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THIOSTEROIDS—18[1] (BILE ACIDS AND STEROIDS XXXIII)

OPTICAL ROTATORY POWER OF STEROIDAL EPISULFIDES AND OXATHIOLANES

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Abstract—An examination of the rotatory properties of a number of steroidal episulfides and oxathiolanes leads to an important generalization, which is deduced from a semi-quantitative treatment of the n–σ^* transition. The sector rule relates the sign and amplitude of the Cotton effect exhibited by episulfides and oxathiolanes to the disposition of atoms in space about the sulfur atom.

IN PREVIOUS papers[2] we have reported that steroidal episulfides have a Cotton effect at about 260 mμ, but no theoretical interpretation of the results has been advanced. Subsequently, Bays *et al.*[3] have discussed the CD curves of some episulfides in terms of a simplified orbital diagram.

We have now measured the ORD curves and the CD curves of a large number of steroidal episulfides. Some of these compounds are particularly favourable for the study of the optical properties because the rotatory contribution of a methyl group at different positions around the chromophore can be estimated by means of a comparison of a series of compounds. The episulfides show regular patterns of rotatory contribution comparable with those shown by ketones. The pattern can be interpreted by a semiquantitative treatment based on molecular orbital theory.

From the theoretical standpoint,[4] the rotational strength R_K affords a useful measure of the asymmetry of the surroundings of the chromophore: the concomitant asymmetry induced in the electron distribution within the chromophore can be deduced from the calculation of R_K. The rotational strength R_K is related to the expression for the wave function of the optically active molecule by

$$R_K = I_m (N |\mu_e| K)(K |\mu_m| N) \quad (1)$$

where N and K are the wave functions for the electronic states N and K respectively, "I_m" denotes the imaginary part of the expression, and μ_e and μ_m are, respectively, the electronic and the magnetic dipole operators. The operators, μ_e and μ_m, are

$$\mu_e = \mathbf{er}$$

$$\mu_m = \frac{e}{2mc} (\mathbf{r} \times \mathbf{p}) \quad (2)$$

[1] K. Takeda, T. Komeno, N. Tokutake and Y. Kanematsu, *Chem. Pharm. Bull.* **13**, 687 (1965).
[2] C. Djerassi, H. Wolf, D. A. Lightner, E. Bunnenberg, T. Takeda, T. Komeno and K. Kuriyama, *Tetrahedron* **19**, 1547 (1963).
[3] D. E. Bays, R. C. Cookson, R. R. Hill, J. F. McGhie and G. E. Usher, *J. Chem. Soc.* 1563 (1964).
[4] C. Djerassi, *Optical Rotatory Dispersion: Applications to Organic Chemistry.* McGraw-Hill, New York (1960).

As we are primarily interested in the sign of the Cotton effect rather than placing emphasis upon its absolute magnitude, the wave functions at the position of nuclear equilibrium are adopted in the calculation of R_K. Moreover, it is assumed that the molecular orbitals can be expressed as linear combinations of atomic orbitals ϕ_r on centers r,

$$\psi_j = \sum_r C_{rj}\phi_r \tag{3}$$

Under these conditions, the electric transition moment becomes

$$\begin{aligned}\mu_e &= \langle N|\mu_e|K\rangle \\ &= e\left\{\sum_i C_{iN}C_{iK}r_{ii} + 2\sum_{\substack{i,j \\ (i\neq j)}} C_{iN}C_{jK}r_{ij}\right\}\end{aligned} \tag{4}$$

where

$$r_{ii} = \int \phi_i r \phi_i \, dz$$

$$r_{ij} = \int \phi_i r \phi_i \, dz$$

The integrals r_{ii} are replaced roughly by the coordinate of the atom i. If the integrals r_{ij} are neglected, just as the overlap integrals $S_{ij} = \int \phi_i \phi_j \, dz$ are neglected, equation (4) becomes

$$\mu_e = e\sum_i C_{iN}C_{iK}r_{ii} \tag{5}$$

Also the magnetic transition moment μ_m becomes

$$\mu_m = \langle K|\mu_m|N\rangle = \sum_{i,j} C_{iK}C_{jN}\langle \phi_i|\mu_m|\phi_j\rangle \tag{6}$$

Then, the calculation of R_K resolves itself into the calculation of the molecular orbitals. Since our main concern here is with signs, we shall be content with the simple LCAOMO calculations. In most simple LCAO-MO methods it has been found convenient to represent the Coulomb and the resonance integrals by expressions of the type:

$$\alpha_r = \alpha_0 + h_r\beta_0$$

and:

$$\beta_{rs} = k_{rs}\beta_0$$

where α_0 and β_0 are standard parameters, usually those of benzene, and h_r and k_{rs} are arbitrary constants.

We assumed, for the sake of simplicity, that the 3p orbitals $3p_x$ and $3p_y$, of the sulfur atom are connected to two carbon atoms whose orbitals are described by the same hybridization as in cyclopropane.[5] Also the donor orbital of a substituent is capable of overpalping slightly with both the σ orbitals and the lone-pair orbital $3p_z$, of the sulfur atom. Thus, the classification of orbitals into n and σ no longer holds in the strictest sense, for the effect is to mix some σ character with non-bonding orbital n. The effect of this small amount of admixed σ-character is to cause the

[5] J. E. Kilpatrick and R. Spitzer, *J. Chem. Phys.* **14**, 463 (1946).

n-σ^* transition. (We neglect the possible mixing of 3d orbitals.) The geometry[6] and the framework orbital notation of the episulfide ring are indicated in Fig. 1.

The coulomb integral for each orbital of the episulfide is estimated from its ionization potential,[7] and the resonance integral is assessed so that this integral is proportional to the overlap integral. As a further simplification, we shall use the 2s orbital of carbon atom for the donor orbital of the substituent. The episulfide ring has two symmetry planes: the plane of the ring and the plane AA′ perpendicular to it.

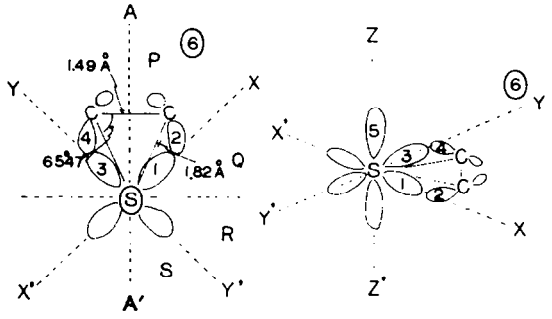


FIG. 1. The geometry and the frame work orbital notation of the episulfide ring.

Therefore, it is sufficient for us to examine the rotatory contribution of a substituent only above the plane of the ring in the spaces, P, Q, R and S divided by four planes AA′, XX′, BB′ and YY′. Now, we consider that there is a substituent at a fixed distance from the sulfur atom; its positional vector makes a fixed angle from the Z-axis. Under these conditions, we solved the secular equation, using the parameters listed in Table 1.

TABLE 1. COULOMB INTEGRALS AND RESONANCE INTEGRALS

$\alpha_1 = \alpha_3 = \alpha_0 + 0{\cdot}1\beta_0$	$\beta_{12} = \beta_{34} = 1{\cdot}7\beta_0$
$\alpha_2 = \alpha_4 = \alpha_0 + 0{\cdot}7\beta_0$	$\beta_{14} = \beta_{23} = 0{\cdot}5\beta_0$
$\alpha_5 = \alpha_0$	$\beta_{24} = 0{\cdot}5\beta_0$
$\alpha_6 = \alpha_0 + 3\beta_0$	$\beta_{56} = 0{\cdot}1\beta_0$

β_{16} (i $\neq$ 5) varies depending on the position of the substituent.

The resulting energy level diagram is shown in Fig. 2.

The molecular orbital calculations indicate that there are two exited states in the episulfide chromophore; one with an A symmetry in group C_2 of the molecule, σ_6^*, and the other with a B symmetry, σ_5^*. As the unoccupied level, σ_5^*, lower than the σ_6^* level, a low-intensity band at about 260 mμ is thus due to the promotion of one of the nonbonding pair of electrons on the sulfur atom to the σ_5^* level. The higher-energy absorption band, n-σ_6^*, must be in the shorter wavelength region. Actually, as shown in Fig. 3, we note that the Cotton effect centered near 205 mμ is detected by both ORD and CD, although the corresponding maximum in the ultraviolet spectrum is not detectable owing to the presence of strong absorption bands of shorter wavelengths. The MO's of the episulfide for n, σ_5^* and σ_6^* levels are summarized in Table 2.

[6] G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers, W. D. Gwinn and W. I. Levan, *J. Chem. Phys.* **19**, 676 (1951).

[7] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.* **84**, 540 (1962).

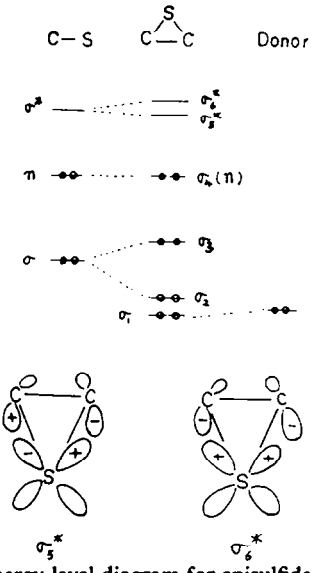


FIG. 2. The energy-level diagram for episulfide chromophore.

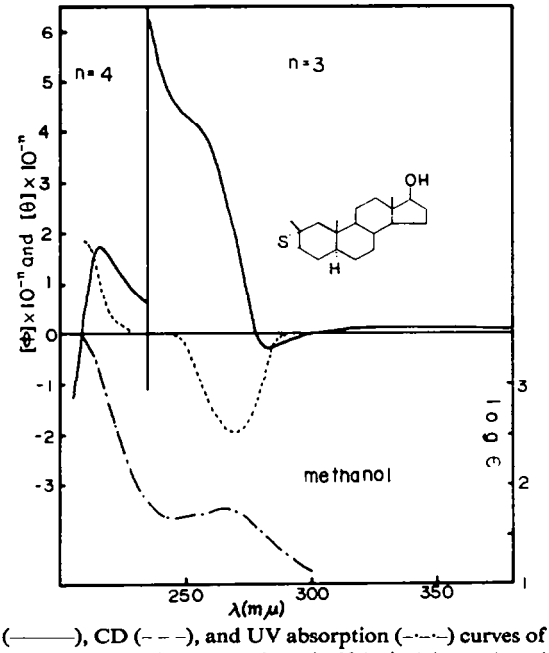


FIG. 3. ORD (———), CD (– – –), and UV absorption (–·–·–) curves of 2β-methyl-17β-hydroxy-5α-androstan-2α,3α-episulfide (VI) in methanol.

If we choose an arbitrary reference point at the sulfur atom, the electric μ_e, and magnetic transition moment, μ_m, are calculated from Eq. (6) and (7) using the wave function listed in Table 2. By scalar multiplication of (6) and (7), the rotational strength R_{ab} is found. From the result, the signs of the contributions made by the atoms (alkyl groups) in different sectors are given in Fig. 4A for n-σ_5* and in Fig. 4B for n-σ_6* transition. The signs given are those above the plane of the episulfide ring. However, the boundary lines are not so definite.

TABLE 2

An electron-donating substituent in the upper P sector

$\psi\sigma_6^* = +0{\cdot}563\phi_1 - 0{\cdot}443\phi_2 + 0{\cdot}550\phi_3 - 0{\cdot}427\phi_4 - 0{\cdot}003\phi_5 + 0{\cdot}047\phi_6$
$\psi\sigma_5^* = -0{\cdot}499\phi_1 + 0{\cdot}483\phi_2 + 0{\cdot}519\phi_3 - 0{\cdot}497\phi_4 + 0{\cdot}004\phi_5 - 0{\cdot}045\phi_6$
$\psi_n = -0{\cdot}007\phi_1 + 0{\cdot}003\phi_2 + 0{\cdot}002\phi_3 + 0{\cdot}000\phi_4 - 0{\cdot}999\phi_5 + 0{\cdot}033\phi_6$

An electron-donating substituent in the upper Q sector

$\psi\sigma_6^* = +0{\cdot}557\phi_1 - 0{\cdot}436\phi_2 + 0{\cdot}558\phi_3 - 0{\cdot}435\phi_4 + 0{\cdot}001\phi_5 - 0{\cdot}014\phi_6$
$\psi\sigma_5^* = -0{\cdot}510\phi_1 + 0{\cdot}490\phi_2 + 0{\cdot}510\phi_3 - 0{\cdot}490\phi_4 - 0{\cdot}000\phi_5 - 0{\cdot}000\phi_6$
$\psi_n = +0{\cdot}004\phi_1 + 0{\cdot}003\phi_2 - 0{\cdot}001\phi_3 - 0{\cdot}002\phi_4 - 0{\cdot}999\phi_5 + 0{\cdot}034\phi_6$

An electron donating substituent in the upper R sector

$\psi\sigma_6^* = +0{\cdot}556\phi_1 - 0{\cdot}434\phi_2 + 0{\cdot}559\phi_3 - 0{\cdot}436\phi_4 + 0{\cdot}001\phi_5 - 0{\cdot}014\phi_6$
$\psi\sigma_5^* = -0{\cdot}512\phi_1 + 0{\cdot}490\phi_2 + 0{\cdot}509\phi_3 - 0{\cdot}488\phi_4 - 0{\cdot}002\phi_5 + 0{\cdot}019\phi_6$
$\psi_n = +0{\cdot}001\phi_1 + 0{\cdot}002\phi_2 + 0{\cdot}001\phi_3 - 0{\cdot}003\phi_4 - 0{\cdot}999\phi_5 + 0{\cdot}033\phi_6$

An electron-donating substituent in the upper S sector

$\psi\sigma_6^* = +0{\cdot}556\phi_1 - 0{\cdot}434\phi_2 + 0{\cdot}558\phi_3 - 0{\cdot}436\phi_4 - 0{\cdot}001\phi_5 + 0{\cdot}022\phi_6$
$\psi\sigma_5^* = -0{\cdot}511\phi_1 + 0{\cdot}490\phi_2 + 0{\cdot}509\phi_3 - 0{\cdot}489\phi_4 - 0{\cdot}001\phi_5 + 0{\cdot}010\phi_6$
$\psi_n = -0{\cdot}001\phi_1 + 0{\cdot}000\phi_2 - 0{\cdot}001\phi_3 + 0{\cdot}003\phi_4 - 0{\cdot}999\phi_5 + 0{\cdot}033\phi_6$

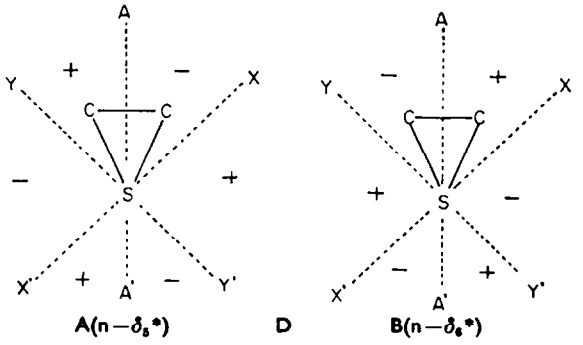
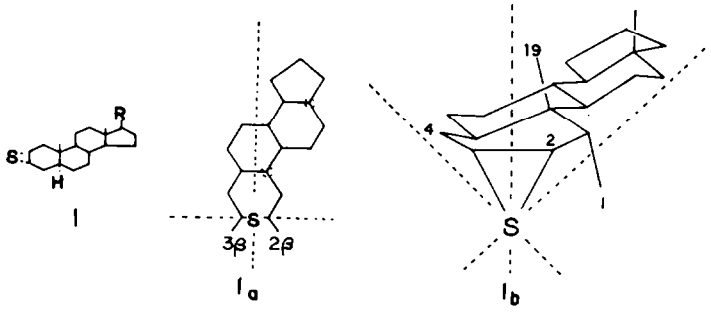


FIG. 4. The signs of the contributions made by the atoms in different sectors above the plane of episulfide ring for the n-σ_5^* transition (about 260 mμ) (4A) and for the n-σ_6^* transition (4B).

It is necessary to consider two views of each molecule in order to predict the sign of its Cotton effect from the episulfide rule. These are (a) the view along the bisectrix of the c–s–c angle and (b) the view of the molecule from above, projected on to the plane of the episulfide ring. In Table 3 are collected the ORD and CD data together with some relevant spectral measurements for the 2α,3α-episulfide and its derivatives. Projections for 17β acetoxy-5α-androstan-2α,3α-episulfide (1) are shown (1a) and (1b)



When the molecule is viewed along the bisectrix of the c–s–c angle, it lies entirely in the back upper sector (1a); projection (1b) shows that all atoms except atoms 4, 5, 6, 7 lie in the region of negative contribution. This is in keeping with the experimental results, a = -70 $[\theta]_{269}^{max}$ -5990 in dioxan.

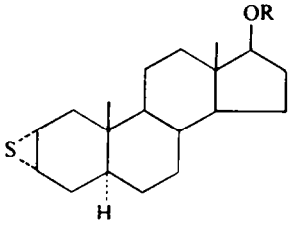
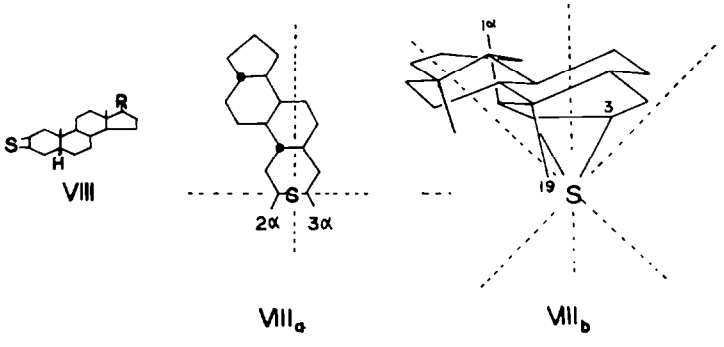


TABLE 3. OPTICAL DATA FOR 2α,3α-EPISULFIDE DERIVATIVES

Substituent	ORD a	ORD Δa	CD λ_{max}	CD $[\theta] \times 10^{-3}$	CD $\Delta[\theta] \times 10^{-3}$	UV λ_{max}	UV ε	Sign of second Cotton effect
R = Ac								
none (I)	−66	—	270	−37·30	—	267	40	+
2β-CH_3 (II)	−38	+28	271	−14·30	+23·0	263	30	+
3β-CH_3 (III)	−124	−58	273	−77·20	−39·9	270	158	−
1α-CH_3 (IV)	+31	+97	262	+27·30	+64·6	262	74	+
R = H								
none (V)	−70	—	269	−59·9		267	44	+
2β-CH_3 (VI)	−37	+33	270	−24·9	+35	267	58	+
1α-CH_3 (VII)	+35	105	263	+38·4	+98·3	263	96	+

Introduction of 2β-methyl group gives the positive contribution to the amplitude and the [θ] maximum of the 260 mμ Cotton effect; Δa + 33, $\Delta[\theta]_{max}$ +3500. This is just in keeping with the expectation that the 2β-methyl group in the lower p-sector makes positive contribution. For the 3β-methyl group a negative contribution would be predicted by the rule. In fact the 3β-methyl group makes a negative contribution to the magnitude of the 273 mμ Cotton effect; Δa −25,Δ[θ] −2030. We would expect a large positive contribution of the 1α-methyl group because it lies in close proximity to the sulfur atom in the region of positive contribution. The amplitude contribution, Δα 105, of the 1a-methyl group is in accord with our prediction.

The data for 17β-hydroxy-5α-androstan-2β-3β-episilfide (VIII) and its methyl derivatives (VIII-XI) are summarized in Table 4. In 2β,3β-episulfide (VIII), as shown in its projections (VIIIa, VIIIb), the rings A and B and the rings C and D lie nearly symmetrically in regard to AA′ and YY′ planes, respectively, so that the rotatory power



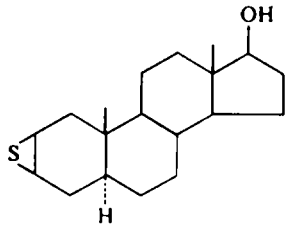
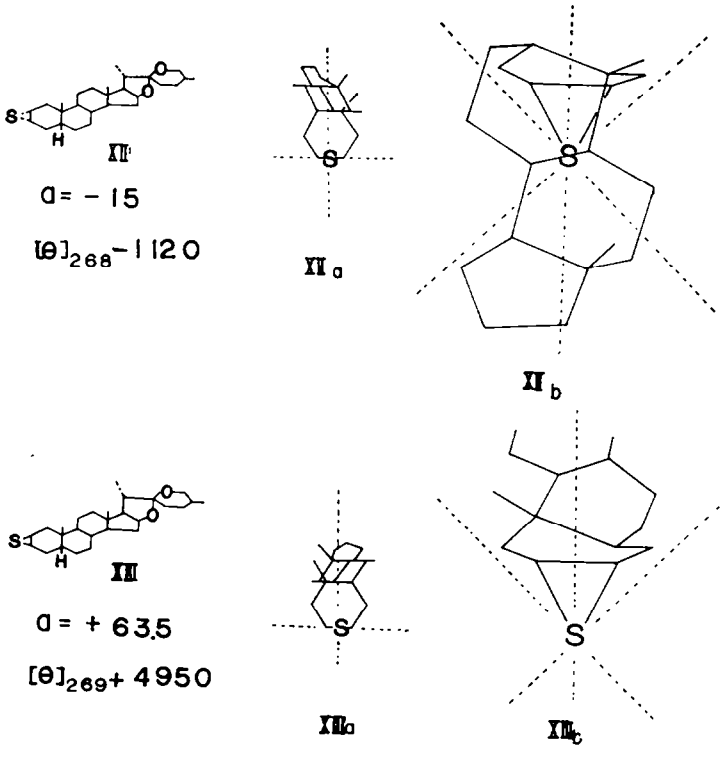


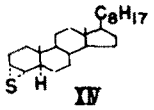
TABLE 4. OPTICAL DATA FOR 2β,3β-EPISULFIDE DERIVATIVES

Substituent	ORD a	ORD Δa	CD λ_{max}	CD $[\theta] \times 10^{-3}$	CD $\Delta[\theta] \times 10^{-3}$	UV λ_{max}	UV ε	Sign of second Cotton effect
none (VIII)	+3		263	+4·1		266	48	—
2α-CH_3 (IX)	+58	−61	276	−51·4	−55·5	271	65	−
3α-CH_3 (X)	+32	+29	273	+32·4	+28·3	268	70	+
1α-CH_3 (XI)	+51·5	+48·5	269	+42·5	+38·4	269	66	−

of the n-σ_5* transition will be zero or very weakly positive. Thus the observed weakly positive Cotton effect is understandable. In passing from 2β,3β-episulfide (VIII) to its 2α-methyl derivative (IX), the change in the rotatory power of n-σ_5* transition is associated with the effect of the 2α-methyl group: Its negative contribution is understandable from the position of the 2α-methyl group entering into the negative region. On the other hand, the 3α-methyl group gives the positive contribution, as expected from its projected location. In 1α-methyl-17β-hydroxy-5α-androstan-2β,3β-episulfide (XI), the 1α-methyl group enters into the positive region, so that its positive contribution results.

The sign and magnitude of the rotational strengths of the other steroidal episulfides is all explained by the episulfides sector rule, as shown in their projections.

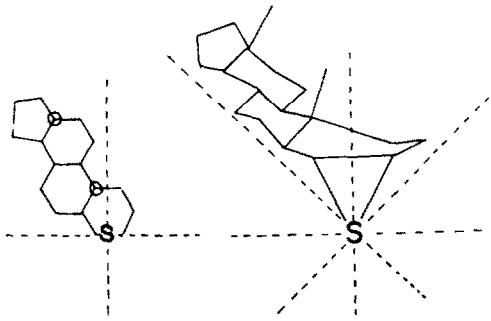




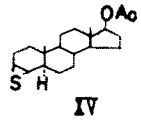
XIV

$\alpha = +102$

$[\theta]_{270} + 8600$



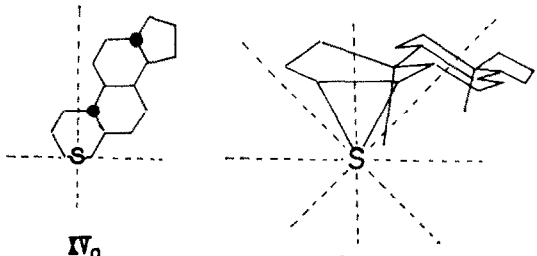
XIVa XIVb



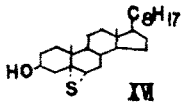
XV

$\alpha = +4$

$[\theta]_{266} + 325$



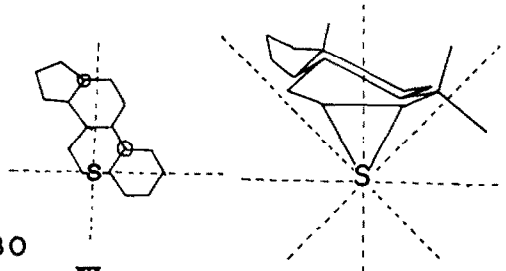
XVa XVb



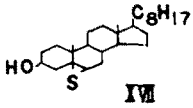
XVI

$\alpha = +78$

$[\theta]_{272} + 6680$



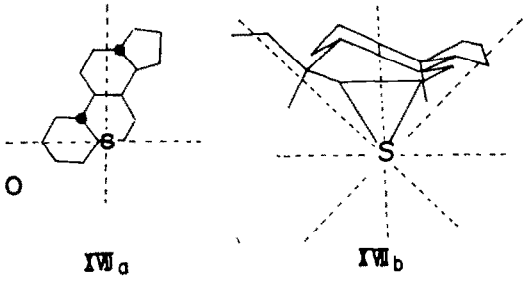
XVIa XVIb



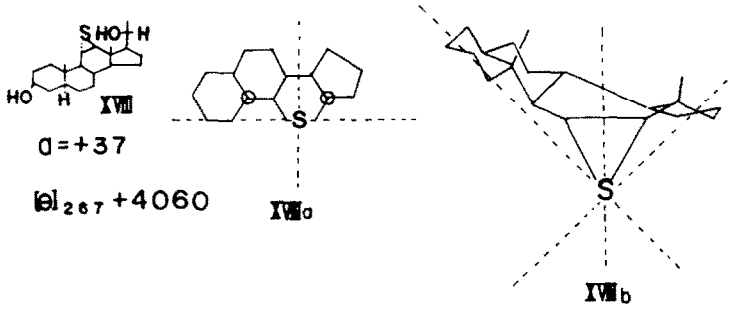
XVII

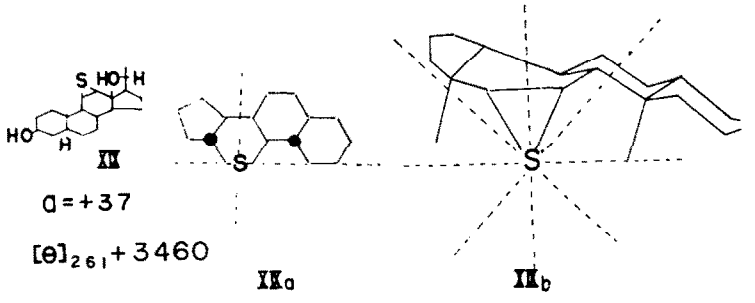
$\alpha = -45$

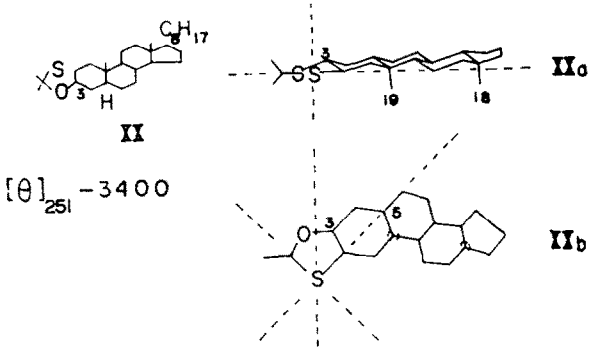
$[\theta]_{268} - 4460$

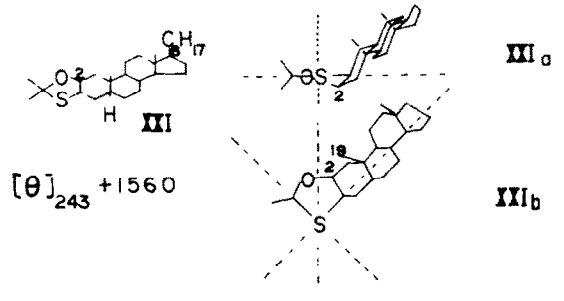


XVIIa XVIIb


S HO H
HO
H
XVIII
α=+37
[θ]267 +4060
XVIIIa
XVIIIb

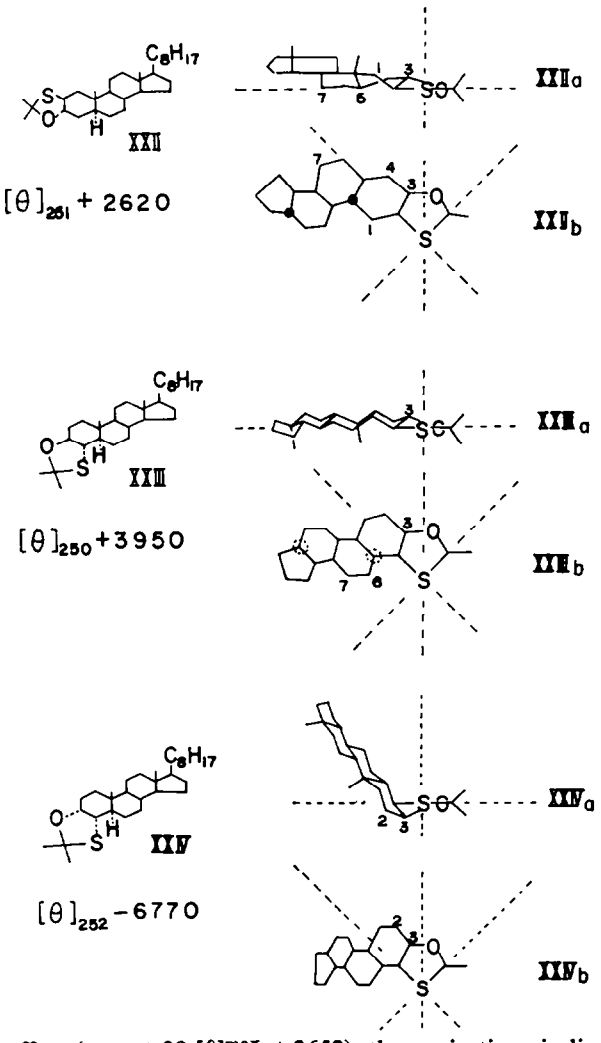

S HO H
HO
H
XIX
α=+37
[θ]261 +3460
XIXa
XIXb


C8H17
S
O
3
H
XX
[θ]251 -3400
3
19
18
XXa
O
3
5
S
XXb


C8H17
O
2
S
H
XXI
[θ]243 +1560
XXIa
2
19
2
O
S
XXIb

Oxathiolanes,[8] in which the chromophoric ring is fused to the steroid skeleton, have an optically active transition near 250 mμ as shown in Fig. 5, and it has been noted that the sign of the Cotton effect depended greatly on the chirality of the chromophoric ring.

If the nature of the transition near 250 mμ is to be the same as that of episulfides the sector rule must be applied to predict the sign of the 250 mμ Cotton effect. This, in fact, is the case. The rule gives consistent predictions in agreement with the observation. For example, in the case of the 2β(s), 3α(o)-acetonide (XXII) which shows a



positive Cotton effect (a = +29,$[\theta]_{251}^{max}$ +2652), the projections indicate that the large positive contributions of the atom 3 overweigh the negative contributions of atoms 1, 10, and 19 and the C and D rings. Cholestan-3α(o),4α(s)-acetonide (XXIV) has a negative Cotton effect (a-110, $[\theta]_{252}^{max}$ −6770). Its projections show that all atoms except C-1 lie in the negative region.

[8] D. A. Lighner, C. Djerassi, K. Takeda, K. Kuriyama and T. Komeno, *Tetrahedron* **21**, 1581 (1965).

From above examples, it will probably be understandable that the sector rule is applicable to the sign predictions of the 250 mμ Cotton effect of the steroidal spiro-oxathiolanes. If the conformations of these hemithioketals are known, or if a substituent making a large rotatory contribution is in the neighbourhood of the chromophore, the sector rule can be used to serve for the prediction of the sign of the n-σ^* Cotton effect.

We have hitherto considered only about the n-σ_5^* Cotton effect of episulfides and oxathiolanes. As stated in the beginning, episulfides generally show two absorptions in their ORD and CD spectra; one appears near 260 mμ, whereas a second more intense band is noted near 200 mμ. The latter may be considered to be the n-σ_6^* transition. But the admixture of the promotion from a sulfur 3p to a sulfur 3d orbital and of the σ-σ^* transition is possible, because of the proximity of their transition energies.

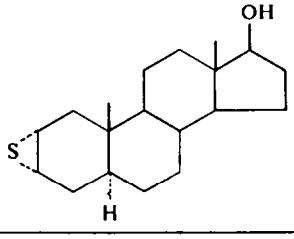


TABLE 5. OPTICAL DATA OF 17β-HYDROXY-5α-ANDROSTAN-2α,3α-EPISULFIDE AND ITS DERIVATIVES IN METHANOL

	First Cotton effect					Second Cotton effect		
	ORD			CD		ORD		
Substituent	a	Δa	λ_{max} (mμ)	$[\theta]_{max} \times 10^{-3}$	$\Delta[\theta] \times 10^{-3}$	$[\phi]$ (peak)	λ (mμ)	sign
none V	−68		266	−36·1	—	+8030	215	+
2β-Me VI	−46	+22	270	−19·5	+16·6	+17400	216	+
1α-Me VII	+28	+96	260	+17·8	+53·9	+8800	217	+

The spectral data of 2α,3α-episulfides in methanol are collected in Table 5. If our semiquantitative calculations is correct, the two transitions are to appear oppositely signed. As shown in the case of 1α-methyl-2α,3α-episulfide (VII), however, two Cotton effect are of the same sign. Moreover, in passing from 2α,3α-episulfide (V) to its 2β-methyl derivative (VI), the second Cotton effect remains positive and its magnitude increases. These facts suggest that reflection of the position of a group through the plane AA′ at right angles to the episulfide ring will reverse its rotatory contribution, but reflection through the plane of the ring will not do so. Therefore, the failure of the sector rule for this Cotton effect seems to be due to the admixture of some other transition with the n-σ_6^* transition rather than to an inadequate choice of the parameters. We do not think that the present semiquantitative treatment for episulfides gives a sufficient basis for a solution of these optical behaviour, but, so far as the first Cotton effect is concerned, the sector rule deduced from our treatment is capable of explaining the rotatory properties.

EXPERIMENTAL

The ORD, CD and UV curves were determined using a Japan Spectroscopic Co. (Nippon Bunko) automatically recording spectropolarimeter (Model ORD/UV-5) equipped with CD. The ORD[9]

[9] C. Djerassi and W. Klyne, *Proc. Chem. Soc.* **55** (1957).

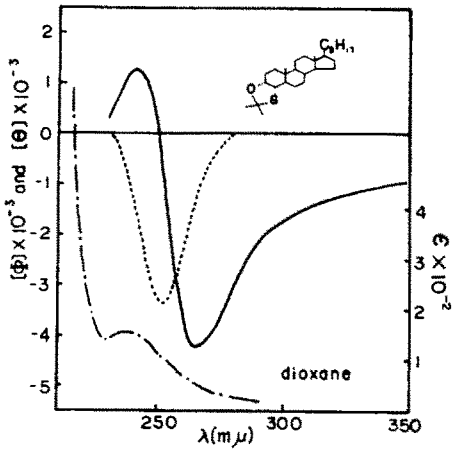


FIG. 5. ORD (———), CD (– – –), and UV absorption (–·–·–) curves of 5α-cholestan-3α(o),4α(s)-acetonide (XXIV) in dioxan.

and CD[10] data are listed according to a convention recorded elsewhere in detail. The synthesis of all samples will be published in the near future.

17β-Acetoxy-5α-androstan-2α,3α-episulfide (I) dioxan: *c* 0·0309, CD, $[\theta]_{305}$ 0, $[\theta]_{270}$ −3730, $[\theta]_{240}$ 0, ORD, $[\phi]_{400}$ −230, $[\phi]_{332}$ −2300, $[\phi]_{316}$ +4330, $[\phi]_{326}$ +3160, $[\phi]_{325}$ +3950, UV, λ_{307}^{max} ε 40.

2β-Methyl-17β-acetoxy-5α-androstan-2α,3α-episulfide (II) dioxan: *c* 0·0184, CD, $[\theta]_{305}$ 0, $[\theta]_{271}$ −1430, $[\theta]_{250}$ 0, ORD, $[\phi]_{400}$ +120, $[\phi]_{334}$ −230, $[\phi]_{315}$ +3550, $[\phi]_{320}$ +12820, UV, λ_{302}^{max} ε 30.

3β-Methyl-17β-acetoxy-5α-androstan-2α,3α-episulfide (III) dioxan: *c* 0·0628, CD, $[\theta]_{300}$ 0, $[\theta]_{272.5}$ −7720, $[\theta]_{240}$ 0, ORD, $[\phi]_{400}$ +115, $[\phi]_{284.5}$ −4470, $[\phi]_{261}$ +7970, $[\phi]_{225}$ +580, UV, λ_{270}^{sh} ε 79.

1α-Methyl-17β-acetoxy-5α-androstan-2α,3α-episulfide (IV) dioxan: *c* 0·0613, CD, $[\theta]_{300}$ 0, $[\theta]_{302}$ +2730, $[\theta]_{288}$ 0, ORD, $[\phi]_{400}$ +1120, $[\phi]_{278}$ +4850, $[\phi]_{258}$ +1710, $[\phi]_{225}$ +3370, UV, λ_{303}^{max} ε 74.

17β-Hydroxy-5α-androstan-2α,3α-episulfide (V) dioxan: *c* 0·0595, CD, $[\theta]_{305}$ 0, $[\theta]_{269}$ −5990, $[\theta]_{240}$ 0, ORD, $[\phi]_{400}$ +300, $[\phi]_{281}$ −1060, $[\phi]_{256}$ +5920, $[\phi]_{240}$ +5040, $[\phi]_{230}$ +7060, UV, λ_{307}^{max} ε 44. MeOH: *c* 0·022, CD, $[\theta]_{300}$ 0, $[\theta]_{267}$ −3610, $[\theta]_{228}$ 0, ORD, $[\phi]_{400}$ +290, $[\phi]_{350}$ +440, $[\phi]_{330}$ −1290, $[\phi]_{288}$ +5550, $[\phi]_{287}$ +4900, $[\phi]_{315}$ +8000, $[\phi]_{300}$ −3650, UV, λ_{302}^{max} ε 62.

2β-Methyl-17β-hydroxy-5α-androstan-2α,3α-episulfide (VI) dioxan: *c* 0·0764, CD, $[\theta]_{305}$ 0, $[\theta]_{270}$ −2490, $[\theta]_{245}$ 0, $[\theta]_{230}$ +10500, ORD, $[\phi]_{400}$ +320, $[\phi]_{335}$ 0, $[\phi]_{315}$ +3690, $[\phi]_{240}$ +7130, UV, λ_{307}^{max} ε 58. MeOH: *c* 0·0474, CD, $[\theta]_{290}$ 0, $[\theta]_{270}$ −1950, $[\theta]_{245}$ 0, $[\theta]_{230}$ +19500, ORD, $[\phi]_{400}$ 120, $[\phi]_{333}$ −270, $[\phi]_{350}$ +4330, $[\phi]_{316}$ +17400, $[\phi]_{305}$ −12900, UV, λ_{306}^{max} ε 58.

1α-Methyl-17β-hydroxy-5α-androstan-2α,3α-episulfide (VII) dioxan: *c* 0·0662, CD, $[\theta]_{300}$ 0, $[\theta]_{303}$ +3840, $[\theta]_{285}$ 0, ORD, $[\phi]_{400}$ +1070, $[\phi]_{274}$ +4750, $[\phi]_{254}$ +1260, $[\phi]_{225}$ +6300, UV, λ_{303}^{max} ε 96. MeOH: *c* 0·0357, CD, $[\theta]_{280}$ 0, $[\theta]_{261}$ +1780, $[\theta]_{240}$ 0, $[\theta]_{215}$ +4150, ORD, $[\phi]_{400}$ +720, $[\phi]_{272}$ +3910, $[\phi]_{251}$ +1080, $[\phi]_{217}$ +8800, $[\phi]_{210}$ +5560, UV, λ_{281}^{max} ε 81.

17β-Hydroxy-5α-androstan-2β,3β-episulfide (VIII) dioxan: *c* 0·0773, CD, $[\theta]_{280}$ 0, $[\theta]_{262}$ +410, $[\theta]_{240}$ 0, ORD, $[\phi]_{340}$ +100, $[\phi]_{279}$ +700, $[\phi]_{252}$ +360, $[\phi]_{224}$ +670, UV, λ_{266}^{max} ε 48.

2α-Methyl-17β-hydroxy-5α-androstan-2β,3β-episulfide (IX) dioxan: *c* 0·0576, CD, $[\theta]_{300}$ 0, $[\theta]_{276}$ −5140, $[\theta]_{250}$ 0, $[\theta]_{225}$ −4040, ORD, $[\phi]_{400}$ +200, $[\phi]_{286}$ −1890, $[\phi]_{265}$ +3890, $[\phi]_{225}$ −2450, UV, λ_{271}^{max} ε 65.

3α-Methyl-17β-hydroxy-5α-androstan-2β,3β-episulfide (X) dioxan: *c* 0·0522, CD, $[\theta]_{295}$ 0, $[\theta]_{272}$ +3240, $[\theta]_{250}$ 0, $[\theta]_{225}$ 0, $[\theta]_{215}$ +4050, ORD, $[\phi]_{400}$ +490, $[\phi]_{285}$ +2822, $[\phi]_{262}$ −370, $[\phi]_{225}$ +6260, UV, λ_{266}^{max} ε 70. MeOH: *c* 0·0685, CD, $[\theta]_{295}$ 0, $[\theta]_{274}$ +1740, $[\theta]_{245}$ 0, $[\theta]_{225}$ 0, $[\theta]_{211}$ +15400, ORD, $[\phi]_{400}$ +120, $[\phi]_{284}$ +2170, $[\phi]_{262}$ +230, $[\phi]_{221}$ +6090, $[\phi]_{210}$ −12600, UV, λ_{265}^{max} ε 62.

1α-Methyl-17β-hydroxy-5α-androstan-2β,3β-episulfide (XI) dioxan: *c* 0·0535, CD, $[\theta]_{290}$ 0, $[\theta]_{269}$ +4250, $[\theta]_{245}$ 0, ORD, $[\phi]_{400}$ +810, $[\phi]_{280}$ +3120, $[\phi]_{256}$ −2030, $[\phi]_{242}$ −1830, $[\phi]_{225}$ −3660, UV, λ_{269}^{max} ε 66.

[10] C. Djerassi and E. Bunnenberg, *Proc. Chem. Soc.* 299 (1963).

5β,25D-*Spirostan*-2α,3α-*episulfide* (XII) dioxan: *c* 0·1068, CD, $[\theta]_{295}$ 0, $[\theta]_{268}$ −1120, $[\theta]_{240}$ 0, ORD, $[\phi]_{400}$ −810, $[\phi]_{279}$ −2340, $[\phi]_{257}$ −890, $[\phi]_{230}$ −1690, UV, λ_{265}^{max} ε 46.

5β,25D-*Spirostan*-2β,3β-*episulfide* (XIII) dioxan: *c* 0·0948, CD, $[\theta]_{295}$ 0, $[\theta]_{269}$ +4950, $[\theta]_{245}$ 0, ORD, $[\phi]_{340}$ −270, $[\phi]_{282}$ +1450, $[\phi]_{256}$ −4900, $[\phi]_{234}$ −3630, UV, λ_{240}^{max} ε 54.

5α-*Cholestan*-3α,4α-*episulfide* (XIV) dioxan: *c* 0·0621, CD, $[\theta]_{300}$ 0, $[\theta]_{270}$ +8600, $[\theta]_{240}$ 0, ORD, $[\phi]_{400}$ +260, $[\phi]_{281\cdot5}$ +4150, $[\phi]_{252}$ −6090, $[\phi]_{227}$ −4280, $[\phi]_{225}$ −5830.

5α-*Cholestan*-3β(0),4α(s)-*acetonide* (XXIII)[8] dioxan: *c* 0·0404, CD, $[\theta]_{275}$ 0, $[\theta]_{250}$ +3950, $[\theta]_{230}$ 0, ORD, $[\phi]_{400}$ −230, $[\phi]_{287}$ +2390, $[\phi]_{234}$ −7130, $[\phi]_{225}$ −6270.

5α-*Cholestan*-3α(o),4α(s)-*acetonide* (XXIV)[8] dioxan: *c* 0·0359, CD, $[\theta]_{280}$ 0, $[\theta]_{252}$ −6770, $[\theta]_{230}$ 0, ORD, $[\phi]_{400}$ −1100, $[\phi]_{305}$ −8470, $[\phi]_{240}$ +2570, $[\phi]_{220}$ +770.