

## Radical-anions of the Isomeric 9-Substituted Thioxanthen S-Oxides

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Radical-anions of 9-substituted thioxanthen S-oxides have been prepared and their e.s.r. spectra measured. For the two 9-methyl isomers the S-O group has the pseudoaxial conformation, in contrast to its pseudoequatorial conformation in the neutral compounds. The spectra of decomposition products are also observed.

ALTHOUGH radical-anions of diphenyl sulphone and related molecules are now well known,<sup>1-3</sup> there are only two reports of radical-anions containing the sulphoxide group.<sup>4,5</sup> In the case of the sulphones one of the motives which prompted a study of this system was the possibility that the way in which the phenyl ring interacts with the sulphone group might show a significant dependence upon the mutual orientations of these two fragments.<sup>6</sup> In the event this did not prove to be detectable in the e.s.r. spectrum but there were reasons to think that this might not be the case for the sulphoxides. Thus the *cis*- and *trans*-thianthren SS-dioxides have radical-anions which are very different both in their stability and e.s.r. spectral parameters<sup>4</sup> and this implies that the interaction between a pseudoaxial S-O bond and a phenyl ring is very different from that between a pseudoequatorial S-O bond and a phenyl ring.

A difficulty with this system is however that although *cis*-thianthren SS-dioxide is known to have both S-O bonds in the pseudoequatorial conformation,<sup>7</sup> its radical-anion might well have inverted, a phenomenon which we observed in the radical-anions of 9-substituted thioxanthen SS-dioxides.<sup>8</sup>

We have therefore studied the analogous 9-substituted thioxanthen S-oxide radical-anions, where the conformation of the ring is revealed by the coupling of the proton in the 9-position.

### EXPERIMENTAL

The two isomers of 9-methylthioxanthen S-oxide and 9,9-dimethylthioxanthen S-oxide were prepared by a reported method.<sup>9</sup> The two isomeric 9-phenyl derivatives were prepared by an analogous method and the pure isomers separated from the reaction mixture (A : B ca. 2 : 1) by t.l.c. using a 9 : 1 benzene-acetone mixture as eluent, and recrystallised from ether, isomer A m.p. 148 °C (prisms), isomer B m.p. 187 °C (platelets). The corresponding deuteriated compounds were obtained using trideuteriomethyl iodide and pentadeuteriobromobenzene respectively as the sources of the Grignard reagent. Satisfactory analysis and 100 MHz n.m.r. spectra were obtained.

Dimethoxyethane was dried over and distilled from lithium aluminium hydride and the radicals were prepared at -80 °C by reaction with a bright mirror of potassium under nitrogen in a sealed tube. E.s.r. spectra were measured on

a JEOL ME/XI spectrometer. The final analysis of the spectra was based on simulation using QCPE program 160.

### RESULTS AND DISCUSSION

The radical-anions of these sulphoxides are extremely unstable even at the lowest usable temperature, -80 °C, just above the freezing point of dimethoxyethane, and attempts to use mixed solvents for which the freezing point would be lower, or indeed the use of any other

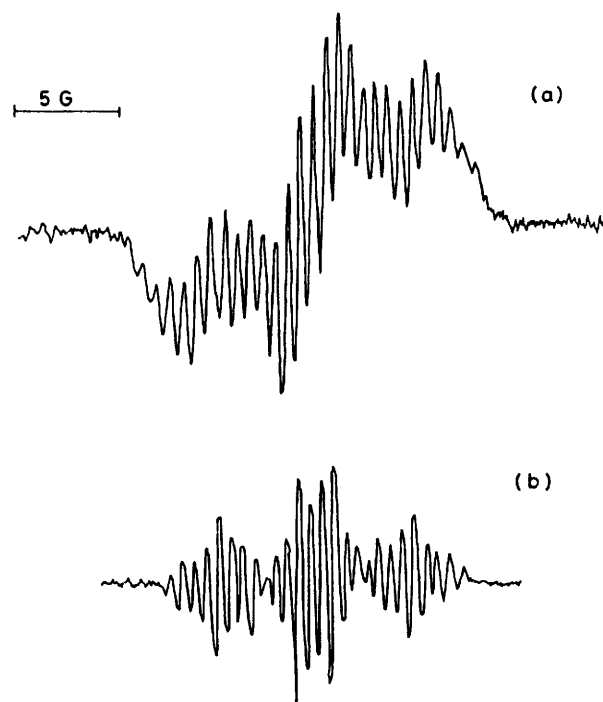


FIGURE 1 Spectra of the radical-anions of 9,9-dimethylthioxanthen S-oxide: (a) normal molecule; (b) perdeuteriomethylated derivative

solvent than dimethoxyethane, gave none of the desired radical-anion. Furthermore all our many attempts to produce the radical-anion of unsubstituted thioxanthen S-oxide itself were completely unsuccessful. Even for the substituted derivatives the concentration of the radical decreased steadily throughout the measurement

<sup>1</sup> R. Gerdil and E. A. C. Lucken, *Proc. Chem. Soc.*, 1963, 144.

<sup>2</sup> D. H. Eargle and E. T. Kaiser, *Proc. Chem. Soc.*, 1964, 22.

<sup>3</sup> R. Gerdil and E. A. C. Lucken, *Mol. Phys.*, 1965, 9, 529.

<sup>4</sup> E. T. Kaiser and D. H. Eargle, *J. Chem. Phys.*, 1963, 39, 1353.

<sup>5</sup> A. Trifunac and E. T. Kaiser, *J. Phys. Chem.*, 1970, 74, 2236.

<sup>6</sup> H. P. Koch and W. E. Moffit, *Trans. Faraday Soc.*, 1951, 47, 7.

<sup>7</sup> S. Hosoya, *Acta Cryst.*, 1966, 21A, 104.

<sup>8</sup> P. Lambelet and E. A. C. Lucken, *J.C.S. Perkin II*, 1976, 164.

<sup>9</sup> A. L. Ternay, L. Ens, J. Herrmann, and S. A. Evans, *J. Org. Chem.*, 1969, 34, 940.

of the spectrum and the signal-to-noise ratio, particularly in the wings of the spectrum where the lines are of low intensity, was never very satisfactory.

A further complication, particularly as far as spectral analysis is concerned, lies in the fact that the protons in

computer simulation of the observed spectrum (see Figure 2c)

Even with these precautions it was not possible to obtain unambiguous analyses of all the observed spectra. Figure 2 shows the spectra of the radical-anions of the

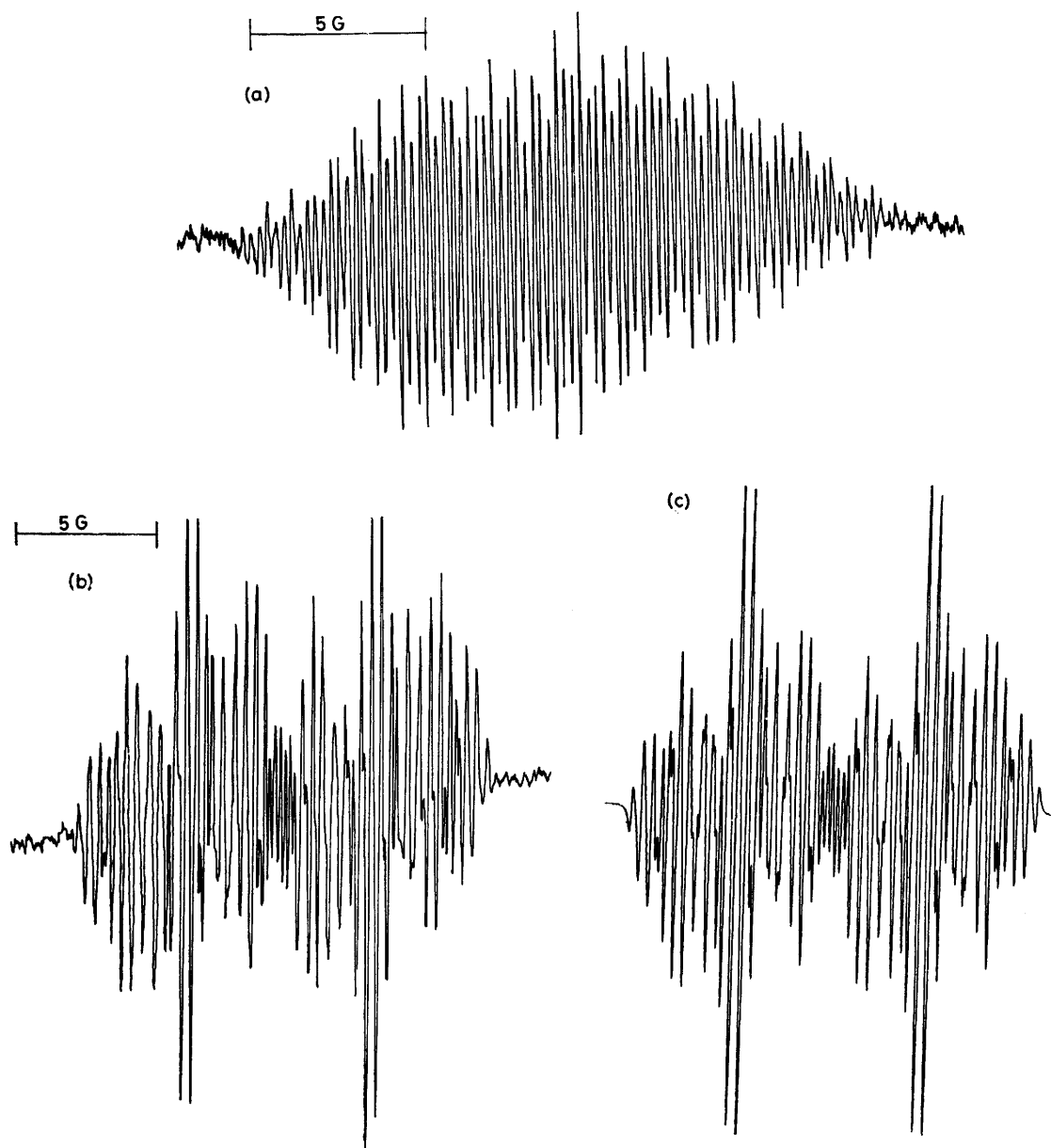


FIGURE 2 Spectra of the radical-anions of (a) *cis*-9-perdeuteriomethylthioxanthen *S*-oxide; (b) *trans*-9-perdeuteriomethylthioxanthen *S*-oxide; (c) computer simulation of (b) using the coupling constants given in the Table

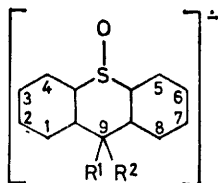
the alkyl or aryl substituent in the 9-positions have an appreciable coupling constant. Spectra suitable for analysis can therefore only be obtained if the 9-substituent is completely deuteriated. An example is shown in Figure 1. The final difficulty is that in all cases hyperfine splitting from the  $^{39}\text{K}$  nucleus ( $I = 3/2$ ) is also visible. In these circumstances it is absolutely essential to check the assignment of the e.s.r. parameters by

*trans*- and *cis*-isomers of 9-perdeuteriomethylthioxanthen *S*-oxide. The presence of a large coupling constant due to the proton in position 9 simplifies the spectrum of the former isomer sufficiently to make spectral analysis straightforward. This coupling is however much smaller for the *cis*-isomer and this fact together with the poor signal-to-noise ratio, makes an unambiguous assignment impossible. For this and for the analogous case

of the 9-phenyl isomer B all that can be said with certainty is that the coupling of the 9-proton is small, certainly  $<5.0$  G and probably no more than 1–2 G.

simply those of a too bulky substituent in the 9-position,<sup>12</sup> the SO group appears to prefer the pseudoequatorial position. In view of the fact that the radical-anions are

Coupling constants of the radical-anions of 9-substituted thioxanthen S-oxides



Radical-anion	R <sup>1</sup>	R <sup>2</sup>	Isomer	Coupling constant (G)					
				<i>a</i> <sub>1</sub>	<i>a</i> <sub>2</sub>	<i>a</i> <sub>3</sub>	<i>a</i> <sub>R'</sub>	<i>a</i> <sub>R''</sub>	<i>a</i> <sub>K</sub>
9-Perdeuteriomethylthioxanthen S-oxide	H	CD <sub>3</sub>	<i>trans</i>	0.74	1.94	4.40	13.82	$<0.10$	0.74
9-Perdeuteriomethylthioxanthen S-oxide	H	CD <sub>3</sub>	<i>cis</i>				$<5.0$		
9-Perdeuteriophenylthioxanthen S-oxide	H	C <sub>6</sub> D <sub>5</sub>	A	0.74	1.84	4.08	17.76	$<0.10$	0.74
9-Perdeuteriophenylthioxanthen S-oxide	H	C <sub>6</sub> D <sub>5</sub>	B				$<5.0$		
9,9-Dimethylthioxanthen S-oxide	CH <sub>3</sub>	CH <sub>3</sub>		0.75	1.95	4.33	0.55	$<0.12$	0.64
9,9-Bisperdeuteriomethylthioxanthen S-oxide	CD <sub>3</sub>	CD <sub>3</sub>		0.75	1.95	4.33	$<0.10$	$<0.10$	0.64

The Table shows the spectral parameters of the five molecules studied here. Apart from the coupling from the proton in the 9-position and the <sup>39</sup>K splitting, the assignment of coupling constants to particular protons is not experimentally available. The assignment given here is based on the hypothesis that sulphoxide is an overall electron-withdrawing group so that the spin-density in the radical-anions will be in the order *a*<sub>para</sub> > *a*<sub>ortho</sub> > *a*<sub>meta</sub>. These coupling constants are therefore not discussed further.

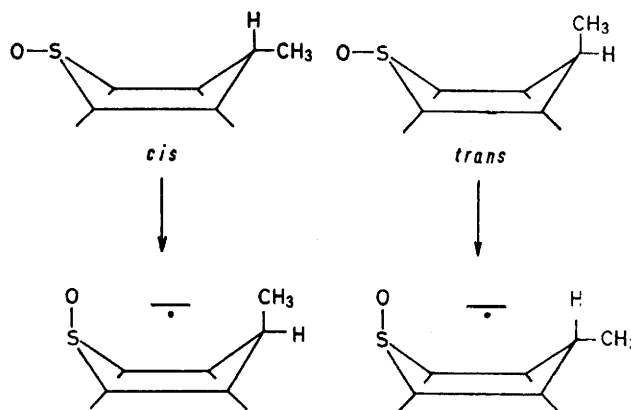
The coupling constants of the protons in the 9-positions show unambiguously that the radical-anions of *cis*-9-methylthioxanthen S-oxide and of isomer B of 9-phenylthioxanthen S-oxide have the substituent in the pseudoaxial position. The crystal structure of the *cis*-9-methyl derivative, however, shows it to take the inverted conformation where the methyl group is in a pseudoequatorial position.<sup>10</sup> At least for this compound, and possibly for isomer B of the 9-phenyl derivative, the conformation has inverted on formation of a radical-anion.

There is likewise evidence from n.m.r. spectroscopy that *trans*-9-methylthioxanthen S-oxide has the substituent in the pseudoequatorial position<sup>9</sup> and there is no doubt that the corresponding radical-anion has the substituent in the pseudoaxial position so that once more inversion appears to have occurred. There is no doubt whatsoever for both the 9-methyl derivatives that in the radical anions the S–O bond is pseudoaxial. This is exactly the opposite of the situation for the neutral compounds where, unless there are steric effects such as those caused by methyl substituents adjacent to the SO group, e.g. *cis*-1,4-dimethylthioxanthen S-oxide,<sup>11</sup> or

<sup>10</sup> J. Jackobs and M. Sundaralingam, *Acta Cryst.*, 1969, **25B**, 2487.

<sup>11</sup> S. S. C. Chu and B. Chung, *Acta Cryst.*, 1974, **30B**, 235.

present as contact ion-pairs it is however not certain whether this would also be the case for the isolated



radical-anion or whether this change in preferred orientation must be ascribed to the presence of the counter-ion.

**Decomposition Products.**—As for the xanthen<sup>13</sup> and thioxanthen SS-dioxide<sup>8</sup> radical-anions, the radical-anions discussed here also decompose if the temperature is allowed to rise much above  $-80$  °C and the products are similar to those observed previously. Thus at  $-50$  °C in contact with potassium, 9-methyl-9-phenylthioxanthen S-oxide yields the 9-methyl-9-phenylfluorene radical-anion while under the same conditions at  $-25$  °C both the 9-perdeuteriophenylthioxanthen S-oxides give *only* the 2,3,4,5,6-pentadeuteriobiphenyl radical-anion.

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<sup>12</sup> S. S. C. Chu, *Acta Cryst.*, 1975, **31B**, 1082.

<sup>13</sup> P. Lambelet and E. A. C. Lucken, *J.C.S. Perkin II*, 1975, 1652.