Optical Activity of the 260 nm Transition of Chiral Thiirans

By **Giovanni Gottarelli** * and **Bruno Samorì**, Istituto di Chimica degli Intermedi, Facolta' Chimica Industriale, Viale Risorgimento 4, 40136 Bologna, Italy
Irene Moretti and **Giovanni Torre**, Istituto di Chimica Organica, Universita' di Modena, Modena, Italy

The optical activity of the 260 nm $n \longrightarrow \sigma^*$ transition of chiral thiirans is rationalized in terms of a dynamic coupling mechanism. From the treatment a symmetry rule is derived.

RECENTLY, the nature of the electronic transitions observed between 45 000 and 35 000 cm^{-1} in thiirans has been studied using information obtained from a comparison between the experimental and theoretical c.d. and absorption spectra of (+)-*R*-methylthiiran.[1] From this study it was concluded that two transitions are present in the region, on the low energy side a symmetry allowed but weak $n \longrightarrow 4s$ ($B_1 \longleftarrow A_1$) transition, on the higher energy side an electrically forbidden and magnetically allowed $n \longrightarrow \sigma^*$ ($A_2 \longleftarrow A_1$) transition. The *n* orbital given by the MO treatment is an almost pure $3p_x$ sulphur AO, 4*s* is also an almost pure sulphur AO, while σ^* is an antibonding orbital involving sulphur $3p_y$, $3d_{yz}$, and carbon 2*s* and $2p_z$ AOs (Figure 1).

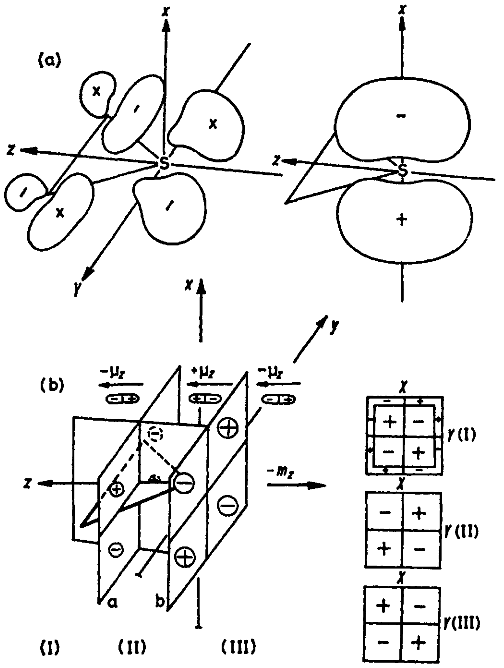


FIGURE 1 (a) Orbitals of the ground and excited states of the $n \longrightarrow \sigma^*$ transition; (b) interaction of the resulting multipolar transition charge distribution with the dipole induced in a polarizable perturber and its expected contribution to the optical activity in the regions (I)—(III) of space surrounding the chromophore (lower left and right)

Although direct MO calculations of optical activity are quite frequent,[2] for molecules of the type considered here, their use is problematic because of conformational uncertainties and the dimensions of the molecules. Furthermore, experimental chemists often prefers a more pictorial description such as those given by perturbation approaches such as the static[3] and dynamic[4] coupling mechanisms. Using these theories it is often possible to obtain symmetry rules which allow a rapid evaluation of the effect of substituents and variations in conformation on the optical activity.

In this paper we use the assignment given above to rationalize by means of the dynamic coupling theory the c.d. spectra of several thiirans.[5] In the examples considered here, the optical activity due to the $n \longrightarrow 4s$ transition is of little interest as its weak c.d. is not resolved from the stronger band due to the $n \longrightarrow \sigma^*$ transition. Only in the case of t-butylthiiran is this transition clearly detected; we shall therefore deal almost exclusively with the $n \longrightarrow \sigma^*$ transition.

RESULTS AND DISCUSSION

The orbitals involved in the 260 nm transition of the parent thiiran (ethylene sulphide) are shown in Figure 1(a); the magnetic dipole moment M_z is directed along the two-fold symmetry axis and its calculated value is —0.517 a.u.[1] Rotational strengths were calculated using the approximations described by Eyring *et al.*[6] following equation (1) where the index *j* refers to perturbing groups

$$R_{0a} = \frac{2}{\hbar}\sum_j\sum_b Im\left(V_{0a,j0b}\,\vec{\mu}_{j0b}\cdot\vec{m}_{a0}\,\frac{\nu_{0b}}{\nu_{0a}{}^2 - \nu_{0b}{}^2}\right) \quad (1)$$

whose excited states are labelled by *b*, μ_{j0b} are the electric dipole transition moments of the $0 \longrightarrow b$ transition of the perturber, and m_{a0} is the magnetic moment of the $0 \longrightarrow a$ transition of the chromophore. $V_{0a,j0b}$ is the perturbation energy between the charge distributions of the $0 \longrightarrow a$ and the $0 \longrightarrow b$ transitions and in this case was approximated by a charge dipole interaction in the extended multipole approach [equation (2)].

$$V_{0a,j0b} = \sum_i q_{i0a}\frac{\vec{r}_{ij}\cdot\vec{\mu}_{j0b}}{r_{ij}{}^3} \quad (2)$$

The summation is extended over the *i* monopoles of the $0 \longrightarrow a$ chromophoric transition. The distance from the monopoles to the perturbers' transition dipole centres is indicated by $r_{ij} = (r_j - r_i)$. Owing to the large distances between the monopoles which are comparable to

---

[1] G. L. Bendazzoli, G. Gottarelli, and P. Palmieri, *J. Amer. Chem. Soc.*, 1974, **96**, 11.

[2] R. E. Geiger and G. H. Wagniere, *Helv. Chim. Acta*, 1975, **58**, 738.

[3] J. A. Schellmann, *J. Chem. Phys.*, 1966, **44**, 55.

[4] E. G. Hohn and O. E. Weigang, jun., *J. Chem. Phys.*, 1968, **48**, 1127.

[5] Preliminary communication, G. Gottarelli, B. Samorì, and G. Torre, *J.C.S. Chem. Comm.*, 1974, 398.

[6] W. H. Inskeep, D. W. Miles, and H. Eyring, *J. Amer. Chem. Soc.*, 1970, **92**, 3866.

the molecular dimensions (see Table 1) it seemed unrealistic to use dipole–quadrupole interactions.

The multipolar charge distribution associated with the transition is depicted in Figure (1b). The transition monopoles were derived using equations (3) and (4),[7] q_i

$$q_i = \sqrt{2}\, e\langle n|\sigma^*\rangle_i \tag{3}$$

$$r_i = \frac{\langle n|\hat{\mathrm{r}}|\sigma^*\rangle_i}{\langle n|\sigma^*\rangle_i} \tag{4}$$

and r_i being the charge and the co-ordinate of the ith monopole respectively. The ith integral is taken over the region of space in which the product $n.\sigma^*$ has a constant sign. The factor $\sqrt{2}$ results from the double occupation of the n orbital. The nodal surfaces bisecting the thiiran ring were approximated by planes, the positions of which were evaluated from computed drawings of the charge density.[8] The exponents of the AO were those used for the MO calculations.[1] All integrals were calculated by numerical methods. The characteristics of the monopoles are reported in Table 1.

The monopoles derived from the overlap of the $3p_x$ sulphur AO with the rear lobe of the sp hybrid orbitals on the carbon atoms were extremely small and were neglected as individuals; their overall contribution was however taken into account by extending the integration space across the nodal plane on the C–C bond of the thiiran ring. The transition monopoles induce in a dissymmetrically positioned polarizable group a dipole in a sense that is attractive. Such a dipole provides a component along the z direction which can be parallel or antiparallel to the magnetic moment of the $n \longrightarrow \sigma^*$ transition giving a non-vanishing scalar product and hence optical activity.

TABLE 1

Characteristics of the monopoles

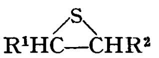
Front	Rear
$q = \pm 0.658 \times 10^{-10}$ e.s.u.	$q = \pm 0.08 \times 10^{-10}$ e.s.u.
$x = \pm 0.586$ Å	$x = \pm 0.489$ Å
$y = \pm 0.577$ Å	$y = \pm 0.640$ Å
$z = -0.266$ Å	$z = +1.16$ Å

As expected, the charge of the monopoles located near the sulphur atom (' front monopoles ' arising mainly from the one-centre $3p_x$, $3p_y$ integral) are larger than those of the monopoles lying near the carbon atoms (' rear monopoles ' arising mainly from two-centre integrals); the latter are however by no means negligible and, at a small distance, *i.e.* for substituents located near the ring carbon atoms behind the plane containing the monopoles, their effect becomes dominant over that of the ' front monopoles '.

The values of the electric dipole transition moments for the aliphatic C–C bonds and the relative frequency were taken from ref. 6. The contributions from the C–H bonds were neglected.[6] The t-butyl group was considered to be in a staggered conformation. For the phenyl groups only transitions which are long-axis polarized were considered, as their electric dipole does not change orientation by rotation of the aromatic ring around the exocyclic C–C bond. Quantitative values were taken from experimental spectra.[9] The point dipoles were located at the centre of the benzene rings and the C–C bonds of the alkyl groups.

The results obtained are reported in Table 2 together with the experimental data. The quantitative experimental values of the rotational strength are however affected by two sources of error: the presence of a contribution to the optical activity from the $n \longrightarrow 4s$ transition and, for the aromatic derivatives, a possible contribution from the ^1L_b transition. These contributions, because of the limited resolving power of the dichrograph, could not be evaluated separately. They are however unlikely to affect the qualitative values. Only in the c.d. spectrum of (+)-*R*-t-butylthiiran are two transitions clearly seen in this region (Figure 2). This confirms the existence of a second weak transition in the region.[1] The

TABLE 2

Rotation strength of thiirans 

$$R^1HC\overset{S}{\frown}CHR^2$$

R¹	R²	Absolute configuration	$10^{40}R$ (exp.)	$10^{40}R$ (calc.)
H	Me	*R*-(+)	−1.0	−1.27
H	t-Bu	*R*-(+)	+0.4	+0.15
H	Ph	*R*-(−)	−4.5	−0.95
Ph	Me (*trans*)	2*R*,3*R*-(+)	−6.7	−2.2
Ph	Me (*cis*)	2*S*,3*R*-(−)	+3.8	+0.3
Ph	Ph (*trans*)	2*R*,3*R*-(+)	−4.7	−1.9

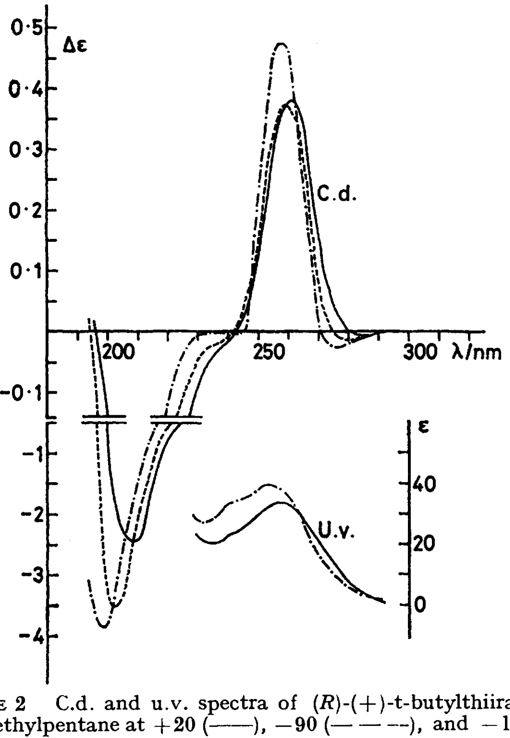


FIGURE 2 C.d. and u.v. spectra of (*R*)-(+)-t-butylthiiran in 3-methylpentane at +20 (——), −90 (— — —), and −180 °C (— · — · —)

---

[7] R. W. Woody and I. Tinoco, jun., *J. Chem. Phys.*, 1967, **46**, 4927.

[8] G. L. Bendazzoli, G. Gottarelli, P. Palmieri and G. Torre, *Mol. Phys.*, 1973, **25**, 473.

[9] G. Gottarelli, S. F. Mason, and G. Torre, *J. Chem. Soc.* (*B*), 1970, 2349.

$n \longrightarrow 4s$ transition has a very small electric moment and, from the point of view of atomic symmetry is magnetically forbidden; hence, there are no important sources of optical activity. On the other hand, the value of R calculated for this transition in the case of (+)-*R*-methylthiiran is about one order of magnitude smaller than that calculated for the $n \longrightarrow \sigma^*$ transition.[1]

For what concerns the ^1L_b aromatic transition, in arylthiirans its typical fine structure is not detectable in the c.d. band at *ca.* 260 nm, the shape of which is very similar to those of alkylthiirans.

In the light of the quantitative uncertainties in the experimental data, and considering the crude approximations used in the calculations, we believe that the agreement found between experimental and calculated data is very good. This is particularly true if one thinks that the characteristics of the monopoles result directly from calculations, without changing the AO exponents of the original MO and without rearranging the positions of the monopoles. The good agreement obtained is probably related to the self-cancellation of different types of errors. However, we believe that the physical model outlined is consistent with the experimental data.

Unfortunately, because of the complex form of the perturbation energy, it is impossible to deduce an analytical expression which defines a symmetry rule. However, considering that $V_{0a,j0b}$ vanishes in the xz and yz planes and using the signs of rotational strengths calculated for a few examples, one can deduce the following approximate picture. There is a first region at the back of the plane containing the rear monopoles where the polarization induced in a perturber by these monopoles is dominant. Perturbing groups directly bonded to the carbons of the thiiran ring or lying near the rear monopoles should give contributions to the optical activity having the signs depicted in (I) [Figure 1(b)]; the front monopoles give opposite polarisation, hence opposite contributions to the optical activity but, owing to their larger distance, their contribution is smaller. However a substituent still lying in this region but further away from the rear monopoles feels a polarisation effect mainly from the stronger front monopoles and gives a contribution to the optical activity which, however small, is opposite to that depicted in (I) (central part). We have therefore indicated a limiting contour line in Figure 1.

There is a second region between the planes containing the front and the rear monopoles where a perturber is polarized in the same direction by both the front and the rear monopoles. The optical activity observed should have the signs depicted in (II). The effect of groups in this region should be higher than in region (I). Finally, there is a third region limited by the plane containing the front monopoles in which a perturber mainly feels their effect. The optical activity observed should have the signs depicted in (III).

The rule proposed easily explains the fact that (+)-*R*-t-butylthiiran has c.d. opposite to that of (+)-*R*-methylthiiran, the reversal in sign being caused by the large contribution of a methyl group of the former derivative in region (II) (see also the quantitative calculations).

The c.d. spectrum of (+)-*R*-isopropylthiiran shows at *ca.* 263 nm a negative Cotton effect of intensity similar to that of methylthiiran.[10] This is in agreement with our predictions as it is known that the isopropyl group in cyclic systems is in a conformation in which the alkyl groups lie outside the ring.[11]

The experimental data reported for steroidal episulphides by Kuriyama *et al.** [12] and Cookson *et al.*[13] fit our predictions reasonably well, as discussed below.

2α,3α-*Epithio*-5α-*derivatives*.—The *X*-ray structure of 2α,3α-epithio-5α-androstane 17β-*p*-bromobenzoate has recently been determined.[14] Rings B and C have chair and ring A and D half-chair conformations. In particular in ring A C(1)—(4) are nearly coplanar and C(5) and C(10) are displaced by −0.44 and 0.36 Å to opposite sides of this plane.

Using this conformation (see Figure 3) it can easily be seen that the C(1)–C(2) and C(3)–C(4) bonds are in the back region (I) and should give equal and opposite contributions; the C(4)–C(5) bond enters region (II) and should give a negative contribution; the C(1)–C(10) bond is in region (I) and should give a small negative contribution. All the other bonds should have negligible effects. In fact 2α,3α-epithiocholestane [13] and 2α,3α-epithioandrostane [12] both show a negative c.d.

Introduction of a 2β-methyl group should give a positive contribution (Δθ −2 300); [12] a 3β-methyl group, instead, a negative contribution (Δθ −3 390)[12]; a 1α-methyl group falls in region (II) and should give a large positive contribution (Δθ +6 400).[12] The case of 2α,3α-epithiolanostane is more complicated because of the conformational uncertainties introduced by the presence of the 4β-methyl group which, by interaction with the angular methyl at C(10) might cause a distortion of ring A. If ring A adopts the same half-chair conformation as the parent cholestane or androstane, then the 4α-methyl is in region (II), very near to the nodal plane and should give a small negative contribution (see Figure 3). If ring A is distorted in order to keep the angular and the 4β-methyl away from each other, then the 4α-methyl group is markedly in region (II) and should give a large negative contribution; in this case however the C(4)–C(5) bond is no longer in region (II) and the optical activity should be similar to that of the androstane and cholestane derivative.

---

* Ref. 12 also reports a Huckel MO treatment of chiral episulphides in which a carbon $2s$ AO is considered as a dissymmetric electric donor substituent. The calculations are repeated each time by shifting the $2s$ AO into different positions. In this way a symmetry rule is obtained which, although possessing different nodal planes, is for practical qualitative purposes substantially equivalent to the one described here.

[10] N. Spassky, personal communication.

[11] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Wiley, New York, 1965, pp. 44, 458.

[12] K. Kuriyama, T. Komeno, and K. Takeda, *Tetrahedron*, 1966, **22**, 1039.

[13] D. E. Bays, R. L. Cookson, R. R. Hill, and J. E. McGhie, *J. Chem. Soc.*, 1964, 1563.

[14] K. Utsumi-Oda and K. Koyama, *J.C.S. Perkin II*, 1973, 1866.

Experimentally, the lanostane derivative gives a negative Cotton effect slightly larger than that of the cholestane derivative.

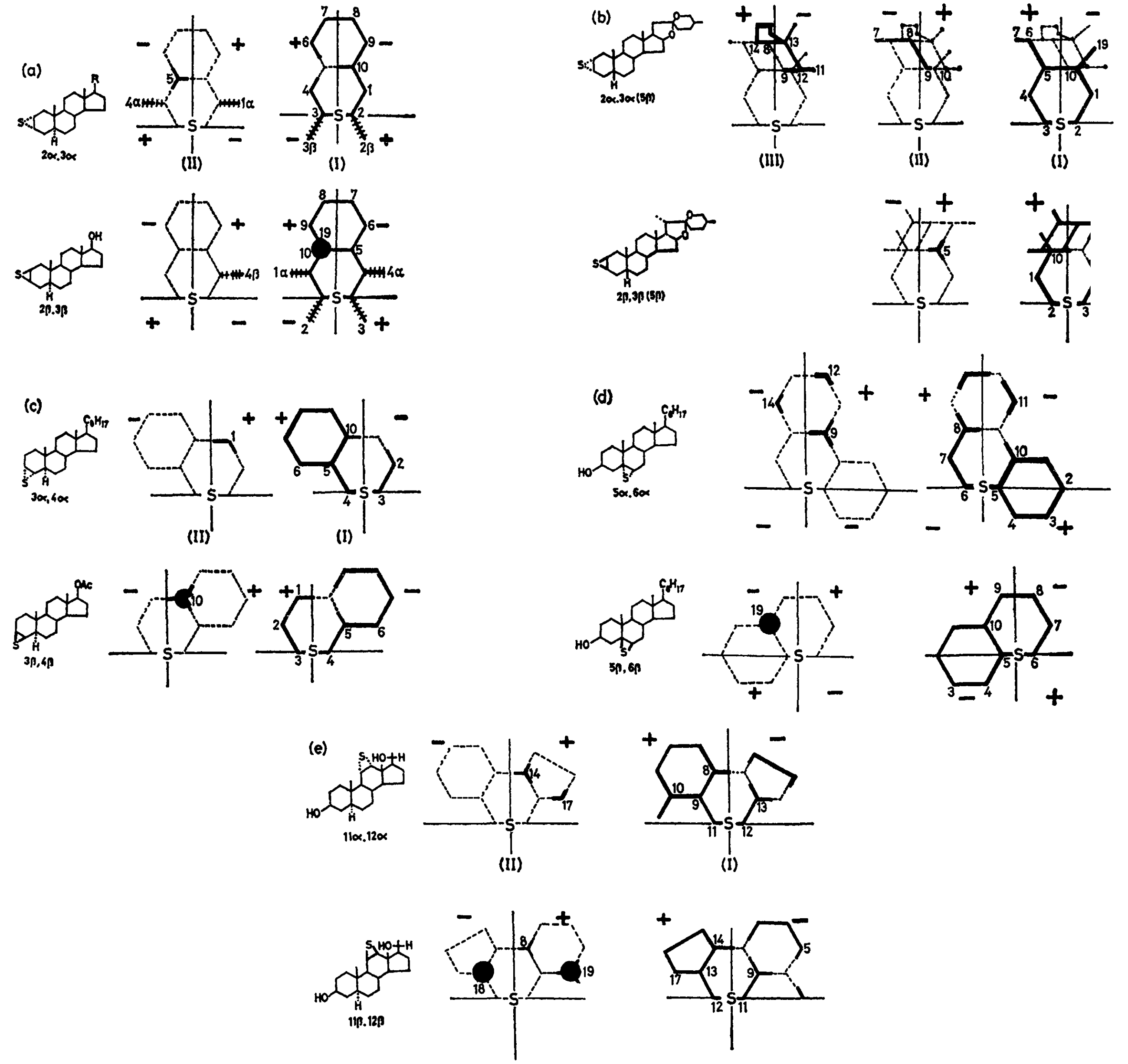


FIGURE 3 Sector projections of steroidal episulphides, looking along the twofold symmetry axis of the thiiran ring (+ Z direction). Full lines represent the parts of the molecule which enter the region considered in the specific drawing; broken lines indicate the part of the molecule lying outside this region

2β,3β-*Epithio*-5α-*derivatives*.—Again the conformation of ring A is not known. If the half-chair conformation is assumed for this system, interactions between angular methyl at C(10) and the epithio-ring are avoided. In this case all the bonds around the chromophore are in region (I), although the methyl group is very near to the nodal plane with region (II). Small optical activity is predicted (θ_{obs} +415).[12]

Introduction of a 2α-methyl group gives a negative contribution ($\Delta\theta$ −5 500);[12] methyl groups in positions 1α and 3α [all region (I)] give [12] the expected effects. In the lanostane derivative the 4β-methyl group is in region (II) and should give a positive contribution, as is experimentally observed.[13]

2α,3α-*Epithio*-5β-*spirostane*.—If ring A is in the half-chair and B and C in the chair conformation, the steroidal skeleton is folded on the epithiochromophore. The C(9)–C(10) bond is in region (II) (positive); the C(9)–C(11) and C(11)–C(12) bonds as well as ring D are probably in region (III) (negative). On this basis the observed [12] negative Cotton effect can be explained.

2β,3β-*Epithio*-5β-*spirostane*.—Again if ring A is in the half-chair, and B and C in the chair conformation, then C(4)–C(5) is in region (II) (positive); C(1)–C(10) is in region (I) (positive). The 10-methyl group is always in region (I) although quite distant from the chromophore. The 2β,3β-epithio-5β spirostane derivative described [12] gives a positive cotton effect (θ +4 950).

3α,4α-Epithio-5α-cholestane.—C(1) is in region (II) and should give a positive contribution, the C(5)–C(10) bond is in region (I) (positive), ring B is also in a positive region, but probably only the C(5)–C(6) bond is near enough to the chromophore. 3α,4α-Epithio-5α-cholestane shows positive dichroism.[12]

3β,4β-Epithio-5α-androstane.—In this case also, in the half-chair conformation there is considerable interaction between the angular methyl and the episulphide ring (similar to the 2β,3β-epithio-5α-derivatives). If this conformation is considered, a positive c.d. is predicted (Figure 3) which is larger than experimentally found (θ +325). If the half-chair is distorted in order to keep the two interacting groups further apart, the angular methyl approaches the nodal plane between region (I) and (II) and a smaller positive c.d. is expected.

5α,6α-Epithiocholestane.—The C(10)–C(1) and C(3)–C(4) bonds near the nodal plane between region (I) and (II) should have equal and opposite effects, C(4)–C(5) and C(7)–C(8) [region (I)] give positive contributions and also C(9)–C(10) [region (II)]. 3β-Hydroxy-5α,6α-epithiocholestane has in fact θ +6 680.[12]

5β,6β-Epithiocholestane.—From molecular models, when ring A is in a chair conformation and B in a half-chair all the groups around the chromophore are in region (I) and should roughly compensate for each other, except the angular methyl group, which is in region (II) and should give a large negative contribution. 3β-Hydroxy-5β,6β-epithiocholestane has θ −4 460.[12]

11α,12α-Epithiopregnane.—The main contribution to rotation should be that of C(13)–C(14) [region (II), positive]. The C(13)–C(17) bond is also in region (II) but further from the chromophore. 3β,20β-Dihydroxy-11α,12α-epithiopregnane shows θ +4 060.

11β,12β-Epithiopregnane.—The 13-methyl group is in region (II) (negative); the C(10)–C(19) and C(9)–C(10) bonds are also in region (II) (positive); C(8) also probably approaches region (II). It is difficult to predict the quantitative contributions; however the effect from the three positive groups in region (II) should overcome the large negative effect of the 13-methyl group. The model pregnane derivative [12] has θ +3 460.

We have also carried out calculations on methylthiiran using equation (5) [15] where j refers to perturbing groups, i is the number of monopoles considered, X_{ij}, Y_{ij}, and Z_{ij} are the components of the distance r_{ij} be-between the charge q_{i0a} and the centre of the perturbing group j, and θ_j and χ_j are the Eulerian angles connecting the co-ordinates of the chromophores to those of the perturber.[4,13,16] The main difference between equations (1) and (5) is that (5) specifically takes into consideration the polarizability perpendicular to the bond, while equation (1), in the approximations described in ref. 6, takes into consideration only the transition moments of substituents directed along the bonds the quantitative values of which are deduced from bond anisotropies. Using equation (5) we have also taken into account the hydrogen atoms. We have used either the complete equation, or, considering isotropic polarizability, ($\alpha^{\perp} = \alpha^{\parallel} = \bar{\alpha}$), only part (5a). In both cases, however, the wrong sign was obtained. This is not surprising, considering isotropic polarizability (Denbigh values [17]): the C–H bond is

$$R_{0a} =$$

$$\frac{i}{2} m_{a0}{}^{z} \sum_j \sum_i \frac{q_{i0a}}{r_{ij}{}^3} [2(\alpha_j{}^{\parallel} \cos^2 \Theta_j + \alpha_j{}^{\perp} \sin^2 \Theta_j)\, Z_{ij} - \qquad \text{(a)}$$

$$\text{(5)}$$

$$(\alpha_j{}^{\parallel} - \alpha_j{}^{\perp})(\sin 2\,\Theta_j \cos \chi_j X_{ij} - \sin 2\,\Theta_j \sin \chi_j Y_{ij})] \qquad \text{(b)}$$

more polarizable than C–C, and further, the C–H bonds of the methyl group, which are relatively distant from the rear monopoles, mainly feel the effect of the front monopoles and give contributions opposite to that of the C–C bond. The contributions to the optical activity of the ring hydrogen atoms therefore becomes greater than that of the methyl group and the wrong sign is obtained. The same also happens using the complete equation (5). Again the C–H bond of the thiiran ring gives higher contributions than the methyl group. Obviously it would be possible to obtain good results, taking into account the C–H bonds, by increasing the distance of the rear monopoles from the thiiran ring, but we believe this procedure to be without much scope. Instead we believe that the general picture arising from considering the two sets of monopoles is satisfactory. This approach allows a semiquantitative explanation of the experimental data reported here and by other authors, and also applies to very complex molecules.

EXPERIMENTAL *

U.v. and c.d. spectra were recorded on a Cary 17 spectrophotometer and a Roussel–Jouan CD II dichrograph, respectively, using pathlengths of 0.5—1.0 mm, and cyclohexane as a solvent. Low temperature u.v. and c.d. spectra were recorded in 3-methylpentane solution. The chiroptical properties of alkyl- and aryl-thiirans at room temperature, in cyclohexane solution, are reported in Tables 3 and 4 respectively.

(S)-(−)-*Methylthiiran.* (*R*)-(+)-Methyloxiran (5.8 g, 0.1 mol),[18] $[\alpha]_D{}^{20}$ + 13.4° (neat), was added dropwise, with stirring, to a mixture of thiourea (8.0 g, 0.105 mol), ice (1.14 g), and water (17 ml). The temperature was controlled at 20° by efficient stirring for 4 h. Distillation of the products was effected without undue delay, fractionation giving a product (60%), b.p. 75—76°, $[\alpha]_D{}^{20}$ −44° (neat) {lit.,[19] b.p. 73—75°, $[\alpha]_D{}^{10}$ −51.2° (neat)}.

---

* The data reported in Tables 2—4, and Figure 2 refer to the *R* configuration in order to make easier comparison between different derivatives.

[15] R. H. Seal, Ph.D. Thesis, London, 1975.

[16] For a definition of Eulerian angles see E. R. Wilson, jun., J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955, p. 285.

[17] K. G. Denbigh, *Trans. Faraday Soc.*, 1940, **36**, 936.

[18] C. C. Price and M. Osgan, *J. Amer. Chem. Soc.*, 1956, **78**, 4787.

[19] T. Tsunetsugu, J. Furkawa, and T. Fueno, *J. Polymer Sci.*, 1971, **9**, 3529.

(S)-(−)-*t-Butylthiiran.*[20] This compound, $[\alpha]_D^{25}$ −39.00° (neat) was kindly supplied by Dr. N. Spassky, Paris University.

(R)-(−)-*Phenylthiiran.* A 50% aqueous dioxan solution of potassium thiocyanate was stirred with optically active (*S*)-(−)-phenyloxiran,[21] $[\alpha]_D^{20}$ −26.7° (neat), following the method of Guss and Chamberlain [22] modified by Stewart,[23] giving the product with b.p. 65—66° at 1.5 mmHg, n_D^{25} 1.599 5, $[\alpha]_D^{20}$ −35.0° (*c* 1.03, cyclohexane) {lit.,[24] b.p. 60° at 1 mmHg, n_D^{25} 1.597 0, $[\alpha]_D^{25}$ −15.7° (heptane)}, 35.8% optical purity.

TABLE 3

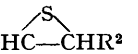
Chiroptical properties of methyl- and t-butyl-thiirans

	Absolute configuration	U.v.[a] $\lambda_{max.}$/nm	U.v.[a] $\varepsilon_{max.}$	$10^{38}D$ (c.g.s.)	C.d.[a] $\lambda_{max.}$/nm	C.d.[a] $\Delta\varepsilon_{max.}$ [b]	$10^{40}R$ [b] (c.g.s.)
Methylthiiran	(*R*)-(+)	262	40.0	3.0	264	−0.84	−1.2
		246infl	25.9				
		199	2 739.0	207.0	205	−4.53	−8.1
t-Butylthiiran	(*R*)-(+)				285	−0.01	
		259	40.1	3.7	260	+0.33	+0.4
		244infl	33.6		233—	−0.02 to	
					240	−0.03	
		202	1 904.0	160.0	209	−2.36	−3.5
		190	1 954.0		190	+1.31	

[a] Cyclohexane solution. [b] Corrected to the maximum optical value reported in the literature.

(2S,3S),(−)-trans-2-*Methyl-*3-*phenylthiiran.* A mixture of (2*R*,3*R*)-(+)-*trans*-2-methyl-3-phenyloxiran (13.4 g, 0.1 mol),[25] $[\alpha]_D^{20}$ +66° (ethanol) {lit.,[23] $[\alpha]_D^{20}$ +70.8° (ethanol)}, potassium thiocyanate (10 g, 0.104 mol), dioxan (20 ml), and water (20 ml) was stirred at room temperature for 40 h. Then the top layer of mixed sulphide and oxide was separated and then stirred for three days with a fresh aqueous dioxan solution of potassium thiocyanate. This mixture was extracted with ether (3 × 25 ml). The ether extracts were washed with water (2 × 50 ml) and dried (K_2CO_3; 24 h). The ether was removed by evaporation under reduced pressure at room temperature. The *residue* was fractionated through a short column, yield 38%, b.p. 77—79° at 2 mmHg, n_D^{20} 1.581 0, $[\alpha]_D^{20}$ −68° (*c* 1.02 cyclohexane) (Found: C,71.8; H, 6.8; S, 21.4. $C_9H_{10}S$ requires C, 71.95; H, 6.7; S, 21.3%).

TABLE 4

Chiroptical properties of arylthiirans 
$R^1HC\overset{S}{\text{—}}CHR^2$

R^1	R^2	Absolute configuration	U.v.[a] $\lambda_{max.}$/nm	U.v.[a] $\varepsilon_{max.}$	$10^{38}D$ (c.g.s.)	C.d.[a] $\lambda_{max.}$/nm	C.d.[a] $\Delta\varepsilon_{max.}$ [b]	$10^{40}R$ [b] (c.g.s.)
Ph	H	(*R*)-(−)	269	541		276	−2.20	−4.5
			261	517		250sh	+0.29	
			226	9 295		226	+14.60	+20.4
			192	43 362		205	−9.70	−21.5
Ph	Me (*trans*)	(2*R*,3*R*)-(+)	263	695		277	−3.00	−6.7
			226sh	10 546	775	250sh	+0.36	
			216sh	12 147	680	228	+16.30	+25.5
			194	39 523		207	−11.20	−20.2
Ph	Me (*cis*)	(2*S*,3*R*)-(−)	261	374		262	+2.13	+3.8
			226sh	5 731		228	+14.48	+15.1
			216	9 325		215	−7.50	−5.9
			192	43 260		201	+12.85	+11.8
Ph	Ph	(*R*,*R*)-(+)				292	−2.50	−4.7
			269	1 453		262sh	+5.23	
			238	17 856	1 886	240	+63.46	+124.4
			215infl	23 000		217	−63.25	−67.8
						206	−54.26	−44.4
			190	53 360	7 700	193	−42.63	

[a] Cyclohexane solution. [b] Values corrected to the optical purity reported in the literature for the thiirans or for the corresponding oxirans.

(2S,3R)-(−)-cis-2-*Methyl-*3-*phenylthiiran.* A mixture of (2*R*,3*S*)-(+)-*cis*-2-methyl-3-phenyloxiran (13.4 g, 0.1 mol),[24] $[\alpha]_D^{20}$ +36.5° (ethanol) {lit.,[24] $[\alpha]_D^{20}$ +41.45° (ethanol)}, potassium thiocyanate (10 g, 0.104 mol), 95% ethanol (40 ml), and water (40 ml) was stirred at room temperature for 48 h. The mixture was diluted with water and extracted with ether. The combined ether layers were dried (K_2CO_3; 12 h) and the ether was removed by evaporation under reduced pressure at room temperature. The residue was again dissolved in 95% ethanol and treated for 48 h with a fresh solution of potassium thiocyanate as previously described. After extraction with ether the combined ether layers were dried (K_2CO_3; 24 h). The solvent was removed in the usual way and the residue was fractionally distilled through a short column, yield 20%, b.p. 84—85° at 5 mmHg, n_D^{20} 1.572 0, $[\alpha]_D^{20}$ −15.3 (*c* 1.70 cyclohexane) (Found: C, 71.85; H, 6.8; S, 21,3. $C_9H_{10}S$ requires C, 71.95; H, 6.7; S, 21.35%).

---

[20] P. Dumas, N. Spassky, and P. Sigwalt, *Makromol. Chem.*, 1972, **156**, 55.

[21] D. J. Pasto, C. C. Cumbo, and J. Fraser, *J. Amer. Chem. Soc.*, 1966, **88**, 2194.

[22] C. O. Guss and D. L. Chamberlain, jun., *J. Amer. Chem. Soc.*, 1952, **74**, 1342.

[23] J. M. Stewart, *J. Org. Chem.*, 1963, **28**, 596.

[24] E. Chiellini, M. Marchetti, and G. Ceccarelli, *Internat. J. Sulfur Chem. A*, 1971, **1**, 73.

[25] H. E. Audier, J. F. Dupin, and J. Jullien, *Bull. Soc. chim. France*, 1966, 2811.

(S,S)-(−)-trans-2,3-*Diphenylthiiran*. The compound was prepared from (*R*,*R*)-(+)-*trans*-2,3-diphenyloxiran,[26] $[\alpha]_D^{20}$ +367° (benzene) {lit.,[25] $[\alpha]_D^{20}$ +357° (benzene)} with an optical purity of *ca.* 95%, as described by Ketcham and Shah for the racemic compound,[27] m.p. 58—59°, $[\alpha]_D^{20}$ −314° (*c* 1.12 cyclohexane) (Found: C, 79,5; H, 5.35; S, 15.3. $C_{14}H_{12}S$ requires C, 79.2; H, 5.7; S, 15.1%).

We thank Dr. N. Spassky for data on (*R*)-(+)-isopropylthiiran and C.N.R. (Rome) for financial support.

[5/2364 *Received, 5th December,* 1975]

---

[26] G. Berti, F. Bottari, P. L. Ferrarini, and B. Macchia, *J. Org. Chem.*, 1965, **30**, 4091.

[27] R. Ketcham and V. P. Shah, *J. Org. Chem.*, 1963, **28**, 229.