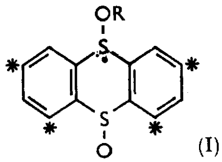
965. 1,4-*Dithiinium Radical-cations.*

By E. A. C. Lucken.

The radical produced by the action of concentrated sulphuric acid on thianthrene is shown to have the structure (II), and not (I) as previously proposed. The perchlorate and pentachloroantimonate of this cation have been isolated and the formation of these radical-cations has been shown to be a property of the 1,4-dithiin system.

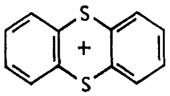
Thianthrene dissolves in concentrated sulphuric acid, giving a magenta solution;[1] which has been shown by electron-spin resonance spectroscopy,[2-4] to contain a free-radical whose resonance spectrum is given in Fig. 1a. The same radical is produced by dissolving thianthrene or its monosulphoxide or disulphoxide in trifluoroacetic acid, and on the basis of this and other experiments Fava, Sogo, and Calvin[4] postulated that it had the structure (I).

The hyperfine splitting was supposed to arise from the four starred protons, assumed to have approximately the same spin-density, with only low spin-density at the remaining four protons. For some reason structure (II) was not considered by these authors although their observations can be equally well, if not better, explained by it. Thus structure (II) contains two groups of four equivalent protons and the only assumption needed to explain the observed electron-spin resonance spectrum is that the splitting produced is smaller than the line width for one set and greater for the other. The rapid production of the radical by the reaction between thianthrene and trifluoroacetic acid, in contrast to its slow production when thianthrene is replaced by the corresponding monosulphoxide or disulphoxide, militates against structure (I). Moreover, there is no need to postulate that thianthrene strongly adsorbs oxygen to explain the formation of the radical in deoxygenated trifluoroacetic acid. The problem was therefore reinvestigated, the observations of Fava, Sogo, and Calvin were confirmed, and the results of further experiments are presented here.



(I)

(R = $CF_3 \cdot CO-$ or HSO_3-)



(II)

Thianthrene dissolves in acetic anhydride containing 1% of perchloric acid to a magenta, radical-containing solution whose visible (Fig. 2a) and electron-spin resonance spectra * are very similar to those of thianthrene in concentrated sulphuric acid. Addition of chloroform to this solution slowly precipitates red-black hexagonal plate-like crystals of formula $C_{12}H_8ClO_4S_2$. An attempt to obtain an infrared spectrum of this substance in a potassium bromide disc yielded the superimposed spectra of thianthrene and potassium perchlorate, the disc having a red-brown colour presumably due to the liberation of bromine. This compound is only weakly paramagnetic, its electron-spin resonance spectrum being shown in Fig. 1b, but it dissolves in nitromethane to a magenta-coloured solution whose visible and electron-spin resonance spectra * were again similar to that of

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* To obtain well-resolved electron-spin resonance of this radical in acetic anhydride or nitromethane it is essential to deoxygenate the solution by bubbling nitrogen through it.

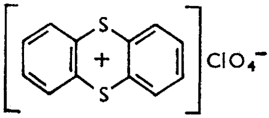
[1] Graebe, *Annalen*, 1876, **179**, 180.

[2] Hirshon, Gardner, and Fraenkel, *J. Amer. Chem. Soc.*, 1953, **75**, 4115.

[3] Wertz and Vivo, *J. Chem. Phys.*, 1955, **23**, 2193.

[4] Fava, Sogo, and Calvin, *J. Amer. Chem. Soc.*, 1957, **79**, 1078.

thianthrene in sulphuric acid. The visible reflection spectrum of the solid (Fig. 2b) was, however, very different from its spectrum in solution. The solution spectra mentioned so far fail to obey Beer's law and they change with temperature and solvent. Attempts to follow these changes quantitatively have been frustrated by slow decomposition.



(III)

The above observations are completely in accordance with the formulation of thianthrene perchlorate, and hence the radical species such as (III), which, however, dimerises in the solid state and is probably in equilibrium with the dimer in solution. Structure (I) is not, however, completely eliminated because of the presence of oxygen in the anion, although the reaction with solid potassium bromide renders this rather unlikely.

If to a solution of thianthrene in chloroform one mol. of antimony pentachloride is added a red-violet microcrystalline precipitate, $C_{12}H_8Cl_5S_2Sb$, is immediately formed.

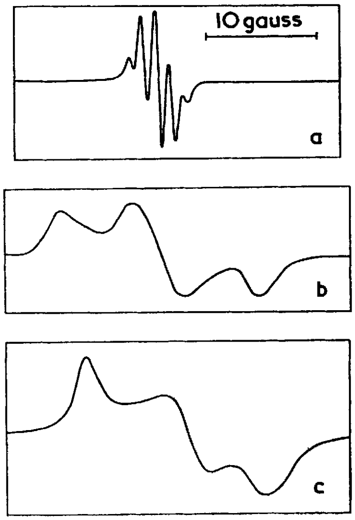


Fig. 1. Electron-spin resonance spectra of thianthrenium radical cations: (a) thianthrene in concentrated sulphuric acid; (b) thianthrenium perchlorate (solid); (c) thianthrenium pentachloroantimonate (solid).

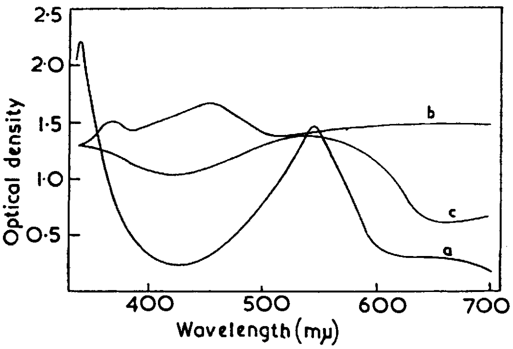


Fig. 2. Ultraviolet and visible absorption and reflectance spectra of thianthrenium radical cations: (a) thianthrene in concentrated sulphuric acid; (b) thianthrenium perchlorate (reflectance); (c) thianthrenium pentachloroantimonate (reflectance).

This contains essentially one unpaired spin per thianthrene molecule, its spin-resonance spectrum being shown in Fig. 1c. Its visible reflectance spectrum (Fig. 2c) is similar to that shown in Fig. 2a. The solid dissolves in nitromethane, giving a solution spectrum similar to that in Fig. 2a and an electron-spin resonance spectrum similar to that of Fig. 1a.

Thianthrene monosulphoxide reacts slowly with acetic anhydride–perchloric acid, to give the magenta radical. Neither of the two isomeric disulphoxides appears to react. All three sulphoxides react slowly with antimony pentachloride in chloroform, to give non-paramagnetic addition products.

These observations leave no reasonable doubt that structure (II) is the correct structure for the radical in question. In the product with antimony pentachloride there were no indications in the spin-resonance spectrum of the radical $SbCl_5^-$, so the anion is presumably $Sb_2Cl_{10}^{2-}$.

Since the central ring in thianthrene is an eight-electron system it is possible that the formation of radical (II) is due to a tendency to achieve the Hückel number 6. To test this hypothesis, diphenyl sulphide, 6-methyl-1,4-benzodithiin, and 2,5-diphenyl-1,4-dithiin were allowed to react with antimony pentachloride in chloroform solution. Diphenyl sulphide gave a non-paramagnetic white crystalline adduct, and the dithiin derivatives gave coloured 1 : 1 paramagnetic adducts whose spin-resonance spectra resembled that in Fig. 2c.

Thus the structure of the radical derived from thianthrene in sulphuric acid has been established as (II) and its formation is a property of the 1,4-dithiin ring system.

EXPERIMENTAL

Ultraviolet and visible absorption spectra were measured with a Cary model 11 recording spectrophotometer, reflectance spectra with a Beckman D.U. spectrophotometer with a diffuse-reflectance attachment. Infrared spectra were measured on a Perkin-Elmer model 221 recording spectrophotometer. Electron-spin resonance spectra were measured on a modified " Microspin " X-band spectrometer with 100 kc./sec. field modulation.

Thianthrene Perchlorate.—Sublimed thianthrene (0·43 g., 0·002 mole) was dissolved in hot acetic anhydride (50 ml.), and a solution of perchloric acid (0·6 ml., 70% w/v of H_2O) in acetic anhydride (100 ml.) was added. To the resultant magenta solution, chloroform (100 ml.) was added and after 12 hr. the crystalline *product* (0·4 g.) was filtered off (Found: C, 45·5; H, 2·7; S, 20·1%; equiv., 316. $C_{12}H_8ClO_4S_2$ requires C, 45·7; H, 2·6; S, 20·3%; equiv., 316).

Thianthrene Pentachloroantimonate.—Sublimed thianthrene (0·43 g., 0·002 mole) was dissolved in anhydrous chloroform (20 ml.), and a solution of antimony pentachloride (0·66 g., 0·0022 mole) in chloroform (20 ml.) added. The *product,* a red-violet precipitate (0·9 g.), was filtered off, washed with chloroform, and dried *in vacuo* (Found: C, 27·4; H, 1·8; S, 12·1; Cl, 34·8. $C_{12}H_8Cl_5S_2Sb$ requires C, 27·9; H, 1·6; S, 12·4; Cl, 34·4%).

2,3-*Dihydro*-6-*methyl*-1,4-*benzodithiin.*—To a refluxing solution of 4-methylbenzene-1,2-dithiol (5·00 g.) and ethylene dibromide (6·05 g.) in ethanol (100 ml.) was added dropwise a solution of sodium ethoxide (4·36 g.) in absolute ethanol (100 ml.). The mixture was refluxed overnight, then distilled to remove 180 ml. of ethanol. To the residue were added ether (100 ml.) and water (100 ml.). The aqueous layer was separated and twice re-extracted with ether (100 + 50 + 50 ml.). The combined extracts were washed twice with water, dried ($MgSO_4$), and evaporated, and the *product* (3·8 g.) was distilled (b. p. 98·5°/0·02 mm.) (Found: C, 59·1; H, 5·8; S, 34·9. $C_9H_{10}S_2$ requires C, 59·3; H, 5·5; S, 34·8%).

6-*Methyl*-1,4-*benzodithiin.*—The dihydro-derivative (10 g.) was dehydrogenated with chloranil by the method of Parham *et al.*[5] Redistillation yielded a pure *product* (3·5 g.), b. p. 82·5—83·5°/0·05 mm. (Found: C, 59·9; H, 4·5; S, 35·4. $C_9H_8S_2$ requires C, 59·9; H, 4·5; S, 35·6%).

6-*Methyl*-1,4-*benzodithiin Pentachloroantimonate.*—This *salt* was prepared as above (0·8 g. from 0·36 g. of dithiin) (Found: C, 21·8; H, 1·8; S, 13·1; Cl, 37·3. $C_9H_8Cl_5S_2Sb$ requires C, 22·5; H, 1·7; S, 13·4; Cl, 37·0%). Unlike the other two pentachloroantimonates this compound was decomposed in air to a black resin.

2,5-*Diphenyl*-1,4-*dithiin Pentachloroantimonate.*—2,5-Diphenyl-1,4-dithiin[6] gave this *salt* in the same way (Found: C, 33·4; H, 2·1; S, 11·2; Cl, 31·0. $C_{16}H_{12}S_2SbCl_5$ requires C, 33·8; H, 2·1; S, 11·3; Cl, 31·2%).

CYANAMID EUROPEAN RESEARCH INSTITUTE,
91, ROUTE DE LA CAPITE, COLOGNY-GENEVA.

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[5] Parham, Roder, and Hasek, *J. Amer. Chem. Soc.*, 1953, **75**, 1647.
[6] Barker and Barkenbus, *J. Amer. Chem. Soc.*, 1936, **58**, 262.