Electron Spin Resonance and Nuclear Magnetic Resonance Studies of Cation Radicals Derived from 9,9-Dialkylthioxanthenes

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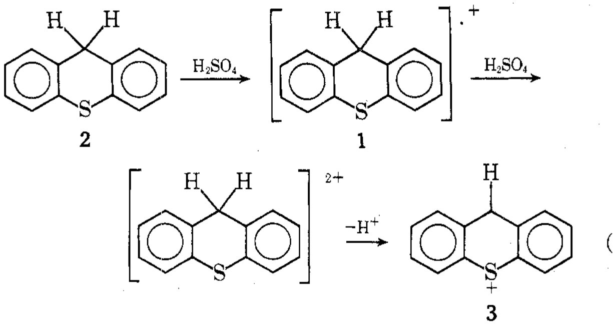
The cation radical of 9,9-dimethylthioxanthene has been prepared in acidic solution and characterized by esr and pmr spectroscopy. Broadening of the aryl region of the pmr is discussed in terms of exchange phenomena. A MO calculation of spin densities in the cation radical is presented. An acidic solution of 9-methyl-9-isopropylthioxanthene is weakly paramagnetic and is presumed to contain the corresponding radical cation.

While the so-called "magic acids" appear to protonate sulfides and sulfoxides with little immediate decomposition,[1,2] sulfuric acid or other one-electron oxidants convert diaryl sulfides into the cation radical of the diaryl sulfides.[3] The treatment of diaryl sulfoxides with sulfuric acid also affords the cation radical of the corresponding diaryl sulfide.[3d] One limitation on this route to cation radicals is that the diaryl compound must be substituted with at least one electron-donating group. Thus Shine and coworkers[3b] were unable to form diphenyl sulfide cation radical while Oae and Kunieda[3d] formed a poorly characterized radical from phenyl *p*-tolyl sulfoxide.

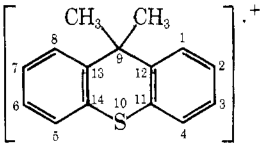
Previous attempts[4] to prepare and detect the cation radical of thioxanthene (**1**) have been fruitless, although it has been postulated[4] as an intermediate in the conversion of thioxanthene (**2**) to the thioxanthylium cation (**3**) (eq 1). It occurred to us that replacement of the methylene hydrogens of **2** with alkyl groups would prevent the formation of **3** by proton loss and that a stable cation radical of the thioxanthene system might, therefore, result. This expectation has been realized and we describe below our electron spin resonance and nuclear magnetic resonance studies of the 9,9-dialkylthioxanthene system in oxidizing acidic media. Because of their significance in other nmr studies,[5] we have employed 9,9-dimethylthioxanthene (**4**) and 9-methyl-9-isopropylthioxanthene (**5**) in this investigation.



(1)

Results

Electron Spin Resonance. When 5 μl of 9,9-dimethylthioxanthene (**4**) is treated with 0.5 ml of 97% sulfuric acid, an immediate green color is observed. The resulting solution gives an electron spin resonance (esr) spectrum consisting of 21 lines. Analysis indicates that the spectrum is a quintet of quintets with four lines lost by overlap. The hyperfine splittings are $a^{H}(4\ H) = 3.10 \pm 0.05$ G and $a^{H}(4\ H) = 0.68 \pm 0.05$ G, with a g value of 2.00668 ± 0.00003. Shine and coworkers[3b] found for *p*-tolyl sulfide cation radical $a_{CH_3}^{H} = 4.9$ G, $a_{o\text{-}H}^{H} = 2.7$ G, and $a_{m\text{-}H}^{H} = 0.6$ G, with a g value of 2.00737. The initial color of their solution also was green. This similarity of splitting constants and color supports our assignment of this spectrum to the cation radical of 9,9-dimethylthioxanthene (**6**), with the $a^{H} = 3.10$ G splitting coming from the ortho- and para-like positions 4 and 2 and $a^{H} = 0.68$ G splitting arising from the meta-like positions 3 and 1. We would anticipate that a_4^{H} and a_2^{H} are really different and likewise a_3^{H} and a_1^{H}, but that these differences are obscured by the line widths (*ca.* 0.3 G). The radical could also be formed in 75% CH_3NO_2–25% H_2SO_4, but there was no improvement in the resolution.



6

Reaction of 5 μl of **4** with 0.5 ml of trifluoroacetic acid gave a spectrum consisting of a single broad line which defied further attempts to resolve it. The total width of the line coincided exactly with the total width at the resolved spectrum in H_2SO_4. A broad unresolved line was also obtained using 50% CH_3NO_2–50% CF_3COOH as a medium. We believe this result can best be interpreted in connection with the nmr results (*vide infra*).

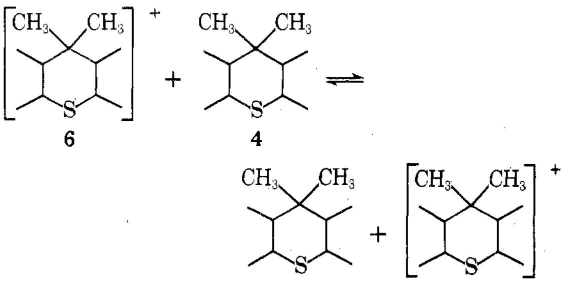
Nuclear Magnetic Resonance. A 10% (w/v) solution of **4** in trifluoroacetic acid produces a light green solution whose nmr spectrum consists of a sharp singlet (CH_3) at δ 1.69 and two broad, *unstructured* resonances centered at δ 7.2 and 7.6. This is to be contrasted to the spectrum of **4** in carbon disulfide which possesses a sharp singlet (CH_3) at δ 1.63 and a highly structured aromatic absorption extending from 6.9 to 7.7.[6] The presence of broadened aryl absorptions in trifluoroacetic acid indicates that a paramagnetic species is produced; however, its presence does not broaden the resonance of the methyl groups at C-9. This is interpreted in terms of eq 2, with rapid exchange between a low concentration of radical cation **6** and the parent sulfide, **4**.

This result is consistent with what is known of electron exchange between radical anions[7] and cations[8] and their neutral precursors. In the nmr spectra the lines are broad-

Table I
Theoretical and Experimental Spin Densities in the 9,9-Dialkylthioxanthene System[a]

	Exptl ρ	ρ, K_{CS} = 0.65	ρ, K_{CS} = 0.8	ρ, K_{CS} = 1.0
ρ_1[b]	−0.024	−0.040	−0.042	−0.045
ρ_2	+0.111	+0.098	+0.105	+0.122
ρ_3	−0.024	−0.022	−0.021	−0.026
ρ_4	+0.111	+0.067	+0.087	+0.112
ρ_{11}		+0.040	+0.019	+0.002
ρ_{12}		+0.087	+0.108	+0.129
$\rho_{10}(\rho_S)$		+0.540	+0.490	+0.411

[a] Experimental spin densities calculated from McConnell's equation with $Q_{CH}{}^{H} = -28.0$ G. Signs of experimental spin densities are assigned from the theoretical calculations. For the McLachlan calculations $\lambda = 1.2$. [b] See structure 6 for numbering.



(2)

ened and shifted with the amount of the broadening proportional to the square of the hyperfine splitting. Since the methyls of 6 have no measurable hyperfine splitting, they remain unbroadened.

Attempts to obtain resolved nmr spectra of 4 in 96% sulfuric acid have been foiled, thus far, by the insolubility of 4 in this medium at 25–30°. Even at elevated temperatures (~60°) the solubility did not improve sufficiently to provide acceptable data while prolonged contact with 96% acid at elevated temperatures appeared to lead to decomposition.[9]

The behavior of 9-methyl-9-isopropylthioxanthene (5) in 96% sulfuric acid was similar to that of 4 in 96% sulfuric acid and useful nmr data could not be obtained.[10]

Molecular Orbital Calculations. A very thorough molecular orbital study of *p,p′*-dihydroxydiphenyl sulfide and diphenyl ether cation radicals has been carried out by Sullivan and Shine.[3c] These authors calculated spin densities from McConnell's equation $a_{CH}{}^{H} = \rho Q_{CH}{}^{H}$[11] using a $Q_{CH}{}^{H}$ value of 28 G. Theoretical spin densities were obtained *via* McLachlan's modification of simple HMO theory,[12] using a fixed set of parameters for the OH group and adjusting the sulfur parameters. A set of sulfur parameters which they found satisfactory was $h_S = 1.11$ and $K_{CS} = 0.65$.[13] We carried out a similar set of calculations using those parameters. The inductive effect of the dimethyl-substituted carbon was accounted for by assigning C-12 and -13 (see 6 for numbering) a parameter $h_{C\text{-sub}} = -0.5$.

The benzene rings of *p,p′*-dihydroxyldiphenyl sulfide are presumed to be twisted, a condition which undoubtedly exists in di-*p*-tolyl sulfide and its cation radicals. Crystallographic studies show that the thioxanthene system is folded rather than planar.[14] The cation radical, however, may be more planar than its parent. When one compares the *g* values of 9,9-dimethylthioxanthene and di-*p*-tolyl sulfide cation radicals, the smaller *g* value of the former (about 0.0007 less) indicates less spin density on the sulfur in the thioxanthene radical. This is consistent with a closer approach to planarity in 6, as opposed to the tolyl sulfide radical, with increased spin delocalization on the rings. One expects that as radical cation 6 approaches planarity the value of the carbon–sulfur resonance integral should increase. To model this behavior, we also carried out calculations for $K_{CS} = 0.8$ and 1.0. The results of these calculations and the experimental spin densities are shown in Table I.

Those calculations carried out with $K_{CS} = 1.0$ seem to fit the experimental data reasonably well. An increase in K_{CS} results in a decrease in sulfur spin density and a concomitant increase in ring spin density. The spin densities at C-2 and -4, with $K_{CS} = 1.0$, are sufficiently similar that one might expect the splitting constant differences to be lost in the line width. One might have expected to see differences between C-1 and -3 but, of course, the theoretical spin densities need not exactly equal the experimental spin densities.

It is also possible to use the *g* value to see which of our sulfur spin densities are in agreement with the results of Sullivan and Shine. As pointed out by these authors, Stone's theory of *g* values[15] gives the following expression for the *g* value of a π organic radical

$$g_{\text{rad}} = 2.0023 + \Sigma_{\text{Het}}\rho_{\text{Het}}\gamma_{\text{Het}} + \Sigma_{C}\rho_{C}\gamma_{C}$$

In this equation, the first term expresses the *g* value for a free electron. The second term accounts for the effects of heteroatoms with the γ parameter dependent on the spin–orbit coupling of the particular heteroatom and the energy of the molecular orbital containing the unpaired electron. The third term is an identical expression for carbon atoms. If one ignores the sulfur lone pair, diphenyl sulfide cation radicals are isoelectronic with diphenylmethyl radical. Stone's theory predicts that the *g* values of neutral odd alternant radicals should be 2.0027. Therefore, we take $\Sigma_C\rho_C\gamma_C$ as $\simeq 0.0004$. The *g* value of *p,p*-dihydroxydiphenyl sulfide cation radical is 2.00687. Using parameters $K_{CS} = 0.65$ and $h_S = 1.11$, Sullivan and Shine calculated for this radical that $\rho_S = 0.434$ and $\rho_O = 0.026$. Defining Δg as the difference between the experimental *g* value and 2.0027, we derive the following expression

$$\frac{\Delta g(\text{dihydroxydiphenyl sulfide radical})}{\Delta g(\text{dimethylthioxanthene radical})} = \frac{\rho_S\zeta_S + 2\rho_O\zeta_O}{\rho_S\zeta_S}$$

In this expression we have assumed that the orbital energies are about the same so that we can replace γ with ζ, the spin–orbit coupling parameter. We can put in the requisite numbers and solve for ρ_S in the thioxanthene derivative. The answer obtained is

$$\frac{0.00417}{0.00397} = \frac{0.434(382) + 2(0.026)(151)}{\rho_S(382)}$$

$\rho_S = 0.433$. This, too, is fairly close to the value obtained for $K_{CS} = 1.0$.

Our results above can be used to estimate ρ_S for di-*p*-tolyl sulfide cation radical. It should be simply 0.00397/0.00467 = 0.433/ρ_S, which gives $\rho_S = 0.509$.

The experimental results of Sullivan and Shine were obtained in the $AlCl_3$–CH_3NO_2 system. Considering the differences in solvent systems, our lack of experimental resolution, and the deficiencies in the theory, it is gratifying that our results are reasonably consistent with those of Sullivan and Shine.

Experimental Section

Nmr spectra were recorded on a Varian Model HA-100D spectrometer operating at 100 MHz with a probe temperature of 34.5°. Chemical shifts are reported with respect to internal tetramethylsilane. Esr spectra were obtained with a Varian V-4500 epr spectrometer equipped with a Varian Fluxmeter and a Hewlett Packard 5245L electronic counter. The solutions were not deoxygenated prior to obtaining the esr spectra. The *g* values were determined with reference to a 2.2×10^{-3} *M* solution of 4-acetamido-2,2,6,6-tetramethylpiperidinyl-1-oxyl in benzene, sealed in a capillary tube and taped to the aqueous sample cell. The *g* value of the standard was first determined with reference to that of *p*-benzosemiquinone in *n*-butyl alcohol. The semiquinone value given by Segal *et al.* is 2.004679.[16] Allendoerfer has pointed out[17] that the values of Segal *et al.* should be lowered by 14×10^{-6}. The value we used was 2.004665. The measured *g* value for the nitroxyl is 2.00603 ± 0.00003 with $a^N = 15.29 \pm 0.10$ G. The latter splittings were directly determined with the fluxmeter. By comparison, the g value of di-*tert*-butyl nitroxide in toluene is 2.00606 ± 0.00001 with $a^N = 15.26 \pm 0.07$ G.[18] To test our procedure in a similar solvent system, we measured a *g* value of 2.00808 for thianthrene cation radical in sulfuric acid. The literature value is 2.0081.[19]

9,9-Dimethylthioxanthene (4) was prepared as described earlier.[20]

9-Methyl-9-isopropylthioxanthene (5). A suspension of 9-methylthioxanthene[21] (3.50 g, 16.5 mmol) in 100 ml of ether was cooled to 0-5° (ice bath) and treated with 6.75 ml of a 22.3% solution of *n*-butyllithium in hexane. After stirring for 10 min at 25°, a solution of isopropyl bromide (2.01 g, 16.4 mmol) in 25 ml of ether was added to the suspension containing the carbanion of 9-methylthioxanthene. The resulting suspension was stirred at room temperature for 10 hr and then diluted with water (100 ml). The ethereal layer was separated, washed with water (2 × 100 ml), dried ($MgSO_4$), and concentrated (stream of nitrogen gas) to afford a viscous, orange oil. Molecular distillation (60° (0.1 Torr)) of this oil yielded 4.10 g (16.2 mmol, 99%) of **5** as a clear, light-yellow oil. This material was essentially homogeneous on tlc; mp 39°.

Anal. Calcd for $C_{17}H_{18}S$: C, 80.26; H, 7.13; S, 12.60. Found: C, 80.30; H, 7.19; S, 12.42.

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Registry No.—**4**, 19019-10-4; **5**, 51966-11-1; 9-methylthioxanthene, 16860-11-0.

References and Notes

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(2) Thioxanthene forms an S-protonated cation while 9-methylthioxanthene forms a mixture of cis and trans S-protonated isomers in $HF-SbF_5-SO_2$. In this mixture thioxanthene slowly is converted into the thioxanthylium ion; manuscript in preparation.

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(9) Solutions of **4** in 96% sulfuric acid which were quenched (water) immediately after preparation did not produce any readily discernible secondary reaction products (tlc, silica gel, chloroform eluent, uv and iodine visualization).

(10) A solution of **5** in a 1:1 mixture of trifluoroacetic acid–trifluoroacetic anhydride, prepared on a vacuum line, exhibited normal methyl and isopropyl resonances and a highly structured aryl multiplet (δ 7.05–7.60). The spectrum of this sealed sample was essentially unchanged after 28 days at 25°. Admission of pure oxygen produced an immediate blue-green hue and an nmr spectrum which possessed normal, but slightly broadened, alkyl resonances and an aryl region exhibiting only two broad, unstructured humps centered near δ 7.5 and 8.1.[6] Although relatively insoluble, a mixture of 10.2 mg of **5** in 0.5 ml of 97% sulfuric is *faintly* green and exhibits an esr spectrum (an order of magnitude less intense than **4**). Some hyperfine structure was discernible but spectral analysis was impossible. These data suggest the formation of a radical cation similar to **6**.

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