

The Circular Dichroism of (-)-(S)-3-Methylthian: a Study of the Electronic Transitions and Stereochemistry of Cyclic Sulphur Derivatives

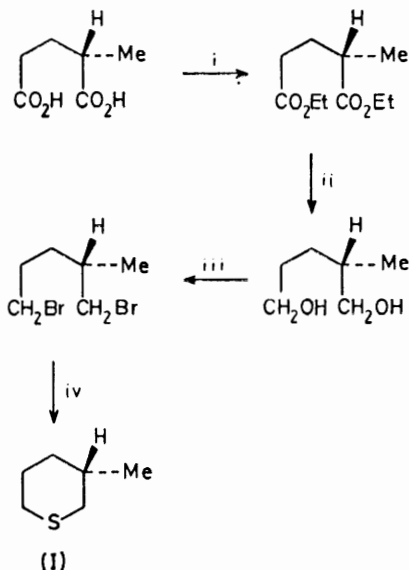
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The u.v. and c.d. spectra of (-)-(S)-3-methylthian and the u.v., l.d., and m.c.d. spectra of thian have been analysed by means of non-empirical MO calculations. While the $n \rightarrow \sigma^*$ assignment of the transition at *ca.* 232 nm is confirmed, the absorption at *ca.* 214 nm is assigned to a $\sigma \rightarrow \sigma^*$ ($A_1 \leftarrow A_1$) transition. The stereochemistry of cyclic sulphur derivatives is discussed in the light of a symmetry rule previously proposed.

THE chiroptical properties of sulphur derivatives have been the subject of recent interest.¹ Thiiran derivatives have been investigated by several authors and the c.d. associated to the $n \rightarrow \sigma^*$ transition at *ca.* 260 nm has been correlated with the molecular geometry by means of symmetry rules.^{2,3}

The c.d. spectra of cyclic five- and six-membered sulphides were analyzed by Rosenfield and Moscovitz by MO semi-empirical calculations.⁴ More recently, Hagishita and Kuriyama⁵ used a symmetry rule previously proposed for thiirans in an attempt to interpret the c.d. spectra of several thiahydrindans; however the effect of β -axial substituents could not be predicted.

In a continuation of previous research on the chiroptical properties and electronic transitions of thiirans,^{3,6} we have extended our studies to 3-methylthian (I) in order to (i) contribute to a conclusive assignment of electronic transitions of aliphatic sulphides; (ii) evaluate the effect of the $C-\hat{S}-C$ angle on the energy levels; and (iii) obtain further information on the relations between the stereochemistry and chiroptical properties.



SCHEME Reagents: i, $\text{CH}(\text{OEt})_3$; ii, LiAlH_4 ; iii, PBr_3 ; iv, Na_2S

We thought 3-methylthian would be a suitable model on account of its limited size which allows the use of nonempirical MO calculations; the conformation of the molecule is well known,⁷ and its absolute configuration was correlated with that of 2-methylglutaric acid through the synthesis depicted in the Scheme (see Experimental section).

C.d. and u.v. spectra of (I) are reported in Figure 1 and

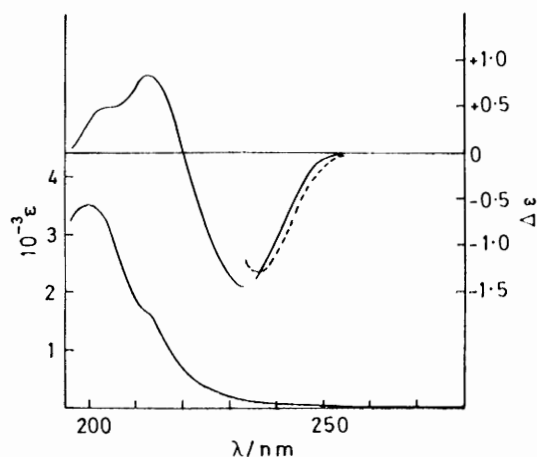
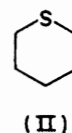


FIGURE 1 Absorption and c.d. spectra of (-)-3-methylthian in n-hexane (—) and chloroform (---)

show the typical trend of aliphatic sulphides. In particular the moderately intense negative c.d. band at *ca.* 230 nm is related to a very weak absorption without a clearly detectable maximum; the positive c.d. at *ca.* 214 nm corresponds to an inflection and the positive c.d. at *ca.* 200 nm to a maximum^{4,5} (ϵ_{max} , 3 500).

The u.v., l.d., and m.c.d. spectra of thian (II) are shown in Figure 2. M.c.d. shows the presence of a very weak additional transition in the region around 260 nm.

Computations and Assignments.—3-Methylthian (I)



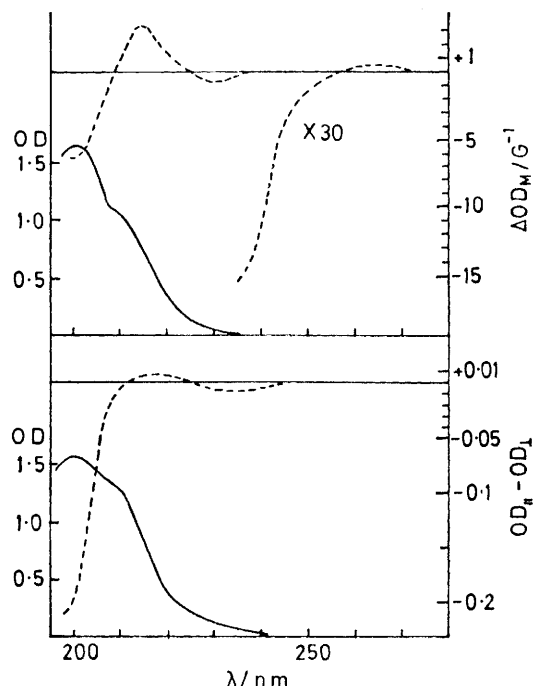
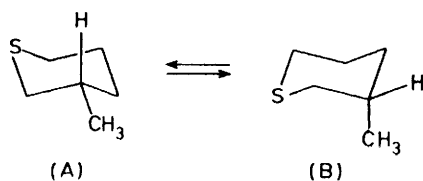


FIGURE 2 Absorption (—) and m.c.d. (----) spectra of thian in n-hexane (upper part). Absorption (—) and l.d. (----) of thian in a nematic eutectic bicyclohexyl mixture (lower part). The m.c.d. scale is in $\Delta OD_M/G^{-1}$.

has two possible conformers (A) and (B). The absorption and c.d. spectra are determined by the equatorial conformer, which is by far the most abundant species present in solution.⁷ We have performed MO and



configuration interaction (CI) computations for both species, since recent c.d. measurements have shown that cyclic sulphides with a β -substituent in the axial position do not follow the symmetry rules proposed for the sign of the rotational strengths of the electronic transition in episulphides.⁵ The computations have been performed with a modified version of the Gaussian 70⁸ system of programs, using a standard set of STO/3G orbitals.

The orbital diagram for the two conformers is typical of the sulphide chromophore. The highest MOs are two σ and one lone pair orbital (n); the lowest virtual MOs are two σ^* ones, which in Figure 3 have a label appropriate to C_{2v} symmetry.

The value of the $\widehat{C-S-C}$ bond angle being the main factor responsible for the orbital ordering in the various classes of sulphides, the correlation of the orbital levels of the thian to the MO levels of thiiran is easily understood by a Walsh-type diagram as shown in Figure 3.

Using this orbital diagram, the thian is expected to exhibit at low energy two $n \rightarrow \sigma^*$ transitions

($n \rightarrow a_1^*$, $n \rightarrow b_2^*$) and at higher energy two $\sigma \rightarrow \sigma^*$ ($a_1 \rightarrow a_1^*$, $a_1 \rightarrow b_2^*$). On qualitative grounds, this one-electron description of electronic excitation in thian is to a large extent found to hold for the two isomers. Nonetheless, the mixing of the various electronic configurations due to CI is required to discuss the chiroptical properties of this molecule. In fact after CI, the $n \rightarrow b_2^*$ and $a_1 \rightarrow a_1^*$ transitions in the

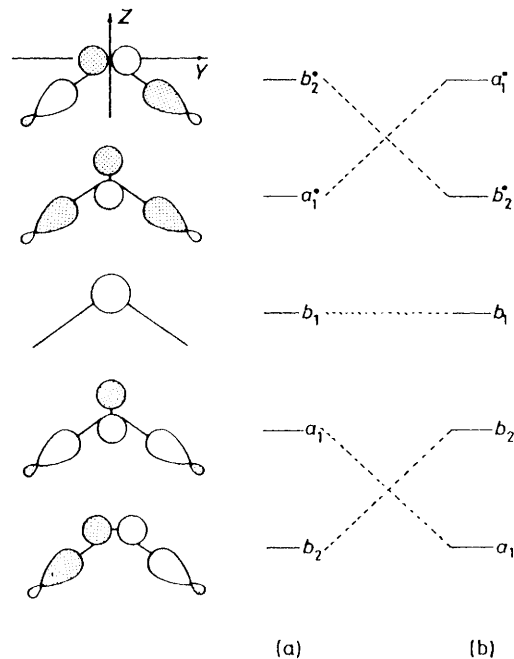


FIGURE 3 Walsh-type correlation diagram of the orbital levels of the thian (a) and the MO levels of thiiran (b)

axial conformer and the $n \rightarrow a_1^*$ and $a_1 \rightarrow b_2^*$ transitions in the equatorial form reverse the sign of the rotational strengths.

A further improvement in the description of the electronic excitations is easily obtained by using the 'random phase' approximation (RPA). This procedure allows the inclusion of some important correlation energy contributions to the optical activity. In addition, as discussed by Bouman and Hansen,⁹ RPA is the only single particle-hole scheme, defined with reference to a single determinant H-F ground state, which satisfies the general hypervirial theorem; this ensures, in the limit of a complete orbital expansion, the equivalence of the rotational strengths computed by different representations of the electric dipole operator. In one case, the RPA method was found to offer significant advantages over the CI method in the calculations of natural c.d. intensities.¹⁰

From a comparison of the computed and experimental results, the following interpretation of the spectral data emerges. At low energy the c.d. spectrum is dominated by a large negative band, which is assigned to the $n \rightarrow b_2^*$ transition. This transition is nearly forbidden in absorption but is magnetically allowed and therefore gives rise to the intense (negative) c.d. at ca. 230 nm.

The orbital diagram in Figure 3 indicates that the transition is shifted to lower energies in episulphides. Accordingly, most of the assignments of the u.v. absorptions and c.d. intensities of this class of molecule locates this transition at *ca.* 260 nm.

Since the two conformers of the unsubstituted thian molecule are energetically equivalent, one can classify the electronic transitions of this molecule according to the C_{2v} (M) molecular symmetry group.¹¹

The thian molecule is expected to assume in a liquid crystalline matrix a disc-like orientation, *i.e.* molecular packing with the mesomorphic molecules preventing orientation of the 'mean molecular plane' perpendicular to the local director.

In the structure of the liquid crystal used as solvent the presence of two cyclohexyl moieties certainly strengthens the disc-like orientation of the thian molecule.

With this expectation a negative and a positive linear dichroism ($A_{\parallel} - A_{\perp}$) must be assigned to the out-of-plane or in-plane polarized transitions respectively.^{12,13}

Rotational strength (10^{-40} cgs) computed for the lowest electronic transitions of the equatorial and the axial conformers of 3-methylthian in the single configuration (a), CI (b), and RPA (c) using the dipole length (d) and the dipole velocity (e) representation of the electric dipole operator

Electronic transition	Equatorial conformer						Axial conformer					
	(a), (d)	(a), (e)	(b), (d)	(b), (e)	(c), (d)	(c), (e)	(a), (d)	(a), (e)	(b), (d)	(b), (e)	(c), (d)	(c), (e)
$n \rightarrow a_1^*$	1.3	0.8	-0.7	-0.5	-0.4	-0.5	0.5	0.7	0.8	0.9	1.0	0.8
$n \rightarrow b_2^*$	-5.3	-4.3	-1.9	-1.8	-1.9	-2.0	1.1	0.6	-0.5	-0.5	-0.6	-0.6
$a_1 \rightarrow a_1^*$	0.7	0.8	1.0	1.0	1.1	1.2	-1.0	-0.8	3.4	3.5	2.3	2.5
$a_1 \rightarrow b_2^*$	-0.1	0.5	-11.2	-5.4	-9.0	-4.9	-16.4	-9.6	-36.2	-24.1	-33.8	-21.0

The l.d. spectrum indicates out-of-plane polarization for the 230 nm band, probably due to a vibronic interaction of the excited nb_2^* state. Rosenfield and Moscovitz⁴ have assigned the next transition to higher energy to the na_1^* excited state. The l.d. spectrum clearly indicates that the transition at 212 nm has in-plane polarization. In addition, the rotational strength computed in the more correct approximation for the $n \rightarrow a_1^*$ transition has the sign opposite to the measured c.d.

For these reasons we propose for the u.v. and c.d. band at 212 nm the assignment $a_1 \rightarrow a_1^*$, which is, according to our RPA and CI computations, the only transition in Figure 3 with positive c.d.

No definitive conclusions can be reasonably obtained for the assignment of the 200 nm band and for the location of the $n \rightarrow a_1^*$ and $a_1 \rightarrow b_2^*$ transitions in the measured spectra. In particular, the $n \rightarrow a_1^*$ transition is an unlikely candidate for the very intense 200 nm

* The magnetic rotational strength for the $n \rightarrow \sigma^*$ transition is proportional to the quantity in equation (i). With the assumption

$$B_{\sigma n} = \mu_{\sigma n} [\sum_s (m_{ns} \times \mu_{s\sigma}) / (E_s - E_n) - \sum_s (\mu_{ns} \times m_{s\sigma}) / (E_s - E_{\sigma})] \quad (i)$$

that the first term dominates the expansion, the B terms for the two $n \rightarrow b_2^*$ and $n \rightarrow a_1^*$ transitions are predicted to have opposite values and in fact the 230 and 260 nm m.c.d. bands show opposite signs.

$$B_{na_1^*} = \mu_{na_1^*} \cdot m_{a_1^*b_2^*} \times \mu_{nb_2^*} / (E_{nb_2^*} - E_{na_1^*}) \quad (ii)$$

$$B_{nb_2^*} = \mu_{nb_2^*} \cdot m_{b_2^*a_1^*} \times \mu_{na_1^*} / (E_{na_1^*} - E_{nb_2^*}) = -B_{na_1^*} \quad (iii)$$

absorption, since this transition should have lower energy (see Figure 3) and negative c.d. (Table).

The m.c.d. spectrum (Figure 2) reveals a very weak negative band at *ca.* 260 nm. This observed magnetic rotational strength could originate from the $n \rightarrow a_1^*$ transition* or a Rydberg-like transition.⁶ We favour the latter assignment, since the low absorption intensity in the 260 nm region is not compatible with an allowed $n \rightarrow a_1^*$ transition.

Since the $n \rightarrow b_2^*$ and the $n \rightarrow a_1^*$ transitions are predicted to be nearly degenerate, it is possible that the two transitions appear in the same spectral region, with the $n \rightarrow a_1^*$ transition being in fact responsible for most of the absorbed intensity (the l.d. of thian has the correct sign) and the $n \rightarrow b_2^*$ transition carrying most of the c.d. activity.

As the $a_1 \rightarrow b_2^*$ transition has positive l.d. and negative c.d. (Table), the absorption at *ca.* 200 nm cannot be assigned to this state. Excitations from the lone pair to virtual MOs of the alicyclic ring, not con-

sidered in Figure 3, should be considered for the absorption at 200 nm.

Optical Activity and Stereochemistry of Cyclic Sulphides.—Since the assignment of the lowest $n \rightarrow b_2^*$ transition appears unambiguous, and considering that the symmetry rule previously proposed on the grounds of a dynamic coupling approach is related to this transition,³ stereochemical considerations will be derived only from the low energy band of the c.d. spectrum.

On going from the symmetric thian to the methyl derivative, 'dynamic' optical activity arises due to the mixing of the $\sigma \rightarrow \sigma^*$ transition of the methyl substituent.

In the case of the 3-methylthian molecule, this is especially evident in the expression of the virtual MOs, which have a considerable contribution from the σ^* C-C exocyclic anti-bonding MO.

In the CI wave functions, the two important configurations for the description of the excited states are given by expression (1). As the mixing coefficient λ is

$$|\sigma \bar{\sigma} n \bar{b}_2^*| + \lambda |\sigma \sigma^* n \bar{n}| \quad (1)$$

proportional to the two electron repulsion integral ($nb_2^* | \sigma \sigma^*$), electrostatic arguments and multipole expansion of the matrix element can be used to make *a priori* estimates of the relative phases of the two components of the excited state.³ For this purpose, it is useful to make a distinction between the quadrupolar fields arising from the one- and two-components of the nb_2^*

charge distribution. The polarization of the substituent resulting from the $\sigma \rightarrow \sigma^*$ excitation will in general minimize the electrostatic interaction between the $\sigma\sigma^*$ dipole and the one- or two-centre components of the quadrupolar field depending on the position of the substituent. This determines the direction of the induced dipole moment in the substituent. With the assumption that this contribution is the most important in determining the optical activity, the scalar product of the induced electric dipole with the intrinsic magnetic dipole of the $n \rightarrow b_2^*$ transition gives the sign of the lowest c.d. band. By this procedure, a sector rule is obtained, where the chromophore region is divided into 12 sub-regions or sectors as shown in Figure 4.

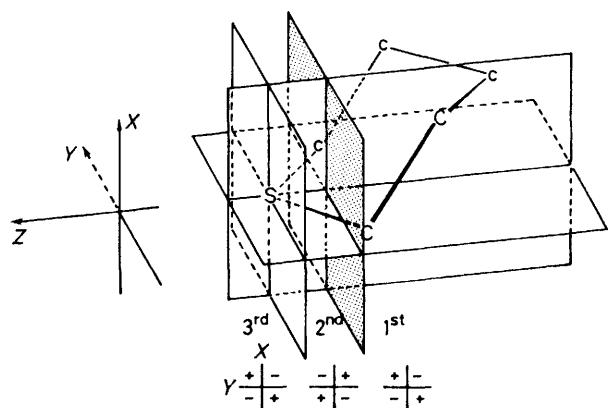


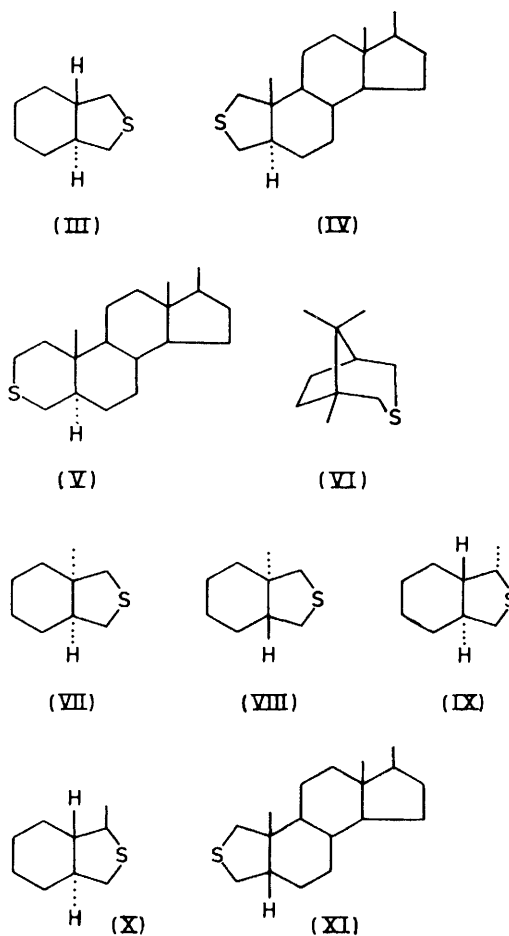
FIGURE 4 Sector rule for the thian chromophore

This sector rule is obeyed by all sulphur compounds investigated by Rosenfield and Moscovitz⁴ when the substituent in (III)—(V) and the methyl substituent in (VI) are placed into the first region, the contribution of the ethylenic bridge in (VI) being neglected, due to its symmetric nature. The c.d. spectra of equatorial 3-methylthian investigated in the present study and of a number of sulphur compounds studied by Hagishita and Kuriyama⁵ are also consistent with the sector rules in Figure 4 when the substituents in the α -position with respect to the sulphur atom are placed into the second region [compounds (IX) and (X)].

The only apparent exception is provided by the contribution of β -axial substituents [present in derivatives (VII), (VIII), and (XI)], for which the sector rule gives a rotational strength opposite in sign to the experimental value when the substituent is assigned to the first region.

Given the assignment proposed in the previous section for the $n \rightarrow b_2^*$ electronic transition of 3-methylthian with an axial conformation, the value of the rotational strengths computed by the CI and RPA methods are in qualitative agreement with the experimental results of Hagishita and Kuriyama. On the other hand, the sector rules in Figure 4 can be reconciled with the experimental measurements of Hagishita and Kuriyama and with the CI and RPA rotational strengths for the axial conformer, by shifting the sector plane between regions I

and II, as a result of the opening of the $\widehat{C-S-C}$ bond angle in five- and six-membered rings. The position of this plane is determined by the two centre overlap between the $3p_x$ lone pair and the $2p$ orbitals of C-2 and -6 in the b_2^* antibonding MO. By opening the $\widehat{C-S-C}$ angle,



the contribution of the $2p_y$ orbitals increases considerably (in thirans the $2p_z$ component is dominant) and therefore the plane shifts towards the carbons.

Although this interpretation seems satisfactory, one cannot in principle disregard other contributions to the optical activity such as static couplings and through bond interactions.^{14,15} With regard to this last point the considerable contributions to the description of the σ^* excited orbital of the equatorial bonds in the C-3 and -5 positions, which are in a **W** relation to the sulphur lone pair, seem remarkable.

EXPERIMENTAL

C.d. and m.c.d. spectra were measured using a JASCO J-500A spectropolarimeter with DP-500 data processor. U.v. spectra were measured using a Cary 14 spectrophotometer. L.d. spectrum was recorded by a modulated technique (JASCO l.d. attachment to the J-500A spectropolarimeter) using a bicyclohexyl nematic liquid crystalline matrix transparent to the u.v. radiation (E. Merck; ZLI 1167) and a surface coupling agent in order to get linearly

anisotropic samples. The calibration and the experimental details of the technique will be discussed elsewhere.¹³ M.p.s are uncorrected. Optical rotations were measured using a Bendix NPL polarimeter.

(+)-(S)-2-Methylglutaric acid was prepared by resolution of the racemate with strychnine following the method described in ref. 16. The acid had $[\alpha]_D +22.5^\circ$ (*c* 2, absolute ethanol), m.p. 77–81 °C {lit.,¹⁶ m.p. 81 °C, $[\alpha]_D +21.7^\circ$ (*c* 5, absolute ethanol)}. (+)-(S)-Diethyl 2-methylglutarate was prepared as described in ref. 7 for the racemate, $[\alpha]_D 22.5^\circ$ (*c* 2, ether). (-)-(S)-2-Methylpentane-1,5-diol was prepared from the diester by reduction with LiAlH₄,⁷ $[\alpha]_D -8.5^\circ$ (*c* 2, ether). (-)-(S)-2-Methyl-1,5-dibromopentane was prepared from the diol as described in ref. 7 for the racemate. The product had $[\alpha]_D -3.9^\circ$ (*c* 2, ether). (-)-(S)-3-Methylthian was prepared as described in ref. 7 for the racemate, $[\alpha]_D -3.1^\circ$ (*c* 2, n-hexane). The ¹H n.m.r. spectrum agreed with that reported in ref. 7.

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