

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 92, NUMBER 7

APRIL 8, 1970

Physical and Inorganic Chemistry

The Direct Calculation of Optical Rotatory Strengths

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Abstract: We describe a program for evaluating the optical rotatory strength of any molecule for which a Slater basis molecular orbital wave function is available. The electric transition moment is evaluated in the gradient formalism. No integrals are neglected. Extended Hückel wave functions are then used to calculate the rotatory strength of some methyl cyclohexanones. The effect of methyl group conformation is found to be significant. Similar calculations yield rotatory strengths for different excited configurations of a twisted butadiene. Perturbation by a nearby σ level affects the strength of two configurations. Configuration interaction among butadiene excitations introduces cross terms which subtract from the pure configuration strength near an *s-cis* geometry. Quantitative agreement with experiment is not achieved for any of the cases studied.

A quantum mechanical theory of optical rotation was first given by Rosenfeld¹ in 1928. The fundamental quantity for the k th electronic excitation from the lower state Ψ_0 to the upper state Ψ_k is the rotational strength R_k

$$R_k = \text{Im}\{\langle\Psi_0|\mathbf{u}_e|\Psi_k\rangle\cdot\langle\Psi_k|\mathbf{u}_m|\Psi_0\rangle\} \quad (1)$$

where \mathbf{u}_e and \mathbf{u}_m are the electric and magnetic moment vectors, respectively. A one-electron version of the theory was applied to molecules in a brilliant series of investigations by the Princeton group.² Fundamental to their approach was a factorization of the problem into localized symmetric chromophores asymmetrically perturbed by neighboring groups of atoms. The perturbation often took the form of mixing into the symmetric chromophore functions asymmetric contributions from atomic orbitals of higher principal quantum number, e.g., 3d orbitals on carbon. There existed a pertinent rationale for this approach in the 1930's. The procedure was retained in the course of the remarkable theoretical and experimental revival of optical dispersion studies that occurred some 20

years later,^{3,4} and was fundamental in providing the theoretical basis for such far-reaching generalizations as the octant rule.⁵

The primary advantage of the one-electron perturbational formulation^{2,4} is that it provides a physically visualizable and realistic model. The disadvantage in extracting quantitative predictions from this model is one common to the calculation of other observables as well: one has perforce to deal with approximate wave functions for molecules of chemical interest. In addition it has been traditional to make a number of simplifying approximations, e.g., neglect of two-center integrals in evaluating the rotational strength from eq 1. When the computed observable is not in agreement with an experimental value, one consequently does not know whether to blame the approximate nature of the wave function or the approximations made in the process of computing the expectation values.

Wave functions of varying degrees of accuracy are becoming available for chiral molecules. Extended

(3) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960, and the chapter by A. Moscovitz therein.

(4) A. Moscovitz, *Advan. Chem. Phys.*, **4**, 67 (1962), and references therein.

(1) L. Rosenfeld, *Z. Phys.*, **52**, 161 (1928).
(2) (a) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940); (b) E. U. Condon, W. Altar, and H. Eyring, *J. Chem. Phys.*, **5**, 753 (1937); (c) E. Gorin, J. Walter, and H. Eyring, *ibid.*, **6**, 824 (1938); (d) E. Gorin, W. J. Kauzmann, and J. Walter, *ibid.*, **7**, 327 (1939).

(5) W. Moffitt, R. B. Woodward, A. Moscovitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, **83**, 4013 (1961); A. Moscovitz, *Tetrahedron*, **13**, 48 (1961).

Hückel⁶ and CNDO/2⁷ wave functions are now readily computed for molecules containing up to 25 atoms. *Ab initio* wave functions at the Hartree-Fock level for systems with approximately ten atoms will shortly become available. Each of these molecular orbital methods generates symmetry-adapted wave functions which are maximally delocalized. In particular orbitals which approximately describe levels involved in an electronic transition are inherently asymmetric, *i.e.*, they extend out to the asymmetric carbon, if such a carbon is the source of chirality in the molecule. Since one-electron integrals are routinely computed, it has become possible, given a molecular wave function, to evaluate the rotational strength exactly. Disagreement with observed rotations can thus be traced directly to deficiencies in the wave functions. We would like to describe in this contribution a program for such computations and to present some preliminary results. Comparisons will be made with experiment and with results obtained by Pao and Santry,⁸ who in a study similarly motivated to ours, used delocalized CNDO/2 SCF wave functions but neglected two-center integrals in order to maintain consistency with the neglect of overlap charge distributions in the approximate SCF method used to generate their wave functions.

Theory

The electric and magnetic moment vectors in eq 1 are sums of one-electron operators.

$$\mathbf{u}_e = e \sum_k \mathbf{r}_k \quad (2)$$

$$\mathbf{u}_m = \frac{e\hbar}{2mci} \sum_k \mathbf{r}_k \times \nabla_k \quad (3)$$

The evaluation of the matrix elements of \mathbf{u}_e could be carried through using the dipole length expression 2. However it can be shown that the rotational strength so calculated is origin dependent.^{9,10} The equations of motion allow a transformation of the following type.¹¹

$$\langle i | \mathbf{r} | j \rangle = \frac{\hbar^2}{m} \langle i | \nabla | j \rangle / (E_j - E_i) \quad (4)$$

It may be shown⁹ that rotational strengths evaluated in the dipole velocity or gradient formalism are origin independent. However, the rotational strengths evaluated in the gradient form do not satisfy the rotational sum rule, *i.e.*, that the sum of all such rotational strengths should vanish.¹² Moreover since the transformation 4 is valid only for exact wave functions, gradient and length forms of rotatory strengths will not coincide for the approximate wave functions which are available to us. This problem has been discussed many times,¹³ and it appears to us that on balance

(6) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers.

(7) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, 129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, 136 (1965), and subsequent papers.

(8) Y.-H. Pao and D. P. Santry, *J. Amer. Chem. Soc.*, **88**, 4158 (1966).

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

(10) W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956).

(11) H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One and Two Electron Systems," Academic Press, New York, N. Y., 1957, p 251.

(12) R. A. Harris, *J. Chem. Phys.*, **50**, 3947 (1969).

(13) S. Chandrasekhar, *Astrophys. J.*, **102**, 223 (1945); S. S. Huang, *ibid.*, **108**, 354 (1948); D. R. Bates, *J. Chem. Phys.*, **19**, 1122 (1951);

there would be some advantage to using the dipole velocity formalism.¹⁴

It is convenient to work with a dimensionless reduced rotational strength $[R_k]$, defined by

$$[R_k] = \frac{100R_k}{D\mu_B} \sim 1.08 \times 10^{40} R_k \quad (5)$$

where D is the Debye unit and μ_B is the Bohr magneton. Assuming single configuration wave functions for ground and excited states, the k th excited state being described by a simple excitation from orbital i to orbital j , and substituting explicitly for μ_e and μ_m , we obtain

$$[R_{ij}] = \frac{-254}{E_j - E_i} \cdot \langle \psi_i | \nabla | \psi_j \rangle \cdot \langle \psi_j | \mathbf{r} \times \nabla | \psi_i \rangle \quad (6)$$

with the gradient operator and the transition energy denominator in atomic units.

In the LCAO MO approximation the ground and excited state molecular orbitals may be written

$$\psi_i = \sum_A \sum_r c_{ir} \chi_r^A \quad (7)$$

and

$$\psi_j = \sum_B \sum_s c_{js} \chi_s^B \quad (8)$$

where the sum on A (or B) is over all atoms in the molecule, and the sum on r (or s) is over all atomic orbitals on atom A (or B) used in the basis set. The present calculation used extended Hückel wave functions⁶ derived from a basis set of 2s and 2p orbitals on all first-row atoms and a 1s orbital on all hydrogens. From (7) and (8) we have

$$\langle \psi_i | \nabla | \psi_j \rangle = \sum_{A,B} \sum_{r,s} c_{ir} c_{js} \langle \chi_r^A | \nabla | \chi_s^B \rangle \quad (9)$$

The one-center integrals are nonvanishing only between a 2s and a 2p orbital, and are easily evaluated.¹⁵ Each two-center integral, however, must be performed in a local coordinate system. We accordingly define a σ direction along the internuclear line, and a π direction perpendicular to σ and lying in the plane containing the z axis and both atoms, as shown in Figure 1. The π' direction is then determined by $\hat{\pi}' = \hat{\sigma} \times \hat{\pi}$.

Now

$$\frac{\partial}{\partial x} = \frac{\partial \sigma}{\partial x} \frac{\partial}{\partial \sigma} + \frac{\partial \pi}{\partial x} \frac{\partial}{\partial \pi} + \frac{\partial \pi'}{\partial x} \frac{\partial}{\partial \pi'} \quad (10)$$

and similarly for $\partial/\partial y$ and $\partial/\partial z$. Hence the nine coefficients $\partial\sigma/\partial x$, $\partial\pi/\partial x$, etc., all of which are easily expressed in terms of the angles θ and φ shown in Figure 1, comprise a transformation matrix M , found to be

H. Shull, *ibid.*, **20**, 18 (1952); M. Wolfsberg, *ibid.*, **23**, 793 (1955); S. R. LaPaglia and O. Sinanoglu, *ibid.*, **44**, 1888 (1966); E. Rothenberg and E. R. Davidson, *J. Mol. Spectrosc.*, **22**, 1 (1967); A. E. Hansen, *Mol. Phys.*, **13**, 425 (1967); D. P. Chong, *ibid.*, **14**, 275 (1968).

(14) Oscillator strengths calculated from transition gradients appear to be in better agreement with experiment: A. J. McHugh and M. Gouterman, *Theor. Chim. Acta*, **13**, 249 (1969).

(15) S. Ehrenson and P. E. Phillipson, *J. Chem. Phys.*, **34**, 1224 (1961).

$$M = \begin{bmatrix} \sin \varphi \sin \theta & \cos \varphi \sin \theta & -\cos \theta \\ \sin \varphi \cos \theta & \cos \varphi \cos \theta & \sin \theta \\ \cos \varphi & -\sin \varphi & 0 \end{bmatrix} \quad (11)$$

such that

$$M^{-1} \left(\frac{\partial}{\partial \sigma}, \frac{\partial}{\partial \pi}, \frac{\partial}{\partial \pi'} \right) = \left(\frac{\partial}{\partial x'}, \frac{\partial}{\partial y'}, \frac{\partial}{\partial z} \right) \quad (12)$$

It may also be seen that

$$M(c_x p_x, c_y p_y, c_z p_z) = (c_\sigma p_\sigma, c_\pi p_\pi, c_{\pi'} p_{\pi'}) \quad (13)$$

That is

$$\begin{aligned} c_\sigma p_\sigma &= c_x p_x \sin \varphi \sin \theta + c_y p_y \cos \varphi \sin \theta - c_z p_z \cos \theta \\ c_\pi p_\pi &= c_x p_x \sin \varphi \cos \theta + c_y p_y \cos \varphi \cos \theta + c_z p_z \sin \theta \\ c_{\pi'} p_{\pi'} &= c_x p_x \cos \varphi + c_y p_y \sin \varphi \end{aligned} \quad (14)$$

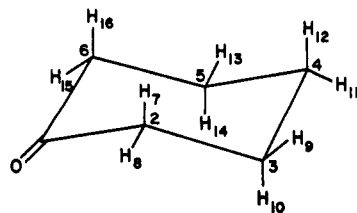
Thus, writing (9) more explicitly and transforming to the local coordinate system according to (12) and (13), we have for the x component of $\langle \psi_i | \nabla | \psi_j \rangle$

$$\begin{aligned} \left\langle \psi_i \left| \frac{\partial}{\partial x} \right| \psi_j \right\rangle &= \sum_{A,B} \left\langle c_{1s} s^A + c_{1z} p_x^A + c_{1y} p_y^A + \right. \\ &\quad \left. c_{1z} p_z^A \left| \frac{\partial}{\partial x} \right| c_{jz} s^B + c_{jz} p_x^B + c_{jy} p_y^B + c_{jz} p_z^B \right\rangle = \\ &\sum_{A,B} \left\langle c_{1s} s^A + c_{1\sigma} p_\sigma^A + c_{1\pi} p_\pi^A + c_{1\pi'} p_{\pi'}^A \left| \sin \varphi \sin \theta \frac{\partial}{\partial \sigma} + \right. \right. \\ &\quad \left. \left. \sin \varphi \cos \theta \frac{\partial}{\partial \pi} + \cos \varphi \frac{\partial}{\partial \pi'} \right| c_{jz} s^B + \right. \\ &\quad \left. c_{j\sigma} p_\sigma^B + c_{j\pi} p_\pi^B + c_{j\pi'} p_{\pi'}^B \right\rangle \quad (15) \end{aligned}$$

where the coefficients of the transformed p orbitals are found from (13). A similar procedure yields the other two components. The matrix elements of $\partial/\partial\pi$ and $\partial/\partial\pi'$ on the right-hand side of (15) are evaluated in terms of overlap integrals,¹⁶ while those of $\partial/\partial\sigma$ are expressed in terms of the $C_{\alpha\beta} \gamma \delta \epsilon$ functions,^{15,17} which are functions of the Slater exponents and the separation between the two atoms A and B . In the cases we studied, only carbon, oxygen, and hydrogen atoms were involved, and the corresponding Slater exponents were 1.625, 2.275, and 1.3. A computer program to carry out the above calculations, using extended Hückel wave functions, was constructed. Its present capacity is for molecules with up to 80 orbitals, and the computation times for rotational strengths are comparable to those necessary to obtain the approximate wave functions.

The Carbonyl Chromophore

We studied initially a favorite system of calculators, the methyl cyclohexanones. The basic molecule is shown below, with the hydrogen numbering system



(16) G. Wagnière and H. Labhart, *J. Chem. Phys.*, **39**, 2386 (1963).

(17) K. Ruedenberg, C. C. J. Roothaan, and W. Jaunzemis, *ibid.*, **24**, 201 (1956); W. C. Hamilton, *ibid.*, **26**, 1018 (1957).

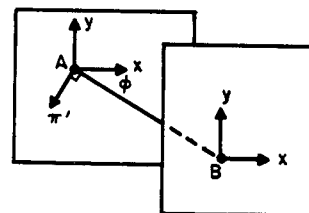
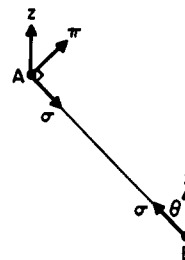


Figure 1. Transformation from an absolute to a local system. The drawing at top is in the plane containing atoms A and B and the z direction. Local coordinates σ and π are defined as described in the text. $\hat{\sigma} \cdot \hat{z} = \cos \theta$. The drawing at bottom is a view of the same coordinate system from along the z axis. The local coordinate π' lies in a plane perpendicular to the z axis. ϕ is the angle between the projection of the line AB on an xy plane through A , and the x axis.

conforming to the convention of Pao and Santry.⁸ We then replaced selected hydrogens by methyl groups, staggered or eclipsed with respect to their adjacent carbon.

Table I shows our calculated rotational strengths, using the gradient form of the electric moment operator and an excitation energy of 4.0 eV. Use of the length form of the electric moment operator yields very similar values. The average deviation is about 10%

Table I. Calculated Rotatory Strengths for Cyclohexanone Derivatives

Proton substituted ^a	[R]		
	Calcd	Calcd ^b	Obsd ^c
H ₇ (s)	+9.92	+0.00	+Small
H ₇ (e)	+10.57		
H ₈ (s)	+5.96	+3.51	
H ₈ (e)	+6.32		
H ₉ (s)	-15.11	-2.26	-
H ₉ (e)	-18.11		
H ₁₀ (s)	+5.24	+2.35	
H ₁₀ (e)	+2.23		
H ₇ , H ₁₃	+5.53	+3.6	+1.8
H ₇ , H ₈ , H ₁₃	+6.36	+5.3	+6.7

^a Staggered methyl group = s, eclipsed methyl group e. ^b Reference 8. ^c See literature references in footnote 8.

and is nonsystematic. While we have not evaluated the effect of changing origins on the dipole length result, the agreement between the two methods is encouraging. The agreement with experiment and previous calculations, except for sign, is not good.

The conformation of the methyl group has a negligible effect on some rotational strengths (substitution at C₂), a more serious effect on others (substitution at C₃). This is reinforced by a calculation on the rotatory

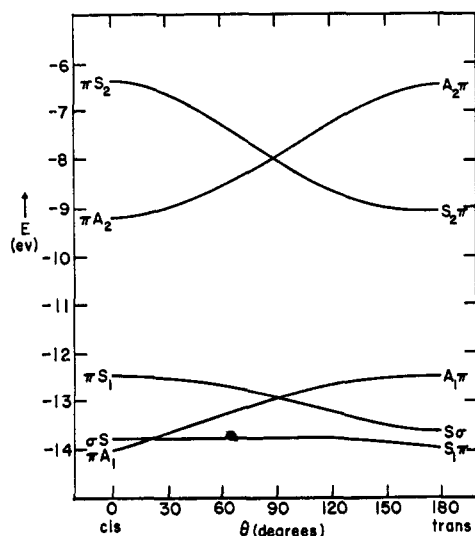


Figure 2. Extended Hückel energy levels of a butadiene. The π levels are numbered in order of ascending energy within each symmetry species.

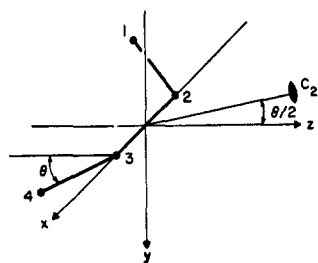
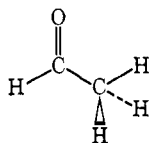


Figure 3. Coordinate choice for butadiene. The initial geometry, $\theta = 0^\circ$, is *s-cis* with the molecule in the *xz* plane. The twisting motion keeps carbon atoms 1, 2, and 3 fixed and rotates carbon 4 down by a dihedral angle θ . At $\theta = 90^\circ$ carbon 4 would be in the *xy* plane. The twofold axis migrates from lying along the *z* axis to a position along the *y* axis in the *s-trans* conformation.

strength of a model acetaldehyde molecule.



Conformations with one hydrogen eclipsing the carbonyl group are, of course, achiral. The maximum rotatory strength is obtained for a conformation in which the methyl group is twisted 30° away from this symmetric geometry, and $[R]$ reaches a value of 2.31. The effect of conformation can thus be a serious one. A more detailed discussion of the sources of rotational strength of the carbonyl chromophore will be given in a forthcoming study.¹⁸

The Skewed Butadiene Chromophore

A nonplanar butadiene is characterized by C_2 symmetry and is thus an inherently chiral entity. The optical activity of skewed dienes has been carefully analyzed by Charney and coworkers,¹⁹ and their studies

(18) J. Howell and R. Hoffmann, unpublished results.

(19) (a) E. Charney, *Tetrahedron*, **21**, 3127 (1965); (b) A. Moscovitz, E. Charney, U. Weiss, and H. Ziffer, *J. Amer. Chem. Soc.*, **83**, 4661 (1961); (c) E. Charney, H. Ziffer, and U. Weiss, *Tetrahedron*, **21**, 3121 (1965); U. Weiss, H. Ziffer, and E. Charney, *ibid.*, **21**, 3105 (1965).

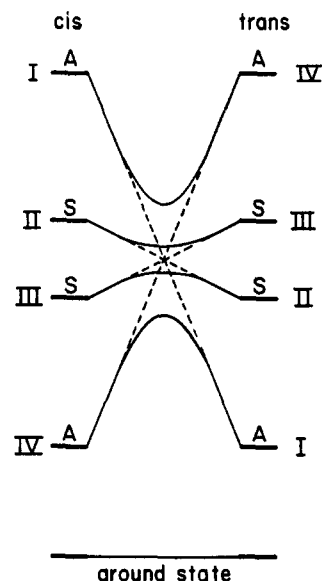


Figure 4. Schematic correlation of butadiene configurations as the molecule is twisted.

contributed to the origin of our work. Figure 2 shows the extended Hückel energy levels of a butadiene²⁰ as the molecule is progressively twisted around the central formal single bond from an *s-cis* ($\theta = 0^\circ$) to an *s-trans* ($\theta = 180^\circ$) geometry. The only symmetry element which is preserved in the course of such twisting is a twofold rotation axis, which migrates in its position from lying in the diene plane in *s-cis* to a position perpendicular to the diene plane in *s-trans*. We classify all levels as symmetric (S) or antisymmetric (A) with respect to this axis. The coordinate system in which the butadiene is located is shown in Figure 3.

Note that in the extended Hückel calculations a σ S level intrudes between the occupied π levels. This σ level does not interact with the π levels in the C_{2v} *s-cis* and C_{2h} *s-trans* geometries, but it does mix at angles other than 0° and 180° . The mixing affects primarily the nearest π level of similar symmetry, S_1 . The interaction is most severe on the *trans* side. Figure 2 shows clearly the avoided crossing of the two S levels between $\theta = 140$ and 180° ; the S_1 level on the *cis* side is forced to correlate with the σ level in the *trans* conformation. We will see below that the perturbation of the S_1 level by σ will cause further difficulties in our computations, but for the moment let us continue our discussion solely in terms of the π levels.

There are four singly excited butadiene configurations.

I	$(S_1)^1(A_1)^1(S_2)^1$	A overall symmetry ²¹
II	$(S_1)^2(A_1)^1(A_2)^1$	S
III	$(S_1)^1(A_1)^2(S_2)^1$	S
IV	$(S_1)^1(A_1)^2(A_2)^1$	A

The state diagram showing the correlation of configurations I through IV is drawn in Figure 4. Electron interaction will prevent the intended crossing which arises from the lowest excitation on the *s-trans* side

(20) $C=C$, 1.34; $C-C$, 1.482; $C-H$, 1.08; all angles 120° .

(21) The proper group theoretical designations are, of course, A for the symmetric, and B for the antisymmetric levels.

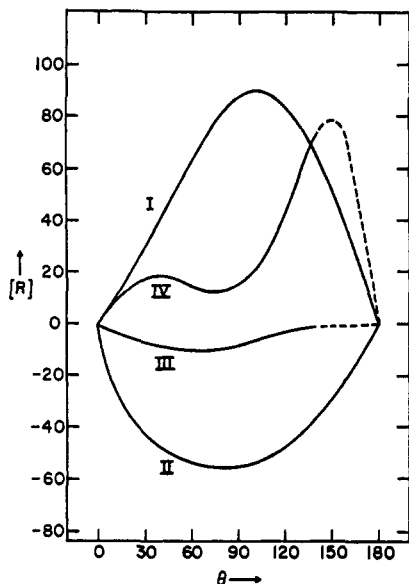


Figure 5. Reduced rotational strengths for configurations I-IV of butadiene. See text for explanation of dashed-line portion on configurations III and IV.

being I, but on the *s-cis* side being IV. The lowest excited singlet wave function will have the final form

$$\psi_A = c_1\psi_I + c_4\psi_{IV} \quad (16)$$

with $c_1 > c_4$ near the *s-trans* geometry, $c_1 \sim c_4$ at $\theta = 90^\circ$, and $c_4 > c_1$ near the *s-cis* geometry. The configurational mixing for the S states is complicated by the initial proximity of configurations II and III in energy. Moreover several recent π -electron SCF calculation on butadiene, carried out with *complete* configuration interaction, indicate that the low-lying S level contains a heavy admixture of a doubly excited configuration.²² Because of the ambiguity of description of this low-lying S state we will concentrate on the rotatory properties of the lower A state.

We first calculated the rotational strengths corresponding to excitations from the ground state to the pure configurations I through IV. The results are shown in Figure 5. The calculated energy gaps were here used in computing the reduced rotational strengths.

The behavior of the rotational strengths of configurations I and II are normal and in agreement with previous work.^{19a} The curves for configurations III and IV are anomalous. We believe the source of the anomaly is the mixing of the S_1 level with the nearby σ level. This interaction should be maximum on the *trans* side, near the avoided crossing. We have, in fact, put a dashed line in that region in Figure 5, since we do not really know which level is to be identified there as a π level. The mixing of σ and S_1 we believe also is responsible for the anomalous behavior of configuration IV near the *cis* side.

If eq 16 is used for the excited state in the expression for the rotational strength one obtains the following relation.

(22) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); W. Th. A. M. van der Lugt, Thesis, Leiden, 1968; R. K. Nesbet, *Proc. Roy. Soc., Ser. A*, **230**, 322 (1954); C. A. Coulson and J. Jacobs, *ibid.*, **206**, 287 (1951); C. M. Moser, *J. Chem. Soc.*, 3455 (1954); N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, **87**, 2081 (1965); A. Imamura, private communication.

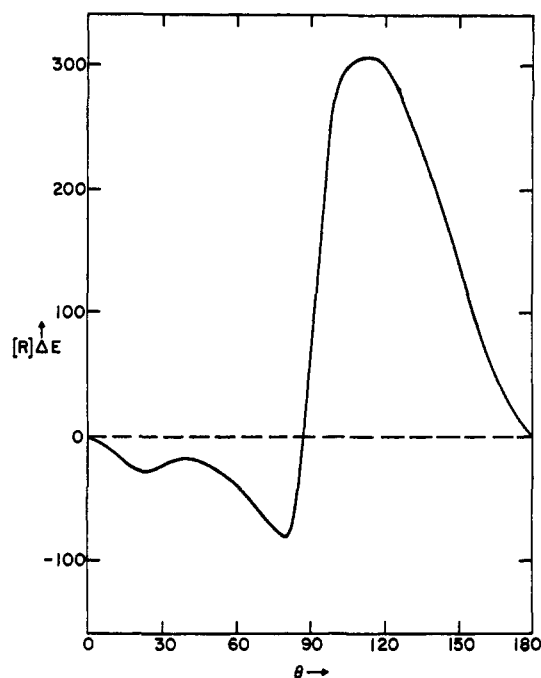


Figure 6. Total reduced rotational strength, multiplied by ΔE , including configurational mixing, for the antisymmetric butadiene excited state. To obtain $[R]$ the vertical scale must be divided by the appropriate transition energy in electron volts.

$$[R] \sim c_1^2 \langle \psi_2 | \nabla | \psi_3 \rangle \cdot \langle \psi_3 | \mathbf{r} \times \nabla | \psi_2 \rangle + c_4^2 \langle \psi_1 | \nabla | \psi_4 \rangle \cdot \langle \psi_4 | \mathbf{r} \times \nabla | \psi_1 \rangle + c_1 c_4 (\langle \psi_2 | \nabla | \psi_3 \rangle \cdot \langle \psi_4 | \mathbf{r} \times \nabla | \psi_1 \rangle + \langle \psi_1 | \nabla | \psi_4 \rangle \cdot \langle \psi_3 | \mathbf{r} \times \nabla | \psi_2 \rangle) \quad (17)$$

Note that in addition to the pure configuration contributions there come in cross terms which consist of scalar products of the electric moment of one configuration with the magnetic moment of the other. If the directions of these moments match, as they do in the case at hand, the contribution of these cross terms may be large. Moreover if c_1 and c_4 are of opposite sign the cross terms can diminish the pure configuration rotational strength or even change its sign.

The configuration mixing coefficients c_1 and c_4 in eq 16 were obtained from a Pariser-Parr-Pople π -electron-only SCF calculation specifically designed to incorporate the effects of torsional motions.²³ c_4 emerges with an opposite sign to c_1 , and one has to approach quite close to $\theta = 90^\circ$ to obtain significant configurational mixing. The net rotatory strength we calculate, Figure 6, is positive and well behaved in the region $90^\circ < \theta < 180^\circ$. In the region $0^\circ < \theta < 90^\circ$ the rotatory strength is small and negative. The dominance of the cross terms is responsible for the negative sign in this region. Many uncertainties in the calculation at this stage, for example, the σ - π mixing and the consequent erratic behavior of pure configuration IV and the approximation involved in getting the configuration interaction coefficients, make us hesitant to say anything definite about the rotation in the

(23) The special features of this program, originally written by A. Imamura, are described in R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967). The butadiene calculations with this program were kindly provided for us by R. Gleiter, Universität Basel.

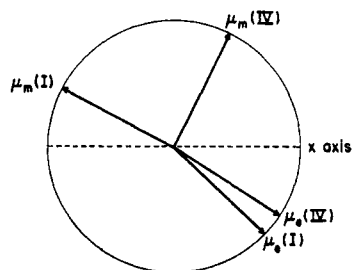


Figure 7. Direction of electric and magnetic transition moments for configurations I and IV in a 60° twisted butadiene. The view is along the twofold axis, and all vectors lie in the plane perpendicular to that axis.

s-cis region except to point out the importance of configurational mixing and the possibility of an actual sign reversal due to cross terms.

In deciding on the symmetry properties of the electric and magnetic moments it is useful to depart from the rigid coordinate system used previously to one which follows the twisting motion. This rotating coordinate system may be defined by keeping the x axis (along C_2-C_3) fixed and rotating the y and z axes in such a way as to have the z axis always along the twofold rotation. The transformation properties of the electric and magnetic transition in this rotating coordinate frame are easily obtained; they are summarized in Table II. In the same coordinate system the electronic

Table II. Transformation Properties of Electric and Magnetic Transition Moments

	C_{2v}	C_2	C_{2h}
μ_{ez}	B_1	B	B_u
μ_{ey}	B_2	B	B_u
μ_{ez}	A_1	A	A_u
μ_{mx}	B_2	B	B_g
μ_{my}	B_1	B	B_g
μ_{ms}	A_2	A	A_g

transitions have definite symmetries shown in Table III. This table also indicates the resultant polarizations of the electric and magnetic moments of these electronic transitions. The rotational strength vanishes, as it must, in the C_{2v} *cis* and C_{2h} *trans* geometries, but it is interesting to note that the reasons for its vanishing encompass all the three possible outcomes. Thus the rotational strength vanishes because either $\mu_e = 0$ (A transition, *trans* side), or $\mu_m = 0$ (B , *trans*; A , *cis*), or because \mathbf{u}_e and \mathbf{u}_m are perpendicular (B , *cis*).

Our detailed calculations concur with the group theoretical conclusions regarding the polarizations of

Table III. Polarizations of Electric and Magnetic Moments of Butadiene Excited Configurations

	C_{2v}	C_2	C_{2h}
Configurations I, IV			
State	B_1	B	B_u
symmetry	B_1	B	B_u
μ_e	x	x,y	x,y
μ_m	y	x,y	0
Configurations II, III			
State	A_1	A	A_g
symmetry	A_1	A	A_g
μ_e	z	z	0
μ_m	0	z	z

the various moments. The actual orientation of the various moments of configurations I and IV is shown in Figure 7 for a twist angle of 60° from the *cis* side. The view is along the local z axis; *i.e.*, all moments lie in the plane perpendicular to that axis. Note the good alignment of μ_e (I) and μ_m (I), the near orthogonality of μ_e (IV) and μ_m (IV) (compensated by a large relative magnitude of μ_e (IV)), and the excellent alignment of μ_m (I) and μ_e (IV), which leads to large cross-term contributions.

The electric transition moments were also recalculated in the length formalism. The directions of the resultant vectors were at all angles of twist within 6° of the gradient results, and often identical to the latter. The magnitudes were comparable, and in particular showed the anomalous behavior of curves III and IV in Figure 5.

Conclusions

The direct procedure of evaluating the rotatory strength correctly from approximate wave functions has been applied by us to the carbonyl and twisted diene chromophores. The results are of the correct order of magnitude but cannot be considered to be quantitatively useful to an experimentalist. The inadequacy of the results must be blamed on the poorness of the wave functions. There are, nevertheless, interesting qualitative insights we have gained: the influence of conformation on rotatory strength and the effect of configuration interaction. With further qualitative results in mind, we are continuing our exploration of optical activity.

Acknowledgment. We are grateful to J. M. Howell for the use of his dipole length program, and numerous discussions as well. Discussions with E. Charney and G. Wagnière were also of great benefit to us. This work was supported by the Public Health Service (GM-13468) and the National Science Foundation (GP 8013)