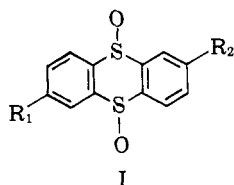


### Stereoisomeric Thianthrene Sulfoxides. Configurational Assignments and Thermal Equilibria<sup>1</sup>

Sir:

We have found that the configurations of a variety of ring-substituted thianthrene 5,10-dioxides may be conveniently and unequivocally assigned on the basis of ultraviolet and infrared spectral comparisons and by the position of the isomerization equilibria. This has forced us to conclude that a previous assignment of configuration<sup>2</sup> to If is in error.



- I  
 a, R<sub>1</sub> = R<sub>2</sub> = H  
 b, R<sub>1</sub> = R<sub>2</sub> = Cl  
 c, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>  
 d, R<sub>1</sub> = R<sub>2</sub> = CH<sub>2</sub>COOCH<sub>3</sub>  
 e, R<sub>1</sub> = H; R<sub>2</sub> = Br  
 f, R<sub>1</sub> = H; R<sub>2</sub> = COOCH<sub>3</sub>

The isomeric mixtures of I were obtained by hydrogen peroxide oxidation of the corresponding thianthrene precursors and the separations could, in most cases, be accomplished by chromatography on Florisil. The isomer which was eluted first (chloroform) proved to have the *cis* configuration in every case.<sup>3</sup>

Configurations were primarily assigned on the basis of the ultraviolet spectra in 95% ethanol (Fig. 1 and 2). The stereoisomers of Ia have been identified<sup>4</sup> and the ultraviolet spectra of *cis*- and *trans*-Ia differ markedly in the position and shape of the principal absorption band, and in the appearance of the long wave length region. Relative to *cis*-Ia, the principal band of *trans*-Ia has been displaced toward longer wave lengths (from 212 to 221 m $\mu$ ) and has become a good deal narrower, while the region above 260 m $\mu$  has become notably intensified. These striking characteristics are shared by every pair of isomers studied (Fig. 1 and 2) and while the spectra suffer displacement with ring substitution, the *relative* positions of the bands in each set are essentially insensitive to the nature of the substituents. The present results clearly express the angular dependence of spectroscopic coupling between sulfoxide and benzenoid transitions. This interaction is a function of the dihedral angle ( $\theta$ ) between the orbital axis of the lone 3sp<sup>3</sup> pair on sulfur and the neighboring benzene 2p  $\pi$ -orbital axes.<sup>5</sup> The two oxygen atoms in *cis*-I are stereochemically equivalent; in the solid state,<sup>4</sup> as in solution,<sup>6</sup> the *e'*,*e'*-conformation is preferred.<sup>7</sup> In *trans*-I, the two oxygen atoms are nonequivalent (*a'*,*e'*-conformation). Hence both of the two n-electron pairs in *cis*-I are *a'* ( $\theta \sim 0^\circ$ ), whereas in *trans*-I

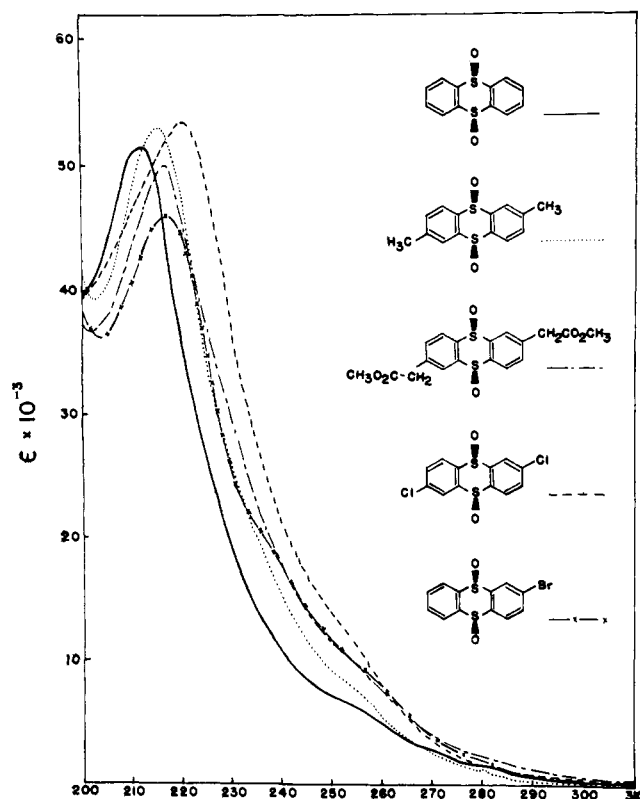


Figure 1.

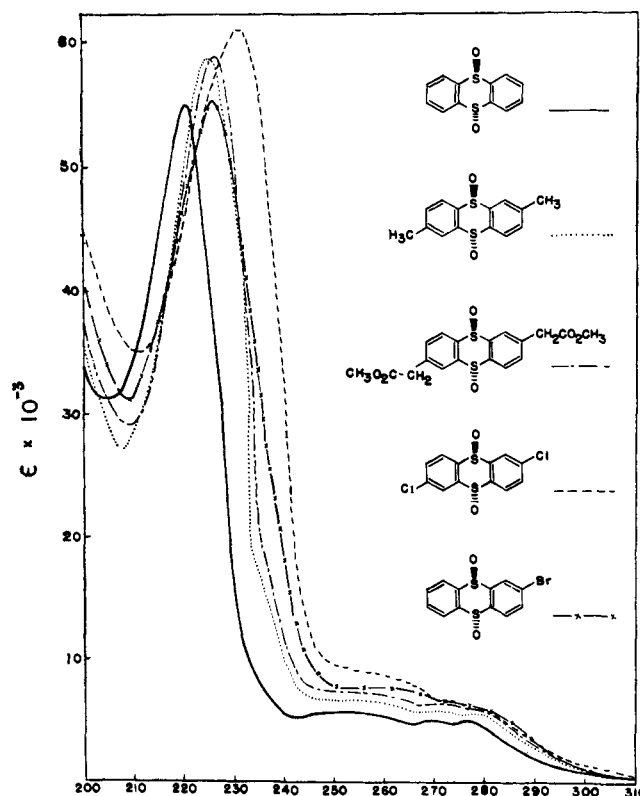


Figure 2.

one is *a'* and the other *e'* ( $\theta \sim 90^\circ$ ). It follows that the stereoisomers are distinct chromophoric entities.<sup>8</sup>

(8) The distinctive e.s.r. spectra of *cis*- and *trans*-Ia also reflect this difference in stereochemistry (E. T. Kaiser and D. H. Eargle, Jr., *J. Chem. Phys.*, **39**, 1353 (1963)).

(1) We gratefully acknowledge support by the National Science Foundation (Grant No. G-9205).

(2) M. Janczewski and M. Dec, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **10**, 605 (1962).

(3) All new compounds gave satisfactory elemental analyses.

(4) S. Hosoya, *Acta Cryst.*, **16**, 310 (1963).

(5) G. Leandri, A. Mangini, and R. Passerini, *J. Chem. Soc.*, 1386 (1957).

(6) T. W. J. Taylor, *ibid.*, 625 (1935).

(7) We adopt the stereochemical nomenclature employed for the 9,10-disubstituted 9,10-dihydroanthracenes (A. H. Beckett and B. A. Mulley, *ibid.*, 4159 (1955)).

