Hindered Rotation in Xanthenyl-type Radicals

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The e.s.r. spectra of the 9-phenylxanthenyl, 9-phenylthioxanthenyl, and 9-phenylselenoxanthenyl radicals have been interpreted; unambiguous assignments of the hyperfine splitting constants have been made by use of a number of selectively deuteriated derivatives. Although the theoretical models used to interpret the experimental data failed to explain all the details of the spin-density distribution, they allowed certain conclusions to be drawn with respect to the stereochemistry of the molecules.

The results show that the phenyl groups do not rotate freely, but are locked at an angle of *ca.* 70—80° degrees to the heterocyclic plane.

NEUTRAL radicals containing the xanthenyl ring with a variety of substituents have been recently investigated.[1-4]

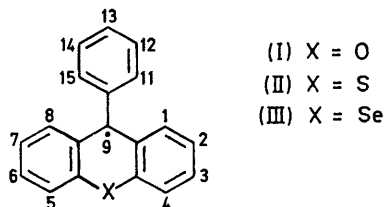The incorrect interpretation of the e.s.r. spectra of some aryl derivatives however,[1,2] prevented the observation of an unusual spin-density distribution on the phenyl ring which can give useful information on the steric hindrance experienced by the phenyl group.

[1] M. D. Sevilla and G. Vincow, *J. Phys. Chem.*, 1968, **72**, 3641.
[2] K. Maruyama, M. Yoshida, and K. Marukami, *Bull. Chem. Soc. Japan*, 1970, **43**, 152.

[3] L. Lunazzi, A. Mangini, G. Placucci, C. Vincenzi, and I. Degani, *Mol. Phys.*, 1970, **19**, 543.
[4] M. D. Sevilla and G. Vincow, *J. Phys. Chem.*, 1968, **72**, 3635, 3647.

This effect (namely the inversion in the magnitude of the *ortho-para* hyperfine splitting) has been observed in the phenylthioxanthenyl radical [3] (II); since it has been interpreted in terms of restricted rotation experienced by the phenyl group owing to the steric repulsion of

(I) X = O
(II) X = S
(III) X = Se

hydrogens 1 and 8, it should also be expected in compounds (I) and (III). In order to check this assumption we made a thorough analysis of the e.s.r. spectrum of compound (III), whose previous interpretation [2] we found incorrect, as well as that of (I) where an error in the assignment had been already suspected.[3]

A further point concerning this series of radicals is the theoretical interpretation of the spin densities in the position 1,8 and 3,6 of the heterocyclic ring. Experimental assignments [3,4] clearly indicate that a_{H3}, a_{H6} are greater than a_{H1}, a_{H8} while the MO calculations so far performed lead to the opposite conclusion. Since this discrepancy indicates that such MO calculations do not give reliable results when applied to this kind of heterocyclic ring, assignments on analogous derivatives,[5] lacking experimental support should be treated with caution.

RESULTS AND DISCUSSIONS

The e.s.r. spectrum of compound (I) has been exactly interpreted (Figure 1) on the basis of the hyperfine splittings reported in Table 1.

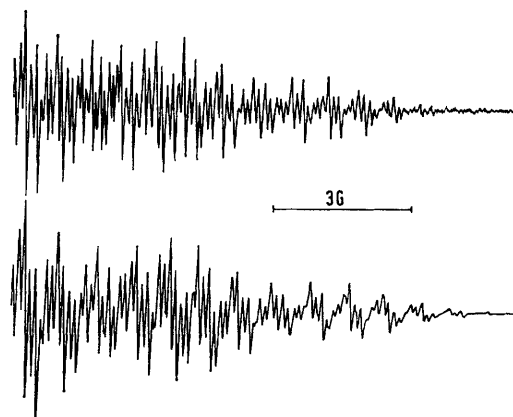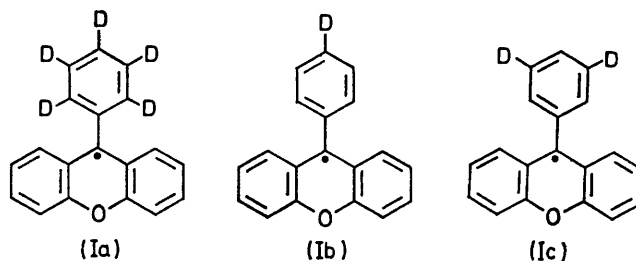2.07_5 MHz, and 4 hydrogens with $a_H = 2.35_5$ MHz. The assignments of ref. 2 are also incorrect.

FIGURE 1 Experimental (upper) and simulated half e.s.r. spectrum of the 9-phenylxanthenyl radical (I). The scale of the simulated spectrum is slightly larger than that of the experimental one

The second task, after finding the correct symmetry for the splitting constants, is to assign them unam-

(Ia)   (Ib)   (Ic)

biguously to particular positions on the radical. A number of labelled derivatives (Ia), (Ib), and (Ic), con-

TABLE 1

Experimental hyperfine splittings (MHz) for the 9-phenylxanthenyl radical (I) and its deuteriated derivatives (Ia), (Ib), and (Ic). The spin densities calculated with the McLachlan method (see text), are reported in columns 6 and 7 for twisting angles of 60 and 80° respectively; their corresponding best Q values are 74.12 and 69.52 MHz respectively

| Positions | Hyperfine splitting constants (MHz) | | | | Spin densities | |
	(I)	(Ia)	(Ib)	(Ic)	$\theta = 60°$	$\theta = 80°$
1—8	9.19_5	9.17	9.25	9.17	0.1413 (10.47)	0.1521 (10.57)
2—7	2.35_5	2.41	2.24	2.41	−0.0460 (3.45)	−0.0510 (3.53)
3—6	10.57	10.65	10.65	10.65	0.1132 (8.39)	0.1187 (8.24)
4—5	2.07_5	2.13	2.24	2.13	−0.0325 (2.41)	−0.0349 (2.41)
11—15 (*ortho*)	2.35_5			2.24	2.41	0.0313 (2.32)	0.0039 (0.28)
12—14 (*meta*)	1.68	0.29_5 (D)	2.24	0.24 (D)	−0.0115 (0.85)	−0.0015 (0.11)
17 (*para*)	1.68			1.17	0.0286 (2.12)	0.0034 (0.22)
9					0.5191	0.5625
18 (oxygen)					0.0180	0.0143
Line-width (gauss)	0.08	0.17	0.35	0.075		

The failure, reported in ref. 1, in simulating the intensities is not due to ' small line-width variations ', but to an incorrect attribution of the smallest splittings to the number of hydrogens, the correct assignment being: 3 hydrogens with $a_H = 1.68$ MHz, 2 hydrogens with $a_H =$

taining respectively 5, 1, and 2 deuterium atoms were, therefore, synthesized.

The e.s.r. spectrum of the 9-[$^2H_5$]phenylxanthenyl radical (Ia) clearly shows that the two greater couplings ($a_H = 10.57$ MHz, $a_H = 9.19_5$ MHz) belong as expected to the heterocyclic ring (Figure 2a). On the basis of the experimental assignments performed on similar cases,[3,4]

[5] M. F. Chin, B. C. Gilbert, and P. Hanson, *J. Chem. Soc. (B)*, 1970, 1700.

a_{H1}, a_{H8} were set equal to 9.19_5 MHz and a_{H3}, a_{H6} to 10.57 MHz. The same spectrum also shows that the two other couplings in the heterocyclic ring cannot be
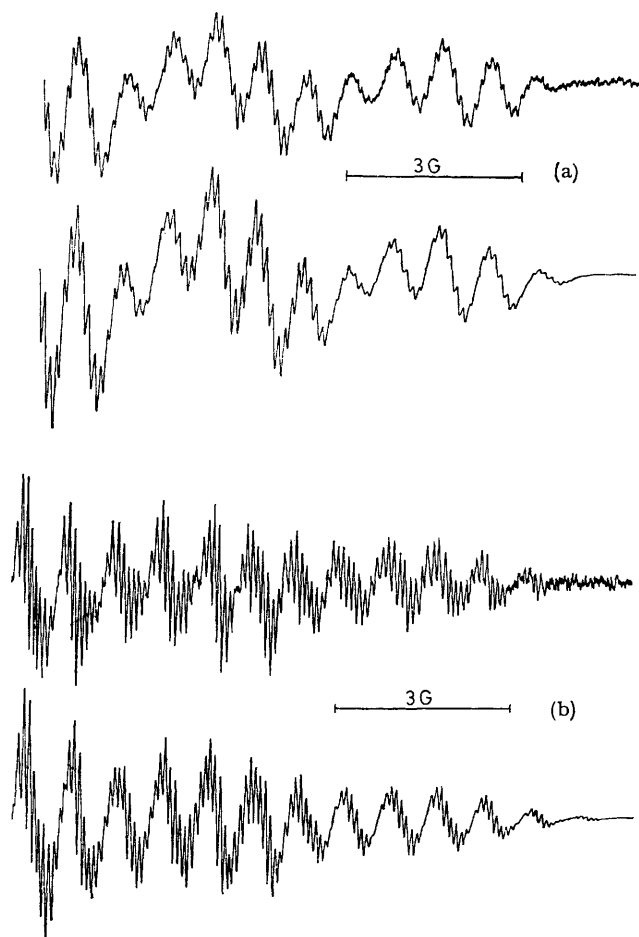

FIGURE 2 (a) Experimental (upper) and simulated half e.s.r. spectrum of the 9-[2,3,4,5,6-$^2H_5$]phenylxanthenyl radical (Ia). (b) Experimental (upper) and simulated half e.s.r. spectrum of the 9-[3,5-^2H]phenylxanthenyl radical (Ic)

equivalent and in particular the values 2.35_5 and 2.07_5 MHz best reproduce the intensity patterns. Indeed, assuming for the heterocyclic ring the pairs 1.68 and 2.35 MHz or 1.68 and 1.07_5 MHz, the simulated spectrum does not exactly match the experimental one.

As pointed out in a similar situation,[3] the assignment of the two smaller heterocyclic ring splittings has been made on theoretical grounds (2.33_5 MHz to positions 2,7 and 2.07_5 MHz to 4,5) because of the uncertainties which are likely to occur even in an experimental checking. The odd number (three) of the hydrogens with the 1.68 MHz splittings and the molecular symmetry allows us to assign one of these constants to the *para*-position; a further proof of this conclusion is given by the spectrum of the 9-[*p*-$^2H_1$]phenylxanthenyl radical (Ib) where one of the smallest couplings was found to disappear because of the deuterium substitution. In order to decide

whether the remaining 1.68 MHz splitting belonged to the two protons in the *ortho*- or *meta*-positions, the spectrum of the 9-[*m,m'*-$^2H_2$]phenylxanthenyl radical (Ic) was investigated. Its spectrum (Figure 2) allowed us to decide that since the four splittings with $a_H = 2.35_5$ MHz were still present, two of them had thus to be assigned to the *ortho*-position. The value of the measured a_D splitting (0.24 MHz) further confirms that a 1.68 MHz coupling has been substituted in the *meta*-position.

It is also worth noting that the spectrum of (Ic) does exclude that the two pairs 1.68, 2.35_5 MHz or 1.68, 2.07_5 MHz, belong to the heterocyclic ring: the assignment to the latter of the pair 2.07_5, 2.35_5 MHz is thus confirmed.

For the selenium derivative (III) (Figure 3), a_H values similar to those reported for the sulphur analogues were observed. The hyperfine splittings for the radicals (II) and (III) are similar to those for the xanthenyl radical with one exception: that is, the *meta* splitting is not equal to the *para*, but is almost zero. In order however to ascertain that the a_H *meta* and not the *ortho* is equal to zero, we recorded the spectrum of the 9-[*m,m'*-$^2H_2$]phenylselenoxanthenyl radical (IIIc). In contrast to the results for (Ic), no appreciable change of the patterns was observed, thus showing that the isotopic substitution had occurred in a position with negligible splitting. Moreover, to avoid the possibility of a proton–deuteron exchange during the synthesis of the labelled radicals, the *m,m'*-dimethyl derivatives (Id), (IId), and (IIId) were also examined

The spectra of the 9-(*m,m'*-dimethylphenyl)thioxanthenyl (IId) and 9-(*m,m'*-dimethylphenyl)selenoxanthenyl radicals (IIId) were closely similar to those of the
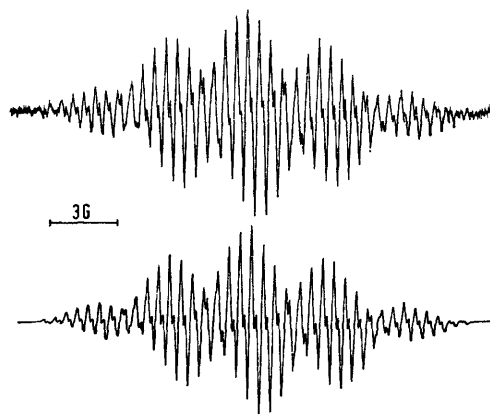

FIGURE 3 Experimental (upper) and simulated e.s.r. spectrum of the 9-phenylselenoxanthenyl radical (III)

corresponding unsubstituted radicals (II) and (III); the spectrum for the 9-(*m,m'*-dimethylphenyl)xanthenyl radical (Id) clearly showed an additional methyl splitting ($a_{Me} = 1.68$ MHz); this parallels the relatively large $a_{H-m,m'}$ value observed in (I). Little doubt remains therefore that there is a negligible spin density in the *meta*-position of the 9-phenylthio- and -selenoxanthenyl

radicals whilst in the corresponding oxygen derivative the splitting is as large as in the *para*-position.

In order to explain the greater than unity *ortho*/*para* ratio of the spin density in (II), an overlapping effect on the *ortho* protons had to be assumed. This contribution takes the form:[3]

$$a_H^* = 1420\cdot4 \sum_i \rho^\pi c_i\, [\psi c_i(H)]^2 \qquad (1)$$

where 1420·4 is the proton hyperfine splitting (MHz) due to a whole electron, $\rho^\pi c_i$ is the spin density of the carbon on the heterocyclic ring and $[\psi c_i(H)]^2$ the probability of finding the c_i *p*-orbital electron at the nucleus of the *ortho*-hydrogen. This model also requires that the phenyl ring is not free to rotate, but experiences a restricted motion with a preferred conformation strongly twisted from planarity. This model, when applied to the selenoxanthenyl derivative, gives the same good results obtained for the corresponding sulphur radical.[3] As reported in Table 2, the McLachlan spin densities

TABLE 2

Experimental hyperfine splittings (MHz) for the 9-phenyl-selenoxanthenyl radical (III) and its derivatives (IIIc), and (IIId). The spin densities have been calculated with the McLachlan method ($h_{Se} = 1\cdot2$, $k_{CSe} = 0\cdot55$) for a twisting angle of 72° (see text). The best Q value was found 70·22 MHz

	Hyperfine splitting constants (MHz)		
		(IIIc)	
Positions	(III)	(IIId)	Spin densities
1—8	8·85	8·85	0·1467 (10·35)
2—7	2·81	2·81	−0·0495 (3·48)
3—6	10·34	10·34	0·1178 (8·28₅)
4—5	2·81	2·81	−0·0368 (2·58₅)
11—15 (*ortho*)	1·40₅	1·40₅	0·0122 (0·87)
12—15 (*meta*)	0·14		−0·0046 (0·35)
13 (*para*)	0·50₅	0·50₅	0·0109 (0·76)
9			0·5470
18			
Line width (gauss)	0·12	0·18	

give the best fitting with the experimental results at the same angle (72°) of ref. 3 and the a_H *ortho* calculated on this basis (−0·84 MHz) is smaller than the experimental value. If however a locked configuration is assumed and the a_H^* contribution computed according to ref. 3 (2·00₅ MHz) the a_H *ortho* value becomes 1·16₅ MHz, in agreement with the experimental splitting value. Also in the case of the 9-phenylxanthenyl radical, the twisting angle θ was estimated by a least-squares fitting procedure between the carbon spin density and the corresponding hydrogen hyperfine splittings; the angle corresponding to the smallest deviation being 60° as in ref. 1. Since however not only the *ortho*, but also the *meta* splittings are, for X = O, in disagreement with the conventional picture of a π radical, they cannot be included in the best fit and therefore the value of 60° is a rough approximation. Moreover, as shown in ref. 2, the shape

of this curve is very flat in the 60—90° range and therefore the uncertainty on the twisting angle is relatively large. We observed, for instance, that an angle of 80° still gives reasonable agreement for the spin density on the heterocyclic ring and also explains the large value of the *ortho* splitting (Table 1). Thus, the McLachlan value of −0·28 MHz has to be added to $a_H^* = 2\cdot58$ MHz [see equation (1)]; the resulting splitting (2·30 MHz) is then in agreement with the experimental one (2·35₅ MHz). This model, however, does not explain the relatively large value for the *meta*-position, a problem which does not arise for the radicals (II) and (III). A possible explanation could be the σ–π interaction effect that Pople and his co-workers took into account in the INDO method. They showed[6] that for a sufficiently high rotation angle a_H *ortho* and particularly a_H *meta* may become greater than a_H *para*. The occurrence of a_H *meta* even larger than *ortho* and *para* has been recently observed in other radicals[7,8] and, at least in one case,[8] the INDO calculations seem well able to explain the experimental data assuming a locked configuration instead of a free rotation model. Unfortunately a complete theoretical calculation based on the INDO method of ref. 6, could not be performed in the present case owing to the size of the radicals which exceed the capability of the computer program.[9] This method, however, was used on the unsubstituted xanthenyl radical[4] to see whether it was at least possible to rationalize theoretically the greater splittings at positions 3,6 in respect to positions 1,8. Unfortunately even the INDO results (Table 3) parallel the trend of the Mc-

TABLE 3

Hyperfine splitting constants calculated by the INDO method for the xanthenyl radical. Values in parentheses are the experimental values of ref. 4

Positions	Hyperfine splitting constants (MHz)
1—8	−14·41 (9·60)
2—7	8·49₅ (2·77)
3—6	−12·08 (11·34)
4—5	8·13 (2·51)
9	−37·79 (35·68)

Lachlan spin densities, and both are opposite to the experimental findings. Therefore a definite interpretation of these radicals cannot be reached even using the INDO method; moreover, since it leads to high values for the *meta*-positions in order to explain *ortho*/*para* ratio greater than unity, INDO is not likely to be successfully applied to sulphur and selenium derivatives because of the negligible spin densities experimentally observed at the *meta*-positions.

We can nevertheless conclude that, whilst the approaches employed do not explain all the features of this series of radicals, they do at least agree in respect of the stereochemical interpretation. There is therefore little

[6] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 1968, **90**, 4201; J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 1968, **49**, 4725.

[7] A. Calder, A. R. Forester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481.

[8] P. J. Krusic and J. A. Rettig, *J. Amer. Chem. Soc.*, 1970, **92**, 722.

[9] Kindly supplied by the Q.C.P.E., Bloomington, Indiana.

doubt that in all the three cases examined the phenyl ring is not allowed to freely rotate but is locked at an angle of 70—80° out of the heterocyclic plane.

The reason for the different behaviour for the $X = O$ and $X = S$ and Se cases as far as the spin density in the *meta*-position is concerned remains, however, unclear.

Calculations.—The MO calculations were carried out by means of the McLachlan approximation. For the 9-phenylxanthenyl radical, the same parameters of ref. 1 have been used ($h_O = 2.0$, $k_{CO} = 0.75$, $\lambda = 1$ or 2) and in Table 1 the spin densities for twisting angles of the phenyl ring equal to 60 and 80° are reported.

For the 9-phenylselenoxanthenyl radical, two sets of parameters have been tested; the first ($h_{Se} = 1.1$, $k_{CSe} = 0.65$) only differs from those proposed for the sulphur atom [10] by the value of the coulomb integral, owing to the lower electronegativity of the selenium atom.[11]

The second set ($h_{Se} = 1.2$, $k_{CSe} = 0.55$), taken from ref. 10, gives similar results and in both cases the best twisting angle (72°) is unchanged: this confirms that the angle is not greatly depending on the parameters used.[3]

For the INDO calculations [9] the bond lengths of ref. 6 and angles of 120° degrees have been employed.

EXPERIMENTAL

Spectral Measurements.—The radicals were obtained directly in the e.s.r. sample tubes by zinc dust reduction of the corresponding perchlorates in methylcyclohexane solution. The samples were carefully degassed and sealed off *in vacuo* in order to increase the lifetime of the radical as well as to obtain a better resolution; the latter reached its best value at *ca.* −60 °C.

The spectra were recorded on a Varian 4502 spectrometer with a 100 KHz field modulation and simulated on a IBM 7094 computer, assuming a Lorentzian line shape.

For the 9-phenylxanthenyl radical the *g* factor (2·00289) of ref. 1 has been used.

In the case of the 9-phenylselenoxanthenyl radical the *g*-factor (2·0068$_5$) was measured by comparison with Fremy's salt (standard *g*-factor = 2·00550).

Syntheses of the Products.—The 9-phenylxanthenylium

perchlorate (I) was prepared [12] by reaction of xanthone with phenylmagnesium bromide followed by addition of 70% aqueous perchloric acid. The corresponding deuteriated derivatives (Ia), (Ib), and (Ic) were obtained in the same way as (I), starting respectively from bromo[2,3,4,5,6-$^2H_5$]benzene, bromo[4-^2H]benzene,[3] and bromo[3,5-$^2H_2$]benzene.[13]

9-(m,m′-Dimethylphenyl)xanthenylium Perchlorate (Id).— The 3,5-dimethylbromobenzene was converted into the corresponding Grignard reagent and allowed to react with xanthone; the mixture was then worked up as described in ref. 12, to yield yellow crystals, m.p. 252—253° (dec.) from acetic acid (Found: C, 65·3; H, 4·5. $C_{21}H_{17}ClO_5$ requires C, 65·5; H, 4·45%).

9-(m,m′-Dimethylphenyl)thioxanthenylium Perchlorate (IId).—This compound was prepared [14] from thioxanthone and the Grignard reagent from 3,5-dimethylbromobenzene; it formed red crystals, m.p. 245° (dec.) from acetic acid (Found: C, 62·2; H, 3·9; S, 7·4. $C_{21}H_{17}ClO_4S$ requires C, 62·9; N, 4·3; S, 8·0%).

9-Phenylselenoxanthenylium Perchlorate (III).—To an ethereal solution of phenylmagnesium bromide (1·2 equiv.) was added selenoxanthone (1·8 g) [15] dissolved in benzene (30 ml). The mixture was refluxed and stirred for 5 h and then washed with water, dried, and evaporated. The residue, dissolved in methylene chloride, was cooled at 0 °C and treated with 70% perchloric acid (2 ml). The violet precipitate, obtained upon addition of anhydrous ether, was crystallized from acetic acid to yield compound (III) (2·1 g), m.p. 167—168° (dec.) (Found: C, 54·0; H, 3·2. $C_{19}H_{13}SeClO_4$ requires C, 54·4; H, 3·1%).

The corresponding deuteriated derivatives (IIIa) and (IIIc) were prepared in the same way as compound (III) starting from bromo[2,3,4,5,6-$^2H_5$]benzene and bromo-[3,5-$^2H_2$]benzene.[13]

9-(m,m′-Dimethylphenyl)selenoxanthenylium Perchlorate.— This compound was prepared in the same way as compound (III) by reaction of selenoxanthone [15] and the Grignard reagent from 3,5-dimethylbromobenzene, m.p. 164—165° (dec.) from acetic acid (deep violet crystals) (Found: C, 56·1; H, 3·8. $C_{21}H_{17}ClO_4Se$ requires C, 56·3; H, 3·8%).

[10] P. D. Sullivan, *J. Amer. Chem. Soc.*, 1968, **90**, 3618.
[11] A. Streitwieser, jun., 'Molecular Orbital Theory', Wiley, New York, 1961.
[12] R. L. Shriner and Calvin N. Wolf, *J. Amer. Chem. Soc.*, 1951, **73**, 891.
[13] R. T. Akawie, J. M. Scarbrough, and J. G. Burr, *J. Org. Chem.*, 1959, **24**, 946.
[14] C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, 1963, **85**, 2278.
[15] R. Lesser and R. Weiss, *Ber.*, 1914, **47**, 2523.