An Electron Resonance Study of Some Substituted Phenoxymethyl Radicals

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A large number of substituted phenoxymethyl radicals formed by the reaction of t-butoxyl radicals with substituted anisoles, thioanisole, phenetole, and thiophenetole have been investigated by e.s.r. The methylene hyperfine couplings are only slightly dependent on the nature of substituents in the aromatic ring; in all cases coupling to ring protons and fluorine atoms has been resolved. The methylene couplings of several of the radicals exhibit line-width alternation at ~35°. Evidence is presented for long-range coupling to ring atoms when *ortho*-substituents force the methylene group out of the plane of the aromatic system.

THE reactions of t-butoxyl radicals, formed both thermally and photochemically, with aromatic ethers have been studied by a number of authors.[1-5] Both methods of formation yielded phenoxymethyl radicals, but the subsequent reaction was different in the two cases. The main product from the photochemical reactions at 40° was a dimeric 1,2-diphenoxyethane, while the thermal reaction at temperatures over 100° proceeded *via* attack of the phenoxymethyl radical on the aromatic ring of another ether molecule.

Aliphatic ether radicals have been extensively studied by e.s.r. both in solution [6-11] and in *X*-irradiated single crystals containing the ether as an inclusion compound [12] but there is no comparable investigation on aromatic ethers. The e.s.r. spectrum of the phenoxymethyl radical † was briefly reported; [13] we have now resolved the ring hyperfine couplings for this radical and have extended the investigation to include a large number of related species. The radicals have been observed during the steady-state photolysis of solutions containing di-t-butyl peroxide by use of techniques recently applied in the investigation of a variety of neutral species including aliphatic radicals,[14] organosilicon and germanium radicals,[13,15] the trichloromethyl radical,[16] and a large number of substituted methyl radicals.[13]

EXPERIMENTAL

The e.s.r. spectra were recorded with a Varian E3 spectrometer and variable-temperature attachment as described.[13] The microwave power was 2·5 mw, and all spectra were measured at −35°. The radicals were prepared by photolysing 5 : 1 mixtures of di-t-butyl peroxide and the respective anisole or phenetole. For solids a saturated solution of the compound in the peroxide was used.

The field sweep of the spectrometer was calibrated with

aqueous solutions of Fremy's salt ($a_N = 13·091 \pm 0·004$ G) and the methylene coupling constants are believed to be accurate to $\pm1\%$. The accuracy of the ring coupling constants depends on the resolution of the particular spectrum. The compounds were all as obtained commercially. The results are given in Table 1, and typical spectra are shown in Figures 1—3.

TABLE 1

Hyperfine coupling constants (gauss) of substituted phenoxymethyl radicals

Substrate	a_H^α	a_H^β	a^o	a^m	a^p	ΔH [a]
Anisole	17·77	—	0·54	0·27	0·49	2·15
Thioanisole	16·47	—	0·79	0·32	0·69	2·91
Pentafluoroanisole	19·16	—	4·45 [b]	<0·10 [b]	0·52 [b]	
p-Bromoanisole	17·77	—	0·61	0·27	—	1·72
p-Chloroanisole	17·80	—	0·61	0·28	—	1·78
p-Fluoroanisole	17·61	—	0·62	0·30	1·14 [b]	3·01 [c]
p-Methoxyanisole	17·36	—	0·52	0·26	—	1·63
m-Fluoroanisole	17·83	—	0·59	0·22	0·43	1·84 [c]
m-Methoxyanisole	17·61	—	0·56	0·25	0·40	1·77
3-Methoxy-4,6-di-bromoanisole	17·73	—	0·86	<0·15	—	—
o-Bromoanisole	17·86	—	0·74	0·44 0·12	0·44	1·73
o-Chloroanisole	17·86	—	0·79	0·43 <0·15	0·43	1·68
Phenetole	14·21	22·37	0·47	0·22	0·36	1·78
Thiophenetole	16·80	20·76	—	—	—	—

[a] Total width of low-field multiplet. [b] Coupling to ^{19}F nuclei. [c] Includes coupling to one ^{19}F nucleus.

RESULTS AND DISCUSSION

With a few exceptions all the compounds investigated gave well resolved spectra attributable to a phenoxymethyl radical. The spectrum obtained from the reaction of t-butoxyl with anisole is shown in Figure 1, A. A similar but weaker spectrum was obtained from thioanisole. The ring proton structure arises essentially from a quartet of triplets with the triplet splitting half that of the quartet. Similar spectra were obtained from

† E.s.r. studies involving phenoxymethyl radicals are also described by R. O. C. Norman and R. J. Pritchett, *J. Chem. Soc. (B)*, 1967, 926; E. J. Baum and R. O. C. Norman, *J. Chem. Soc. (B)*, 1968, 227.

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[15] S. W. Bennett, C. Eaborn, A. Hudson, H. A. Hussain, and R. A. Jackson, *J. Organometallic Chem.*, 1969, **16**, P36.
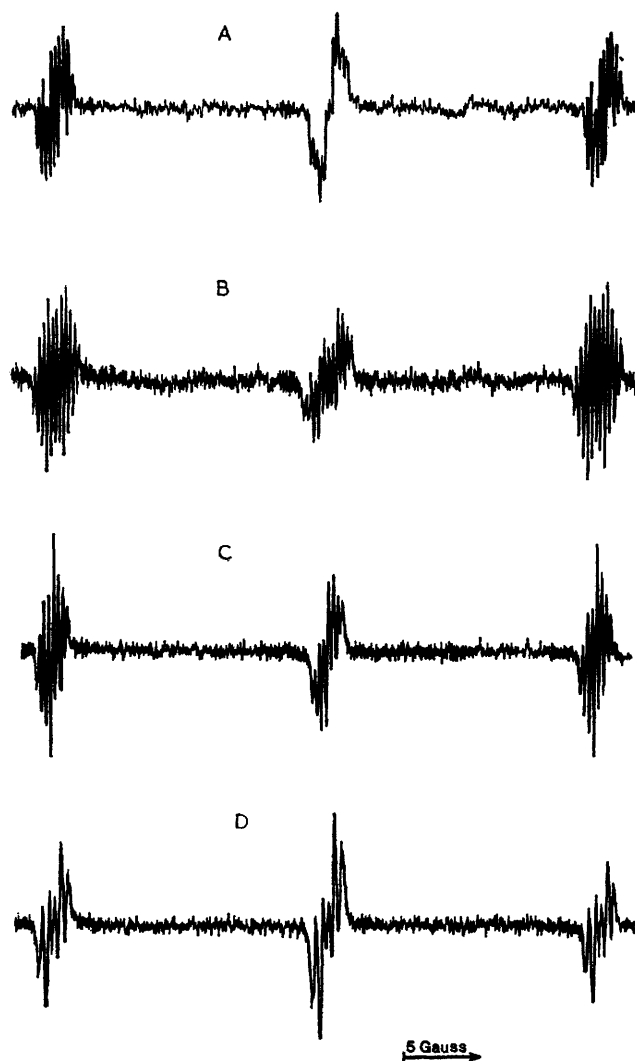[16] A. Hudson and H. A. Hussain, *Mol. Phys.*, 1969, **16**, 199.

FIGURE 1 The e.s.r. spectra of the radicals A, phenoxymethyl; B, *p*-fluorophenoxymethyl; C, *p*-bromophenoxymethyl; and D, *o*-bromophenoxymethyl
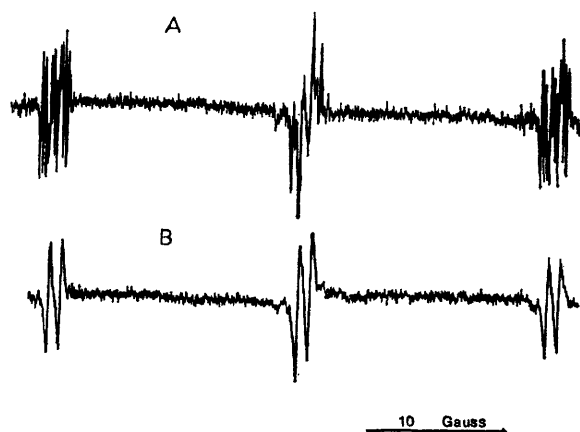

FIGURE 2 The e.s.r. spectra of the radicals A, *m*-fluoro-phenoxymethyl and B, 3-methoxy-4,6-dibromophenoxymethyl

p-chloro-, *p*-bromo-, and *p*-methoxy-anisole (Figure 1, C) and in each case the ring proton structure consisted of a triplet of triplets, the magnitude of the splittings being very similar to those observed in the unsubstituted phenoxymethyl radical, and confirms the assignment of a splitting of *ca.* 0·5 G to the *para*-proton. The *p*-fluoro-phenoxymethyl radical (Figure 1, B) also has similar proton coupling constants and a doublet of 1·14 G from the ^{19}F nucleus. This is in accord with previous work on fluorine-containing aromatic radicals: [17] proton splittings are often little changed on fluorine substitution

FIGURE 3 The e.s.r. spectrum of the pentafluorophenoxy-methyl radical

and the fluorine splittings are about 2—2·5 times those of a proton in the same position. We assign the larger of the two remaining splittings to the *ortho*-protons. This is consistent with the results on *ortho*- and *meta*-sub-stituted phenoxymethyl radicals to be discussed later and also with molecular orbital calculations on PhO·CH$_2$· by use of McLachlan's approximate SCF procedure.[18] With $\alpha_0 = \alpha + 1\cdot6\beta$ and $\beta_{CO} = 1\cdot3\beta$ the calculations predict $a(ortho) > a(meta)$ and a negative spin density in the *meta*-position.

All radicals discussed so far exhibit line-width altern-ation at $-35°$: the central group of lines of the 1 : 2 : 1 triplet from the methylene protons is broader than the outer ones (Figure 1, A, B, and C). This departure from the expected intensity ratio is similar to effects found in the related radicals ·CH$_2$OMe[11] and ·CH$_2$OH[19] and can be associated with a restricted rotation about the CH$_2$–O bond. Before discussing the spectra ob-tained from *ortho*- and *meta*-substituted radicals it is helpful to consider the conformational properties of phenoxymethyl radicals in more detail.
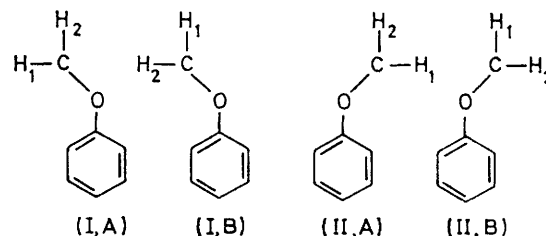

FIGURE 4 Modes of internal motion of phenoxymethyl radicals

The radicals ArOCH$_2$· have two modes of internal motion as shown in Figure 4. First, rotation about the

[17] A. Carrington, A. Hudson, and H. C. Longuet-Higgins, *Mol. Phys.*, 1965, **9**, 377.
[18] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.
[19] A. Hudson, *J. Chem. Soc. (A)*, 1969, 2513.

·CH$_2$–O bond interchanges the positions of protons H(1) and H(2). These two positions are not related by a plane of symmetry and there is now substantial evidence to suggest that they will have different coupling constants. In particular the internal rotation in the radicals ·CH$_2$OH [19] and ·CH$_2$·OCH$_3$ [11] has been ' frozen out ' at low temperatures to give doublet splittings for H(1) and H(2) differing by about 1 G.

The second internal rotation is about the Ar–O bond. This motion interchanges the coupling constants of the two *ortho*-, and also the two *meta*-protons. Alternating line-widths due to this type of motion have been observed in many radicals including the *p*-dimethoxy-benzene cation.[20] In species such as the benzaldehyde radical anion the motion is restricted even at room temperature and the five ring protons all have different coupling constants.[21] In the radicals studied here there is no evidence for line-width alternation in the ring proton hyperfine structure at the temperature of our experiments although the small hyperfine splittings and only partially resolved lines make it difficult to detect small changes in line-widths. However the influence of ring substituents on the motion about the Ar–O bond is important in what follows.

The spectrum of the radical from *o*-bromoanisole is shown in Figure 1, D. An essentially identical although weaker spectrum was obtained from *o*-chloroanisole. Clearly in these radicals there is a definite redistribution of spin density whereas in the *para*-substituted species the ring coupling constants are relatively insensitive to the nature of the substituent. This is most easily understood in terms of a restricted rotation about the O–Ar bond such that structure (III) is preferred to structure (IV). In support of this we note that only one conformer is observed in the e.s.r. spectrum of the *o*-fluorobenzaldehyde radical anion, whereas two overlapping spectra are observed with the *m*-fluoro-compound.[22] Similarly the radical cation of 2,5-dimethyl-quinol exists in a single form.[23]

We have also recorded the spectrum of the 3-methoxy-4,6-dibromophenoxymethyl radical (V) (Figure 2, B).

(III)   (IV)   (V)
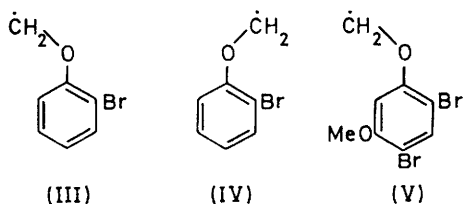
A single doublet splitting of 0·86 G was resolved and from the line-width we can place an upper limit on a second doublet splitting of 0·15 G. We assign the larger splitting to the *ortho*-proton and the smaller to the *meta*-proton. This seems most likely by comparison with the results on the *para*-substituted radicals and is consistent with the radicals described below. By analogy we can then assign the largest doublet in the *o*-bromo- and *o*-chloro-radicals to the *ortho*-proton and the small doublet to the *meta*-proton *trans* to the methylene group. The triplet of 0·44 G is attributed to the *para*-proton and the remaining *meta*-proton. As might be expected the *para*-proton coupling is relatively insensitive to conformational changes.

The ring hyperfine structure of the *m*-fluorophenoxy-methyl radical (Figure 2, A) and the overall width of the low-field multiplet are very similar to those of the *m*-methoxy-radical. If we assign the coupling constants to the ring protons in the same way for both radicals, then the *meta*-fluorine coupling constant must be less than the line-width of 0·15 G. We shall return to this point later.

The reaction of t-butoxyl radicals with pentafluoro-anisole gives the well resolved spectrum shown in Figure 3. The small doublet splitting of 0·52 G is presumably from the *para*-fluorine and we assign the triplet of 4·45 G to the *ortho*-positions. As in the *m*-fluoro-radical the remaining splitting is less than the line-width. The methylene proton coupling of 19·16 G is significantly larger than in any of the other radicals and the *para*-fluorine splitting is only half that of the *p*-fluorophenoxymethyl radical. The *ortho*-fluorine coupling constant is much larger than would be predicted from the *ortho*-proton splittings in the other radicals.

We believe the most probable explanation for these observations is that the steric interaction of the two *ortho*-fluorine atoms forces the methylene group out of the plane of the benzene ring. Similar interactions have been postulated to explain the unusually large ^{14}N splitting in the alkoxynitroxide radical formed on irradiation of pentafluoronitrobenzene in tetrahydro-furan.[17] The result will be decreased conjugation with the ring, thus explaining the low *para*-fluorine splitting, and an increase in the spin density on the methylene group. Moreover the π-orbital of the latter will be perpendicular to the aromatic π-orbitals and in a favourable position for a direct interaction with the *ortho*-fluorine atoms. This will give a positive contribution to the fluorine splitting in addition to the contribution from spin density in the ring which is also probably positive. The *ortho*-splitting is thus enhanced. However if, as molecular orbital calculations suggest, the spin density at the *meta*-positions is negative, the two possible contributions to the *meta*-fluorine coupling constant will be of opposite sign.

Long-range coupling to fluorine [24-26] is expected to be

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[22] A. Hudson and J. W. E. Lewis, to be published.

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[24] J. L. Gerlock and E. G. Janzen, *J. Phys. Chem.*, 1968, **72**, 1832.

[25] R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, 1967, **71**, 14.

[26] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (B), 1967, 981.

more important than for protons since a $2s$ electron in a fluorine atom is predicted to have a coupling constant of 17,200 G. Only a small amount of spin density is, therefore, required to account for the observed splittings. Although this explanation is satisfactory for the *ortho*-positions in it less convincing in the *meta* case. In particular it does not account for the low ^{19}F splitting in the *m*-fluoro-radical where steric interactions are expected to be small.

Another effect which might affect the coupling constants arises from the difference between the reduced moments of inertia [27] about the Ar–O bond of the *cis*- and *trans*-isomers of the *m*-fluoro-radical. This is because the Ar–O bond is not a principal axis of the inertial tensor. In the absence of steric interactions, the potential function for the internal rotation probably consists of two nearly identical valleys. However the energy levels in the two wells are not the same because the two rotamers have different reduced moments of inertia. This type of effect is well known in the study by i.r. spectroscopy of torsional frequencies in molecules such as *m*-fluorophenol [28] and *m*-fluorobenzaldehyde.[29] As a result the *cis*- and *trans*-rotamers are not necessarily present in equal amounts at equilibrium. Free-energy differences between rotamers can also be investigated by e.s.r.: the *cis*- and *trans*-forms of the *m*-fluorobenz-aldehyde ketyl exist in unequal amounts at room temperature as do the isomeric forms of the ketyls of thiophen-2-carbaldehyde and 2-acetylthiophen [22] although, in the last two examples, steric interactions are probably important. In the present case the re-distribution of spin from this mechanism appears to be rather small since the proton coupling constants are similar to those of the unsubstituted species. It seems unlikely therefore that the small ^{19}F splitting is simply attributable to a low spin density on the adjacent carbon atom although this occurs at one of the *meta*-positions in the *ortho*-substituted radicals.

Most attempts to interpret ^{19}F splittings in aromatic radicals in terms of π-electron spin densities [17,30,31] have used the two term equation (1), although three-

$$a_{\mathrm{F}} = Q^{\mathrm{F}}_{\mathrm{CC}}\rho_{\mathrm{C}} + Q^{\mathrm{F}}_{\mathrm{FF}}\rho_{\mathrm{F}} \qquad (1)$$

term equations have also been suggested,[32,33] It has frequently been assumed that, by analogy with the theory of proton coupling constants, the first term which accounts for spin polarisation of the C–F σ bonding electrons by the π-electron spin density on carbon, is negative. As the second term which allows for the direct effects of π-electron density on fluorine, is positive, the observed splitting arises as the difference between

two terms of opposite sign. A low coupling constant could occur if the two contributions accidentally cancel. However two recent investigations have assigned positive signs to $Q^{\mathrm{F}}_{\mathrm{CC}}$.[34,35] If this is the case, then no cancellation can occur unless ρ_{C} and ρ_{F} are of opposite sign which seems improbable. We suggest that these difficulties arise because the extremely large coupling constant [36] of a single fluorine $2s$ electron makes $Q^{\mathrm{F}}_{\mathrm{CC}}$ sensitive to small changes in the hybridisation of the C–F bond.

Clearly a number of uncertainties still exist in the theory of ^{19}F hyperfine coupling constants. We conclude this somewhat speculative discussion by noting that our observation of a low splitting from a *meta*-fluorine is not unprecedented. In their n.m.r. studies of the contact shifts of *o*-, *m*-, and *p*-fluorophenyl-aminotroponeimineate nickel complexes Eaton and his co-workers [31] found that, whereas the *ortho*- and *para*-compounds gave couplings roughly twice those of protons in the same positions, in the *meta*-compound the ^{19}F coupling was much smaller than that of proton.

The line-width alternation which we have already discussed for the *para*-substituted radicals is much less marked in the remaining species at the same temperature (Figures 1, D and 2 and 3). This implies that the barrier to rotation about the CH$_2$–O bond is lower in the unsymmetrically substituted radicals than in the symmetrical ones. This is to be expected if, as we have suggested, *ortho*- and *meta*-substitution makes out of plane conformations of the methylene group more favourable.

With the exception of pentafluorophenoxymethyl, the methylene proton coupling constants of the ether radicals in Table 1 show only small variations. There is, however, a significant reduction on going from anisole to thioanisole, accompanied by an increase in the ring proton splittings. To gain further insight into this variation we have also investigated the radicals from phenetole and thiophenetole. The spectrum from phenetole consists of a quartet (22·37 G) of doublets (14·21 G) and is attributed to the 1-phenoxyethyl radical. The splitting from the ring protons is slightly smaller than in the phenoxymethyl radical. A similar spectrum was obtained from thiophenetole but the signal was too weak for us to resolve the ring hyperfine structure. However, the low-field multiplet was broader than that of the 1-phenoxyethyl radical indicating a larger de-localisation on to the ring in agreement with the results from anisole and thioanisole. The low reactivity of thioethers towards t-butoxyl radicals is also found in chemical investigations.[26]

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[31] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, 1962, **5**, 407.

[32] A. Hinchliffe and J. N. Murrell, *Mol. Phys.*, 1968, **14**, 147.
[33] P. V. Schastnev and G. M. Zhidomirov, *J. Struct. Chem.*, 1964, **5**, 778; 1967, **8**, 127.
[34] J. Sinclair and D. Kivelson, *J. Amer. Chem. Soc.*, 1968, **90**, 5074.
[35] W. G. Esperen and R. W. Kreilick, *Mol. Phys.*, 1969, **16**, 577.
[36] D. H. Whiffen, ref. 28, p. 137.

It is possible to correlate the effects of substituents on the spin distribution in alkyl radicals by use of a method suggested by Fischer.[37] He introduces a parameter $\Delta(X_i)$ for each substituent X_i and writes (2) for the spin density, ρ_α, on the radical carbon atom.

$$\rho_\alpha = \Pi_i [1 - \Delta(X_i)] \qquad (2)$$

If one of the substituents is methyl for which $\Delta(Me) = 0.081$, ρ_α can be determined from the methyl proton splitting and (3) with $Q_H^{Me} = 29.30$ G. Values of

$$a_H^{Me} = Q_H^{Me} \rho_\alpha \qquad (3)$$

$\Delta(OPh)$ and $\Delta(SPh)$ calculated from our results are given in Table 2, together with values [37,38] for Me, OH and OEt. The Fischer treatment is not strictly valid for strongly perturbing substituents but is still useful for showing trends in a series of related radicals. It is

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[38] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.
[39] R. W. Fessenden, *J. Phys. Chem.*, 1967, **71**, 74.

TABLE 2

$\Delta(X)$ values for MeCHX· radicals

X	a^{Me}	$\Delta(X)$	Ref.
Me	24·68	0·081	38
OH	22·61	0·160	37
OEt	22·28	0·172	37
OPh	22·37	0·169	*
SPh	20·76	0·229	*

* This work.

noteworthy that the α-proton coupling constants in the two ethyl radicals show an opposite trend to the methyl splittings. We believe that the oxygen-containing radical is less planar than its sulphur analogue and thus has a smaller α-proton coupling [39] in spite of a larger spin density on the radical carbon. The ^{13}C splitting of ·CH_2OH (47·6 G) suggests that it is slightly non-planar.[39] The very similar electronegativities of carbon and sulphur support the idea of a more nearly planar structure for the thio-radical.