Substituted Benzene Cations formed by Radiolysis: an Electron Spin Resonance Study
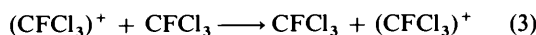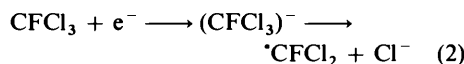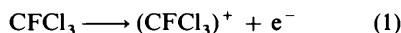
D. N. Ramakrishna Rao and Martyn C. R. Symons *
Department of Chemistry, The University, Leicester LE1 7RH

Exposure of dilute solutions of substituted benzenes in trichlorofluoromethane to ^{60}Co γ-rays at 77 K gave the corresponding radical cations, which were detected and characterised by e.s.r. spectroscopy. In general, the e.s.r. results show that the SOMO is that predicted by theory and found from photoelectron spectroscopic studies, but several interesting facets have emerged. For the monosubstituted cations, (Ph–X)$^+$, where X = CHO or CMeO, the SOMO is largely confined to the benzene ring, with no evidence for cations with a SOMO largely confined to the *n* oxygen orbital. For styrene and substituted styrene cations there is considerable delocalisation on to the olefin moiety (*ca.* 30%). Nitrobenzene cations have a nodal plane through the nitro group with zero spin density on nitrogen (a_2), but they rearrange on annealing to give (RONO)$^+$ cations with the unpaired electron strongly confined to the nitro group. For the disubstituted cations, the effect of a methyl group *para* to a nitro group is of interest since the alternative SOMO is selected (b_1), giving a high spin density on the methyl group (A_{Me} = 20 G). However, delocalisation on to the nitro group remains small. The effect of *para*-cyano groups on the cations of halogenobenzenes is to increase the extent of delocalisation on to halogen, but no hyperfine splitting from ^{14}N is detectable. The effect of a *para*-nitro group is to increase the spin density on the halogen still further.

Benzyl derivatives, (PhCH$_2$X)$^+$, are of interest because of the range of conformations available. When X = Me, the methyl group lies close to the plane of the ring, giving maximum σ–π interaction with the methylene protons [A(^{1}H) = 29 G]. Curiously, for *p*-diethylbenzene cations, the major species seems to have the two methyl groups well removed from the nodal plane. Halogen substituents (X = Cl, Br) also give variable conformations, the in-plane site being favoured for chlorine, and the maximum out-of-plane site for bromine. However, the cation of *p*-nitrobenzyl chloride has a high spin density on chlorine. As with benzaldehyde, the SOMO for phenylacetaldehyde cations is clearly confined to the benzene ring rather than being the *n* oxygen orbital. In this case, the CHO group sits close to the plane of the ring, whereas the CMeO group is well removed from this plane.

Although there have been extensive e.s.r. studies of aromatic radical anions during the past 25 years,[1] relatively few radical cations have been studied by this technique apart from various condensed-ring cations.[2] The cation of benzene itself has been studied in frozen sulphuric acid[3] and on silica surfaces,[4] as have various methyl derivatives.[5,6] We showed some time ago that hexamethylbenzene cations are stable in sulphuric acid at room temperature,[7] and later published e.s.r. results for pentamethylbenzene cations and 1,2,4,5-tetramethylbenzene cations.[8] Also, cations containing amino[9] and alkoxy[10] substituents are relatively stable and have been studied in fluid solution by e.s.r. spectroscopy.

Recently, however, there has been an upsurge of interest in organic radical cations following the use of halogeno derivatives as solvents, pioneered by Hamill and co-workers.[11,12] The basic chemistry leading to good yields of such cations, (S)$^+$, is summarised in reactions (1)—(4). Following ionization, the

$$CFCl_3 \longrightarrow (CFCl_3)^+ + e^- \qquad (1)$$

$$CFCl_3 + e^- \longrightarrow (CFCl_3)^- \longrightarrow$$
$$\qquad \qquad \qquad \qquad \cdot CFCl_2 + Cl^- \qquad (2)$$

$$(CFCl_3)^+ + CFCl_3 \longrightarrow CFCl_3 + (CFCl_3)^+ \qquad (3)$$

$$(CFCl_3)^+ + S \longrightarrow CFCl_3 + (S)^+ \qquad (4)$$

thermalised electrons react efficiently with solvent molecules (2), the resulting radicals giving very broad e.s.r. features that do not generally interfere with those from the trapped radical cations.

In contrast, the solvent cations are mobile *via* charge transfer (3) until they are close to a solute molecule (S), which reacts to give (S)$^+$ (4), provided its ionization potential is less than that of the solvent. The most popular solvent for these studies is trichlorofluoromethane, CFCl$_3$, and this is the solvent we have used herein.

A wide range of organic radical cations have now been studied using this technique. They include alkane cations,[13,14] amide cations,[15] phosphine cations,[16] peroxide and persulphide cations,[17] alkyl halide cations,[18] and cations of silicon, germanium, and tin alkyls.[19,20] We,[21] and Tabata and Lund,[22] have shown that various methylbenzene cations give relatively well resolved e.s.r. spectra in Freon solvents, and Iwasaki and co-workers have nicely established that at very low temperatures the benzene cation is Jahn–Teller distorted, the distortion becoming dynamic in the 90—100 K region.[23] This result is of particular interest since no-one has yet been able to detect benzene anions in their static distorted form by e.s.r. spectroscopy.
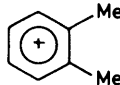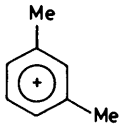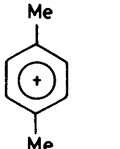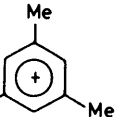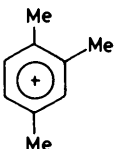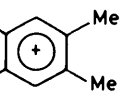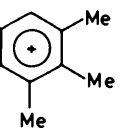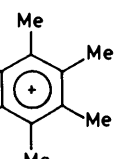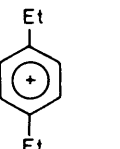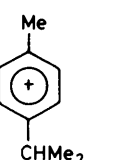
We have shown that well defined e.s.r. spectra can be obtained from halogenobenzene cations prepared in this way.[24,25] The results show that the SOMO (semi-occupied molecular orbital) is extensively delocalised on to halogen in these cations, especially that of iodobenzene. Cations of ethylbenzene are of interest because they show very large hyperfine coupling to the two methylene protons (29 G), showing that the methyl group lies close to the plane of the ring, in the sterically least favoured site.[26] We have also found that chlorine favours a similar in-plane site, whereas bromine lies well out of the plane, giving large σ–π delocalisation *via* the C–Br bond.[27]

Table 1. E.s.r. parameters for benzene and monosubstituted benzene cations in Freon solvent

Cation	Hyperfine coupling constants (G)[a]		
	Ring protons[a]	Alkyl protons[a]	Other nuclei[a]
$C_6H_6^{+}$ [b]	4.5 (6H)		
$C_6H_6^{+}$ [c]	4.4 (6H)		
$C_6H_6^{+}$ [d]	8.2 (2), 2.4 (4)		
$PhMe^{+}$ [b]	12 (1)	18.5(3)	
$PhMe^{+}$ [c]	12.5 (1)	20 (3)	
$PhCH_2Me^{+}$ [e]	12 (1)	29 (2)	
$PhCHMe_2^{+}$ [e]	12 (1)	(i) 6 (1) (ii) 21 (1)	
$PhSiH_3^{+}$ [e]	11 (1)	9 (3)	
$PhC(H)(=O)^{+}$	11 (1)		
$PhC(Me)(=O)^{+}$	9 (1)		
$PhC(OMe)(=O)^{+}$	10.5 (1)	5.5 (2)	
$PhC(OEt)(=O)^{+}$	10.5 (1)	4 (1), 7.5 (1)	
$PhCN^{+}$	10 (1)		
$PhCH{=}CH_2^{+}$	11 (1)	9.5 (2)	
$PhCMe{=}CH_2^{+}$	11 (1)	9.5 (2)	
$PhC{\equiv}CH^{+}$	10 (1)	10 (1)	
$PhC{\equiv}CMe^{+}$	9.5 (1)	12.5 (3)	
$PhCH{=}CHCO_2Et^{+}$	10 (1)	10 (1)	
$PhOMe^{+}$ [f]	9.97 (1) $\left.{4.52 \atop 5.51}\right\}$ (2) $\left.{0.21 \atop 1.00}\right\}$ (2)	4.83 (3)	
$PhOMe^{+}$	10 (1), 5 (2)	5 (3)	
$PhOEt^{+}$	10 (1), 4.5 (2)	7 (2)	
$PhNMe_2^{+}$	5 (3)	12 (6)	^{14}N 30 (z), ca. 0 (x, y)
$PhN(Me)C(=O)(H)^{+}$	8 (1)	8 (3)	^{14}N 18 (z), ca. 0 (x, y)
$PhNO_2^{+}$	6 (4)		
PhF^{+} [g]	10.5 (1)		^{19}F 155 (z), 25.3 (x, y)
$PhCl^{+}$ [g]	9 (1)		^{35}Cl 28 (z)
$PhBr^{+}$ [g]			^{81}Br 185 (z)
PhI^{+} [g]			^{127}I 210 (z)

[a] G = 10^{-4} T isotropic data only: the number of equivalent nuclei is given in parentheses. [b] Ref. 21. [c] Ref. 22. [d] Ref. 23. [e] Ref. 26. [f] Ref. 10. [g] Ref. 25.

Table 2. E.s.r. parameters for polysubstituted benzene cations

Cation	Hyperfine coupling constants (G)		
	Ring protons	Alkyl protons	Other nuclei
o-dimethylbenzene cation	a 7.5 (2) b 5.5 (2)	12.8 (6) 13.2 (6)	
m-dimethylbenzene cation	a 8.5 (2) b 8.5 (2)	12.0 (2) 12.0 (2)	
p-dimethylbenzene cation	a 2.5 (4) b 3.0 (4)	18.2 (6) 18.3 (6)	
1,3,5-trimethylbenzene cation	11.4 (1) ~2 (2)	17 (3) 5.7 (6)	
1,2,4-trimethylbenzene cation	5.3 (1)	16 (6) 5.3 (3)	
1,2,4,5-tetramethylbenzene cation	c 0	11.0	
pentamethylbenzene cation	c	10.85 (6) 10.30 (6) 0.56 (3)	
hexamethylbenzene cation	c	6.45	
p-diethylbenzene cation		(i) 7 (2), 15 (2) (ii) Σ (4H) = 78	
p-methyl-isopropylbenzene (cymene) cation CHMe₂		18 (3) (i) 0 (1) (ii) 18 (1) (iii) 28 (1)	

Table 2 (*continued*)

Cation	Hyperfine coupling constants (G)		
	Ring protons	Alkyl protons	Other nuclei
p-methylbenzaldehyde cation		19.0 (3)	
dimethyl terephthalate cation		5.5 (6)	
1,4-dicyanobenzene cation	e		
benzodioxole (CH₂) cation		22.4 (2)	
p-nitrotoluene cation	ca. 3 (?)	20 (3)	
m-nitrotoluene cation	12 (1)	20 (3)	
o-nitrotoluene cation	12 (1)	18 (3)	
p-bromonitrobenzene cation			⁸¹Br 217 (z)
p-chlorotoluene cation		17.5 (3)	³⁵Cl 27 (z) (1)
p-bromotoluene cation		15 (3)	⁸¹Br 170 (z) (1)

a Ref. 21. *b* Ref. 22. *c* Ref. 8. *d* Ref. 25. *e* Unresolved singlet.
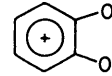
Table 2 (*continued*)

Cation	Ring protons	Alkyl protons	Other nuclei
Et-(ring)-Br		20 (1), 35 (1)	^{81}Br 160(z)(1)
CN-(ring)-Br			^{81}Br 185(z)(1)
Br-(ring)-Br d			^{81}Br 143(z)(2)
Me-(ring)-F d	2.9 (4)	19 (3)	^{19}F 136 (z), 22.5 (x, y)
OH-(ring)-Br d			^{81}Br 113(z)(1)
OMe-(ring)-Br d			^{81}Br 113(z)(1)
SH-(ring)-Br d			^{81}Br 100(z)(1)
Me-(ring)-I c			^{127}I 185 (z)
Me-C=O, HN-(ring)-NO$_2$	8 (1), 6 (1)	8 (1)	^{14}N 18 (z), ca. 0 (x, y)

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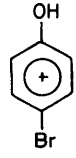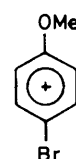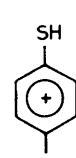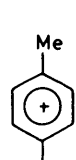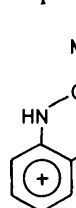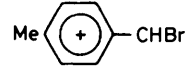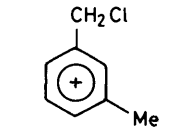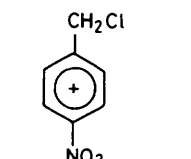
Table 3. E.s.r. parameters for various substituted benzyl radical cations

Cation	Hyperfine coupling constants (G)		
	Ring protons	Alkyl protons	Other nuclei
PhCH$_2$CHO$^+$	12 (1)	24 (1), 27.5 (1)	
PhCH$_2$C(Me)O$^+$	10.5 (1)	7 (1), 10.5 (1)	
PhCH$_2$C(=O)OMe$^+$	11 (1)	5 (1), 14 (1)	
PhCH$_2$OCOMe$^+$	11 (1)	5 (1), 15 (1)	
PhCH$_2$Cl$^+$	12 (1)	21.5 (1), 26 (1)	^{35}Cl 0
PhCH$_2$Br$^+$			^{81}Br 193 (z); 133 (z)
Me-(ring)-CHBr	15		^{81}Br 162 (z)
CH$_2$Cl-(ring)-Me	12 (1)	24 (1), 27 (1)	^{35}Cl 0
CH$_2$Cl-(ring)-NO$_2$		8 (2)	^{35}Cl 30 (z)

The aim of the present study was to bring these studies together, and to add a range of other substituted benzene cations so as to provide a general survey of the e.s.r. spectra of such cations. The results are compared with the results of photoelectron spectroscopy (p.e.s.) and of theoretical calculations. Of particular interest to us was the possibility that there might be inversion of certain levels as a result of distortion or medium effects, such as can be observed for various substituted pyridine cations, where either the $n(\sigma)$ orbital on nitrogen, or the π orbital of the ring, can be the SOMO depending on the substituent.[28]

Experimental

All the aromatic compounds used in this study were commercial samples whose purity was checked by n.m.r. spectroscopy. They were purified as necessary by standard procedures. Dilute solutions (*ca.* 0.001 mole fraction) in CFCl$_3$ were degassed and frozen as small beads in liquid nitrogen. These were exposed to ^{60}Co γ-rays in a Vickrad cell to doses of *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 B-H12E field probe, which were standardised with a sample of diphenylpicrylhydrazyl (DPPH). Samples were annealed by decanting the nitrogen from the insert Dewar and allowing the samples to warm with continuous monitoring of the spectra. They were re-cooled to 77 K for study whenever significant spectral changes were observed.

Results and Discussion

The majority of our results, and those of others, are summarised in Tables 1—3. Some selected spectra are given in Figures 1—8. These have been somewhat arbitrarily selected as being typical

of certain types of spectra to which others, not shown, can be related. In all cases, the radicals detected after exposure at 77 K are identified as the parent radical cations. All workers in this field agree that the only species likely to be detectable under our conditions are the parent radical cations or unimolecular breakdown products thereof, the evidence for this claim being overwhelming. In a few cases, unimolecular breakdown does apparently occur on annealing. These are discussed specifically below. In other cases, on annealing or when more concentrated solutions were studied, dimer cations were detected. These are not discussed herein.

Alkylbenzene Cations.—There are few surprises in the results given in Tables 1 and 2. Most of the spectra were unambiguously interpreted, but some difficulty was experienced with the spectra of the trimethyl derivatives because of the lack of symmetry and consequent inequivalence of the methyl protons. For the 1,2,4-derivative, we find two of the methyl groups nearly equivalent (*A ca.* 16 G), the third showing only a small coupling (5.3 G) approximately equal to that of a single ring proton. Thus the nodal plane must fall close to the other two protons, as in (1). For the 1,3,5-derivative the spectrum can be interpreted in terms of one strongly and two weakly coupled methyl groups, again with very small coupling to two of the ring protons. We suggest a structure of the type shown in (2) for this cation. A typical e.s.r. spectrum is shown in Figure 1.

Results for ethylbenzene and 1,4-diethylbenzene cations make an interesting contrast. We have previously shown that there are two strongly coupled methylene protons (*ca.* 29 G) for the monoethyl derivative, which we interpreted in terms of structure (3), with θ close to 30°.[26] Hence, for the diethyl derivative we had expected to find a quintet spectrum with a similar splitting. In fact, the spectrum was clearly due to at least two species, but the total splitting of 78 G is far less than predicted. At 77 K the major species had $A(2H) = 7$ G and $A(2H) = 15$ G, which on annealing to *ca.* 140 K became a quintet, $A(4H) = 11$ G. A second species giving a total splitting of 78 G was in much lower abundance. If the four protons are equivalent, this gives $A(4H) = 19.5$ G. We suggest that the main species adopts structure (4), with θ *ca.* 60°. In no case were we able to induce 'free' rotation of these groups on annealing, prior to radical loss at *ca.* 160 K. Although these results are reasonable, they correspond to average values (*i.e.*, for θ = 45°) greater than those for the corresponding methyl derivatives for which free rotation was found at 77 K.[21,22] For the major diethyl cation, we calculate an average coupling of 22 G, which is clearly greater than the value of 18.2 G[21] (18.3 G[22]) obtained for *p*-xylene cations. At present, we are unable to offer any convincing reasons for this switch in conformation on going from the mono- to the di-ethyl derivative or for the numerical discrepancy.

The e.s.r. spectrum for PhCHMe$_2^+$ cations was far more complicated than expected and changed on annealing.[26] We intrepreted this in terms of several different conformations of nearly equal energy.

Carbonyl Derivatives.—Results for benzaldehyde radical cations are of interest since, in CFCl$_3$ solvent, a 1:2:1 triplet was obtained, whereas for solutions in CCl$_4$ the spectrum was a 9 G doublet. We suggest that the extra doublet splitting in CFCl$_3$ is due to coupling to ^{19}F nuclei. A similar extra doublet splitting has been observed for (C$_2$F$_4$)$^+$ cations,[28] but coupling to chlorine is more common.[18] However, for acetophenone, only the expected doublet splitting from the *para*-proton was obtained using Freon solvent [Figure 2(*a*)]. Also, for the *para*-methyl derivative in Freon, no extra splitting was seen, the spectrum comprising a major 1:3:3:1 quartet assigned to the methyl protons, the splitting being *ca.* 19 G, which is close to

(1)   (2)

(3)   (4)

3250 G

20 G
├──┼──► H

+6 +5 +4

+3

+2

-4 -5 -6

-3

+1 0   -1 -2

Figure 1. First-derivative *X*-band e.s.r. spectrum for 1,2,4,5-tetramethylbenzene in CFCl$_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the radical cations

that for toluene cations [Figure 2(*b*)]. Splitting from the ring protons and the aldehydic proton was not resolved, but there was slight asymmetry which we assign to *g*-value anisotropy. A reasonable fit was obtained with $g_{max.} = 2.005$ and $g_{min.} = 2.002$. We suggest that this increase in Δg stems from spin density on the carbonyl oxygen, but delocalisation cannot be very great in view of the large splitting obtained from the methyl protons. It is noteworthy that whilst the methyl proton splitting suggests no loss of spin density, the *para*-proton splitting for the unsubstituted derivatives, including that for acetophenone cations (*ca.* 9 G), suggests a reduction of *ca.* 20%.

For all these cations, the SOMO is clearly the π(*b$_1$*) orbital indicated in (5), rather than the non-bonding oxygen orbital shown in (6). This is not populated for the aldehydes since we have established that the aldehydic proton should give a large hyperfine coupling (*ca.* 130 G).[29]

These results make an interesting comparison with that for the isoelectronic radical (7) derived by hydrogen-atom addition to cyanobenzene.[30] This gave a coupling of 78 G to the added
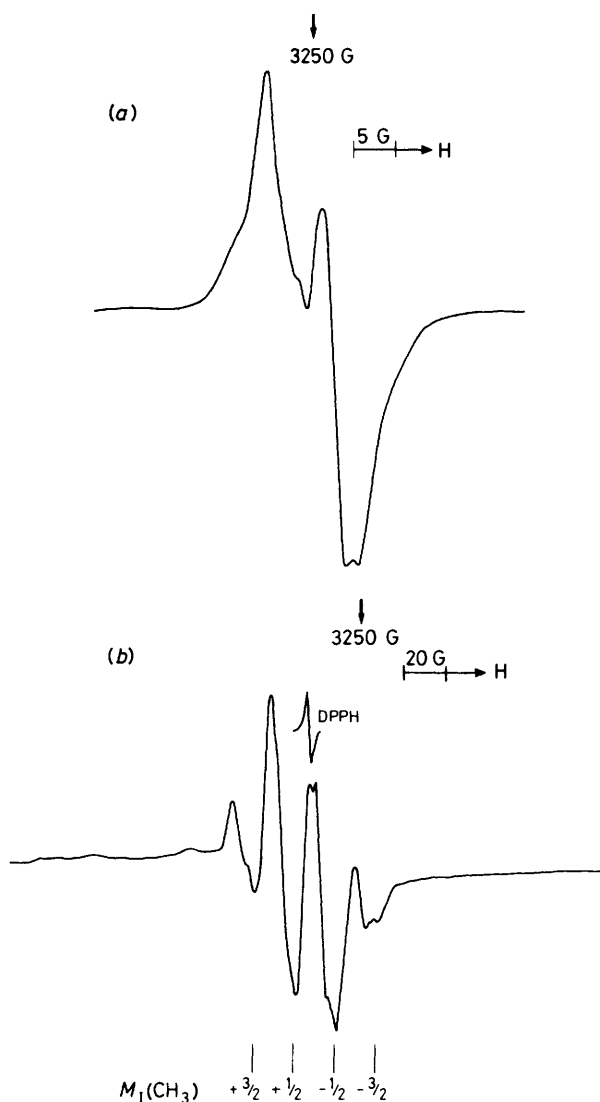
Figure 2. First-derivative X-band e.s.r. spectrum for (a) acetophenone and (b) p-methylbenzaldehyde in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the corresponding cations

hydrogen, the orbital being unambiguously the $n(N)$ orbital [$A(^{14}N) = 11.3$ G]. Calculations and p.e.s. studies suggest that the π and $n(\sigma)$ orbitals are very close for $PhCOH^+$ and $PhCOMe^+$ and their derivatives.[31-33] One group[31] definitely conclude that the HOMO is the $a'n(O)$ rather than the $a''(\pi)$, related to the b_1 orbital (5), whilst another[33] propose the reverse order. Our results are conclusively in favour of the $a''(b_1)$ assignment for the SOMO.

Benzoate Ester Cations.—Both the methyl and ethyl derivatives gave major 10.5 G doublets, with subsidiary splittings from the alkyl protons. For the methyl ester two methyl protons gave 5.5 G, the other splittings being unresolved. Thus the methyl group adopts a preferred conformation with one C–H proton close to the radical plane. A similar conformation was found for the cation of methyl formate,[34,35] the two strongly coupled protons giving splittings of 23 G. Assuming a linear dependence of $A_{iso.}$ on spin density, we estimate a spin density of *ca.* 24% on the ester group of methyl benzoate cations. Alternatively, assuming a coupling of *ca.* 12 G for the *para*-proton in the absence of delocalisation we estimate *ca.* 16% on the ester group.
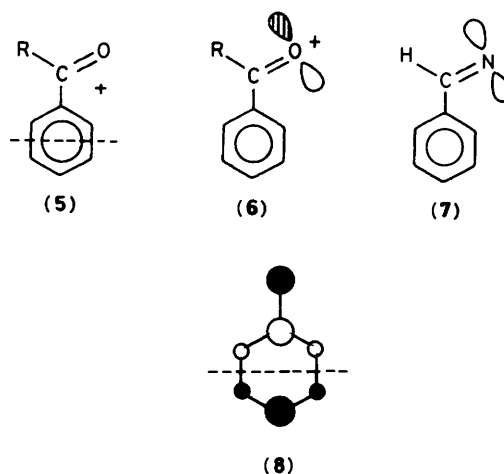
As with the alkyl esters, the possible alternative structure with the unpaired electron largely confined to the in-plane oxygen orbital, $n(O)$, was not detected. In this case, both p.e.s. results and calculations agree in placing this level below the two π levels, although these were not distinguished in the p.e.s. study of McGlynn and co-workers,[36] and must therefore be quite close together.

Our results for dimethyl phthalate are interesting in that at 77 K a very broad feature was obtained, but this became a quartet on warming to *ca.* 120 K, with a splitting of *ca.* 10 G. This suggests three approximately equivalent protons, which is a difficult result to accommodate since it implies a highly asymmetric conformation. However, at *ca.* 140 K shoulders appeared between each major component. This suggests a septet from six equivalent protons with splitting of *ca.* 5 G, with selective broadening of the $M_1 = \pm 2$ and 0 components. This could arise if there was an alternation of spin density on the two ester groups, induced, for example, by concerted out-of-plane vibrations of each CO_2Me unit. This would leave the ± 3 and ± 1 lines unaffected and broaden the remainder. However, in the light of the results for methyl benzoate, we should also consider concerted hindered rotation of the two methyl groups. We do not think that jumps between structures of this type could lead to the observed line-width alternation.

Cyanobenzene Cations.—Our spectra for $(PhCN)^+$ cations comprised broad doublets with $A(^1H) = 10$ G. We were unable to resolve splitting from other ring protons but conclude that $A_{\|}(^{14}N) \leqslant 9$ G. Also, there was no major g-shift. Hence we conclude that the spin density of nitrogen is low. The SOMO is clearly the $b_1(\pi)$ orbital indicated in (8), with nodes close to the cyanide carbon and between the *ortho* and *meta* CH groups. Other cyano-derivatives are discussed below.

Phenylacetylene (Ethynylbenzene) Cations.—Phenylacetylene is isostructural with the cyano derivative and hence their cations are expected to be similar. Our results clearly support the expected $b_1(\pi)$ SOMO, and the small g-shifts show that this is well removed from the in-plane quasi-π orbital (Table 1).

The e.s.r. spectrum for the phenylacetylene cation comprised a well defined 1:2:1 triplet with $A = 10$ G. There can be little doubt that the two protons involved are the *para* ring proton and the acetylenic proton. The spectrum for the methyl derivative, $(PhC{\equiv}CMe)^+$, showed a 1:3:3:1 quartet ($A = 12.5$ G) and an extra doublet ($A = 9.5$ G); again, assignment is unambiguous.

Judging from the *para*-proton splitting, the spin-density distribution is similar to that for the cyano derivative. The reduction in the *para*-proton splitting suggests a shift of 15—
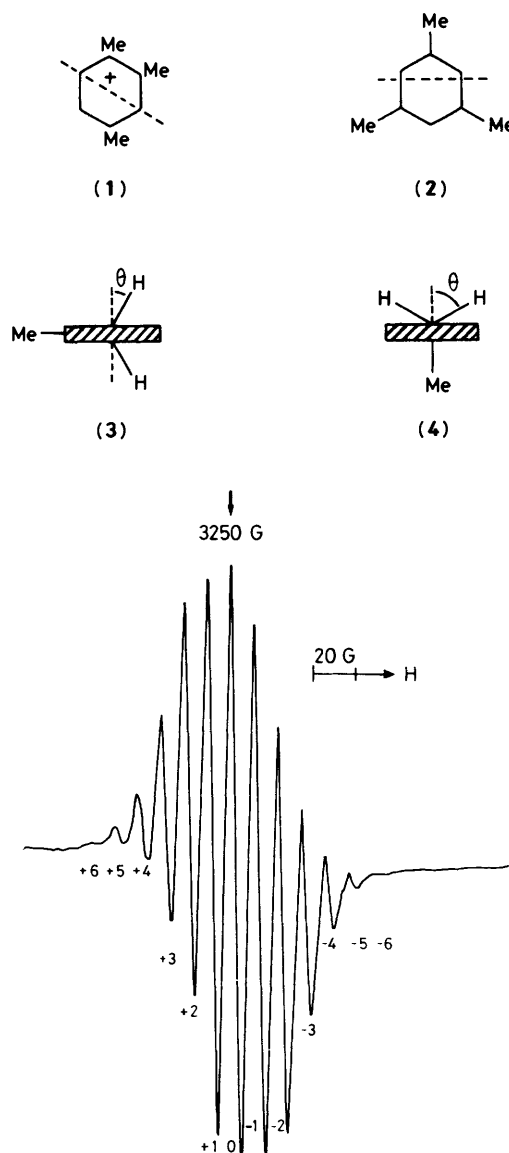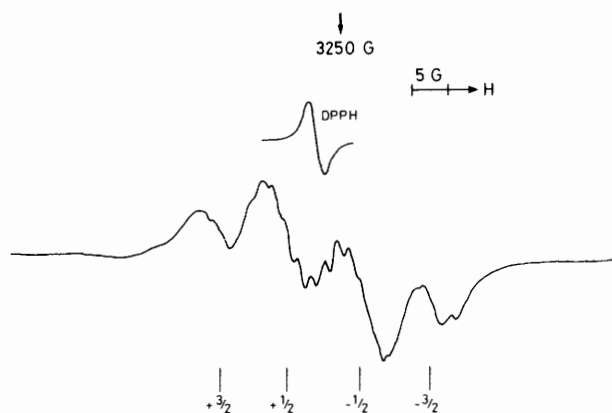
Figure 3. First-derivative X-band e.s.r. spectrum for styrene in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the styrene radical cations

(9)
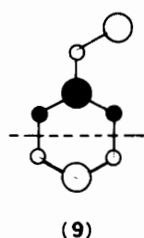
20% spin density on to the C≡N or C≡CR groups. The ^{14}N coupling, assuming $A_\perp$ ca. 0, suggests a spin density of ca. 18% on nitrogen in good agreement. The acetylenic C–H coupling suggests a spin density of 30—40% on carbon, which is surprisingly high. It is difficult to estimate the ĊMe spin density from the methyl splitting since this depends strongly on the effective positive charge on the C≡CMe unit. If this were comparable to that for the toluene cation (A_{Me} = 18 G) we could argue that the spin density is ca. 23% (assuming an effective spin density of 0.33 for the C–Me unit in the toluene cation). However, if, as we suspect, there is a lower effective positive charge on the C≡CMe unit, the spin density must be >23%. Unfortunately, we cannot be more precise than this in our estimates at present.

Styrene and Related Cations.—Our results (Figure 3) show strong coupling (ca. 10 G) to three nearly equivalent protons with extra couplings of ca. 3 G to other protons. The results are in good accord with expectation for the predicted SOMO (9) [33,37] giving quite high spin density (ca. 30—40%) on the CH_2 carbon atom, and on the *para*-carbon atom. The cation for α-methylstyrene gave a very similar e.s.r. spectrum, thereby confirming that the spin density on the α-carbon atom must be small.

The spectrum of the cation derived from ethyl cinnamate showed coupling to two nearly equivalent protons (ca. 10 G). This shows that the HOMO is very similar to that of styrene cations (9), with little delocalisation on to the ester group.

Aryl Ether Cations.—Anti-bonding between the b_1 orbital and the oxygen $p(\pi)$ orbital raises the b_1 HOMO well above the a_2 orbital, and there is quite strong delocalisation on to oxygen for these cations.[31] They are relatively stable, and the methoxy derivative (anisole cation) has been studied in the liquid-phase by e.s.r. spectroscopy.[10] Our spectra were less well resolved, but the parameters are very similar to those previously reported, thus supporting the assignment. In this case, the methyl group is still 'freely' rotating even at 77 K. It is noteworthy that the nodal

(10)

Figure 4. First-derivative X-band e.s.r. spectrum for various nitrobenzene derivatives in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned (a) to $(PhNO_2)^+$ cations, (b) p-methylnitrobenzene cations, and (c) o-methylnitrobenzene cations

surface has moved away from the methoxy group so as to fall close to the *meta* C–H groups thereby enhancing the hyperfine coupling to the *ortho*-protons (ca. 5 G) and reducing that to the *meta*-protons (ca. 0.6 G). The liquid-phase results show that the two *ortho*- and two *meta*-protons are not equivalent (Table 1), but this is too small an effect for us to detect.

The e.s.r. spectrum for the ethoxy derivative was an unresolved broad line at 77 K, but above ca. 130 K a relatively well resolved spectrum gave the results indicated in Table 1. The ring proton splittings are close to those for the methoxy cation, but the CH_2 protons have an appreciably larger coupling (ca. 7 G), which suggests that the preferred conformation is one in which the methyl group lies in the molecular plane. These results can be compared with those for dialkyl ethers.[38–40] These give an average β-proton coupling of ca. 43 G. Again, if we assume an approximately linear correlation, we estimate a spin density of ca. 12% on oxygen. This is probably an underestimate because the reduction in the positive charge on oxygen should reduce the tendency towards hyperconjugative electron release thus reducing the coupling more rapidly then predicted by a linear correlation.

The cyclic acetal (10) gave a cation having an unusually large

(11)

coupling to the methylene protons of *ca.* 21.5 G. This was expected because of our results for saturated acetals, which have splittings of *ca.* 150 G to the methylene protons.[40] Assuming linearity this gives *ca.* 15% delocalisation but, as before, we suggest that this is probably an underestimate.

Aniline and Related Cations.—Because of their low ionization potentials, these cations have been extensively studied by e.s.r. in the liquid phase.[9] The SOMO is clearly the b_1 orbital which is well removed from the a_2 orbital. Our results for the dimethyl derivative, $(PhNMe_2)^+$ are in good accord with liquid-phase data,[9] and give, in addition, a measure of the anisotropic ^{14}N coupling ($A_{\|} = 30$ G, $A_{\perp}$ *ca.* 0). From this we obtain $A_{iso.}$ *ca.* 10 G and $2B$ *ca.* 20 G. It is preferable to use the room-temperature value of $A_{iso.} = 11$ G,[9] which gives $2B = 19$ G. This can be used to give an approximate estimate of the spin density on nitrogen in the usual way.[41] This gives 56%, which is remarkably high. From the *para*-proton coupling we obtain a delocalisation of *ca.* 50%, and from the methyl proton coupling (*ca.* 12 G) we obtain a spin density of *ca.* 45% using the data for Me_3N^+ cations as a yard-stick. We conclude that the spin density on nitrogen is indeed *ca.* 50% As with anisole cations, the estimate from the *N*-methyl groups is probably low because of the extra positive charge effect.

Nitrobenzene and Related Cations.—Our results for $PhNO_2^+$ cations (4H, *A ca.* 6.0 G) [Figure 4(*a*)] are in good accord with expectation for the a_2 orbital, which has been predicted to be the SOMO for these cations.[31.32] However, there is a remarkable inversion of levels for the *para*-methyl derivative, as can be judged from Figure 4(*b*). This shows a quartet for the methyl protons [$A(^1H) = 20$ G] with an extra splitting of *ca.* 3 G, probably assignable to the ring protons. There are no clear parallel features from ^{14}N, so the spin density on nitrogen must be low. It is interesting to note that the more approximate INDO theory predicts that this orbital, the b_1 orbital, should be the SOMO for the nitrobenzene cations,[42] but the switch found herein has not been predicted theoretically nor deduced from the p.e.s. spectra.

Results for the *ortho*-derivative again show the strong control exercised by the methyl group, since it dominates the structure [Figure 4(*c*)], which must be close to that shown in (11). The methyl proton coupling is *ca.* 18 G and the *para*-proton coupling *ca.* 12 G, these results being very similar to those for toluene cations. Clearly, delocalisation on to the nitro group is trivial for these cations, even when orbital overlap is favourable, in marked contrast with results for the corresponding radical anions. The spectrum for the *meta*-derivative was very similar to that for the *ortho*-cation, giving $A(Me) = 20$ G and $A(para$-H$) = 12$ G, so again, the nitro group does not significantly participate in the SOMO.

In our study of nitroalkane cations we suggested that the parent cations having a SOMO confined to a combination of oxygen $2p$ orbitals readily rearrange to the isomeric nitrite cations, $RONO^+$.[43.44] Similar rearrangements for various nitroaryl cations are described later.

Halogenobenzene Cations.—We have already published our results for the mono-halogenobenzene cations,[35] the results

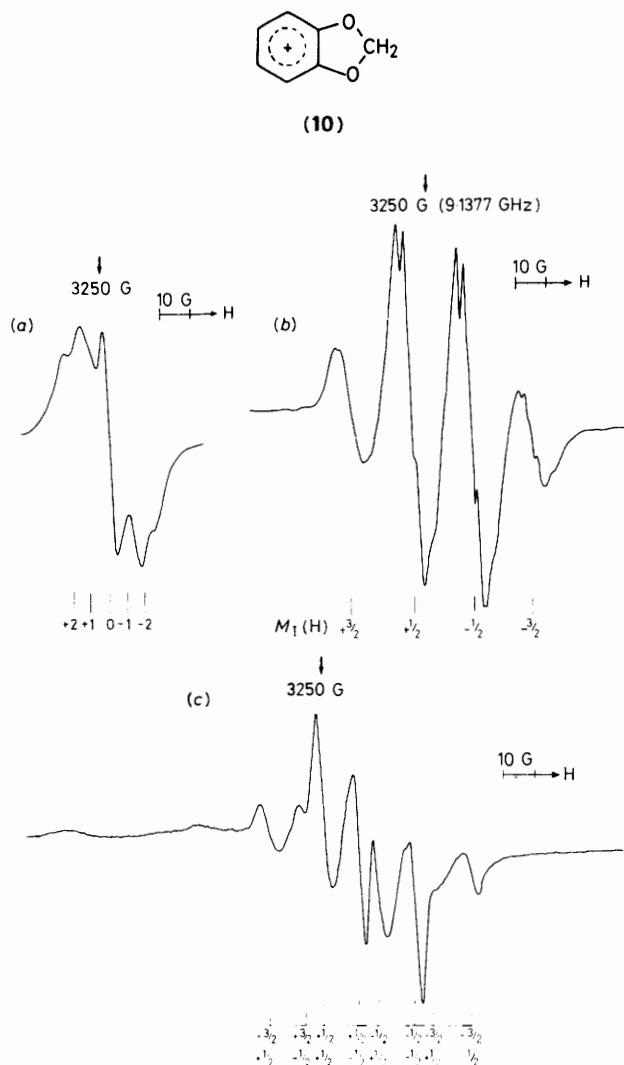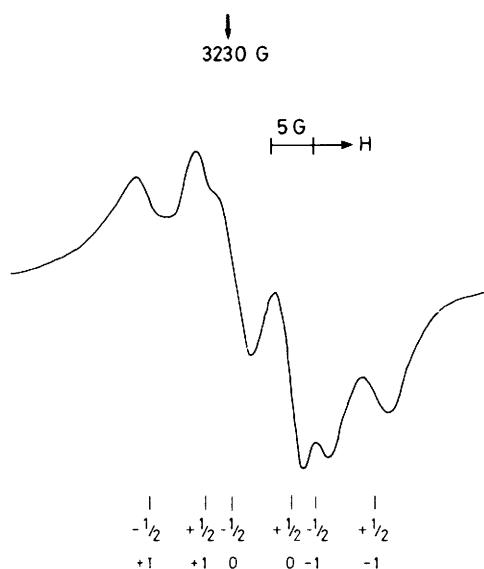Figure 5. First-derivative *X*-band e.s.r. spectrum for *p*-ethyl-bromobenzene in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features for the radical cations. The *z*-features are indicated in the stick diagram

being included in Tables 1 and 2. They were analysed in terms of an uppermost b_1 orbital, delocalisation on to halogen increasing from *ca.* 8% for fluorine to 23, 30, and *ca.* 46% on Cl, Br, and I, respectively. Thus delocalisation on to fluorine is slightly less than that on to oxygen for the anisole cation, the order being F > OR > Cl > Br > I ≈ NR_2.

We have extended this study to cover a variety of substituted halogenobenzene cations, including *para*-methyl; *para*-ethyl (Figure 5); *para*-nitro; and *para*-cyano-bromobenzene cations (Table 2). In all cases, the same (b_1) orbital is involved, but several trends in the value of A_z for the halogen substituent are of interest. Unfortunately, except for fluorine, it is difficult to obtain good values for $A_{\perp}$ (A_x, A_y) for the halogen interaction. Even with the best simulation techniques, matching spectra is not very precise, and we prefer to use the precisely measured A_z values to illustrate trends. Also, reasonably good values of halogen spin densities can be obtained using the empirical equation established by Oloff and Hüttermann[45] (ρ_x = spin

$$\rho_x = A_z f_x/2B° \qquad (5)$$

density on halogen, A_z = the maximum hyperfine coupling, $2B°$ is the calculated coupling for unit populaton of the halogen p_z orbital, and $f_x = 0.81$ for ^{35}Cl and ^{81}Br, and 1.0 for ^{127}I).

In all cases, *para*-methylation leads to a small reduction in A_z and calculated spin density on halogen. For fluorine there is a *ca.* 1% decrease but for chlorine and bromine the decrease is *ca.* 3%. Delocalisation on to the methyl group is between 5 and 10%, depending on the contributions of spin polarisation and genuine declocalisation to the proton coupling. Clearly this is distributed between the ring and the halogen substituent.

It is curious that the reduction in spin density on bromine induced by OR groups (*ca.* 12%) is greater than that induced by a second bromine (*ca.* 7%), since delocalisation on to bromine in $(PhBr)^+$ (*ca.* 30%) is greater than that on to OR groups, if our estimates, given above, are correct. However, the most interesting result is the large increase in spin density on bromine of *ca.* 5% caused by a *para*-nitro group. We have shown above that the nitro group is unable to act as an electron donor in the *para*-methylnitrobenzene cation. It is, however, a powerful electron acceptor. Thus its presence encourages electron donation from bromine to help reduce the electron deficiency on the *para*-carbon.

Benzyl Derivatives.—These are of interest because of the range of possible conformations of the CH_2X group, which may

Figure 6. First-derivative X-band e.s.r. spectrum for benzyl methyl ketone in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the radical cations

Figure 7. First-derivative X-band e.s.r. spectrum for p-nitrobenzyl chloride in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the radical cations

Figure 8. First-derivative X-band e.s.r. spectrum for 2-nitro-N-phenylacetamide in $CFCl_3$ after annealing to *ca.* 120 K, showing features assigned to the rearranged radical cation

be largely sterically or largely electronically controlled. In all cases studied, the orbital selected is the b_1 orbital, placing high spin density on the carbon to which the CH_2X group is bound. Hence, from the point of view of e.s.r. spectroscopy the cations are of far greater interest than the corresponding anions, since these generally have a nodal plane passing through the CH_2X unit (a_2).

We have shown above that when X = Me, electronic control just dominates, and we conclude that C–H hyperconjugation is favoured over C–C hyperconjugation. That the balance between steric and electronic control is subtle is shown by the results for the isopropyl (cumene) cation, and for the *para*-diethyl cation.

Phenylacetaldehyde and Related Cations.—The results for phenylacetaldehyde show that the two methylene protons are inequivalent but with hyperfine coupling constants (24 and 27.5 G) greater than the normal average (*ca.* 19 G). Thus the conformation must be as in (3), the CHO group being *ca.* 4° out of the radical plane. In marked contrast, with the more bulky CMeO group the structure has clearly switched to that shown in (4), with the CMeO group close to the 90° out-of-plane limit (Figure 6). Again the balance between electronic and steric control is clearly extremely subtle.

Results for the C(OMe)O derivative cations are similar to those for benzyl methyl ketone cations except that the degree of asymmetry is greater, the two methylene protons giving 14 and 5 G splitting. Interestingly, results for benzyl acetate cations are almost identical (Table 3).

Benzyl Halide Cations.—We have already drawn attention to an interesting switch in conformation on going from $(PhCH_2Cl)^+$ to $(PhCH_2Br)^+$ cations.[27] The e.s.r. results show unambiguously that the chlorine atom lies close to the radical plane, as in (3), whilst the bromine atom sits close to the 90° site, as in (4). This was a surprise since it is well established that in neutral β-chloroalkyl radicals the chlorine favours the out-of-plane site, especially at low temperatures.[46,47] We suggest that the difference must rest again on subtle factors, and this is well illustrated by our results for the *para*-nitro derivative (Figure 7). In this case, the e.s.r. spectrum is clearly dominated by the normal anisotropic hyperfine coupling to chlorine, with
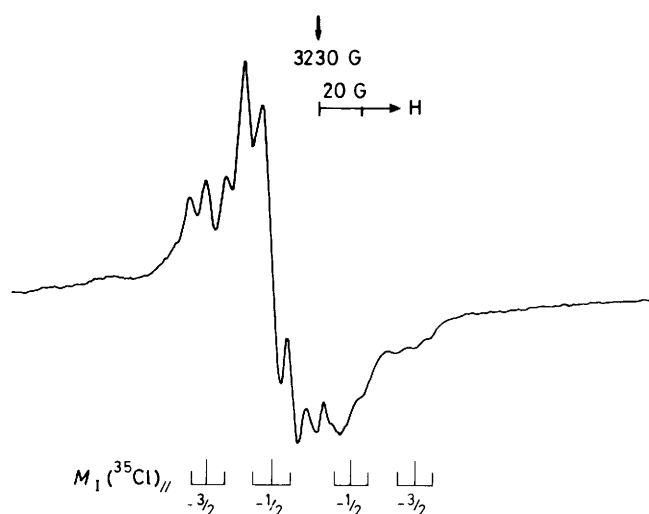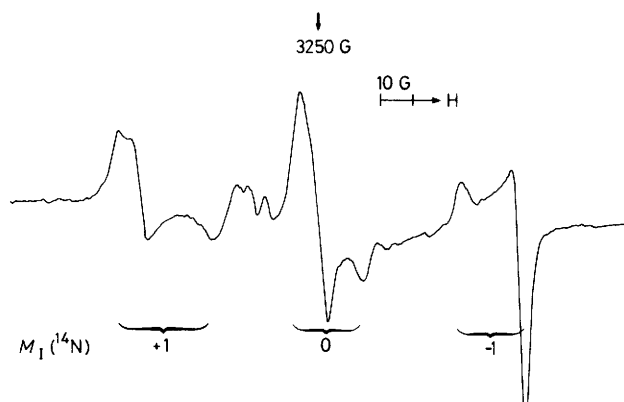
$A_\parallel(^{35}Cl) = 30$ G and an 8 G splitting from the two methylene protons. Thus the nitro substituent has induced a complete switch from the in-plane site for chlorine (3) to the out-of-plane site (4). It is not clear to us why this change should occur. What is clear is that when θ is small, delocalisation on to halogen is large.

Aspects of the Mechanism.—There was clear evidence for the formation of dimer cations in several cases on annealing, or when the concentration of substrate was too high. However, except for the halogenobenzene cations, the resulting e.s.r. spectra were poorly defined and will not be discussed herein. Our results for $(Ph-hal)_2^+$ dimer cations have already been reported.[25]

The other reaction of interest that we observed in our annealing experiments is the apparent rearrangement of cations containing nitro groups. We have previously suggested that, for nitroalkane cations, rearrangement (6) is facile.[43,44] The e.s.r.

$$R\text{-}NO_2^{+\cdot} \longrightarrow RONO^+ \qquad (6)$$

spectra for $(RONO)^+$ cations closely resembles that for $^\cdot NO_2$ radicals, but there are measurable differences. In all cases studied herein, nitro-derivative cations gave these characteristic

e.s.r. features on annealing; a typical example being shown in Figure 8. (The parent cations in this case gave a well resolved e.s.r. spectrum. The derived parameters, given in Table 2, show that the spin density on the amide nitrogen atom is *ca.* 36%).

The facility of this rearrangement shows that $RONO^+$ radicals must be remarkably stable. This undoubtedly arises for the same reasons that confer stability on the structurally similar $\cdot NO_2$ radicals. Nevertheless, since there is no e.s.r. evidence for the formation of cations having a SOMO similar to that for normal $RNO_2^{+\cdot}$ cations, the initial incentive for rearrangement must differ for the two types of nitro derivatives. It is noteworthy that the yield of $RONO^+$ cations was very low for nitrobenzene and other nitro cations for which the HOMO has a node at the C–N bond. Since, as concluded above, the a_2 orbital is close in energy to the b_1 orbital for nitrobenzene cations, we suggest that there is a low population of the $(a_2)^2(b_1)^1$ configuration, and that this is the form that rearranges to $(RONO)^+$. Even so, a σ–π excitation would appear to be necessary before there is a real incentive for the phenyl group to migrate to oxygen.

Finally, we should mention that in our study of $^{13}CH_3NO_2$ in Freon,[44] we obtained evidence for yet another intermediate, namely the σ radical $(Me\cdot NO_2)^+$. This rearranged readily to the $(O\dot{N}OMe)^+$ cation. The ^{14}N hyperfine coupling and g-tensor components are remarkably similar for these cations, but the former has a large ^{13}C hyperfine coupling which is absent for the latter. It is possible that the aromatic derivatives also give σ* intermediates since we would be unable to distinguish these from the nitro cations without the use of ^{13}C labelling.

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