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Optical Activity of Chiral Disulfide Chromophores[1]

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Abstract: The optical rotatory properties of inherently dissymmetric disulfide structures are calculated from LCAO–MO–SCF–CI wave functions constructed on a semiempirical CNDO molecular orbital model. Sulfur 3d functions are included in the atomic orbital basis set and electronic excited states are constructed in the virtual orbital configuration interaction approximation. Transition energies, oscillator strengths, reduced rotatory strengths, and dissymmetry factors are calculated and reported for the five lowest energy singlet–singlet transitions of H_2S_2, $(CH_3)_2S_2$, and 1,2-dithiolane in various conformations. All two-center as well as one-center contributions to the transition integrals are included in the calculation. The results suggest that, although the sulfur 3d orbitals apparently have little influence on the ground-state electronic properties of the disulfide moiety, the spectroscopic properties associated with the lowest lying disulfide transitions strongly reflect d-orbital participation in the excited states. The influence of d orbitals is especially apparent in the rotatory strengths calculated as a function of the XSS/SSX dihedral angle.

The natural optical rotatory properties of chiral disulfide systems have been the subject of considerable research activity in recent years. Perhaps the most extensive studies and intense interest have focused on the natural optical activity exhibited by the disulfide chromophore in cystine and in cystine derivatives.[2,3] Other small disulfide systems whose optical rotatory properties have been measured include the antibiotic gliotoxin,[4] substituted 1,2-dithianes and 1,2-dithiolanes,[5] and anomeric di-5-(2′-deoxyuridilyl) disulfides.[6] The optical activity associated with cystine residues in proteins has received special attention since, in addition to providing structural and chemical information about the disulfide linkages, it can be used as a probe for following structural changes in the protein environment about the disulfide groups.[2k,l,7] Although the utility of disulfide optical activity as a probe of protein structure and reactivity has been demonstrated in a number of experimental studies (see especially the work of Beychok and coworkers[2k,l,7e–g]), the successful application of this technique is hindered by (1) the difficulties in separating the contributions made by aromatic side chains to the near ultraviolet optical activity from the disulfide con-

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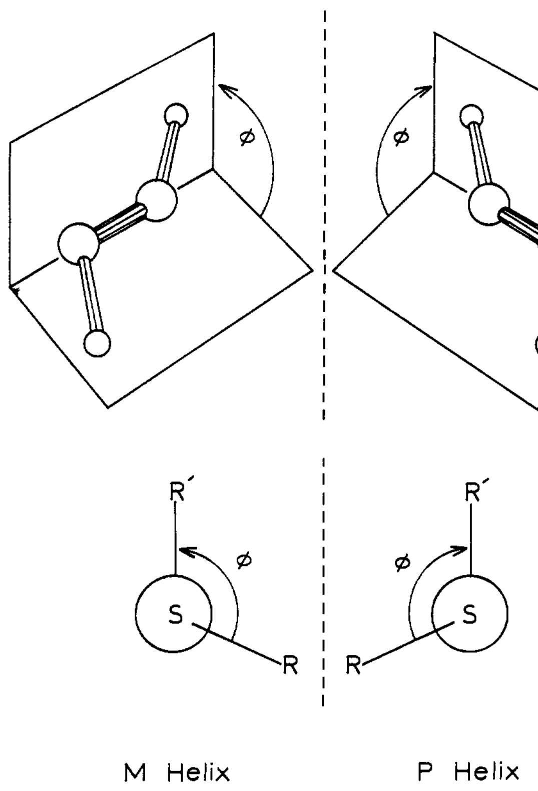

Figure 1. The dissymmetric disulfide group.

tributions; and (2) an incomplete theoretical understanding and empirical characterization of disulfide optical activity in terms of specific structural parameters (inherent and environmental). These problems have been discussed thoroughly in the recent literature for proteins,[7e–g] and the problem of spectra–structure correlation in smaller disulfide model systems also has received detailed attention.[2h,3,8] There is little question that natural optical activity has provided considerable stereochemical and spectroscopic information about chiral systems. However, it can be accurately stated that a great deal of ambiguity still exists, especially with respect to a sound theoretical understanding of the relationships between the spectroscopic observables of optical activity, stereochemical variables, and the electronic states of the disulfide group.

Linderberg and Michl[8] were the first to carry out theoretical calculations of the rotatory strengths associated with electronic transitions in a chiral disulfide system. They focused their attention on the optical activity exhibited by the first two (lowest energy) electronic transitions (spin allowed) in the disulfide chromophore and restricted their study to the inherently dissymmetric structures of HSSH characterized by dihedral angles $\phi \neq 0,180°$[9] (see Figure 1). To analyze the optical activity observables in terms of electronic structural variables, Linderberg and Michl examined and compared two different representations of the disulfide electronic states. They first adopted the very simple LCAO–MO model proposed by Bergson.[10] With this model the two lowest lying singlet–singlet transitions are ascribed to excitations from lone-pair electron orbitals localized on the two sulfur atoms to a σ-type molecular orbital which is antibonding with respect to the two sulfur atoms. In its simplest form, Bergson's model represents the highest energy sulfur lone-pair orbitals as pure $3p_s$ atomic functions, excluding any $3s_s$ character. Electric dipole character in the two lowest energy transitions must arise, therefore, from an admixture of the $3s_s$ and $3p_s$ atomic functions in the σ^*_{ss} molecular orbital. This simple model has been used with some success in explaining, qualitatively, the rotational barrier about the disulfide bond in H_2S_2,[10] the frequency shifts and band splittings observed as a function of dihedral angle ϕ in the near-ultraviolet absorption spectra of cyclic and acyclic disulfide molecules,[5g,11,12] and the dependence of the ionization potential upon ϕ.[13] Similarly, Linderberg and Michl found that the Bergson model, when applied to the optical activity of chiral disulfides, provided descriptions of the underlying spectroscopic processes and of the optical rotatory parameters (signs and relative magnitudes as a function of ϕ) which are in qualitative agreement with those obtained by use of more sophisticated models of the electronic states.

Linderberg and Michl carried out a second set of calculations on the rotatory strengths of chiral H_2S_2 structures based on a semiempirical CNDO molecular orbital model[14,15] of the molecular valence-shell electronic structure. They used the Sichel–Whitehead variant of the CNDO model[16] and restricted their atomic orbital basis set to 3s and 3p STO's on the sulfur atoms and 1s STO's on the hydrogen atoms. Electric dipole transition integrals were calculated in the dipole length formalism, and all off-diagonal elements of the electric dipole transition matrix (in an atomic orbital basis) were set equal to zero except for those between a 3s and a 3p orbital located on the same sulfur atom. That is, all two-center contributions to the electric dipole transition integrals were neglected (consistent with the complete neglect of differential overlap approximation used in obtaining the molecular orbitals). Matrix elements of the angular momentum operator were calculated from resonance integrals (semiempirically determined); this method avoids direct calculation of angular momentum transition integrals and circumvents the need for specifying, explicitly, the radial parts of the atomic orbital (AO) basis functions.

The CNDO calculations performed by Linderberg and Michl for various ground-state properties of H_2S_2 are in reasonable agreement with experiment. The calculated values for the two lowest ionization potentials are estimated to be about 10–15% too high, and the computed transition energies to the two lowest singlet states are approximately 10–15% lower than the experimental values. For all values of the dihedral angle ϕ and for all sets of geometrical parameters (bond

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angles and distances) used, the lowest unoccupied molecular orbital was characterized as σ^*_{ss}. Furthermore, the highest occupied molecular orbital was, in most cases, similar to that proposed by Bergson (a linear combination of nonbonding 3p orbitals on the sulfur atoms). The lowest energy transition for all calculations was characterized as $n(3p_s) \rightarrow \sigma^*_{ss}$, which is in agreement with the assumptions of Bergson's simple model. Near $\phi = 0$, the first excited state was calculated to be of B symmetry (antisymmetric with respect to 180° rotation about the molecular C_2 axis). Between $\phi = 70$ and 90° (depending upon the parameters used in the calculation), a crossover between this B state and an excited state of A symmetry occurs, and from $\phi = 90$ to 180° the A state is the lowest energy excited state.

Lindenberg and Michl calculated that the rotatory strength of the first transition is positive for $\phi > 90°$ (left-handed helix, M configuration, and A state lowest). This result was reported to be relatively insensitive to choice of parameters (geometrical and computational). For $\phi < 90$ (left-handed helix, B state lowest), they found that the computed rotatory strength is somewhat more sensitive to the details of the calculation, but that it is generally negative in sign.

The primary purpose of the present study is to extend the work of Lindenberg and Michl (L–M) on chiral disulfides. To obtain a description of the disulfide electronic structure, we employ the semiempirical CNDO model[14,15] in performing SCF–MO calculations. Unlike L–M, however, we include in our AO basis set the 3d orbitals on each sulfur atom. Furthermore, we use the "standard" CNDO parameters as set forth by Pople and coworkers.[17] Excited states are represented as linear combinations of singly excited configurational wave functions, the coefficients determined by CI calculations. Electric dipole transition integrals are calculated in the dipole velocity formalism. Before calculating the electric dipole and magnetic dipole transition matrix elements, the CNDO wave functions are renormalized including overlap ("deorthogonalized").[18–20] Using these renormalized wave functions, both the one-center and two-center terms in the transition matrices are calculated and both one-center and two-center contributions are included in the computed rotatory strengths. In addition to various chiral structures of H_2S_2, the present study includes calculations on several structures of $(CH_3)_2S_2$, dimethyl disulfide, and on two 1,2-dithiolane structures in which the five-membered ring is nonplanar and dissymmetric (possessing only a C_2 symmetry element).

The two most significant differences between the L–M study and the present work are the inclusion of sulfur 3d orbitals in the AO basis set and the calculation of both one-center and two-center contributions to the rotatory strength. Molecular rotatory strengths are known to exhibit an extraordinary sensitivity to the detailed spatial distribution and nodal pattern of the electron orbitals involved in spectroscopic transitions.[21–30] This sensitivity was demonstrated quite forcefully in a study of the $n\pi^*$ rotatory strength of optically active saturated ketones reported by Bouman and Moscowitz.[28] It might be expected that the presence of d orbitals, with their rich nodal structure, in the AO basis set will yield a better spatial representation of the spectroscopic states associated with the disulfide chromophore. Results from recent calculations of rotatory strengths based on molecular orbital models suggest that the two-center contributions to the computed values are not negligible.[19,20]

Method

The semiempirical CNDO molecular orbital model has been well described in the literature[15,17] and need not be elaborated upon here. We obtained our copy of the molecular orbital program CNINDO from Dr. Paul Dobash and made several minor modifications to permit its use on the CDC 6400 computer at the University of Virginia. Although the program has an option to perform INDO calculations,[17] we were restricted to CNDO calculations since we include d orbitals in our basis set. The SCF–MO's are expressed as linear combinations of atomic orbitals.

$$\phi_i = \sum_{\mu} C_{i\mu}\chi_{\mu} \qquad (1)$$

The excited states are represented by linear combinations of Slater determinants constructed in the virtual orbital approximation. The ground state is taken to be the Slater determinant comprised of the doubly occupied molecular orbitals of lowest energy. An excited state determinant is obtained by replacing an orbital in the ground-state determinant with one of the virtual orbitals. Considering only singlet states obtained by the excitation of one electron we have

$$^1\psi_a = \sum_{p,q} C^a{}_{p,q}\,(^1/_2)^{1/2}\,[\psi_{\bar{p}\to\bar{q}} - \psi_{p\to q}] \qquad (2)$$

where

$$\Psi_{\bar{p}\to\bar{q}} = |\phi_1(1)\bar{\phi}_1(2)\ldots\phi_p(2p-1)\bar{\phi}_q(2p)\ldots\bar{\phi}_m(2m)| \qquad (3)$$

is an excited state determinant and the sum in eq 2 extends over all molecular orbital excitations considered. The coefficients $C^a{}_{p,q}$ are obtained by configuration interaction (CI) calculations in which the requisite electron repulsion integrals as well as the molecular orbitals and eigenvalues are taken from CNINDO.

In a previous publication[19] we described the computer program ANGMOMT, which calculates the rotatory strengths for transitions from the ground state to excited states approximated by eq 2. We have trans-

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lated this program from Algol into Fortran and have made several modifications on it. The revised version of ANGMOMT will be described briefly below.

The optical activity associated with a single electronic transition can be expressed conveniently in terms of the reduced rotatory strength

$$[R_{0\rightarrow a}] = (100/\beta D)\ \mathrm{Im}[\langle\psi_0|\hat{\boldsymbol{\mu}}|\psi_a\rangle\cdot\langle\psi_a|\hat{\mathbf{m}}|\psi_0\rangle] \quad (4)$$

where β is the Bohr magneton, D is the Debye unit, $\hat{\mu}$ is the electric dipole operator, and $\hat{\mathbf{m}}$ is the magnetic dipole operator. The operators are defined by

$$\hat{\boldsymbol{\mu}} = e\sum_j \hat{\mathbf{r}}_j \quad (5)$$

$$\hat{\mathbf{m}} = \frac{e\hbar}{2mci}\sum_j(\hat{\mathbf{r}}_j\cdot\hat{\nabla}_j) = \frac{e}{2mc}\sum_j\hat{\mathbf{L}}_j \quad (6)$$

where j labels electrons. The current version of ANGMOMT calculates reduced rotatory strengths for singlet–singlet transitions where the states are approximated by eq 2. The state transition integrals in eq 4 are calculated including all two-center moment integrals over atomic orbitals in addition to the one-center integrals. To be consistent with the CNDO approximations inherent in the MO calculation, we first "deorthogonalize" the atomic orbital basis set. This step is accomplished by operating on the matrix of MO coefficients with $\mathbf{S}^{-1/2}$ where $\mathbf{S}$ is the matrix of atomic overlap integrals. This procedure has been shown to produce improved charge distributions[31] and, recently, Imamura, *et al.*,[20] have shown that it yields more accurate rotatory strengths.

The calculations proceed in two parts. The first deals with the computation of the transition integrals in terms of atomic orbitals and their projection onto the molecular coordinate system, while the second involves the assembly of the projected moments to yield the reduced rotatory strengths. A local coordinate system is defined for each atom such that it is parallel to the reference molecular coordinate system in which the relative positions of all atoms are described. Thus, the one-center transition integrals are readily projected onto the molecular coordinate system. Two-center integrals are calculated in a "local diatomic" coordinate system and are projected onto the origin in two steps. In the first step the atomic orbitals on the two centers are rotated into alignment with the molecular system, while in the second the operator is rotated.

Having computed the projected dipole velocity and angular momentum matrix elements in terms of atomic orbitals, we may compute these quantities in terms of molecular orbitals according to

$$\langle\phi_i|\hat{\mathbf{O}}|\phi_j\rangle = \sum_k\sum_l C_{ik}C_{jl}\langle\chi_k|\hat{\mathbf{O}}|\chi_l\rangle \quad (7)$$

where $\hat{\mathbf{O}}$ is $\hat{\nabla}$ or $\hat{\mathbf{L}}$. For transitions from the ground state to an excited state given by eq 2, the transition moments are given by

$$\langle\psi_0|\hat{\mathbf{O}}|\psi_a\rangle = \sum_{p,q}C^a{}_{p,q}\langle\phi_k|\hat{\mathbf{O}}|\phi_l\rangle \quad (8)$$

After the dipole velocity and angular momentum matrix elements have been calculated we use the following equations to obtain the state electric and magnetic dipole transition moments in cgs units.

$$\langle\psi_0|\hat{\boldsymbol{\mu}}|\psi_a\rangle = (e\hbar^2/m)\langle\psi_0|\hat{\nabla}|\psi_a\rangle(E_a - E_0)^{-1} \quad (9)$$

$$\langle\psi_a|\hat{\mathbf{m}}|\psi_0\rangle = (e/2mc)\langle\psi_a|\hat{\mathbf{L}}|\psi_0\rangle \quad (10)$$

In addition to reduced rotatory strengths, other properties calculated for each singlet–singlet electronic transition are

(a) dipole strength

$$D_{0a} = \langle\psi_0|\hat{\boldsymbol{\mu}}|\psi_a\rangle\cdot\langle\psi_a|\hat{\mu}|\psi_0\rangle \quad (11)$$

(b) oscillator strength

$$f_{0a} = (4\pi m\nu_{0a}/3\hbar e^2)D_{0a} \quad (12)$$

(c) dissymmetry factor

$$g_{0a} = 4R_{0a}/D_{0a} \quad (13)$$

where

$$R_{0a} = \mathrm{Im}[\langle\psi_0|\hat{\boldsymbol{\mu}}|\psi_a\rangle\cdot\langle\psi_a|\hat{\mathbf{m}}|\psi_0\rangle] \quad (14)$$

Structure Variables

Three different chemical species were included in the present study. They are hydrogen disulfide, H_2S_2, dimethyl disulfide, $(CH_3)_2S_2$, and 1,2-dithiolane, $(CH_2)_3S_2$. Two 1,2-dithiolane structures were studied. In each structure the five-membered ring is nonplanar and possesses P chirality (right-handed helical sense). For one structure (DT-1), the structural parameters for the ring were taken from the X-ray diffraction data on single crystals of DL-6-thioctic acid (α-DL-lipoic acid) reported by Stroud and Carlisle.[32] The $-(CH_2)_4$-COOH ring substituent of the 6-thioctic acid molecule was replaced by a hydrogen atom to obtain our DT-1 structure. The ring structural parameters for our second 1,2-dithiolane isomer (DT-2) were taken from the X-ray diffraction data on single crystals of 1,2-dithiolane-4-carboxylic acid reported by Foss, Hordvik, and Sletten.[33] In this case, the –COOH ring substituent was replaced by a hydrogen atom to generate our DT-2 structure.

The CSS/SSC dihedral angle (ϕ) in DT-1 is 35.5° and in DT-2 it is 26.6°. The sulfur–sulfur and sulfur–carbon bond lengths and the sulfur–sulfur–carbon bond angles in DT-1 and DT-2 are as follows: r(S′S) = 2.053 Å, r(S′C′) = 1.79 Å, r(SC) = 1.83 Å, ∠C′S′S = 95.5°, and ∠CSS′ = 92.8° for DT-1; r(S′S) = = 2.096 Å, r(S′C′) = 1.803 Å, r(SC) = 1.808 Å, ∠C′S′S = 91.6°, and ∠CSS′ = 96.3° for DT-2. Note that neither DT-1 nor DT-2 has exact C_2 point group symmetry, although departures from this symmetry are small.

Five geometrical isomers of dimethyl disulfide were considered. Four of these structures were generated by fixing the bond distances and bond angles at r(SS) = 2.04 Å, r(SC) = 1.78 Å, r(CH) = 1.09 Å, ∠SSC = 103°, and ∠SCH = 109°, while varying the dihedral angle ϕ through the values 60, 75, 90, and 120°. The structure parameters chosen for the fifth isomer are as follows: r(SS) = 2.03 Å, r(SC) = 1.82 Å, r(CH) = 1.09 Å, ∠SSC = 104.5°, ∠SCH = 109°,

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Table I. H_2S_2,[a] Computed Orbital Energies and Total Ground-State Energies (in atomic units)

	Dihedral angle (ϕ), deg								
	0	30	60	75	85	90	95	120	180
					HOMO				
1(n′); a	−0.426	−0.433	−0.448	−0.458	−0.466	−0.470	−0.474	−0.496	−0.572
2(σ'_{SH}); b	−0.548	−0.593	−0.622	−0.635	−0.642	−0.646	−0.654	−0.660	−0.666
3(σ_{SS}); a	−0.550	−0.551	−0.553	−0.554	−0.554	−0.554	−0.554	−0.555	−0.533
4(n); b	−0.572	−0.527	−0.499	−0.485	−0.477	−0.470	−0.468	−0.449	−0.426
5(σ_{SH}); a	−0.699	−0.694	−0.678	−0.668	−0.661	−0.646	−0.648	−0.636	−0.590
					LUMO				
$\bar{1}$(σ^*_{SH}); a	0.016	0.025	0.043	0.052	0.057	0.060	0.061	0.068	0.079
$\bar{2}$(σ^*_{SS}); b	0.051	0.049	0.045	0.043	0.041	0.040	0.039	0.045	0.061
$\bar{3}$(π_d); a	0.107	0.116	0.118	0.120	0.121	0.122	0.126	0.128	0.144
$\bar{4}$($\sigma^{*\prime}_{SH}$); b	0.112	0.091	0.072	0.065	0.062	0.060	0.060	0.034	0.031
$\bar{5}$(π'_d); b	0.130	0.129	0.129	0.128	0.128	0.122	0.122	0.119	0.107
Total ground-state energy	−23.480	−23.490	−23.500	−23.502	−23.505	−23.506	−23.505	−23.500	−23.492

[a] $r(SS) = 2.05$ Å, $r(SH) = 1.34$ Å, $\angle SSH = 92°$.

and $\phi = 75°$. The structure parameters of the CSSC group in single crystals of L-cystine (hexagonal L-cystine) are nearly identical with those adopted for the fifth isomer (the dihedral angle in hexagonal L-cystine is 73.7°).[34,35] All five structures of $(CH_3)_2S_2$ have P chirality.

Calculations were performed on 12 different geometrical isomers of H_2S_2. To generate nine of these structures, bond distances and bond angles were held constant while the dihedral angle ϕ (see Figure 1) was varied. For these nine structures, the bond distances and bond angles were fixed at $r(SS) = 2.05$ Å, $r(SH) = 1.34$ Å, and $\angle SSH = 92°$, and the angle ϕ was varied through the following values: 0(cis), 30, 60, 75, 85, 90, 95, 120, and 180° (trans). Three additional structures were studied in which the bond distances were fixed at $r(SS) = 2.05$ Å and $r(SH) = 1.34$ Å, the SSH angle was fixed at 102°, and the dihedral angle was varied through $\phi = 30$, 75, and 90°. Each of the ten dissymmetric structures of H_2S_2 has P chirality.

Results

H_2S_2. In Table I are displayed the energies (in atomic units) computed for the five highest occupied and five lowest unoccupied molecular orbitals of H_2S_2 for various values of the dihedral angle ϕ. Each orbital is assigned a symmetry designation, a or b, depending upon whether it is symmetric (a) or antisymmetric (b) with respect to 180° rotation about the C_2 molecular symmetry axis. The total energies computed for the ground states of the various rotational isomers of H_2S_2 are also given in Table I. HOMO's 2 and 5 are comprised almost entirely of hydrogen 1s and sulfur 3s and 3p atomic orbitals and their nodal patterns correspond to S–H σ bonding and S–S π bonding. HOMO's 1(n′) and 4(n) are comprised mostly of sulfur 3s and 3p atomic orbitals and correspond to Bergson's nonbonding or "lone-pair" sulfur functions. However, for certain geometries, the 1(n′) orbital has considerable S–S π antibonding character and 4(n) has S–S π bonding character.

Among the set of five LUMO's shown in Table I, $\bar{1}$ and $\bar{4}$ reflect both S–H and S–S antibonding character due to sulfur 3p and hydrogen 1s combinations, but also have significant S–H and S–S bonding character due to sulfur 3d and hydrogen 1s admixtures. Orbital $\bar{2}$ is a S–S antibonding σ function (comprised mostly of sulfur 3s and 3p atomic orbitals), and the dominant participants in both $\bar{3}$ and $\bar{5}$ are sulfur 3d functions in π bonding combinations.

The 1(n′) molecular orbital remains highest in energy among the occupied orbitals for all angles $\phi < 90°$. Between $\phi = 0$ and 65°, $\bar{1}$ is the lowest energy virtual orbital, and, from $\phi \cong 65$ to 90°, $\bar{2}$ is the lowest lying virtual orbital. We note that there is only minimal sulfur 3d orbital character in each of the occupied SCF molecular orbitals. However, there is significant 3d character in each of the five lowest lying vacant orbitals, and the 3d orbitals are dominant in LUMO's $\bar{3}$ and $\bar{5}$. If one accepts the validity of the virtual orbital approximation for representing spectroscopic excited states (with due reservations), the present molecular orbital calculations strongly suggest the importance of sulfur d orbitals in the excited states of the disulfide chromophore.

In Table II are listed the transition energies, oscillator strengths, and dissymmetry factors computed for the four lowest energy transitions in the H_2S_2 structural isomers. Additionally, each transition is characterized in terms of one-electron orbital excitations. Since our excited states are constructed as linear combinations of singly excited configurational wave functions, these characterizations reflect only the predominant configurational contributions to each excited state. We note that d orbital participation is *dominant* only in transition IV (at values of $\phi < 60$). However, for all values of ϕ, each of the four lowest energy transitions (I–IV of Table II) includes nonnegligible contributions from 3s → 3d and 3p → 3d excitations. In most cases, the terminal state is computed to have between 5 and 30% d orbital character. A and B designate the symmetries of the excited states (defined with respect to the molecular C_2 symmetry element).

The sums of the reduced rotatory strengths computed for transitions I and II, $[R_I] + [R_{II}] = [R^a_{net}]$, and for transitions III and IV, $[R_{III}] + [R_{IV}] = [R^b_{net}]$, are given in Table III.

The data presented in Tables I and II are for H_2S_2 structures in which $\angle SSH = 92°$. Calculations were also performed at several values of ϕ for H_2S_2 structures in which $\angle SSH = 102°$. This alteration in structural

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Table II. H_2S_2[a] Computed Properties for First Four Transitions[b]

Transition		0	30	60	75	85	90	95	120	180
		Dihedral Angle (ϕ), deg								
I	ΔE =	2.71	3.07	3.51	3.83	3.96	4.00	3.92	3.51	2.89
	f =	0.001	0.007	0.102	0.129	0.141	0.130	0.101	0.073	0.101
	$[R]$ =	0	−51.0	261	275	189	−296	−301	−199	0
	g =	0	0.034	0.014	0.012	0.008	0.012	0.018	0.017	0
		$A(n'\sigma^*_{SH})$	$A(n'\sigma^*_{SH})$	$B(n'\sigma^*_{SS})$	$B(n'\sigma^*_{SS})$	$B(n'\sigma^*_{SS})$	$A(n\sigma^*_{SS})$	$A(n\sigma^*_{SS})$	$A(n\sigma^*_{SS})$	$A(n\sigma^{*\prime}_{SH})$
II	ΔE =	3.00	3.16	3.87	4.04	4.04	4.02	4.10	3.96	3.62
	f =	0.124	0.130	0.038	0.097	0.158	0.129	0.096	0.111	0.006
	$[R]$ =	0	230	−126	−232	−241	196	207	255	0
	g =	0	0.008	0.019	0.015	0.013	0.005	0.013	0.012	0
		$B(n'\sigma^*_{SS})$	$B(n'\sigma^*_{SS})$	$A(n'\sigma^*_{SH})$	$A(n'\sigma^*_{SS})$	$A(n\sigma^*_{SS})$	$B(n'\sigma^*_{SS})$	$B(n'\sigma^*_{SS})$	$B(n'\sigma^*_{SS})$	$B(n\sigma^*_{SH})$
III	ΔE =	4.41	4.43	4.37	4.66	4.79	4.89	4.81	4.32	3.73
	f =	0.077	0.128	0.093	0.025	0.020	0.019	0.057	0.025	0.011
	$[R]$ =	0	207	134	75.3	66.9	123	−11.0	−17.3	0
	g =	0	0.015	0.029	0.021	0.024	0.048	0.002	0.004	0
		$B(n'\sigma^{*\prime}_{SH})$	$B(n'\sigma^{*\prime}_{SH})$	$B(n'\sigma^{*\prime}_{SH})$	$B(n'\sigma^{*\prime}_{SH})$	$B(n'\sigma^{*\prime}_{SH})$	$B(n'\sigma^{*\prime}_{SH})$	$A(n\sigma^{*\prime}_{SH})$	$A(n\sigma^{*\prime}_{SH})$	$A(n\sigma^*_{SS})$
IV	ΔE =	5.06	5.28	5.42	5.14	4.99	4.92	4.97	5.56	5.06
	f =	0.495	0.422	0.126	0.079	0.043	0.111	0.023	0.049	0.432
	$[R]$ =	0	−200	−55.6	−30.1	−4.6	−20.0	53.1	91.5	0
	g =	0	0.004	0.005	0.003	0.008	0.008	0.018	0.016	0
		$A(n'\pi_d)$	$A(n'\pi_d)$	$A(n\sigma^*_{SS})$	$A(n\sigma^{*\prime}_{SH})$	$A(n\sigma^{*\prime}_{SH})$	$A(n\sigma^{*\prime}_{SH}]$	$B(n'\sigma^{*\prime}_{SH})$	$B(n'\sigma^{*\prime}_{SH})$	$B(n'\sigma^*_{SS})$

[a] $r(SS) = 2.05$ Å, $r(SH) = 1.34$ Å, $\angle SSH = 92°$. [b] Units: ΔE, eV; R = reduced rotary strength = $1.08 \times 10^{40} \times R$(cgs); g = dissymmetry factor = $4R$(cgs)/D(cgs).

Table III

ϕ, deg	$[R^a_{net}]$	$[R^b_{net}]$
30	179	7
60	135	78
75	44	45
85	−52	62
90	−100	103
95	−94	42
120	56	74

parameters resulted in changes in the detailed composition of the HOMO's, LUMO's, and spectroscopic states, but the qualitative features (energy orderings, state symmetries, molecular orbital identities in terms of general bonding or antibonding patterns) did not change significantly *except* for the H_2S_2 ($\phi = 90°$) structure. Similarly, the signs and relative magnitudes of the calculated rotatory strengths remained unchanged when the SSH angle was increased from 92 to 102°, *except* in the case of H_2S_2 ($\phi = 90°$). The transition energies and reduced rotatory strengths computed for the first four transitions of H_2S_2 ($\phi = 90°$, $\angle SSH = 102°$) are given in Table IV. Additionally, $[R^a_{net}] = 6$ and $[R^b_{net}] = 71$ for this structure. We note that in going from $\angle SSH = 92$ to102° at $\phi = 90°$ the relative energies of the $B(n'\sigma^*_{SS})$ and $A(n\sigma'_{SS})$ states change. The signs of the rotatory strengths associated with transitions to these two states remain unchanged, but the relative magnitudes of the computed rotatory strengths and, consequently, $[R^a_{net}]$ change.

Table IV

	I	II	III	IV
ΔE, eV	4.33	4.37	4.61	4.73
$[R]$	173	−167	160	−89.3
	$B(n'\sigma^*_{SS})$	$A(n\sigma^*_{SS})$	$B(n'\sigma^{*\prime}_{SH})$	$A(n\sigma^{*\prime}_{SH})$

Table V. $(CH_3)_2S_2$,[a] Computed Orbital Energies and Total Ground-State Energies (in atomic units)

	60	75	90	120
	Dihedral angle (ϕ), deg			
	HOMO			
1(n′); a	−0.409	−0.423	−0.433	−0.457
2(n): b	−0.463	−0.452	−0.433	−0.405
3(σ_{SS}); a	−0.494	−0.499	−0.494	−0.496
4(σ'_{SC}); b	−0.566	−0.571	−0.574	−0.596
5(σ_{SC}); a	−0.622	−0.617	−0.612	−0.577
	LUMO			
$\bar{1}$(σ^*_{SC}); a	0.058	0.061	0.069	0.095
$\bar{2}$(σ^*_{SS}); b	0.072	0.067	0.074	0.073
$\bar{3}$(σ^*_{SC}); b	0.091	0.076	0.078	0.053
$\bar{4}$(π_d); a	0.154	0.152	0.159	0.162
$\bar{5}$(π'_d); b	0.163	0.162	0.164	0.157
Total ground-state energy	−40.8821	−40.8830	−40.8849	−40.8794

[a] $r(SS) = 2.04$ Å, $r(SC) = 1.78$ Å, $r(CH) = 1.09$ Å, $\angle SSC = 103°$, and $\angle SCH = 109°$.

$(CH_3)_2S_2$. In Table V are displayed the energies (in atomic units) computed for the five highest occupied and five lowest unoccupied molecular orbitals of dimethyl disulfide for ϕ = 60, 75, 90, and 120°. The total energies computed for the ground states of the rotational isomers are also given in Table V. Occupied orbitals 1(n′) and 2(n) are comprised mostly of sulfur 3s and 3p atomic orbitals and correspond to Bergson's nonbonding or "lone-pair" sulfur functions. Orbital $\bar{3}$ is a S–S σ bonding function. The atomic orbital compositions and nodal patterns of orbitals $\bar{4}$ and $\bar{5}$ exhibit both S–C σ bonding and S–S π bonding character. As was the case for H_2S_2, very little d orbital character is found in any of the occupied molecular orbitals.

The lowest energy vacant orbital for each isomer of $(CH_3)_2S_2$ is primarily a S–C σ antibonding orbital as reflected in the sulfur 3p and carbon 2s, 2p combinations; however, it also exhibits considerable S–S and S–C σ and π bonding character due to sulfur 3d and

Table VI. $(CH_3)_2S_2$, Computed Properties for First Five Transitions

Transition		Dihedral angle (ϕ), deg				
		60[a]	75[a]	75[b]	90[a]	120[a]
I	ΔE (eV) =	3.83	4.20	4.19	4.39	3.62
	f =	0.013	0.101	0.101	0.066	0.038
	$[R]$ =	20.8	186	187	112	−38.0
	g =	0.009	0.012	0.012	0.011	0.006
		$A(n'\sigma^*_{SC})$	$B(n'\sigma^*_{SS})$	$B(n'\sigma^*_{SS})$	$B(n'\sigma^*_{SS})$	$A(n\sigma^{*\prime}_{SC})$
II	ΔE (eV) =	3.89	4.28	4.29	4.42	3.91
	f =	0.120	0.015	0.016	0.014	0.173
	$[R]$ =	186	22.6	21.6	18.9	−193
	g =	0.008	0.010	0.009	0.009	0.006
		$B(n'\sigma^*_{SS})$	$A(n'\sigma^*_{SC})$	$A(n'\sigma^*_{SC})$	$A(n\sigma^*_{SS})$	$A(n\sigma^*_{SS})$
III	ΔE (eV) =	4.41	4.42	4.43	4.64	4.35
	f =	0.077	0.051	0.053	0.074	0.029
	$[R]$ =	166	118	118	125	−105
	g =	0.014	0.015	0.015	0.012	0.024
		$B(n'\sigma^{*\prime}_{SC})$	$B(n'\sigma^{*\prime}_{SC})$	$B(n'\sigma^{*\prime}_{SC})$	$B(n'\sigma^{*\prime}_{SC})$	$B(n\sigma^*_{SC})$
IV	ΔE (eV) =	5.56	5.19	5.18	4.74	5.40
	f =	0.137	0.149	0.148	0.151	0.068
	$[R]$ =	−168	−186	−184	−192	138
	g =	0.010	0.009	0.009	0.009	0.017
		$A(n\sigma^*_{SS})$	$A(n\sigma^*_{SS})$	$A(n\sigma^*_{SS})$	$A(n\sigma^{*\prime}_{SC})$	$B(n'\sigma^*_{SS})$
V	ΔE (eV) =	5.67	5.77	5.78	5.59	5.65
	f =	0.165	0.214	0.215	0.216	0.294
	$[R]$ =	−25.4	−12.0	−12.2	−0.01	11.5
	g =	0.001	0.001	0.001	0	0
		$B(\sigma_{SS}\sigma^*_{SS})$	$B(\sigma_{SS}\sigma^*_{SS})$	$B(\sigma_{SS}\sigma^*_{SS})$	$A(n'\sigma^*_{SC})$	$B(\sigma_{SS}\sigma^*_{SS})$

[a] See footnote *a* of Table V for structure parameters. [b] $r(SS) = 2.03$ Å, $r(SC) = 1.82$ Å, $r(CH) = 1.09$ Å, $\angle SSC = 104.5°$, and $\angle SCH = 109°$.

carbon 2s, 2p admixtures. The second lowest energy vacant orbital is $\underline{a}$ S–S σ antibonding function. Orbital $\overline{3}$ is similar to $\overline{1}$ except for its symmetry, and orbitals $\overline{4}$ and $\overline{5}$ are essentially S–S π bonding functions constructed from sulfur 3d atomic orbitals.

The transition energies, oscillator strengths, reduced rotatory strengths, and dissymmetry factors computed for the first five (lowest energy) singlet–singlet transitions of the five $(CH_3)_2S_2$ isomers are listed in Table VI. The sums of the reduced rotatory strengths for transitions I and II, $[R^a_{net}]$, and for transitions III and IV, $[R^b_{net}]$, are given in Table VII.

Table VII

ϕ deg	$[R^a_{net}]$	$[R^b_{net}]$
60 (1)	207	−2
75 (1)	209	−68
75 (2)	209	−66
90 (1)	131	−67
120 (1)	−231	33

Table VIII

		I	II	III	IV	V
DT-1	ΔE (eV) =	2.67	3.56	4.52	5.22	5.65
	$[R]$ =	259	91.0	181	46.7	−184
DT-2	ΔE (eV) =	2.68	3.27	4.53	5.62	5.79
	$[R]$ =	234	82.1	155	34.1	−149

$(CH_2)_3S_2$. The transition energies and reduced rotatory strengths computed for the five lowest energy singlet–singlet transitions of the two 1,2-dithiolane structures, DT-1 and DT-2, are given in Table VIII. Recall that the CSS/SSC dihedral angle in DT-1 is 35.5° and in DT-2 it is 26.6°. Furthermore, the bond distances and bond angles in the two structures differ slightly, and neither structure possesses exact C_2 symmetry due to the inequivalence of S–C and S′–C′ bond distances, of S′SC and SS′C′ bond angles, and of the three C–C bond distances. The symmetries and orbital character of the computed transitions are the same for the two structures and the assignments are as follows: I, $A(n'\sigma^*_{SC})$; II, $B(n'\sigma^*_{SS})$; III, $B(n'\sigma^{*\prime}_{SC})$; IV, $B(n\sigma^*_{SC})$; V, $B(n'\pi_d)$. We note that the rotatory strengths computed for DT-1 ($\phi = 35.5°$) are slightly larger than those computed for DT-2 ($\phi = 26.6°$), and that the signs of $[R]$ for the two structures are identical for each transition. Additionally, it is important to point out that the orbitals designated σ^*_{SC} and $\sigma^{*\prime}_{SC}$ contain significant S–S π antibonding character as well as S–C σ antibonding character, and that very little d orbital character is found in any of the occupied molecular orbitals.

Discussion

The calculated transition energies displayed in Table II reveal a hypsochromic (blue) shift in transition I of H_2S_2 on going from $\phi = 0$ to 90°. The computed values of λ(I) *vs.* ϕ are plotted in Figure 2 and a least-squares fit of the data yields a straight line with slope $(d\lambda(I)/d\phi) = -1.67$ nm/deg. Transition I of H_2S_2 also exhibits hyperchromicity on going from $\phi = 0$ to 85°. These calculated results are in substantial agreement with the experimentally determined ultraviolet absorption data obtained on various cyclic and acyclic disulfide systems.[5g,10–12] The hypsochromic shift also can be rationalized on Bergson's simple LCAO–MO model of the disulfide chromophore.[10] However, contrary to the predictions of Bergson's model, we calculate a small hypsochromic shift for

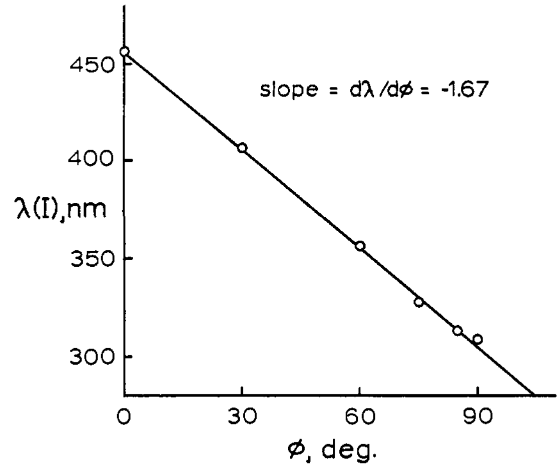

Figure 2. Computed wavelengths for transition I of H_2S_2 at various values of ϕ between 0 and 90°.

transition II of H_2S_2 on going from $\phi = 0$ to 90°. The transition wavelength, λ(II), is only a weak function of ϕ, and at 90°, λ(I) = λ(II). The blue shift predicted for transition II cannot be ascertained from the presently available ultraviolet absorption spectra of disulfide systems. Polarized spectra on single crystals of these systems would appear to provide the only reliable means of making unambiguous assignments of the bands in the near ultraviolet region. We note that for all dihedral angles ϕ, transitions I and II of H_2S_2 terminate in excited states of opposite symmetries (with respect to the molecular C_2 axis).

Transitions I and II of $(CH_3)_2S_2$ also exhibit a hypsochromic shift between $\phi = 60$ and 90°. For transition I, $(d\lambda(I)/d\phi) = -1.43$ nm/deg. Note, however, a suggested hypochromic effect in the computed oscillator strengths of the $n' \rightarrow \sigma^*_{SS}$ transition in $(CH_3)_2S_2$ isomers, $\phi = 60$, 75, and 90°.

Although the relative excitation energies computed for transition I of the various rotational isomers of H_2S_2 and $(CH_3)_2S_2$ are in substantial agreement with experiment, the absolute values of these computed quantities are generally about 15% lower than the experimental values. Using the same set of CNDO parameters as we used (*i.e.*, those recommended by Santry and Segal[15]), but including 3s and 3p functions on the sulfur atoms, Linderberg and Michl[8] computed the lowest singlet–singlet excitation energy for H_2S_2 ($\phi = 90°$ and $\angle SSH = 94°$) to be 5.00 eV. This value is about 5% higher than the experimental value of ~4.8 eV. As might be expected, inclusion of sulfur 3d functions in the basis set for the CNDO calculation leads to lower energy excited states constructed in the virtual orbital approximation.

The spectroscopic properties we calculate for the lowest energy singlet–singlet transition of H_2S_2 rotamers differ in several respects from those previously reported by Linderberg and Michl. Whereas L–M calculated a lowest excited state of B symmetry throughout the range $\phi = 0$ to 90°, we find the lowest excited state to be of A symmetry between $\phi = 0$ and 35° and of B symmetry for $35° < \phi < 90°$. For the H_2S_2 isomers we find a strict correlation between excited state symmetries and the signs of computed rotatory strengths in all four transitions listed in Table II. The computed values of $[R]$ are <0 for excited states of A symmetry and are >0 for excited states of B symmetry. Since each of our H_2S_2 isomers has P chirality, these symmetry correlations are in agreement with those predicted by Wagniere and Hug[26,36] for other dissymmetric molecular systems which possess a C_2 symmetry axis (*e. g.*, skewed diones[37] and dienes[38,39]).

The results obtained by L–M suggest that the net rotatory strength associated with the two lowest lying transitions in H_2S_2 at $\phi = 90°$ should be very small due to the mutual cancellation of R_I and R_{II}. Our calculations yield a substantial net rotatory strength for transitions I and II of H_2S_2 when $\phi = 90°$ and $\angle SSH = 92°$. However, this net value does go through a minimum close to $\phi = 75°$. For H_2S_2 ($\phi = 90°$, $\angle SSH = 102°$), the net rotatory strength of transitions I and II is very small ($[R^a_{net}] = 6$).

The rotatory strengths computed for the five lowest lying singlet–singlet transitions of $(CH_3)_2S_2$ at $\phi = 60$, 75, 90, and 120° differ in several respects from those calculated for H_2S_2. First, there is no simple correlation between excited state symmetries and the signs of the computed rotatory strengths. Second, for $0 < \phi < 90°$ (*i.e.*, cisoid structures) the rotatory strengths of the first three transitions are positive in sign, and for the transoid structure ($\phi = 120°$) the rotatory strengths of the first three transitions are negative in sign. The opposition in signs of the rotatory strengths for cisoid and transoid structures of like chirality is in agreement with the L–M results and our own calculations on H_2S_2. However, like signs for the rotatory strengths of all three of the lowest energy transitions in $(CH_3)_2S_2$ (for each isomer) are at variance with our calculations (and those of L–M) on H_2S_2.

The rotatory strengths computed for the first four transitions in both DT-1 and DT-2 are all positive in sign. The fifth transition in each structure exhibits a large negative rotatory strength. As was the case for the $(CH_3)_2S_2$ isomers, the excited state symmetries are not simply correlated with the signs of the computed rotatory strengths of DT-1 and DT-2.

Within the approximations of the CNDO molecular orbital model and the virtual orbital CI representation of excited electronic states, the results obtained in this study clearly demonstrate the strong influence of sulfur 3d orbitals on the optical rotatory properties computed for chiral disulfide chromophores. The virtual orbitals $\bar{1}$, $\bar{3}$, $\bar{4}$, and $\bar{5}$ of H_2S_2 all possess considerable sulfur 3d character, and the lower excited states for several values of ϕ are dominated by configurations in which these orbitals are half occupied. Although the occupied orbitals, 1(n') and 4(n), and the virtual orbital, $\bar{2}(\sigma^*_{SS})$, of H_2S_2 are nearly free of d-orbital character for all values of ϕ, the singly excited configurations $(n'\sigma^*_{SS})$ and $(n\sigma^*_{SS})$, mix extensively with singly excited configurations which do involve significant d-orbital participation. This ubiquity of the sulfur 3d orbitals in the disulfide excited states most probably accounts for the rather complex dependence

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of the computed rotatory strengths on dihedral angle ϕ. Our results on H_2S_2 certainly are less simple than those reported by L–M, and the complications introduced by the presence of 3d orbitals in our basis set preclude meaningful analogies with Bergson's simple representation of disulfide chromophoric properties.

Four of the five lowest lying vacant orbitals of $(CH_3)_2S_2$, $\bar{1}$, $\bar{3}$, $\bar{4}$, and $\bar{5}$, also possess considerable d-orbital character and, as was the case for the H_2S_2 isomers, the optical rotatory properties computed for the lowest lying transitions of $(CH_3)_2S_2$ reflect the presence of significant d-orbital participation in the disulfide excited states. Our results on the $(CH_3)_2S_2$ and $(CH_2)_3S_2$ isomers are in agreement with the rule set forth by Carmack and Neubert[5a] that "in simple 1,2-dithiane ring systems a positive CD band corresponding to the lowest frequency ultraviolet absorption band of the disulfide group (in the case of 1,2-dithianes in the range 280–290 nm) is associated with a right-handed (P) screw sense of the helix containing the atoms C–S–S–C,. . . ." Similar conclusions concerning the relationship between the chirality of the disulfide moiety in 1,2-dithianes and the sign of the lowest energy Cotton effect were independently reached by Claeson[5b] and by Dodson and Nelson.[5c] The dihedral angle ϕ in most of the 1,2-dithianes which have been studied is probably close to 60°.[40] The dihedral angle ϕ in most of the dissymmetric 1,2-dithiolanes studied is probably around 30°.[32,33] CD studies coupled with conformational analysis on these five-membered ring compounds also lead to an empirical rule which relates P chirality to a positive Cotton effect in the lowest energy electronic transition.[5d–g,41] X-Ray analysis reveals that the CSS/SSC dihedral angle in gliotoxin is ~14° and that the C–S–S–C chromophoric group has a left-handed screw sense (M chirality).[4] The CD band assigned to the lowest energy disulfide transition (*ca.* 340 nm) is negative in sign. These CD data on dissymmetric 1,2-dithiolanes and on gliotoxin suggest that the empirical rule proposed by Carmack and Neubert for 1,2-dithianes has general applicability to disulfides with $\phi < 60°$. The theoretical results obtained on the $(CH_3)_2S_2$ and $(CH_2)_3S_2$ isomers are in consonance with such a rule for any disulfide chromophore with a cisoid structure ($0° < \phi < 90°$).

Recently, Ludescher and Schwyzer[2p] studied the nmr and CD spectra of [2,7-cystine]gramicidin S. From molecular models they estimated that the CSS/SSC dihedral angle in this homodietic–heterodietic bicyclic decapeptide is approximately 120°, and from an analysis of proton nmr spectra they assigned a P chirality to the twisted C–S–S–C moiety. Linderberg and Michl predicted that the sign of the lowest energy CD band for a transoid disulfide structure of P chirality should be negative. Our results on H_2S_2 and on $(CH_3)_2S_2$ lead to the same prediction. Additionally, for $(CH_3)_2S_2$ at $\phi = 120°$, our calculations suggest a weak negative Cotton effect for the first transition followed by two substantially more intense negative Cotton effects at higher energies. These theoretical results are in remarkable agreement with the CD spectra reported by Ludescher and Schwyzer for the [2,7-cystine]gramicidin S compound in solution.

Our discussion and comparison of experimental and theoretical results have been based on the implicit assumption that only the inherent chirality of the disulfide chromophore contributes to the optical rotatory observables. This assumption is probably quite valid in analyzing the optical activity of the lowest energy transition in many of the 1,2-dithianes and 1,2-dithiolanes which do not include substituents with chromophores that absorb at wavelengths >220 nm. However, for systems such as gliotoxin, [2,7-cystine]-gramicidin S, and the large number of acyclic cystine derivatives whose optical rotatory properties have been studied, it is clear that interactions between the disulfide moiety and peripheral chromophoric groups could lead to chiroptic effects comparable in magnitude to, or larger than, those attributable to inherent dissymmetry within the disulfide group. These "vicinal" contributions to the optical activity of disulfide systems are not examined in the present study. Instead, our primary objective was to place in sharper focus the relationships between the electronic structure variables, stereochemical features, and spectroscopic properties of inherently dissymmetric disulfide groups. Vicinal effects can be treated only after the *inherent* chiroptical properties of the chromophore are reasonably well understood.

This study has been somewhat limited in scope with respect to both the computational parameters used in the molecular orbital model and the range of structure variables considered. All molecular orbital calculations were carried out on the CNDO model using the "standard" parameters.[17] For the molecular systems treated in this study *a priori* considerations reveal no compelling reasons for adopting one set of CNDO parameters over any other when electric and magnetic dipole transition integrals are the quantities to be calculated. Reparameterization is possibly essential to a good representation of the electronic properties calculated here. However, the use of a minimal valence shell + 3d basis set of atomic orbitals, and the employment of the virtual orbital approximation with limited configuration interaction in constructing excited states, are probably somewhat more serious approximations in calculating spectroscopic properties such as dipole strengths and rotatory strengths. Parameter optimization and a thorough parameter *vs.* rotatory strength sensitivity analysis were beyond the scope of the present study. For this reason, the qualitative behavior of $[R]$ as a function of the structure variable ϕ is emphasized over the absolute magnitudes computed for $[R]$.

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