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THE CIRCULAR DICHROISM AND ABSOLUTE CONFIGURATION OF ARYL-THIIRANES.

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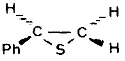
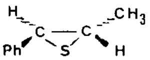
In earlier work we have studied the circular dichroism of aryl-oxiranes.[1] We wish now to report some preliminary results concerning the extension of our investigation to the optical activity of aryl-thiiranes.

Compounds I-IV were synthesised from the corresponding optically active oxiranes of known absolute configurations and optical purity, by reaction with potassium thiocyanate (I, II, III)[2] and with thiourea (IV).[3] The reactions are known to occur with inversion of configurations at both of the carbon atoms of the ring.[4] The absolute configurations given in chart I are assigned on this basis. As the percent of inversion during the reactions is not exactly known, we are unable to give the optical purities of the thiiranes, the C.D. spectra were however corrected to 100% optical purity of the starting epoxides.

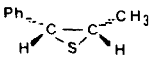
Chart I



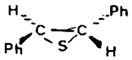
(+)(S) - I



(-)(1S, 2S) - II



(-)(1R, 2S) - III



(-)(S,S) - IV

The absorption and circular dichroism spectra of compounds I-IV are reported in fig. 1: they show quite clearly the transitions characteristic of the thiirane and aromatic rings.

The C.D. spectra of the compounds studied show a positive transition at 277 mµ for I and II, and at 262 and 292 for III and IV respectively. These bands should correspond to the thiirane transition described at around 262 mµ by Kuriyama et al.[5] for a number of steroidal episulphides as $n \longrightarrow \sigma^{*}_{5}$.[†] The sign of the C.D. band is in agreement with the sector rule for episulphides[5], within the limits of possible conformational changes, mainly of the phenyl group, but also other interpretations based on a different mechanism of optical activity seem to be possible.[7] Further proof of the non aromatic nature of this band is the presence of an inflection showing vibronic fine structure in the negative part of the spectrum at about 250 mμ, evident in compounds I, II, IV; this part of the spectrum is likely to correspond to the aromatic ^1L_b band shifted to shorter wavelength by overlapping and cancellation with the opposite signed thiirane band. The negative sign of the multiple Cotton effects are related to the chirality of the carbon directly attached to the aromatic ring as was previously pointed out.[1,8,9] In compound III, since the sign of the thiirane ring transition and of the benzene ^1L_b band are the same, only one band of positive sign is observed.

Going to shorter wavelength the main feature of the spectra is the system of two bands of opposite signs and elevated $\Delta\varepsilon$ value each corresponding to definite maxima or inflections in the absorption in the spectral region between 210-240 mμ; and this suggests the existence of exciton optical activity.[10] The shorter wavelength absorption observed at about 205 mμ in steroidal episulphides is given as $A_1 \longrightarrow B_1$[5,6] and should have an electric transition moment perpendicular to the plane of the ring. This transition can couple with the ^1L_a benzene transition and should give for the S configuration of the atom bearing the phenyl, as shown in Fig. 2, a long wavelength negative Cotton effect and a short wavelength positive one, or a positive Cotton effect at long wavelength and a negative at short wavelength for the R configuration. This is indeed observed in the spectra of compounds I-III.

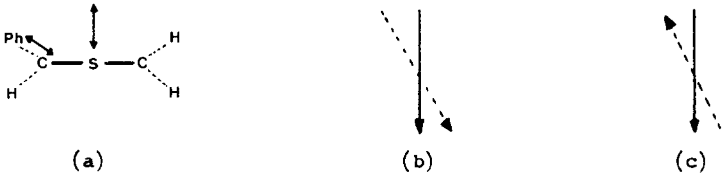


Fig. 2 - The dipole-coupling mechanism for benzene ^1L_a and thiirane $A_1 \longrightarrow B_1$ transitions in (+)-(S) phenyl-thiirane (a). The optical factor is positive for the high-energy band (b) and negative for the low energy one (c).

[†] The transition is described in group theoretical terms as $A_1 \longrightarrow A_2$ in the group C_{2v} and should be electrically forbidden and magnetically allowed with magnetic moment along the symmetry axis of the thiirane ring. This transition together with the one at about 235 mμ has recently been put on a more firm theoretical basis using CNDO/2 calculation including d-orbitals.[6]

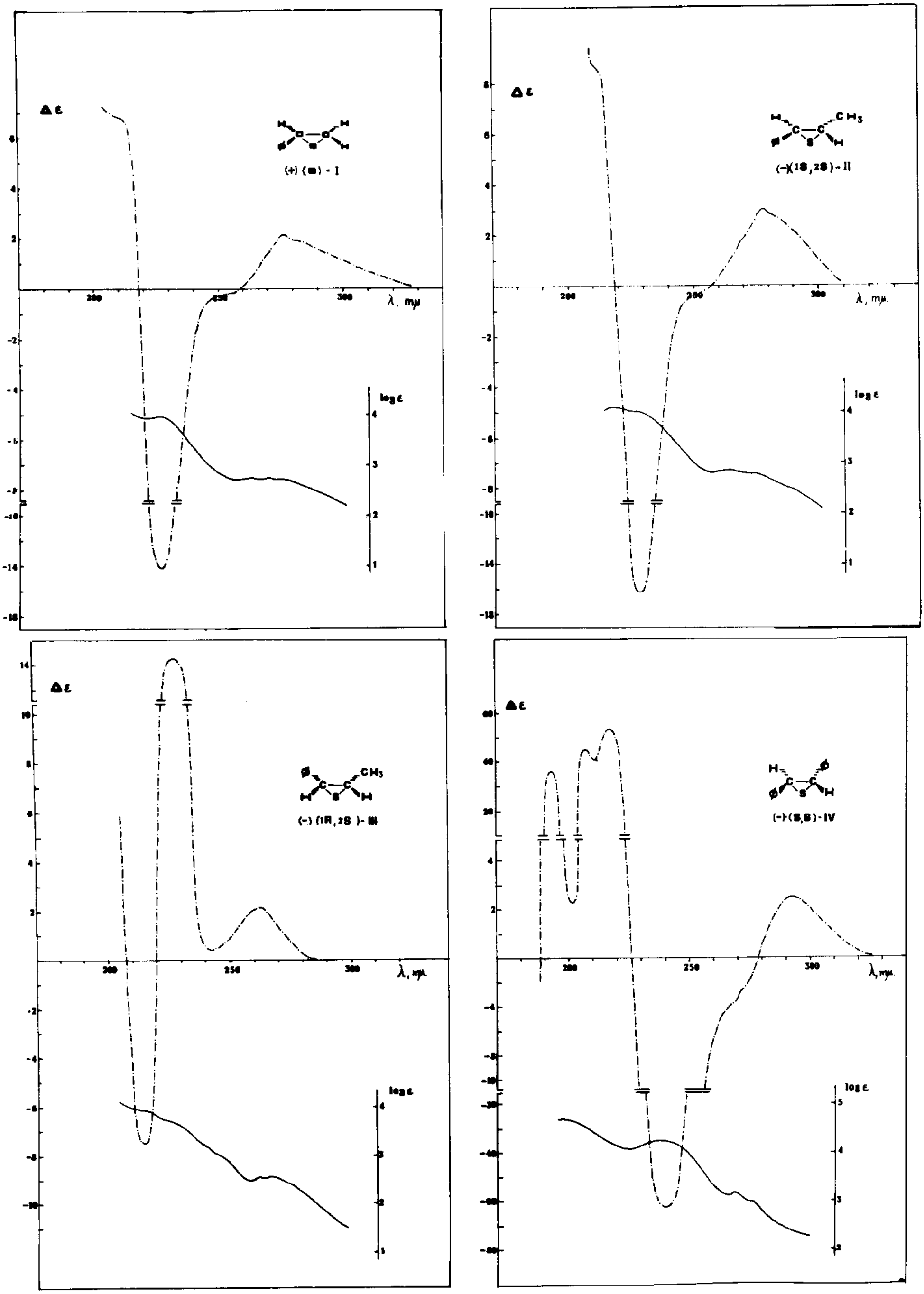


Fig. 1 - C.D. (-.-) and U.V. (——) spectra of thiiranes (I-IV) in Cyclohexane.*

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* The C.D. spectra in 95% ethanol did not show any significant difference with respect to those in cyclohexane.

In compound IV there is the further complication of the presence of the new phenyl group and a more complex exciton treatment is needed. The importance of the coupling of the episulphide ring in compound IV is also emphasized by the unsatisfactory results of a simple calculation based only on the coupling of ^1L_a aromatic transitions in comparison with the satisfactory results obtained from (+)trans-stilbene oxide[1b] and (-)trans-1,2-diphenyl-cyclopropane.[11]

Dipole-dipole and electric-magnetic coupling calculations are in progress in order to put on a quantitative basis the contribution of the two mechanism to the optical activity of these systems.

Acknowledgements.

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