Distonic isomerisations of imine radical cations: aspects of the reactivity of heteroatomic subunits damaged by ionising radiation

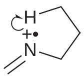
Christopher J. Rhodes,* Harry Morris, Hikmet Agirbas, Mark Standing and Yaming Zhang

School of Pharmacy and Chemistry, Liverpool John Moores University, Byrom St., Liverpool, UK L3 3AF

Radical cations have been prepared by exposure of imines, PhCH=NR, to ionising radiation in a fluorotrichloromethane matrix at 77 K, and studied by EPR spectroscopy. They are found to rearrange mainly *via* a 5-centre transition state in which intramolecular H-atom transfer occurs from the alkyl chain (R) to the initially ionised nitrogen atom, yielding radicals of the general type PhCH=NH$^+$–C–C–C.

Introduction

In previous studies,[1,2] we have determined some structural features of imine radical cations, as matrix isolated species, by means of EPR spectroscopy. In the main, these are σ-type radicals and are highly reactive, undergoing facile H-atom transfer reactions in solution,[3,4] and even in cryogenic matrices are prone to intramolecular abstraction of H-atoms from the *N*-alkyl chain (=N$^{\bullet +}$–R) when this is at least three carbon units long, giving distonic 'iminium' substituted radicals, C=NH$^+$–C–C–C$^\bullet$, apparently *via* a 5-centre transition state (**I**). The



I

imine unit may be considered a functional building block for heterocyclic bases, and indeed imine units, derived from dicyanamide, are implicated in the formation of nucleotides during the prebiotic phase of evolution.[5] The properties of fundamental electron-loss centres of this kind may dictate the subsequent outcome of the radiolytic events in the more complex, *e.g.* protein/membrane systems.

Of central relevance to reactivity is the question of the electronic ground-state: for imines of the type PhCH=NR (R = Me, Et, Pr^i, Bu^t) we found that the σ-electronic state was formed by charge transfer to halocarbon radical cations derived from the matrix material.[1,2] EPR spectroscopy is definitive in this regard since large (*ca.* 85 G) couplings are observed from the unique (C*H*=N) proton, which is *trans* to the nominally N-centred orbital, the latter being strongly s-p hybridised. This agrees with photoelectron[6] and theoretical[7,8] results for simple imines; however the nearest π-state is very similar in energy (within the Koopmans approximation) and a 'switch' is predicted as more extensive π-conjugation is introduced to the structure—this was confirmed by our results[1] for Ph$_2$C=NBu$^{t(\bullet +)}$ and Ph$_2$C=NH$^{\bullet +}$.

Additionally, the nature of substituents switches between σ- and π-states in a rather subtle way, and furthermore, for R = CH$_2$Bu^t or -(CH$_2$)$_3$Me, abstraction from the γ-carbon atom occurs to form distonic 'iminium' isomers (C=NH$^+$–C–C–C$^\bullet$). Given the well established propensity for σ-radicals to abstract H-atoms,[3,4] we propose that the ground state ions here are also σ, but rearrange spontaneously. Intermolecular H-atom abstractions were observed previously for unsubstituted 1,2-, 1,3- and 1,4-diazabenzene radical cations,[9] and also for 1,3,5-triazine$^{\bullet +}$,[10] all of which possess σ-ground states; π-states of radical cations instead tend to form π-dimer species.[11] In the following, we examine the distonic ionisation phenomenon for a series of *N*-alkyl substituted imines in an effort to probe the mechanism.

Table 1 EPR hyperfine coupling constants for radicals derived from *N*-alkylimines

Radical	Coupling constants/G = 10^{-4} T
PhCH=NH$^+$–(CH$_2$)$_2$CH$_2^\bullet$	(1H) 5.0, (1H) 32.0, (2H) 21.0
PhCH=NH$^+$–(CH$_2$)$_2$CH$^\bullet$CH$_3$	(3H) 26.0, (1H) 17.2, (1H) 9.2, (1H) 22.0
PhCH=NH$^+$–CH$_2$CHMeCH$_2^\bullet$	(2H) 19.0
PhCH=NH$^+$–(CH$_2$)$_2$CMe$_2$CH$_2^\bullet$	(2H) 19.0
PhCH=NH$^+$–(CH$_2$)$_2$CHMeCH$_2^\bullet$	(1H) 18.1, (2H) 21.1 [a] (1H) 36.2, (2H) 22.2 [b]
PhCH=NH$^+$–(CH$_2$)$_2$CH$^\bullet$CH$_2$CH$_3$	(1H) 34, (3H) 22
PhCH=N$^{\bullet +}$–Me	(1H) 78, (3H) 33, (^{14}N)$_\parallel$ 50, (^{14}N)$_\perp$ 8, (19F) 10
Ph$_2$C=N$^{\bullet +}$–CH$_2$Ph	(1H) 76, (1H) 19, (^{14}N)$_\parallel$ 47, (^{14}N)$_\perp$ 13, (^{19}F) 9

[a] Recorded at 77 K. [b] Recorded at 77 K after annealing to 155 K.

Results and discussion

In each case, the dominant radical species is a carbon-centred radical formed by intramolecular H-atom transfer, presumably to the initially ionised σ-nitrogen atom; all *g*-values are close to 2.003. In those cases where residual signals were also present from the primary nitrogen-centred σ-cation, it is significant that annealing does not result in their thermal rearrangement; this suggests that the rearrangement process is assisted by thermal energy available from the exoergicity of the electron transfer process to the freon matrix, probably by promoting the attainment of the correct conformation of the alkyl chain for H-atom abstraction to occur. This is similar to our result for Bu$^n_4$Sn$^{\bullet +}$ radical cations which once thermalised are not further decomposed to *n*-butyl radicals, although these apparently arise during the initial ionisation event.[12,13] The coupling constant data are collated in Table 1, to which we refer in our discussion of individual precursor imines.

PhCH=NR: R = *n*-butyl, *n*-pentyl, *n*-hexyl

The *n*-butyl case was discussed previously,[1] when on the basis of a study of a number of specifically deuterium labelled derivatives we were able to make an assignment to the rearranged radical, PhCH=NH$^+$–(CH$_2$)$_2$CH$^\bullet$–Me. The most significant aspect of this observation is that a 5-centre transition structure must be involved, and while either 5- or 6-centre geometries can readily be envisaged for an intramolecular H-atom abstraction of this kind it is possible that the former alternative is selected

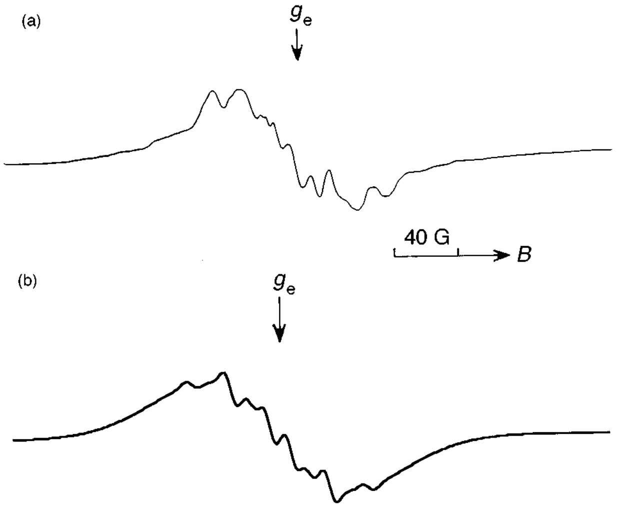


Fig. 1 (a) EPR spectrum recorded from PhCH=N(CH$_2$)$_4$CH$_3$–CFCl$_3$ at 77 K, following γ-irradiation, (b) simulation based on parameters in Table 1

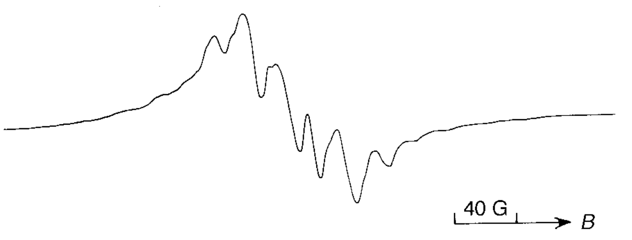


Fig. 2 EPR spectrum recorded from PhCH=N(CH$_2$)$_5$CH$_3$–CFCl$_3$ at 77 K, following γ-irradiation

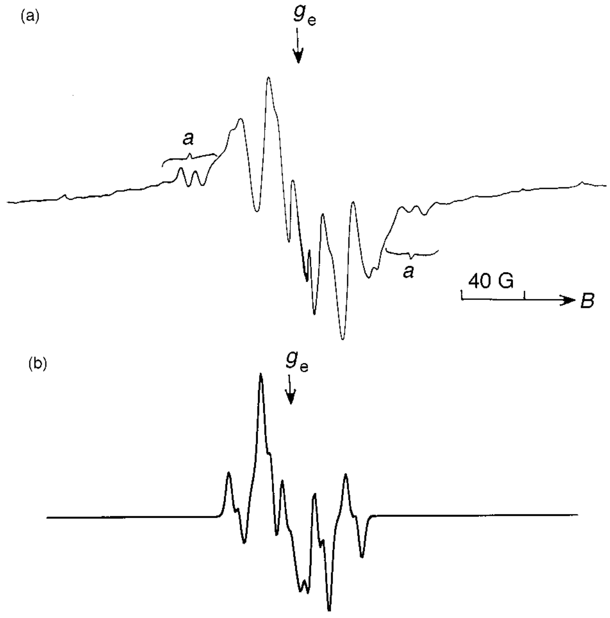


Fig. 3 (a) EPR spectrum recorded from PhCH=N(CH$_2$)$_2$CH$_3$–CFCl$_3$ at 77 K, following γ-irradiation (features marked *a* from primary radical cations); (b) simulation of central features from distonic ion, using parameters from Table 1

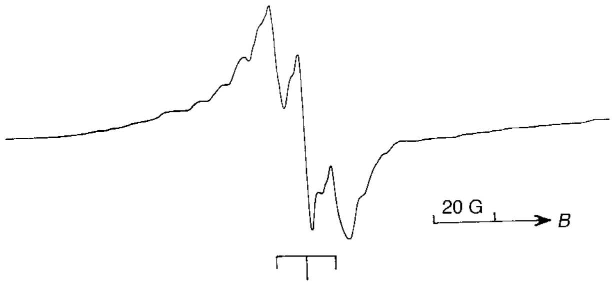


Fig. 4 EPR spectrum recorded from PhCH=N(CH$_2$)$_2$CMe$_3$–CFCl$_3$ at 77 K, following γ-irradiation

on the grounds of abstracting a secondary hydrogen atom rather than one primary from the methyl group terminal on the alkyl chain. Possible reconstructions for the *n*-pentyl analogue (*e.g.* Fig. 1) eliminate the possibility of a structure in which the methyl group is attached directly to the radical centre, and so abstraction from a more remote methylene group must occur: we propose the structure PhCH=NH$^+$–(CH$_2$)$_2$CH$^•$–CH$_2$Me, which again implicates the involvement of a 5-centre transition state. The spectrum of the *n*-hexyl derivative is very similar (Fig. 2) to that for the *n*-pentyl case [Fig. 1(a)] but we are less certain of an assignment regarding the two possibilities, PhCH=NH$^+$–(CH$_2$)$_2$CH$^•$–CH$_2$CH$_2$Me or PhCH=NH$^+$–(CH$_2$)$_3$-CH$^•$–CH$_2$Me, since either structure is compatible with the analysis based on two methylene groups adjacent to the radical centre. As we show later, there is no evidence for abstraction *via* a lower number centre arrangement. Since the analysis is in terms of four protons, the possibility is raised that both radicals arise from abstraction at the methyl terminus, leading to radicals of type RCH$_2$CH$_2^•$; however, the patterns are quite different from that obtained from a genuine radical of this kind (see below), and we do not consider it likely that separate 7- or 8-centre arrangements would be involved for these compounds, certainly not in a condensed phase where extensive molecular motion will be impeded.[14] In further support of our assignment we note that estimation of the required dihedral angles for the CH$_2$ groups flanking the radical centre in relation to the SOMO, using the standard $B\cos^2\theta$ dependence[15] with a value for $B = 54$ G, and the couplings in Table 1, leads to values of 37, 50, 50 and 90° (taking one coupling as zero, since it is not resolved). We have shown previously[16] that in the absence of extensive conformational averaging, the couplings for two methylene protons should give dihedral angles which sum to 120°: if we take the 37 and *ca.* 90° angles as referring to one methylene group and the two 50° angles for the other, this condition is approximately fulfilled; however, the departure from 120° for both segments of the alkyl chain indicates that some degree of torsional motion exists. We believe the model to be reasonable and that very similar conformations are adopted by the alkyl chains in both *n*-pentyl and *n*-hexyl distonic isomers.

PhCH=N(CH$_2$)$_2$Me

Although this compound is similarly an *n*-alkyl derivative, we discuss it separately because the results are different from those obtained in the other cases: specifically, the H-atom is now abstracted from the terminal methyl group which leads to a quite distinct spectral pattern (Fig. 3). In this case there are two protons with a coupling of 21.0 G (*α*), and two more (β) at 33 and 5 G, the angles for the latter summing to 112°. According to our previous discussion of conformational effects in radicals,[16] this indicates that residual torsional averaging occurs, as might be expected for this light 3-carbon alkyl chain. Additionally, there are wing features present from the primary radical cations.

PhCH=N(CH$_2$)$_2$CMe$_3$ and PhCH=NCH$_2$CHMe$_2$

The spectra (Figs. 4 and 5) from these compounds both comprise a triplet pattern with a splitting of 19 G, which is surprising. The coupling is lower than normal for an RCH$_2^•$ radical and suggests a measure (up to 17%) of spin delocalisation in the system; even in the PhCH=NH$^+$–(CH$_2$)$_2$CH$_2^•$ radical, above, there is some reduction. We believe that these are, nonetheless, RCH$_2^•$ type radicals because the other possible radicals resulting from abstraction elsewhere from the alkyl chains do not agree with the observed coupling constants. In particular, we

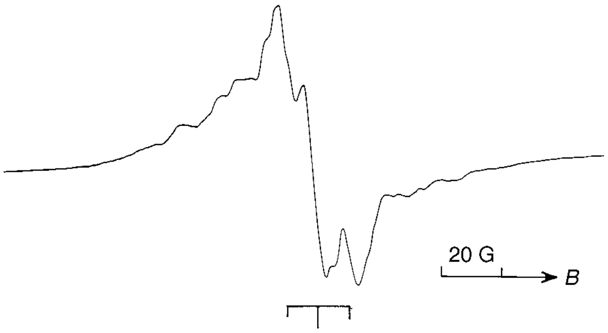


Fig. 5 EPR spectrum recorded from $PhCH{=}NCH_2CHMe_2$–$CFCl_3$ at 77 K, following γ-irradiation

might envisage the 'allylic' structures, $PhCH{=}NH^+{-}CH^{\cdot}{-}R$, which are expected to be very stable: indeed, we found that the radical cation $PhCH{=}CHCH_2SnBu^n{}_3{}^{\cdot+}$ decomposed spontaneously to form the structurally related $PhCH{=}CH{-}CH_2{}^{\cdot}$ radical at 77 K;[13] however, the couplings to the 'allyl' protons were only 10 G, far smaller than we now observe, and the absence of coupling from the protons of the group R which this implies (the triplet arising from the two 'allyl' protons) is certainly incompatible with the radical derived from $PhCH{=}N(CH_2)_2CMe_3$.

We propose that, following H-abstraction, the resulting carbon radical centre remains in sufficiently close proximity to the C=N unit that some spin transfer takes place. An interaction of this kind would also explain the fact that the larger β-proton coupling in the $PhCH{=}NH^+{-}(CH_2)_2CH_2{}^{\cdot}$ radical is lower than that in, say, the *n*-butyl radical which we measured at 45 G also in a solid freon matrix.[12,13] Our remaining problem concerns the fact that we do not resolve any coupling to the unique β-proton in the imputed $PhCH{=}NH^+{-}CH_2C\mathit{H}MeCH_2{}^{\cdot}$ radical, and must mean that it lies close to the nodal plane of the radical centre—yet this contrasts with results for other primary alkyl radicals such as isobutyl[15] and either the axial or equatorial isomer of the cyclohexylmethyl radical,[17] which also possess a similar unique β-hydrogen atom, but all with couplings >30 G. We consider that this apparent discrepancy is also best explained in terms of an interaction between the carbon radical centre and the C=N group, alluded to earlier.

$PhCH{=}N(CH_2)_2CHMe_2$

The radical derived from this compound, $PhCH{=}NH^+{-}(CH_2)_2{-}CHMeCH_2{}^{\cdot}$, contrasts with its lower isomer, $PhCH{=}NH^+{-}CH_2CHMeCH_2{}^{\cdot}$, discussed above, since coupling to the β-proton is now resolved [Fig. 6(a)], though still smaller at 18 G than is typical for $R_2CHCH_2{}^{\cdot}$ radicals.[15,17] On annealing for some minutes at 155 K, this increases to 36 G [Fig. 6(c)] while the $a(CH_2)$ proton coupling also resumes a normal value (*ca.* 22 G): we interpret this observation in terms of an initial weak $C^{\cdot}{-}{-}C{=}N$ interaction, stable at 77 K, which is lost at higher temperatures.

Location of the steric minimum

In previous work,[1,2] we investigated the minimum energy conformations of the alkyl groups (R′) ethyl, isopropyl and *tert*-butyl and were able to estimate the orientation of these groups with respect to the nitrogen-centred SOMO, which can be interpreted in terms of a compromise between steric and electronic (hyperconjugative) control. In order to increase the bulk of the alkyl group in an attempt to locate the true steric minimum—as in a previous study of very hindered alkyl radicals by Griller and Ingold[18]—we studied the compounds $PhCH{=}NCH_2CMe_3$ and $Ph_2C{=}NCH_2CMe_3$ but, as discussed earlier, observed instead only the rearranged (distonic) radical cations, $PhCH{=}NH^+{-}CH_2C(Me_2)CH_2{}^{\cdot}$ and $Ph_2C{=}NH^+{-}CH_2{-}C(Me_2)CH_2{}^{\cdot}$ which we proposed arose through the 5-centre arrangement **I**. We adopted a similar approach with the compound $Ph_2C{=}NCH_2Ph$, and predicted that while an analogous 5-centre geometry (**II**) can be envisaged, the sp^2 C–H hydrogen atom would be less prone to abstraction, given the greater C–H bond strength.[19]

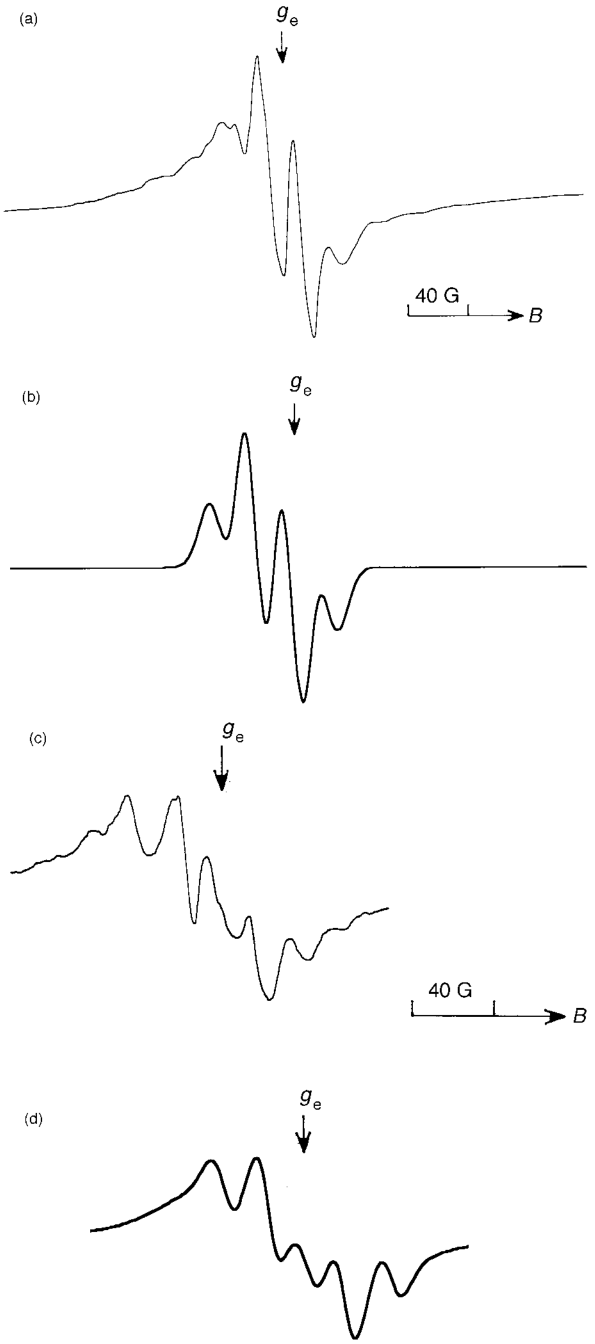


Fig. 6 EPR spectrum recorded from $PhCH{=}N(CH_2)_2CHMe_2$, (a) at 77 K, (b) simulation, (c) at 77 K, after annealing at 155 K for 5 min, (d) simulation

The spectrum shown in Fig. 7 was recorded following exposure of this material, in a solid $CFCl_3$ matrix at 77 K, to γ-radiation and can indeed be assigned to the primary radical cation, with the hyperfine data given in Table 1. It is significant that the rearranged radical $Ph_2C{=}NH^+{-}CH^{\cdot}{-}Ph$ is not formed by a 1,2-hydrogen atom shift, and shows that despite its far greater stability—we estimate by certainly 20 kcal mol^{-1} (ref. 19)—the 3-centre arrangement **III** does not provide a sufficiently low energy pathway for the required shift to occur.

In a previous publication,[1] we showed that the couplings to the β-hydrogens ($C{=}N^{\cdot+}{-}C\mathit{H}R_2$) in imine radical cations could be accounted for by the usual $B\cos^2\theta$ angular dependence, if

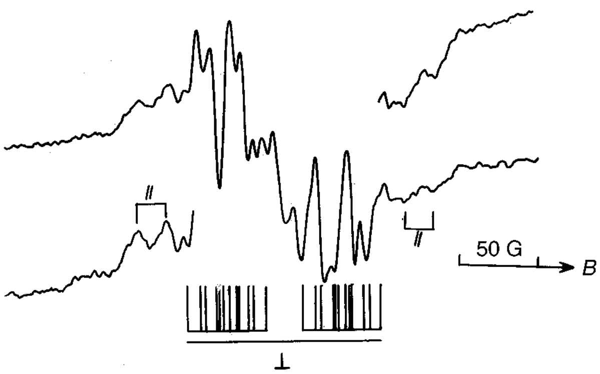


Fig. 7 EPR spectrum recorded from $Ph_2C{=}NCH_2Ph$–$CFCl_3$ at 77 K; wing regions (inset) are recorded at 5 × the gain of the central signal

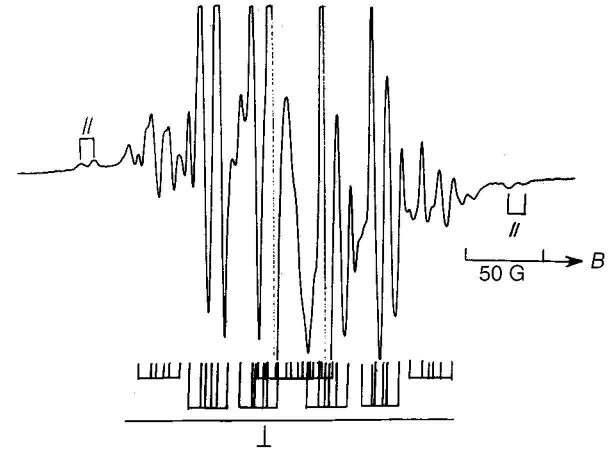
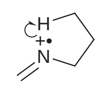
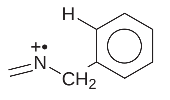


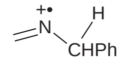
Fig. 8 EPR spectrum recorded from $PhCH{=}NMe$–$CFCl_3$ at 77 K



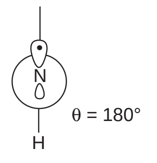
I



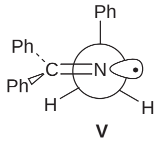
II



III



IV



V

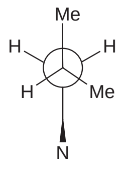
different values for B were used for the ranges 0–90° (33 G) and 90–180° (91 G); θ is defined in **IV**. Accordingly, we propose a conformation close to **V** to account for the unequal β-H couplings (19, 76 G) that we observe in the $Ph_2C{=}N^{\bullet+}$–CH_2Ph radical cation. This structure can only be undergoing torsion of the $PhCH_2$ group at a low frequency on the EPR timescale because the calculated angle between the two C–H bonds is 115°: close to the 120° expected for a true *rigid* structure.[16] For the fully bisected geometry **V** with dihedral angles of 30 and 150° between the C–H bonds and the SOMO, couplings of 25 and 68 G are calculated[1] and are close to those (19 and 76 G) observed, showing that steric control prevails in this case, to minimise the interactions between the three phenyl groups; at the electronic (hyperconjugative) maximum, a larger coupling to one C–H proton ($\theta = 180°$) of *ca.* 90 G is observed—as for $Ph_2C{=}N^{\bullet+}$–Et radical cations[1]—but this is avoided for $Ph_2C{=}N^{\bullet+}$–CH_2Ph because it would bring two of the phenyl groups into close proximity. For comparison, we studied the radical cation of $PhCH{=}NMe$, in which the alkyl group (Me) is freely rotating (Fig. 8); this coupling is very close to that measured for other *N*-methylimine radical cations[1,2] and supports the value of B derived previously for the lower (0–90°) range,[1] defined in **IV**. We note that both $Ph_2C{=}N^{\bullet+}$–CH_2Ph and $PhCH{=}N^{\bullet+}$–Me show additional 8–10 G doublet splittings which are due to ^{19}F matrix superhyperfine couplings, since they are of similar magnitude to those observed previously for similar species, and are not present when CCl_4 is used as the matrix. Furthermore, the imine primary radical cation is stable to rearrangement to the more thermodynamically stable (allylic) isomer, $PhCH{=}NH^+$–$CH_2^{\bullet}$.

Table 2 Regioselectivity[a] of intramolecular H-atom abstraction in imine radical cations

Imine	Rearrangement	T-State
$C{=}N$–CH_3	N	
$C{=}N$–CH_2Ph	N	
$C{=}N$–CH_2CH_3	N	
$C{=}N$–$CH(CH_3)_2$	N	
$C{=}N$–$C(CH_3)_3$	N	
$C{=}N$–$CH_2CH_2CH_3$*	Y[b]	5-centre
$C{=}N$–$CH_2CH(CH_3)_2$*	Y	5-centre
$C{=}N$–$CH_2C(CH_3)_3$*	Y	5-centre
$C{=}N$–$CH_2CH_2CH_2$*CH_3	Y	5-centre
$C{=}N$–$CH_2CH_2CH(CH_3)_2$*	Y	6-centre
$C{=}N$–$CH_2CH_2C(CH_3)_3$*	Y	6-centre

[a] Asterisk (*) shows abstraction at carbon to left from it. [b] Rearrangement is only partial, the spectrum being partly from the primary radical cation.

Nature of transition states for distonic rearrangement of imine radical cations. The observed regioselectivities (given in Table 2) permit a quite detailed view of possible transition states for the imine radical cation rearrangement. Judging by the nature of the radicals produced, it appears that the 5-centre transition structure **I** is favoured in most cases; the exceptions being $PhCH{=}N(CH_2)_2CMe_3$ and $PhCH{=}N(CH_2)_2CHMe_2$ for which a 6-centre process must operate. For the latter radical cation, it is especially surprising that the 5-centre process does not occur because this would lead to the formation of the relatively stable tertiary $PhCH{=}NH^+$–$(CH_2)_2CMe_2^{\bullet}$ radical, but probably is a consequence of a stereoelectronic effect in which the conformation **VI**, which should be favoured as the steric minimum, places the $CHMe_2$ hydrogen atom in a position that is unfavourable for transfer to the nitrogen atom. Obviously, the 5-centre process is impossible for the $PhCH{=}N(CH_2)_2CMe_3^{\bullet+}$ radical cation with no γ-hydrogen, but it is the 6- rather than the 4-centre process which is chosen as the alternative; indeed, we have no evidence for the latter even in the $PhCH{=}NCH_2$-$CHMe_2^{\bullet+}$ species in which the γ-hydrogen should be activated for abstraction.



VI

In no case do we observe an 'allylic' isomer, $R_2C{=}NH^+$–$CR_2^{\bullet}$, formed by a 1,2-shift (3-centre transition state), despite the expectedly high thermodynamic stability of such a species: this is emphasised particularly for the potential $Ph_2C{=}NH^+$–$CHPh^{\bullet}$ radical, which, as discussed in the previous section should be *ca.* 20 kcal mol^{-1} more stable than the primary A′ structure (the electronic ground state for the radical). Clearly kinetic control operates, and there is no access to a suitably low energy pathway for the required 3-centre arrangement.

Table 3 EPR hyperfine coupling constants for imine π-radical cations

Radical	Coupling constants/10^{-4} T
$PhCH{=}NSO_2Me^{\bullet +}$	(1H) 7.5, $(^{14}N)_{\parallel}$ *ca.* 10
$PhCH{=}NSO_2N{=}CHPh^{\bullet +}$	(1H) 7.0, $(^{14}N)_{\parallel}$ not resolved
$PhCH{=}NSO_2C_6H_4Me^{\bullet +}$	(3H) 15.0
p-$MeOC_6H_4CH{=}NSO_2$-9-anthryl	Unresolved singlet

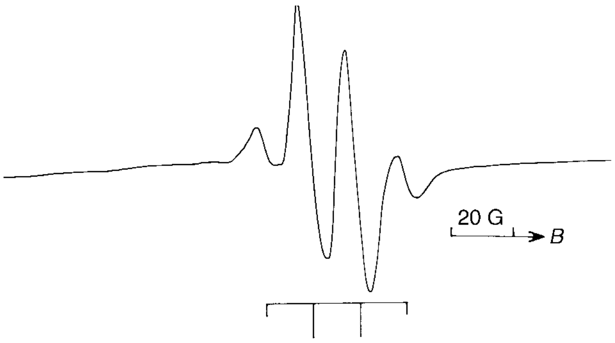


Fig. 9 EPR spectrum recorded from $PhCH{=}NSO_2C_6H_4Me$–$CFCl_3$ at 77 K

π-Radical cations

As alluded to earlier, given the close energetic proximity of the σ and π states for imine radical cations, the formation of the σ state is sometimes observed, as is the case for the compounds whose EPR parameters are listed in Table 3. For the anthracene derivative, *p*-$MeOC_6H_4CH{=}NSO_2$-9-anthryl, a singlet with poor resolution and a *g*-value of 2.003 is recorded, and so the electron loss is most likely from the anthracene unit, given the absence of hyperfine structure, particularly from ^{14}N, which is evident in the spectra of the other derivatives.

The spectral parameters are very similar for the radicals $PhCH{=}NSO_2C_6H_4CO_2Me$, $PhCH{=}NSO_2Me$ and $PhCH{=}NSO_2$-$N{=}CHPh$, showing coupling to the *para*-proton of the aromatic group of *ca.* 7.5 G and a parallel ^{14}N coupling of *ca.* 9 G. Comparison with data for monosubstituted benzene radical cations, in which the *para*-proton coupling is *ca.* 11 G, suggests that *ca.* 30% of the spin density is withdrawn by the C=N unit, *ca.* 20% being localised onto the nitrogen atom. In the case of $PhCH{=}NSO_2C_6H_4Me$, the EPR spectrum (Fig. 9) shows a 15 G coupling to the methyl protons, immediately telling which ring is ionised, and comparison with the 18 G methyl proton coupling in the toluene cation[20] shows that 17% of the spin density is delocalised onto the iminesulfonyl substituent.

Experimental

The *N*-alkylbenzalimines were prepared by the following general method. Benzaldehyde (2 g) was stirred in dichloromethane solution (50 ml) with the stoichiometric quantity of the appropriate amine for 2 h in the presence of anhydrous sodium sulfate (to absorb water produced in the reaction). The mixture was filtered and the dichloromethane was evaporated; the imine was purified by chromatography on alumina, under dry nitrogen gas, using diethyl ether as the eluent. Other materials were kindly supplied by Dr P. B. Wyatt. The identity and purity of each compound were checked using ^1H NMR spectroscopy.

For EPR measurements, dilute solutions of each imine were prepared in fluorotrichloromethane, and were frozen at 77 K, prior to exposure to γ-radiation to a dose of 1 Mrad. The spectra were recorded using a Varian E9 spectrometer, fitted with variable temperature facilities.

Acknowledgements

We thank the EPSRC, Ceram Research Ltd., NATO and John Moores University for financial support of this work.

References

1 C. J. Rhodes and H. Agirbas, *J. Chem. Soc., Perkin Trans. 2*, 1992, 397.
2 C. J. Rhodes and H. Agirbas, *J. Chem. Soc., Faraday Trans.*, 1990, 3303.
3 A. R. Forrester, M. Gill, R. J. Napier and R. H. Thompson, *J. Chem. Soc., Perkin Trans. 2*, 1979, 632.
4 D. H. Bae, P. S. Engel, A. K. M. M. Hoque, D. E. Keys, W. K. Lee, R. W. Shaw and H. J. Shine, *J. Am. Chem. Soc.*, 1985, **107**, 2561.
5 M. Calvin, *Chemical Evolution*, Clarendon, Oxford, 1969.
6 L. Klasinc, B. Rusic, A. Sabljic and N. Trisajstic, *Int. J. Quantum Chem.*, 1983, **23**, 1667.
7 M. H. Lien and A. C. Hopkinson, *Can. J. Chem.*, 1984, **62**, 922.
8 M. T. Nguyen, A. F. Heggarty and P. Brint, *J. Chem. Soc., Dalton Trans.*, 1985, 1915.
9 G. W. Eastland, D. N. R. Rao and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2833.
10 C. J. Rhodes, *J. Chem. Res.* (*S*), 1989, 76, and unpublished results.
11 M. Iwasaki, K. Toriyama and K. Nunome, *J. Chem. Soc., Chem. Commun.*, 1983, 320.
12 E. C. Butcher, C. J. Rhodes, R. S. Davidson and R. Bowser, *J. Organometal. Chem.*, 1992, **436**, 5.
13 E. C. Butcher, C. J. Rhodes, M. Standing, R. S. Davidson and R. Bowser, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1469.
14 C. J. Rhodes, *J. Am. Chem. Soc.*, 1988, **110**, 4446.
15 J. K. Kochi, *Adv. Free Radical Chem.*, 1975, **5**, 189.
16 C. J. Rhodes and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 1187.
17 K. U. Ingold and J. C. Walton, *J. Am. Chem. Soc.*, 1985, **107**, 6315.
18 D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, 1973, **95**, 6459.
19 D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.*, 1982, **33**, 493.
20 M. C. R. Symons and L. Harris, *J. Chem. Res.* (*S*), 1982, 268; (*M*) 1982, 2746.

Paper 8/01066H
Received 5*th February* 1998
Accepted 1*st April* 1998