

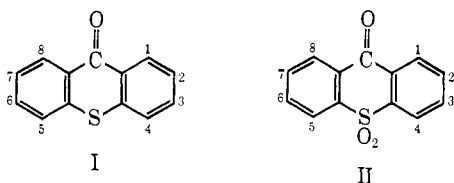
The Electron Paramagnetic Resonance Spectra of Thioxanthone and Thioxanthone Sulfone Anion Radicals

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Abstract: Anion radicals were prepared from thioxanthone and thioxanthone sulfone by alkali metal reduction in 1,2-dimethoxyethane solutions. The anion radical of thioxanthone sulfone was also prepared by autoreduction in basic ethanol. Epr spectra of the radicals have been observed and nuclear coupling constants measured. Proton coupling constants have been assigned by examining the epr spectra of radicals obtained from methyl-substituted compounds.

In the last few years several papers have appeared discussing the epr spectra of anion radicals of thioxanthone (I)² and thioxanthone sulfone (II).²⁻⁵ No coupling constants were reported for the thioxanthone radical. Vincow³ has measured the epr spectrum of the sulfone anion radical prepared in basic ethanol. He did not determine the assignments of coupling constants to positions experimentally but assumed that the spin distribution was similar to that in benzophenone anion radical. He was able to calculate a theoretical spin distribution which agrees well with experiment assuming his assignment of coupling constants.



Kaiser and Eargle² found that the epr spectrum of thioxanthone sulfone anion radical prepared by alkali metal reduction in 1,2-dimethoxyethane (DME) solution was quite different from that prepared in alcohol solutions. They were not able to obtain proton coupling constants from their spectrum.

With this in mind, we decided to repeat these experiments, measure coupling constants which have not been previously reported, and assign proton coupling constants to positions in these anion radicals.

Results and Discussion

I. Thioxanthone Anion Radical Thioxanthone was reduced with Na and K metals in DME solutions. The coupling constants measured from these spectra are given in Table I.

The epr spectrum of the radical prepared by K metal reduction and the spectrum simulated using our constants are shown in Figure 1.

The assignment of proton coupling constants was done by examining the epr spectra of anions prepared from 2-methyl-, 2,4-dimethyl-, and 1,4-dimethylthioxanthone. The assignment is based on the fact that Q_{CH_3} is about equal to Q_{H} for most aromatic systems.

(1) To whom inquiries concerning this paper should be addressed.

(2) E. T. Kaiser and D. H. Eargle, Jr., *J. Am. Chem. Soc.*, **85**, 1821 (1963).

(3) G. Vincow, *J. Chem. Phys.*, **37**, 2484 (1962).

(4) H. Heymann, *J. Am. Chem. Soc.*, **71**, 260 (1949).

(5) E. A. Fehnel, *ibid.*, **71**, 1063 (1949).

Table I. Coupling Constants from the Epr Spectra of Thioxanthone Anion Radicals

Position	$A_{\text{H}}(\text{K metal})^a$, gauss	$A_{\text{H}}(\text{Na metal})$, gauss
1	3.380	3.35
2	0.950	0.90
3	3.750	3.80
4	0.345	0.45
Metal	0.110	0.45

^a The spectrum of this radical was simulated for us by Dr. M. Sakamoto of the Computer Division of Jeolco, Medford, Mass. The coupling constants given here give a simulated spectrum which is in very good agreement with the experimental spectrum.

Thus the width of the epr spectrum of a methyl-labeled aromatic anion radical is approximately equal to the width of the parent radical plus twice the coupling constant at the position of methyl substitution. For some of the radicals we were able to measure methyl group coupling constants directly, and these measured coupling constants were generally in good agreement with the aromatic proton coupling constants in the parent radical. The measured widths for the above anion radicals are given in Table II along with those expected on the basis of our assignments.

Table II. Widths in Gauss of Epr Spectra of the Anion Radicals of Methyl-Substituted Thioxanthenes

Compd	K metal		Na metal	
	Measd	Exptd	Measd	Exptd
Thioxanthone	17.18		18.4	
2-Methyl	18.9	18.92	19.5	20.2
2,4-Dimethyl	19.5	19.6	20.1	21.2
1,4-Dimethyl	23.8	24.48	26.0	26.0

The outer portion of the spectrum of the radical prepared by the reduction of 2-methylthioxanthone with K metal consists of a pentuplet which arises from splitting by the three protons of the methyl group and the proton at the 7 position with coupling constants of 0.95 gauss. The width of the spectrum from the potassium reduction of 2,4-dimethylthioxanthone shows that the coupling constant at the 4 position must be very small and leads to the assignment of $A_4 = 0.345$ gauss.

The widths of the epr spectra of the radicals from the reaction of sodium and potassium with 1,4-dimethylthioxanthone show that A_1 must be large. The

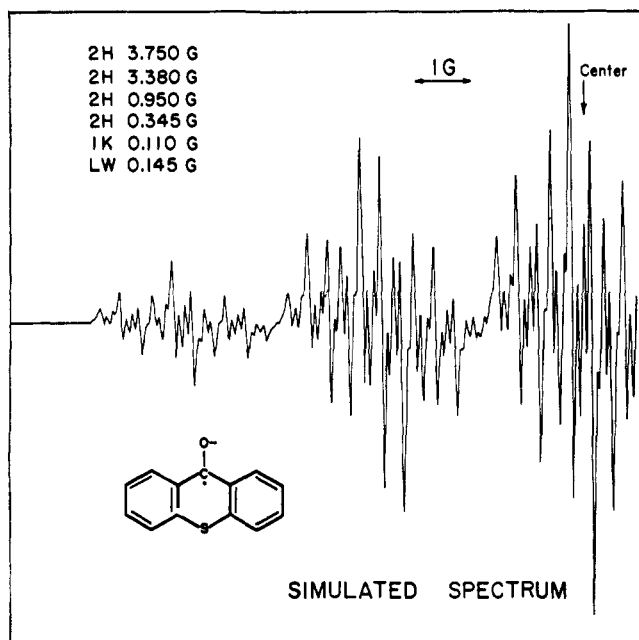
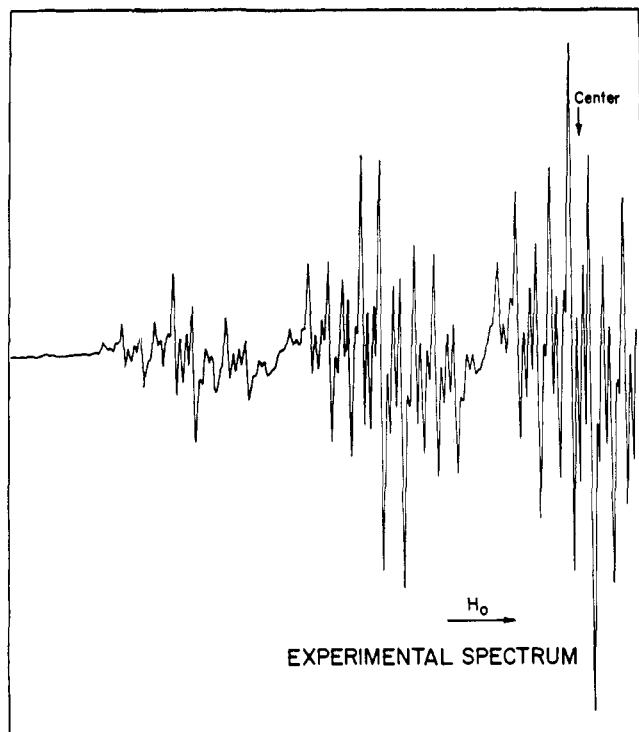


Figure 1.

spectra are too complex and too poorly resolved to see any significant structure, but the measured widths are in good agreement with our assignments. The order of coupling constants is similar thus to the situation in benzophenone ketyl and in the thioxanthone sulfone anion radical in which A_1 is less than A_3 .

II. Thioxanthone Sulfone Anion Radical. Vincow³ reported proton coupling constants for thioxanthone sulfone anion radical prepared in basic alcoholic solutions. These coupling constants are given in Table III as he assigned them. We repeated this experiment and observed a spectrum which agreed well with Vincow's coupling constants.⁶

(6) After the completion of our work a note appeared by J. P. Keller

Table III. Proton Coupling Constants for Thioxanthone Sulfone Anion Radical Prepared in Basic Ethanol^{2 a}

Position	A_H , gauss	Position	A_H , gauss
1	2.35	3	3.10
2	0.52	4	0.84

^a No metal splittings are seen in alcohol solutions.

The measured widths of the epr spectra for methyl-substituted thioxanthone sulfone anion radicals prepared by this method are given in Table IV along with the widths predicted on the basis of Vincow's assignments.

Table IV. Observed Widths of Spectra of Methyl-Substituted Thioxanthone Sulfones Prepared in Alcohol Solutions

Compound	Obsd width, gauss	Predicted width, gauss
Thioxanthone sulfone	13.62	
2,7-Dimethyl	15.9	15.70
2-Methyl	14.3	14.66
2,4-Dimethyl	16.1	16.34
1,4-Dimethyl	17.2	20.0 (21.50 if A_1 were 3.10 gauss)

The agreement between measured and predicted widths is generally quite good. The epr spectrum of the radical prepared from 2,7-dimethylthioxanthone sulfone is well resolved, and the measured methyl group splitting is 0.55 gauss which agrees well with 0.52 gauss measured from the parent radical spectrum. The width of the epr spectrum of 1,4-dimethylthioxanthone sulfone anion radical does not agree exactly with that predicted by either of the two possible assignments of A_1 , but it is in much better agreement with $A_1 = 2.35$ gauss than with $A_1 = 3.10$ gauss. This assignment also agrees with Vincow's calculated spectrum. The change in the oxidation state from the sulfide to the sulfone seems to make the first unfilled orbital more polarizable.

To complete this study the anion radical of thioxanthone sulfone was prepared by K metal reduction in DME solution. Table V gives the coupling constants

Table V. Coupling Constants for Thioxanthone Sulfone Anion Radical in DME Solution

Position	A_H , gauss	Position	A_H , gauss
1	2.04	4	0.78 ± 0.03
2	0.36	K metal	0.11
3	3.07		

which were measured from the epr spectrum of this radical. These coupling constants are quite similar to those measured in alcohol solution but are uniformly smaller.

Measured epr spectral widths for methyl-substituted thioxanthone sulfones in DME solutions are given in Table VI along with the predicted widths which are calculated from our assignment and the agreement is again quite good.

and R. G. Hayes, *J. Chem. Phys.*, **46**, 816 (1967), in which similar results were reported for the spectrum of the thioxanthone sulfone anion radical in alcohol.

Table VI. Widths of the Spectra of the Anion Radicals of Substituted Thioxanthone Sulfones in DME

Compound	Width, gauss	
	Measd	Exptd
Thioxanthone Sulfone	12.80	
2-Methyl	13.4	13.52
2,4-Dimethyl	15.1	15.08
1,4-Dimethyl	17.0 ± 0.5	18.44 (20.50 if $A_1 = 3.07$ gauss)

The spectrum of 1,4-dimethylthioxanthone sulfone consists of 19 broad lines which arise from a triplet splitting ($A_H = 2.9$ gauss) further split by two pentuplets ($A_H = 1.85$ and $A_H = 0.75$ gauss). This is consistent with $A_1 = 2.04$ and $A_3 = 3.07$ gauss and is further evidence for these assignments.

The spectrum we observed for thioxanthone sulfone anion radical in DME is quite different in structure and width from that reported by Kaiser and Eargle.² Their spectrum may be attributed to an impurity in their sample. Dr. Eargle has recently made a radical from some of our thioxanthone sulfone which had not been purified completely and found a poorly resolved epr spectrum which is 15 gauss wide.⁷ The spectrum previously reported was 14.5 gauss wide. The spectrum from purified material is well resolved and reproducible from sample to sample. The number and degeneracy of the coupling constants are consistent with the structure of the molecule and agree well with those reported for the radical prepared in alcohol solution. We are confident that this is the correct spectrum and that the earlier one was in error.

Experimental Section

Radicals prepared by alkali metal reduction were prepared using the usual high vacuum techniques. To prepare the alcohol solutions, the thioxanthone sulfone was dissolved in ethanol. A pellet of KOH or NaOH was added, and the solution became blue as the base dissolved. If no color was formed, a reducing agent such as sucrose or sodium dithionite was added. The anion radical of 1,4-dimethylthioxanthone sulfone was prepared by dissolving equal portions of 1,4-dimethylthioxanthone sulfone and 1,4-dimethylthioxanthanol sulfone (prepared by the method of Fehnel⁵) in ethanol. The solution was poured into the epr probe, a small pellet of KOH was added, and the probe was sealed under vacuum. On gentle heating the KOH dissolved and a blue color appeared. The color and the epr spectrum remained for several days when the sample was stored in a dark place.

Spectra were recorded on a Varian 4500 spectrometer equipped with a 9-in. magnet with Fieldial control. Spectra of the alcohol solutions were observed at room temperature and spectra of the DME solutions were observed at -50° . A Varian variable-temperature controller was used to control the temperature to $\pm 0.5^\circ$.

(7) Private communication from Dr. D. H. Eargle, Department of Chemistry, University of Illinois at Chicago.

Thioxanthone was obtained from Aldrich and was recrystallized several times from ethanol.

2-Methylthioxanthone was prepared by the method of Mayer⁸ (mp $123-124^\circ$, lit.⁸ 123°).

1,4- and 2,4-dimethylthioxanthone were prepared by the method of Marsden and Smiles⁹ (1,4- mp $112-113^\circ$, lit.⁹ 112°) (2,4- mp $142.5-143^\circ$, lit.⁹ 127°). The elemental analysis, mass spectrum, and nmr spectrum of this sample of 2,4-dimethylthioxanthone are consistent with its structure. We believe that the low melting point reported for this compound in the literature is due to contamination with 1,3-dimethylthioxanthone which is formed as a by-product. Evidence for this by-product was seen in the epr spectra recorded for the anion radicals of 2,4-dimethylthioxanthone if the samples were not carefully purified. The spectra obtained from such samples show a broad structureless absorption beyond the outside lines of the measured spectrum. This absorption is not seen if the compound is recrystallized several times from ethanol.

Each of the thioxanthenes was oxidized to the corresponding sulfone by the following procedure. The thioxanthone (0.5 g) was dissolved in 10 ml of glacial acetic acid. The solution was heated to reflux and about 3 ml (about 500% excess) of 30% H_2O_2 was added in 1-ml portions at 0.5-hr intervals. After refluxing for about 3 hr, the mixture was cooled and poured into water. Crystals usually formed on cooling. The yellow compound was isolated by filtration, decolorized with Norit, and recrystallized from ethanol. It was then dissolved in chloroform and passed through a column of Merck acid-washed alumina. The compound came through in the first 50-ml portion of chloroform, and a yellow band remained at the top of the column. The colorless solid thus obtained was again treated with Norit, recrystallized from ethanol, and dried in a vacuum desiccator. Infrared spectra for all of the substituted sulfones were closely related to that of thioxanthone sulfone. Yields were of the order of 90-100%. The melting points observed are listed in Table VII. The mass spectra of all compounds measured were in agreement with their structures.

Table VII

Compound	Mp, $^\circ C$		Mass spectrum parent peak
	Found	Lit. ^a	
Thioxanthone sulfone	186-187	187	
2-Methylthioxanthone sulfone	200-201	199	258
2,4-Dimethylthioxanthone sulfone	181-182		272
1,4-Dimethylthioxanthone sulfone	149-150		272

^a F. Ullman and A. Lehner, *Ber.*, **38**, 729 (1905).

2,7-Dimethylthioxanthone sulfone was prepared by the method of Shirley, *et al.*,¹⁰ mp $237-239^\circ$, lit.¹⁰ $237-238^\circ$.

Acknowledgments. The support of the Petroleum Research Fund is gratefully acknowledged. M. M. U. wishes to thank the National Science Foundation for predoctoral fellowships.

(8) F. Mayer, *Ber.*, **43**, 588 (1910).

(9) E. G. Marsden and S. Smiles, *J. Chem. Soc.*, 1353 (1911).

(10) D. A. Shirley, *et al.*, *J. Org. Chem.*, **22**, 1073 (1957).