there is justification to attempt a more sophisticated calculation which would allow calculation of the splitting constant of the sp^3 carbons;[22] there are simply too many unknown parameters.

Obviously one should not attach too much significance to such a crude calculation, but qualitatively 3 protonation (IX) is much easier to accommodate than 1 protonation; the proton next to the sp^3 center has considerably too high a calculated spin density, but we have not reasonably accommodated this sp^3 center in the calculation. We feel that these calculations do rule out VIII, which should show three ring protons with large splittings. It is difficult to see why 3 protonation of the 1,6-di-*t*-butyl anhydride (IIB, X = O) would give a_3 (2 H) only half as large as for 2,5 or unsubstituted anhydride, but 1 protonation is definitely ruled out, for that product would have two large splittings instead of the one observed. It is possible that a completely different species was formed from IIB (X = O).

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Electron Spin Resonance Studies on the Anion Radical of Dibenzo[*b*,*f*]thiepin

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Abstract: The anion radical of dibenzo[*b*,*f*]thiepin has been prepared in 1,2-dimethoxyethane solution by potassium metal reduction. The esr spectrum of the radical has been recorded, and proton coupling constants have been assigned to positions by examining the esr spectra of anion radicals formed from several methyl-substituted derivatives of dibenzo[*b*,*f*]thiepin.

Esr studies of the conjugative effects of sulfur in aromatic sulfide anion radicals have been limited to planar systems. Dibenzothiophene[3-5] and thioxanthone[6,7] anion radicals have esr spectra which can be best explained by assuming that the sulfur $3p_y$ orbital is responsible for sulfur π bonding. This interaction should be very dependent on the geometry of the molecule. In order to investigate the dependence on molecular geometry of sulfur π bonding in aromatic sulfide anion radicals, we felt that it would be desirable to examine the esr spectrum of the anion radical of a nonplanar aromatic sulfide.

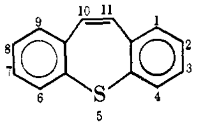
We have been unable to prepare anion radicals from diphenyl sulfide or thianthrene which are stable enough for esr studies. Dibenzo[*b*,*f*]thiepin, however, does form an anion radical which proved to be quite stable below −40°, and we decided therefore that it would be an appropriate system to examine for this study.

Results

The esr spectrum of the anion radical of dibenzo[*b*,*f*]thiepin (DBTP) is shown in Figure 1. Table I lists the coupling constants which we measured from this spectrum.

The assignment of coupling constants was done by examining the esr spectra of anion radicals prepared from 2-methyl-, 2,4-dimethyl-, 1,4-dimethyl-, and 10,11-dimethyl-DBTP. The widths of these spectra are given in Table II.

Table I. Proton Coupling Constants for the Anion Radical of Dibenzo[*b*,*f*]thiepin



Posn	A_H, gauss	Posn	A_H, gauss
1	1.41	4	1.41
2	0.00	10	3.79
3	3.79		

Table II. Widths of the Esr Spectra of Methyl-Substituted DBTP Anion Radicals

Compound	Spectral width, gauss
DBTP	20.59
2-Methyl-DBTP	20.6
2,4-Dimethyl-DBTP	21.5
1,4-Dimethyl-DBTP	23.4
10,11-Dimethyl-DBTP	38.3

Figure 2 shows the esr spectrum of the anion radical formed from 2-methyl-DBTP. It is very similar to the spectrum of the parent radical and shows no evidence for a methyl group splitting. This demonstrates that A_2 = 0.00 gauss.

The esr spectrum of 2,4-dimethyl-DBTP is not completely resolved, but if one examines the outer portions of the spectrum, one sees a quartet with a coupling constant of 1.4 guass, and a quartet with a coupling

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[3] R. Gerdil and E. A. C. Lucken, *J. Am. Chem. Soc.*, 87, 213 (1965).

[4] R. Gerdil and E. A. C. Lucken, *Proc. Chem. Soc.*, 144 (1963).

[5] D. H. Eargle, Jr., and E. T. Kaiser, *ibid.*, 22 (1964).

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

[7] M. M. Urberg and E. T. Kaiser, *ibid.*, 89, 5179 (1967).

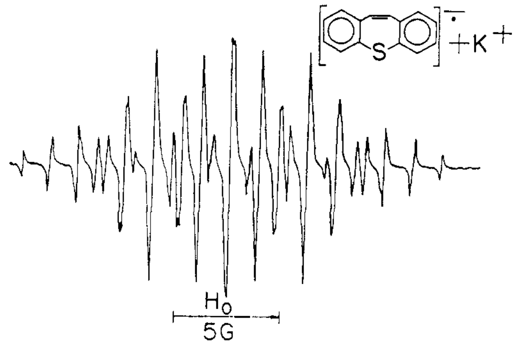


Figure 1.

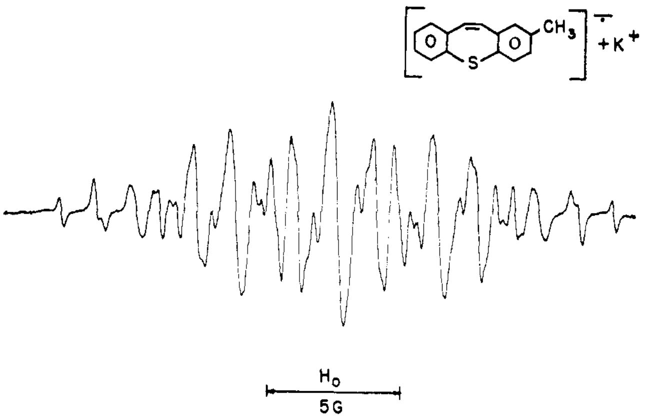
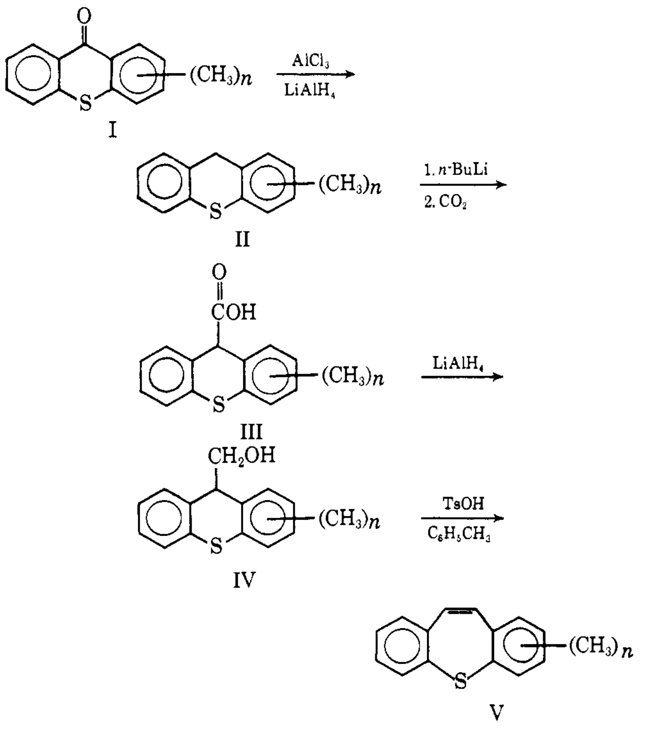
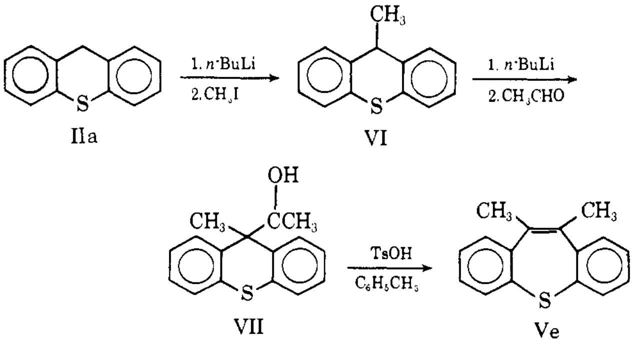


Figure 2.





constant of 0.8 gauss. These splittings arise from the three ring protons in the 1, 6, and 9 positions, and from the three protons on the methyl group in the 4 position, respectively, indicating that A_4 = 1.41 gauss in the parent radical.

The anion radical of 1,4-dimethyl-DBTP gives a poorly resolved esr spectrum. The width of this spectrum indicates that A_1 cannot be as great as 3.79 gauss. Thus we assign A_1 = 1.41 gauss.

The width of the esr spectrum of the anion radical of 10,11-dimethyl-DBTP indicates that A_{10} must be large. A septuplet with a coupling constant of 4.3 gauss is seen which arises from the six methyl protons, and this confirms our assignment of A_{10} = 3.79 gauss. Because of the complexity of the spectrum, we did not analyze it further.

Experimental Section

Radicals were prepared by potassium metal reduction in 1,2-dimethoxyethane (DME) solutions using the usual high vacuum techniques. Esr spectra were recorded at −50° since the radicals were found to decompose rapidly at higher temperatures. Spectra were recorded on a Varian Model V4500 spectrometer equipped with a 9-in. magnet and Fieldial control.

Preparation of Compounds. The preparation of dibenzo[*b,f*]-thiepin was first reported by Bergmann and Rabinovitz[8] in 1960. We found it advisable to revise their method of synthesis somewhat in order to make methyl-substituted derivatives of this compound.

Our synthetic route for DBTP and ring-methylated DBTP is given by steps I–V. A similar route (steps IIa–Ve) yielded 10,11-dimethyl-DBTP. Thioxanthone and ring-methylated thioxanthones (I) were prepared as described in a previous paper.[7]

Thioxanthenes (II). Thioxanthene (IIa) was prepared from thioxanthone (Ia) by the method of Graebe and Schultess,[9] or by the method of Bergmann and Rabinovitz.[8]

We found that we were unable to use HI and red phosphorus for the reduction of methyl-substituted thioxanthones. The method which Blackwell[10] used to reduce benzophenone to diphenylmethane was modified to accomplish this reduction.

$AlCl_3$ (0.35 mole, 46.7 g) was dissolved in 100 ml of ether, and the solution was added slowly to a suspension of 0.175 mole (6.6 g) of $LiAlH_4$ in 100 ml of ether. This solution was cooled in an ice bath and 0.1 mole of I was added as a solid over a period of 10 min. The solution was then refluxed for 0.5 hr and the excess $LiAlH_4$ was carefully destroyed with water. The solution was then made basic with NaOH to destroy the fine gray residue which was present as an impurity in the $LiAlH_4$. It was acidified again with HCl to dissolve the aluminum oxide which had precipitated. The layers were separated, and the aqueous layer was washed with ether. The combined ether layers were washed with water and dried over $MgSO_4$, and the ether was evaporated.

2-Methylthioxanthene (IIb) was crystallized from cyclohexane giving an 87% yield of white prisms, mp 79.5–81.5°.

2,4-Dimethylthioxanthene (IIc) was dissolved in hexane and decolorized with Merck acid-washed alumina. Evaporation of the hexane gave a 66% yield of a colorless oil which solidified on standing, mp 38–39°.

1,4-Dimethylthioxanthene (IId) was recrystallized from ethanol giving a 75% yield of white needles, mp 81–82°.

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[8] E. D. Bergmann and M. Rabinovitz, *J. Org. Chem.*, **25**, 828 (1960).

[9] C. Graebe and O. Schultess, *Ann.*, **263**, 1 (1891).

[10] J. Blackwell, *J. Chem. Soc.*, 1405 (1961).

Thioxanthene-9-carboxylic Acids (III). II (0.05 mole) was dissolved in 250 ml of dry ether. The solution was cooled in an ice bath and 35 ml of 1.6 *M n*-butyllithium (Foote) was slowly added with a hypodermic syringe. The solution was then refluxed for 1 hr and allowed to cool. A large excess of Dry Ice was then added as rapidly as possible, and the reaction was worked up by conventional procedures. Yields depend very much on the rate of addition of Dry Ice. If it is added too slowly, yields are poor, and a red impurity is formed which is difficult to remove. Almost quantitative yields could be obtained for each of the acids with this procedure.

Thioxanthene-9-carboxylic acid (IIIa) was recrystallized from chloroform-cyclohexane, mp 226–227° (lit.[11] 228–229°).

2-Methylthioxanthene-9-carboxylic acid (IIIb) was recrystallized from acetone, mp 223–223.5°.

2,4-Dimethylthioxanthene-9-carboxylic acid (IIIc) was recrystallized from acetone giving white needles, mp 221–222.5°.

1,4-Dimethylthioxanthene-9-carboxylic acid (IIId) was recrystallized from acetone giving white needles, mp 242–247° dec.

9-Hydroxymethylthioxanthenes (IV). LiAlH$_4$ (0.1 mole) was dissolved in 200 ml of dry ether. The solution was cooled in an ice bath, and 0.05 mole of III was added as a solid over a period of 10 min. The solution was refluxed for 2 hr and worked up by conventional procedures. Yields varied from 85 to 100% for each compound.

9-Hydroxymethylthioxanthene (IVa) was recrystallized from CCl$_4$, mp 110–111° (lit.[8] 110–111°).

2-Methyl-9-hydroxymethylthioxanthene (IVb) was purified by chromatography on Merck alumina in hexane–chloroform solvent. It was obtained as a colorless oil which solidified on standing, mp 48–50°.

2,4-Dimethyl-9-hydroxymethylthioxanthene (IVc) was recrystallized from ethanol giving white needles, mp 114.5–116°.

1,4-Dimethyl-9-hydroxymethylthioxanthene (IVd) was recrystallized from ethanol giving white needles, mp 122.5–123.5°.

9-Methylthioxanthene (VI). IIa was lithiated as before, and the lithium salt was treated with a large excess of freshly distilled methyl iodide. The red color of the lithium salt disappeared within a few minutes after the methyl iodide was added. The solution was worked up as usual. Recrystallization from methanol give a 50% yield of white needles, mp 81–82° (lit.[12] 84.5°).

9-Methyl-9-(α-hydroxyethyl)thioxanthene (VII). VI was lithiated by the same procedure as IIa had been in the preparation of VI. A large excess of freshly distilled acetaldehyde was added to the solution of the lithium salt. The solution was worked up as usual. Evaporation of the ether solvent yielded a yellow oil. This was dissolved in ethanol and decolorized with Norit A. The ethanol was then evaporated leaving a 75% yield of colorless oil which was finally crystallized by dissolving it in a minimum of ether and storing in the freezer for a day. The *dl* alcohol melted at 71–72.5°.

Dibenzo[*b,f*]thiepins (V). One gram of IV or VII and 5 g of *p*-toluenesulfonic acid were added to 50 ml of toluene. The mixture was refluxed for 3.5–4 hr, during which time a red or purple color formed. Most of the toluenesulfonic acid precipitated on cooling. Water was added to dissolve the sulfonic acid. The toluene layer was separated and the toluene evaporated, leaving an oil. This oil was dissolved in ether and the aqueous layer extracted with ether. The combined ether solution was washed with water until the water layer was no longer acid to litmus. The ether layer was then dried with MgSO$_4$ and the ether evaporated to give the crude product.

Dibenzo[*b,f*]thiepin (Va) was passed through a silica gel column using hexane as the solvent, and then recrystallized from methanol, giving 0.74–0.85 g (80–91% of theory) of pale yellow needles, mp 87–88° (lit.[8] 89–90°).

2-Methyl-DBTP (Vb) was recrystallized several times from methanol. Pale yellow plates were obtained in 50% yield, mp 76.5–77.5°.

Anal. Calcd for $C_{15}H_{12}S$: C, 80.31; H, 5.39. Found: C, 80.50; H, 5.58.

2,4-Dimethyl-DBTP (Vc) was passed through a silica gel column using a mixed solvent of 20% HCCl$_3$ in hexane. It was crystallized by placing a methanol solution in the freezer for a day, giving a 65% yield of yellow needles, mp 39–40°.

Anal. Calcd for $C_{16}H_{14}S$: C, 80.62; H, 5.92. Found: C, 80.15; H, 5.86.

1,4-Dimethyl-DBTP (Vd) was recrystallized from methanol. The first crop yielded 0.56 g (60% of theory) of pale yellow needles, mp 81–81.5°.

Anal. Calcd for $C_{16}H_{14}S$: C, 80.62; H, 5.92. Found: C, 80.82; H, 5.94.

10,11-Dimethyl-DBTP (Ve) was recrystallized from methanol giving a 60% yield of white plates, mp 94–95°.

Anal. Calcd for $C_{16}H_{14}S$: C, 80.62; H, 5.92. Found: C, 80.53; H, 5.96.

Discussion

The spin distribution in the dibenzo[*b,f*]thiepin anion radical is much more similar to that found for the stilbene anion radical[13] than that for the dibenzocyclooctatetraene species.[14] The coupling constants for these radicals are compared in Table III.

Table III. Coupling Constants Measured from the Esr Spectra of the Stilbene, Dibenzo[*b,f*]thiepin, and 1,2:5,6-Dibenzocyclooctatetraene Anion Radicals (in gauss)

Ring position	Stilbene[a]	DBTP	Dibenzocyclo-octatetraene
1	1.90, 2.96	1.41	0.20
2	0.30, 0.81	0.0	1.80
3	3.89	3.79	1.80
4	0.81, 0.30	1.41	0.20
Vinyl	4.37	3.79	2.60

[a] In the stilbene anion radical neither the two *ortho* nor the two *meta* positions are equivalent. It is not known to which *ortho* or *meta* position the coupling constants correspond.

The observation that the spin density in the dibenzo[*b,f*]thiepin radical at the position *para* to the sulfide residue is small indicates that conjugation through the sulfide bridge is much weaker than conjugation through the vinyl residue. It would be anticipated that the interaction between the sulfide sulfur and the aromatic system should be weak if only the 3p$_y$ orbital is available for conjugation.

Acknowledgments. We gratefully acknowledge the support of the Petroleum Research Fund, and we wish to thank Professor E. D. Bergmann who kindly gave us a sample of DBTP for preliminary studies.

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(13) R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, **41**, 3272 (1964); C. S. Johnson, Jr. and R. Chang, *ibid.*, **43**, 3183 (1965); R. Chang and C. S. Johnson, Jr., *ibid.*, **46**, 2314 (1967). Esr studies on the rate of electron transfer between the stilbene radical and *trans*-stilbene suggest that the radical has the *trans* configuration.

(14) A Carrington, H. C. Longuet-Higgins, and P. F. Todd, *Mol. Phys.*, **8**, 45 (1964).