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OPTICAL ACTIVITY OF NON-PLANAR CONJUGATED DIENES—III

HMO CALCULATION OF THE SKEW ANGLE DEPENDENCE

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Abstract—In two previous communications,[1,2] the results of an investigation of the rotational contribution of a dienic system which is constrained to be non-planar (skewed) have demonstrated that the sign of the rotational strength, and of the resulting Cotton effect, associated with the longest wavelength electronic transition of the system is determined by the skew or helical sense of the four carbon system of which it is composed. The theoretical basis of this conclusion is discussed here and calculations are reported of the intensity of the absorption bands, and of the rotational strength of this transition, as well as that of the transition of next higher energy as a function of the skew angle. In addition, making use of experimentally observed band widths, the contributions of these two transitions to the optical rotatory dispersion have been calculated, also as a function of skew angle, and it is demonstrated that for the one case for which X-ray data are available to determine the skew angle, the shape of the experimentally observed ORD curve is in excellent qualitative agreement with the calculation.

THE role that a dissymmetric chromophore plays in imparting optical activity to molecules containing the chromophoric system has recently been explored extensively, and in two earlier communications,[1,2] we have presented the results of the investigation of one such system in two alternate configurations, namely a conjugated four carbon group constrained by its molecular environment to be non-planar in *cisoid* and *transoid* configurations. In the first of these,[1] a successful calculation was reported of the rotational strength associated with the longest wavelength V ← N transition in a diene with a skew angle of 17·5° (as measured from a Dreiding model of the compound), but no discussion has been presented of the angular dependence of the rotatory dispersion.[3] The optical activity results from the rotational strength associated with, in this case, the electronic absorption strengths of the electric and magnetic dipole transition matrix elements, $(a\,|\mathbf{R}|\,b)$ and $(b\,|\mathbf{M}|\,a)$, between the ground and excited state configurations a and b. The rotational strength is given by[4] the imaginary part of their vector dot product.

$$R_{ba} = Im\,\{(a\,|\mathbf{R}|\,b)\cdot(b\,|\mathbf{M}|\,a)\} \tag{1}$$

The calculation of the electric dipole moment matrix element also leads to a measure of the absorption intensity of the $a \rightarrow b$ transition because the oscillator strength, f,

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[1] A. Moscowitz, E. Charney, U. Weiss, and H. Ziffer, *J. Amer. Chem. Soc.* **83**, 4661 (1961).

[2] E. Charney, H. Ziffer and U. Weiss, *Tetrahedron* **21**, 3121 (1965).

[3] A related calculation of the rotational strength and the optical activity at 350 mμ for angles to 40° has been made by R. Deen, Ph.D. thesis, U. of Leiden, September (1961). The results are compatible so far as parity is concerned, but Deen's calculation predicts a red rather than a blue shift of the long wavelength transition as the angle increases.

[4] L. Rosenfeld, *Z. für Physik.* **52**, 161 (1929).

is proportional to the square of this matrix element. A calculation of the rotational strength, which is the purpose of this investigation has as a fruitful byproduct, then, the capability of calculating the absorption intensities. The required matrix elements in their integral form are given in Eqs (6), (9), (14) and (15). These integrals require a knowledge of the molecular wave functions and geometry, and the approximation inherent in the present discussion is that the atomic wave functions from which the molecular functions are formed, are invariant to the skew angle of the diene except insofar as this is reflected in changes in bond distances. The integrals and therefore the matrix elements are, of course, strongly dependent on the skew angle.

The basis of the present calculations is Hückel Molecular Orbital (HMO) theory using the method of linear combination of atomic orbitals (LCAO) which was used so successfully to predict the rotational strength of the lowest energy singlet excitation of hexahelicene[5] and which was used to obtain the earlier results,[1,2] but several new refinements and approximations have been made to permit a full calculation of the angular dependence. The results are compatible with earlier calculations of the absorption intensity of the long wavelength transition of butadiene[6] and with the symmetry requirements which forbid the second singlet transition in *trans*-butadiene, but allow it for *cis*-butadiene.

The HMO LCAO treatment of the π electronic system of butadiene produces a set of four molecular orbitals from which ground and excited state configurations are made respectively, by filling the lowest two of these orbitals and by successive higher orbitals. The coefficients c_{jr} of the MO's, which are constructed from the atomic orbitals, φ_r

$$\Psi_j = \sum_r c_{jr}\varphi_r \tag{2}$$

are obtained by setting the normalization condition, $\int \Psi^2 \, d\tau = 1$, in the form,

$$\sum_r c_{jr}^2 = 1.$$

In its simplest form, due to Hückel, the resonance integrals

$$\beta_{rs} = \int \varphi_r H \varphi_s \, d\tau$$

are taken to be equal for all similar bonds in the molecule between adjacent bonded atoms r and s, but zero for nonbonded atoms, and the Coulomb integrals $\alpha = \int \varphi_r H \varphi_r \, d\tau$ are taken to be equal for the electrons of the π lattices (the σ electrons are ignored in this treatment). The final assumption is that the atomic orbitals are orthonormal, so that the overlap integrals

$$S_{rs} = \int \varphi_r \varphi_s \, d\tau$$

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[5] A. Moscowitz, Ph.D. thesis, Harvard University, March (1957).

[6] R. S. Mulliken, *J. Chem. Phys.* 7, 121 (1939); while this manuscript was in preparation, the calculation of the near-UV spectral intensities of butadiene by N. L. Allinger and M. A. Muller, *J. Amer. Chem. Soc.* **86**, 2811 (1964), appeared which uses the Pariser and Parr approximation. *Except* for the fact that the oscillator strength which they calculate for the first and second transition (N → V_1 and N → V_2 in their notation) goes to zero for $\theta = 90°$, the present results are in reasonable agreement with the results from their more sophisticated treatment, which employs normalized antisymmetrized product wave functions.

are equal to zero for $r \neq s$ and equal to unity for $r = s$. In the present treatment, the latter two of these approximations are retained, at least for the purpose of solving the secular equation to obtain the coefficients, c_{jr}, which are required for the calculation of the absorption intensities and the rotational strengths; however, for reasons which will be discussed, other approximations are made with respect to the β's.

The variation of β with skew angle. The resonance integral, β, represents the interaction energy between atomic orbitals and, in the Hückel approximation, between the orbitals of bonded atoms only. Obviously, this interaction varies with bond distance and a number of relations have been proposed[7] to relate the value of β with bond distance or other parameters which depend on bond distance. Frequently these are ignored in HMO calculations, the bond or resonance integrals being assumed equal for nearest neighbors in a conjugated system. Calculations of the resonance and/or transition energies of butadiene have been made in both ways.[8] In the present case, it was deemed especially desirable to account for the inequality of the resonance interaction because the transition moments required for the calculation of absorption intensity and rotational strengths are strongly dependent on bond lengths which may vary considerably as the angle of skew varies; the electric and magnetic dipole transition moments, in turn are calculated using the coefficients which are obtained from the solution of the secular determinant in which the chosen values of β are incorporated.

β depends on skew angle in still another way. Since the interaction energy between adjacent $2p\pi$ orbitals of carbon is likely to be a maximum when the orbitals are axially parallel and a minimum when they are orthogonal to each other, we have assumed that the resonance integral between carbons 2 and 3 of the diene system (the central carbons in our nomenclature) goes to zero when the C1–C2 bond becomes perpendicular to the C3–C4 bond and attains its maximum value when the four carbon system is planar.

This result is concomitant with the assumption that as the diene system is progressively skewed out of a plane, the $2p\pi$ orbitals of carbons 1 and 2, and similarly those of carbons 3 and 4, remain substantially parallel to each other. Thus the $2p\pi$ orbitals of carbons 2 and 3 which are also parallel in the planar diene become perpendicular to each other at the 90° skew angle and return to the parallel condition at the 180° skew angle. This assumption is based on the fact that although the resonance energy for butadiene is reasonably large, the experimentally determined bond distance for the central bond is very much larger than that of the two side bonds, and consequently, the interaction between the π orbitals of the carbons 1 and 2, and of 3 and 4, must be much larger than that between 2 and 3. In the Hückel treatment, this is borne out by values of the bond order for the 1, 2 and 3, 4 bonds of about 0·9, while a value of about 0·5 or less is obtained for the 2, 3 bond. In more refined treatments even lower values are found for the 2, 3 bond; typical values now accepted are in the range of 0·15.[9]

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[7] See, for example, the discussion in A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* J. Wiley New York (1961).

[8] R. S. Mulliken, *Rev. Mod. Phys.* **14**, 265 (1942); A. Almennigen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.* **12**, 1221 (1958).

[9] C. A. Coulson, Personal Communication.

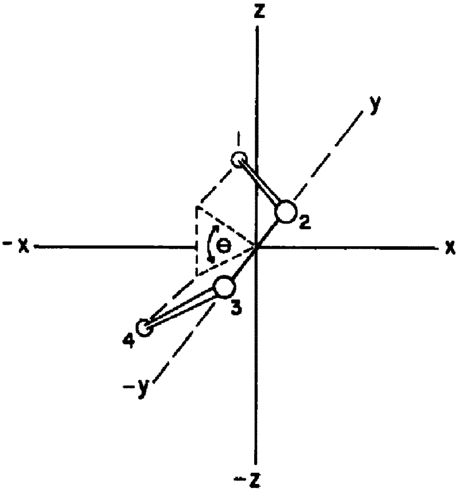

Fig. 1. Coordinate axes of the diene system.

The procedures for calculating β follow:

β_{12}: values are calculated using Mulliken's relation for β as a function of the overlap integral as plotted in Ref. 7. The required bond distances utilized are those in *trans*-butadiene for the planar molecule ($\theta = 0°$, see Fig. 1) and the normal single and double bond distances for the 90° case. For all intermediate angles, the bond distance is assumed to vary as cos θ, i.e.

$$r_{12} = 1{\cdot}33 + 0{\cdot}04\ |\cos\theta|$$

β_{23}: the same method is used to calculate values of β_{23}' with $r_{23} = 1{\cdot}54 - 0{\cdot}07\ |\cos\theta|$ and β_{23} is calculated[10] next from

$$\beta_{23} = \beta_{23}'\ |\cos\theta|$$

so that $\beta_{23} = \beta_{23}'$ for $\theta = 0$, 180° i.e. for *cis* and *trans*-butadiene and $\beta_{23} = 0$, for $\theta = 90°$.

Energies and intensities. With the foregoing values of β, the usual 4 × 4 secular determinant is solved to obtain the eigenvalues and eigenvectors, the latter of which, suitably normalized, are the AO coefficients of the molecular orbitals. These are listed in Table 1. From the eigenvalues, the energies of the lowest singlet $\pi^* \leftarrow \pi$ transition (${}^1B_u \leftarrow {}^1A_g$ in *trans*- and ${}^1B_2 \leftarrow {}^1A_1$ in *cis*-butadiene) as well as that of the second transition (${}^1A_g \leftarrow {}^1A_g$ in *trans*- and ${}^1A_1 \leftarrow {}^1A_1$ in *cis*-butadiene) have been calculated and are plotted in frequency units in Fig. 2, after adjusting the calculated energy of the planar butadiene ($\theta = 0°$) to a mean value representative of the average of observed *cis* and *trans* configurations.[11]

[10] R. G. Parr and B. L. Crawford, Jr., *J. Chem. Phys.* **16**, 526 (1948); M. J. S. Dewar, *J. Amer. Chem. Soc.* **74**, 3345 (1952); H. Suzuki, *Bull. Chem. Soc. Japan* **35**, 1715 (1962).

[11] *trans*-Butadiene has an observed absorption band at about 217 mμ in hexane attributed (W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* **A174**, 220 (1940)) to the ${}^1B_u \leftarrow {}^1A_g$ transition. The mean value of the corresponding absorption bands of about six each of *cisoid* and *transoid* dienic compounds of similar type was used to evaluate the difference (28 mμ) between the band positions of the two configurations. The position of the absorption band of the starting planar configuration is therefore taken as 231 mμ from which the energy of this transition in a hypothetical linear butadiene is calculated to be 43,300 cm^{-1}.

TABLE 1. EIGENVALUES AND AO COEFFICIENTS OF THE HMO'S OF SKEWED BUTADIENE

Skew Angle	$\epsilon_2, \epsilon_2'(\mp)$[a]	$\epsilon_1, \epsilon_1'(\mp)$[a]	c_1[b]	c_2[b]
0°	1·56925	0·68925	0·3906	0·5894
10°	1·52790	0·70790	0·3979	0·5845
20°	1·49397	0·72397	0·4040	0·5803
30°	1·46339	0·75339	0·4122	0·5745
40°	1·40801	0·79801	0·4253	0·5649
50°	1·34882	0·84882	0·4394	0·5540
60°	1·28659	0·90659	0·4546	0·5416
70°	1·22773	0·96773	0·4695	0·5288
80°	1·16692	1·03692	0·4850	0·5145
90°	1·11000	1·11000	0·5000	0·5000

[a] See text below for definition of subscripts

[b] See note (13) for definition of subscripts

It is interesting to note the almost astounding agreement between the calculated transition energy of the long wavelength band corresponding to the diene twisted into two ethylene molecules ($\theta = 90°$), with the observed transition energy for ethylene.

In the simple HMO treatment we are using here, the neglect of electronic interactions leads to an accidental degeneracy in the transition energies for the two excitations corresponding to the promotion of an electron from the lowest energy MO to the first unfilled MO and from the highest filled MO to the second unfilled MO. Both of these are ${}^1A_g \leftarrow {}^1A_g$ in *trans*- and ${}^1A_1 \leftarrow {}^1A_1$ in *cis*-butadiene. It is well-known that at least insofar as the calculation of the excited state energies is concerned, this aspect of simple HMO treatment may be seriously deficient. We are encouraged,

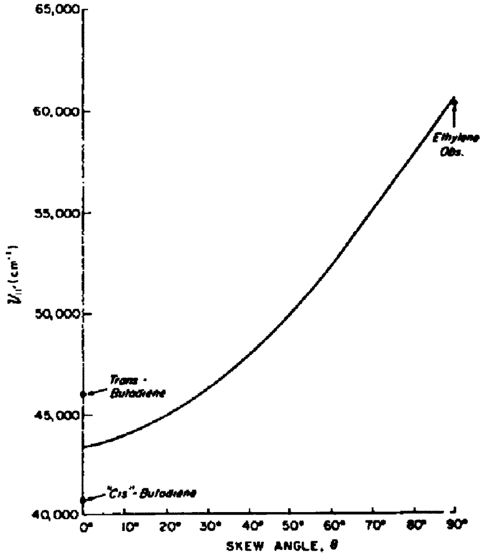

FIG. 2. Calculated transition energies for butadiene as a function of skew angle.

however, to be satisfied with this treatment, because of its success in describing qualitatively and semi-quantitatively the dispersion of the optical activity of dienic compounds and because of its ease of use. The degeneracy in transition energies is, however, accompanied by identical values for the electric and magnetic dipole transition moments, a fact which leads to rather large values (the sum of the two) for the absorption intensity of the second $\pi^* \leftarrow \pi$ transition in *cis*-butadiene and for the rotational strength arising from this transition. Since the available experimental information, as well as any quantum mechanical treatment, which accounts for electron correlation or includes overlap or configuration interaction destroys the accidental degeneracy, we have not doubled the oscillator strength or the rotational strength of the second transition for the purpose of making comparisons with experimental data.

In the discussion which follows, in order to avoid confusion between the labeling of carbon atoms in the diene system, the MO's will be labeled by subscripts 2, 1, 1′, 2′ in order of increasing energy, so that the promotion of an electron in the ground electronic configuration, from the filled Ψ_1 to the unfilled Ψ_1', is the ${}^1\mathrm{B_u} \leftarrow {}^1\mathrm{A_g}$ transition in *trans*-butadiene while $\Psi_1 \rightarrow \Psi_2'$ is the forbidden ${}^1\mathrm{A_g} \leftarrow {}^1\mathrm{A_g}$ transition for the same molecular configuration. The intensities may be calculated in the usual form from dipole length matrix elements $\int \Psi_a^* \mathbf{r} \Psi_b \, d\tau$ but, as has been pointed out,[3,5] it is convenient and in this case perhaps preferable, from the point of view of consistency in the treatment of absorption intensities and rotational strengths, to utilize dipole velocity matrix elements.[12] These are related by:

$$\int \Psi_a^* \mathbf{r} \Psi_b \, d\tau = \frac{1}{E_b - E_a} \frac{h^2}{4\pi^2 m} \int \Psi_a^* \nabla \Psi_b \, d\tau$$

where $\mathbf{r}$ is a coordinate of the electron (the radius vector from the origin), m is the electronic mass, h, Planck's constant and the nabla, ∇, represents, as usual, the operator $\partial/\partial \mathbf{r}$, the Ψ_a and Ψ_b being respectively the molecular orbitals occupied by the electron in the ground and excited state configurations, in our case, Ψ_1 and Ψ_1' or Ψ_2'. In the one-electron HMO approximation, the matrix elements over molecular orbitals may be expressed as a sum of matrix elements over atomic orbitals

$$\int \Psi_a^* \nabla \Psi_b \, d\tau = \sum_{ij} c_i c_j \int \varphi_i^* \underset{ij}{\nabla} \varphi_j \, d\tau$$

for which we will use the shorthand notation $(a\,|\nabla|\,b)$; the matrix element of the longest wavelength singlet transition is thus designated $(1\,|\nabla|\,1')$ and the second singlet transition is designated $(1\,|\nabla|\,2')$. The calculation of these elements will yield the oscillator strength, f, for these transitions through

$$f = \frac{64h}{3\pi\, mc\bar{\nu}_{ab}} |(a\,|\nabla|\,b)|^2 \qquad (5)$$

where $hc\,\bar{\nu}_{ab}$ is the energy associated with the transition from the ground configuration to the excited state, $\bar{\nu}_{ab}$ being the associated frequency in units of cm^{-1}. In practice, $\bar{\nu}_{ab}$ may be approximated by the peak positions of the observed absorption band or, as in this investigation, by the frequency calculated from the HMO treatment adjusted

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[12] M. Wolfsberg, *J. Chem. Phys.* **23**, 793 (1955).

to be consistent with the experimental observations for the planar molecule. The other physical constants have their usual meaning with m representing the mass of the electron. Expressing the matrix elements in terms of the coefficients c_1 and c_2 of the atomic orbitals[13] and the values of the integrals $\int \varphi_i^* \nabla \varphi_j \, d\tau$, for the longest wavelength singlet transition we obtain

$$(1\,|\nabla|\,1') = -2c_1c_2\left[\int \varphi_1^*\nabla\varphi_2\,d\tau + \int \varphi_2^*\nabla\varphi_4\,d\tau\right] - 2c_1^2\int \varphi_2^*\nabla\varphi_3\,d\tau \qquad (6)$$

$$\equiv -2c_1c_2[\nabla_{12} + \nabla_{34}] - 2c_1^2\nabla_{23} \qquad (7)$$

In cartesian coordinates, in terms of the unit vectors **i**, **j**, **k**

$$\nabla_{12} = (\mathbf{i}\cos x_{12} + \mathbf{j}\cos y_{12} + \mathbf{k}\cos z_{12})\,\langle\nabla_{12}\rangle$$

etc. where $\cos x_{12}$ is the direction cosine of the directed line joining carbon atom 1 to atom 2 with respect to the x axis. Similarly for y and z; $\langle\nabla_{12}\rangle$ is the absolute value of the $\int \varphi_1^*\nabla\varphi_2\,d\tau$.[14] The atomic orbitals φ_i are all identical so that $\langle\nabla_{12}\rangle = \langle\nabla_{34}\rangle$. Making this substitution and eliminating terms which add to zero because of the geometry of the system, the matrix element reduces to

$$(1\,|\nabla|\,1') = -4c_1c_2(\mathbf{j}\cos y_{34} + \mathbf{k}\cos z_{34})\,\langle\nabla_{34}\rangle + 2c_1^2\mathbf{j}\,\langle\nabla_{23}\rangle \qquad (8)$$

Values of the square of this matrix element as a function of the skew angle, θ, are given in Table 2. Similarly the matrix elements, $(1\,|\nabla|\,2')$ and $(2\,|\nabla|\,1')$, for the 2nd and 3rd singlet transitions

$$(1\,|\nabla|\,2') = (c_1^2 + c_2^2)\left[\int \varphi_3^*\nabla\varphi_4\,d\tau - \int \varphi_1^*\nabla\varphi_2\,d\tau\right] \qquad (9)$$

$$(1\,|\nabla|\,2') = 2\mathbf{i}(c_1^2 + c_2^2)\cos x_{34}\,\langle\nabla_{34}\rangle \qquad (10)$$

The oscillator strengths calculated from the squares of these matrix elements values are plotted in Fig. 3. As is usual[15] in calculations of this type, the calculated oscillator strengths are rather larger than the experimentally observed values, but the ratio of the calculated intensities for the ($^1B_u \leftarrow {}^1A_g$) in the *trans* to the ($^1B_1 \leftarrow {}^1A_1$) in the *cis* configuration is 1·44, whereas from experimental observations[16] of the absorption intensities of this band in dienic compounds of the steroid and terpene types, the ratio is between 1·5 and 1·8 in quite good agreement with the calculation. It should be noted that the intensity does not reduce to zero for $\theta = 90°$, but instead to a finite value presumably expected from the now ethylene-like absorptions of the

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[13] The atomic orbitals, φ_i, for which hydrogenlike functions with the effective nuclear charge $Z_r = 3{\cdot}18$ are used in the present treatment, combine to give the following four MO's of the diene π electronic system in order of decreasing energy.

$$\begin{aligned}\Psi_2' &= c_1\varphi_1 - c_2\varphi_2 + c_2\varphi_3 - c_1\varphi_4\\ \Psi_1' &= c_2\varphi_1 - c_1\varphi_2 - c_1\varphi_3 + c_2\varphi_4\\ \Psi_1 &= c_2\varphi_1 + c_1\varphi_2 - c_1\varphi_3 - c_2\varphi_4\\ \Psi_2 &= c_1\varphi_1 + c_2\varphi_2 + c_2\varphi_3 + c_1\varphi_4\end{aligned}$$

[14] The only component of ∇_{ij} which contributes to this integral is the one directly along the bond from atom i to atom j when, as is the case for $2p_\pi$ orbitals, the symmetry is such that the value of the integral remains unchanged by reflection in the plane perpendicular to the orbital axis. This can be shown to be true even when the orbitals are not parallel, as is the case for skew angles greater than zero, provided only that the approximation made in the first paragraph of this paper, with respect to the invariance of the atomic wave functions to skew angles, is valid. Obviously, the approximation will be best for skew angles near 0°, 90° and 180°.

[15] See for example, the paper by Suzuki—Ref. 10.

[16] Unpublished observations.

TABLE 2. SQUARE OF THE INTENSITY MATRIX ELEMENTS

Skew angle $\theta°$	$(1\,|\nabla|\,1')^2$ A^2	$(1\,|\nabla|\,2')^2$ A^2
0 (*cis*)	$0{\cdot}249 \times 10^{16}$	$0{\cdot}125 \times 10^{16}$
10	0·245	0·122
20	0·234	0·121
30	0·217	0·117
40	0·199	0·112
50	0·180	0·105
60	0·164	0·097
70	0·151	0·088
80	0·144	0·077
90	0·140	0·068
100	0·168	0·055
110	0·196	0·043
120	0·227	0·032
130	0·258	0·023
140	0·289	0·015
150	0·315	0·008
160	0·337	0·004
170	0·351	0·001
180 (*trans*)	0·354	0·000

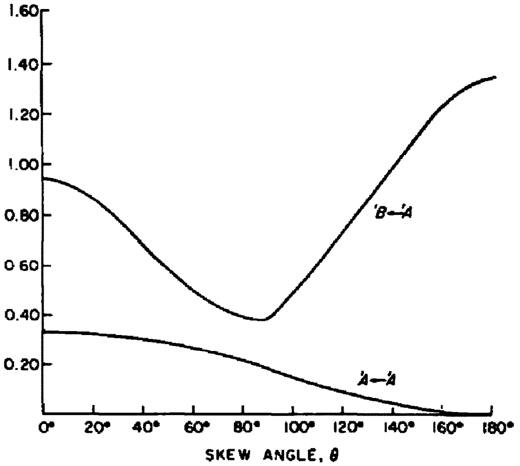

FIG. 3. Calculated oscillator strengths for the first two singlet transitions in butadiene.

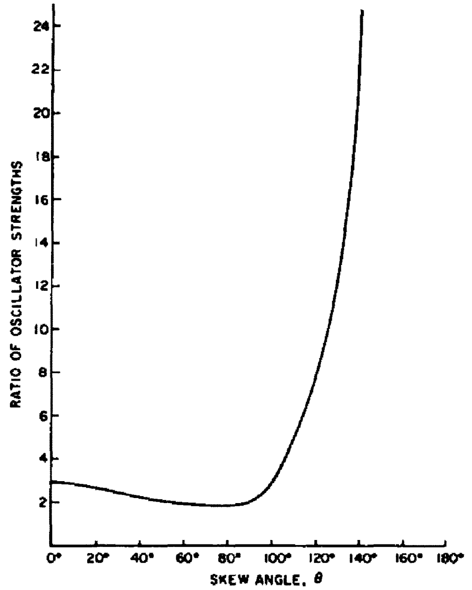

FIG. 4. Ratio of the calculated intensities of the ${}^1A \leftarrow {}^1A$ to that of the ${}^1B \leftarrow {}^1A$ transitions in butadiene.

resulting molecule. Furthermore, the ratios of the calculated intensity of the second transition, ${}^1A_1 \leftarrow {}^1A_1$ to that of the first, as plotted in Fig. 4, fits reasonably well with experimental observations.[17]

Rotational strengths

Of the matrix elements required for the calculation of the rotational strength, the magnetic dipole transition moment remains to be calculated. In the shorthand notation used above, the elements required are $(1\,|\mathbf{r} \times \nabla|\,1')$ and $(1\,|\mathbf{r} \times \nabla|\,2')$, where $\mathbf{r}$ is the radius vector from the origin of the coordinates to the electron in the molecular orbital under consideration. These matrix elements can be expressed as sums over the integrals connecting the atomic orbitals,

$$(1\,|\mathbf{r} \times \nabla|\,1') = -2c_1c_2\left[\int \varphi_1^*(\mathbf{r} \times \nabla)\,\varphi_2\,d\tau + \int \varphi_3^*(\mathbf{r} \times \nabla)\,\varphi_4\,d\tau\right] -2c_1^2\int \varphi_2^*\,(\mathbf{r} \times \nabla)\,\varphi_3\,d\tau \tag{11}$$

$$(1\,|\mathbf{r} \times \nabla|\,2') = (c_1^2 + c_2^2)\left[\int \varphi_3^*(\mathbf{r} \times \nabla)\,\varphi_4\,d\tau - \int \varphi_1^*\,(\mathbf{r} \times \nabla)\,\varphi_2\,d\tau\right] \tag{12}$$

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[17] Experimental measurement of the integrated intensities of the absorption bands of the ${}^1A_1 \leftarrow {}^1A_1$ transitions which occur at about 200–210 mμ superimposed on a band of still higher energy is somewhat difficult. But in the four compounds we have measured, the ratio of the intensity of this ${}^1B_2 \leftarrow {}^1A_1$ to that of the ${}^1A_1 \leftarrow {}^1A_1$ has a mean value of 4·8 ± 2·3; (1·8 in 1,3-cholestadiene, 3·6 in 2,4-cholestadiene, 7·7 in lumisterol and 6·3 in ergosterol). These are to be compared to calculated values of about 3·0 (Fig. 4) for the small angles expected in the diene system in these compounds. In the treatment by Allinger and Miller (Ref. 6), in which the ${}^1A_1 \leftarrow {}^1A_1$ ($N \rightarrow V_2$) is not accidentally degenerate, the calculated intensity ratio for the first two transitions is of the order of 10 for small angles.

and in turn, these integrals for $2p_\pi$ orbitals, can be expressed as

$$\int \varphi_1{}^*(\mathbf{r} \times \nabla)\, \varphi_j\, d\tau = \boldsymbol{\rho}_{ij} \times \nabla_{ij} \tag{13}$$

where $\boldsymbol{\rho}_{ij}$ are the radius vectors from the origin of coordinates to the midpoint of the bond connecting atoms i and j, so that in terms of the cartesian coordinates,

$$\boldsymbol{\rho}_{ij} = \mathbf{i}\bar{x}_{ij} + \mathbf{j}\bar{y}_{ij} + \mathbf{k}\bar{z}_{ij}$$

where $\bar{x}_{ij}$, $\bar{y}_{ij}$ and $\bar{z}_{ij}$ are the coordinates of the midpoint of the $i \rightarrow j$ bond. The magnetic moment matrix elements $(1\,|\mathbf{r} \times \nabla|\, 1')$ and $(1\,|\mathbf{r} \times \nabla|\, 2')$ in terms of these parameters are:[18]

$$(1\,|\mathbf{r} \times \nabla|\, 1') = 4c_1c_2[\mathbf{j}(\bar{z}_{34} \cos x_{34} - \bar{x}_{34} \cos z_{34}) + \mathbf{k}(\bar{x}_{34} \cos y_{34} - \bar{y}_{34} \cos x_{34})]\, \langle\nabla_{34}\rangle \tag{14}$$

$$(1\,|\mathbf{r} \times \nabla|\, 2') = 2(c_1{}^2 + c_2{}^2)[\mathbf{i}(\bar{y}_{34} \cos z_{34} - \bar{z}_{34} \cos y_{34}]\, \langle\nabla_{34}\rangle \tag{15}$$

Combining these with equations (8) and (10) and noting that $(\bar{z}_{34} \cos x_{34} - \bar{x}_{34} \cos z_{34})$ is identically zero for all values of the parameters, the rotational strengths are given by

$$R_{11}' = 16c_1{}^2c_2{}^2(\bar{x}_{34} \cos z_{34} \cos y_{34} - \bar{y}_{34} \cos x_{34})\, \langle\nabla_{34}\rangle^2 \tag{16}$$

$$R_{12}' = 4(c_1{}^2 + c_2{}^2)^2 \cos x_{34}\, (\bar{y}_{34} \cos z_{34} - \bar{z}_{34} \cos y_{34})\, \langle\nabla_{34}\rangle^2 \tag{17}$$

Values of R_{11}' and R_{12}' as a function of skew angle are plotted in Fig. 5. Several rather interesting features are observed. Most noticeable is the fact that the optical activity of the two transitions is comparable, in contradistinction to their oscillator strengths, which differ markedly. As the angle of skew increases the magnitude of the

[18] In the formalism used in this treatment, the magnetic moment matrix elements do not contain a component connecting the atomic orbitals on atoms 2 and 3, because for this case $(\boldsymbol{\rho} \times \nabla)_{23}$ reduces to zero for the C_2 symmetry of the skewed diene as well as for the C_2h and C_2v symmetries of the planar dienes. A. Moscowitz has pointed out (personal communication) that in the treatment of the absolute configuration of cycloöctene [A. Moscowitz and K. Mislow, *J. Amer. Chem. Soc.* **84**, 4605 (1962)] it is demonstrated that a contribution to the rotational strength arises from still another component connecting 2p orbitals positioned on adjacent atomic (bonded) centers, and that this contribution is proportional to $\sin 2\theta$. Thus, for $\theta = 0$ (parallel 2p orbitals of the 2,3 bond in planar butadiene) as well as for $\theta = 90°$ (perpendicular 2p orbitals of 2,3 bond in butadiene twisted to 90°), the contribution is zero. However, at intermediate angles this term contributes a component which, in the case of a twisted olefin, appears to give rise to a large optical activity. In the present case, with a longer distance between the bonds, this term would give rise to a significant but somewhat smaller contribution to the activity and creates a maximum in the absolute value of the rotational strength at about 40°. We have no evidence at present to indicate whether or not the inclusion of this term would improve or reduce the agreement with experimentally observed activities. In ethylene itself, the N → V transition which probably gives rise to a major part of this activity may be to a "perpendicular" ethylene, so as to give a rotational strength *opposite in sign* from that expected from the sense of twist in the ground state. There is no reason to believe that a similar situation would be expected with respect to the nominal single bond of the dienes, but if it did it would reduce rather than increase the absolute value of the rotational strength at intermediate angles of twist. To the extent that this would bring the calculated and experimental curves for lumisterol into better agreement, a small amount of experimental evidence is provided. However, as we have pointed out (see text), factors connected with just the geometry of the diene in lumisterol probably preclude using the experimental results at the present time, as evidence for or against this mechanism and this contribution.

rotational strength increases, somewhat more sharply for the $^1B_2 \leftarrow {}^1A_1({}^1B_u \leftarrow {}^1A_g)$ than for the $^1A_1 \leftarrow {}^1A_1({}^1A_g \leftarrow {}^1A_g)$ transition. Furthermore, the treatment predicts that the activity arising from each transition will be greatest for angles near 90°, where the system is no longer really a conjugated diene. The validity of the treatment for really large angles (say greater than 25°) is open to question; nevertheless, a diene skewed to 90° (C_2 symmetry with only a two-fold rotation axis but no plane of symmetry), should be optically active, for simple considerations will show that each of the ethylene-like chromophores will give rise to both an electric and magnetic transition moment which in the asymmetric environment of the other will combine to give a finite rotational strength. The rotational strengths are, in fact, equal in magnitude but opposite in sign for the first and second transitions of the 90° diene, so that in the simplest HMO approximation where the transition energies would collapse to the same value, the net optical activity from these transitions would be zero. To what extent the present treatment satisfactorily predicts the result is unknown because as far as is known, no experimental data exist with which to test the calculation at angles near 90°. Fortunately, for smaller angles, estimates of the angles may be made from Dreiding models[1] and at least one case exists for which a diene skew angle may be calculated from X-ray data.[19] This case is discussed below.

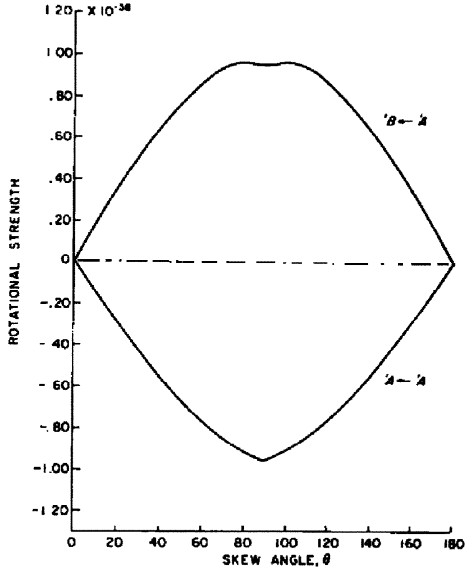

FIG. 5. Rotational strengths of the $^1B \leftarrow {}^1A$ and $^1A \leftarrow {}^1A$ transitions of butadiene.

Rotatory dispersion

The specific and the molar rotatory dispersion may be calculated from the rotational strength with the aid of experimental data on the half widths of the absorption bands either using the gaussian techniques[20] or with the aid of a Lorentz

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[19] D. C. Hodgkin and D. Sayre, *J. Chem. Soc.* 4561 (1952).

[20] A. Moscowitz, *Rev. Mod. Phys.* 32, 440 (1960).

expression for the band shape. In terms of the latter, the molar rotatory dispersion is given by

$$[\mathrm{M}(\nu)] = \frac{4800\, N\hbar^2 e^2}{m^2 c^2} \sum_i R_i \frac{\nu^2(\nu_i^2 - \nu^2)}{(\nu_i^2 - \nu^2)^2 + \nu^2 \gamma_i^2}$$

where the frequency ν, the frequency of the ith transition, ν_i, and the half-band width, γ_i, are given in cm^{-1}, e and m are respectively the charge and the mass of the electron, in c.g.s. units, N is Avogadro's number, c is the velocity of light in cm/sec and $\hbar = h/2\pi$ where h is Planck's constant. The frequencies ν_i may be chosen as the positions of the experimental absorption band maxima, as has been done in Fig. 7 for the compound lumisterol, or from the frequencies obtained from the HMO calculation as in the calculations which are plotted in Fig. 6. The very large rotational strengths associated with these transitions are seen to give rise to large values for the optical activity, a prediction which received the experimental confirmation reported in earlier papers in this series. In Fig. 7 the calculated and observed rotatory dispersions for lumisterol are plotted, with the very gratifying result that as far as it has been possible to make measurements to date, the shapes of the two curves are very similar. The absolute values, of course, are in only reasonable agreement, the discrepancies undoubtedly arising in part from deficiencies in the theoretical treatment, but also in part from the fact that the only geometrical parameter introduced in these calculations is the 8·3° skew angle calculated from the X-ray data of Hodgkin and Sayre.[19] Actually, structural values determined by X-ray crystallography lead to interbond distances which differ considerably, for at least one of the nominal double bonds, from the butadiene values used in the calculations. Also the interbond angles differ slightly from those used here. The angles and distances are listed in Table 3. The atomic wave functions as well as the matrix elements are fairly sensitive[8] to these parameters, so that better quantitative agreement can hardly be expected.

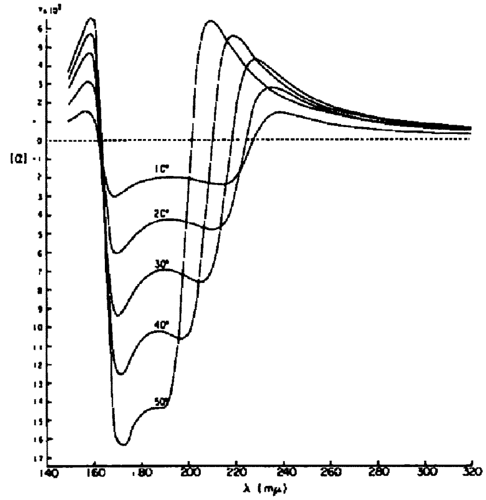

FIG. 6. Calculated rotatory dispersion of butadiene as a function of skew angle.

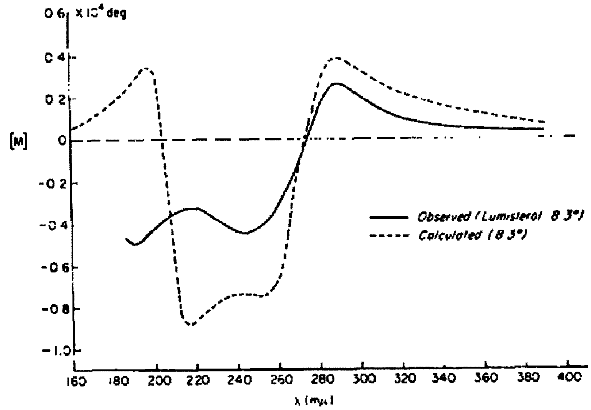

FIG. 7. Rotatory dispersion of lumisterol.

There are available a number of more refined treatments of butadiene including, among others, valence bond[21] and LCAO-SCF[22] treatments which could be utilized to obtain MO coefficients for butadiene other than, and perhaps better than those utilized here. Especially, improvement could be expected for the $^1A \leftarrow {}^1A$ transitions and some work on this is under way. At the present state, however, it would seem more important to obtain experimental structural parameters of additional optically active dienes by X-ray determination in order to put the semi-quantitative aspects of the theory to a more thorough test.

TABLE 3

	r_{56}	$r_{6,7}$	r_{78}	$\gamma_{56,67}$	$\gamma_{67,78}$
obs[a]	$1{\cdot}36_8$	$1{\cdot}51_6$	$1{\cdot}25_3$	121°42′	122°12′
calc[b]	$1{\cdot}36_9$	$1{\cdot}47_1$	$1{\cdot}36_9$	124°	124°

[a] Calculated from X-ray data of Ref. 19; distance in angstroms.
[b] The bond distances are calculated using cosine functions as described in the text.

Acknowledgments—We wish to thank Professor C. A. Coulson for an interesting discussion and valuable comments and Professor A. Moscowitz for pointing out the possibility of treating a twisted diene as an inherently dissymmetric chromophore.

[21] J. Fain and F. A. Matsen, *J. Chem. Phys.* **26**, 376 (1957).

[22] C. A. Coulson and J. Jacobs, *Proc. Roy. Soc.* **A206**, 287 (1951); H. Kon, *Bull. Chem. Soc. Japan* **28**, 275 (1955); R. G. Parr and R. S. Mulliken, *J. Chem. Phys.* **18**, 1338 (1950).