involving various radicals arising from the butyl chloride and acetone.

Comparison with Polyvinyl Chloride. It is interesting to compare the Φ(HCl) and G(HCl) values for 1,3-DCB (Table I) with corresponding data in the literature for pure PVC films. The relevant data for this comparison are those of Miller[17] who obtained G(HCl) = 13 for the electron irradiation of PVC *in vacuo* at 30°, and those of Petit and Zaitoun[18] who obtained Φ(HCl) = 0.13 for the uv irradiation at 3023 Å of PVC films *in air*. Since it has been shown[19] that the G(HCl) for irradiation of PVC in air is ~2.3 times the G value for irradiation under vacuum, a value of 0.13/2.3, or 0.057, might be indicated for Φ(HCl) for PVC *in vacuo*. On this basis, we notice a striking similarity between the ratio of G(HCl) values for vacuum irradiation of PVC and its likely model compound, 1,3-DCB (13/4.8, or ~2.7), and the corresponding ratio of Φ(HCl) values (0.057/0.026, or ~2.2). A similar correlation was noted previously connecting the photo- and radiation-induced production of unsaturation (due to HCl elimination) in PVC containing residual ketonic solvent with corresponding results for solvent-free PVC.[4]

In view of the correlation between 1,3-DCB and PVC noted in this study, the Φ(HCl) ~ 0.01 recently reported by Reinisch and Gloria[20] for PVC irradiation at 2537 Å appears quite low. These workers previously reported[21] an initial Φ(HCl) ~0.06–0.10 for polychromatic irradiation of PVC which decreased to ~0.02–0.03 after extended irradiation. Further work on the photolysis of PVC and other model compounds should help to clarify this question of quantum yields.

Acknowledgment. The author is indebted to Drs. J. A. Parker and T. H. Anderson for their support during this study, and to Dr. T. Mill for helpful discussions regarding reaction mechanisms.

---

(17) A. A. Miller, *J. Phys. Chem.*, **63**, 1755 (1959).

(18) J. Petit and G. Zaitoun, *C. R. Acad. Sci., Paris*, **256**, 2610 (1963).

(19) G. Zeppenfeld and L. Wuckel, *Proc. Tihany Symp. Radiat. Chem., 2nd, 1966*, 765 (1967); *Chem. Abstr.*, **68**, 59913 (1968).

(20) R. F. Reinisch and H. R. Gloria, *Amer. Chem. Soc., Div. Polym. Chem., Prepr.*, 9, 349 (1968).

(21) R. F. Reinisch, H. R. Gloria, and D. E. Wilson, *ibid.*, **7**, 372 (1966).

On the Inherent Optical Activity of Organic Disulfides

Jan Linderberg and Josef Michl[1]

Contribution from the Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark. *Received November 5, 1969*

Abstract: A consideration of the simple Bergson model and a semiempirical CNDO calculation lead to a natural explanation of the lack of inherent optical activity of the first uv transition in open-chain disulfides and strong inherent activity in cyclic disulfides. Inherent activity of sign opposite to the latter is predicted for the so-far hypothetical disulfides with dihedral angles considerably larger than 90°. Matrix elements of the angular momentum operator were calculated in a simple way from resonance integrals; this procedure might be of general interest in semiempirical methods.

A thorough understanding of the relation between stereochemistry and circular dichroism (CD) of disulfides would be helpful in investigations of the conformation of numerous biologically important compounds.[2,3] The first step in this direction was made when the antibiotic gliotoxin, with a negative first band in the CD spectrum, was found to have left-handed chirality at the disulfide linkage.[4] From an investigation on 1,2-dithianes with known absolute configuration, Carmack and Neubert formulated the following rule[5]: six-membered ring systems with the disulfide chromophore twisted in the sense of a left-handed helix have first uv transitions of negative rotatory strength (at 280–290 mμ). The rotatory strength is quite high (~-0.2×10^{-38} cgs unit), typical of "inherently dissymmetrical" chromophores. The authors cautioned against indiscriminate use of the rule for rings of different size and open-chain disulfides until more is known about effects of perturbations due to asymmetry of the environment. The second uv band (at 240 mμ) gives a CD band of sign opposite to the first band; however, its dichroism is more sensitive to minor perturbations (solvent, etc.), and the authors do not recommend it for diagnostic purposes.[5]

Similar conclusions concerning the optical activity of 1,2-dithianes were independently reached by Dodson and Nelson,[6] and by Claeson,[7] who pointed out that the observed optical activity is due to inherent dissymmetry of the chromophore, which usually greatly outweighs effects due to environmental perturbations, so that the rule should be applicable to disulfides in general. However, he also noted that the magnitude of the inherent optical activity must depend on the dihedral angle ϕ, since for ϕ = 0 or 180°, the chromophore is planar and thus inherently inactive, and suggested that in instances of low inherent activity, the effects of peripheral asymmetry may become dominant. Bey-

---

[1] To whom correspondence should be addressed at the Department of Physics, University of Utah, Salt Lake City, Utah 84112.

(2) S. Beychok, *Science*, **154**, 1288 (1966).

(3) S. Beychok and E. Breslow, *J. Biol. Chem.*, **243**, 151 (1968).

(4) A. F. Beecham, J. Fridrichsons, and A. McL. Mathieson, *Tetrahedron Lett.*, 3131 (1966); A. F. Beecham and A. McL. Mathieson, *ibid.*, 3139 (1966); J. Fridrichsons and A. McL. Mathieson, *Acta Crystallogr.*, 23, 439 (1967).

(5) M. Carmack and L. A. Neubert, *J. Amer. Chem. Soc.*, **89**, 7134 (1967).

(6) R. M. Dodson and V. C. Nelson, *J. Org. Chem.*, **33**, 3966 (1968).

(7) G. Claeson, *Acta Chem. Scand.*, **22**, 2429 (1968).

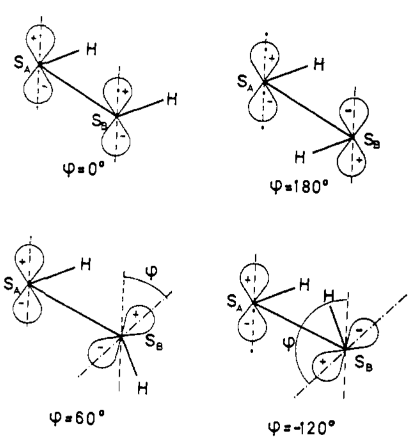

Figure 1. 3p orbitals χ_A and χ_B on sulfur atoms S_A and S_B.

chok and Breslow[3] mention briefly in a footnote that the effects of asymmetrical environments follow the quadrant rule.

The empirical rule for the optical activity of the first uv band of disulfides has since been invoked in studies of additional simple six- and five-membered ring compounds.[8,9] In the former,[10] the dihedral angle ϕ is probably close to 60°, in the latter,[11] to 30°. No exceptions have been found so far, and for such values of ϕ, the rule seems to be generally accepted. The weak and complicated CD spectrum of the five-membered ring disulfide, 6,8-thioctic acid,[12] seems to have been satisfactorily explained as due to partial cancelling of contributions from the two conformers differing by the skew sense of the S–S bridge and present in comparable amounts.[9]

Studies of disulfides with dihedral angles close to 90° (λ_{max} ~250–260 mμ) have led to an entirely different picture. Coleman and Blout[13] conclude that the sign of the rotatory strength of the first uv band is dominated by peripheral effects rather than the screw sense of the disulfide linkage. The rotatory strength of the first band in their open-chain compounds is indeed quite low (~0.02×10^{-38} cgs unit). This cannot be due to a nearly equal distribution of the two possible disulfide conformers, since the second transition had large rotatory strength ($0.3–0.9 \times 10^{-38}$ cgs unit). The authors suggest that only the second band (λ_{max} ~200 mμ) reflects the inherent dissymmetry of the chromophore and can be used for diagnostic purposes. Beychok and Breslow[3] also noted the high sensitivity of the first CD band of the disulfide chromophore in several polypeptides to minor changes in structure and remarked that there may be no simple relationship between the screw sense and the sign of the first CD band.

Clearly, the strange fact which calls for an explanation is the lack of strong inherent optical activity of the first uv band at $\phi = 90°$, given that it is quite strong at $\phi = 60°$ or smaller. From a consideration of the molecular shape, one might have been tempted to expect an even stronger inherent activity for $\phi = 90°$. The suggested explanation[13] that the first, as opposed to the second, uv band has very low inherent activity because it is essentially a localized atomic transition, does not explain why this transition has a high inherent activity for smaller values of ϕ and rests on shaky theoretical grounds (all of the lone-pair molecular orbitals of Bergson's model[14] which these authors use to account for the first two uv bands are delocalized to exactly the same degree).

In the present paper, we analyze the consequences of the Bergson model which accounts satisfactorily for other dihedral angle dependent properties of disulfides. In addition, we report results of calculations using the semiempirical CNDO model.[15] The principal results of both are identical and provide a simple explanation of the apparent discrepancy. Moreover, they allow a tentative prediction of the optical activity for the as yet unobserved dihedral angles considerably larger than 90°.

Bergson's Model.[14] The most striking property of the weak lowest frequency band in the uv spectra of simple disulfides is the red shift it undergoes when the dihedral angle ϕ is distorted from the most stable value of 90° toward smaller values.[16] At the same time, the ionization potential decreases (estimated from charge-transfer spectra[17]). An elementary molecular orbital model proposed by Bergson[14] provides a simple explanation. It assumes that the only molecular orbitals affected by a change in ϕ are the fully occupied lone-pair electron orbitals, ψ_+ and ψ_-, with energies E_+ and E_-, respectively, formed from those 3p sulfur atomic orbitals which are not used up for bonding (χ_A and χ_B)

$$\psi_+ = (1/\sqrt{2})(\chi_A + \chi_B) \qquad \psi_- = (1/\sqrt{2})(\chi_A - \chi_B)$$

The mutual orientation of χ_A and χ_B is determined by the dihedral angle ϕ. Their phases are defined in Figure 1, which also shows our definition of ϕ ($\phi > 0$ for a left-handed helix; $-180° < \phi < +180°$). From simple molecular orbital theory

$$E_\pm = [\alpha \pm \beta \cdot \cos\phi]/[1 \pm S \cdot \cos\phi] \tag{1}$$

where α, β, and S are the Coulomb, resonance, and overlap integral for $\phi = 0°$. Equation 1 provides an immediate explanation of the rotational barrier and the dependence of the ionization potential on ϕ. Bergson found[14] that the same value of β will account for the rotational barrier and for the observed shifts of the lowest frequency band in the uv spectrum, using eq 1 and assuming that this band is due to a transition from the highest occupied molecular orbital into a virtual orbital whose energy is independent of ϕ (probably the σ^* S–S antibonding molecular orbital). The other two lone pairs are in sulfur 3s orbitals, much more firmly bound and presumably of little importance for spectral properties.

The transition, though weak, is electrical dipole moment allowed, as evidenced by the coincidence of shapes

---

[8] G. Claeson and J. Pedersen, *Tetrahedron Lett.*, 3975 (1968); M. Carmack and C. J. Kelley, *J. Org. Chem.*, 33, 2171 (1968).

[9] A. F. Beecham, J. W. Loder, and G. B. Russell, *Tetrahedron Lett.*, 1785 (1968).

[10] O. Foss, K. Johnsen, and T. Reistad, *Acta Chem. Scand.*, 18, 2345 (1964).

[11] O. Foss and O. Tjomsland, *ibid.*, 12, 1810 (1958).

[12] C. Djerassi, H. Wolf, and E. Bunnenberg, *J. Amer. Chem. Soc.*, 84, 4552 (1962).

[13] D. L. Coleman and E. R. Blout, *ibid.*, 90, 2405 (1968).

[14] G. Bergson, *Ark. Kemi*, 12, 233 (1958); 18, 409 (1962).

[15] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 43, S129 (1965).

[16] J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, 76, 4348 (1954).

[17] W. M. Moreau and K. Weiss, *ibid.*, 88, 204 (1966).

of uv and CD spectra[7] (for a discussion of this point see ref 18). Within the Bergson model, nonzero oscillator strength originates from admixture of s character into the σ^* orbital and from overlap-dependent terms which would normally be neglected in a zero differential overlap theory.

One could expect that Bergson's highly successful simple model will also provide a rough idea of the dependence of the rotational strength of the first uv band on the dihedral angle ϕ. Since the model only considers orbitals on sulfur, any optical activity predicted for disulfides will be of the "inherent" type. We shall assume that the virtual orbital involved in the first uv transition is the σ^* S–S antibonding orbital. The chromophore belongs to the point symmetry group C_2; the orbitals σ^* and ψ_+ transform according to the B representation, ψ_- according to the A representation. The two available excited states are of different symmetries ($\psi_- \rightarrow \sigma^*$: B, $\psi_+ \rightarrow \sigma^*$: A) and do not interact. According to eq 1, for $|\phi| < 90°$, ψ_- is the highest occupied molecular orbital and B the first excited state, for $90° < |\phi| < 180°$, ψ_+ is the highest occupied and A the first excited state, while for $|\phi| = 90°$, ψ_- and ψ_+ have the same energy and the excited states B and A are degenerate. Thus, according to the simple model, the expression "the lowest-frequency absorption band in the uv spectrum of disulfides" must mean different things for different values of ϕ.

Because of the mirror-image relation between conformations with dihedral angles $\phi = \pm\phi_0$ (Figure 1), the only respect in which either the $\psi_- \rightarrow \sigma^*$ or the $\psi_+ \rightarrow \sigma^*$ transitions differ in the two conformations is the sign of the rotatory strength; if it is R_0 for $\phi = \phi_0$, it is $-R_0$ for $\phi = -\phi_0$. Figure 1 shows further that a change of ϕ by 180° has no effect on χ_A, but converts χ_B into $-\chi_B$. Thus, the orbital ψ_+ in a conformation with dihedral angle $\phi = \phi_0$ is identical with the orbital ψ_- in a conformation with $\phi = \phi_0 \pm 180°$; similarly, ψ_- for $\phi = \phi_0$ is identical with ψ_+ for $\phi = \phi_0 \pm 180°$. Since the σ^* orbital is assumed independent of ϕ, the transitions $\psi_- \rightarrow \sigma^*$ for $\phi = \phi_0$ and $\psi_+ \rightarrow \sigma^*$ for $\phi = \phi_0 \pm 180°$ are identical in all respects, in particular energy, oscillator and rotatory strength, and polarization in the absolute framework of Figure 1. However, as the C_2 axis itself rotates by 90° when ϕ is changed by 180°, the polarizations with respect to the molecular C_2 axis differ and so do the excited state symmetry labels (B and A, respectively).

Thus, Bergson's model predicts a "quadrant" rule for the inherent optical activity of disulfides. Let R_0 denote the rotatory strength of the first uv transition in a conformation with $\phi = \phi_0, 0° < \phi_0 < 90°$. Then, for $\phi = -\phi_0$, the rotatory strength is $-R_0$. In both cases, the symmetry of the excited state is B ($\psi_- \rightarrow \sigma^*$ transition). According to the preceding paragraph, the $\psi_+ \rightarrow \sigma^*$ transition in a conformation with $\phi = 180° - \phi_0$ has rotatory strength equal to $-R_0$ and in conformation with $\phi = \phi_0 - 180°$ equal to R_0. Since $0° < \phi_0 < 90°$, for the latter two conformations $\psi_+ \rightarrow \sigma^*$ is the first uv transition (excited state of A symmetry). In the cases of $\phi = 0°$ and $\phi = 180°$, the rotatory strength is clearly equal to zero. In the remaining cases, $\phi = \pm 90°$, the "first" uv transition consists of a superposition of the now degenerate transitions $\psi_- \rightarrow \sigma^*$ and $\psi_+ \rightarrow \sigma^*$. The same argument as above shows that their rotatory strengths are equal and of opposite signs. Within the framework of Bergson's model, they should exactly cancel and the first band should be inactive.

The model does not permit absolute sign predictions, because of uncertainty in the sense of the electric dipole transition moment, but accepting the experimental result $R < 0$ for $\phi \cong 60°$, the following "quadrant" rule is obtained

Dihedral angle	−180°		−90°		0°		90°		180°
Rotatory strength	0	−	0	+	0	−	0	+	0

It is difficult to estimate the reliability of these conclusions. Perhaps the largest shortcoming of the model is the neglect of hybridization of the lone electron pairs and complete neglect of the presence of bonds from sulfur atoms to substituents. Other uncertainties are related to the one-electron approximation: estimate of excitation energy as difference of orbital energies and neglect of configuration interaction. Still another source of problems may be the neglect of d-orbital participation.

Because of the sensitivity of calculated optical activity to details of the wave function, we do not consider the prediction of exact antipode properties of conformations with $\phi = \phi_0$ and $\phi = \phi_0 \pm 180°$ as meaningful. However, in view of the other successes of the Bergson model, the basic result is probably correct: the excited state which is responsible for the first uv band at ϕ close to 0° is of B symmetry, and its energy increases continuously as ϕ goes to 180°. From experiment, the inherent rotatory strength of the transition into this state is large and negative for $\phi \cong 60°$. The excited state which is responsible for the first uv band at ϕ close to 180° is of A symmetry and its energy grows continually as ϕ goes to 0°. The energies of the two states are similar for ϕ close to 90°, and the two transitions merge in the spectrum to give a single absorption band. The presence of two transitions in the 250-mμ absorption band of dimethyl disulfide had been postulated in the spectral study of McGlynn, *et al.*,[19] but has apparently gone unnoticed. The inherent rotatory strengths of the two transitions are of similar magnitude and opposite signs. Since the CD band is not resolved, the observed inherent activity is very small.

The CD curves of some of the open-chain disulfides reported by Beychok[3] indeed show similarities to the CD spectrum of 6,8-thioctic acid,[12] and the drawing in ref 9 showing effects of incomplete cancellation illustrates our point. In ref 9 the two nearly cancelling contributions came from two conformers, each having one transition near 335 mμ; in our case, they are both due to the same conformer, which has two transitions near 250 mμ. This situation provides an excellent opportunity for asymmetrically disposed substituents to induce "extraneous" optical activity by perturbing the balance. Also, small changes in conformation will have large effects. As soon as ϕ is changed sufficiently for the two transitions to be resolved as two separate CD bands, as obviously happens for $\phi \cong 60°$, the true inherently active nature of both transitions is revealed.

---

(18) A. Moscowitz in "Modern Quantum Chemistry," Part III, O. Sinanoğlu, Ed., Academic Press, New York, N. Y., 1965, p 31.

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

It is likely that the weak 1,2-dithiane band at 240 mμ with sign of rotatory strength opposite to that of the first band (~280–290 mμ) indeed is the other (A) state. The absorption spectra[7] show that it overlaps partially with stronger absorption due to other transitions at shorter wavelengths. This could explain the sensitivity of its observed rotatory strength to small perturbations. In our interpretation, the band close to 200 mμ in disulfides[13] with ϕ close to 90° must be assigned to some other transition and cannot be discussed within Bergson's model.

Most of the objections to the applicability of the Bergson model, particularly the neglect of hybridization, can be removed in an all-valence electron calculation. Also, it could be claimed that the bonds between the sulfur atoms and the substituents should be explicitly included in the "chromophore" used for definition of the "inherent" rotatory strength. The best compromise between an effort to limit the calculation to the "chromophore" only and an effort to represent it in a more realistic way seems to be a model calculation on hydrogen disulfide.

Calculation of the Optical Activity of H_2S_2. Method. Of the several available degrees of complexity, we have chosen the semiempirical CNDO model,[15] which has been used recently by numerous authors for calculations of electronic spectra of various organic molecules[20] and of optical activity of twisted ethylenes.[21] We have used the version described in detail by Sichel and Whitehead.[22,23] The only modification was a neglect of resonance integrals between nonneighbors, which is consistent with the zero differential overlap approximation and the use of effective charge $Z = 1$ on hydrogen. The two formulas for two-center electron repulsion integrals investigated by these authors (Ohno and Nishimoto–Mataga approximations) gave very similar results for the rotatory strength of about a dozen conformations of H_2S_2; thereafter, only the Nishimoto–Mataga parametrization was used. As in their work, only s and p orbitals were included in the basis set.

Rotatory strengths were calculated from the well-known formula

$$R_i = \operatorname{Im}(\langle 0|\vec{m}|i\rangle\langle i|\vec{\mu}|0\rangle)$$

where R_i is the rotatory strength of the transition from the ground state $|0\rangle$ to the ith excited state $|i\rangle$, Im stands for "imaginary part of," and $\vec{m}$ and $\vec{\mu}$ are the electric and magnetic dipole moment operators, respectively.

The ground state was represented by Slater determinant D_0 constructed from the seven lowest self-consistent-field (SCF) molecular orbitals ψ_k, $k = 1$–7. Two approximations were used to represent the excited states: (1) a single configuration wave function $D_{k\rightarrow k'}$ obtained from D_0 by removing one ψ_k, adding one of the virtual orbitals $\psi_{k'}$, and projecting out a singlet state (SCF approximation); (2) a configuration interaction wave function φ_i constructed in the usual manner from all singly excited configurations

$$\varphi_i = \sum_{k\rightarrow k'} C_{i,\,k\rightarrow k'} D_{k\rightarrow k'} \quad \text{(CI approximation)}$$

The calculation of R_i was reduced to the evaluation of matrix elements of $\vec{m}$ and $\vec{\mu}$ over atomic orbitals in the usual manner

$$\langle\varphi_i|\vec{\mu}|D_0\rangle = \sqrt{2}\sum_{k\rightarrow k'}\langle\psi_{k'}|\vec{\mu}|\psi_k\rangle C_{i,\,k\rightarrow k'}$$

$$\langle\psi_{k'}|\vec{\mu}|\psi_k\rangle = \sum_{\kappa \mathrm{a}}\sum_{\mu \mathrm{b}}\langle\chi_{\kappa\mathrm{a}}|\vec{\mu}|\chi_{\mu\mathrm{b}}\rangle c_{k,\mu\mathrm{b}}c_{k',\kappa\mathrm{a}}$$

and similarly for $\vec{m}$. Here, $\chi_{\kappa a}$ is the κth atomic orbital on atom a and $c_{k,\kappa\mathrm{a}}$ is its expansion coefficient in the kth molecular orbital.

The elements of $\vec{m}$ over atomic orbitals were approximated according to Pople.[24] For diagonal elements, $\langle\chi_{\kappa\mathrm{a}}|\vec{m}|\chi_{\kappa\mathrm{a}}\rangle = e\cdot\vec{r}_\mathrm{a}$, where e is electron charge and $\vec{r}_\mathrm{a}$ is the position vector of atom a. Off-diagonal elements are zero except for those between a 3s and a 3p orbital located on the same sulfur atom, in which case $\langle \mathrm{s}|\vec{m}|\mathrm{p}_x\rangle = 1.112\ ea_0, 0, 0$; $\langle \mathrm{s}|\vec{m}|\mathrm{p}_y\rangle = 0, 1.112\ ea_0, 0$; and $\langle \mathrm{s}|\vec{m}|\mathrm{p}_z\rangle = 0, 0, 1.112\ ea_0$, where a_0 is the Bohr radius (using the formula $\langle \mathrm{s}|z|\mathrm{p}_z\rangle = (2n + 1)/2\mu\sqrt{3}$ in atomic units, with $\mu = 1.817$ and $n = 3$, valid for Slater orbitals). This is a rough approximation and it might be argued that better values should be obtained from atomic SCF orbitals or experimental atomic intensities. However, since we found that these off-diagonal elements contribute by far most to the resultant values of the electric dipole transition moments for the two transitions of interest, a change of the value 1.112 ea_0 would only multiply the calculated moments by a positive constant. Since we are only interested in orders of magnitude of oscillator and rotatory strengths, this is of little importance.

The elements of $\vec{\mu}$ over atomic orbitals are reduced to elements of the linear momentum operator $\vec{p}$ in the usual way: $\vec{\mu} = (e/2mc)\vec{l}$, where m is electron mass, c the velocity of light, and $\vec{l} = \vec{r} \times \vec{p}$ the angular momentum operator ($\vec{r}$ is the position vector operator). To evaluate $\langle\chi_{\mathrm{a}\kappa}|\vec{l}|\chi_{\mathrm{b}\mu}\rangle$ we define an auxiliary angular momentum operator $\vec{l}^{\mathrm{b}}$ for which atom b is the center of coordinates $\vec{l}^{\mathrm{b}} = (\vec{r} - \vec{r}_\mathrm{b}) \times \vec{p}$, where $\vec{r}_\mathrm{b}$ is a constant vector operator defined by the position vector of atom b. Then, $\langle\chi_{\mathrm{a}\kappa}|\vec{l}|\chi_{\mathrm{b}\mu}\rangle = \langle\chi_{\mathrm{a}\kappa}|\vec{l}^{\mathrm{b}}|\chi_{\mathrm{b}\mu}\rangle + \vec{r}_\mathrm{a} \times \langle\chi_{\mathrm{a}\kappa}|\vec{p}|\chi_{\mathrm{b}\mu}\rangle$. The first term on the right-hand side is easily reduced to overlap integrals using the basic properties of atomic orbitals such as $l_z|\mathrm{p}_x\rangle = i\hbar|\mathrm{p}_y\rangle$, and simplifies even further using $S_{\mathrm{a}\kappa,\mathrm{b}\mu} = \delta_{\mathrm{a}\kappa,\mathrm{b}\mu}$.

The elements of $\vec{p}$ are usually calculated directly assuming an explicit radial form for the atomic orbitals. However, in semiempirical calculations, particularly those using the ZDO approximation, one has little or no need to specify uniquely the radial form of atomic orbitals for any other purpose. For instance, in the procedure of Sichel and Whitehead,[22,23] used in our calculations, the only purpose for which the Slater radial dependence is actually needed is to calculate overlap integrals which are, in turn, used only for

---

(20) C. Giessner-Prettre and A. Pullman, *Theor. Chim. Acta*, **13**, 265 (1969), and references therein.

(21) M. Yaris, A. Moscowitz, and R. S. Berry, *J. Chem. Phys.*, **49**, 3150 (1968).

(22) J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, **7**, 32 (1967).

(23) J. M. Sichel and M. A. Whitehead, *ibid.*, **11**, 220 (1968).

(24) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 43, S136 (1965).

the determination of the resonance integrals β from $\beta_{\mathrm{a}\varkappa,\mathrm{b}\mu} = -S_{\mathrm{a}\varkappa,\mathrm{b}\mu}(\beta_\mathrm{a}{}^0 + \beta_\mathrm{b}{}^0)/2$, where $\beta_\mathrm{a}{}^0$ and $\beta_\mathrm{b}{}^0$ are empirically adjusted atomic constants. It is likely that after a suitable adjustment of the β^0's one could recover an essentially identical set of β integrals using almost any reasonable radial part for the χ's, *e.g.*, Clementi's SCF orbitals. This is somewhat analogous to the finding[23] that both Ohno and Nishimoto–Mataga formulas can be used for two-center electron repulsion integrals in such calculations, giving almost the same results if the β^0's are adjusted properly in each case. As a second example, we may cite the usual π-electron calculations in which the radial part of the atomic orbitals need not be specified at all since not even overlap integrals are calculated. Thus, committing oneself to a specific choice of the radial part of the χ's may mean sacrificing some of the flexibility of semiempirical methods. It seems preferable to relate the elements of $\vec{p}$ to some of the quantities already present in the semiempirical theory. Such a possibility is suggested by the relation

$$i\hbar\langle\chi_{\varkappa\mathrm{a}}|\vec{p}|\chi_{\mu\mathrm{b}}\rangle = (\vec{r}_\mathrm{a} - \vec{r}_\mathrm{b})\beta_{\varkappa\mathrm{a},\mu\mathrm{b}} \qquad (2)$$

recently derived by one of us from the commutation relation between $\vec{r}$ and H in the framework of the semiempirical model.[25] The values of β derived from eq 2 for second-row atoms, assuming that χ's are Slater or Clementi's SCF orbitals, are rather close to those obtained empirically,[25] so that it does not matter much whether the elements of $\vec{p}$ are calculated from eq 2 or directly assuming Slater radial parts. In actual practice, it seems simpler to use eq 2 particularly if atoms of several different kinds or bonds of various lengths are present. For third-row atoms, the situation may be different: the values of β we have derived from eq 2 assuming either Slater or Clementi radial form for the χ's are much lower than those recommended.[23,26] Since the recommended values of β are used in our calculations, it is consistent to use eq 2 to evaluate the elements of $\vec{p}$.

Our final formula for the matrix elements of the λth component of $\vec{\mu}$ between p orbitals is

$$\langle\chi_{\mathrm{a}\varkappa}|\mu_\lambda|\chi_{\mathrm{b}\mu}\rangle = i(e\hbar/2mc)[e_{\lambda\mu\varkappa}\delta_{\mathrm{ab}} + (1/\hbar^2)\sum_{\sigma,\tau} e_{\lambda\sigma\tau}r_{\mathrm{a}\sigma}r_{\mathrm{b}\tau}\beta_{\varkappa\mathrm{a},\mu\mathrm{b}}]$$

where λ, $\varkappa$, μ, σ, τ are x, y, z; $r_{\mathrm{a}\sigma}$ is the σth component of $\vec{r}_\mathrm{a}$, and $e_{\lambda\mu\varkappa}$ is equal to 1 (-1) if $\lambda\mu\varkappa$ is an even (odd) permutation of xyz and equal to zero otherwise. The same expression is obtained if an auxiliary operator $\vec{l}^\mathrm{a}$ is introduced instead of $\vec{l}^\mathrm{b}$. When one or both of the orbitals $\chi_{\mathrm{a}\varkappa}$, $\chi_{\mathrm{b}\mu}$ are of the s type, the first term in the brackets is absent.

The S–S bond length used in the calculations was 2.05 Å, the S–H bond length 1.34 Å. These values were chosen as representative after a survey of available experimental data on disulfides and are close to the recent values reported for H_2S_2 itself.[27] The calculations were done for S–S–H angles of 90, 94, 100, and 108°, which span the whole range so far reported for any disulfide (H_2S_2,[27] 91° 32′; five-membered ring disulfides, ~95°;[11] six-membered ring disulfides, ~99°;[10] open-chain alkyl disulfides, ~104°[10,28,29]). For several of the values of the S–S–H angle, the calculations were repeated with modified values of $\beta_\mathrm{S}{}^0$ and $\beta_\mathrm{H}{}^0$ parameters as well as the one-center electron repulsion integrals in order to find out how sensitive the results were to the details of parametrization. Each calculation was performed for 20–25 values of the dihedral angle ϕ.

Results

The calculations using Sichel–Whitehead parameters[22,23] reproduce the basic properties of the ground state. The preferred conformation is defined by a very flat minimum: ϕ is 90° and S–S–H angle is 90–94° in reasonable agreement with experiment[27] (S–S–H angle 90° 36′), the bonding energy is 8.70 eV, and the experimental value[30] including zero-point energy[31] is 10.44 eV. The rotational barrier calculated for the S–S–H angles 90° or 94° is 2.7 kcal/mol; the experimental value is 3.0 ± 0.5 kcal/mol.[32] The barrier is symmetrical in agreement with experiment.[27] The lowest two calculated ionization potentials are 11.1 and 11.2 eV for S–S–H angle 94°, $\phi = 90°$. This is a little higher than the range 9.5–10.3 eV we guessed from available data on related molecules[33] (H_2S, 10.46; $(CH_3)_2S$, 8.69; CH_3SH, 9.44; $(CH_3S)_2$, 8.46 eV). The experimental difference between diethyl disulfide and trimethylene disulfide has been estimated[17] at 0.7 eV; the calculated difference of the ionization potentials of H_2S_2 at $\phi = 90°$ and $\phi = 30°$ is 0.4 eV at S–S–H angles 90–94°. The nature of the highest occupied molecular orbital ψ_7 is the same as in Bergson's model (ψ_- or ψ_+, depending on the value of ϕ). However, for some of the parameter choices tested, particularly for values of ϕ close to 90°, an orbital of basically σ S–S bonding character becomes comparable in energy or even less stable. The lowest empty orbital ψ_8 is always of σ^* S–S antibonding nature, as in Bergson's model. It is always slightly bonding, indicating a very high value for electron affinity. We assign no quantitative significance to this result, but it is in qualitative agreement with the very easy reducibility of disulfides.

Although the same parametrization need not be optimum for excited states (*cf.* ref 20, 34–36), we used the Sichel–Whitehead values, taking two precautions. First, we attach little importance to calculated absolute magnitudes and concentrate on trends and changes occuring as ϕ changes; second, we repeat the calculations with various modified values of the parameters and investigate how sensitive the results are. For all values of the S–S–H angles, and for all parametrizations used, both series of calculations (SCF and CI)

---

(25) J. Linderberg, *Chem. Phys. Lett.*, **1**, 39 (1967).

(26) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 47, 158 (1967).

(27) G. Winnewisser, M. Winnewisser, and W. Gordy, *ibid.*, 49, 3465 (1968).

(28) C. Szantay, M. P. Kotick, E. Shefter, and T. J. Bardos, *J. Amer. Chem. Soc.*, **89**, 713 (1967).

(29) "Tables of Interatomic Distances and Configurations in Molecules and Solids," Special Publication No. 11, The Chemical Society, London, 1958.

(30) F. Fehér and G. Winkhaus, *Z. Anorg. Allg. Chem.*, **292**, 210 (1957).

(31) F. Fehér, W. Laue, and G. Winkhaus, *ibid.*, 288, 113 (1956).

(32) F. Fehér and K. Seyfried, *ibid.*, **322**, 162 (1963).

(33) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1959).

(34) P. A. Clark and J. L. Ragle, *J. Chem. Phys.*, **46**, 4235 (1967).

(35) D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, **9**, 412 (1968).

(36) D. T. Clark, *ibid.*, **10**, 111 (1968).

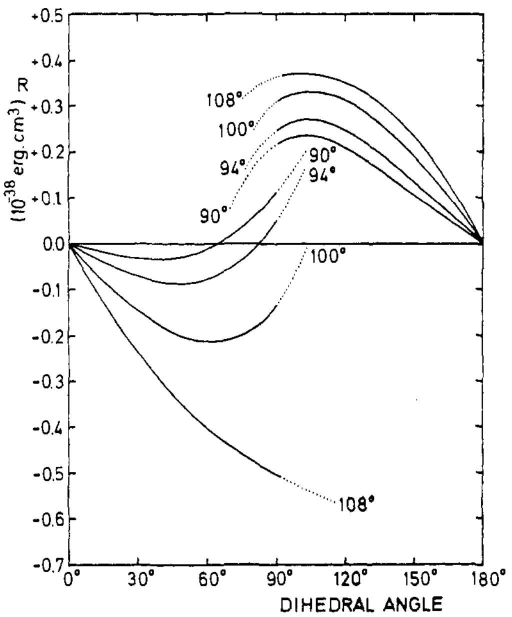

Figure 2. Calculated rotatory strength R of the lowest (solid) and second-lowest (dotted) transitions in H_2S_2 for several values of the S–S–H angle.

lead to very similar results for the lowest excited state. In the SCF approximation, it is represented by the configuration $D_{k\rightarrow k'}$ where k is always the less stable of the two lone-pair orbitals (even for parametrizations in which this is not the highest occupied orbital as mentioned above), and k' is the σ^* S–S antibonding orbital. In the CI approximation, it is represented by a linear combination of configurations in which this $D_{k\rightarrow k'}$ prevails by far. This is in agreement with the assumption made in Bergson's model. In the following, results of SCF and CI calculations are discussed together.

As in Bergson's model, the first excited state is of B symmetry for ϕ close to 0°, and its energy grows as ϕ increases. A typical difference between $\phi = 30°$ and $\phi = 90°$ is 0.6–1.2 eV, depending on the details of the calculations (SCF or CI, S–S–H angle, parameter values). Experimentally,[17] the difference in the first excitation energies in thioctic acid and diethyl disulfide is 1.2 eV. As ϕ approaches 90°, an excited state of A symmetry becomes lower in energy. In most calculations, it becomes the second excited state somewhere near $\phi = 30°$, and near $\phi = 90°$ its energy is equal to that of the B state. (The crossover may occur anywhere in the region ϕ = 70–90°.) As ϕ grows further, the energy of the A (now lowest) state continues to decrease until for $\phi = 180°$ it is virtually the same as that of the B state at $\phi = 0°$. Simultaneously, the B state keeps shifting to higher energies, for some time being second-lowest, and soon becoming third or higher. Experimentally, the excited-state symmetries are unfortunately not known. In all calculations, the preferred molecular geometry in the excited state turns out to be planar, the *cis* and *trans* forms being almost equal in energy. This would also be predicted from the simple Bergson model; it is in agreement with the shape of the absorption band of H_2S_2.[37] Undoubtedly, the length of the S–S bond increases on excitation, but we have made no attempt to locate a minimum on the energy surface. If it exists, it is very shallow (S–S bond dissociation energy in H_2S_2 is 3.13 eV,[38] comparable to the excitation energy; photodissociation of the S–S bond is a well-known process[16,39]).

Unlike these general trends, the absolute magnitude of the excitation energies is sensitive to the choice of parameters. For the Sichel–Whitehead parameters,[22,23] and for S–S–H angle 94°, $\phi = 90°$, the SCF result for the first two excited states is 2.66 and 4.40 eV (the crossover point is at $\phi = 70°$); the CI result is 2.47 and 2.47 eV. Experimentally,[37] the maximum of the first absorption band lies at 4.8 eV. The band is very broad and reaches down to about 3 eV; it can certainly easily accommodate two transitions. The relatively poor agreement may be related to the neglect of one-center exchange integrals (singlet–triplet splitting is almost exactly zero). It can be improved artificially by increasing the resonance integrals. For the values recommended by Santry and Segal,[26] and all other parameters unchanged, the SCF excitation energies are 5.57 and 5.59 eV, CI energies 5.00 and 5.00 eV. This change also lowers the calculated ionization potential by about 0.3 eV, bringing it in a little better agreement with experiment. However, this adjustment of resonance integrals is known to lead to too high ionization potentials in most molecules.[40] We have made no effort to find the best parameter values.

The calculated oscillator strengths of the first two transitions are usually 0.01–0.05 and rarely exceed 0.1, depending on ϕ and details of calculations. This is in qualitative agreement with experiment. The measured value[19] for the first band of dimethyl disulfide is 0.03, but this probably represents a sum for the first two overlapping transitions. The calculated oscillator strength of the first transition does not depend very sharply on ϕ. The details of the dependence are sensitive to parametrization and the S–S–H angle. In most cases, the calculated intensity grows slowly as ϕ approaches 90° from either side; it is larger when the B state is lowest than when the A state is lowest.

As in Bergson's model, the calculated rotatory strength R of the first transition is positive for $\phi > 90°$ (left-handed helix, A state lowest), irrespective of the choice of parameters, S–S–H angle, and procedure used (SCF or CI). It would be interesting to verify this experimentally.

For $\phi < 90°$ (B state lowest), the value of R is more sensitive to details of calculation. Generally, it becomes more negative as the S–S–H angle increases. For the Sichel–Whitehead parametrization, the CI result is shown in Figure 2. The SCF result is similar. An increase in the one-center electron repulsion integrals to their theoretical values does not change the picture qualitatively. All of these results are in fair agreement with experiment:[5] $R \cong -0.20 \times 10^{-38}$ cgs units in cyclic disulfides with probable angles ϕ = 60°, S–S–H = 99°. However, when the β^0's are increased, the calculated values of R become less

---

(37) F. Fehér and H. Münzner, *Chem. Ber.*, **96**, 1131 (1963).

(38) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 17.

(39) R. B. Whitney and M. Calvin, *J. Chem. Phys.*, **23**, 1750 (1955).

(40) J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, **11**, 239 (1968).

negative. For the values of Santry and Segal,[26] negative R is obtained only for the S–S–H angle = 108°. Already for the S–S–H angle of 100°, R is positive for all ϕ between 0° and 180°, in disagreement with experiment. In summary, those parametrizations which lead to agreement with experiment for ϕ = 60° give results basically similar to those obtained from the Bergson model.

It is possible that an improvement of the calculations such as inclusion of d orbitals with their complicated nodal properties into our basis set would make the changes of the calculated rotatory strength with the dihedral angle less simple. However, it is unlikely that it could change the basic results: (i) the transition into the lowest excited state of disulfides is inherently optically active, but for dihedral angles close to 90°, the inherent activities of two such transitions, which both contribute to the observed first band in the uv or CD spectra, nearly cancel so that environmental effects dominate; (ii) for dihedral angles sufficiently larger than 90°, the first uv band would again become strongly inherently active and the left-handed helix would give positive rotatory strength.

Acknowledgment. The authors are indebted to Dr. Göran Claeson, A. B. Bofors, Nobel-Pharma, Mölndal, Sweden, and Dr. Albert Moscowitz, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, for valuable discussions.

Conductometric Pulse Radiolysis of Sulfur Hexafluoride in Aqueous Solutions. Rate of Hydrolysis of Sulfur Tetrafluoride[1]

K.-D. Asmus,[2a] W. Grünbein,[2a] and J. H. Fendler[2b]

Contribution from the Hahn-Meitner Institut für Kernforschung, Berlin, Germany,
and the Radiation Research Laboratories, Mellon Institute,
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.
Received December 15, 1969

Abstract: Changes in the conductivity of pulse-irradiated aqueous solutions saturated with SF_6 (*ca.* 2 × 10^{-4} M) have been observed as a function of time. In neutral solutions the conductivity increases in two steps. The fast first step is attributed to the reactions $e_{aq}^- + SF_6 \rightarrow \cdot SF_5 + F^-$ and $\cdot SF_5 + 2H_2O \rightarrow \cdot OH + SF_4 + H_3O^+ + F^-$. A lower limit for the rate constant of the reaction of $\cdot SF_5$ with H_2O of 6.3 × 10^3 M^{-1} sec^{-1} could be derived. The slow second step is due to the hydrolysis of SF_4. The observed pseudo-first-order rate constant for this reaction increases linearly with hydronium and hydroxide ion concentration and can be described by $k_\psi = k_0 + k_a[H_3O^+] + k_b[OH^-]$. The rate constant k_0 for the pH-independent hydrolysis is 9.5 × 10^3 sec^{-1}, and k_a and k_b for the acid- and base-catalyzed hydrolyses are 8.5 × 10^7 M^{-1} sec^{-1} and 7.0 × 10^9 M^{-1} sec^{-1}, respectively. Mechanisms for the hydrolysis of SF_4 are discussed.

Sulfur hexafluoride is known as an efficient electron scavenger in irradiated liquid and gaseous systems.[3–7] Recently it has been shown that the hydrated electron produced in the radiolysis of water

$$H_2O \rightsquigarrow e_{aq}^-, H_3O^+, \text{etc.} \qquad (1)$$

reacts with SF_6 according to

$$e_{aq}^- + SF_6 \xrightarrow{H_2O,\ \cdot OH} 6F^- + SO_4^{2-} + 7H_3O^+ \qquad (2)$$

and that the rate constant is equal to 1.65 × 10^{10} M^{-1} sec^{-1}.[6] SF_6 scavenges all hydrated electrons in γ-irradiated aqueous solutions under 6–10 atm of sulfur hexafluoride (*ca.* 10^{-3} M). A detailed mechanism for the overall process given in eq 2 has been proposed,[6] according to which the formation of SF_5 and the oxidation of water by SF_5 are the first two steps.

$$SF_6 + e_{aq}^- \longrightarrow \cdot SF_5 + F^- \qquad (3)$$

$$\cdot SF_5 + 2H_2O \longrightarrow \cdot OH + F^- + H_3O^+ + SF_4 \qquad (4)$$

The sulfur tetrafluoride formed in reaction 4 then hydrolyzes according to

$$SF_4 + 9H_2O \longrightarrow SO_3^{2-} + 4F^- + 6H_3O^+ \qquad (5)$$

and the sulfite subsequently is oxidized by species such as $\cdot OH$, H_2O_2, or $\cdot SF_5$.

$$SO_3^{2-} + (\cdot OH, H_2O_2, \cdot SF_5) \longrightarrow SO_4^{2-} \qquad (6)$$

Since the reaction of SF_6 with e_{aq}^- leads to charged products, conductivity measurements appeared to be a useful means for tracing the elementary processes described in reactions 3–6. A pulse radiolysis study in which changes in the conductivity of solutions containing SF_6 were recorded after a short electron pulse has, therefore, been carried out. The simultaneous observation of changes in optical absorption and conductivity has been utilized in several investigations and has been found to be a very suitable technique for studying elementary processes which involve the creation or destruction of charges.[8]

---

(1) Supported in part by the U. S. Atomic Energy Commission.

(2) (a) Hahn-Meitner Institut für Kernforschung, Berlin, Germany; (b) Radiation Research Laboratories, Mellon Institute, Carnegie-Mellon University, Pittsburgh, Pa. 15213.

(3) G. R. A. Johnson and J. M. Warman, *Trans. Faraday Soc.*, **61**, 1709 (1965).

(4) J. M. Warman, K.-D. Asmus, and R. H. Schuler, Advances in Chemistry Series, No. 82, American Chemical Society, Washington, D. C., 1968, p 25, and references cited therein.

(5) G. R. A. Johnson and M. Simic, *J. Phys. Chem.*, **71**, 2775 (1967).

(6) K.-D. Asmus and J. H. Fendler, *ibid.*, **72**, 4285 (1968).

(7) K.-D. Asmus and J. H. Fendler, *ibid.*, **73**, 1583 (1969).