Stereoisomeric Thianthrene Sulfoxides. Configurational Assignments and Thermal Equilibrations¹

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 configuration² to If is in error.



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.³

Configurations were primarily assigned on the basis of the ultraviolet spectra in 95% ethanol (Fig. 1 and 2). The stereoisomers of Ia have been identified⁴ 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 μ) and has become a good deal narrower, while the region above $260 \text{ m}\mu$ 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 (θ) between the orbital axis of the lone 3sp³ pair on sulfur and the neighboring benzene 2p π -orbital axes.⁵ The two oxygen atoms in cis-I are stereochemically equivalent; in the solid state,⁴ as in solution,⁶ the e',e'-conformation is preferred.⁷ 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

(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)).



one is a' and the other e' ($\theta \sim 90^{\circ}$). It follows that the stereoisomers are distinct chromophoric entities.⁸

(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)).



Since the ultraviolet spectra serve as diagnostic tests of configuration in this series, it is easy to identify the stereoisomers of If (Fig. 3). The *trans* isomer is the higher melting $(208-209^{\circ})$ and the *cis* isomer the lower melting $(196-197^{\circ})$ form. This result is contrary to a previous assignment.² Accordingly, the configurations claimed² for the related acid and other derivatives must now be reversed.

The above conclusions are borne out by an inspection of the S–O stretching region in the infrared. The *cis* isomers of Ia–f all have a strong band at 1087–1094 cm.⁻¹ (KBr). The *trans* isomers on the other hand all have *two* regions of strong absorption, one at 1070–1079 cm.⁻¹ and the other at 1018–1044 cm.⁻¹. The low frequency band presumably corresponds to the a'-stretching mode.⁹

The isomerization¹⁰ of Ia on heating¹¹ is classically the first example of a thermal stereomutation in the sulfoxide series. Ib has also been thus isomerized¹² and this method has recently been extended to monosulfoxides.¹³ We find that the *trans* isomers of Ia-f all isomerize to the *cis* isomers at elevated temperatures $(200-300^\circ)$. The misassignment² of configuration was the result of the assumption, based on earlier erroneous conclusions,¹⁴ that the acid precursor of *trans*-If is the more stable form.

(9) T. Cairns, G. Eglinton, and D. T. Gibson, Spectrochim. Acta., 20, 159 (1964).

- (10) K. Fries and W. Vogt, Ber., 44, 756 (1911).
- (11) F. Krafft and R. E. Lyons, *ibid.*, 29, 435 (1896).
- (12) H. Baw, G. M. Bennett, and P. Dearns, J. Chem. Soc., 680 (1934).
- (13) H. B. Henbest and S. A. Khan, *ibid.*, 56 (1964).
 (14) E. Bergmann and M. Tschudnowsky, *Ber.*, 65, 457 (1932); *cf.* ref. 6.
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Interconvertible Four-, Five-, and Six-Coordinate Cobalt Complexes¹

Sir:

Acetone solutions of salts of one or both of the interesting square-planar complexes, $Co(MNT)_2^-$ and $Co(TDT)_2^{-,2}$ undergo color changes in the presence of the ligands pyridine, o-phen, triphenylarsine, triphenylphosphine, MNT²⁻, and diars.³ In most cases crystalline complexes precipitate from the solutions on addition of ether. Elemental analyses reveal that the color changes follow from the formation of new complexes in which the coordination number of cobalt has increased to five or six. Six crystalline compounds giving good analyses have been isolated. They are the fivecoordinate species $[(n-C_4H_9)_4N][Co(MNT)_2(C_5H_5N)]$ and $[(n-C_4H_9)_4N][Co(MNT)_2(P(C_6H_5)_3)]$ and the sixcoordinate species $[(n-C_4H_9)_4N][Co(MNT)_2(o-phen)],$ $[(n-C_4H_9)_4N][Co(MNT)_2(diars)],^4 [(n-C_4H_9)_4N]_3[Co (MNT)_3$], and $[(n-C_4H_9)_4N][Co(TDT)_2(o-phen)]$. In addition, the five-coordinate complex [Co(MNT)₂- $(As(C_6H_5)_3)$]⁻ and the six-coordinate complexes [Co- $(MNT)_2(C_5H_5N)_2$ and $[Co(TDT)_2(diars)]^-$ were identified spectroscopically in solution. The solids are all diamagnetic and $[Co(MNT)_2(P(C_6H_5)_3)]^-$ is diamagnetic in acetone solution. The final observation that, with the exception of $[Co(MNT)_2(C_5H_5N)]^-$, excesses of ligand do not modify the solution spectra leads to the conclusion that these stable adducts include the first examples of diamagnetic, truly fivecoordinate cobalt in the formal oxidation state, "Co-(III)."⁵

Table I contains a summary of the spectra of the new complexes in acetone. Spectra of the pyridine solutions show an absorption maximum developing at $705 \text{ m}\mu$ at low pyridine concentration which then decreases again at high pyridine concentration, leading finally to a weak band with a maximum at $700 \text{ m}\mu$. This is interpreted by the reactions

$$[Co(MNT)_{2}]^{-} + C_{\delta}H_{\delta}N \xrightarrow{} [Co(MNT)_{2}(C_{\delta}H_{\delta}N)]^{-} + C_{\delta}H_{\delta}N \xrightarrow{} [Co(MNT)_{2}(C_{\delta}H_{\delta}N)_{2}]^{-}$$

Fortunately, the successive stages of complex formation are fairly well separated. The successive formation constants for five- and six-coordination at 25° may be estimated as 3.5×10^3 and 5.5, respectively, and the spectrum of the five-coordinate species determined.

Formation constants for several of the other adducts were also determined spectrophotometrically. This could be done either by directly observing dissociation

(3) Abbreviations used: o-phenylene bis(dimethylarsine) = diars, 1,10-phenanthroline = o-phen



(4) Samples of this compound could not be obtained free of residual $[(n-C_4H_9)_4N]Br$.

(5) Five-coordinate, paramagnetic Co(III) complexes of the type Co-(PR₈)₂X₃ have recently been prepared by K. A. Jensen, P. H. Nielsen, and C. T. Pedersen, Acta Chem. Scand., **17**, 1115 (1963).

⁽¹⁾ Acknowledgment is made to the National Science Foundation for support of this research. This research was also supported by Public Health Service Research Grant No. CA-07016-01 from the National Cancer Institute.

^{(2) (}a) H. B. Gray and E. Billig, J. Am. Chem. Soc., 85, 2019 (1963);
(b) E. Billig, H. B. Gray, S. I. Shupack, J. H. Waters, and R. Williams, Proc. Chem. Soc., 110 (1964).