Electron Spin Resonance Study of Halogenated Aromatic Cation-radicals

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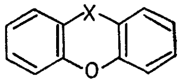
Hyperfine splitting constants, McLachlan spin densities, and experimental line-width parameters are reported for some fluorinated dibenzo-*p*-dioxin and phenoxathiin cation-radicals. The main differences between the spectra of the heterocycles are assigned to the influence of the heteroatoms.

E.S.R. studies on aromatic ions are usually concerned with the relationship between the experimental splitting constants and the spin density distribution. Additional information on the spin density pattern may be provided by the study of line-width effects. The e.s.r. spectra of the fluorinated dibenzo-*p*-dioxin (1) and phenoxathiin (2) cation-radicals are suitable for such analysis, the line-width parameters and hyperfine splitting constants outlining differences in the electronic structure of the heterocycles.



(1) X = O

(2) X = S

RESULTS AND DISCUSSION

Fluorine Compounds.—Hyperfine splittings. The spectra of 2,7-difluorodibenzo-*p*-dioxin and 2,8-difluorophenoxathiin cation-radicals were interpreted in terms of the coupling of two pairs of equivalent nuclei with $I = 1/2$ (Table 1). The fluorine splittings were assigned on the expectation of larger line widths from ^{19}F than from proton splittings.

The ratio of fluorine and proton splitting at the same site in the unsubstituted ion ($a_F : a_H$) exceeds the experimental value found in most e.s.r. studies on fluorine radicals (2·0—2·7),[1-4] the largest departure being obtained for the 2,7-difluorophenoxathiin ion. As the $a_F : a_H$ ratios reported by Thomson and MacCullock [5] in their study on fluoronaphthalene cation-radicals were also greater than 2·0—2·7, we assume that such higher values are characteristic for fluorinated aromatic cations.

TABLE 1

Hyperfine splitting constants (G) of unsubstituted and substituted radicals

Ion-radical	a_2	a_3	a_7	a_8	$a_F : a_H$	g
Dibenzo-*p*-dioxin	2·12	2·12	2·12	2·12		2·0035
2,7-Difluorodibenzo-*p*-dioxin	6·50	2·45	2·45	6·50	3·07	2·0042
Phenoxathiin	1·04	2·08	2·08	1·04		2·0061
2,8-Difluoro-phenoxathiin	4·15	2·07	2·07	4·15	3·99	2·0064

The spectrum of 2,7-difluorodibenzo-*p*-dioxin ion is better resolved in sulphuric acid and a further splitting of 0·2 G can be observed on the central triplet corresponding to $M_F = 0$. This splitting can be ascribed either to the 1,6- or to the 4,9-protons.

The *g* factors of the substituted and unsubstituted ions are also collected in Table 1. The main effect is provided by the replacement of sulphur by oxygen rather than by fluoro-substitution in agreement with the larger spin–orbital coupling constant of sulphur than oxygen.

Line-width effects. The e.s.r. spectra of the fluorinated ions in sulphuric acid at room temperature present a remarkable line-width effect, the experimental intensities

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differing from the theoretical values (Figures 1 and 2). In the spectrum of 2,8-difluorophenoxathiin ion, the effect is observed mainly for the high field lines, whereas for the 2,7-difluorodibenzo-*p*-dioxin ion, the intensities on both sides of the spectrum are altered. By increasing the temperature to 70 or 85°, the spectra became more symmetrical, the diminution of the line-width effect being determined by the large decrease in solvent viscosity in this temperature range. Such line broadening arising from an electron–nucleus anisotropic magnetic interaction has been reported previously for other fluorinated radicals, but owing to the high viscosity of the solvent the effect is greatly enhanced.[6-10]

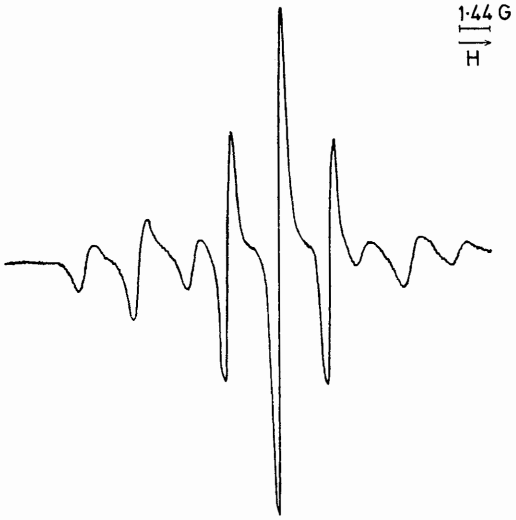

FIGURE 1 E.s.r. spectrum of the 2,7-difluorodibenzo-*p*-dioxin ion in sulphuric acid at 35°: theoretical intensities, 1 : 2 : 1 : 2 : (4) : 2 : 1 : 2 : 1; experimental intensities, 0·4 : 0·8 : 0·4 : 2 : (4) : 2 : 0·2 : 0·4 : 0·2

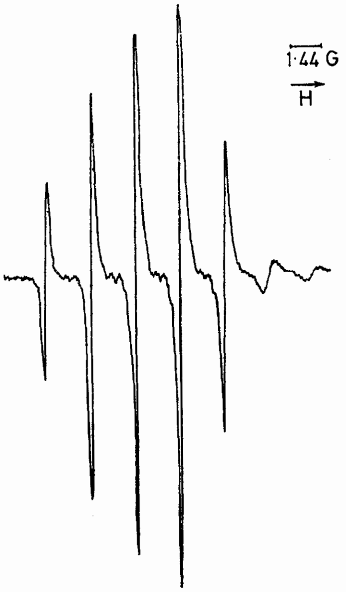

FIGURE 2 E.s.r. spectrum of the 2,8-difluorophenoxathiin ion in sulphuric acid at 35°: theoretical intensities, 1 : 2 : 3 : (4) : 3 : 2 : 1; experimental intensities, 1·3 : 2·6 : 3·5 : (4) : 2 : 0·23 : 0·1

In terms of the Freed–Fraenkel theory on line widths in e.s.r. spectra,[11,12] the width of a fluorine line can be determined by equation (1) where $\tilde{M}_{\mathrm{F}}$ is the spectral index number, A is the line-width of the central line

$$T_{2\mathrm{F}}^{-1} = A + B\tilde{M}_{\mathrm{F}} + C\tilde{M}_{\mathrm{F}}^{2} \qquad (1)$$

($M_{\mathrm{F}} = 0$), chosen as reference, and B and C are correlated with the spectral densities $j_i^{(\mathrm{DG})}$ and $j_{ij}^{(\mathrm{D})}$. While the theoretical expression for B is similar for both ions, the expression for C is different, as the fluorine atoms are completely equivalent in 2,7-difluorodibenzo-*p*-dioxin [equations (2)] and only equivalent in the 2,8-difluorophenoxathiin ion [equations (3)]. $j_{\mathrm{F}}^{(\mathrm{DG})}(0)$, The spectral density for the cross-term between the dipolar and

$$B_{\mathrm{F}} = 16 j_{\mathrm{F}}^{(\mathrm{DG})}(0) B_0/3 \qquad C_{\mathrm{F}} = 8 j_{\mathrm{FF}}^{(\mathrm{D})}(0) \qquad (2)$$

$$B_{\mathrm{F}} = 16 j_{\mathrm{F}}^{(\mathrm{DG})}(0) B_0/3 \qquad C_{\mathrm{F}} = 8 j_{\mathrm{FF'}}^{(\mathrm{D})}(0) \qquad (3)$$

g tensor interaction is given by relation (4) in which $g^{(0)} = 1/\sqrt{6}[2g_3 - (g_1 + g_2)]$, $g^{(2)} = 1/2(g_1 - g_2)$, and

$$j_{\mathrm{F}}^{(\mathrm{DG})} = \frac{\tau_{\mathrm{R}}}{1 + \omega^2\tau_{\mathrm{R}}^2}\,\frac{\pi|\beta_{\mathrm{e}}|}{5\hbar}\,\zeta_{\mathrm{F}}[D_{\mathrm{F}}^{(0)}g^{(0)} + (D_{\mathrm{F}}^{(2)} + D_{\mathrm{F}}^{(-2)})g^{(2)}] \qquad (4)$$

g_1, g_2, and g_3 are the anisotropic components of the g-tensor; D represents the dipolar coefficients and can be calculated from information about the geometry of the molecule and the spin density distribution, $\zeta_{\mathrm{F}} = |\gamma_{\mathrm{e}}||\gamma_{\mathrm{F}}|\hbar/2\pi$; and τ is the rotational correlation time. $j_{\mathrm{FF}}^{(\mathrm{D})}(0)$ Is a purely dipolar term which depends on the spin density distribution and mainly on the 'local' spin density [equation (5)]. The other quantities included in relation (5) have the same significance as before.

$$j_{\mathrm{FF}}^{(\mathrm{DG})}(0) = \frac{\tau_{\mathrm{R}}}{1 + \omega^2\tau_{\mathrm{R}}^2}\,\frac{4\pi^2}{5}\,\zeta_{\mathrm{F}}\zeta_{\mathrm{F}},\sum_{m=-2}^{m=2} D_{\mathrm{F}}^{(m)} \,.\, D_{\mathrm{F}}^{(-m)} \qquad (5)$$

To obtain A, B, and C we followed the method of Freed and Fraenkel, defining a relative width parameter W_i, for the ith hyperfine line with respect to the central line. In terms of the relative width parameters, the line-width expression (1) can be rewritten as (6) where equations (7) and (8) apply. The new coefficients B' and

$$W_{\mathrm{F}} = 1 + B'\tilde{M}_{\mathrm{F}} + C'\tilde{M}_{\mathrm{F}}^2 \qquad (6)$$

$$B' = \frac{B}{A} = \frac{B}{\frac{\sqrt{3}}{2}|\gamma_{\mathrm{e}}|\delta_{\mathrm{ref}}} \qquad (7)$$

$$C' = \frac{C}{A} = \frac{C}{\frac{\sqrt{3}}{2}|\gamma_{\mathrm{e}}|\delta_{\mathrm{ref}}} \qquad (8)$$

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C' were estimated by fitting relation (6) to the experimental relative widths by the least-squares method.

TABLE 2

Line-width parameters (s^{-1}) for the difluoro-substituted cation-radicals

Ion-radical	10^6A	$10^6B'$	$10^6C'$	10^6B	10^6C
2,7-Difluorodibenzo-*p*-dioxiin	5·795	0·278	0·895	1·611	5·505
2,8-Difluorophenoxathiin	1·677	0·925	0·773	1·549	1·295

The results obtained from six different scans for each spectrum are presented in Table 2. It may be seen that while the B values are not too different, the C value in the dibenzo-*p*-dioxin derivative is *ca.* 4 times that for 2,8-difluorophenoxathiin. Neglecting, as usual, the nonlocal contributions to the $D_F^{(0)}$ components and assuming the same rotational correlation time, this difference between the spectral densities $j_{FF}^{(D)}$ and $j_{FF'}^{(D)}$ results from larger spin density on the fluorine atom in the first ion [equation (9)].

$$\frac{C^{(1)}}{C^{(2)}} = \frac{j_{FF}^{(D)}}{j_{FF'}^{(D)}} = \left[\frac{\rho_F^{(1)}}{\rho_F^{(2)}}\right] \qquad (9)\dagger$$

TABLE 3

Splitting constants calculated from Hückel and McLachlan spin densities

$a_H = |27|\rho\pi_c$ (i) $a_F = 93{\cdot}1\rho\pi_c$ (ii)* $a_F = 63{\cdot}3\rho\pi_c + 298{\cdot}9\rho\pi_F$ (iii)*

		a_H (G)			a_F (G)				
Ion-radical	h_F	Hückel (i)	McLachlan (i)	Exp.	Hückel (ii)	McLachlan (ii)	Hückel (iii)	McLachlan (iii)	Exp.
2,7-Difluorodibenzo-*p*-dioxin	1·8	2·01	2·26		6·19	6·62	9·75	8·18	
	2·0	1·98	2·21	2·45	6·21	6·62	8·45	7·28	6·50
	2·2	1·96	2·17		6·21	6·61	7·54	6·67	
2,8-Difluorophenoxathiin	1·8	1·95	2·28		4·99	3·65	7·54	3·79	
	2·0	1·93	2·25	2·07	4·93	3·47	6·48	3·31	4·15
	2·2	1·92	2·23		4·87	3·32	5·75	2·95	

* The larger broadening of the high field lines is considered as evidence for the positive sign of a_F.

An empirical estimation of the fluorine spin density ratio in both ions, using the C values from Table 2, leads to relation (10) that is, the fluorine spin density in the

$$\rho_F^{(1)}/\rho_F^{(2)} \simeq 2 \qquad (10)$$

2,7-difluorodibenzo-*p*-dioxin ion is twice that in 2,8-difluorophenoxathiin.

The similar values for B may be explained by high g factor anisotropy in the sulphur-containing radicals,[13] which compensates for the low value of the D coefficient for 2,8-difluorophenoxathiin, the reverse being true for the other ion.

The line-width parameters indicate that the main contribution to line broadening in the dibenzo-*p*-dioxin derivative is provided by pure anisotropic dipolar interactions, as a consequence of greater delocalisation of the unpaired electron on the fluorine atoms; for the difluorophenoxathiin ion g tensor anisotropic effects predominate. This is supported by the occurence of a similar but smaller effect in the unsubstituted phenoxathiin ion,[14] whereas for dibenzo-*p*-dioxin line broadening is apparent only upon substitution.

Spin densities. Hückel and McLachlan spin densities were calculated for both ions using the oxygen and sulphur parameters for the unsubstituted ions,[15] and fluorine parameters in the range h_F 1·5—2·2 and k_F 0·7. The choice of the best parameters was difficult as the proton splittings generally used for this purpose were insensitive to h_F values (Table 3). Secondly, the relationship between the fluorine hyperfine splitting and the spin densities is still unclear. Besides a McConnell type formula, more general relationships have also been suggested, implying a large range of σ–π polarisation parameters.[16-19] In our case we chose the formulae and Q values given by Thomson and MacCullock,[5] as their paper provides the only extensive study on fluorine cation-radicals.

In spite of the real objections to a McConnell type relation (the variable value of the $\rho_F : \rho_c$ ratio) the results are excellent for the difluorodibenzo-*p*-dioxin ion, and satisfactory for the difluorophenoxathiin ion. By using the two parameter formula it was not possible to obtain a_F values matching the experimental data when employing the same h_F for both ions. For difluorodibenzo-*p*-dioxin the best value is h_F 2·2 whereas for the phenoxathiin derivative the results diverge. The Hückel approach requires a higher value and the McLachlan method a smaller one.

If we consider for each ion the fluorine parameter which leads to the best agreement with the experimental splittings (h_F 2·2 for 2,7-difluorodibenzo-*p*-dioxin and h_F 1·8 for 2,8-difluorophenoxathiin), the ratio of the fluorine spin densities is 1·7, close to the value obtained from line-width analysis in spite of the rough approximations made. Perhaps a more refined calibration of parameters will improve the results, but as long as the

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† $C^{(1)}$ and $C^{(2)}$ are the C coefficients for 2,7-difluorodibenzo-*p*-dioxin and 2,8-difluorophenoxathiin respectively.

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spin polarisation parameters are uncertain, this seems unnecessary.

Chlorine Compounds.—The spectrum of 2,7-dichlorodibenzo-*p*-dioxin ion consists of three lines only, similar to the spectra previously reported for dichloro-derivatives of thianthren and phenoxathiin.[20,21] The experimental hyperfine splitting of 2·59 G was assigned to unsubstituted positions of high spin density, *i.e.* positions 3 and 8. The 2-chlorophenoxathiin ion in sulphuric acid gave a spectrum with broad lines, assigned the coupling constants a_1 2·04 and a_2 1·30 G. In perchloric acid better resolution was reached, but the spectrum could not be interpreted with certainty.

EXPERIMENTAL

The positive ions of 2,7-difluoro- and 2,7-dichloro-dibenzo-*p*-dioxin and 2-chloro- and 2,8-difluoro-phenoxathiin were prepared by three methods: dissolving the neutral compounds in sulphuric acid (*d* 1·84) and adding a drop of H_2O_2 for the dibenzo-*p*-dioxin derivatives, oxidation with $SbCl_5$ in CH_3NO_2 in an inert atmosphere, and oxidation with $K_3[Fe(CN)_6]$ in $HClO_4$.

E.s.r. spectra were taken with a JES 3 B spectrograph in the X band, using a variable temperature cavity. The best resolution for the spectra in $SbCl_5$–CH_3NO_2 was obtained at −40° and line-width observations in sulphuric acid solution were taken at 35—85°. For 2,7-difluorodibenzo-*p*-dioxin the upper limit was 70° as at higher temperature the radical concentration decays. The 2,7-dichlorodibenzo-*p*-dioxin ion was not stable in $HClO_4$–$K_4[(Fe(CN)_6]$ and therefore was obtained only by the first two methods.

The *g* factors were measured in H_2SO_4 using peroxyaminodisulphonate (*g* 2·0056) as the standard.

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