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## Possible Assignments for the Three Lowest Lying Singlets in Dialkyl Sulfides<sup>1a</sup>

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**Abstract:** The three lowest lying electronic transitions of the C-S-C sulfide chromophore fall at approximately 240, 220, and 200 nm. These transitions are assigned on the basis of symmetry considerations and the optical absorption and optical activity data. In order to inquire further into the nature of these transitions and their assignments, semiempirical calculations of oscillator strengths and rotational strengths are performed for a number of dialkyl sulfides and the results compared with experiment. The assignments which have been made are as follows, where the designations refer to the irreducible representations of the group  $C_{2v}$ : (a) the very weak 240-nm transition is  $b_1 \rightarrow b_2^*$  and is electric dipole forbidden, magnetic dipole allowed; (b) the 220-nm transition is  $b_1 \rightarrow a_1^*$  and is electric dipole allowed; and (c) the band at 200 nm is an atomic-like  $b_1 \rightarrow 3d$  transition. The orbital  $b_1$  is a nonbonding 3p sulfur orbital,  $b_2^*$  and  $a_1^*$  are orbitals antinodal in the plane of the C-S-C chromophore and antibonding between the sulfur and carbon atoms, and 3d represents a linear combination of sulfur 3d atomic orbitals.

The object of this paper is to characterize the lower lying electronic transitions of saturated dialkyl sulfides. The assignments rest on a comparison of experimental and theoretical energies, intensities, and especially optical activity. As is well known, the optical activity associated with an electronic transition is a signed quantity that depends on both the electric and magnetic dipole transition moments. Hence optical activity data, like absorption data, provide important criteria with which to test the merit of a particular set of assignments.

The isolated sulfide chromophore, belonging to the point group  $C_{2v}$ , exhibits optical activity only when dissymmetrically substituted. The point of view which we shall adopt is that the optical activity of dialkyl sulfides arises because the dissymmetrically disposed substituents perturb the wave functions of the erstwhile isolated chromophore in such a way that the rotational strengths are no longer all zero. Both the merits and the shortcomings of such an approach have been discussed elsewhere.<sup>2-4</sup> In this work, tentative assignments of the three lowest lying singlets in dialkyl

sulfides are made, based on the experimental data and symmetry considerations. In order to understand more fully the optical properties associated with these transitions, wave functions are obtained semiempirically for the symmetric sulfide chromophore, in an eight-electron Wolfsberg-Helmholz approximation.<sup>5</sup> The effects of hydrocarbon substituents on these wave functions are treated by a perturbation approach: the perturbing Hamiltonian is taken as the electrostatic field of the incompletely shielded carbon and hydrogen nuclei (plus their electrons)<sup>6-9</sup> which make up the molecular framework. The perturbed wave functions are then used to calculate the absorption intensity and the optical activity of some sulfides of known absolute configuration which are conformationally rigid.

As the reader will find, the quantitative agreement with experiment will not be particularly good. However, as the analysis presented below will show, the precise magnitudes and even some of the signs of the

(1) (a) Part of the Ph.D. Thesis of J. S. R., University of Minnesota, 1969. (b) National Science Foundation Cooperative Graduate Fellow, 1963-1966.

(2) C. W. Deutsche, D. A. Lightner, R. W. Woody, and A. Moscovitz, *Annu. Rev. Phys. Chem.*, **20**, 407 (1969).

(3) E. G. Höhn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).

(4) J. A. Schellman, *Accounts Chem. Res.*, **1**, 144 (1968).

(5) (a) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952). (b) Both the Wolfsberg-Helmholz and the extended Hückel<sup>10</sup> formalisms were considered. As will be elaborated in the body of the paper, some consequences of the inclusion of overlap in the diagonalization of the secular equations lead us to prefer the Wolfsberg-Helmholz approximation in the present work. (c) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(6) A. Moscovitz, *Advan. Chem. Phys.*, **4**, 67 (1962).

(7) E. Gorin, J. Walter, and H. Eyring, *J. Chem. Phys.*, **6**, 824 (1938).

(8) E. Gorin, W. Kauzmann, and J. Walter, *ibid.*, **7**, 327 (1939).

(9) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940).

optical activity will depend critically on the exact values of the molecular orbital coefficients. As such, in view of the crudeness of the semiempirical approach employed, any better agreement would be fortuitous. Indeed, better agreement could be obtained in particular instances by a more elaborate parameterization, e.g., different parameters for five- and six-membered rings. However, our stated purpose is an assignment of the transitions and an understanding of the origins of the pertinent transition moments, rather than a strict quantitative accounting of the optical activity and intensities of absorption. In this context, the calculated molecular orbitals serve the function of a scaffolding on which to hang a discussion, rather than as a primary predictive structure. This being the case, further elaborations in the construction of the orbitals appear unnecessary to our purposes. We do hasten to add our belief that the analyses given provide a reasonable defense of the ultimate assignments chosen.

### Summary of Experimental Data

The ultraviolet vapor spectrum of dimethyl sulfide<sup>10,11</sup> shows two main absorption bands in the region from 200 to 230 nm, a structured band around 220 nm, and a relatively structureless band at about 200 nm. These two bands have oscillator strengths of about 0.016 and 0.06, respectively. Thompson and coworkers<sup>10</sup> have examined the vibrational structure of the 220-nm band and have assigned the frequencies to progressions and combinations of the symmetrical C-S-C stretch and the parallel methyl rock (symmetry  $a_1$ ) built on the 0-0 transition. This is consistent with an electric dipole allowed transition.

On going from vapor to solution,<sup>10</sup> the 220-nm band loses its structure and is blue shifted, so that it appears as a shoulder under the 200-nm absorption. There is further blue shifting with increasing solvent polarity. In addition, the solution spectrum reveals a very weak transition on the long wavelength edge of the absorption with an  $\epsilon_{\text{max}}$  of about 20. In cyclic sulfides, this transition undergoes a red shift as the C-S-C angle decreases on going from larger to smaller rings and appears at about 265 nm in three-membered rings (episulfides).<sup>11</sup>

The spectra of both methyl sulfoxide<sup>11</sup> and hydrogen sulfide<sup>10</sup> show a band at 200 nm of approximately the same intensity as that in methyl sulfide. Cumper and coworkers<sup>12</sup> observed a band with roughly the same wavelength and intensity when the carbons bonded to sulfur were replaced by silicon and germanium, for example, in  $(R_3Si)_2S$ , where R is a methyl group. The relative insensitivity of the position and intensity of this band to the nature of the atoms bonded to sulfur suggests an atomic-like transition, say  $3p \rightarrow 3d$  or  $3p \rightarrow 4s$  on sulfur.

Optical rotatory dispersion and circular dichroism (CD) properties are known in the range 200–260 nm for some dissymmetric sulfides.<sup>13,14</sup> For cyclic sulfides, three Cotton effects are observed in this spectral region, at about 200, 220, and 240 nm. The midpoint of the large Cotton effect associated with the very weak long wavelength transition red shifts from about 235 nm in six-membered ring sulfides to about 265 nm in episulfides,<sup>15,16</sup> paralleling the absorption spectrum. The magnitudes of the rotational strengths observed are of the order of  $10^{-40}$  cgs.

In summary, the following low-energy transitions in dialkyl sulfides are observed: a very weak band,  $\epsilon_{\text{max}} \sim 20$ , at about 240

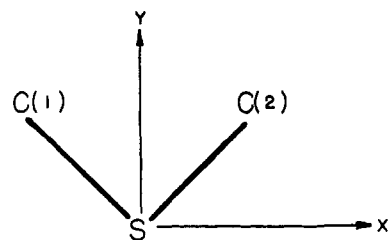


Figure 1. Coordinate system of sulfide chromophore ( $z$  axis is toward reader).

nm; a band,  $f \sim 0.016$ , at about 220 nm; and a moderately strong band,  $f \sim 0.06$ , at about 200 nm. All the bands are optically active in the dissymmetric sulfides considered in this paper. Another transition is known at about 195 nm; however, since there are no data available on the optical activity of this band we have not considered it.

In the course of what follows, we shall ultimately suggest the following assignments, where the designations refer to the irreducible representations of  $C_{2v}$  given in Table I: (a) the very weak

Table I.  $C_{2v}$  Character Table<sup>a</sup>

| $C_{2v}$ | $E$ | $C_2(y)$ | $\sigma_v(yz)$ | $\sigma_v'(xy)$ |
|----------|-----|----------|----------------|-----------------|
| $A_1$    | 1   | 1        | 1              | 1               |
| $A_2$    | 1   | 1        | -1             | -1              |
| $B_1$    | 1   | -1       | 1              | -1              |
| $B_2$    | 1   | -1       | -1             | 1               |

<sup>a</sup> The coordinate system is that of Figure 1.

band at 240 nm is assigned to an electric dipole forbidden, magnetic dipole allowed  $b_1 \rightarrow b_2^*$  transition; (b) the band at 220 nm to an electric dipole allowed  $b_1 \rightarrow a_1^*$  transition; (c) the band at 200 nm to an atomic-like  $b_1 \rightarrow 3d$  transition. The orbital  $b_1$  is a nonbonding  $3p$  orbital on the sulfur atom;  $b_2^*$  and  $a_1^*$  are orbitals antinodal in the plane of the C-S-C chromophore and antibonding between the sulfur and carbon atoms, and  $3d$  represents a linear combination of sulfur  $3d$  atomic orbitals. These orbitals are further elaborated later in the text.

The assignments just noted are based on the calculations and comparisons made in sections A-E, and for convenience we state now the subject matter of these sections. In part A, we discuss what conclusions, based on qualitative symmetry considerations, one can come to about the sulfide assignments. In part B, molecular orbitals and orbital energies are obtained for the isolated sulfide chromophore in a Wolfsberg-Helmholz approximation. In part C, the optical activity of the  $b_1$  (lone pair)  $\rightarrow b_2^*$  transition in some dissymmetrically substituted sulfides is calculated, using a first-order perturbation approach. In part D, eight transitions corresponding to lone pair promotions are mixed together in a perturbation calculation of the oscillator and rotational strengths of certain dissymmetric sulfides. Part E concerns the molecule 2-thia-5 $\alpha$ -androstan-17 $\beta$ -ol which is considered as a special case.

### Computations

**A. Assignments Based on Symmetry Considerations.** We shall describe the sulfide chromophore in terms of a basis set consisting of the  $3s$ ,  $3p$ ,  $3d$ , and  $4s$  Slater-type atomic orbitals (AO's) on the sulfur atom, plus a  $2sp^3$  hybrid orbital on each carbon atom. These hybrids, denoted by  $c_1$  (centered on  $C_1$ ) and  $c_2$  (centered on  $C_2$ ), are directed toward the sulfur atom. The coordinate system and the labeling of the atoms are shown in Figure 1. The valence shell of the sulfide chromophore is assumed to have eight electrons, six from the valence shell of the sulfur atom and one from each carbon atom. Crude molecular orbitals (MO's), constructed as linear combinations of the AO's, are listed in Table II in approximate order of the orbital energies;

(10) S. D. Thompson, D. G. Carroll, F. Watson, M. O'Donnell, and S. P. McGlynn, *J. Chem. Phys.*, **45**, 1367 (1966).

(11) L. B. Clark and W. T. Simpson, *ibid.*, **43**, 3666 (1965).

(12) C. W. N. Cumper, A. Melmkoff, and A. I. Vogel, *J. Chem. Soc. A*, 242 (1966).

(13) P. Laur, H. Häuser, J. E. Gurst, and K. Mislow, *J. Org. Chem.*, **32**, 498 (1967).

(14) (a) R. M. Dodson, private communication. (b) P. Salvadori (*Chem. Commun.*) 1203 (1968) treats open chain sulfides. Because of their conformational mobility, we have not treated these molecules specifically in this work.

(15) C. Djerassi, H. Wolf, D. A. Lightner, E. Bunnenberg, K. Takeda, T. Komeno, and K. Kuriyama, *Tetrahedron*, **19**, 1547 (1963).

(16) K. Kuriyama, T. Komeno, and K. Takeda, *ibid.*, **22**, 1039 (1966).

**Table II.** Crude MO's Constructed as Linear Combinations of the AO Basis Set<sup>a,b</sup>

| Orbital designation                       | Linear combination  | Symmetry       |
|---|---|----------------|
| 4s  |   | a <sub>1</sub> |
| 3d <sub>xy</sub>                          |   | b <sub>2</sub> |
| 3d <sub>x<sup>2</sup>-y<sup>2</sup></sub> |   | a <sub>1</sub> |
| 3d <sub>yz</sub>                          |   | b <sub>1</sub> |
| 3d <sub>xz</sub>                          |   | a <sub>2</sub> |
| 3d <sub>z<sup>2</sup></sub>               |   | a <sub>1</sub> |
| a <sub>1</sub> *                          | 3s + 3p <sub>y</sub> - (c <sub>2</sub> + c <sub>1</sub> ) | a <sub>1</sub> |
| b <sub>2</sub> *                          | 3p <sub>x</sub> - (c <sub>2</sub> - c <sub>1</sub> )      | b <sub>2</sub> |
| XX b <sub>1</sub>                         | 3p <sub>z</sub>   | b <sub>1</sub> |
| XX 2a <sub>1</sub>                        | 3s - 3p <sub>y</sub> - (c <sub>2</sub> + c <sub>1</sub> ) | a <sub>1</sub> |
| XX b <sub>2</sub>                         | 3p <sub>x</sub> + (c <sub>2</sub> - c <sub>1</sub> )      | b <sub>2</sub> |
| XX 1a <sub>1</sub>                        | 3s + 3p <sub>y</sub> + (c <sub>2</sub> + c <sub>1</sub> ) | a <sub>1</sub> |

<sup>a</sup> The energy increases from bottom to top. <sup>b</sup> X denotes that the orbital is occupied in the ground state.

the energies are assumed to increase with the number of nodes. The ordering of the 3d and 4s levels is arbitrary. The orbitals are also classified according to the appropriate irreducible representation of C<sub>2v</sub>.

There are 32 excited singlet states arising from this manifold of orbitals. Of these, the ones corresponding to promotions from the highest three orbitals are tabulated in Table III along with the directions of the

**Table III.** Electric and Magnetic Dipole Moments of Transitions

| Transition  | State symmetry | <b>u</b> | <b>m</b> |
|---|----------------|----------|----------|
| b <sub>1</sub> → b <sub>2</sub> *                           | A <sub>2</sub> | 0        | y        |
| b <sub>1</sub> → a <sub>1</sub> *                           | B <sub>1</sub> | z        | x        |
| b <sub>1</sub> → 3d <sub>z<sup>2</sup></sub>                | B <sub>1</sub> | z        | 0        |
| b <sub>1</sub> → 3d <sub>xz</sub>                           | B <sub>2</sub> | x        | 0        |
| b <sub>1</sub> → 3d <sub>yz</sub>                           | A <sub>1</sub> | y        | 0        |
| b <sub>1</sub> → 3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>  | B <sub>1</sub> | 0        | 0        |
| b <sub>1</sub> → 3d <sub>xy</sub>                           | A <sub>2</sub> | 0        | 0        |
| b <sub>1</sub> → 4s   | B <sub>1</sub> | z        | 0        |
| 2a <sub>1</sub> → b <sub>2</sub> *                          | B <sub>2</sub> | x        | z        |
| 2a <sub>1</sub> → a <sub>1</sub> *                          | A <sub>1</sub> | y        | 0        |
| 2a <sub>1</sub> → 3d <sub>z<sup>2</sup></sub>               | A <sub>1</sub> | y        | 0        |
| 2a <sub>1</sub> → 3d <sub>xz</sub>                          | A <sub>2</sub> | 0        | y        |
| 2a <sub>1</sub> → 3d <sub>yz</sub>                          | B <sub>1</sub> | z        | x        |
| 2a <sub>1</sub> → 3d <sub>x<sup>2</sup>-y<sup>2</sup></sub> | A <sub>1</sub> | y        | 0        |
| 2a <sub>1</sub> → 3d <sub>xy</sub>                          | B <sub>2</sub> | x        | z        |
| 2a <sub>1</sub> → 4s  | A <sub>1</sub> | y        | 0        |
| b <sub>2</sub> → b <sub>2</sub> *                           | A <sub>1</sub> | y        | 0        |
| b <sub>2</sub> → a <sub>1</sub> *                           | B <sub>2</sub> | x        | z        |
| b <sub>2</sub> → 3d <sub>z<sup>2</sup></sub>                | B <sub>2</sub> | x        | 0        |
| b <sub>2</sub> → 3d <sub>xz</sub>                           | B <sub>1</sub> | z        | x        |
| b <sub>2</sub> → 3d <sub>yz</sub>                           | A <sub>2</sub> | 0        | y        |
| b <sub>2</sub> → 3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>  | B <sub>2</sub> | x        | z        |
| b <sub>2</sub> → 3d <sub>xy</sub>                           | A <sub>1</sub> | y        | 0        |
| b <sub>2</sub> → 4s   | B <sub>2</sub> | x        | 0        |

electric and magnetic dipole transition moments, **u** and **m**. Some of the zero values of **u** and **m** follow from the fact that the atomic orbitals involved are on the same center and that this center is the origin of coordinates.

The rotational strength of a transition 0 → *i* is given by<sup>17</sup>

$$R_{0i} = \text{Im} \{ \langle 0 | \mathbf{u} | i \rangle \cdot \langle i | \mathbf{m} | 0 \rangle \} \quad (1)$$

On examining Table III, one sees that in order that there be some electric and magnetic transition moment in the same direction, it is necessary to mix either an

(17) E. U. Condon, *Rev. Mod. Phys.*, **9**, 432 (1937).

A<sub>1</sub> excited state with an A<sub>2</sub> or a B<sub>1</sub> with a B<sub>2</sub> state. The states are mixed by a perturbation V which arises from the neutral carbon and hydrogen atoms making up the extrachromophoric framework of the molecule.<sup>6-9</sup> One of the important features of V is that it is a one-electron operator and, hence, will not mix directly configurations which differ in more than one molecular orbital. Thus, configurations which do differ in more than one orbital can be mixed together only in second or higher order.

There are a number of things, based on qualitative considerations, that one can say about the nature of the sulfide transitions. In looking for the assignments, we will confine ourselves to promotions from the lone pair, 3p<sub>z</sub>, of symmetry b<sub>1</sub>. In defense of this procedure we note that (1) the lone pair on sulfur is expected to be the highest filled orbital; (2) sulfones, which have no nonbonding electrons on sulfur, are transparent in the region of the spectrum we are considering.

For the very weak transition at about 240 nm, which is strongly optically active, we are looking for an electric dipole forbidden, magnetic dipole allowed transition. There is only one lone pair promotion that qualifies, namely b<sub>1</sub> → b<sub>2</sub>\*, where b<sub>2</sub>\* is a σ antibonding MO.

For the 220- and 200-nm bands, we want electric dipole allowed promotions from the lone pair, and there are a number of possibilities: b<sub>1</sub> → a<sub>1</sub>\*, b<sub>1</sub> → 3d<sub>z<sup>2</sup></sub>, b<sub>1</sub> → 3d<sub>xz</sub>, b<sub>1</sub> → 3d<sub>yz</sub>, b<sub>1</sub> → 4s. The experimentally observed vibrational structure of the 220-nm band shows a progression in the C-S-C symmetric stretching frequency. This would suggest that the equilibrium carbon-sulfur bond length changes on going from the ground to the excited state. So a plausible assignment of this band would be a promotion to the antibonding orbital, a<sub>1</sub>\*, rather than to the atomic-like 3d or 4s. For the 200-nm band, the relative insensitivity of the position and intensity of this band to the nature of the atoms bonded to sulfur suggests an atomic-like 3p → 3d or 3p → 4s on sulfur. The promotions b<sub>1</sub> → 3d<sub>z<sup>2</sup></sub> and b<sub>1</sub> → 4s are z polarized, but there are no states with which they can mix in first order to gain some magnetic moment in the z direction.

Oscillator strengths of the electric dipole allowed transitions 3p<sub>z</sub> → 4s, 3p<sub>z</sub> → 3d<sub>z<sup>2</sup></sub>, 3p<sub>z</sub> → 3d<sub>xz</sub>, and 3p<sub>z</sub> → 3d<sub>yz</sub> were calculated, using the dipole velocity form of the matrix element ⟨0|**u**|*i*⟩.<sup>18</sup> Table IV shows the

**Table IV.** Calculated<sup>a-d</sup> Oscillator Strengths of Some Lone Pair Promotions

|                 | 3p <sub>z</sub> → 4s                          |        |        |        |        |
|-----------------|---|--------|--------|--------|--------|
| Z <sub>4s</sub> | 1.0   | 1.2    | 1.4    | 1.6    |        |
| f               | 0.0001  | 0.0003 | 0.0008 | 0.0017 |        |
|                 | 3p <sub>z</sub> → 3d <sub>z<sup>2</sup></sub> |        |        |        |        |
| Z <sub>3d</sub> | 0.5   | 1.0    | 1.5    | 2.0    | 2.5    |
| f               | 0.0009  | 0.0360 | 0.2081 | 0.5669 | 1.0460 |
|                 | 3p <sub>z</sub> → 3d <sub>xz</sub>            |        |        |        |        |
| Z <sub>3d</sub> | 0.5   | 1.0    | 1.5    | 2.0    | 2.5    |
| f               | 0.0007  | 0.0090 | 0.1561 | 0.4252 | 0.7845 |

<sup>a</sup> Z<sub>3p</sub> = 5.45. <sup>b</sup> Based on transition energy corresponding to 200 nm. <sup>c</sup> f for 3p<sub>z</sub> → 3d<sub>yz</sub> is equal in magnitude to that for 3p<sub>z</sub> → 3d<sub>xz</sub>. <sup>d</sup> The orbital exponent is Z/n.

results for a range of effective nuclear charges of the sulfur 3d and 4s orbitals. It is evident that the oscill-

(18) A. Moscowitz, "Modern Quantum Chemistry," Vol. 3, O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, p 31.

ator strengths are extremely sensitive to the effective nuclear charges  $Z$  of the excited-state orbitals. This was previously shown for  $3p \rightarrow 4s$  in  $H_2S$  by Cusachs, Miller, and McCurdy.<sup>19</sup> However, one can pick out values of  $Z_{3d}$  for which the oscillator strength of the promotion  $3p_z \rightarrow 3d$  agrees well with experiment for either the 220- or the 200-nm band. For the  $3p_z \rightarrow 4s$  transition, however,  $Z_{4s}$  values in the range  $0 \rightarrow 2$  lead to  $f$  values at least an order of magnitude smaller than the experimental ones for either of the electric dipole allowed transitions. But more important, recall that there is no state that  $3p_z \rightarrow 4s$  can mix with in first order to give optical activity. We thus eliminate the 4s orbital from further consideration as the upper state orbital in either the 200- or the 220-nm transition.<sup>20</sup>

As a result of these qualitative arguments, we come to the following tentative conclusions. The only electric dipole forbidden, magnetic dipole allowed lone pair promotion is  $b_1 \rightarrow b_2^*$ ; this we assign to the very weak 240-nm band. For the 220- and 200-nm bands we have to consider  $b_1 \rightarrow a_1^*$  and three possible  $b_1 \rightarrow 3d$  electric dipole allowed promotions. As we saw, the experimental evidence suggests that the 200-nm band is atomic-like and that the upper state orbital in the 220-nm band has antibonding character. Thus we tentatively assign  $b_1 \rightarrow a_1^*$  to the 220-nm band, and a  $b_1 \rightarrow 3d$  promotion (which one we cannot say) to the 200-nm band.

**B. Calculated MO's and Energies for the Sulfide Chromophore.** In order to provide molecular orbital coefficients for order of magnitude calculations of oscillator and rotational strengths, a Wolfsberg-Helmholz<sup>5</sup> type of calculation was performed for the sulfide chromophore, using a Slater basis set consisting of the 3s, 3p, 3d, and 4s atomic orbitals on sulfur and a  $2sp^3$  hybrid on each carbon. In evaluating the secular determinant  $|H_{ij} - ES_{ij}|$ , the following approximations were used. (1) The diagonal matrix elements,  $H_{ii}$ , were chosen as the negative of neutral atom valence state ionization potentials (VSIP's). (2) One-center and nearest-neighbor off-diagonal matrix elements were approximated as

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij} \quad (2)$$

(3) Non-nearest-neighbor  $H_{ij}$  were neglected.

Quantities we regarded as variable parameters were  $K$ , the VSIP of the sulfur 3d AO, and  $Z_{3d}$ , the effective nuclear charge of the sulfur 3d AO. Fixed VSIP's and nuclear charges used in the calculations are given in Tables V and VI.

We found that the ordering of the ground-state MO's was independent of  $K$ , but that the ordering of the excited state MO's was markedly dependent on  $K$ . The relative position of the levels also depended on whether or not the off-diagonal overlaps in the Hückel matrix were included. The ordering of the levels is of concern here because this ordering affects the relative signs of the coefficients in the MO's, and these signs are im-

(19) L. C. Cusachs, D. J. Miller, and C. W. McCurdy, Jr., *Spectrosc. Lett.*, 2(5), 141 (1969).

(20) Cusachs and coworkers<sup>19,21</sup> have also investigated the effective nuclear charges of the 3d and 4s orbitals of sulfur. They too note the sensitivity of the oscillator strengths to the values of the effective nuclear charges, but their considerations lead them to effective nuclear charges outside the range we considered.

(21) W. W. Fogleman, D. J. Miller, H. B. Jonassen, and L. C. Cusachs, *Inorg. Chem.*, 8, 1209 (1969).

**Table V.** Valence State Ionization Potentials<sup>a</sup>

| Atomic orbital                           | VSIP, eV |
|--|----------|
| Sulfur 3s                                | 21.29    |
| Sulfur 3p <sub>z</sub>                   | 11.38    |
| Sulfur 3p <sub>x</sub> , 3p <sub>y</sub> | 12.50    |
| Sulfur 4s                                | 3.6      |
| Carbon 2s                                | 21.2     |
| Carbon 2p                                | 11.4     |
| Carbon 2sp <sup>3</sup>                  | 13.85    |

<sup>a</sup> Taken from L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, 43, S160 (1965); L. C. Cusachs, J. W. Reynolds, and D. Barnard, *ibid.*, 44, 835 (1966); L. C. Cusachs and J. R. Linn, Jr., *ibid.*, 46, 2919 (1967).

**Table VI.** Effective Nuclear Charges<sup>a,b</sup>

| Atomic orbital     | $Z$  |
|--------------------|------|
| Sulfur 3s, 3p      | 5.45 |
| Sulfur 4s          | 1.00 |
| Carbon 2s, 2p      | 3.25 |
| Perturber carbon   | 3.25 |
| Perturber hydrogen | 1.00 |

<sup>a</sup> Slater values. <sup>b</sup> The nonorthogonality between 3s and 4s was neglected because, for these  $Z$  values,  $\langle 3s|4s \rangle = 0.0114$ .

portant for the rotational strength calculations. Indeed, such considerations provide motivation, in the present instance, for the neglect of the off-diagonal overlaps in the Hückel matrix.

In Hückel theory, the ordering of the state energies follows that of the orbital energies. Hence we want  $b_2^*$  to be the lowest energy excited orbital, in which case the lowest energy transition calculated would be the electric dipole forbidden, magnetic dipole allowed  $b_1 \rightarrow b_2^*$ , which is our candidate for the very weak band at 240 nm. When one omits the off-diagonal overlaps, and chooses a  $K$  near 1, the  $b_2^*$  orbital is the lowest excited one, followed by  $a_1^*$ , and then the 3d and 4s levels. As  $K$  increases to 2, the orbitals  $b_2^*$  and  $a_1^*$  become higher in energy, and the lowest excited state orbitals become mainly 3d and 4s. If one includes the off-diagonal overlaps in the Hückel matrix, one cannot choose  $K$  near 1, since this causes the MO's to go over to the AO's.<sup>5c</sup> So for the case when the off-diagonal overlaps are included,  $K$ 's larger than 1 must be used. However, these larger  $K$ 's lead to an unacceptable ordering of virtual orbitals. For these reasons, the off-diagonal overlaps were omitted, and a  $K$  near 1 was chosen, which ensures that the lowest excited state orbitals are  $b_2^*$ , then  $a_1^*$ , followed by the 3d and 4s levels.

The orbitals and energies are given in Table VII for the case  $K = 1$ ,  $Z_{3d} = 1.5$ , and 3d VSIP = 1.0 eV. We note the following from these results. (1) The highest filled orbital is a pure  $3p_z$  atomic orbital on sulfur. (2) With these parameters, the lowest excited state orbitals are  $b_2^*$  and  $a_1^*$ , which are antinodal in the plane of the C-S-C chromophore and antibonding between the sulfur and carbon atoms. (3) With a total spread of about 0.03 eV, the 3d levels are all clustered around the value -1.0 eV. This was the input diagonal element for the d orbitals, and the reasons for this choice will be discussed later.

The oscillator strengths of the transition  $b_1 \rightarrow a_1^*$  ( $\phi_4 \rightarrow \phi_6$  in the notation of Table VII) were calculated using these  $K = 1.0$  MO's. The calculated result was

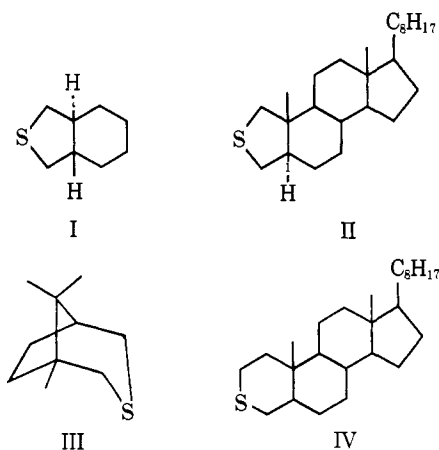
**Table VII.** Molecular Orbitals and Energies for the Sulfide Chromophore<sup>a-c</sup>

|                                   | 3d <sub>z<sup>2</sup></sub> | 3d <sub>xz</sub> | 3d <sub>yz</sub> | 3d <sub>x<sup>2</sup>-y<sup>2</sup></sub> | 3d <sub>xy</sub> | 3p <sub>y</sub> | 3p <sub>x</sub> | 3p <sub>z</sub> | c <sub>1</sub> | c <sub>2</sub> | 3s      | 4s      | Energy, eV |
|-----------------------------------|-----------------------------|------------------|------------------|---|------------------|-----------------|-----------------|-----------------|----------------|----------------|---------|---------|------------|
| φ <sub>12</sub> (b <sub>2</sub> ) | 0                           | 0                | 0                | 0   | 0.9981           | 0               | 0.0305          | 0               | 0.0381         | -0.0381        | 0       | 0       | -0.9733    |
| φ <sub>11</sub> (a <sub>1</sub> ) | 0.9638                      | 0                | 0                | -0.2572                                   | 0                | 0               | 0               | -0.0280         | 0.0408         | 0.0408         | -0.0285 | -0.0033 | -0.9826    |
| φ <sub>10</sub> (b <sub>1</sub> ) | 0                           | 0                | 1                | 0   | 0                | 0               | 0               | 0               | 0              | 0              | 0       | 0       | -1.0000    |
| φ <sub>9</sub> (a <sub>2</sub> )  | C                           | 1                | C                | 0   | 0                | 0               | 0               | 0               | 0              | 0              | 0       | 0       | -1.0000    |
| φ <sub>8</sub> (a <sub>1</sub> )  | 0.2579                      | 0                | 0                | 0.9662                                    | 0                | 0               | 0               | 0               | 0              | 0              | 0       | 0       | -1.0000    |
| φ <sub>7</sub> (a <sub>1</sub> )  | 0.0139                      | 0                | 0                | -0.0037                                   | 0                | 0               | 0               | 0.0776          | -0.0875        | -0.0875        | 0.0621  | 0.9872  | -3.5813    |
| φ <sub>6</sub> (a <sub>1</sub> )  | 0.0658                      | 0                | 0                | -0.0176                                   | 0                | 0               | 0               | 0.4959          | -0.5184        | -0.5184        | 0.4322  | -0.1590 | -4.2311    |
| φ <sub>5</sub> (b <sub>2</sub> )  | 0                           | 0                | 0                | 0   | -0.0587          | 0               | 0.7424          | 0               | 0.4719         | -0.4719        | 0       | 0       | -6.6260    |
| φ <sub>4</sub> (b <sub>1</sub> )  | 0                           | 0                | 0                | 0   | 0                | 1               | 0               | 0               | 0              | 0              | 0       | 0       | -11.3800   |
| φ <sub>3</sub> (a <sub>1</sub> )  | -0.0065                     | 0                | 0                | 0.0017                                    | 0                | 0               | 0               | 0.8405          | 0.2144         | 0.2144         | -0.4489 | 0.0003  | -14.5180   |
| φ <sub>2</sub> (b <sub>2</sub> )  | 0                           | 0                | 0                | 0   | 0.0196           | 0               | 0.6693          | 0               | -0.5252        | 0.5252         | 0       | 0       | -19.7507   |
| φ <sub>1</sub> (a <sub>1</sub> )  | -0.0061                     | 0                | 0                | 0.0016                                    | 0                | 0               | 0               | 0.2020          | 0.4195         | 0.4195         | 0.7791  | 0.0095  | -28.9270   |

<sup>a</sup>  $K = 1.0$ . <sup>b</sup> These orbitals pertain to the six-membered ring sulfide chromophore (see section C). <sup>c</sup> Orbitals φ<sub>1</sub>-φ<sub>4</sub> are occupied in the ground state.

$f = 0.012$  for a transition centered at 220 nm, which compares well with the experimental value of 0.016. This lends support to the assignment of the 220-nm band as  $b_1 \rightarrow a_1^*$ .

**C. First-Order Perturbation Calculations. 1. Assignment of the 240-nm Transition.** Using the zero-order states built from these molecular orbitals we calculated, to first order, the rotational strength of the electric dipole forbidden  $b_1 \rightarrow b_2^*$  transition for the dissymmetric sulfides I-IV. These are the five-membered ring sulfides, (8*R*,9*R*)-*trans*-2-thiahydrindan (I) and *A*-nor-2-thiacholestane (II), and six-membered ring sulfides, 1,8,8-trimethyl-3-thiabicyclo[3.2.1]octane (III) and 3-thia-5- $\alpha$ -cholestane (IV). The experimental



rotational strengths for these compounds are given in Table VIII.

Referring to Table III, we see that there are two states with which  $b_1 \rightarrow b_2^*$  can mix to gain electric transition moment in the same direction as the magnetic transition moment, namely  $b_1 \rightarrow 3d_{yz}$  and  $b_2 \rightarrow b_2^*$ . The perturbation operator  $V$ , which is the potential energy of an electron in the field of the incompletely shielded carbon and hydrogen atoms of the molecule, has the form<sup>6-9</sup>

$$V = \sum_{\text{C atoms}} V_{\text{C}} + \sum_{\text{H atoms}} V_{\text{H}} \quad (3)$$

where

$$V_{\text{C}}(r) = -\frac{e^2}{a_0} Z_{\text{C}} \left[ \frac{Z_{\text{C}}^2 r^2}{6a_0^2} + \frac{Z_{\text{C}} r}{a_0} + 3 + \frac{4a_0}{Z_{\text{C}} r} \right] \exp(-Z_{\text{C}} r/a_0) \quad (4)$$

**Table VIII.** Experimental Rotational Strengths<sup>a</sup> of Sulfides

| Compound   | $\lambda_{\text{max}}$ , nm | $R$               | $\lambda_{\text{max}}$ , nm | $R$               | $\lambda_{\text{max}}$ , nm | $R$               |
|--|-----------------------------|-------------------|-----------------------------|-------------------|-----------------------------|-------------------|
| (8 <i>R</i> ,9 <i>R</i> )- <i>trans</i> -2-Thiahydrindan (I) | 244                         | -4.0 <sup>b</sup> | 217                         | 4.0 <sup>b</sup>  | 202                         | -4.0 <sup>b</sup> |
| <i>A</i> -Nor-2-thiacholestane (II)                          | 244                         | 4.0 <sup>b</sup>  |                             | <i>b, c</i>       | 202                         | 4.0 <sup>b</sup>  |
| 1,8,8-Trimethyl-3-thiabicyclo[3.3.1]octane (III)             | 233                         | -0.7 <sup>d</sup> | 215                         | -2.4 <sup>d</sup> | 202                         | 1.9 <sup>d</sup>  |
| 3-Thia-5- $\alpha$ -cholestane (IV)                          | 235                         | 1.8 <sup>e</sup>  | 216                         | 1.3 <sup>b</sup>  | 200                         | -1.4 <sup>e</sup> |

<sup>a</sup> In units of  $10^{-40}$  cgs. <sup>b</sup> Reference 13. <sup>c</sup> The 217-nm band appears to be absent in this compound. <sup>d</sup> Calculated from CD spectra taken by R. Nagarajan, assuming Gaussian shape; C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, New York, N. Y., 1960, Chapter 12, p 165. <sup>e</sup> Calculated from CD spectra taken by L. Verbit, assuming Gaussian shape.

and

$$V_{\text{H}}(r) = -\frac{e^2}{a_0} Z_{\text{H}} \left[ 1 + \frac{a_0}{Z_{\text{H}} r} \right] \exp(-2Z_{\text{H}} r/a_0) \quad (5)$$

$Z_{\text{C}}$  and  $Z_{\text{H}}$  are the effective nuclear charges for C and H, and  $a_0$  is the Bohr radius. In deriving these expressions, it was assumed that the wave functions of the shielding electrons can be approximated by Slater AO's and that the 1s electrons of carbon are perfectly shielding. In evaluating matrix elements of  $V$  with respect to atomic orbitals, three-center integrals were neglected.

Our unnormalized perturbed state  $b_1 \rightarrow b_2^*$  is then

$$(b_1^{-1}b_2^*)' = (b_1^{-1}b_2^*) + A(b_1^{-1}3d_{yz}) + B(b_2^{-1}b_2^*) \quad (6)$$

where, in first order

$$A = \langle b_2^* | V | 3d_{yz} \rangle / (E_{b_1 \rightarrow b_2^*} - E_{b_1 \rightarrow 3d_{yz}}) \quad (7)$$

$$B = \langle b_2^* | V | b_1 \rangle / (E_{b_1 \rightarrow b_2^*} - E_{b_2 \rightarrow b_2^*}) \quad (8)$$

In the numerical calculations (1) the alkyl side chains in II and IV were neglected; (2) all six-membered rings were assumed to be in the chair form; (3) bond angles were assumed tetrahedral except  $\angle \text{CSC} = 100^\circ$  in six-ring sulfides,  $\angle \text{CSC} = 92^\circ$  in five-ring sulfides; (4) bond distances used were C-C, 1.54 Å; C-H, 1.09 Å; C-S, 1.82 Å; (5)  $Z_{3d}$  for sulfur was taken as 1.5. Other effective nuclear charges are given in Table VI.

The mixing coefficients and the contributions of  $(b_1^{-1}3d_{yz})$  and  $(b_2^{-1}b_2^*)$  to the rotational strength are shown in Table IX. In the calculations, for order of magnitude purposes, both states  $(b_1^{-1}3d_{yz})$  and  $(b_2^{-1}b_2^*)$  were assumed to lie 1.5 eV above the  $(b_1^{-1}b_2^*)$  state.

Table IX. First-Order Calculated Rotational Strengths of the  $b_1 \rightarrow b_2^*$  Transition<sup>a</sup>

| Compd | $A^b$                   | $B^b$                   | Total contribution of states to rotational strength |                         | Exptl                  |
|-------|-------------------------|-------------------------|---|-------------------------|------------------------|
|       |                         |                         | $(b_1^{-1}3d_{yz})$                                 | $(b_2^{-1}b_2^*)$       |                        |
| I     | $-3.841 \times 10^{-3}$ | $1.296 \times 10^{-6}$  | $-0.64 \times 10^{-40}$                             | $-1.56 \times 10^{-43}$ | $-4.0 \times 10^{-40}$ |
| II    | $1.057 \times 10^{-2}$  | $-1.065 \times 10^{-4}$ | $1.75 \times 10^{-40}$                              | $1.28 \times 10^{-42}$  | $4.0 \times 10^{-40}$  |
| III   | $-5.565 \times 10^{-3}$ | $-3.041 \times 10^{-5}$ | $-0.91 \times 10^{-40}$                             | $3.61 \times 10^{-43}$  | $-0.7 \times 10^{-40}$ |
| IV    | $7.459 \times 10^{-3}$  | $3.131 \times 10^{-6}$  | $1.23 \times 10^{-40}$                              | $-3.72 \times 10^{-43}$ | $1.8 \times 10^{-40}$  |

<sup>a</sup>  $Z_{3d} = 1.5$ . <sup>b</sup>  $A$  and  $B$  are the mixing coefficients, defined in eq 7 and 8.

We see that the  $(b_2^{-1}b_2^*)$  contribution is the wrong sign in two cases, as well as being three orders of magnitude too low. In contrast, the sign of the  $(b_1^{-1}3d_{yz})$  contribution is correct for the four cases. In addition, the order of magnitude is correct, except perhaps for compound I which is about a factor of 6 too low. Thus the calculations suggest the assignment of the 240-nm band to the  $b_1 \rightarrow b_2^*$  promotion. The main contribution to the optical activity here comes from a mixing of the  $(b_1^{-1}b_2^*)$  state with the higher lying  $(b_1^{-1}3d_{yz})$  state.

An important point to bring out is that the sign of the contribution of the state  $(b_1^{-1}3d_{yz})$  to the rotational strength of  $(b_1^{-1}b_2^*)$  is correct only because the orbital  $b_2^*$  has some admixture of  $3d_{xy}$ . To see this one must examine the contributions of the AO matrix elements to the MO perturbation matrix element  $\langle b_2^* | V | 3d_{yz} \rangle$  which governs the mixing coefficient  $A$ . For our starting MO's, this matrix element is

$$\langle b_2^* | V | 3d_{yz} \rangle = -0.0587 \langle 3d_{xy} | V | 3d_{yz} \rangle + 0.7424 \langle 3p_z | V | 3d_{yz} \rangle \quad (9)$$

The AO matrix elements, in turn, for the representative case of compound II, are

$$\langle 3d_{xy} | V | 3d_{yz} \rangle = 3.708 \times 10^{-1} \quad (10)$$

$$\langle 3p_z | V | 3d_{yz} \rangle = 8.683 \times 10^{-3} \quad (11)$$

For this case

$$\langle b_2^* | V | 3d_{yz} \rangle = -1.585 \times 10^{-2} \quad (12)$$

The 3p-3d and 3d-3d contributions come in with different signs, and the 3d-3d AO matrix element is three orders of magnitude larger than the 3p-3d integral. Thus the sign and magnitude of the mixing coefficient, and hence the rotational strength, are determined by the amount of sulfur  $3d_{xy}$  in the  $b_2^*$  orbital.

**2. The 220-nm Transition.** We turn now to the  $b_1 \rightarrow a_1^*$  transition, which we are considering assigning to the 220-nm band. There are two transitions with which  $b_1 \rightarrow a_1^*$  can mix to become optically active, namely,  $(b_1^{-1}3d_{xz})$  and  $(b_2^{-1}a_1^*)$ . In preliminary first-order perturbation calculations, neither state made contributions to the optical activity which were of the correct sign and order of magnitude for all four sulfides. The contribution of  $(b_1^{-1}3d_{xz})$  was roughly two orders of magnitude larger than that of  $(b_2^{-1}a_1^*)$ . It is of note that, in both this case and the previous one, the mixings of the lone pair promotions with promotions from the  $\sigma$  bonding levels, that is the  $(b_1^{-1}b_2^*) - (b_2^{-1}b_2^*)$  and the  $(b_1^{-1}a_1^*) - (b_2^{-1}a_1^*)$  mixings, were roughly two orders of magnitude smaller than the lone pair promotion - lone pair promotion mixings,  $(b_1^{-1}b_2^*) - (b_1^{-1}3d_{yz})$  and  $(b_1^{-1}a_1^*) - (b_1^{-1}3d_{xz})$ .

Since the Wolfsberg-Helmholz 3d molecular orbitals were nearly degenerate, and since the first-order calculation of the rotational strength of  $b_1 \rightarrow a_1^*$  was unsuccessful, it was decided to perform a degenerate perturbation type of calculation, in which all the lone pair transitions were mixed together.

**D. Degenerate Perturbation Calculation.** Calculations were carried out in which all eight states arising from the lone pair promotions were mixed together under the perturbation. The ground state and states arising from promotions from the  $\sigma$  bonding levels were not included because they would not mix significantly with the lone pair transitions as we saw in the last section. All the carbon and hydrogen perturbers were included, not just those dissymmetric with respect to the symmetry planes of the sulfide chromophore. Although those perturbers which are symmetrically disposed would not contribute to the optical activity they would contribute to the splittings of the orbitals, and in particular the 3d orbitals.

The input unperturbed orbital energies of the  $b_2^*$  and  $a_1^*$  were chosen so that the transition energies (calculated as simple differences of orbital energies) of the two perturbed states  $(b_1^{-1}b_2^*)'$  and  $(b_1^{-1}a_1^*)'$  matched the experimental ones for the 240- and 220-nm transitions. We saw that the orbital energies of the 3d levels were clustered around the negative of the VSIP of the sulfur 3d AO. This quantity was selected so that the energy of the lowest perturbed  $b_1 \rightarrow 3d$  state matched the experimental one corresponding to the 200-nm transition. This procedure necessitated values of the sulfur 3d VSIP of about 1 eV.

The perturbation matrix was diagonalized, and the oscillator and rotational strengths were calculated for transitions from the lone pair to the perturbed excited state orbitals. The ordering of the excited state MO's for a typical case is shown in Table X, while the MO

Table X. Ordering of Excited State MO's before and after Perturbation for 3-Thiacholestane. Orbital Energies (eV) Are in Parentheses

| Before perturbation                              |         | After perturbation          |
|--|---------|-----------------------------|
| $\varphi_{12}(3d)$                               | (-0.97) |                             |
| $\varphi_{11}(3d)$                               | (-0.98) |                             |
| $\varphi_8(3d), \varphi_9(3d), \varphi_{10}(3d)$ | (-1.0)  | $\varphi'_{12}(3d)$ (-1.54) |
|  |         | $\varphi'_{11}(3d)$ (-1.72) |
|  |         | $\varphi'_{10}(3d)$ (-2.47) |
|  |         | $\varphi'_7(4s)$ (-3.62)    |
|  |         | $\varphi'_6(3d)$ (-3.79)    |
| $\varphi_7(4s)$                                  | (-3.58) | $\varphi'_5(3d)$ (-5.42)    |
| $\varphi_6(a_1^*)$                               | (-4.8)  | $\varphi'_4(a_1^*)$ (-5.64) |
| $\varphi_5(b_2^*)$                               | (-5.5)  | $\varphi'_3(b_2^*)$ (-6.20) |

coefficients of the lowest energy 3d level are presented in Table XI. In the case of the five-membered ring

**Table XI.** MO Coefficients of Lowest 3d Level Given by Perturbation Calculation<sup>a</sup>

| Compd                                     | I       | II      | III     | IV      |
|---|---------|---------|---------|---------|
| 3d <sub>z<sup>2</sup></sub>               | 0.4709  | 0.4314  | 0.0442  | 0.2782  |
| 3d <sub>xz</sub>                          | -0.0202 | 0.0475  | -0.0476 | 0.0636  |
| 3d <sub>yz</sub>                          | 0       | -0.1620 | 0.6674  | 0.5499  |
| 3d <sub>x<sup>2</sup>-y<sup>2</sup></sub> | 0.7841  | 0.7821  | 0.5334  | 0.6382  |
| 3d <sub>xy</sub>                          | 0       | 0.1438  | 0.1017  | -0.1577 |
| 3p <sub>z</sub>                           | 0       | 0       | 0       | 0       |
| 3p <sub>x</sub>                           | 0       | 0.0089  | 0.0049  | -0.0098 |
| 3p <sub>y</sub>                           | -0.0673 | -0.1106 | 0.2016  | 0.0636  |
| c <sub>1</sub>                            | 0.0755  | 0.1275  | -0.2062 | -0.0724 |
| c <sub>2</sub>                            | 0.0755  | 0.1102  | -0.2163 | -0.0539 |
| 3s  | -0.0556 | -0.0919 | 0.1787  | 0.0575  |
| 4s  | -0.3794 | -0.3222 | -0.3059 | -0.4104 |

<sup>a</sup> Z<sub>3d</sub> = 1.5, K = 1.01.

sulfides, I and II, the lowest 3d level is predominantly 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub> and 3d<sub>z<sup>2</sup></sub>, while for the six-membered ring sulfides, III and IV, it is mainly 3d<sub>yz</sub> and 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub>.

Tables XII and XIII show the calculated rotational

**Table XII.** Calculated Rotational Strength of the b<sub>1</sub> → a<sub>1</sub>\* Transition as a Function of K<sup>a,b</sup>

| Compd | K   | R     |      | K     |       | R     | R <sub>exptl</sub> of 220-mμ band |
|-------|-----|-------|------|-------|-------|-------|-----------------------------------|
|       |     | R     | K    | R     | K     |       |                                   |
| I     | 1.0 | -0.05 | 1.01 | 0.02  | 1.025 | 0.17  | 4.0                               |
| II    | 1.0 | -0.11 | 1.01 | -0.42 | 1.025 | -1.35 |                                   |
| III   | 1.0 | -1.20 | 1.01 | -0.82 | 1.025 | -0.94 | -2.4                              |
| IV    | 1.0 | 0.71  | 1.01 | 0.39  | 1.025 | -0.33 | 1.3                               |

<sup>a</sup> Z<sub>3d</sub> = 1.5. <sup>b</sup> Rotational strength (R) in units of 10<sup>-40</sup> cgs.**Table XIII.** Calculated Rotational Strength of the Lowest b<sub>1</sub> → 3d Transition as a Function of K<sup>a,b</sup>

| Compd | K   | R     |      | K     |       | R     | R <sub>exptl</sub> of 200-mμ band |
|-------|-----|-------|------|-------|-------|-------|-----------------------------------|
|       |     | R     | K    | R     | K     |       |                                   |
| I     | 1.0 | -0.05 | 1.01 | -0.14 | 1.025 | -0.37 | -4.0                              |
| II    | 1.0 | -0.06 | 1.01 | 0.46  | 1.025 | 1.36  | 4.0                               |
| III   | 1.0 | 1.56  | 1.01 | 1.51  | 1.025 | 1.70  | 1.9                               |
| IV    | 1.0 | -1.63 | 1.01 | -1.20 | 1.025 | -0.97 | -1.4                              |

<sup>a</sup> Z<sub>3d</sub> = 1.5. <sup>b</sup> Rotational strength (R) in units of 10<sup>-40</sup> cgs.

strengths of the perturbed b<sub>1</sub> → a<sub>1</sub>\* and b<sub>1</sub> → 3d (the lowest 3d level) transitions when the zero-order molecular orbitals were obtained with three slightly different values of the parameter K. It is evident that the magnitudes and even the signs of the rotational strengths of these transitions are extremely sensitive to small changes in the MO coefficients. We saw before that the inclusion of some 3d<sub>xy</sub> in the b<sub>2</sub>\* MO was necessary for a calculation of the optical activity of the b<sub>1</sub> → b<sub>2</sub>\* transition. Now we find that the optical activity of the b<sub>1</sub> → a<sub>1</sub>\* and b<sub>1</sub> → 3d transitions also depends critically on the precise coefficients of the 3d and 4s AO's in the unperturbed MO's. This is because the contributions of the various AO matrix elements to the MO matrix elements of V contribute with different signs. However, with our set of assignments, we were able to find a set of MO coefficients, by varying K, which gave the correct sign for the rotational strengths of the three transitions in all four compounds. This was the only set of assignments, out of the many we considered in preliminary calculations, which led to this agreement.

The entire calculation, the Wolfsberg-Helmholz followed by a mixing of the eight lone-pair promotions under the perturbation, was performed for three different values of the effective nuclear charge of the sulfur 3d orbital, 1.5, 2.0, and 2.5. For each Z<sub>3d</sub>, the MO coefficients were optimized with respect to the experimental data, by varying the parameter K. Each time, the VSIP of the sulfur 3d AO was selected so that the final b<sub>1</sub> → 3d transition energy matched the experimental value. The final parameters are listed in Table XIV. The resulting oscillator and rotational strengths

**Table XIV.** Wolfsberg-Helmholz Parameters

| Z <sub>3d</sub> | K    | VSIP of 3d AO's |
|-----------------|------|-----------------|
| 1.5             | 1.01 | 1.0 eV          |
| 2.0             | 1.02 | 1.0 eV          |
| 2.5             | 0.98 | 1.5 eV          |

of the three lowest transitions are given in Table XV. The experimental oscillator strengths are  $f \sim 0.06$  for the 200-nm band and  $f \sim 0.016$  for the 220-nm band.

The oscillator strengths resulting from the Z<sub>3d</sub> = 1.5 calculation agree best with experiment. Other values of Z<sub>3d</sub> give  $f$  values for b<sub>1</sub> → 3d which are too high because the matrix element  $\langle 3p | \nabla | 3d \rangle$  increases with Z<sub>3d</sub> in the manner shown in Table IV.

Looking at the rotational strengths of the six-membered ring compounds, III and IV, the best agreement with experiment is given by the Z<sub>3d</sub> = 1.5 calculation. For the five-membered ring compounds, although the signs of the rotational strengths are correct, the magnitudes are too low by as much as two orders of magnitude. The first-order mixing described in section C of the states (b<sub>1</sub>-<sup>1</sup>b<sub>2</sub>\*) and (b<sub>1</sub>-<sup>1</sup>3d<sub>yz</sub>) gave rotational strengths for I and II of the correct order of magnitude, for the b<sub>1</sub> → b<sub>2</sub>\* transition (see Table IX). However, when the eight lone pair promotions are mixed together, the optical activity of this transition in I and II drops drastically. The main reason for this is that in the first-order calculation, the energy separation of the states was set at 1.5 eV for all compounds, whereas in the higher order calculation the energy separations were determined mainly by the differences in the diagonal elements of the perturbation operator. The 3d<sub>yz</sub> levels are lowered by a much smaller amount in I and II (particularly I) than in III and IV. Table XVI shows the perturbation matrix element  $\langle 3d_{yz} | V | 3d_{yz} \rangle$  for the four compounds for Z<sub>3d</sub> = 1.5 and 2.0. So the energy differences of the relevant states are much greater in I and II than in III and IV. These results indicate that the perturbation calculation is a poor way of determining energy separations in a quantitative way, although the relative ordering of levels may very well be correct.

There is a marked improvement in the rotational strengths of I and II on going to Z<sub>3d</sub> = 2.0. One reason for this is the increased amount of 3d in the b<sub>2</sub>\* and a<sub>1</sub>\* molecular orbitals, which arises from the increased magnitudes of the overlaps of the sulfur 3d with the carbon 2sp<sup>3</sup> AO's, with increased Z<sub>3d</sub>. Another factor is that the transition dipole moment integral,  $\langle 3d | \nabla | 3p \rangle$ , increases with Z<sub>3d</sub>. However, the good agreement of III and IV is lost on going to Z<sub>3d</sub> = 2.0.

Table XV. Calculated Oscillator Strengths ( $f$ ) and Rotational Strengths ( $R$ ) from Perturbation Calculation<sup>a</sup>

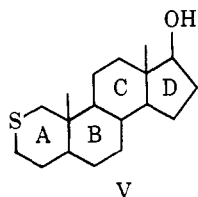
| Compd | $b_1 \rightarrow b_2^*$ |                    |                    | $b_1 \rightarrow a_1^*$  |                    |                    | $b_1 \rightarrow 3d$ |                    |                    |
|-------|-------------------------|--------------------|--------------------|--------------------------|--------------------|--------------------|----------------------|--------------------|--------------------|
|       | $f$                     | $R_{\text{calcd}}$ | $R_{\text{exptl}}$ | $f$                      | $R_{\text{calcd}}$ | $R_{\text{exptl}}$ | $f$                  | $R_{\text{calcd}}$ | $R_{\text{exptl}}$ |
|       |                         |                    |                    | $Z_{3d} = 1.5, K = 1.01$ |                    |                    |                      |                    |                    |
| I     | 0.000                   | -0.06              | -4.0               | 0.012                    | 0.02               | 4.0                | 0.035                | -0.14              | -4.0               |
| II    | 0.000                   | 0.53               | 4.0                | 0.017                    | -0.42              |                    | 0.033                | 0.46               | 4.0                |
| III   | 0.000                   | -0.47              | -0.7               | 0.034                    | -0.82              | -2.4               | 0.074                | 1.51               | 1.9                |
| IV    | 0.000                   | 1.00               | 1.8                | 0.008                    | 0.39               | 1.3                | 0.067                | -1.20              | -1.4               |
|       |                         |                    |                    | $Z_{3d} = 2.0, K = 1.02$ |                    |                    |                      |                    |                    |
| I     | 0.000                   | -1.67              |                    | 0.055                    | 0.72               |                    | 0.079                | -0.66              |                    |
| II    | 0.000                   | 4.77               |                    | 0.070                    | -1.71              |                    | 0.060                | 1.09               |                    |
| III   | 0.002                   | -12.84             |                    | 0.272                    | 9.67               |                    | 0.123                | 4.95               |                    |
| IV    | 0.001                   | 3.54               |                    | 0.031                    | 0.10               |                    | 0.184                | -4.45              |                    |
|       |                         |                    |                    | $Z_{3d} = 2.5, K = 0.98$ |                    |                    |                      |                    |                    |
| I     | 0.000                   | -4.00              |                    | 0.128                    | 1.29               |                    | 0.132                | -0.42              |                    |
| II    | 0.000                   | 7.95               |                    | 0.132                    | -1.21              |                    | 0.123                | 0.06               |                    |
| III   | 0.002                   | -0.15              |                    | 0.424                    | -2.26              |                    | 0.335                | 3.51               |                    |
| IV    | 0.001                   | 1.69               |                    | 0.094                    | 0.17               |                    | 0.322                | -2.83              |                    |

<sup>a</sup> Rotational strengths in units of  $10^{-40}$  cgs.

Table XVI. Diagonal Perturbation Matrix Element,  $\langle 3d_{yz} | V | 3d_{yz} \rangle$  in eV

| Compd | $Z_{3d} = 1.5$ | $Z_{3d} = 2.0$ |
|-------|----------------|----------------|
| I     | -0.7747        | -0.9509        |
| II    | -1.6173        | -1.7487        |
| III   | -3.2588        | -3.7355        |
| IV    | -2.4576        | -2.7712        |

E. The Case of 2-Thia-5 $\alpha$ -androstan-17 $\beta$ -ol. The perturbation calculation of the optical activity of the compound 2-thia-5 $\alpha$ -androstan-17 $\beta$ -ol (V) was carried



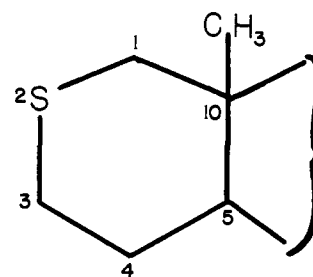
out for the following four conformations of ring A of the steroid skeleton, neglecting the OH group in the D ring: (1) a regular chair; (2) a flattened chair, in which C-5 (see Figure 2) lies in the  $z = 0$  plane (coordinate system of Figure 1); (3) a flattened boat, in which C-4, C-5, and C-10 lie in the  $z = 0$  plane; (4) a regular boat.

The results are shown in Table XVII. It is seen that, for ring A of the steroid structure in a chair conforma-

Table XVII. Calculated Rotational Strengths<sup>a,b</sup> of 2-Thia-5 $\alpha$ -androstan-17 $\beta$ -ol

| Conformation of ring A      | $b_1 \rightarrow b_2^*$   | $b_1 \rightarrow a_1^*$ | $b_1 \rightarrow 3d$ |
|-----------------------------|---------------------------|-------------------------|----------------------|
| Chair                       | 1.51                      | 2.57                    | -3.39                |
| Flattened chair             | 0.97                      | -0.60                   | 0.29                 |
| Flattened boat              | -1.52                     | -0.74                   | 1.97                 |
| Boat                        | -1.52                     | -7.71                   | 10.83                |
| 50% chair, 50% boat         | -0.01                     | -2.57                   | 3.72                 |
|                             | Experimental <sup>c</sup> |                         |                      |
| $\lambda_{\text{max}}$ , nm | 239                       | 217                     | 204                  |
| $R$                         | -0.1 <sup>d</sup>         | -2.6 <sup>d</sup>       | 2.4 <sup>d</sup>     |

<sup>a</sup> Rotational strengths in units of  $10^{-40}$  cgs. <sup>b</sup>  $Z_{3d} = 1.5, K = 1.01$ . <sup>c</sup> There is an additional small CD peak at 253 nm with a rotational strength of  $0.05 \times 10^{-40}$  cgs. <sup>d</sup> Calculated from CD spectra taken by L. Verbit, assuming Gaussian shape.

Figure 2. Numbering of atoms in ring A of 2-thia-5 $\alpha$ -androstan-17 $\beta$ -ol.

tion, the signs of the rotational strengths of all three transitions of interest are in disagreement with experiment. With the flattened boat conformation the signs are correct, although the rotational strength of the  $b_1 \rightarrow b_2^*$  state is an order of magnitude high.

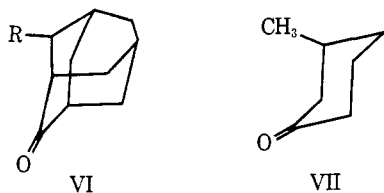
An alternate interpretation of the experimental data is that we have an equilibrium mixture of the boat and chair conformers, which have oppositely signed rotational strengths. The two forms may absorb at slightly different wavelengths, giving rise to the small positive CD band at 253 nm. Wellman and coworkers<sup>22</sup> have shown that when two oppositely signed CD curves, at wavelengths  $\lambda_1$  and  $\lambda_2$ , of similar amplitude overlap strongly, the wavelength interval between the resultant extrema is of the order of the half-width of the component bands, independent of  $(\lambda_1 - \lambda_2)$ , for  $(\lambda_1 - \lambda_2)$  small compared to the band half-width. In addition, the resulting apparent rotational strengths are markedly reduced over those of the contributing curves, by as much as a factor of 25. We may be seeing an example of this in the CD of 2-thia-5 $\alpha$ -androstan-17 $\beta$ -ol, where we have two oppositely signed extrema at 239 and 253 nm, with extremely small magnitudes. The wavelength interval between them, 14 nm, is the same order as the band half-width, *ca.* 9 nm. In fact, it would be difficult to explain the 253-nm band, which does not appear in the other four compounds, on any other basis. The calculated rotational strengths of the  $b_1 \rightarrow a_1^*$  and  $b_1 \rightarrow 3d$  transitions in the boat and chair conformers do not have such similar amplitudes: thus the effect would not be as marked for these transitions.

(22) K. Wellman, P. Laur, W. Briggs, A. Moscowitz, and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 66 (1965).



The results for a 50–50 boat–chair mixture are shown in Table XVII.

It may be further noted that in 2-thia-5 $\alpha$ -androstan-17 $\beta$ -ol (V) the axial methyl at position 10 (see Figure 2) is situated in the same position relative to the sulfur atom, as the 3-axial substituents in the chair cyclohexanones VI and VII are situated relative to the carbonyl group. The experimental work of Snatzke and Eckhardt<sup>23</sup> has shown that 3-axial Cl, Br, and I in the rigid adamantanones (VI) produce a net negative Cotton effect, a result contrary to that predicted by the octant rule.<sup>24</sup> In the approximate SCF calculations of Pao and Santry<sup>25</sup> on methylcyclohexanones, the calculated signs and rotational strengths are in good agreement with the experimental data and with the octant rule for a number of isomers: however, axial 3-methylcyclohexanone (VII) is calculated to have a



negatively signed rotational strength when the ring is in the chair conformation, a result in disagreement with the octant rule. In these calculations, the basis set includes AO's from all of the atoms in the molecules. One might argue then that 3-axially substituted six-membered ring chair sulfides, like 3-axially substituted chair cyclohexanones, may be molecules for which the separation into inherently symmetric chromophore and dissymmetric perturbation is not valid. However,

(23) G. Snatzke and G. Eckhardt, *Tetrahedron*, **24**, 4543 (1968).

(24) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, **83**, 4013 (1961).

(25) Y. Pao and D. P. Santry, *ibid.*, **88**, 4157 (1966).

such an interpretation leaves unexplained the appearance of the band at 253 nm.

### Summary

The three lowest energy transitions in saturated dialkyl sulfides have been assigned on the basis of symmetry considerations and the optical absorption and optical activity data. The nature of these assignments has been elaborated by semiempirical calculations of oscillator and rotational strengths. The assignments are as follows. (1) The very weak band at about 240 nm is assigned to the electric dipole forbidden, magnetic allowed transition,  $b_1(3p_z) \rightarrow b_2^*$ . (2) The band at about 220 nm is assigned to the electric dipole allowed  $b_1(3p_z) \rightarrow a_1^*$  promotion. (3) The band at 200 nm is assigned to the transition  $b_1(3p_z) \rightarrow 3d$ , where 3d is a linear combination of sulfur 3d orbitals. The particular linear combination is dependent on the compound.

It should be noted that these assignments are in disagreement with previous ones, which were based only on absorption data. Thompson and coworkers<sup>10</sup> assigned the 240-nm band to the orbitally forbidden promotion  $3p_z \rightarrow 3d_{xy}$  on sulfur, the 220-nm band to the promotion  $3p_z \rightarrow 3d$  (which was not specified), and the 200-nm band to the promotion  $3p_z \rightarrow 4s$ . Clark and Simpson<sup>11</sup> assigned the 240-nm band to  $3p_z \rightarrow b_2^*$ , as do we. The 220-nm band they assigned to an intensity cancelling linear combination of the orbital promotions  $b_2 \rightarrow b_2^*$  and  $a_1 \rightarrow a_1^*$ . The 200-nm band they assigned to an intensity enhancing linear combination of the orbital promotions  $b_2 \rightarrow a_1^*$  and  $a_1 \rightarrow b_2^*$ . We found, however, that these alternate assignments are less consonant with the optical activity data than our own.

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