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The $n \to \pi^*$ Optical Activity of Chiral Carbonyl Compounds Predicted to be Optically Inactive by the Octant Rule

Chin-yah Yeh and Frederick S. Richardson

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, USA

The "one-electron" model of $n \to \pi^*$ optical activity in chiral carbonyl compounds is carried to second-order in perturbation theory and the results are applied to systems which are predicted by the octant rule to yield zero $n \to \pi^*$ optical activity. It is shown that second-order contributions to the $n \to \pi^*$ rotatory strength lead to sector rules which are qualitatively different from those obtained from first-order contributions. Inclusion of three-way interactions involving the carbonyl chromophore and two different extrachromophoric perturbing groups (or atoms) lead to second-order contributions to the rotatory strength which can account for the $n \to \pi^*$ optical activity in chiral carbonyl systems predicted to be optically inactive by the conventional quadrant and octant rules. These results are shown to be in agreement with the conclusions derived by Ruch and Schönhofer from a purely algebraic theory of molecular chirality.

Key words: Chiral carbonyl compounds - Optical activity in chiral carbonyl compounds

1. Background

The "octant rule" [1, 2] has found wide application in the interpretation of optical activity associated with the $n \to \pi^*$ transition of dissymmetric carbonyl compounds. According to this rule the sign of the Cotton effect (CE) associated with the $n \to \pi^*$ transition (centered near 290 *nm*) is determined by the spatial distribution of substituent atoms or groups about the symmetric carbonyl chromophore. In its simplest application, the octant rule states that the sign of the contribution which a given perturbing (or substituent) atom at point $P(x, y, z)$ makes to the CE will vary as the sign of the product (xyz) of its coordinates (measured with respect to a coordinate origin centered at or near the mid-point of the carbonyl C=O bond). It is presumed that the extrachromophoric perturbing groups contribute *additively* to the $n \to \pi^*$ CE and that the relative magnitudes of their individual contributions are determined in large part by: 1) their distance from the carbonyl group; 2) their intrinsic chemical or electrical nature; and, 3) their proximity to nodal surfaces defined by the "octant rule function", $F(x, y, z)$.

The "octant rule function", $F(x, y, z)$, partitions the space surrounding the carbonyl chromophore into eight regions (or sectors) defined by: 1) the two symmetry planes of an isolated carbonyl chromophore of idealized C_{2v} symmetry; and, 2) a third plane which bisects and is perpendicular to the C=O bond. If these three planes are taken to define a Cartesian coordinate system, then the sign of $F(x, y, z)$ is determined by the sign of (xyz) and $F(x, y, z) = 0$ on each plane. For alkyl perturbing groups and halogen perturbers (excepting fluorine atoms), the sign of $F(x_p, y_p, z_p)$ - where (x_p, y_p, z_p) refers to the Cartesian positional coordinates of perturber p - determines the sign of the contribution made by perturber group p to the $n \rightarrow \pi^*$ CE.

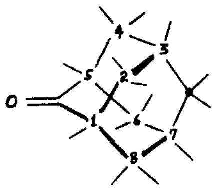
The simplest and most direct rationalization of the "octant rule" for optically active ketones is provided by the so-called "one-electron" theory of molecular optical activity [2–5]. This theory is based on a perturbation model in which the carbonyl chromophore is assumed to zeroth-order to possess exact C_{2v} symmetry and optical activity is generated in the carbonyl transitions via electrostatic interactions between the carbonyl group and dissymmetrically arranged extrachromophoric perturbing groups. To first order in this model $n \rightarrow \pi^*$ optical activity obtains if the interaction potential transforms as the pseudoscaler (A_2) irreducible representation of the C_{2v} point group. To first order, only pairwise interactions between the carbonyl group and perturbing groups are considered so that the overall interaction potential may be written as a sum over individual perturbing moieties (taken as atoms *or* groups), $V = \Sigma_{p=1}^{N} V_p$. The sign and magnitude of the contribution made by perturber p to the $n \rightarrow \pi^*$ CE is determined, then, by V_p. Schellman [6] has shown that the simplest pseudoscalar function (in C_{2v}) which will satisfy the symmetry requirements for generating optical activity in the "one-electron" model applied to dissymmetrically perturbed ketones has an xy-dependence upon perturber positional coordinates (where the z-axis has now been taken to be directed along the carbonyl C=O bond). This suggests that a "quadrant rule" rather than an "octant rule" is the minimum sector rule applicable to the carbonyl chromophore. According to Schellman's one-electron treatment [6] the second simplest pseudoscalar function which will lead to $n \rightarrow \pi^*$ optical activity has the xyz-dependence required of the octant rule.

Although both the "quadrant rule" and the "octant rule" are subsumed in the simple one-electron model for carbonyl $n \rightarrow \pi^*$ optical activity, it is not yet clear when one may expect one or the other of these rules to be most reliable and accurate. The applicability of one or the other will, in general, depend upon the nature and nodal properties of the wave functions associated with the $n \rightarrow \pi^*$ transition and upon the extent to which the carbonyl chromophore retains its C_{2v} microsymmetry in the molecule as a whole [3].

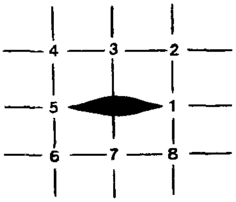
Two crucial features of both the quadrant rule and the octant rule as rationalized on the basis of the one-electron perturbation model (carried to first order) are: 1) the additivity of contributions made by individual perturber groups to the $n \rightarrow \pi^*$ CE; and, 2) the absence of contributions made by groups or atoms located on the respectively defined nodal planes. These features are responsible for the ease with which the quadrant and octant rules may be applied. However, it is also these features which lead to a recognition of the basic limitations and incompleteness of the rules (and the underlying theory). Examples of systems for which application of the octant (or quadrant) rule leads to erroneous conclusions with regard to predicting the absence or presence of carbonyl $n \rightarrow \pi^*$ optical activity may be illustrated as follows:

a) Chiral Systems Predicted to be Achiral

Let us consider the fused ring system, adamantanone, as shown in **Ia.** and **Ib.**

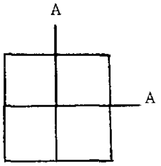


Ia. Side View



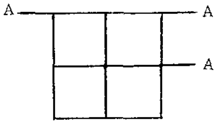
Ib. Front View

Derivatives of adamantanone with substituents either located on nodal planes (as in **II**) or attached symmetrically with respect to nodal planes (as in **III**) are predicted to be optically inactive by the octant rule (as well as the quadrant rule). However, both structures **II** and **III** are chiral and can exist in optically active enantiomeric forms.



II

($A \neq H$)

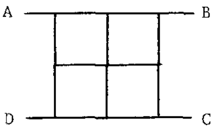


III

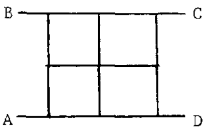
b) Chiral Mixtures Predicted to be Achiral

According to the octant and quadrant rules the $n \rightarrow \pi^*$ CEs in structures **IVa** and **IVb** should be equal in magnitude but opposite in sign. An equimolar mixture of these two geometrical isomers, then, should be optically inactive. More rigorously, since **IVa** and **IVb** are *not* optical isomers and are not enantiomeric, there is no reason to expect that an equimolar mixture of them will be optically inactive (in contradistinction to the predictions based on the octant rule).

As was pointed out by Ruch and Schönhofer in their algebraic treatment of chirality phenomena [7-9], sector rules such as the quadrant and octant rules may not be

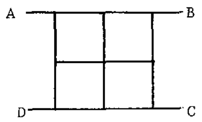


IVa



IVb

"qualitatively complete". In their consideration of substituted adamantanone structures of the general type,



Ruch and Schönhofer [8] showed that the appropriate "chirality function" was of the form,

$$\begin{aligned}\chi(A,B,C,D) &= \lambda_A - \lambda_B + \lambda_C - \lambda_D \\ &\quad + (\mu_A - \mu_C)(\mu_B - \mu_D)(\mu_A - \mu_B + \mu_C - \mu_D), \end{aligned} \tag{1}$$

where λ_p and μ_p represent physical (or chemical) properties unique to the substituent group p. If χ vanishes, then the system is optically inactive. If $A \equiv C$ and/or $B \equiv D$, then the polynomial term in μ_p vanishes and the terms in λ_p provide a qualitatively complete representation of the "chirality function". The terms in λ_p lead to a quadrant (or half-octant) rule in this special case. Assuming that $A \not\equiv B \not\equiv C \not\equiv D$, we see that it is the multiplicative term in μ that allows differentiation between the chiralities of structures **IVa** and **IVb**. In general, Ruch's chirality functions include both *additive terms* (such as those in λ) and *multiplicative terms* (such as those in μ).

In a physical sense, the *additive* terms in Ruch's chirality functions represent pairwise interactions between the chromophoric group and a single nonchromophoric ligand moiety of the molecular structures and the *multiplicative* terms account for three-way and other many-body interactions involving the chromophoric group and at least two nonchromophoric groups. In treating dissymmetric ketone systems by the one-electron model carried to first order in perturbation theory, only pairwise interactions between the carbonyl moiety and individual perturber groups are included and contributions to the $n \rightarrow \pi^*$ CE are *additive* with respect to the perturber groups. If, however, the basic one-electron model is carried to higher orders of perturbation theory, then multiplicative terms enter into the final expressions for $n \rightarrow \pi^*$ rotatory strength (which governs the sign and magnitude of the associated CE).

2. One-Electron Model to Second Order in Perturbation Theory

For an electronic transition, $0 \rightarrow n$, localized on the carbonyl chromophore the rotatory strength expressed to second-order in the chromophore-perturber group pairwise interaction potential (V) is given by:

$$\begin{aligned}R_{0n} &= \mathrm{Im}[P_{0n}^{(0)} \cdot M_{n0}^{(0)} + P_{0n}^{(0)} \cdot M_{0n}^{(1)} + P_{0n}^{(1)} \cdot M_{n0}^{(0)} + P_{0n}^{(1)} \cdot M_{n0}^{(1)} \\ &\quad + P_{0n}^{(0)} \cdot M_{n0}^{(2)} + P_{0n}^{(2)} \cdot M_{n0}^{(0)}] \end{aligned} \tag{2}$$

where $P_{0n}^{(i)} = \langle 0 | \hat{\mu} | n \rangle \equiv$ electric dipole transition moment of ith order in V, $M_{n0}^{(i)} = \langle n | \hat{m} | 0 \rangle \equiv$ magnetic dipole transition moment of ith order in V, and

$\mathrm{Im}(a + ib) = b$. For the $n \to \pi^*$ transition of a carbonyl chromophoric group with exact C_{2v} symmetry, $P_{0n}^{(0)} = 0$, and Eq. (2) reduces to:

$$R_{0n} = \mathrm{Im}[P_{0n}^{(1)} \cdot M_{n0}^{(0)} + P_{0n}^{(1)} \cdot M_{n0}^{(1)} + P_{0n}^{(2)} \cdot M_{n0}^{(0)}], \tag{3}$$

or,

$$R_{0n} = R_{0n}^{(1)} + R_{0n}^{(2)} \tag{4}$$

The first-order rotatory strength, $R_{0n}^{(1)} = \mathrm{Im}\, P_{0n}^{(1)} \cdot M_{n0}^{(0)}$, is just that quantity traditionally dealt with in the perturbation models of carbonyl $n \to \pi^*$ optical activity and leads to the usual quadrant and octant rules [2, 6]. This term has linear dependence upon the interaction potential V and receives contributions from the individual extrachromophoric perturber groups *additively*. For this term to be non-zero, at least one component of the pairwise interaction potential must transform as a pseudoscalar function under the symmetry operations of the C_{2v} point group.

The second-order rotatory strength displayed in Eq. (4) exhibits quadratic dependence upon the interaction potential, V, and allows for three-way interactions involving two perturber groups and the chromophoric group. The interaction potential may be written in the following general form:

$$V = \sum_p V_p(A_1) + \sum_p V_p(A_2) + \sum_p V_p(B_1) + \sum_p V_p(B_2) \tag{5}$$

where $V_p(\Gamma_\alpha)$ denotes a pair-wise interaction between perturber p and the chromophoric group which transforms as the Γ_α irreducible representation of the C_{2v} point group. In this representation each pairwise potential function is presumed to be written in such a form that it provides a basis for one of the four irreducible representations of the C_{2v} point group. Now the signs and relative magnitudes of the second-order rotatory strength terms in Eq. (3) will depend upon the following quantity.

$$U = \sum_p \sum_{p'} [V_p(A_1) V_{p'}(A_2) + V_p(B_1) V_{p'}(B_2)]$$

where the summations are taken over all perturber groups in the extra-chromophoric environment. We note first that U transforms as a pseudoscalar function under the symmetry operations of the C_{2v} point group. Secondly, we note that the terms $V_p(A_1) V_{p'}(A_2)$ must lead to quadrant and/or octant behavior (or, more generally, to sector rule behavior similar to that derived for the first-order rotatory strengths). Thirdly, we note that for $p = p'$ the terms $V_p(B_1) V_p(B_2)$ also lead to sector rule behavior which is similar to that derived for the first-order rotatory strengths. Finally, when $p \neq p'$ the $V_p(B_1) V_{p'}(B_2)$ terms represent contributions to the $n \to \pi^*$ rotatory strength which depend upon the simultaneous perturbative actions of two *different* perturber groups on the carbonyl chromophore. These latter terms may contribute even when the individual perturber groups do not satisfy the symmetry or spatial requirements dictated by the quadrant or octant rules.

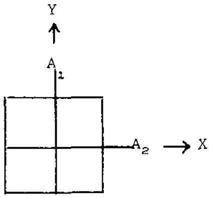
The collection of perturber-chromophore interaction terms giving rise to quadrant or octant behavior (to first *and* second order) is given by:

$$\sum_{p} V_p(A_2) + \sum_{p}\sum_{p'} V_p(A_1)V_{p'}(A_2) + \sum_{p} V_p(B_1)V_p(B_2)$$

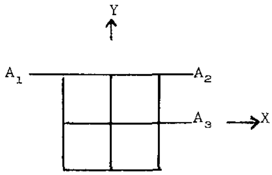
(first-order) (second-order)

It is important to note that although all of these terms lead to similar partitionings of the extrachromophoric environment (that is, similar sector rules) it is *not* readily apparent that the signs to be assigned to the various sectors for the purpose of predicting rotatory strength contributions will be the same for all terms. That is, the space about the carbonyl chromophore will be partitioned similarly with respect to the number and location of nodal surfaces. However, the signs associated with individual sectors may be different for different terms depending upon which of the zeroth-order chromophoric states are being coupled or mixed. Signs cannot be assigned to specific sectors in the absence of a detailed model of the chromophoric electronic states and their associated spectroscopic properties.

Examples of structures for which only terms of the $V_p(B_1)V_{p'}(B_2)$ type will predict a net $n \rightarrow \pi^*$ rotatory strength are given by **V** and **VI**.



V



VI

In these structures (adamantanone derivatives), A_1, A_2, and A_3 are presumed to be identical chemically and the subscripts are merely book-keeping labels. According to the usual quadrant and octant rules, neither of these structures should exhibit $n \rightarrow \pi^*$ optical activity. However, for structure **V** the $V_p(B_1)V_{p'}(B_2)$ term takes the form:

$$\sum_{p}\sum_{p' \neq p} V_p(B_1)V_{p'}(B_2) = V_1(B_1)V_2(B_2) + V_1(B_2)V_2(B_1)$$

Now, expressing V_1 as a polynomial in the Cartesian coordinates of perturber group $A_1(x_1, y_1, z_1)$ and V_2 as a polynomial in the Cartesian coordinates of perturber group $A_2(x_2, y_2, z_2)$, and retaining only terms up to and including order two, we may write:

$$V_1(B_1) = V_1(x_1) + V_1(x_1 z_1) = 0, \qquad V_1(B_2) = V_1(y_1) + V_1(y_1 z_1),$$

$$V_2(B_1) = V_2(x_2) + V_2(x_2 z_2), \qquad V_2(B_2) = V_2(y_2) + V_2(y_2 z_2) = 0.$$

Finally, the quantity governing the second-order perturbed $n \rightarrow \pi^*$ rotatory strength may be written as:

$$V_1(y_1)V_2(x_2) + V_1(y_1)V_2(x_2 z_2) + V_1(y_1 z_1)V_2(x_2)$$

In a physical sense, the substituent A_1 is effective in destroying the xz-plane of symmetry in the C_{2v} chromophore, while the substituent A_2 is effective in destroying the yz-plane of symmetry. Acting together, they render the system optically active. Within the limits of the "one-electron" model (as described by Schellman [6]) this necessary three-way interaction between A_1, A_2, and the carbonyl chromophore is accounted for only when the perturbation treatment is carried to at least second-order (in V).

It is easy to show (using procedures similar to that given for structure **V** above) that the $V_p(B_1)\, V_{p'}(B_2)$ terms can account for differences in the optical activity of **IVa** and **IVb** and for the nonvanishing optical activity of the $n \rightarrow \pi^*$ transition in structure **VI.**

3. Higher Orders

It is possible of course to carry the one-electron model of carbonyl $n \rightarrow \pi^*$ optical activity to higher orders in perturbation theory and this will yield yet more terms in the rotatory strength expressions and will give additional kinds of partitionings within the space occupied by the extrachromophoric groups. However, the perturbation expansion carried to second order yields a "qualitatively complete" representation in so far as every kind of chiral perturbation which can generate optical activity in a C_{2v} chromophore is at least minimally included. Higher order terms may contribute quantitatively to the optical activity, but they will not generate any new sources of chiral perturbations.

Perturbation expansions carried to just second order (within the one-electron model of molecular optical activity) may not provide "qualitatively complete" expressions for the rotatory strengths of electronic transitions in chromophores having symmetries other than C_{2v}. For example, the perturbation treatment of D_{4h} type chromophores in chiral systems must be carried to fifth order before "qualitative completeness" is achieved [10].

4. Discussion

The principal purpose of this communication was to show how the simple "one-electron" perturbation model, when carried to second order, can account for the $n \rightarrow \pi^*$ optical activity in chiral carbonyl compounds predicted to be optically inactive by the conventional quadrant and octant rules. The second-order representation leads to terms in the $n \rightarrow \pi^*$ rotatory strength expression which arise from three-way interactions involving the carbonyl chromophore and *two* extrachromophoric perturber groups. This stands in contrast to the usual first-order "one-electron" model of carbonyl $n \rightarrow \pi^*$ optical activity in which only pairwise chromophore-perturber interactions are represented. There exist several kinds (structural types) of chiral carbonyl compounds whose $n \rightarrow \pi^*$ optical activity is predicted to be zero on the basis of the "one-electron" model carried to first order. Extension of the model to second order and inclusion of three-way perturber-chromophore-perturber interactions leads to a nonvanishing $n \rightarrow \pi^*$ optical activity for these systems and a set of sector rules somewhat different from the quadrant and octant rules. In the absence of detailed calculations it is not possible to estimate the magnitudes of the second-order contributions to the $n \rightarrow \pi^*$ rotatory strengths of the systems considered in this study. For chiral carbonyl compounds in which both first- and second-order terms may contribute to the $n \rightarrow \pi^*$ rotatory strength, it is not at all clear that the first-order terms should always dominate and should determine the relevant sector rules.

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References

1. Moffitt, W., Woodward, R. B., Moscowitz, A., Klyne, W., Djerassi, C.: J. Am. Chem. Soc. **83**, 4013 (1961)
2. Moscowitz, A.: Advan. Chem. Phys. **4**, 67 (1961)
3. Bouman, T. D., Moscowitz, A.: J. Chem. Phys. **48**, 3115 (1968)
4. Kauzmann, W. J., Walter, J. E., Eyring, H.: Chem. Rev. **26**, 339 (1940)
5. Condon, E. U., Altar, W., Eyring, H.: J. Chem. Phys. **5**, 753 (1937)
6. Schellman, J. A.: J. Chem. Phys. **44**, 55 (1966)
7. Ruch, E.: Accounts Chem. Res. **5**, 49 (1972)
8. Ruch, E., Schönhofer, A.: Theoret. Chim. Acta (Berl.) **19**, (1970)
9. Snatzke, G., Snatzke, F. in: Fundamental aspects and recent developments in optical rotatory dispersion and circular dichroism, Ciardelli, F., Salvadori, P. Eds. Chapt. 3.5. London: Heyden and Son Ltd. 1973
10. Richardson, F. S.: unpublished work

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