Unstable Intermediates. Part 205.[1] Radical Cations of Pyrrole, Furan, and Thiophen Derivatives: an Electron Spin Resonance Study

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Exposure of dilute solutions of pyrrole, 2,5-dimethylpyrrole, furan, thiophen, and 2,5-dimethylthiophen in Freon at 77 K to ^{60}Co γ-rays gave the corresponding cations. In all cases, analysis of their e.s.r. spectra established that the unpaired electron occupies the $^1a_2$ (π_3) orbital with a node through the heteroatom. Data for the dimethyl derivatives are close to those recently reported for the 1,3-dimethylcyclopentadienyl radical, whilst those for the unsubstituted radicals are similar to those for the radical cation of cyclopentadiene.

The specific generation of radical-cations by ionizing radiation has long been recognised as a useful preparative procedure, but only recently has a reliable method been forthcoming, in which further reactions of such cations are inhibited, and from which good e.s.r. spectra can be obtained.[2–5] These media include CCl_4, $FCCl_3$, other Freons, and SF_6. In fact, it seems that Shida and Hamill, using optical spectroscopy, were the first to realise the potential of such solvents,[6,7] and they were exploited, in particular by Grimison and Simpson, in a study of the optical spectra of a range of heterocyclic aromatic cations.[8]

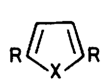
Two recent studies are of especial importance in relation to the present work. One is that of Shida and his co-worker on the pyridine cation,[2] and the other is that of Davies and his co-workers on cyclopentadienyl and substituted cyclopentadienyl radicals.[9–11] Such radicals have also been studied by Sakurai and his co-workers.[12] It is also of interest that Gilbert and his co-workers have postulated the formation of some of these radical cations in their extensive e.s.r. studies.[13] The heterocyclic cations were not detected directly, but various products of their reactions were detected.

Photoelectron spectroscopic studies of pyrrole, furan, and thiophen have been interpreted in terms of electron loss from the $^1a_2$ (π_3) orbital having a node through the heteroatom. It was therefore expected that this would prove to be the SOMO in the present studies, but the possibility that proton loss from the pyrrole cation could generate a σ-radical similar to the pyridine cation [2] was considered, as was the possibility that a similar σ-radical localised on sulphur might be stabilised by ring distortion.

Experimental

All materials were of the highest available grade and were used as supplied. A range of solutions in Freon ($FCCl_3$) in the 0.01—0.1 mole fraction range were studied. Solutions were degassed by repeated freeze–thaw cycles, and were frozen as small glassy beads to 77 K prior to exposure to ^{60}Co γ-rays in a Vickrad source for up to 1 h (*ca.* 1 Mrad).

E.s.r. spectra were measured at 77 K on a Varian E-109 spectrometer calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker BH 12E field probe, which were standardised with a sample of diphenylpicrylhydrazyl. Samples were annealed by decanting the liquid nitrogen from the insert Dewar, and re-cooling whenever significant spectral changes were observed. In selected cases spectra were studied over a range of temperatures using a variable temperature insert.



(1)

Table 1. Hyperfine coupling constants of radical cations derived from pyrrole, furan, and thiophen derivatives (1) and of related radicals

Radical		Hyperfine coupling constants (G) [a]			
X	R	$H_{2,5}$	$H_{3,4}$	$H(CH_3)$	Other nuclei
S	H	13	2.5		
S	CH_3		3.5	18.1	
O	H	14	3.5		
NH	H	16	3.0		*ca.* 3 (^{14}N)
NH	CH_3		3.5	17.5	*ca.* 3 (^{14}N)
NCH_3	H	15.5	3.6		*ca.* 3.5 (^{14}N)
CH_2	H [b]	11.6	3.5		<2 (CH_2)
CH	H [c]	13	3.45		1.0 (CH)
CH	CH_3 [c,d]		3.7	13.5	1.1 (CH)

[a] G = 10^{-4} T. [b] Ref. 14. [c] Ref. 11. [d] These are limiting values estimated in ref. 11.

Results and Discussion

The e.s.r. spectra assigned to the radical cations were invariant within the concentration range used. On annealing, resolution increased, especially for the unsubstituted derivatives. Data are given in Table 1 and some typical spectra are shown in Figures 1 and 2.

Structure.—The results clearly establish that all these cations share a common structure. Indeed, comparison with the results for 1,3-dimethylcyclopentadienyl radicals [11] and for cyclopentadiene cations,[14] also given in this Table, suggests that these also have a comparable SOMO. These are clearly established by the results as the $^1a_2$ (π_3) orbitals in (I) (X = CH, NH, O, S, or CH_2). For cyclopentadienyl radicals (X = CH) (I) and (II) are degenerate and equally populated on average. It seems that when CH is replaced by NH, O, S, or CH_2 π_2 is always more stable than π_3 so the SOMO becomes π_3. For 1,3-dimethylcyclopentadienyl radicals, Davies and his co-workers estimate that π_3 contributes *ca.* 95% and π_2 *ca.* 5% to the observed time-averaged e.s.r. data.[11] Our results give no clear evidence for such admixture.

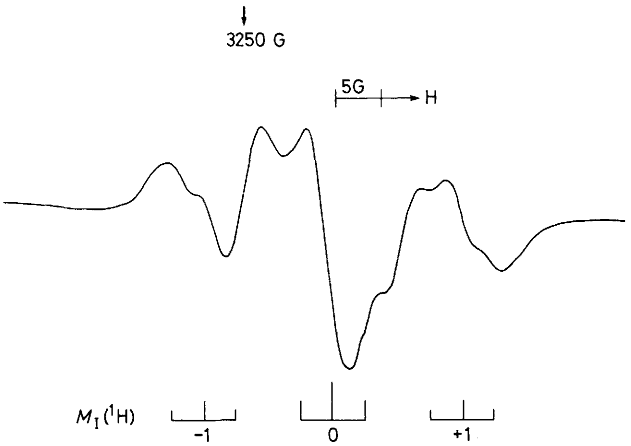


Figure 1. First derivative X-band e.s.r. spectrum (112 K) for furan in Freon (1 : 1 000) after exposure to ^{60}Co γ-rays at 77 K showing features assigned to the furan cation

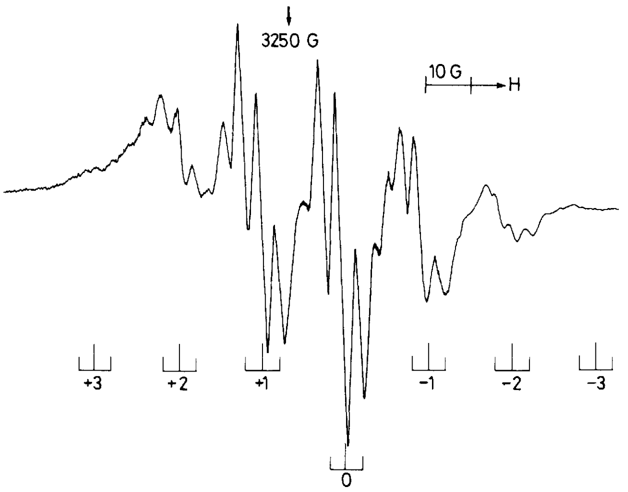
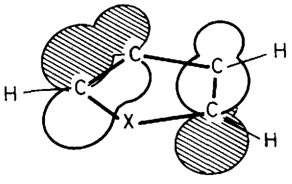
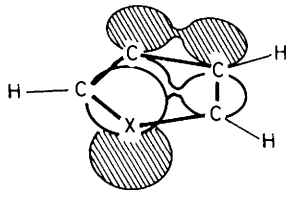


Figure 2. First derivative X-band e.s.r. spectrum (112 K) for 2,5-dimethylthiophen in Freon (1 : 1 000) after exposure to ^{60}Co γ-rays at 77 K showing features assigned to the radical cation

However, there is another orbital that should be considered in this context, namely the $^9a_1$ orbital in (III) which is, in first order, the in-plane lone-pair (n.b.) orbital on X, when X = O or S. This is clearly far deeper than π_2 or π_3 when X = O, but could be within reach when X = S. Photoelectron spectroscopic studies for thiophen suggest energies of 8.9 (π_3), 9.5 (π_2), and 11.9 eV (n.b.) (Table 2) but these relate to the undistorted parent molecules. Loss of e^- from the n.b. orbital would give rise to a distortion which, by analogy with pyridine cations[15] whose SOMO is a similar n.b. orbital on nitrogen,[2] will involve an increase in the $\mathrm{C{-}\widehat{S}{-}C}$ angle. This could move the $^9a_1$ (n.b.) orbital above the two π orbitals, making this the SOMO. However, our results rule out this possibility as the major product. The situation envisaged is quite comparable with those for $(C_6H_5I)^-$ and $(C_6F_5I)^-$ already described[16,17] in which there is π*–σ* competition, both anions being detected in the former case. Our spectra are not well resolved, and the possible presence of $(C_4H_4S)^+$ cations having a $^9a_1$ (n.b.) structure in low concentration cannot be totally ruled out.



(I)



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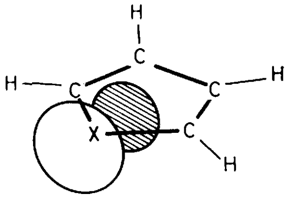

(III)

Table 2. Orbital energies for furan, thiophen, and pyridine (eV)

	$^1a_2$ (I)	$^2b_1$ (II)	$^9a_1$ (*n*)	Δ[(*n*) − $^1a_2$]
Furan[a]	8.9	10.4	12.9	4.07
Thiophen[a]	8.9	9.5	11.9	3.0
Pyridine[b]	9.6	9.75	10.5	0.9

[a] J. A. Sell and A. Kuppermann, *Chem. Phys. Lett.*, 1979, **61**, 355. [b] E. Heilbronner, V. Hornung, F. H. Pinkerton, and S. F. Thames, *Helv. Chim. Acta*, 1972, **55**, 289.

Pyrrole.—The hyperfine coupling for the 2- and 5-protons is remarkably high (*ca.* 16 G). That for the 3- and 4-pair is normal, so we cannot invoke a shift of spin-density to explain the increase. However, we can invoke the positive charge effect noticed, for example, on going from $C_6H_6^-$ (3.4 G) to $C_6H_6^+$ (4.4 G). The increase from the value deduced for π_3 for cyclopentadienyl radicals[11] (*ca.* 13 G) then appears to be quite reasonable.

The 2,5-dimethyl derivative also has an enhanced proton coupling. Thus the value for the dimethylcyclopentadienyl species (π_3) is *ca.* 13.6 G[11] whilst our value is 17.5 G. This is again a positive charge effect. As we established some time ago, hyperconjugative electron release is strongly enhanced by a partial positive charge on carbon.[18,19] The increase observed here is comparable with those found for similar systems.[14,19]

As expected, data for the *N*-methyl derivative are very close to those for the parent cations. It is noteworthy that, for the latter, but not the former, the characteristic blue colour associated with these ions changed to orange on annealing to *ca.* 180 K. There was no well defined change in the e.s.r. spectra during this modification. It is possible that this corresponded to loss of the N–H proton, since this would probably not greatly affect the SOMO.

The small, almost isotropic hyperfine coupling to ^{14}N (*ca.* 3 G) is characteristic of σ-orbital spin polarisation, and hence is probably negative. Spin polarisation of the N–C σ-electrons places spin directly into the 2*s* orbital on nitrogen, whereas π-polarisation only involves the 2*p* (π, *z*) orbital. This anisotropic coupling will partially cancel with the σ-orbital polarisation involving $2p_x$ and $2p_y$ orbitals so that the isotropic coupling dominates.

Furan.—The value of the coupling to the 2-,5-protons is appreciably less than that for pyrrole cations, whilst that for the 3-,4-protons is slightly increased. These changes are presumably a direct consequence of changing from NH to O. This may be a direct electronegativity effect or it may be due to small changes in bond lengths and angles in the ring.

Thiophen.—There is a further decrease in $a(2,5\ ^1H)$ on going from furan cations to thiophen cations, but in this case $a(3,4\ ^1H)$ also falls slightly. We had anticipated that, for this cation, there might be a small population of π_2, but, at least in fast exchange, this would cause $a(2,5\ ^1H)$ to fall, but $a(3,4\ ^1H)$ should increase, so this explanation is improbable.

For the 2,5-dimethyl derivative, $a(CH_3)$ is even larger (18.5 G) than that for the pyrrole derivative (17.5 G). In this case, $a(3,4\ ^1H)$ has increased to the average value of *ca.* 3.5 G.

Conclusions.—We have searched for evidence of proton-loss from methyl groups of these cations such as is postulated by Gilbert *et al.*[13] However, no such change occurred on annealing prior to total spectral loss. This is not a significant result since Freon is a very poor proton acceptor compared with water.

We conclude that the nature of the atom or group at the 1-position for all these radicals has very little effect on the form of the SOMO. There is, however, a marked positive charge effect on the proton hyperfine coupling constants, and particularly on the extent of delocalisation exhibited by methyl groups at the 2- and 5-positions.

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