Electron Spin Resonance Spectrum of the Xanthen Radical Anion

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The radical anions of xanthen and several of its derivatives have been prepared by the action of potassium on a solution of the parent compound in dimethoxyethane at −70°. The e.s.r. spectra of these species are reported and compared with the results of MO calculations. It is suggested that the xanthen radical anion is not symmetrical but that the electron is localised on one of the benzene rings and jumps rapidly between the two sites. The radicals decompose at higher temperatures to yield other radicals some of which have been identified.

THE e.s.r. spectra of radical anions of diaryl ethers other than dibenzofuran[1] have not hitherto been reported even though the spectra of the alkoxybenzenes were observed some years ago.[2,3] All attempts at observing the radical anion of diphenyl ether have yielded the spectrum of the biphenyl radical anion.[4] This is so stable that its spectrum tends to mask that of any other species present. The radical anion of xanthen, however, where scission of the carbon oxygen bond does not yield two separate fragments, seemed unlikely to yield decomposition products having more stable radical anions.

We report here the preparation and e.s.r. spectrum of the radical anion of xanthen and some of its derivatives

xanthen was prepared by reduction of the corresponding xanthhydrol[7] while 9-methyl-9-phenylxanthen resulted from the action of methylmagnesium iodide on 9-phenyl-xanthylium perchlorate, m.p. 104—105° (from ethanol). We thank Professor G. Ourisson for a gift of 3,6-dimethyl-xanthen.

RESULTS AND DISCUSSION

(a) *Xanthen Radical Anions.*—The desired radical anions could only be obtained if the reactions were carried out below −70°. This is in agreement with a previously reported failure to obtain it by electrolytic reduction in dimethylformamide at −40°.[8]

Figure 1 shows the spectrum and Table 1 lists the

TABLE 1

Coupling constants (mT) of xanthene radical anion and several of its derivatives
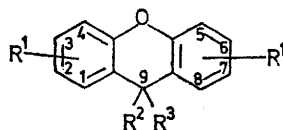
Radical anion	$a_{1,8}$	$a_{2,7}$	$a_{3,6}$	$a_{4,5}$	a_{R_2}	a_{R_3}	a_{R^1}
Xanthen	0.325	<0.01	0.197	0.384	1.280	1.280	
3,6-Dimethylxanthen	0.305	<0.015		0.380	1.010	1.010	0.200
9-Methylxanthen	0.316	<0.015	0.214	0.377	1.015	0.035	
9-Deuteriomethylxanthen	0.316	<0.015	0.214	0.377	1.015		
9-Phenylxanthen *	0.256	<0.01	0.187	0.325	1.230	0.040 0.045	
9-Deuteriophenylxanthen	0.256	<0.01	0.187	0.325	1.230		
2,7-Dimethyl-9-phenylxanthen *	0.266	<0.013	0.177	0.310	1.220	0.080 0.037	<0.01
MO calculations about xanthen	0.28	0.07	0.25	0.37	2.96	2.96	

* The coupling constants a_{R_3} are referred to phenyl group; the first value corresponds to coupling with the two protons, in positions *ortho* or *meta*, and the second with the *para*-proton.

EXPERIMENTAL

Xanthen was a recrystallised commercial (Fluka) product. 9-methyl-[5] and 9-phenyl-xanthen[6] were prepared by published methods, the perdeuterio-methyl and -phenyl derivatives being prepared *via* the appropriately deuteriated methyl iodide or bromobenzene. 2,7-dimethyl-9-phenyl-

proton hyperfine coupling constants of the radical anion of xanthen and several of its derivatives. The assignment is based in part on the spectra of the methyl and phenyl derivatives (for the 2,7; 3,5; and 9,10 positions) and in part on the results of MO calculations,[9] shown likewise in Table 1.

Qualitatively there is excellent agreement between theory and experiment, quantitatively however there is a very noticeable disagreement for the largest coupling

[1] R. Gerdil and E. A. C. Lucken, *J. Amer. Chem. Soc.*, 1965, **87**, 213.

[2] J. K. Brown, D. R. Burnham, and N. A. J. Rogers, *Tetrahedron Letters*, 1966, **23**, 2621.

[3] J. K. Brown and D. R. Burnham, *Mol. Phys.*, 1968, **15**, 173.

[4] A. Carrington and J. dos Santos-Verga, *Mol. Phys.*, 1962, **5**, 21.

[5] J. B. Conant, L. F. Small, and W. Sloan, *J. Amer. Chem. Soc.*, 1926, **48**, 1743.

[6] D. Cram and D. Kollmeyer, *J. Amer. Chem. Soc.*, 1968, **90**, 1795.

[7] J. Reilly and P. J. Drumm, *J. Chem. Soc.*, 1930, 455.

[8] B. J. Tabner and J. R. Zdysiewicz, *J. Chem. Soc. (B)*, 1971, 1659.

[9] G. Orlandi, G. Poggi, F. Barigelletti, and A. Breccia, *J. Phys. Chem.*, 1973, **77**, 1102.

constant, the experimental coupling in the 9,10 positions being approximately half that predicted theoretically. The methylene proton coupling constants were calculated according to the method of Whiffen [10] taking into account
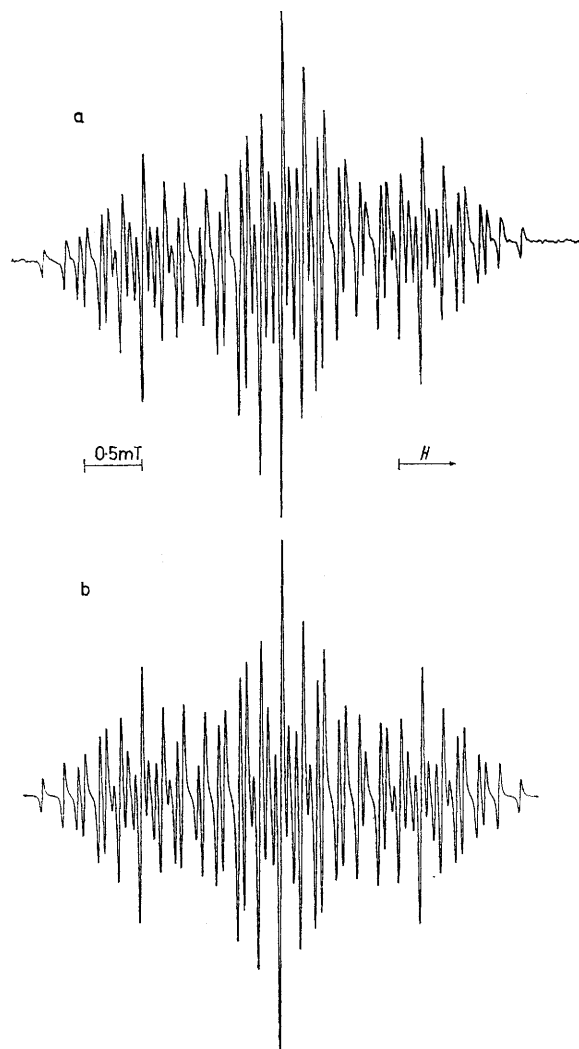

FIGURE 1 a, E.s.r. spectrum of the xanthen radical anion; b, computer simulation based on the coupling constants given in Table 1

their well established angular dependance [11] and the fact that the xanthen radical anion is probably non-planar and inverting rapidly between two equivalent conformations. Whiffen's method indicates that where a C–H fragment is attached to more than one point of a conjugated π-radical the coupling constant is proportional to $(\sum_i c_i)^2$ where c_i are the coefficients of the π-atomic orbitals of the carbon atoms directly linked to the C–H fragment in the singly occupied molecular orbital. If these coefficients are the same in sign and magnitude, as in the present instance, this implies that $a_{CH_2} = Q4c_i^2$. The constant of proportionality, Q, varies with the dihedral angle, θ, between the axis of the neighbouring π-orbital

and the CH bond of the methylene group according to relationship (1) where A is usually taken as 5.8 mT and B

$$Q = A \cos^2\theta + B \qquad (1)$$

is small, $ca.$ 0.3 mT or even zero. If it is assumed that the methylene group retains a regular tetrahedral geometry then the dihedral angles of the two CH groups differ by 120°. If the molecule flips between two equivalent conformations, then the average coupling constant $\bar{a}_{CH_2}$ of the methylene group is given by (2) where θ is the dihedral angle for one of the two CH bonds. In ref. 9

$$\bar{a}_{CH_2} = 4c_i^2 [A/2 + A \sin (2\theta + 30°)/2 + B] \qquad (2)$$

the methylene coupling constant was calculated assuming $\theta = 0°$ and $B = 0$. The term in parentheses then takes the value $5A/8$ and, as seen above, gives rise to a coupling constant twice that observed. On the other hand if we assume the value $c_i^2 = 0.17$, as above, we can use this formula to obtain $\theta - 37°$, $i.e.$ the axis of the neighbouring π orbital bisects the angle between the two methylene protons which have thus dihedral angles of 37 and 83° respectively. Decreasing c_i^2 to 0.15 reduces θ to $-31°$. If the methylene group is not considerably distorted from regular tetrahedral geometry, such a value implies however that the angle between the planes of the benzene rings is abnormally small.

A further difficulty arises if we consider the coupling constants in the 9-substituted derivatives. The two conformations are now no longer equivalent and a rigid structure is almost certainly maintained. As a first approximation, particularly with the methyl group, we may assume that the substituent has no effect on the electron distribution (the ring proton coupling constants indeed strongly support this) but only blocks the molecular geometry. The value of 1.0 mT observed for the remaining methylene proton then implies that the proton previously in the position of the methyl group had a coupling of 1.6 mT to yield the average observed coupling of 1.3 mT. One may then at once deduce from the ratio of the coupling constants, given by expression (3) that

$$\frac{a_{max.}}{a_{min.}} = \left[\frac{\cos \theta}{\cos(\theta + 120°)}\right]^2 \qquad (3)$$

θ has the value 18.5°. This yields a much more reasonable value of the angle between the planes of the benzene
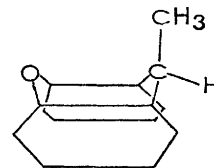

FIGURE 2 Configuration of the 9-methylxanthen radical anion

rings and indicates that the methyl group has occupied the least hindered position (Figure 2) but implies that

[10] D. H. Whiffen, *Mol. Phys.*, 1963, **6**, 223.
[11] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1962, **37**, 1327.

TABLE 2

INDO Calculations of coupling constants (mT) of xanthen and chroman radical anions. In both molecules the angle of fold about the C(9)–O axis is 28°. In the case of chroman the saturated portion of molecule is maintained in the boat configuration, and the coupling constants obtained for the ring protons are divided by two. The numbering of chroman is non-systematic in order to facilitate direct comparison with xanthen

| Radical anion	a_1	a_2	a_3	a_4	a_9	a'_9	$\dfrac{a_9 + a'_9}{2}$
Xanthen	−0.35	0.11	−0.31	−0.23	3.40	1.50	2.45
Chroman	−0.33	0.09	−0.29	−0.28	1.39	0.60	1.00
Experimental	0.384 or 0.325	0.00	0.197	0.325 or 0.384			1.280

c_i^2 is only 0.077. Even if we acknowledge some perturbation by the substituent so that one proton of the methylene group has a coupling in the range 0.7—1.3 mT and the other 1.9—1.3 mT and hence a ratio changing from 2.7 to 1.0 then θ goes from 8 to 30° and c_i^2 goes from 0.083 to 0.075. Both on the grounds of the large coupling constant of the ring protons *ortho* to the oxygen atom in the xanthen radical anion and of the large (0.536 mT) *ortho* coupling constant of the radical anion of anisole [2,3] this value seems far too small. There is in fact no reason to suppose that it differs much from the values given in Table 1.

One possible way out of the impasse would be to assume that the xanthen radical anion does not in fact have a symmetrical structure but that the electron is localised on one of the benzene rings and jumps rapidly between them. The spin densities in the unsymmetrical ion would then be approximately twice those given above and comparable with those observed in, say, the anisole radical anion [3] (a_o 0.536, a_m 0.618, a_p 0.061 mT) but whereas the jumping of the electron between the two benzene rings halves the coupling constants of the ring protons, the methylene splittings remain unchanged since the methylene group is common to both radicals. The spin density at the carbon atom carrying the methylene group in the unsymmetrical radical anion then rises to four times that calculated previously, *i.e.* 0.30 to 0.33, almost exactly twice that calculated for a symmetrical xanthen radical anion and similar to that observed in analogous positions of the anisole radical anion.

Some support for this hypothesis lies in the previously remarked rapid decomposition of the diphenyl ether radical anion presumably by the heterolysis (4). The

$$[\text{Ph-O-Ph}]^{\overline{\cdot}} \longrightarrow \text{PhO}^- + \text{Ph·} \qquad (4)$$
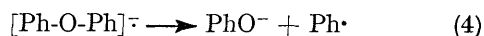
asymmetry of the radical anion may be determined by the neighbourhood of the counter ion and leaves open the

(I)
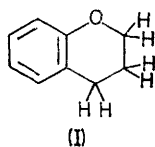
[12] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026.

possibility that the species observed in radiation damaged crystalline xanthen,[9] where the coupling of 2.72 mT is
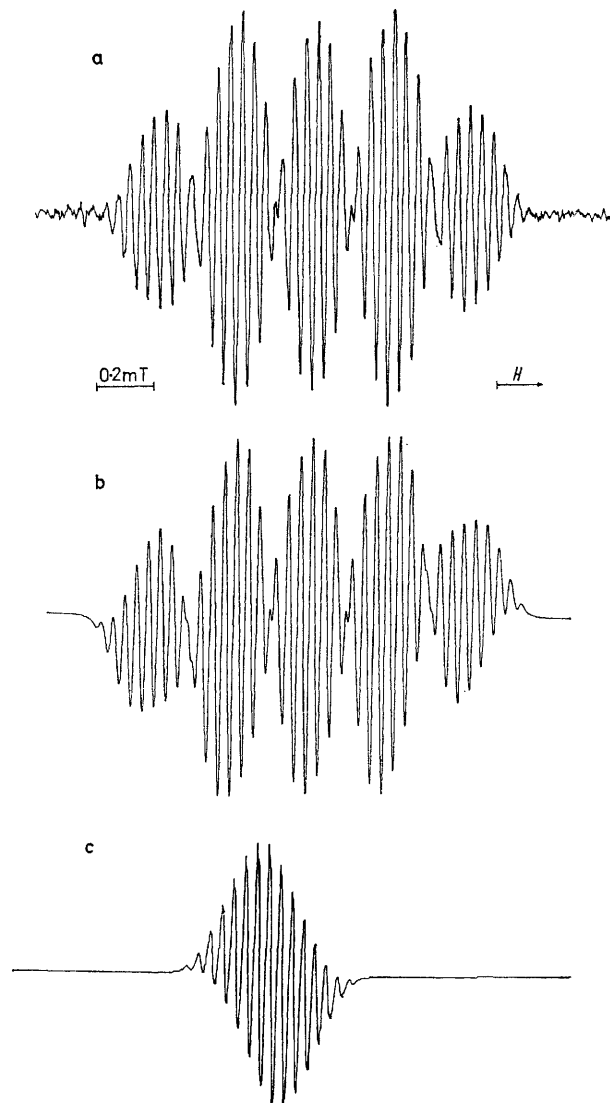

FIGURE 3 a, E.s.r. spectrum arising from the reaction of 9-pentadeuteriophenylxanthen with K at −20°; b, computer simulation of the spectrum of the 1,2,3,4,5-pentadeuteriobiphenyl radical anion; c, computer simulation of the spectrum of the perdeuteriobiphenyl radical anion

assigned to the methylene protons, is indeed the symmetrical xanthen radical anion.

Finally we have carried out INDO calculations [12] on the radical anions of xanthen and of chroman (I) where the saturated portion of the molecule is maintained in the boat conformation. In both molecules the angle of fold about the C(9)–O[C(4)–O] axis was 28°. Table 2 shows the calculated proton coupling constants, those for the ring protons in the chroman radical anion being divided by two to facilitate comparison with the xanthen species. These calculations confirm that the symmetrical xanthen radical anion has a large coupling constant for the methylene protons. The pattern and magnitudes of the ring proton couplings in the two radical anions are similar.

(b) *Decomposition Products.*—If the temperature of these solutions is allowed to rise much above −70° the
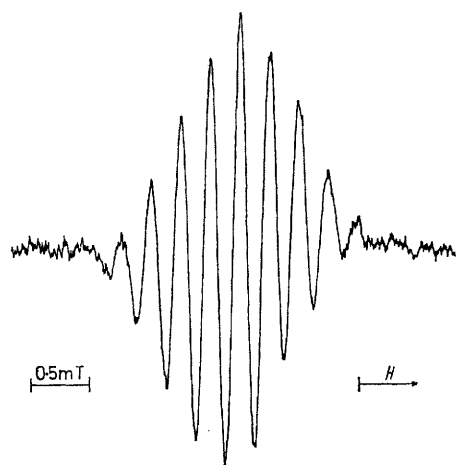

FIGURE 4   E.s.r. spectrum arising from the reaction of 2,7-dimethy-9-phenylxanthen with K at −20°

xanthen radical anions decompose and their spectra replaced by those of other species. Xanthen itself, in agreement with an earlier observation,[8] gives the xanthone radical anion; the same species is observed for 9-methylxanthen. The origin of the oxygen atom in these xanthone radical anions is by no means clear: the most likely source is the solvent but it is difficult to rule out the possibility that these very small quantities of xanthone arise from traces of adventitious alkali metal oxide.

In contrast the radical anion of 9-phenylxanthen decomposes at −20° to yield the biphenyl radical anion. The spectrum arising from the decomposition of the 9-(pentadeuteriophenyl)xanthen radical anion is shown in Figure 3 together with computer simulations of the spectrum of the radical anion of 1,2,3,4,5-pentadeuterio- and perdeuterio-biphenyl. These spectra leave no doubt that the only one of the benzene rings in the biphenyl arises from the 9-phenyl substituent, the remaining ring coming presumably from the xanthen residue. A confirmation of this is afforded by Figure 4 showing the spectrum of the decomposition product of 2,7-dimethyl-9-phenylxanthen. This spectrum is not well resolved but

[13] K. Ishizu, *Bull. Chem. Soc. Japan*, 1964, **37**, 1093.

is very similar to the equally poorly resolved spectrum of the radical anion of 3-methyldiphenyl.[13] This implies that the biphenyl is formed by attack of the phenyl
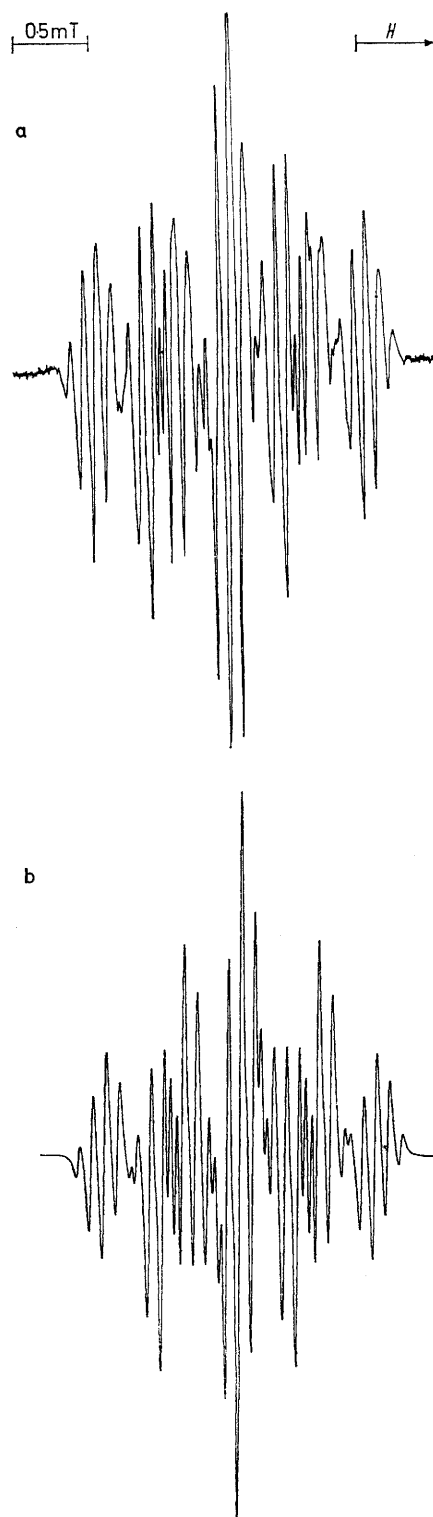

FIGURE 5   a, electron spin resonance spectrum arising from the reaction of 9-methyl-9-phenylxanthen with K at −70°; b, computer simulation based on the coupling constants given in the text

residue on the positions of the benzene rings in xanthen bearing the methylene substituent. The detailed mechanism of this reaction is however far from clear.

All attempts at observing the radical anion of 9-methyl-9-phenylxanthen have yielded the spectrum shown in Figure 5a. In Figure 5b is shown a computer simulation based on the coupling constants a_1 0.090 (4H), a_2 0.40 (2H), a_3 0.535 mT (2H). Since these values are very similar to the hyperfine coupling constants of the ring protons of the fluorene radical anion,[14] the spectrum shown in Figure 5a may be due to the 9-methyl-9-phenylfluorene radical anion.

[14] F. C. Adam and C. R. Kepford, Canad. J. Chem., 1971, 49, 3529.