

### 310. Rotatory Properties of the $n \rightarrow \sigma^*$ Transition of Episulphides.

By D. E. BAYS, R. C. COOKSON, R. R. HILL, J. F. MCGHIE,  
and G. E. USHER.

Whereas the magnetic dipole transition moment of an  $n \rightarrow \pi^*$  transition is directed along the internuclear axis (*e.g.*, C=S in a thione), it may be at right angles in an  $n \rightarrow \sigma^*$  transition (*e.g.*, C-SR in a sulphide). For an examination of the rotatory properties of a class of  $n \rightarrow \sigma^*$  transitions the episulphide group has the advantages of absorbing in an accessible region of the spectrum (about 260  $m\mu$ ) and of having no conformational freedom. On the other hand it has the complication of two possible  $\sigma^*$  orbitals, each with three nodes not exactly at right angles to the straight line between the C and S atoms. The circular dichroism of a number of steroid episulphides and of the 9,10-epithiostearic acids has now been measured and tentatively interpreted in terms of a simplified orbital diagram (probably over-simplified!).

THE weak band in the ultraviolet spectra of episulphides that has recently been reported at about 260  $m\mu$ <sup>1,2</sup> may confidently be assigned, as the transition of lowest energy, to the  $n \rightarrow \sigma^*$  transition of the sulphur atom. The ground state of the episulphide ring is probably best described by  $sp^3$  hybridisation of all three ring atoms.<sup>3</sup> However, in this model the rotatory component of the  $n \rightarrow \sigma^*$  transition is more difficult to analyse than in the equivalent in which the orbitals of the sulphur atom are resolved into  $s$  and  $p$  components (only the  $p$  contributing to rotation), leaving the carbon atoms  $sp^3$  hybridised, and we therefore adopt the latter for the present purpose. There are, then, one  $n$  and two  $\sigma^*$  orbitals, and thus two possible  $n \rightarrow \sigma^*$  transitions. The circular component of the helical motion of an electron arises from the change  $p_z \rightarrow p_y$  or  $p_z \rightarrow p_x$  and the linear component is assumed to come from the transfer of an electron from the donor orbital of a substituent (of lower ionisation potential than hydrogen) to the same anti-bonding C-S orbital.<sup>4</sup> (We neglect the possible mixing with  $3d$  orbitals.) In a symmetric molecule the two  $n \rightarrow \sigma^*$  transitions are equally probable and the transition is optically inactive: in a dissymmetric one the net rotational strength will be the resultant of the strengths of the two  $n \rightarrow \sigma^*$  transitions (often of opposite sign), which can, in principle, be calculated by estimating the magnitude and direction of the electric dipole transition moment for each transition. The net rotational strength is then given by

$$R = \mu\rho_1 \cos \theta_1 + \mu\rho_2 \cos \theta_2$$

where  $\mu$  is the magnetic dipole transition moment, assumed the same in magnitude but at right angles in direction for the two possible transitions,  $\rho_1$  and  $\rho_2$  are the electric dipole transition moments for the two transitions, and  $\theta_1$  and  $\theta_2$  are the angles between the magnetic and electric moments in the respective transitions. The sense of rotation of charge and thus the direction of  $\mu$  in each transition can be obtained by labelling the phases in the usual way, *i.e.*, the donor orbital is put out of phase with the nearest lobes of the  $n$  and  $\sigma^*$  orbitals.†

To use these simple ideas to predict the direction of optical rotation of episulphides from the arrangement of substituents in regions of space near the episulphide ring we need

† This is because the mixed  $n$ -donor orbital of higher energy must be the antisymmetric combination, and the normal selection rules for electric and magnetic dipole transitions are then applied,  $+$   $\rightarrow$   $-$  and  $+$   $\rightarrow$   $+$  respectively.

<sup>1</sup> McGhie and Usher, *Chem. and Ind.*, 1962, 1980.

<sup>2</sup> Takeda and Komeno, *Chem. and Ind.*, 1962, 1793.

<sup>3</sup> Cf. Coulson and Moffitt, *Phil. Mag.*, 1949, **40**, 1; Coulson and Goodwin, *J.*, 1962, 2851; 1963, 3161.

<sup>4</sup> Mason, *Quart. Rev.*, 1963, **17**, 20.

to know the shapes of the episulphide orbitals as well as the relative energies and positions of all the donor orbitals whose contributions do not cancel.

The distribution of the orbitals is roughly indicated in Fig. 1, which shows what is basically the  $3p_z \rightarrow 3p_x$  transition of the sulphur atom, and Fig. 2 for the  $3p_z \rightarrow 3p_y$  transition.† The sulphur  $p_z$  orbital (shaded in the Figures) has the usual form, with a node in the plane of the ring. By analogy with the  $\sigma$  orbitals of cyclopropane,<sup>3</sup> the  $\sigma^*$  orbital is assumed to have the form of what one might call<sup>5</sup> a "bent anti-bond" or "bisected banana." In the first  $\sigma^*$  orbital (Fig. 1) a nodal plane passes through the sulphur atom in the plane  $yy'$ , another through the carbon atom, and there is a third nodal plane

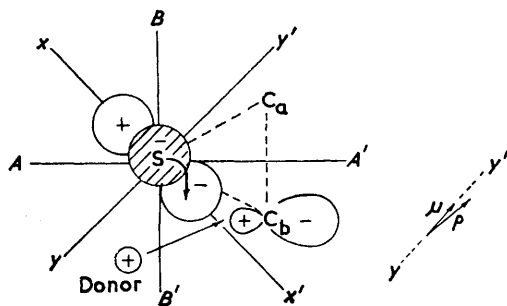


FIG. 1a.  $n \rightarrow \sigma_x^*$ , projection along axis  $zz'$ .

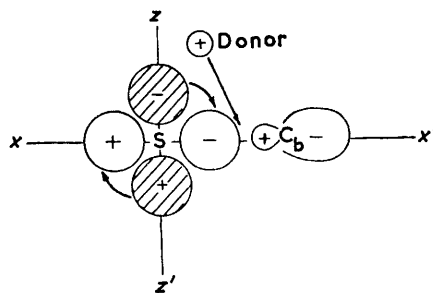


FIG. 1b. Projection along axis  $yy'$ .

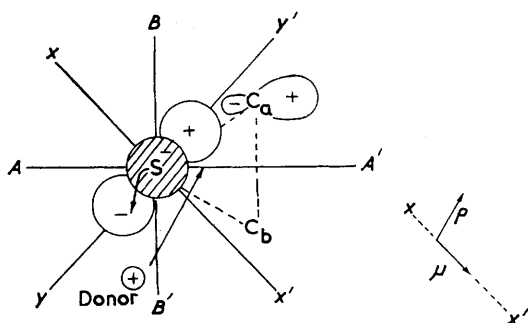


FIG. 2a.  $n \rightarrow \sigma_y^*$ , projection along axis  $zz'$ .

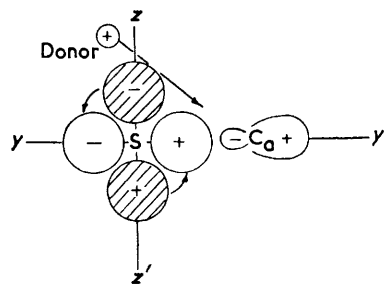


FIG. 2b. Projection along axis  $xx'$ .

surface somewhere between the two atoms, presumably nearer to carbon than to sulphur. As a simple illustration the perturbation is shown for a donor group (*e.g.*, a hydrocarbon  $\sigma$  orbital) above the plane of the ring, to the right when viewed along  $AA'$  and between the nodal surfaces passing through sulphur and the S-C bond. In Fig. 1 the rotatory movement of the promoted electron comes from the sulphur  $p_z \rightarrow p_x$  and the linear displacement from a slight admixture of a high-energy charge-transfer from the donor (D) to the same  $\sigma_x^*$  orbital. The composite transition then involves movement of the electron in a right-handed spiral, producing positive rotatory strength. Or, put in terms of moments, the charge rotates in a sense producing a magnetic field in the direction  $y'y$  or a magnetic moment in the direction  $yy'$ : the linear displacement moves the electron from D to about the middle node of the  $\sigma_x^*$  orbital, producing an electric field with a large component along  $y'y$ , or an electric moment along  $yy'$ . The parallel magnetic and electric moments cause left-hand circularly polarised light to be absorbed more than right, giving the

† For brevity later in the discussion these are referred to as  $\sigma_x^*$  and  $\sigma_y^*$  orbitals, with the episulphide ring set up in this orientation.

<sup>5</sup> Coulson, "Valence," Oxford Univ. Press, 1952, p. 205.

positive rotatory power. On the other hand in this particular geometry the magnetic and electric moments for the  $n \rightarrow \sigma_y^*$  transition (Fig. 2) are approximately at right angles, giving no rotatory strength. The net result then is positive rotation.

Compared with the carbonyl group, analysis of whose  $n \rightarrow \pi^*$  transition ( $n$  electrons in the plane of the group, only one  $\pi^*$  orbital with two nodal planes at right angles) leads to the beautifully simple and effective Octant rule,<sup>6</sup> the  $n \rightarrow \sigma^*$  transition of the epithio-group is extremely complicated. All that can be said with certainty is that reflection of the position of a group through the plane of the ring will reverse its rotatory contribution, as will reflection through the plane  $AA'$  at right angles to the ring. By the same token a group in the plane of the ring or in the plane  $AA'$  will make no contribution to the rotation. Although inspection of the orbital picture allows the unambiguous assignment of the signs of rotatory contributions from certain regions of space, lack of knowledge of the shapes of the orbitals and the nodal surfaces (especially of the middle  $\sigma^*$  node) † makes it impossible to work out even the sign of  $R$  in other regions, so that a complete diagram analogous to the Octant rule cannot yet be constructed. Meanwhile, each case is best treated separately.

The data are summarised in the Table.‡ Except that one  $n$ -heptyl substituent carries a carboxyl group at the end and the other a methyl group, the enantiomorphous *cis*-9,10-

	$\epsilon_1 - \epsilon_r$	Solvent	C.D. max. ( $m\mu$ )	Band width at half $\Delta\epsilon_{\max}$ . ( $m\mu$ )	$[\alpha]_D^\circ$ in $\text{CHCl}_3$
Optically active <i>cis</i> -9,10-epithiostearic acid (I) .....	0	b	—	—	-0.8
(+)- <i>trans</i> -9,10-Epithiostearic acid .....	-1.06	b	264	20	+79
(-)- <i>trans</i> -9,10-Epithiostearic acid .....	+1.16	b	263	20	-71
2 $\alpha$ ,3 $\alpha$ -Epithiocholestane (III) .....	-1.16	a	268	—*	+29
2 $\beta$ ,3 $\beta$ -Epithiocholestane (IV) .....	+0.21	a	264	20	+39
2 $\alpha$ ,3 $\alpha$ -Epithiolanostane (V) .....	-1.98	a	267	21	+13
2 $\beta$ ,3 $\beta$ -Epithiolanostane (VI) .....	+0.58	a	265	19	+68
2 $\alpha$ ,3 $\alpha$ -Epithiolanost-8-ene (VII) † .....	-1.59	a	265	21.5	+18.5
Di-(3 $\beta$ -hydroxyylanostan-2 $\alpha$ -yl) disulphide (VIII) .....	-0.55	a	266	—	+24
Di-(3 $\beta$ -hydroxyylanost-8-en-2 $\alpha$ -yl) disulphide	-0.31	a	260	—	-19

Solvent: a = cyclohexane; b = 95% EtOH.

\* Curve non-Gaussian. † Contained 0.5% of the 7,9-diene.

epithiostearic acid (No. 1) (I) has a plane of symmetry through the ring ( $AA'$  in Fig. 1a) and it is not surprising that it showed no measurable dichroism. The *trans*-isomer (Nos. 2 and 3) approaches  $C_2$  symmetry, and the two side-chains will make approximately equal contributions to the rotation. The precise average conformation in which the two zig-zag chains extend away from the ring may decide the sign of rotation. However, the likely source of the net contribution from the side-chains, *i.e.*, near  $C_b$  in the  $xx'$  plane or near  $C_a$  in the  $yy'$  plane (Fig. 1a), happens to lie in a region of space where  $\rho$  and  $\mu$  for the nearest transition are almost at right angles. The more distant  $n \rightarrow \sigma^*$  transition is therefore probably responsible for much of the rotation in these compounds. The delicate balance of factors makes assignment of absolute configuration hazardous.

In the half-chair conformation of 2 $\alpha$ ,3 $\alpha$ -epithiocholestane (III) the main perturbation comes from around  $C_{10}$ . The contribution of the  $S-C_2$   $\sigma^*$  transition is negative, that of the rather more distant  $S-C_3$   $\sigma^*$  is positive, so the negative rotation is understandable. The dominant effect in the 2 $\beta$ ,3 $\beta$ -epimer (IV) is the proximity of the 10-Me electrons to

† Because the sulphur orbitals are more diffuse than those of carbon and the S-C bonds are bent outward from the ring, the endocyclic lobe of the carbon orbital will usually be unimportant for overlap with donors from across the ring.

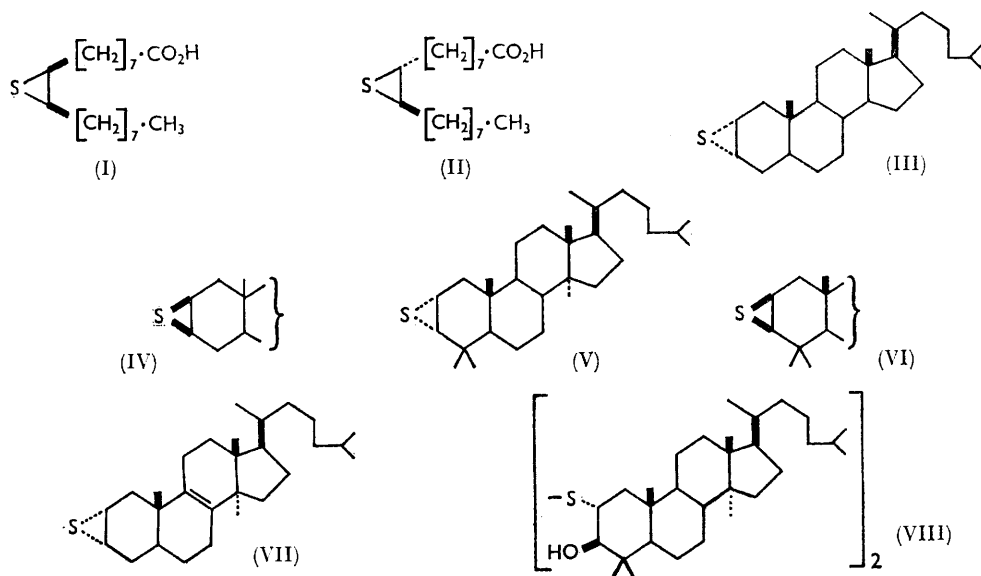
‡ [Added in Proof.] The values of  $\Delta\epsilon$  for (III) and (IV) agree fairly closely with those published by Djerassi, Wolf, Lightner, Bunnenberg, Takeda, Komeno, and Kuriyama (*Tetrahedron*, 1963, **19**, 1547).

<sup>6</sup> Moffitt, Woodward, Moscowitz, Klyne, and Djerassi, *J. Amer. Chem. Soc.*, 1961, **83**, 4013.

1566 *Rotatory Properties of the  $n \rightarrow \sigma^*$  Transition of Episulphides.*

the sulphur atom. The S-C<sub>2</sub>  $\sigma_y^*$  then becomes positive and the S-C<sub>3</sub>  $\sigma_x^*$  more weakly negative, giving the observed positive rotation.

In passing from 2 $\alpha$ ,3 $\alpha$ -epithiocholestane (III) to the lanostane analogue (V) we need consider only the effect of the two 4-methyl groups. There will be a slight change in conformation of ring A to twist the two  $\beta$ -methyl groups on C<sub>4</sub> and C<sub>10</sub> away from each other and to more nearly stagger the C<sub>4</sub>- $\alpha$  and C<sub>6</sub>- $\alpha$  bonds, but it should not significantly change



the negligibly small contribution of the rest of the  $\sigma$  framework. The perturbations from the electrons associated with the 4 $\beta$ -methyl group (especially those in the quaternary C-Me bond) will be almost on the  $xx'$  plane (cf. Fig. 1a, C<sub>a</sub> = C<sub>2</sub>, C<sub>b</sub> = C<sub>3</sub>), so that the effect on the S-C<sub>3</sub>  $\sigma_x^*$  transition will be zero or very weakly positive. The electrons of the 4 $\alpha$ -Me-C bond, being well on the  $y'$  side of the  $xx'$  plane and on the  $x'$  side of the nodal plane through C<sub>3</sub>, are in a good position for simultaneous overlap with the sulphur  $p_z$  orbital and the exocyclic lobe on C<sub>3</sub> of  $\sigma_x^*$ , and thereby confer relatively large negative rotatory power on this transition. The sense of the much weaker perturbations of  $\sigma_y^*$  by C<sub>4</sub> and its methyl groups is uncertain.

In undistorted half-chair conformations of ring A in 2 $\alpha$ ,3 $\alpha$ -epithiolanostane (V) the 4-methyl group *cis* to the epithio-ring is pseudo-equatorial and the one *trans* is pseudo-axial, whereas in the 2 $\beta$ ,3 $\beta$ -epimer (VI) the *cis*-methyl group is *pseudo*-axial and the *trans*-*pseudo*-equatorial. In these conformations the relation of the two methyl groups to the epithio-ring are very different. However, repulsion between the axial 10 $\beta$ - and 4 $\beta$ -methyl groups must cause some twisting of the *gem*-dimethyl group in both cases, which will make the orientation of the group to the epithio-ring in one epimer almost the mirror-image of that in the other. To this extent the opposite effect on the dichroism of 4-dimethylation of cholestane  $\alpha$ - and  $\beta$ -episulphides is understandable.

In other words, the twist introduced into ring A by repulsion between the 10 $\beta$ - and 4 $\beta$ -methyl groups in 2 $\beta$ ,3 $\beta$ -epithiolanostane (VI) will move the two methyl groups close to the plane  $xx'$ , so that they contribute little to the rotation of  $n \rightarrow \sigma_x^*$  and only weakly to the more distant  $n \rightarrow \sigma_y^*$ . The main effect is to force the sulphur atom closer to C<sub>10</sub> and its methyl group, thus increasing the positive rotatory contribution.

We defer comment on the two related disulphides (VIII its 8,9-dehydro-derivative)

[1964]

1567

until more examples have been measured, especially of cyclic compounds of known conformation.

## EXPERIMENTAL

Dichroism was measured with a Rousell-Jouan dichrographe. The results were calculated by substitution in the equation

$$\Delta_{\epsilon} = \frac{\text{sensitivity} \times d \times M \times \text{vol. (ml.)}}{\text{Weight (mg.)} \times \text{path-length (cm.)}}$$

where  $d$  = peak height in mm. The concentration and path length were chosen so that the slits were kept below 1.3 mm. and the sensitivity was kept at  $1.5 \times 10^{-4}$ .

The circular dichroism curves that were obtained for the acids and epithio-compounds (III—VII) had well-resolved maxima, and  $d$  varied from 10 to 60 mm. In contrast to this, the circular dichroism curves for the disulphides (VIII and its 8,9-dehydro-derivatives) were very broad, with  $d$  4.5 and 3 mm., respectively.

R. R. H. gratefully acknowledges a Union Carbide Research Fellowship. This work was partly supported by a contract from the U.S. Army, through its European Research Office.

CHELSEA COLLEGE OF ADVANCED TECHNOLOGY, LONDON.  
THE UNIVERSITY, SOUTHAMPTON.

[Received, July 30th, 1963.]

---