Physical Properties of α-5,8-Oxido-3,9(17),13-duvatrien-1-ol (α-V).—α-V, recrystallized from hexane or pentane, melts at 109–110°, and shows no selective absorption of ultraviolet light; $[\alpha]^{25}\text{D}$ +77.4°. Infrared absorption occurred at 2.95, 6.05, 9.3, 10.2, 11.1, and 11.6 μ; n.m.r. spectrum, 9.13 (6), 8.72 (6), 5.2 (2), and 4.55–4.9 τ (4).

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.60; active H (1), 0.33; mol. wt., 304. Found: C, 78.86; H, 10.69; active H (tritium exchange), 0.29; mass, 304.

Catalytic Hydrogenation of α-5,8-Oxido-3,9(17),13-duvatrien-1-ol (α-V).—Catalytic hydrogenation of 267 mg. of α-V using Adams' catalyst in ethyl acetate (24 hr. at 3 atm.), followed by chromatography of the product on silicic acid, allowed isolation of 250 mg. of hexahydro α-V, m.p. 117–119°. The infrared absorption of hexahydro α-V was identical with that of hexahydro α-IV and a mixture of hexahydro α-V and hexahydro α-IV melted at 118–119°.

Anal. Calcd. for $C_{20}H_{38}O_2$: C, 77.37; H, 12.33; mol. wt., 310. Found: C, 77.53; H, 12.18; mass, 310.

Dehydration of α-5,8-Oxido-3,9(17),13-duvatrien-1-ol (α-V) to 5,8-Oxido-1(15),3,9(17),13-duvatetraene (XIII).—A mixture of 0.20 g. of α-V, 0.40 g. of potassium hydrogen sulfate, and 20 ml. of anhydrous, peroxide-free dioxane was refluxed for 3 hr. The cooled solution was decanted from the potassium hydrogen sulfate, concentrated, and the residue (190 mg.) chromatographed on Florisil. The fractions eluted by 1:99 ether–hexane yielded a colorless oil (90 mg.) which slowly solidified. The solid, XIII, melted at 66–67°. Crystallization from methyl alcohol raised the melting point to 70–71°. XIII showed infrared absorption at 6.08, 6.25, 10.3, 11.3, and 11.6 μ; $\lambda_{\max}^{\text{cyclohexane}}$ 237 mμ (log ε 4.28); n.m.r. spectrum, 9.12 (6), 8.70 (3), 7.07 (2), 5.55 (1), 5.06 (4), and 3.9–4.6 τ (4).

Anal. Calcd. for $C_{20}H_{30}O$: C, 83.85; H, 10.56; mol. wt., 286. Found: C, 83.03; H, 10.46; mass, 286.

Dehydration and Cyclization of α-5,8-Oxido-3,9(17),13-duvatrien-1-ol (α-V).—A solution of α-V (200 mg.) and *p*-toluenesulfonic acid (120 mg.) in benzene (10 ml.) was refluxed for 30 min., cooled to 25°, diluted with ether (50 ml.), and washed with a total of 25 ml. of 5% sodium carbonate solution. The organic phase, after treatment with anhydrous sodium sulfate, was concentrated to yield 190 mg. of a pale yellow, viscous oil. Chromatography on Florisil yielded a colorless oil which readily solidified. The solid (XIV, 90 mg.) melted at 49–50°. Crystallization from hexane at −27° raised the melting point to 50–51°; $\lambda_{\max}^{\text{cyclohexane}}$ 251 mμ (log ε 3.99). Infrared absorption occurred at 6.15, 9.75, and 12.0 μ; n.m.r. spectrum, 9.25 (3), 9.06 (6), 8.77 (3), 8.22 (3), 6.28 (1), and 3.98 τ (1).

Anal. Calcd. for $C_{20}H_{30}O$: C, 83.85; H, 10.56; mol. wt., 286. Found: C, 83.11; H, 10.44; mass, 286.

Cyclization of 5,8-Oxido-1(15),3,9(17),13-duvatetraene.—A mixture of XIII (25 mg.) and *p*-toluenesulfonic acid (10 mg.) in benzene (5 ml.) was refluxed for 30 min. The reaction mixture was processed as in the preceding section to yield 22 mg. of pale yellow oil. Chromatography on Florisil yielded 13 mg. of a colorless solid, m.p. 46–48°, whose infrared and ultraviolet absorption spectra were identical with those previously recorded for the sample of XIV.

Physical Properties of β-5,8-Oxido-3,9(17),13-duvatrien-1-ol (β-V).—β-V, after recrystallization from hexane, melted at 108–109°, $[\alpha]^{25}\text{D}$ +72.5°. β-V shows no selective ultraviolet absorption other than end absorption; infrared spectrum, 3.10, 6.10, 8.95, 9.30, 10.25, 10.82, 11.30, and 11.60 μ; n.m.r. spectrum, 9.12 (6), 8.70 (3), 8.62 (3), 4.50–5.52 (6).

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.60; mol. wt., 304. Found: C, 78.77; H, 10.64; mass, 304.

A mixture of β-V and α-V melted at 70–95°.

Dehydration of β-5,8-Oxido-3,9(17),13-duvatrien-1-ol (β-V).—A mixture of β-V (188 mg.), potassium hydrogen sulfate (400 mg.), and 20 ml. of dioxane was heated under reflux for 3 hr. The residue from concentration of the dioxane solution was chromatographed on Florisil; the dehydration product was eluted with 1% ether in pentane. The infrared, mass, and n.m.r. spectra of the unsaturated ether (61 mg.), m.p. 70–71° after recrystallization from methyl alcohol, were identical with the spectra of the product obtained by potassium hydrogen sulfate dehydration of α-V.

Anal. Calcd. for $C_{20}H_{30}O$: C, 83.85; H, 10.56; mol. wt., 286. Found: C, 84.14; H, 10.25; mass, 286.

Ion Radicals. IV.[1] The Electron Spin Resonance Spectra of Substituted Thianthrenes in Sulfuric Acid Solution

H. J. SHINE, C. F. DAIS, AND R. J. SMALL

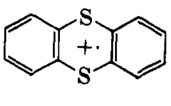
The Department of Chemistry, Texas Technological College, Lubbock, Texas

Received May 20, 1963

Fifteen thianthrenes with substituents in the 1-, 2-, and 2,7-positions have been prepared. Each of the thianthrenes dissolves in 96% sulfuric acid to give a colored, paramagnetic solution. The e.s.r., ultraviolet, and visible spectra of these solutions have been recorded. The hyperfine structures of the e.s.r. spectra are in accord with the recent proposals[1] for the structure of the thianthrene positive ion radical and the major coupling of the 2,3,7,8-protons. The *g*-values of all but one of the thianthrenes were close to 2.008–2.009. The exception was 2,7-dibromothianthrene with a *g*-value of 2.0101. Line widths and hyperfine splittings are reported.

Solutions of thianthrene in concentrated sulfuric acid are purple in color[2,3] and are paramagnetic.[1,4-10] Solutions of thianthrene in solvents containing Lewis acids such as aluminum chloride[1b,8,9] and antimony pentachloride[8,9] exhibit paramagnetic resonance.

The formation of a paramagnetic species in these systems has been interpreted[1,7,9,10] as a one-electron oxidation to give the ion radical I.



I

---

[1] (a) Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963; (b) part I, H. J. Shine and L. Piette, *J. Am. Chem. Soc.*, **84**, 4798 (1962); (c) part II, H. J. Shine, C. F. Dais, and R. J. Small, *J. Chem. Phys.*, **38**, 569 (1963); (d) supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, grants AF-AFOSR-61-48 and AF-AFOSR-23-63, to whom we express our thanks.

[2] K. Fries and W. Vogt, *Ber.*, **44**, 756 (1911).

[3] K. Fries and W. Vogt, *Ann.*, **381**, 312 (1911).

[4] J. M. Hirshon, D. M. Gardner, and C. R. Fraenkel, *J. Am. Chem. Soc.*, **75**, 4115 (1953).

[5] J. E. Wertz and J. Vivo, *J. Chem. Phys.*, **23**, 2193 (1955).

[6] A. Fava, P. B. Sogo, and M. Calvin, *J. Am. Chem. Soc.*, **79**, 1078 (1957).

[7] W. C. Needler, Ph.D. thesis, University of Minnesota, August, 1961 [*Dissertation Abstr.*, **22**, 3873 (May, 1962)]. At the time of submission of our first papers in this series we were not aware of the work of Professor J. E. Werz and Dr. Needler. We wish to thank Dr. E. T. Kaiser, Washington University, for calling our attention to this thesis.

[8] M. Kinoshita and H. Akamatu, *Bull. Chem. Soc. Japan*, **35**, 1040 (1962).

[9] M. Kinoshita, *ibid.*, **35**, 1137 (1962).

[10] E. A. C. Lucken, *J. Chem. Soc.*, 4963 (1962).

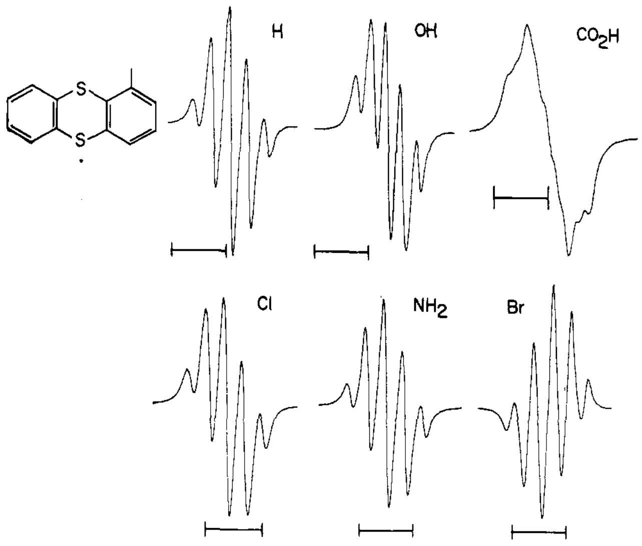


Fig. 1.—E.s.r. spectra of 1-substituted thianthrenes in 96% sulfuric acid. The scale calibration shown is 4 gauss. Field increases from right to left in each case.

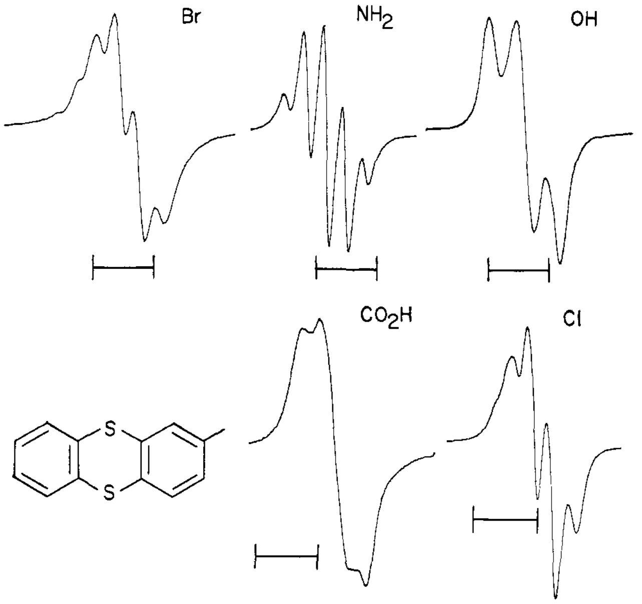


Fig. 2.—E.s.r. spectra of 2-substituted thianthrenes in 96% sulfuric acid. The scale calibration shown is 4 gauss. Field increases from right to left in each case.

Characteristic 5-line, 1:4:6:4:1, e.s.r. spectrum observed is consistent with the symmetrical radical I in which the spin coupling of only four of the protons is large enough to be observed. The four effective protons have been described as those in the 2-, 3-, 7-, and 8-positions.[1] As a test of this assignment a number of substituted thianthrenes were made and the spin and absorption spectra of their sulfuric acid solutions were recorded. The e.s.r. spectra of the 2,7-dimethyl- and 2,7-dichlorothianthrenes in sulfuric acid demonstrated the validity of the assignment.[1c,7] We now wish to report the spectral characteristics of a number of substituted thianthrenes, so that comparisons of 1-substituents with 2- and 2,7-substituents may be made.

Results and Discussion

E.s.r. Spectra.—With some exceptions the hyperfine structures of the e.s.r. spectra (Fig. 1–3) are clearly understandable on the basis of the assignments made previously.[1] Each of the 1-substituted thianthrenes has a 5-line spectrum, except the 1-carboxythianthrene. On the other hand, except for 2-aminothianthrene, substituents in the 2- and 2,7-positions cause marked changes from the 5-line pattern of the parent molecule. The spectra of the 2,7-dihydroxy- and 2,7-di-*t*-butylthianthrenes have hyperfine structures consistent with coupling with the 3,8-protons. The 3-line spectrum of 2,7-dichloro- and the 9-line spectrum of 2,7-dimethylthianthrene already have been discussed.[1c] The details of the variations in hyperfine structures of the 2-substituted thianthrenes are not explainable with certainty at this stage. The spectrum of 2-bromothianthrene shows marked lack of symmetry and this could not be removed by diluting or warming the solution in a capillary tube to about 60°. A similar, but less marked, dissymmetry is obtained with 2-chlorothianthrene. It is possible that these characteristics are due to *g*-anisotropy. The reasons for the 5-line pattern of 2-aminothianthrene and the pattern of the 1-carboxylic acid are also unknown. It is evident, however, that large distortions from the parent 5-line pattern occur mostly when substituents are placed in the 2- and 2,7-positions, and that this is what the earlier assignment[1] of proton coupling predicts.

The *g*-values and hyperfine splittings for the fifteen compounds are listed in Table I. It is seen that all of the *g*-values are larger than the free spin value of 2.0023. The substituents do not cause much variation in the *g*-values except in the case of the 2,7-dibromothianthrene. It is evident from the over-all splittings (about 4 to 13 gauss) that there is a larger spin density on the sufur atoms than on the other ring atoms. The *g*-values indicate also that, as with many other sulfur-containing radicals, spin-orbit coupling is occurring. It is possible that this is responsible for the rather large hyperfine line widths in the thianthrene cation radicals compared say, with those of the anthracene cation radical. This may also be the reason for the single broad line of the 2,7-dibromothianthrene cation radical.

TABLE I

ELECTRON SPIN RESONANCE SPECTRA

Thianthrene derivative	No. of lines	Hyperfine splitting[a]	Over-all splitting[a]	*g*-Values
Thianthrene	5	1.32	5.26	2.0081[d]
Monoxide	5	1.32	5.30	2.0081
1-NH_2	5	1.31	5.24	2.0081
2-NH_2	5	1.27	5.18	2.0080
1-Br	5	1.40	5.54	2.0081
2-Br	4[b]	[c]	6.7	2.0091
1-Cl	5	1.35	5.32	2.0081
2-Cl	3[b]	[c]	4.8	2.0079
1-OH	5	1.27	5.08	2.0081
2-OH	3	1.91	3.81	2.0077
1-COOH	[b]	[c]	5.6	2.0082
2-COOH	3[b]	[c]	3.6	2.0082
2,7-Me_2	9	1.65	13.2	2.0088
2,7-$(OH)_2$	3	1.90	3.79	2.0076
2,7-Cl_2	3	1.49	3.26	2.0083
2,7-Br_2	1	[c]	3.72	2.0101
2,7-(*t*-Bu)$_2$	3	1.60	3.21	2.0078

[a] In gauss. [b] Poorly resolved or unsymmetrical spectrum. [c] Not measurable. [d] Ref. 5 gives 2.0078, 2.0081; ref. 6 gives 2.009; ref. 8 gives 2.0083; ref. 9 gives 2.0080.

TABLE II

ABSORPTION SPECTRA IN THE VISIBLE AND ULTRAVIOLET OF SUBSTITUTED THIANTHRENES DISSOLVED IN 96% SULFURIC ACID

Substituent	Time[a]	λ, mμ	$\epsilon \times 10^{-4}$	Time[a]	λ, mμ	$\epsilon \times 10^{-4}$	λ, mμ	$\epsilon \times 10^{-4}$
H	5 d	546	0.89	5 d	290	3.80	270	3.15
1-NH_2	30 m	539	0.52	70 m	290	2.61	271	2.45
	10 d	539	0.52	10 d	290	2.61	271	2.45
2-NH_2	10 m	531	0.62	25 m	290	3.88	274	3.05
	5 d	524	0.97	1 d	290	4.80	274	sh.[b]
	10 d	524	0.97	10 d	290	5.02	274	sh.[b]
1-OH	30 m	528	0.74	2 h	[c]		273	2.54
	5 d	515	0.77	1 d	[d]		[d]	
	10 d	515	0.77	10 d	[d]		[d]	
2-OH	30 m	597	1.08	2 h	291	6.90	[e]	
	5 d	592	1.01	1 d	291[f]	6.37	[e]	
	10 d	592	0.96	5 d	291[f]	5.50	[e]	
1-Cl	5 d	539	0.85	5 d	291[g]	2.84	274	3.10
	10 d	539	0.85	10 d	291[g]	2.84	274	3.10
2-Cl	5 d	572	1.09	5 d	294	4.91	274	3.13
	10 d	572	1.09	10 d	294	4.91	274	3.13
2-Br	5 d	584	1.18	5 d	295	5.23	275	3.23
	10 d	584	1.18	10 d	295	5.23	275	3.23
1-COOH	10 m	538	1.09	1 h	291	4.26	274	sh.[b]
	5 d	537	1.11	1 d	291	4.44	274	sh.[b]
	10 d	537	1.08	5 d	291	4.44	274	sh.[b]
2-COOH	15 m	539	0.72	1 h	300	3.97	[e]	
	5 d	534	0.96	1 d	300	4.30	[e]	
	10 d	534	0.96	10 d	300	4.63	[e]	
2,7-$(OH)_2$	5 m	604	1.15	1 h	333[h]	2.55	296[h]	3.60
	5 d	540	1.10	1 d	333	3.80	296	3.20
	10 d	540	1.10	10 d	333	5.37	296	2.55
2,7-$(Cl)_2$	6 d	585	1.20	6 d	297	4.80	276	2.62
	10 d	585	1.34	10 d	297	5.00	276	2.76
2,7-$(Br)_2$	14 d	600	[i]	14 d	300	[i]	277	[i]
2,7-$(Me)_2$	30 m	580	1.22	20 m	295	4.40	273	2.59
	4 d	580	1.22	4 d	295	4.40	273	2.59
2,7-(*t*-$Bu)_2$	1 d	585	1.28	1 d	296	4.53	273	2.82
	3 d	585	1.28	3 d	296	4.53	273	2.82

[a] From first contact of solute with acid in minutes (m), hours (h), or days (d). [b] Shoulder. [c] A broad band with broad maxima at 315 (ϵ 2.08 × 10^4) and 295 mμ $(1.88 \times 10)^4$. [d] No maximum at 273 mμ; instead a broad band with maxima at 296 (ϵ 2.52 × 10^4) and 281 mμ (2.32 × 10^4). [e] No maxima in this region. [f] A new small peak appeared at 318 mμ (ϵ 2.60 × 10^4). [g] Shoulder at 299 mμ (ϵ 2.50 × 10^4). [h] The change in absorbance at these λ-values was accompanied by an isosbestic point at 305 mμ. [i] Compound too insoluble to determine reliably.

Electrolytic Oxidation.—The conclusion that the structure of the thianthrene positive ion radical was I suggested that anodic oxidation of thianthrene should give this radical. The oxidation was carried out[11] every elegantly chronopotentiometrically by Dr. J. D. Voorhies, using nitromethane as solvent and magnesium perchlorate as the supporting electrolyte. A red-violet color was obtained at the platinum anode and a value of $E^{1}/_{4}$ = 1.3 v. *vs.* a normal hydrogen electrode was obtained. The wave height was indicative of a one-electron oxidation. Since the thianthrene used in the anodic oxidation was from the same batch as was used for all of the sulfuric acid work,[1] there seemed to be no doubt that the electrolysis experiment had given the ion radical I. This was confirmed only recently when e.s.r. equipment became available in our own laboratory. Oxidation at a platinum electrode, carried out in a cell in the microwave cavity gave the result shown in Fig. 4.

Absorption Spectra in Sulfuric Acid.—Each of the thianthrenes dissolved in 96% sulfuric acid to give a colored solution, the colors varying from blue to wine red. The characteristics of the visible and ultraviolet spectra of the solutions are listed in Table II. The amino-, hydroxy-, carboxy-, and methylthianthrenes dissolved quickly so that their absorption spectra could be recorded fairly soon after making the necessary dilutions. Some of the spectra of this group of compounds changed with time. These changes were more pronounced in the ultraviolet than in the visible spectra. The most extensive changes occurred in the 2-amino, 1- and 2-hydroxy, and the 2,7-dihydroxy compounds. The 1-aminothianthrene solution was very stable. The behavior of 2,7-dihydroxythianthrene is most interesting. In the ultraviolet the initially predominant peak at 296 mμ decreased with time and the one at 333 mμ increased, the transition going through an isosbestic point at 305 mμ. This behavior is the *reverse* of what appears to be the characteristic behavior of the thianthrene oxides in 96% sulfuric acid.[1b,12] Thus, it seems that the 2,7-dihydroxythianthrene is undergoing disproportionation or rearrangement to a hydroxy oxide. The same diagnosis may be made from the change in the visible spectrum of this compound: from 604 to 540 mμ. Indications are present also in the spectra of 2-hydroxythianthene that a small amount of the hydroxy oxide may be forming. That is, a new peak appeared at 318 mμ after the solution was one day old, and there was an accompanying fall in

---

(11) In the laboratories of the American Cyanamid Co., Bound Brook' N. J.

(12) Part III, H. J. Shine and T. A. Bobinson, *J. Org. Chem.*, **28**, 2828 (1963).

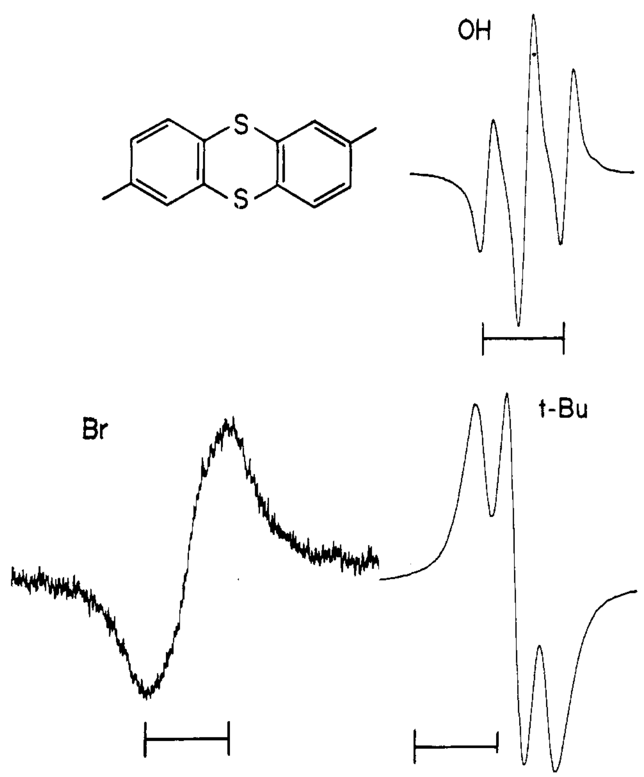


Fig. 3.—E.s.r. spectra of 2,7-disubstituted thianthrenes in 96% sulfuric acid. The scale calibration shown is 4 gauss. Field increases from right to left in each case.

absorbance at the maximum for the 2-hydroxythianthrene. The case of this compound and its oxide with λ_{max} at 319 mμ is discussed in the preceding paper.[12]

The remaining substituted thianthrenes dissolved in 96% sulfuric acid only slowly. The solutions were quite stable. The spectra of 1-chloro-, 2-chloro-, and 2-bromothianthrene were recorded at time intervals while these compounds were dissolving in stoppered cells. No differences were observed between the character of the visible and ultraviolet spectra recorded this way and the character of the spectra of solutions, used for absorbancy calculations, in which a known quantity of solute had taken several days to dissolve.

The spectra of all of the thianthrenes between 400 and 1200 mμ, when first recorded, had the same characteristics; that is, a large slender peak in the visible and two small bands in the near infrared, whose positions near 920 and 1050 mμ did not seem to differ much from one compound to another. On the other hand, the positions of the peaks in visible region clearly reflected the nature and positions of the substituents.

The λ_{max} of thianthrene in 96% sulfuric acid is 546 mμ. All of the 1-substituents cause a hypsochromic shift from 546 mμ, while most of the 2-substituents cause a bathochromic shift. The exceptions among the 2-substituents are the amino and carboxyl groups. Therefore, the transition from ground to excited state is facilitated by electron donors in the 2- and 7-positions, but it is adversely affected by all groups in the 1-position and the $-NH_3^+$ and $-C(OH)_2^+$ groups in the 2-position. It is evident, therefore, that the $\pi \rightarrow \pi^*$ transition occurring in the visible region is polarizing the ion radical along its long axis.

Molecular orbital calculations are being carried out both to define this transition exactly and to provide a clearer understanding of the e.s.r. spectra.

The ultraviolet spectrum of thianthrene in 96% sulfuric acid has maxima at 270 and 290 mμ. Most of the substituted thianthrenes have maxima in these regions. The positions of these maxima do not differ in most cases from those of thianthrene. The absorptivity in the region of 270 mμ does not change so much in going from one compound to another as the absorptivity in the region of 290 mμ. In this region the 2-substituted thianthrenes, with the exception of the 2-carboxy, have the larger absorptivities. Again, the precise analysis of these spectra must await a solution to the transitions which are occurring.

Experimental

Materials. Benzenesulfonyl Chlorides.—The following were obtained from Distillation Products: 2,5-dimethyl-, 2,5-dichloro-, 3,4-dichloro-, and *p*-bromobenzenesulfonyl chloride.

Thiols.—The following thiols were obtained from commercial sources: *p*-methylthiophenol and *p*-*t*-butylthiophenol (Distillation Products), *m*-methylthiophenol and *o*-methylthiophenol (Pitt-Consol Chemical Company). *p*-Bromothiophenol was prepared by the reduction of the corresponding benzenesulfonyl chloride with lithium aluminum hydride following the general procedure of Field and Greenwald,[13] m.p. 74.0–75.5° (lit.[14] 72–74°), after recrystallization from aqueous ethanol. All other thiols were prepared by the reduction of the corresponding benzenesulfonyl chlorides with zinc dust and sulfuric acid, following the general procedure of Vogel.[15] The resulting thiols were used without further purification.

Disulfides.—The general procedure was to dissolve the thiols in aqueous sodium hydroxide and oxidize with a solution of iodine in carbon tetrachloride. The resulting disulfides were recrystallized from ethanol ultraviolet spectra were of ethanol solutions): *p*-tolyldisulfide, m.p. 45.5–46.3° (lit.[16] 48°), λ_{max} 243 mμ; *o*-tolyl disulfide, m.p. 36.2–36.7° (lit.[17] 38–39°), λ_{max} 242 mμ; 4,4′-dibromodiphenyl disulfide, m.p. 93–93.5° (lit.[18] 92–94°), λ_{max} 249 mμ; 4,4′-di-*t*-butyldiphenyl disulfide, m.p. 88.0–88.6°, λ_{max} 243 mμ.

Anal. Calcd. for $C_{20}H_{26}S_2$: C, 73.12; H, 7.36; S, 19.51. Found: C, 73.38; H, 7.34; S, 19.20.

2,2′,5,5′-Tetramethyldiphenyl disulfide had m.p. 51.5–52.5°, λ_{max} 245 mμ.

Anal. Calcd. for $C_{16}H_{18}S_2$: C, 23.36. Found: S, 23.52.

Thianthrenes.—The following compounds were prepared as described by Gilman and Swayampati[19]: 1-aminothianthrene, m.p. 124–125° (lit. 120–121°); 1-chlorothianthrene, m.p. 84.5–85.5° (lit. 85–85.5°); 2-chlorothianthrene, m.p. 83.5–84.5° (lit. 84°); 1-carboxythianthrene, m.p. 228–228.8° (lit. 224–225°); 2-carboxythianthrene, m.p. 225–226° (lit. 227–228°). The 2-aminothianthrene, m.p. 158–159° (lit. 160°), and 2-bromothianthrene, m.p. 85–86° (lit. 88–89°), were prepared as described by Gilman and Swayampati.[20] 1-Bromothianthrene, m.p. 145–146.5° (lit.[21] 145°), was prepared from 1-aminothianthrene in a manner similar to the preparation of 1-chlorothianthrene. The 2-hydroxythianthrene, m.p. 143–144° (lit.[22] 145°), was prepared from 2-bromothianthrene by the procedure of Pützer and Muth.[22,23] 2,7-Dichlorothianthrene, m.p. 181.5–182° (lit.[24] 181.5°), was prepared by the procedure of Baw,

---

(13) L. Field and F. Greenwald, *J. Org. Chem.*, **16**, 946 (1951).

(14) L. Field, *J. Am. Chem. Soc.*, **74**, 394 (1952).

(15) A. Vogel, "A Textbook of Practical Organic Chemistry," Longmans Green and Co., New York, N. Y., 1954, p. 784.

(16) K. Slotta and W. Franke, *Ber.*, **63**, 681 (1930).

(17) F. Taboury, *Ann. Chim.* (Paris), **15**, 47 (1908).

(18) S. Wada, *Yakugaku Zasshi*, **79**, 88 (1959).

(19) H. Gilman and D. R. Swayampati, *J. Am. Chem. Soc.*, **79**, 211 (1957).

(20) H. Gilman and D. R. Swayampati, *ibid.*, **77**, 5947 (1955).

(21) H. Gilman and C. G. Stuckwisch, *ibid.*, **65**, 1461 (1943).

(22) B. Pützer and H. Muth, German Patent 606,350 (November, 1934).

(23) We are grateful to Mr. C. N. Sechrist, American Oil Co., Texas City, Tex., for carrying out the high-pressure hydrolysis.

(24) H. Baw, G. M. Bennett, and P. Dearns, *J. Chem. Soc.*, **680** (1934).

Bennett, and Dearns.[24] 2,7-Dimethylthianthrene and 2,7-dibromothianthrene were prepared by the same procedure and were recrystallized from ethanol. The 2,7-dimethylthianthrene had m.p. 117–118° (lit.[25] 117°). The 2,7-dibromothianthrene had m.p. 204–205°.

Anal. Calcd. for $C_{12}H_6S_2Br_2$: Br, 42.72. Found: Br, 42.44.

2,7-Di-*t*-butylthianthrene.—4,4′-Di-*t*-butyldiphenyl disulfide (3.2 g.) was mixed with 30 ml. of 96% sulfuric acid with shaking; 30 ml. of 30% fuming sulfuric acid was added to the shaking mixture in small portions. The color turned from green to wine red. After 1 hr. the reaction mixture was poured over ice, and the resulting brown solution was extracted with chloroform. The chloroform solution was washed with dilute sodium hydroxide solution and water, dried over anhydrous magnesium sulfate, filtered, and evaporated. A white solid was obtained, which was recrystallized from aqueous ethanol, m.p. 151–152°, 0.11 g. (3%).

Anal. Calcd. for $C_{20}H_{24}S_2$: C, 73.11; H, 7.36; S, 19.36. Found: C, 72.98; H, 7.50; S, 19.36.

2,7-Dihydroxythianthrene was prepared[23] by the hydrolysis of 2,7-dibromothianthrene using the procedure given[22] for 2-hydroxythianthrene. Recrystallization from aqueous methanol gave a product with m.p. 232–233°.

Anal. Calcd. for $C_{12}H_8O_2S_2$: C, 58.03; H, 3.25; S, 25.82. Found: C, 57.85; H, 3.51; S, 25.53.

Attempts to prepare 1,6-dimethyl-, 1,4,6,9-tetramethyl-, 1,4,6,9-tetrachloro-, and 2,3,7,8-tetrachlorothianthrene were unsuccessful.

Spectra.—The e.s.r. spectra were obtained with a Varian spectrometer using 100-kc. field modulation. Line calibrations were made by using potassium nitroso disulfonate in saturated sodium carbonate solution as a standard.[26] A Varian Associates V-4532 dual sample cavity was used. The standard solution was enclosed in a Pyrex capillary and modulated at 400 c.p.s. The thianthrene solutions were placed in Varian Associates flat quartz cells and modulated at 100 kc. A Varian Associates Model G-22 dual channel recorder was used to record standard and sample spectra simultaneously. The klystron frequency was measured with a Hewlett Packard Model 540-B transfer oscillator, in conjunction with a Model 524-C electronic counter, a Model 525-B frequency converter, and a Model X532-B frequency counter. The *g*-values were calculated from the dual recordings, using the value of 2.0057 for the standard.[26] Line splittings were measured as the distance between points on the derivative curves corresponding with the centers of absorption lines. The width of a hyperfine line was measured between the points on the derivative curve corresponding with points of maximum slope on the absorption curve.

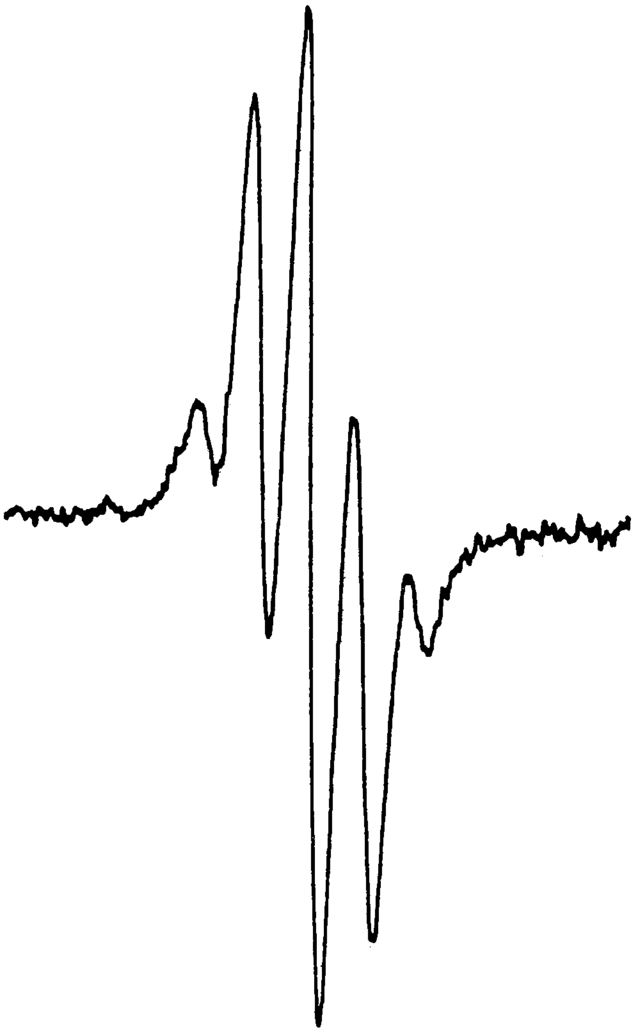


Fig. 4.—E.s.r. spectrum obtained from the anodic oxidation of thianthrene in nitromethane solution.

The hyperfine splittings were found to be constant for all lines in those spectra whose shapes permitted splitting measurement. In some of these spectra, however, line widths were not constant. Line widths were constant in thianthrene (0.56), 1-bromo- (0.57), 1-chloro- (0.55), 2,7-dimethyl- (0.56), and 2,7-dihydroxythianthrene (0.63 gauss). In other cases the central lines were wider than the terminal. Thus, in 1-amino- and 2-aminothianthrene, the three central lines were 0.57 and the two terminals, 0.49 gauss. In 2,7-dichlorothianthrene, the center line was 0.98 and the terminals 0.90 gauss. The corresponding widths in 2,7-di-*t*-butylthianthrene were 0.94 and 0.86 gauss

---

[25] I. N. Tits-Skvortsova, A. I. Leonova, S. Ya. Levina, and E. A. Karaseva, *Sbornik Statei Obshchei Khim., Akad. Nauk SSSR,* **1**, 541 (1953).

[26] J. E. Wertz, D. C. Reitz, and F. Dravnieks, in "Free Radicals in Biological Systems," Academic Press, Inc., New York, N. Y., 1961, p. 186.