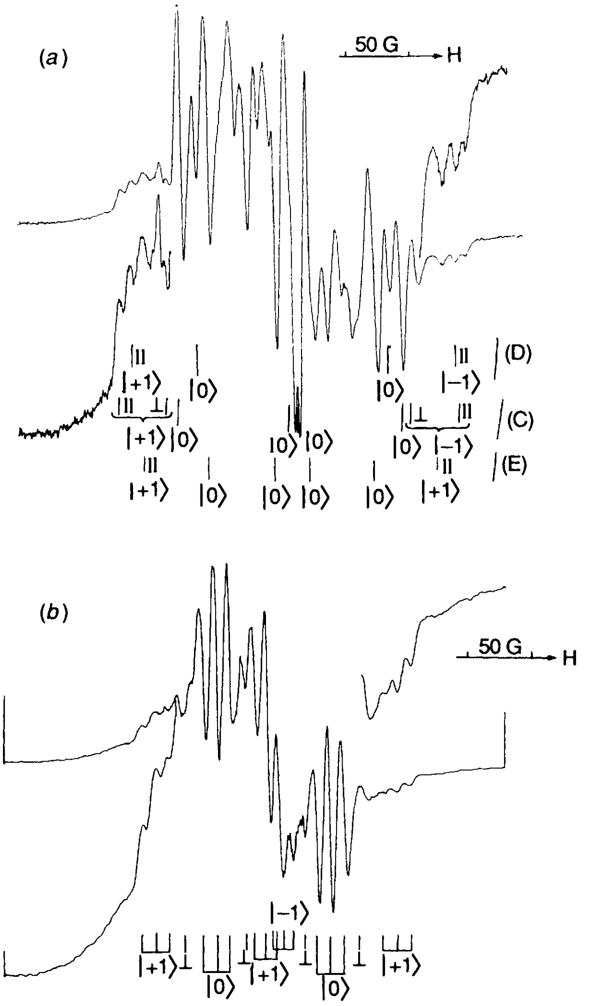


Fig. 3 EPR spectra from: (*a*) $PhCH{=}NEt^{\bullet+}$ radical cations at 77 K, showing three conformations **IV**–**VI**, marked C–E; and (*b*) the deuteriated analogue

In **IV**, hyperconjugation is maximised while in **V** and **VI**, the structure has moved in the direction of reducing steric interactions. Structures **IV** and **VI** are formed in greater abundance than **V**, and are presumably closer to energy minima. We suggest that in **VI**, steric control is not complete, and the ethyl group has twisted slightly through 20° from the true steric minimum, in order to increase hyperconjugation. We presume that a similar mixture of conformers is present in the $PhCD{=}NEt^{\bullet+}$ system: the outer features from C being clearly resolved while the signals from D and E are partly responsible for the overlapping signals in the central region of the spectrum.

$Ph_2C{=}NCHMe_2$ *and* $PhCH{=}NCHMe_2$.—Fig. 4 shows the spectrum recorded from $Ph_2C{=}NCHMe_2$, which given its simple form can be assigned to a single radical species. The ^{14}N coupling data are in the established range for imine radical cations,[4] and the β-proton coupling is identical with that measured for conformer **II** of the $Ph_2C{=}NEt^{\bullet+}$ radical cation. Therefore, a conformation **VII** similar to **II** is implicated.

The spectrum [Fig. 5(*a*)] obtained from $PhCH{=}NCHMe_2$ presents a deceptive appearance since it seemingly comprises a

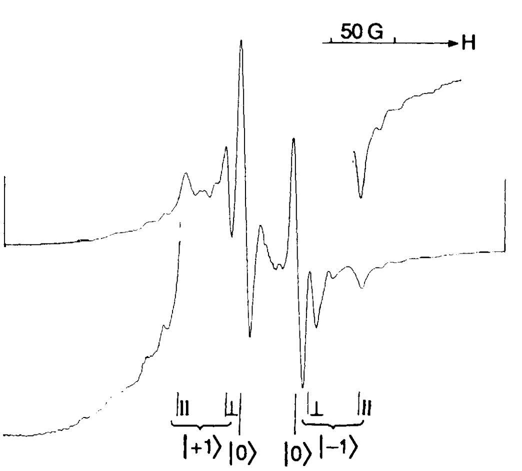


Fig. 4 EPR spectrum from $Ph_2C{=}NCHMe_2^{\bullet+}$ radical cations at 77 K

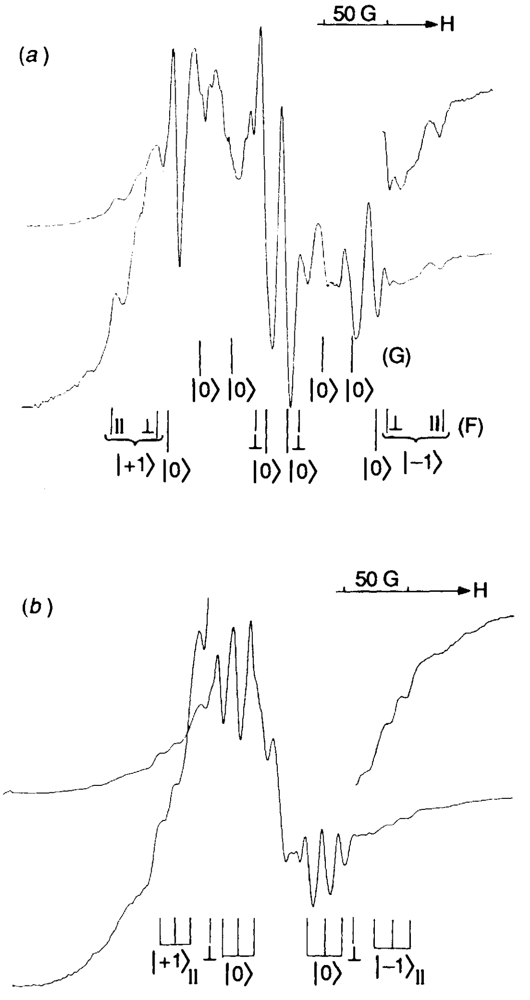


Fig. 5 EPR spectra recorded at 77 K from: (*a*) $PhCH{=}NCHMe_2^{\bullet+}$ radical cations. showing features from two conformations **VIII**, **IX** marked F, G; and (*b*) from $PhCD{=}NCHMe_2^{\bullet+}$ radical cations

triplet (70 G) of doublets (16 G) pattern for the |0⟩ features. The 70 G triplet would need to be assigned to the β-C–H and the CH=N imine protons, but such a considerable decrease in the imine proton coupling from that measured so far (*ca.* 80–86 G) implies a change in the geometry of the radical centre that is not borne out by the ^{14}N data, which are in the typical range. We therefore studied the deuteriated analogue $PhCD{=}NCHMe_2$ in order to check on the CH=N (CD=N) coupling, and obtained the spectrum shown in Fig. 5(*b*).

The |0⟩ features consist of a doublet (69 G) of (deuterium) triplets (13.2 G) and so the β-proton from the isopropyl group has a coupling of 69 G while the imine proton requires a coupling of $13.2(\gamma_H/\gamma_D) = 86$ G, which is in the normal range. It is clear, then, that the |0⟩ components in the spectrum from $PhCH{=}NCHMe_2$ [Fig. 5(*a*)] should be analysed as a doublet (85.9 G) of doublets (69.7 G) pattern, flanked by a set of ^{14}N parallel and perpendicular features. So, additionally, there is a doublet of doublets pattern (85.9 G, 23.2 G) of lower intensity from a second conformer, along with associated parallel ^{14}N components (the perpendicular features from this second species are not resolved due to their overlap with signals from the major conformer).

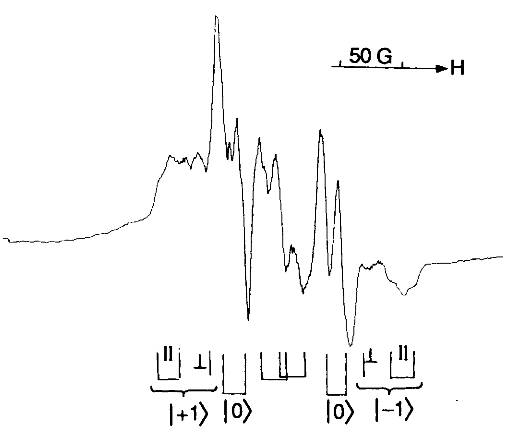


Fig. 6 EPR spectrum recorded at 77 K from $p\text{-}ClC_6H_4CH{=}NBu^{t\bullet+}$ radical cations, showing only the $^2A'$ state

The conformation of the species with the larger β-proton coupling can be assigned to **VIII**; however, that of the radical with the 23 G coupling is more difficult to assign because this coupling is small enough to arise from eclipsing of the C–H bond with either lobe of the SOMO (Fig. 2). Nonetheless, we favour the conformation **IX** because this involves smaller steric interactions than the alternative **X**. Interestingly, when CCl_4 was used as the matrix material, only a species with a total proton coupling of 115 G was observed, suggesting that a single conformer with a relatively small β-proton coupling of *ca.* 29 G was formed.

$p\text{-}MeO\text{-}C_6H_4CH{=}NBu^t$ *and* $p\text{-}Cl\text{-}C_6H_4CH{=}NBu^t$.—We reported previously our results for the $PhCH{=}NBu^{t\bullet+}$ radical cation[4] which was a $\sigma(^2A')$ species. Additionally, we discovered that by extending the conjugation of the π-system, an electronic 'crossover' could be induced, so that $Ph_2C{=}NBu^t$ gave rise to a π-radical cation. It seemed possible, therefore, that by the introduction of a suitable substituent into the aromatic ring the π-highest occupied molecular orbital (HOMO) might be raised in energy above the a′ orbital. For $p\text{-}Cl\text{-}C_6H_4CH{=}NBu^t$, this was found not to be the case, since the spectrum observed (Fig. 6) was that of the $^2A'$ radical cation. However, the sample of $p\text{-}MeO\text{-}C_6H_4CH{=}NBu^t$ became a deep mauve colour following γ-irradiation and its EPR spectrum (Fig. 7) consisted of a narrow singlet feature with no clear substructure. We assign this to the formation of a π-radical cation with couplings of < 5 G, but can say little more except that the spin density on the nitrogen atom must be very low since no ^{14}N parallel features could be detected. The signal was stable to prolonged irradiation with visible light.

$Ph_2C{=}NCH_2Bu^t$ *and* $PhCH{=}NCH_2Bu^t$.—In each case, a 2 H triplet signal was observed with a spacing of 22.5 G (Fig. 8). This we assign to the formation of the distonic radical cations, $Ph_2C{=}\overset{+}{N}HCH_2CMe_2CH_2^{\bullet}$ and $PhCH{=}\overset{+}{N}HCH_2CMe_2CH_2^{\bullet}$, arising from the intramolecular H-atom transfer reaction (1).

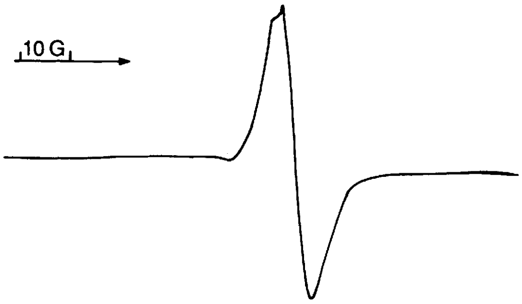


Fig. 7 EPR spectrum recorded at 77 K from p-$MeOC_6H_4CH{=}NBu^{t\bullet+}$ radical cations, assigned to a π-state

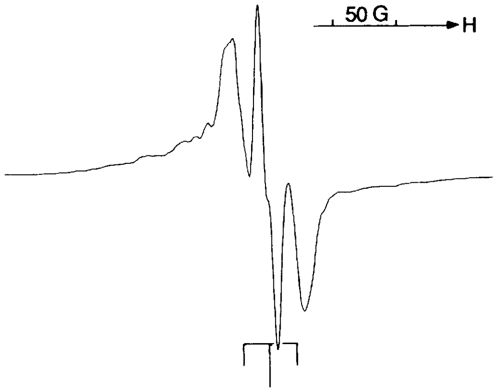


Fig. 8 EPR spectrum recorded at 77 K, following γ-irradiation of $Ph_2C{=}NCH_2Bu^t$ in $CFCl_3$ at 77 K, and assigned to the distonic ion, $Ph_2C{=}\overset{+}{N}H{-}CH_2CMe_2\dot{C}H_2$, formed by the reaction (1)

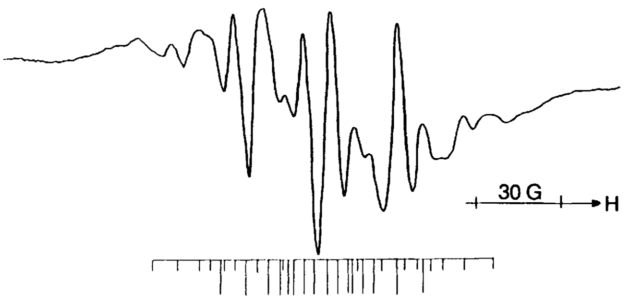
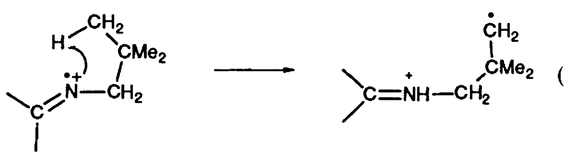


Fig. 9 EPR spectrum recorded at 77 K, following γ-irradiation of $PhCD{=}NCD_2CH_2CH_2CH_3$ in $CFCl_3$ at 77 K, and assigned to the distonic ion $PhCD{=}\overset{+}{N}H{-}CD_2CH_2\dot{C}HCH_3$



(1)

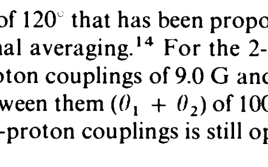
This observation confirms the high reactivity of imine radical cations toward H-atom abstractions[1,2] that is characteristic of σ-radicals in which the SOMO is mainly localised onto a single atom, *e.g.* vinyl and phenyl radicals.

Table 2 Derived orbital populations and bond angles for imine radical cations

Radical	2s[a]	2p	C=N-R[b]
$Ph_2C{=}NEt^{\bullet+}$ A	0.027	0.736	159
B	0.029	0.778	159
$Ph_2C{=}NCHMe_2^{\bullet+}$	0.022	0.792	161
$PhCH{=}NEt^{\bullet+}$ C	0.024	0.806	161
D	0.024	0.816	161
E	0.024	0.821	161
p-$ClC_6H_4CH{=}NBu^{t\bullet+}$	0.030	0.734	158
$PhCH{=}NCHMe_2^{\bullet+}$	0.021	0.835	162

[a] After correcting for the spin polarisation contribution according to the method of ref. 4. [b] Using the equation for C_{2v} symmetry derived by C. A. Coulson, *Volume Commemoritif Victor Henri, Contribution a L'étude de la Structure Moleculaire*, Desoer, Liège, 1948, p. 15.

$PhCH{=}N(CH_2)_3CH_3$.—In a previous publication,[12] we reported an EPR spectrum recorded following γ-irradiation of this compound in $CFCl_3$ at 77 K. This contained features that seemed compatible with the formation of the π-radical cation with a π_4 (styrene type) SOMO. As part of the present work, we have carried out a more detailed study of the selectively deuteriated analogues, $PhCH{=}NCD_2(CH_2)_2CH_3$, $PhCD{=}NCD_2(CH_2)_2CH_3$ and $PhCD{=}N(CH_2)_3CH_3$. Surprisingly, the EPR spectra recorded following irradiation of all four of these compounds in $CFCl_3$ at 77 K are identical, and of the form shown in Fig. 9. Therefore, both the π_4 and $^2A'$ cations are eliminated as potential candidates for this spectrum since both would have SOMOs involving protons at the labelled positions and so the appearance of the spectra should vary with the nature of the deuterium substitution. We had also considered the possibility of a π-cation in which the SOMO was localised to the exocyclic C=N π-orbital, but this can of course also be ruled out. In view of the results for the neopentyl derivatives given in the previous section, where H-atom transfer occurred through a five-centre arrangement, it appears most likely that the species responsible for the signal is the distonic ion $PhCH{=}\overset{+}{N}H(CH_2)_2\dot{C}HCH_3$ in which the unpaired electron is remote from all positions of substitution. The spectrum may be easily reconstructed in terms of the parameters given in the table, and are similar to those previously reported for the 2-pentyl radical in a freon matrix,[13] other than the conformation of the alkyl chain (CH_2CH_2R; R = Me or NH=CHPh). In the present case, the results are compatible with a static conformation (**XI**) since the sum of the angles θ_1 and θ_2 is 121°: close to the value of 120° that has been proposed to indicate the absence of torsional averaging.[14] For the 2-pentyl radical, the inequivalent β-proton couplings of 9.0 G and 34.5 G indicate a dihedral angle between them ($\theta_1 + \theta_2$) of 100° so that torsional averaging of the β-proton couplings is still operating at 77 K.



XI

Couplings vs. *Conformation in σ-Imine Radical Cations*.—From the foregoing, it is clear that imine radical cations are σ-radicals, and are both isoelectronic and isostructural with vinyl radicals. Table 2 shows the derived orbital populations and bond angles associated with the nitrogen centres. As before,[4] we have corrected the nitrogen 2s orbital population for the indirect contribution from spin polarisation in order to determine the true hybridisation state of the SOMO on nitrogen. The bond angles are in the range 158–161°, in accord with our previous study, and are close to the *ab initio* result for the

$H_2C{=}N{-}Me^{\cdot +}$ radical cation which predicts an angle of 158°.[15]

The hyperfine coupling for β-protons in π-radicals follows a dependence on the dihedral angle (θ) between the density axis of the SOMO and the C–H bond that is symmetrical with respect to reflection through the radical plane [*i.e.* $A(\theta{=}0°) = A(\theta = 180°)$], and is normally assumed to take the form of a $B\cos^2\theta$ relationship.[16] For an sp hybridised orbital, this simple dependence breaks down because of the lower symmetry of the orbital and $A(\theta = 0°) \neq A(\theta = 180°)$. With the similar case of $^3J_{H-H}$ couplings in NMR spectroscopy,[17] where the spin–spin coupling interaction is also unsymmetrical and shows two inequivalent maxima for two proton dihedral angles of $\theta = 0°$ and $\theta = 180°$, an empirical approach[17] is to either modify the $B\cos^2\theta$ law to the form $B\cos^2\theta + C\cos\theta$, where the $\cos\theta$ term allows for the smaller interaction when $\theta = 0°$ if C is a negative constant, or to simply take the form of the coupling for the range θ = 0–90° as being distinct from that when θ = 90–180° and to again assume a $B\cos^2\theta$ law, but allow a different value of B for the two ranges.

Thus, if the coupling of 90.1 G corresponds to a proton occupying the $\theta = 180°$ position **I** in an imine radical cation, it may be taken as the value of B in the 90–180° range. Since the methyl groups in the radicals[4] *p*-$Me{-}C_6H_4CH{=}NMe^{\cdot +}$ and $Ph_2C{=}NMe^{\cdot +}$ each show three equivalent protons and are therefore freely rotating, we can estimate a value for B in the 0–90° range by taking the usual value[16] of $\langle\cos^2\theta\rangle = 0.5$ and equal population of the two ranges, so that: $A = 0.25B_{0-90°} + 0.25B_{90-180°}$. A value for A = 31.5 G (an average for the latter two radicals, with their freely rotating methyl groups) was taken, giving $B_{0-90°}$ = 35.9 G. In support of this estimate, we note that it is in reasonable agreement with the coupling to the *ortho* protons in the σ-pyridine radical cation,[18] which are forced to be *cis* with respect to the SOMO. Using the above values for the constants B, the coupling/θ curve in Fig. 2 was calculated.

The overall form of the curve is broadly similar to those reported for other σ-radicals of the acyl,[6] silyl[8] and norbornyl[7] type, but represents by far the largest β-proton hyperfine interaction observed to date for any σ-radical.

Acknowledgements

We thank NATO and the Central Research Fund of the University of London for grants in support of this work, and Dr. Peter Clay (Imperial College) for providing access to ^{60}Co irradiation facilities.

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Paper 1/05271C
Received 16*th October* 1991
Accepted 6*th November* 1991