An Electron Spin Resonance Study of Imidazole Radical Cations

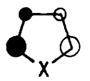
Christopher J. Rhodes
Department of Chemistry, Queen Mary College, University of London, Mile End Road, London E1 4NS

ESR spectroscopy shows that the SOMO in 1-alkylimidazole radical cations corresponds to the π_3 orbital, as is the case for pyrrole, furan, and thiophene cations, but there is a nodal shift in the wavefunction which distributes most of the spin density unsymmetrically between the two nitrogen atoms.

The technique of exposing dilute solutions of substrates in freon solvents to ionising radiation at low temperatures for the production of radical cations for ESR studies is now well established, and a wealth of information regarding the structures of these important intermediates has thus been obtained, as evidenced by two recent reviews of the subject.[1,2] The essence of this technique was used originally for the observation of optical spectra of organic radical cations,[3,4] including heterocyclic derivatives,[5] and rests on the ability of radiolytically produced solvent radical cations to perform single-electron oxidations on substrate molecules following charge migration in the solid matrix.

For the present work, we have studied the ESR spectra of the radical cations of some imidazole derivatives. We are unaware of any previous ESR work on these species, although the optical spectrum of the imidazole radical cation has been reported,[5] and well-defined photoelectron spectra of imidazole derivatives have been obtained.[6] CNDO/2 calculations predict that the highest occupied orbital in the imidazole molecule is the π_3 ($^1a_2$) orbital, and so the lowest energy band in the photoelectron spectra of imidazole and its methyl derivatives has been assigned to ionisation from this orbital.[6]

We note that ESR studies of the radical cations of pyrrole, furan, and thiophene and their alkyl derivatives, formed both by radiolysis in solid $CFCl_3$ and photochemically in the liquid phase, show the SOMO to be a π_3 orbital of type (**1**) with the node passing through the heteroatom.[7,8]



(**1**)

Experimental

The imidazole derivatives were commercial samples (Aldrich) which were purified before use by distillation. Dilute solutions (0.1–1.0 mol %) were prepared in $CFCl_3$ (obtained from Aldrich and purified by being filtered twice through activated alumina) and reduced to small polycrystalline beads by being pipetted into liquid nitrogen. The beads were irradiated to a dose of 1 Mrad† using an X-ray source, and the ESR spectra were recorded, also at 77 K, with a Bruker 200D spectrometer.

Results and Discussion

The hyperfine coupling constants for the imidazole radical cations are given in the Table; for comparison, data for structurally related cations, taken from the literature, are also included. Unfortunately, we were unable to obtain data for the radical cation of imidazole itself, due to its low solubility in $CFCl_3$.

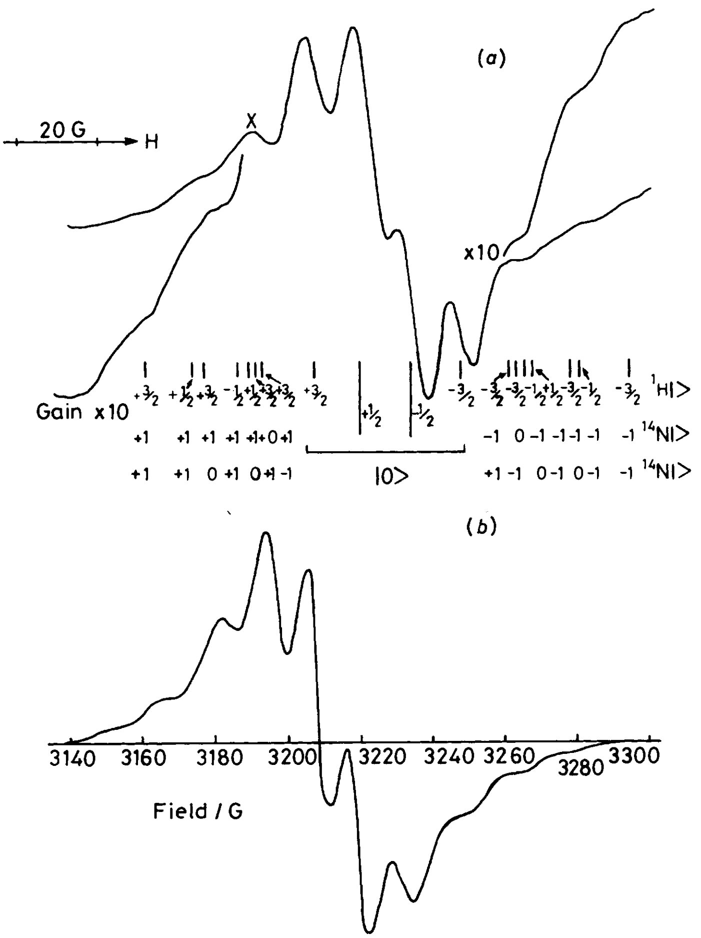


Figure 1. (*a*) X-Band ESR spectrum recorded following X-irradiation of a dilute solution of 1-methylimidazole in $CFCl_3$ at 77 K, and assigned to the primary radical cations; feature marked (×) arises from a coincidence of the parallel features associated with the nuclear spin states shown, and is clearest on the low field side of the spectrum because of *g*-anisotropy. (*b*) Simulation of spectrum in 1(*a*).

Alkyl-substituted Imidazole Radical Cations.—The ESR spectra assigned to 1-methyl- and 1,2-dimethyl-imidazole radical cations are shown in Figures 1(*a*) and 2. These spectra are very similar in appearance, both consisting of a central

---

† 1 rad = 0.01 Gy.

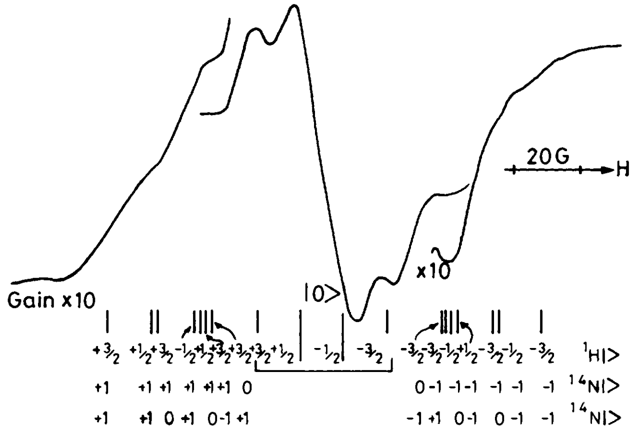


Figure 2. X-Band ESR spectrum assigned to 1,2-dimethylimidazole radical cations.

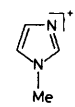
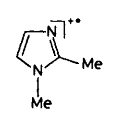
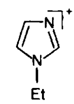
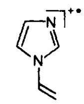
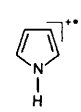
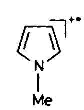
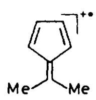
^{14}N|0⟩ feature which is split into a quartet, assigned to coupling to a single methyl group (*ca.* 12 G), and outer 'parallel' features which we interpret in terms of coupling to two non-equivalent nitrogen nuclei. Possible structures for the SOMO of an imidazole radical cation are (*a*) a σ-state, formed by ionisation of the in-plane N-3 lone pair, and (*b*) a π-state, formed by loss of a ring π-electron, in principle from either the π_2 or π_3 orbitals. The σ-state can be ruled out for the following reasons: (*i*) we do not observe a perpendicular $A_\perp$ (^{14}N) splitting as expected since the nitrogen 2s contribution would be relatively large for this type of orbital; (*ii*) the coupling to the CH_3 protons would be very small, in contrast with that observed (*ca.* 12 G); (*iii*) rather than the observed quartet splitting of the central feature, a triplet splitting of *ca.* 20–30 G would be expected from the '*ortho*' protons by analogy with results for other heterocyclic σ-cations.[9] We have carried out anisotropic simulations of the spectra, using the parameters given in the Table. Figures 1(*a*) and 1(*b*) show, respectively, the spectrum of the 1-methylimidazole cation and its simulation. The overall agreement is good, including the reproduction of the feature marked (×) which arises from a coincidence of parallel features, as shown, and is clearest in the low-field region of the spectrum because of the *g*-anisotropy. Most importantly, our assignment of two inequivalent nitrogen atoms is supported: simulated patterns obtained on the basis of the nitrogen nuclei being equivalent are in much poorer agreement with the observed spectra. The fact that there is no evidence of coupling to the second methyl group in the dimethyl derivative other than a slight broadening of the spectral lines (Figure 2) shows that the spin density at the 2-position is very low.

From the ^{14}N data (Table), and taking $A_\perp(^{14}\text{N}) = 0$, we obtain spin densities of *ca.* 0.32 and 0.62 for the two nitrogen atoms. We can use the CH_3 coupling to aid the assignment of these spin densities to particular nitrogen atoms: for a spin density at N-1 of 0.62, a *Q*-value of *ca.* −21 G is obtained from the McConnell-type equation (1); for a spin density of 0.32, a *Q*-value of *ca.* −37 G is obtained. We favour the latter value since it is in better accord with the methyl proton couplings in aminium radical cations[10,11] and therefore assign the spin density of 0.32 to the substituted nitrogen atom (N-3).

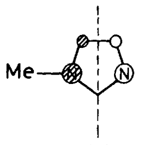
$$a(\text{H}) = Q\rho_\text{N} \qquad (1)$$

Our assignment of the SOMO is therefore as a π_3 type orbital (**2**) with the node passing through carbon-2, and the majority of the spin density on the two nitrogen atoms. Therefore, a nodal shift has occurred with respect to the cations with a single heteroatom (**1**).

Table. ESR data for imidazole and structurally related radical cations.

Radical	Hyperfine coupling constants/G[a] and *g* factors
	(CH_3) 12, $A_\parallel(^{14}\text{N-1})^b$ 16, $A_\parallel(^{14}\text{N-3})^b$ 30, $A_\perp(^{14}\text{N-1}) = A_\perp(^{14}\text{N-3})$ *ca.* 0; $g_\perp = 2.005, g_\parallel = 2.002$
	(CH_3) 13, $A_\parallel(^{14}\text{N-1})^b$ 16, $A_\parallel(^{14}\text{N-3})^b$ 32, $A_\perp(^{14}\text{N-1}) = A_\perp(^{14}\text{N-3})$ *ca.* 0; $g_\perp = 2.005, g_\parallel = 2.002$
	(1-H) 25, (1-H) 14, $A_\parallel(^{14}\text{N-1})$ 16, $A_\parallel(^{14}\text{N-3})$ 32, $A_\perp(^{14}\text{N-1}) = A_\perp(^{14}\text{N-3})$ *ca.* 0; $g_\perp = 2.005, g_\parallel = 2.002$
	(=CH_2) 17.8, $A_\parallel(^{14}\text{N-1})$ 6, $A_\perp(^{14}\text{N-1})$ *ca.* 0; $g_\text{AV.} = 2.003$
	H(2, 5) 16, H(3, 4) 3, $A(^{14}\text{N})$ 3[c]
	H(2, 5) 15.5, H(3, 4) 3.6, $A(^{14}\text{N})$ 3.5[c]
	H(2, 5) 16.8, H(3, 4) 4.5[c]

[a] 1 G = 10^{-4} T. [b] For assignments, see text. [c] From ref. 7. [d] From ref. 13.



(2)

The spectrum of the 1-ethyl derivative (Figure 3) shows identical ^{14}N data (Table), and so the SOMO must also be of

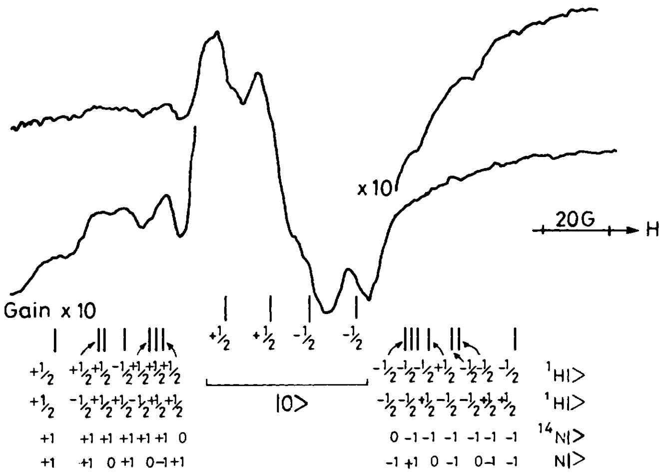


Figure 3. X-Band ESR spectrum assigned to 1-ethylimidazole radical cations.

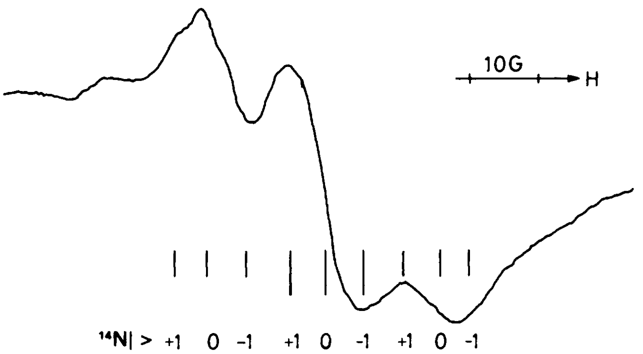
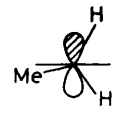
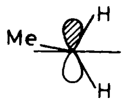


Figure 4. X-Band ESR spectrum assigned to 1-vinylimidazole radical cations.

the form (**2**). The two methylene protons of the ethyl group are inequivalent, since the ^{14}N|0⟩ feature is split into a doublet (25 G) of doublets (14 G). There must thus be a preferred orientation of the ethyl group with respect to the π-system, as in (**3**). This contrasts with the result for the ethylbenzene radical cation, in which the methylene protons are equivalent,[12] indicating a conformation with the methyl group lying in the plane of the aromatic ring (**4**). We suggest that the greater hyperconjugation in the ethylbenzene cation [A(H) = 29 G] overrides the unfavourable steric interaction between the ring and the methyl group; the lower spin density at the nitrogen atom in the ethylimidazole cation results in weaker hyperconjugation and so the resulting conformation (**3**) is partly dictated by the steric interaction.

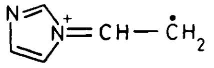


(**3**)



(**4**)

1-*Vinylimidazole Radical Cation*.—The spectrum recorded following X-irradiation of 1-vinylimidazole in $CFCl_3$ at 77 K is shown in Figure 4, and comprises, essentially, a 17.8 G triplet. Since this is completely different from the spectra of the alkyl derivatives, the structure of the cation must also be different. One possibility is that the SOMO is of the type (**2**), with the node passing through one of the nitrogen atoms and strong coupling to two ring protons, since large couplings to 2-H and 5-H have been observed in pyrrole[7,8] and fulvene[13] radical cations (Table). However, the couplings observed in the 1-vinylimidazole cation seem, at 17.8 G, to be rather large for such an assignment. Our INDO calculations for the 1-vinylimidazole cation predict a high spin density at the vinyl $=CH_2$ carbon, for a range of ring geometries, and only small spin densities at the ring positions. We therefore favour the alternative interpretation, in terms of a substantial contribution from the 'limiting' structure (**5**), with *ca.* 77% of the spin density at the terminal $=CH_2$ group.



(**5**)

There appears to be an additional, though poorly resolved, triplet splitting present, which we interpret as a 'parallel' coupling to the N-1 nucleus of *ca.* 6 G. Taking $A_{\perp}$ (^{14}N) = 0, we obtain an isotropic coupling of *ca.* 2 G, and a N_{2p} spin-density of 0.12. From the equation (2), with the values given in

$$a^{\mathrm{N}} = \left\{S^{\mathrm{N}}_{1s} + \sum_{R} Q^{\mathrm{N}}_{\mathrm{N\text{-}R}}\right\}\rho^{\pi}_{\mathrm{N}} \qquad (2)$$

reference 14 for the $1s^2$ core (S^{N}_{1s}) and N–R bond ($Q^{\mathrm{N}}_{\mathrm{N\text{-}R}}$) polarisations we predict an isotropic ^{14}N coupling of 2.34 G. This agrees closely with our estimate, above, and suggests that the perpendicular coupling *is* close to zero, as assumed.

These results show that *ca.* 90% of the spin density is confined to the $N-CH=CH_2$ unit, and so the spin density on the ring is very low, in broad agreement with INDO results.

References

1 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393.
2 M. Shiotani, *Magn. Reson. Rev.*, 1987, **12**, 333.
3 T. Shida and W. H. Hamill, *J. Chem. Phys.*, 1966, **44**, 2369.
4 T. Shida and W. H. Hamill, *J. Chem. Phys.*, 1966, **44**, 4372.
5 A. Grimison and G. A. Simpson, *J. Phys. Chem.*, 1968, **72**, 1776.
6 L. Klasinc, B. Ruscic, F. Kajfez, and V. Sunjic, *Int. J. Quantum Chem., Quantum Biol. Symp.*, 1978, **5**, 367.
7 D. N. R. Rao and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1983, 135.
8 A. G. Davies, L. Julia, and S. N. Yazdi, *J. Chem. Soc., Perkin Trans. 2*, 1989, 239.
9 D. N. R. Rao, G. W. Eastland, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1985, 727.
10 V. N. Belevsky, L. T. Bugaenko, and O. In Quan, *J. Radioanal. Chem.*, 1986, **107**, 67.
11 C. J. Rhodes, in 'Organic Free Radicals,' eds. H. Fischer and H. Heimgartner, Springer Verlag, Berlin, 1988, p. 161.
12 D. N. R. Rao, H. Chandra, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1201.
13 C. J. Rhodes, *J. Chem. Soc., Chem. Commun.*, 1988, 647.
14 C. J. Rhodes, *J. Chem. Soc., Faraday Trans. 1*, 1988, 3215.

Paper 9/00798I
Received 21*st February* 1989
Accepted 19*th October* 1989