Symmetry Rules for Optical Rotation[1]

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Cotton effects arise when the electronic motions of a transition are such that parallel components of electric and magnetic moments are generated. With molecules possessing centers or planes of symmetry, strict group theoretical rules show that this cannot happen. Over the years, three different types of asymmetric interactions have been proposed to account for the generation of Cotton effects. The three mechanisms supplement one another and are not to be regarded as alternatives. The basis for the symmetry rules for the one-electron mechanism are now well understood. The other mechanisms are the coupling of electric transition moments on different groups (Kirkwood–Kuhn) and the coupling of a magnetic moment on one group with the electric moment of another. In this paper all three mechanisms are developed for a basic model system. It is shown that the signs of Cotton effects may be easily correlated with molecular conformation when the transition moment geometry is such that negative and positive energy situations are discernible by inspection. Basic equations are presented for each mechanism.

The importance of optical rotation as a tool in structural chemistry lies in its extraordinary sensitivity to molecular geometry. Most spectral properties of a molecule depend in a more or less additive fashion on the chemical groups of which it is constituted. The relative geometries of the constituent groups alter such properties as a secondary effect of greater or less sensitivity, depending on the method. (At opposite ends of the sensitivity scale are high-resolution nuclear magnetic resonance spectroscopy and molar refractivity.) Optical rotation, on the other hand, is inextricably bound to the interactions among the groups and, therefore, to molecular geometry. Apart from rare molecules which have intrinsically asymmetric chromophores, optical rotation has no primary source within the groups themselves but springs directly from their relative orientations.

When optical rotation or circular dichroism is measured in the neighborhood of an absorption band, characteristic curves of the kind shown in Figure 1 are observed. This absorption–dispersion behavior is called a Cotton effect. The two kinds of curves are related by a well-established mathematical transformation, so that in any theoretical discussion it suffices to discuss one of them. We shall consider circular dichroism, since it has the simplifying property of vanishing except within an optically active absorption band. This will also automatically restrict our discussion to the optical activity generated by a single absorption band, rather than the cumulated contributions of all bands which is required for the understanding of rotatory dispersion in transparent regions. Circular dichroism will be defined as $\Delta\epsilon = \epsilon_l - \epsilon_r$, where ϵ_l and ϵ_r are the molecular extinction coefficients for left and right circularly polarized light, respectively. Conversion to the alternative measure of circular dichroism in terms of molecular ellipticity is easily achieved by means of the formula $[M_\theta] = 2.303(4500/\pi)\Delta\epsilon$.[2]

The integrated intensity of an electronic absorption band may be shown to be directly proportional to the square of the electric dipole moment $\mathbf{\mu}$ for the transition. This is a quantity which plays the same role in quantum theory as the oscillating electric dipole in the classical theory of the absorption and emission of radiation. One principal difference is that the magnitude of the classical dipole depends on the strength of the field which induces it, whereas in quantum mechanics it is a fixed molecular quantity which depends on the wave functions of the ground and the excited states. The magnitude of the transition dipole (apart from an internal field correction) may be determined experimentally by the formula

$$D = \mu^2 \cong \frac{(2303)3hc}{8\pi^3 N \lambda_{max}} \int \epsilon d\lambda \qquad (1)$$

where h, c, N, and ϵ are, respectively, Planck's constant, the velocity of light, Avogadro's number, and the molecular extinction coefficient. If reasonably accurate wave functions are available, D may be calculated by way of the defining relation $\mathbf{\mu} = \int \psi_{excited} \cdot \mu \psi_{ground} \, d\tau$. The transition moment is a vector and has fixed orientation within a molecular group. This is easily seen in measurements of the absorption properties of oriented specimens where the extinction coefficient depends on the direction of polarization of light, $\epsilon = 3\epsilon_0 \cos^2 \theta$, where ϵ_0 is the ordinary extinction coefficient of an unoriented sample and θ is the angle between μ and the electric vector of the polarized beam of light. In optical rotation theory the directions and magnitudes of the transition moments are assumed to be known from experiment or calculation. The square of the transition moment is called the dipole strength, D, of the transition.

Just as the observed absorption of a molecule may be said to arise from its dipole strength, circular dichroism arises from an analogous quantity, the rotatory strength,

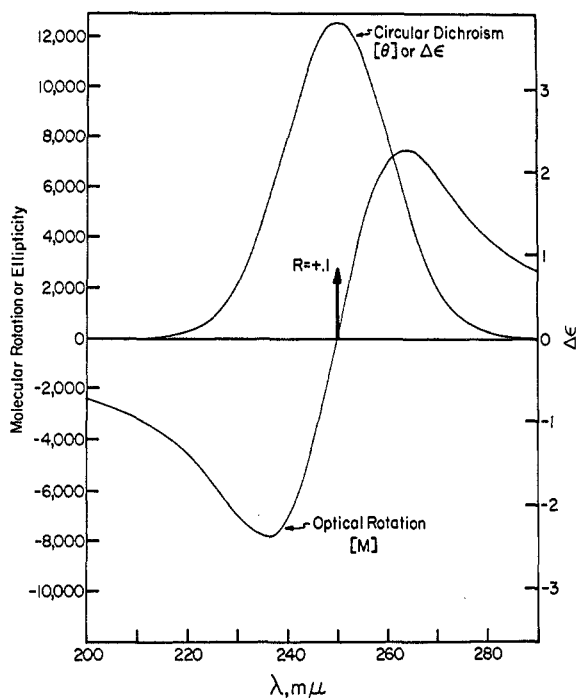(2) A. Moscowitz in "Optical Rotatory Dispersion," C. Djerassi, Ed., McGraw-Hill Book Co., Inc., 1960.

Figure 1. Circular dichroism–optical rotation curves for a Gaussian absorption band. Rotatory strength = 0.1 Debye magnetons (DM), band width = 15 mμ, λ_{max} = 250 mμ.

R, which is obtainable from the area of a circular dichroic band

$$R \cong \frac{1}{4} \frac{(2.303)3hc}{8\pi^3 N \lambda_{max}} \int \Delta\epsilon d\lambda \qquad (2)$$

Quantum mechanics shows that R = Im$[\mathbf{M} \cdot \boldsymbol{\mu}]$. The symbol Im means the "imagninary part of," $\boldsymbol{\mu}$ is the electric transition moment as before, and $\mathbf{M}$ is the magnetic dipole moment of the transition. A convenient unit for R is the Debye magneton (DM), which equals 0.92732×10^{-38} cgs unit. For molecules, in the absence of external fields, the electric moments may be taken as real vectors and the magnetic vectors as pure imaginaries. The physical significance of this difference is that they are out of phase with one another. Consequently, the rotatory strength is a pure imaginary, and its value is obtained by dropping the i in the resulting formulas. This is done in all subsequent formulas. The amplitude of the circular dichroic band thus depends on the magnitude of the electric and magnetic transition moments and on the cosine of the angle between them.

It should be noted that optical rotatory methods detect only the relative orientations of transition moments in its constituent groups, not the positions and orientations of atoms and bonds. Conversion of one kind of information into the other requires a knowledge of the orientations of the transition moments within the groups and the manner in which they are combined to give net molecular moments.

The Origin of Magnetic Transition Moments

Magnetic transition moments can usually be completely ignored in electronic spectroscopy. The es-

sential purpose of molecular theories of rotatory power is to demonstrate how these moments arise in optically active transitions and how they are coupled to electric transition moments to given nonvanishing rotatory strengths. The magnetic moment operator is given by

$$\mathbf{M} = \frac{e}{2mc}(\mathbf{r} \times \mathbf{p}) = \frac{\mathbf{r} \times e\mathbf{v}}{2c} \qquad (3)$$

where the first form shows its proportionality to angular momentum and the second to the current density $e\mathbf{v}$; m is the mass of the electron, e is its charge, $\mathbf{r}$ is distance from a selected origin, $\mathbf{p}$ is the momentum operator, and $\mathbf{v}$, the velocity operator $(= \mathbf{p}/m)$. If the quantity $e\mathbf{v}$ is replaced by its macroscopic equivalent $I d\mathbf{s}$ (where I is the current carried by a small element of conductor $d\mathbf{s}$), the classical formula for the magnetic moment of a current element is obtained. Thus, the quantum mechanical origins of electronic magnetic moments[3] are identical with those in classical mechanics: the net circulation of current about a point of space.

The magnetic transition moment is to be found by integrating between the wave functions of the states linked by the transition $M_t = \int \psi_{excited}\mathbf{M}\psi_{ground} \, d\tau$. Note that changing the order of the wave functions in this integral changes the sign of the transition moment because of the skew symmetric character of M_t. For many transitions it is possible to find an origin such that the magnetic transition moment vanishes. This is because most molecular transitions may be regarded as linear charge displacements which give electric moments but no magnetic moments if the origin is properly selected in the group. There are other cases, however, where the transition represents an intrinsic rotation of charge density. Examples are the p–p and d–d transitions in atoms and the n–π^* transitions of molecules. Here we have an intrinsic magnetic transition moment of the order of a Bohr magneton. To distinguish the two cases we put $\mathbf{r} = \mathbf{R} + \boldsymbol{\varrho}$, where $\mathbf{r}$ is the position vector of the electrons, $\mathbf{R}$ is a fixed vector from an arbitrarily selected origin to the optical center of the group under consideration, and $\boldsymbol{\varrho}$ defines the position of electrons relative to the local center. The magnetic moment is then

$$\mathbf{M} = \frac{\mathbf{R} \times e\mathbf{v}}{2c} + \frac{\boldsymbol{\varrho} \times e\mathbf{v}}{2c} = \frac{\mathbf{R} \times e\mathbf{v}}{2c} + \mathbf{m} \qquad (4)$$

where $\mathbf{m}$ is the local (intrinsic) magnetic moment operator. To simplify the discussion we assume that the transition is either purely electric (has a large linear transition velocity, $\mathbf{v}_t$) or intrinsically magnetic (has a large $\mathbf{m}_t$), but not both. As a consequence, we either have

$$\mathbf{M}_t = \mathbf{m}_t \qquad (5a)$$

(3) We are excluding electron spin from the present discussion. Magnetic moments resulting from jumps in electron spin do not usually make significant contributions to ordinary optical activity, though they must be considered in discussion of magnetic rotation.

or

$$\mathbf{M_t} = \frac{\mathbf{R} \times e\mathbf{v_t}}{2c} \tag{5b}$$

If there is but one group that need be considered, the origin may be placed in the center of the group and there is no magnetic moment from the latter formula ($\mathbf{R} = 0$). This is the case considered in treating absorption spectra. If there are two groups coupled to one another, their combination possesses a magnetic moment even though the charge displacements are locally linear within their groups. It has been shown many times that the combination of two terms of the kind in (5b) causes the position of the arbitrary origin to drop out so that the distance that matters in the final formula is $\mathbf{R_{21}} = \mathbf{R_2} - \mathbf{R_1}$, i.e., the separation of the two coupled groups (see Table I).

Condon, Altar, and Eyring were the first to appreciate the contributions of intrinsic magnetic moments to optical rotation in their one-electron theory. Kuhn and Kirkwood demonstrated the production of magnetic moments by linear electric transitions for the classical and quantal cases, respectively.

We can change eq 5 into a more familiar form by using the quantum mechanical formula for the velocity $e\mathbf{v_t} = i\omega_t\mathbf{\mu_t}$, where ω_t is the circular Bohr frequency, $(2\pi/h)(E_{ex} - E_g)$.[4] The magnetic moment is thus expressible in terms of the electric transition moment from which it originates (eq 5'). As stated above, the position of the origin cancels out in the calculation of

$$\mathbf{M_t} = \frac{i\omega_t}{2c} \mathbf{R} \times \mathbf{\mu_t} \tag{5'}$$

optical rotation, leading to the intuitively satisfactory result that only the relative positions of the groups affect the optical properties.

Symmetry Rules

There is no established language, so we will define a symmetry rule for the purposes of this paper as a simple geometrical construct which provides predictions of the sign and order of magnitude of a Cotton effect from molecular conformation and, hopefully, molecular conformation from the signs and orders of magnitudes of Cotton effects. The octant rule for ketones and the quadrant rule for the peptide link are two examples of regional symmetry rules. They permit one to assay the contribution of a perturbing group to the Cotton effect of a chromophore as being positive, negative, or vanishing, depending on whether or not the group lies in certain regions defined by the symmetry of the chromophore. To incorporate many cases of interest, we will have to generalize to the more complex case where not only the position but also the orientation of the second group is specified. Symmetry rules can only be effective for idealized cases. As a consequence, it is pointless to utilize complex models for their deriva-

tion. For this purpose we will select as a model for optical activity a molecule which has only two groups and only two electronic transitions. Even so, we will be led to three different mechanisms and three sets of symmetry rules. To apply the results to real molecules, one must assume either that other groups and transitions are unimportant or that their effects are additive. If this is not true, symmetry rules are of little value, and the origins of Cotton effects can be comprehended only on the basis of quantitative calculations. Despite their limitations, symmetry rules have great heuristic value and have provided the solution to many practical structural problems.

Three Mechanisms of Molecular Rotatory Power

With the restrictions outlined above that the model has only two electronically excited states, it is easily seen that there are only three ways in which rotatory strength can be developed by two groups. (1) Both transitions are in the same chromophore. One is magnetic and the other electric. The rest of the molecule acts as a perturbing field which partially breaks down the symmetry of the chromophore and "mixes" the two transitions. This is the one-electron or Condon, Altar, and Eyring theory. (2) Both groups have a single electric transition. Because of their proximity, these are coupled by their dipolar fields to produce a magnetic moment as discussed above. This is the Kuhn–Kirkwood mechanism. When the two groups are identical, the excited states are degenerate and the two groups participate equally in the resulting coupled transitions. This is the exciton modification of Moffitt. (3) One group has an electric transition and the other a magnetic transition. These are coupled in the molecule to give rotatory strength to both transitions. This type of interaction has long been recognized as a possibility but has been ignored by most workers in the field. It was considered by Woody and Tinoco[5] in their discussion of the optical rotation of peptide helices; it has been used in my own laboratory for several years, where it is indispensable in understanding the rotatory properties of certain cyclic peptides; it has recently been given a systematic discussion by Höhn and Weigang.[6] We shall call it the μ–m mechanism.

These possibilities are outlined in Table I, together with the formulas which give the rotatory strength for each case. The vector expressions in brackets, which depend directly on the relative geometries of the transition moments, might be called the optical factors for the transition. The symbol V is the perturbation energy between the two excited states which produces coupling with mechanisms 1 and 3 and mixing with mechanism 2. Since the energies of the states are assumed to be known, the unknown factors in the determination of the sign of a given Cotton effect are the optical factor and the potential energy V. The signs of the optical and energy factors are not independent of one another, however; reversal of the direction of a

(4) Note that this formula is also classical. For a classical harmonic oscillator the displacement is given by $x = x_0e^{i\omega t}$; therefore, $ev = edx/dt = i\omega ex = i\omega\mu$.

(5) R. W. Woody and I. Tinoco, J. Chem. Phys., 46, 4927 (1967).
(6) E. G. Höhn and O. E. Weigang, ibid., in press.

Table I

Origins of Optical Activity for a Simple Model with Two Electronic Transitions

Mechanism		Group 1 contributes	Group 2 contributes	Rotary strength
Dipole–dipole coupling	Nondegenerate	μ_1	μ_2	$R_1 = \dfrac{-V_{12}\epsilon_1\epsilon_2}{\hbar c(\epsilon_2{}^2 - \epsilon_1{}^2)}[\mathbf{R}_{21}\cdot\mu_2 \times \mu_1]$
	Degenerate (Moffitt)	μ_1	μ_2	$R_1 = \pm\dfrac{\pi}{2\lambda_1}[\mathbf{R}_{21}\cdot\mu_2 \times \mu_1]$
One electron		μ_β	Static environment	$R_\alpha = \dfrac{-V_{\alpha\beta}}{\epsilon_\beta - \epsilon_\alpha}[\mu_\beta\cdot\mathbf{m}_\alpha]$
		m_α		
μ_2–m_1		m_1	μ_2	$R_1 = \dfrac{-V_{12}}{(\epsilon_2 - \epsilon_1)}[\mu_2\cdot\mathbf{m}_1]$

transition moment changes the sign of both the optical factor and V. It is thus possible to set the optical factor arbitrarily as positive (by selecting the appropriate phase for the two transition moments) and thereafter derive all qualitative symmetry rules from the form of the potential energy of interaction of the two groups. This will be done separately for the three mechanisms.

The One-Electron Mechanism. With this mechanism the optical factor has no geometry dependence at all, since the relative orientations of the two transition moments are entirely determined by the electronic structure of the single chromophoric group. It can be shown that the form of V which is required to induce optical rotation of the chromophore depends on the symmetry of the chromophoric group itself, and a general method for determining the appropriate potential function for different symmetries has been described.[7] The results of the analysis may be paraphrased in a very simple manner: use the natural planes of symmetry of the chromophore to divide all of space into regions bounded by these planes. The contribution to R of a perturbing group changes sign when it passes from one region to another. Once the sign of one region is established (by experiment or detailed calculation), all the others follow. The importance of this mechanism lies in the fact that the lowest energy absorption bands of many molecules containing hetero atoms are essentially p–p transitions with large magnetic moments (n–π^* transitions). The d–d transitions of the transition metals also fall in this category. We shall illustrate the method for the n–π^* transitions of the peptide and ketone groups.

For the peptide group there is only one plane of symmetry, and the above considerations indicate a "planar rule." The rotatory strength changes sign when a given perturbant is switched from one side of the peptide plane to the other. We now come to a minor complication which arises frequently, namely, that the electronic orbitals involved in the transition may effectively have a higher symmetry than the group itself. This is the case of the n–π^* transition of the peptide unit. The n orbital of the CO group has a nodal surface perpendicular to the plane of the peptide group. This surface is planar in symmetrical ketones but somewhat distorted in peptides. Calculations and

experiment show that this surface plays the same role as a true symmetry plane, so that the resultant rule is a quadrant rule (Figure 2a).

With the carbonyl group there are two natural planes of symmetry, perpendicular to one another and intersecting on the C–O axis (Figure 2b). This leads to a quadrant rule. The π^* orbital has, however, a nodal surface orthogonal to both of these which comes between the C and O atoms. Inclusion of this surface is the origin of the octant rule which has been used so
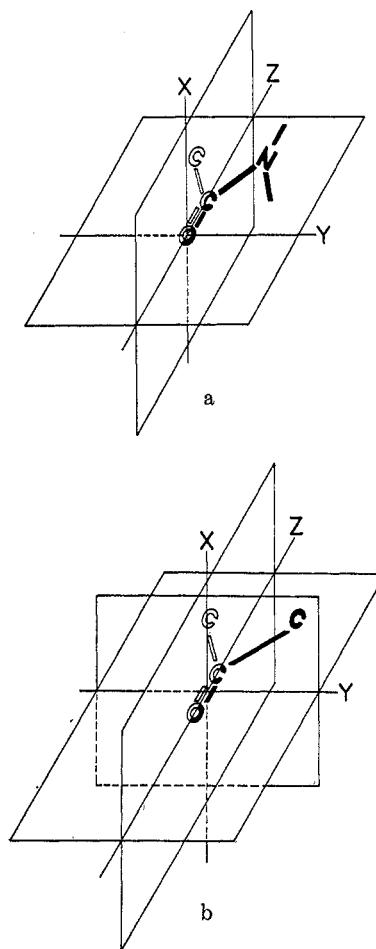

a

b

Figure 2. (a) Quadrant rule for the peptide group. The vertical surface is not planar because of the horizontal distortion of the nonbonding electrons of the C–O group. (b) Octant rule for ketones. The surface separating the C from the O atom is not planar because of the unsymmetrical distribution of the π electrons on the C and O atoms. No attempt is made to depict the deviations from planarity, since these are very sensitive to the wave functions assumed.

(7) J. A. Schellman, J. Chem. Phys., **44**, 55 (1966).

extensively. The author recently posed the question of the relative dominance of the quadrant rule and octant rule contributions, which to a certain extent depend on the selection of wave functions (basis set). Bouman and Moscowitz[8] have recently investigated this point and found not only that the octant set gives larger contributions, but also that the quadrant contributions are strongly suppressed by the assumption of delocalized n orbitals. Accordingly, they reassert the octant rule as the basic symmetry rule for ketones.

It is usually assumed that regional rules of these kinds furnish the basis for the complete interpretation of the Cotton effects of transitions with large magnetic moments. This is not necessarily true. It can easily be shown that effectively the μ–m mechanism can contribute as effectively as the one-electron mechanism. Both mechanisms should always be considered in any application to see which, if either, plays the dominant role.

The Dipole-Coupling Mechanism. For all strong transitions ($\epsilon > 1000$), dipole coupling plays a major part in the development of Cotton effects. To a first approximation the potential energy is given by the point-dipole formula

$$V = \frac{\mu_1 \cdot \mu_2}{R^3} - \frac{3(\mu_1 \cdot R)(\mu_2 \cdot R)}{R^5} \qquad (6)$$

where μ_1 and μ_2 are the transition moments in groups 1 and 2 and R is the distance between them ($R = R_2 - R_1$). We note that both the optical and the energy factors for this case depend only on the relative orientations of transition moments and not on the constitution or symmetry of the groups. The resulting symmetry rule is also independent of group structural features.

A single transition moment is represented by a double-headed arrow which indicates its oscillatory nature. When two transition moments are coupled, their relative motions become important, and the combined system is best represented by pairs of single-headed arrows which indicate the relative phases of motion (Figure 3). The only possibilities for two transition moments are "in phase" and "out of phase." Which of the two is called "in phase" depends on the convention one sets up in drawing the arrows and does not affect the interpretation. It can be shown that the rotatory strengths developed by the two phases are equal in magnitude and opposite in sign. Hence, the only thing to be decided on with the simple model is the effect of geometry on the sign of the Cotton effect of the band of lowest energy. The clue for this assignment comes from the fact that negative coupling energy is always associated with the lowest energy band. One procedure is as follows: assign the transition moment arrows for the given conformation so that the optical factor ($R_{21} \cdot \mu_2 \times \mu_1$) is positive. This means that we are dealing with a positive Cotton effect, and the only question is whether it is to be assigned to the low- or high-energy band. If the arrangement of dipoles is

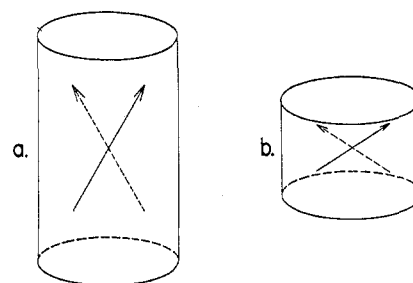(8) Bouman and Moscowitz, *J. Chem. Phys.*, in press.

Figure 3. The dipole-coupling mechanism. The optical factors are positive (right handed) in both cases. The interaction energy is positive on the left, negative on the right, indicating negative and positive Cotton effects, respectively, for the long-wavelength band.

such that the sign of the energy is obvious (as it is in the examples in Figure 3), the positive Cotton effect will be assigned to the high-energy band for positive V and to the low-energy band for negative V. It is easy to show that, if the transition moment arrows have the sense of a right-handed screw or if they appear to wind around one another in a right-handed sense, the optical factor is positive. It is negative for a left-handed sense. Precisely the same considerations apply to the case of degenerate bands ($\epsilon_1 = \epsilon_2$), but the high- and low-energy bands are now the two bands which result from the exciton splitting.

Further insight may be gained by writing out the complete expression for the rotatory strength of the long-wavelength Cotton effect. To simplify the formula, the Z axis is made to coincide with μ_1 and the Y axis perpendicular to μ_2. The vectors may then be written $\mu_1 = (0,0,\mu_{1Z})$; $\mu_2 = (\mu_{1X},0,\mu_{2Z})$; $R_{21} = (X,Y,Z)$ and the rotatory strength is given by eq 7. If μ_2 is

$$R_1 = \frac{2\pi}{hc} \frac{\epsilon_1\epsilon_2}{(\epsilon_2{}^2 - \epsilon_1{}^2)} \frac{(\mu_{1Z})^2}{R^5} [Y(R^2 - 3Z^2)\mu_{2X}\mu_{2Z} - 3(XYZ)(\mu_{2X})^2] \quad (7)$$

perpendicular to μ_1 ($\mu_{2Z} = 0$), the first term in the brackets vanishes, and the result is an octant (XYZ) rule. If the dipoles are essentially parallel (μ_{2X} much smaller than μ_{2Z}), the first term in the brackets dominates. The nodal surfaces of this term are given by $Y = 0$ and the two conical surfaces of $X^2 + Y^2 - 2Z^2 = 0$.

Electric–Magnetic Coupling. Magnetic dipoles do not couple directly with electric dipoles. However, all magnetic transitions which are associated with the orbital motions of electrons produce electric moments as well. If the chromophore has a center or a plane of symmetry, the electric moments can be dipole moments perpendicular to the magnetic moment, quadrupole moments, etc. In particular, if the transition is of the n–π^* type involving a p–p quantum jump in the atomic orbitals, the transition invariably is associated with a large quadrupole moment (Figure 4). This quadrupole moment interacts only very feebly with the radiation field, which is essentially uniform over the group, but can interact strongly with the inhomogeneous field of a neighboring dipole. We shall deal with the symmetry

rules associated with the special case of Figure 4a, which so far has provided the most important applications (carbonyl group, carboxylic acids, peptides). Extension of the method to other chromophores is straightforward if the symmetry of the excited-state wave function is known.

A simple qualitative symmetry rule for this mechanism can often be obtained as follows. Locate the magnetic moment along the positive Z axis and place the quadrupole charges as indicated in Figure 4a. This figure is appropriate for the convention that the n orbitals are p_y and the π orbitals are p_x. If the chromophore is a carbonyl group, this is the standard octant framework. In many cases the symmetry rule may be established as follows. Draw in the transition moment of the second group in such a way that $\mathbf{\mu} \cdot \mathbf{m}$ is positive. The optical factor thus represents a positive Cotton effect. If the energy of the coupled system is negative, the positive Cotton effect belongs with the long-wavelength band; if the energy is positive, it belongs to the short-wavelength band. Normally, the long-wavelength band is the n–π^* transition, but this is not necessary for the application of the rule.

The symmetry requirements on V can be formulated more quantitatively as follows. The potential energy of two arbitrary charge distributions can be developed in a series

$$V = \sum F_{ij}(q_i^{(1)}, q_j^{(2)}, \mathbf{R}) \qquad (8)$$

where q_i is the ith moment of charge in group 1 ($q_0 =$ total charge, q_1 is a vector representing the three components of dipole moment, q_2 is a tensor representing five components of quadrupole moment, etc.) and $\mathbf{R} = (\mathbf{R}_2 - \mathbf{R}_1)$ is the distance between two conveniently chosen origins in the groups. The moments are defined relative to the two origins. The F_{ij} are functions characteristic of each type of interaction.[9] Equation 6 is the appropriate function for $i = j = 1$. For the interaction of a quadrupole on group 1 with a dipole on group 2, we require the term for $i = 2, j = 1$, which is

$$V = F_{21} = \frac{\mathbf{R} \cdot \mathbf{Q}_1 \cdot \mathbf{\mu}_2}{R^5} - \frac{5}{2}\frac{(\mathbf{R} \cdot \mathbf{Q}_1 \cdot \mathbf{R})(\mathbf{R} \cdot \mathbf{\mu}_2)}{R^7} \qquad (9)$$

$\mathbf{Q}_1$ is the quadrupole tensor or diadic of group 1 and is most easily represented by the matrix shown in (10).

$$\mathbf{Q} = \begin{bmatrix} 2Q_{XX} - Q_{YY} - Q_{ZZ} & 3Q_{XY} & 3Q_{XZ} \\ 3Q_{XY} & 2Q_{YY} - Q_{XX} - Q_{ZZ} & 3Q_{YZ} \\ 3Q_{XZ} & 3Q_{YZ} & 2Q_{ZZ} - Q_{XX} - Q_{YY} \end{bmatrix} \qquad (10)$$
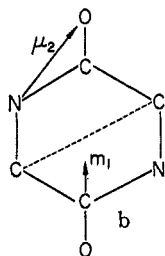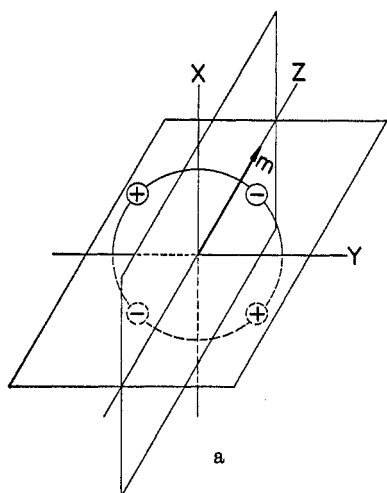

a

b

Figure 4. (a) The quadrupole and magnetic moment associated with an n–π^* transition. The magnetic moment is a pure imaginary, indicating it is out of phase with the quadrupole which is depicted. (b) The electric and magnetic dipoles involved in the μ–m mechanism for diketopiperazines (see text). The coupling takes place by way of the interaction of μ_2 with the quadrupole associated with m_1.

A formula equivalent to the above has recently been given by Höhn and Weigang.[6] The components of quadrupole moment are calculated by means of

$$Q_{\alpha\beta} = -e \int \psi_{ex} \alpha \beta \psi_g d\tau \qquad (\alpha, \beta = X, Y, Z)$$

where e is the protonic charge. For the XY quadrupole of Figure 4, the matrix takes the form

$$\mathbf{Q} = 3\begin{bmatrix} 0 & Q_{XY} & 0 \\ Q_{XY} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

so that

$$\mathbf{R} \cdot \mathbf{Q}_1 \cdot \mathbf{\mu}_2 = 3Q_{XY}(X\mu_{2Y} + Y\mu_{2X})$$

$$\mathbf{R} \cdot \mathbf{Q}_1 \cdot \mathbf{R} = 3Q_{XY}(2XY)$$

(9) The multipolar expansion of two arbitrary charge distributions is difficult to find in the literature in the form most useful to the present application. We give the first eight terms of eq 8.

$$V = \frac{e_1 e_2}{R} \text{ (charge-charge)} + \frac{e_2 \mathbf{R} \cdot \mathbf{\mu}_1 - e_1 \mathbf{R} \cdot \mathbf{\mu}_2}{R^3} \text{ (charge-dipole)} +$$

$$\left[\frac{\mathbf{\mu}_1 \cdot \mathbf{\mu}_2}{R^3} - 3\frac{(\mathbf{\mu}_1 \cdot \mathbf{R})(\mathbf{\mu}_2 \cdot \mathbf{R})}{R^5}\right] \text{ (dipole-dipole)} + \frac{1}{2R^5}\left[(e_1 \mathbf{R} \cdot \mathbf{Q}_2 \cdot \mathbf{R}) + \right.$$

$$\left. (e_2 \mathbf{R} \cdot \mathbf{Q}_1 \cdot \mathbf{R})\right] \text{ (charge-quadrupole)} + \left[\frac{\mathbf{R} \cdot \mathbf{Q}_1 \cdot \mathbf{\mu}_2 - \mathbf{R} \cdot \mathbf{Q}_2 \cdot \mathbf{\mu}_1}{R^5} - \right.$$

$$\left. \frac{5}{2}\frac{(\mathbf{R} \cdot \mathbf{Q}_1 \cdot \mathbf{R})\mathbf{R} \cdot \mathbf{\mu}_2 - (\mathbf{R} \cdot \mathbf{Q}_2 \cdot \mathbf{R})\mathbf{R} \cdot \mathbf{\mu}_1}{R^7}\right]$$

(dipole-quadrupole) + higher terms

$\mathbf{Q}$ and $\mathbf{R}$ are as defined in text.

and

$$V = \frac{3Q_{XY}}{R^7} \left[R^2(X\mu_{2Y} + Y\mu_{2X}) - \right.$$

$$\left. 5XY(\mu_X X + \mu_Y Y + \mu_Z Z) \right]$$

$$= \frac{3Q_{XY}}{R^7} \left[(R^2 - 5X^2)Y\mu_{2X} + \right.$$

$$\left. (R^2 - 5Y^2)X\mu_{2Y} - 5(XYZ)\mu_{2Z} \right] \quad (11)$$

There is no single symmetry rule in general. If the transition moment of group 2 happens to coincide with one of the coordinate axes, one of the three terms can be used to define the regional rule for this component. Notice that the Z component follows an octant rule.

The complete formula for the rotatory strength of the n–π* transition may be written as eq 12. It should

$$R_1 = -\frac{1}{\epsilon_2 - \epsilon_1} \frac{3Q_{XY}}{R^7} \left[(R^2 - 5X^2)Y\mu_{2X} + \right.$$

$$\left. (R^2 - 5Y^2)X\mu_{2Y} - 5(XYZ)\mu_{2Z} \right]\mu_{2Z}m_{1Z} \quad (12)$$

be noted that the convention for the coordinate system is contained in this formula.

Application of the Rules

Since all the results given above depend on a highly oversimplified model for an optically active molecule, the question arises as to their applicability to real molecular problems. The fact is that the mechanisms which have been discussed supply all the ingredients for sophisticated calculations, which consist in the compounding of all three mechanisms for as many groups and excited states as are necessary or feasible. Indeed, if nondegenerate first-order perturbation theory is applicable, one may use the formulas given above for each pair of transitions, and the results of the full calculation are obtained by simply summing the contributions. If it can be decided that a given interaction dominates the development of a Cotton effect, then a simple symmetry rule is applicable.

If the Cotton effect arises from a band with a large electric dipole and no magnetic dipole and if there are no magnetic transitions in the near-ultraviolet, the situation is considerably simplified, since it is a fairly safe assumption that the rotatory strength is developed largely from the dipole–dipole coupling mechanism. If, further, there is another strong band in the molecule of not-too-different energy, it is often a good approximation to assume that the rotatory strength is dominated by its interaction with this band. This is especially appropriate if the two bands are degenerate or nearly degenerate. In this case a rotatory strength "couplet" is developed (Figure 5) which is easily detected experimentally and whose sign can be determined from the symmetry rule for dipole–dipole coupling. Our group has undertaken a long series of investigations of dipeptides, diamides, and diketopiperazines in which such couplets are easily recognizable and have provided clear guidelines for conformational analysis.
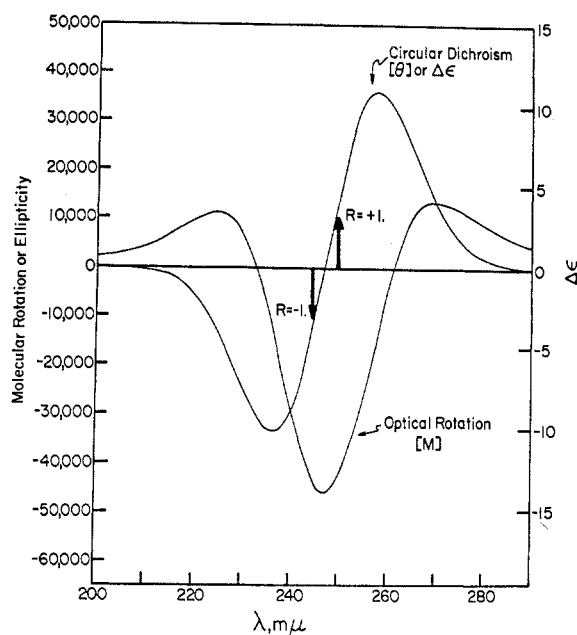

Figure 5. A rotatory strength "couplet" is a characteristic form of dispersion which arises when two Cotton effects of equal but opposite rotatory strength lie less than a band width from one another. In the figure, $R_1 = 1$ DM, $\Delta_1 = 15$ mμ, $\lambda_1 = 250$ mμ; $R_2 = -1$ DM, $\Delta_2 = 15$ mμ, $\lambda_2 = 245$ mμ. The contrast with Figure 1 makes the observation of a couplet an extremely effective way of detecting small band splittings.

Another case is when all the transitions of the second group are far down in the ultraviolet. The totality of bands can often be represented by an effective transition moment with the direction of the principal polarizability of the group and an energy which is obtainable from the dispersion of the polarizability (or, preferably, the dispersion of the optical anisotropy). It was Kirkwood who first showed that the totality of transition moments of distant absorption bands enters into this mechanism as the anisotropy of the group polarizability.

If the transition under consideration is weak and essentially magnetic, it is usually allowable to ignore the μ–μ coupling entirely. The Cotton effect is then usually treated by the one-electron mechanism and by regional rules such as the octant rule. If this procedure is permissible, the symmetry rules are both powerful and simple, since the form of the regional rules is determined entirely by the electronic properties of the chromophore. The remainder of the molecule supplies only a static asymmetric environment. A combination of simple symmetry arguments, plus a few experiments with molecules of known structure, is often sufficient to establish the division into regions and the signs to be attached to each region for a given type of perturbation. This lack of dependency on the details of quantum mechanical calculations provides an especially solid basis for conformational analysis.

A difficulty with this approach is that it ignores the possibility of coupling of the magnetic dipole with strong transitions outside the group. It is not difficult to show, either by general considerations or by detailed

calculations, that the two mechanisms can produce equally large effects. Recent studies in our laboratory bring this out rather clearly. P. M. Bayley and V. Madison have investigated theoretically the rotatory strength of the n–π^* Cotton effect of dipeptides as a function of the two conformational angles φ and ψ. In such a study it is possible to follow the relative contributions of the one-electron mechanism and the μ–m mechanism as a function of conformation. In the α-helical conformation the two mechanisms enforce one another, as was also concluded by Woody and Tinoco.[5] In certain cases where the two peptide units are twisted back toward one another, the one-electron mechanism is by far the major contributor, but in other cases, such as diketopiperazines, where the peptide units are "back-to-back," the entire rotatory strength is calculated to come from the μ–m mechanism.

The situation is represented in Figure 4b which depicts the coupling of the magnetic moment of the n–π^* transition of one peptide unit with the electric moment of the π–π^* transition of the other. (In quantitative calculations, both units simultaneously play both roles.) As can be seen, the optical factor $[\mathbf{\mu}_2 \cdot \mathbf{m}_1]$ is sizable. Glycine diketopiperazine is planar and is not optically active. This arises from the vanishing of V in eq 11. (Put both μ_{2x} and X equal to zero.) With substituted diketopiperazines the molecule is folded along the dotted line of the figure. The energy of interaction of a quadrupole and a dipole at the distances characteristic of these molecules is in the range of 100 cm^{-1}, which is a small coupling energy. It achieves great importance, however, because of the smallness of $\epsilon_2 - \epsilon_1$ in these compounds (see formula in Table I). The n–π^* and π–π^* transitions are almost degenerate. We conclude that this mechanism and the one-electron mechanism are equally important for peptide Cotton effects and that their relative dominance is a matter of geometry, not of principle. Similar conclusions have recently been expressed by Höhn and Weigang[6] for the carbonyl n–π^* transition.

In conclusion, it may be stated that symmetry rules will continue to be used for the settlement of conformation questions and for establishing the mechanism of production of Cotton effects. These rules can only be applied effectively by keeping in mind their implicit assumption of an interaction mechanism. Consequently, a careful evaluation of mechanism must precede the application of a symmetry rule.