J. Am. Chem. Soc. **1983**, *105*, 79-84

concentration of zwitterionic intermediate may be small and a proton transfer involving this intermediate can be rate determining, as in the case of methyl 3-(2-aminophenyl)propionate;[16] i.e., the reaction will be similar to a bimolecular reaction rather than the intramolecular reaction of V. With esters I and II nucleophilic attack involves formation of a 5-membered ring so that the reactions are sterically more favorable than those of VII. Electron withdrawal from the carbonyl of II will also enhance nucleophilic attack. While the pK_a of the nucleophile is low, breakdown of the tetrahedral intermediate formed from I and II is rate determining, although I must lie close to the borderline for a change in rate-determining step.

Acknowledgment. This work was supported by research grants from the National Institutes of Health.

Registry No. I, 35613-44-6; I HCl, 49851-36-7; II, 82571-36-6; II HCl, 82571-38-8; V, 61088-45-7; 2-oxindole, 59-48-3; methyl phenylacetate, 101-41-7; (*o*-nitrophenyl)acetatic acid, 3140-52-1; methyl (*o*-nitrophenyl)acetate, 30095-98-8; 2,2,2-trifluoroethyl (*o*-nitrophenyl)-acetate, 82571-37-7; 2,2,2-trifluoroethanol, 75-89-8; methanol, 67-56-1; trimethylamine, 75-50-3; 2-methoxyethylamine, 109-85-3; Tris, 77-86-1; *N*-ethylmorpholine, 100-74-3; imidazole, 288-32-4; carbonate, 463-79-6; morpholine, 110-91-8; 2-(*N*-morpholino)ethanesulfonic acid, 4432-31-9; cacodylate, 75-60-5; malonate, 141-82-2; acetate, 64-19-7; glycolate, 79-14-1.

Optical Activity of β,γ-Enones: A Quantitative Chirality Rule

P. H. Schippers and H. P. J. M. Dekkers*

Contribution from the Department of Theoretical Organic Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands. Received March 15, 1982

Abstract: Generally the relation between molecular geometry and circular dichroism (CD) of an electronic transition is made via the rotational strength R, which contains the scalar product of the magnetic ($\bar{\mu}$) and electric ($\bar{r}$) dipole moment in that transition. It is assumed that with β,γ-enones the optical properties of the $n \rightarrow \pi^*$ transition derive from a perturbation of the local $n_{CO} \rightarrow \pi^*_{CO}$ transition in the carbonyl chromophore by the remaining part of the molecule. Since the $n_{CO} \rightarrow \pi^*_{CO}$ transition is strongly magnetic dipole allowed (along the C=O bond, z direction) but electric dipole forbidden, the rotational strength in β,γ-enones probes the z component of the admixed extraneous transition moment $\bar{r}$, whose magnitude is measured by the square root of the dipole strength D. It appears advantageous to express the optical activity as $R/(|\bar{\mu}|{\cdot}D^{1/2}) = \cos\theta$ since then it no longer contains the magnitude of $\bar{r}$ and is a direct measure of the angle θ between the C=O bond and the direction of the admixed electric dipole transition moment. For a series of rigid β,γ-enones, a surprisingly high correlation is found between $\cos\theta$ and the cosine of the angle ξ between the C=O bond and the C_γ=C_β bond: to a good approximation, $n \rightarrow \pi^*$ optical activity and enone structure are quantitatively related by the equation $\cos\theta = -(\text{sign } xy)\cdot(\cos\xi)$, where x and y are the coordinates of the olefinic C_β atom in the ketone reference frame and xy is positive in the upper-right quadrant. This transparant relationship indicates that the unique radiative properties of the $^1n\pi^*$ state of β,γ-enones derive from a small ethylenic $\pi_{CC}\pi^*_{CC}$ contamination in the carbonyl $n_{CO}\pi^*_{CO}$ state, which might be electrostatically brought in. Within limits, the chirality rule offers a quantitative tool in the study of β,γ-enone stereochemistry, as is illustrated for some examples.

In many respects $n \rightarrow \pi^*$ transition in β,γ-enones is an intriguing subject. Whereas position, width, and shape of the absorption band closely resemble those of the $n \rightarrow \pi^*$ band in saturated ketones, its intensity is often enhanced by more than an order of magnitude. With chiral enones, this increased dipole strength is sometimes, but not invariably, accompanied by enhanced circular dichroism (CD).[1] From the theoretical point of view, the situation with β,γ-enones is at the same time more simple and more complex than with saturated ketones. On the one hand, the large enhancement of intensity and optical activity in the $n \rightarrow \pi^*$ transition points to the ethylenic group as major perturber, suggesting a description in terms of a two-chromophore model. On the other hand, the ethylenic π orbitals (π_{CC}, π^*_{CC}) overlap those of the homoconjugated carbonyl bond (n_{CO}, π^*_{CO}), which renders the use of a simple electrostatic model admixing $\pi_{CC} \rightarrow \pi^*_{CC}$ character to the $n_{CO} \rightarrow \pi^*_{CO}$ transition questionable. Indeed, many investigators have invoked overlap effects as the main source of the enhanced optical activity[2-4] and absorption intensity.[5,6]

With respect to structure-CD relationship, the work of Moscowitz et al.[3] is of prime importance. These authors put forward a rule that for β,γ-enones of a specified (C=O)—(C=C) geometry (class A in their notation) allows the prediction of the sign of the longest wavelength Cotton effect: Due to n_{CO}–π_{CC} overlap the contribution to the $n \rightarrow \pi^*$ Cotton effect of a C=C group, situated in a rear octant, is consignate with the ketone octant rule, and for class A geometry, it is so large that it solely determines the sign of the CD (generalized octant rule, GOR). In the theoretical formalism underlying the GOR, the $n \rightarrow \pi^*$ electric-dipole transition moment was to result from both $\pi_{CC} \rightarrow \pi^*_{CC}$ and charge-transfer transitions, but the latter were judged to be relatively unimportant.[3] Later this was substantiated by MO-CI calculations[7] that showed that in the $n \rightarrow \pi^*$ transition of bicyclo[2.2.2]octenone the calculated dipole and rotational strengths derive exclusively from a $\pi_{CC}\pi^*_{CC}$ contamination in the $n_{CO}\pi^*_{CO}$ state which is electrostatically brought in.

Recently a major contribution in the field was given by Kuritani et al.[8] To explain the Cotton effect observed with some β,γ-enones, these authors explicitly took the view that the effects originate in the electrostatic admixture of $\pi_{CC}\pi^*_{CC}$ character in the $n\pi^*$ state. On this basis they proposed a new sector rule, complementing the GOR, claimed to predict correctly the sign of the $n \rightarrow \pi^*$ CD of β,γ-enones.[8]

Our interest in the subject was prompted when we observed for β,γ-enones large differences between the optical activities in

---

(1) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1-74.

(2) Ballard, R. E.; Mason, S. F.; Vane, G. W. *Trans. Faraday Soc.* **1963**, *59*, 775-782. Grinter, R.; Mason, S. F.; Vane, G. W. *Ibid.* **1964**, *60*, 285-290.

(3) Moscowitz, A.; Mislow, K.; Glass, M. A. W.; Djerassi, C. *J. Am. Chem. Soc.* **1962**, *84*, 1945-1955.

(4) Cookson, R. C.; MacKenzie, S. *Proc. Chem. Soc., London* **1961**, 423-424.

(5) Labhart, H.; Wagnière, G. *Helv. Chim. Acta* **1959**, *42*, 2219-2227.

(6) Murrell, J. N. "The Theory of the Electronic Spectra of Organic Molecules"; Methuen: London, 1963; pp 164-168.

(7) Moscowitz, A.; Hansen, A. E.; Förster, L. S.; Rosenheck, K. *Biopolym. Symp.* **1964**, *1*, 75-89.

(8) Kuritani, H.; Shingu, K.; Nakagawa, M., *Tetrahedron Lett.* **1980**, 529-530.

0002-7863/83/1505-0079$01.50/0

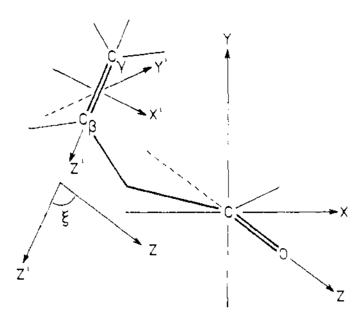


Figure 1. Reference frame for carbonyl group (x, y, z) and ethylenic group (x', y', z') in β,γ-enones. The C_α atom connecting the moieties lies in the xz plane; the y' axis is perpendicular to the plane of the ethylenic group. ξ denotes the angle between z and z' axes.

absorption and fluorescence, pointing to distorted $^1n\pi^*$ states.[9] To evaluate these, we needed a, preferably quantitative, relationship between optical activity and molecular structure. Since only qualitative relations had been given,[3,8,10] we thought it worthwhile to investigate whether such a quantitative relation could be found.

Procedure and Results

The connection between molecular geometry and circular dichroism is laid via the electronic rotational strength R, which is obtained from experiment by integrating the CD associated with the electronic transition over all vibrational fine structure. From theory, R equals the scalar product of the magnetic ($\vec{\mu}$) and electric dipole moment ($\vec{r}$) associated with the transition (eq 1). A further

$$R = \mathrm{Im}\ \vec{\mu}\cdot\vec{r} \qquad (1)$$

quantity of interest is the electric dipole strength D, which can be found from the integrated absorption band and whose theoretical expression is given by eq 2.

$$D = |\vec{r}|^2 \qquad (2)$$

Perhaps the most basic question on β,γ-enone optical activity concerns the state from which the n → π^* transition acquires intensity. If it is $\pi_{CC}\pi^*_{CC}$, i.e., if the result calculated for bicyclo[2.2.2]octenone may by extended to other enones, one may—because of the intimate connection of $\pi_{CC} \rightarrow \pi^*_{CC}$ transition moment with C=C geometry—rely on the existence of a transparent CD-molecular structure relationship. Following common practice, we might have tried to establish from theory a correlation between n → π^* rotational strength and β,γ-enone geometry. Ultimately such a procedure would amount to finding in the perturbed wave function for the $^1n\pi^*$ state (eq 3) both nature (ψ_i) and amount (λ_i) of admixed states.

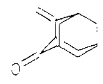
$$n_{CO}\pi^*_{CO} + \sum_i \lambda_i\psi_i \qquad (3)$$

In our opinion, however, in the case at hand a different approach may be useful. For the n → π^* transition of β,γ-enones, one may safely assume that the magnetic-dipole transition moment $\vec{\mu}$ predominantly results from the local carbonyl $n_{CO} \rightarrow \pi^*_{CO}$ transition; i.e., $\vec{\mu}$ is large, is directed along the carbonyl bond (z-axis, Figure 1), and is constant in a series of enones. Since the $n_{CO} \rightarrow \pi^*_{CO}$ transition is electric dipole forbidden, R probes the z component of the admixed extraneous transition moment $\vec{r}$, whose magnitude is measured by D. Unlike D and R, however, the quantity $R/D^{1/2}$ (eq 4) no longer contains the magnitude of

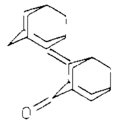
$$\frac{R}{D^{1/2}} = \frac{|\mathrm{Im}\ \vec{\mu}|\cdot|\vec{r}|\cdot(\cos\theta)}{|\vec{r}|} = |\vec{\mu}|\cdot(\cos\theta) \qquad (4)$$

the admixed electric dipole transition moment, i.e., it is independent of the strength of the coupling and offers a direct measure for the angle θ between the C=O axis and $\vec{r}$. Now suppose the n → π^* transition in β,γ-enones derives its intensity and optical activity only from coupling, whatever its nature, with the $\pi_{CC} \rightarrow \pi^*_{CC}$ transition. Since the latter is polarized along the C=C bond (z' direction, Figure 1), this renders the angle θ equal to the angle ξ between the C=O and C=C bond (cf. Figure 1). As a result, a powerful quantitative relationship between optical activity and molecular structure would be obtained: for β,γ-enones the structural parameter ξ follows directly from the observed $R/D^{1/2}$ value.

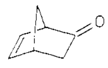
To test the validity of the relation and the various underlying assumptions, we have searched the literature for examples of chiral β,γ-enones with known absolute configuration that satisfy the following criteria: (a) The circular dichroism and absorption spectra, or at least $\Delta\epsilon_{max}$ and ϵ_{max}, of the n → π^* band are known. (b) A strong interaction exists between the carbonyl group and the homoconjugated C=C bond, as manifest from a considerably enhanced ($\epsilon_{max} > 50$, say) n → π^* oscillator strength, being due to the presence of only one, at the most alkyl substituted, ethylenic bond. (c) A reliable value of ξ can be obtained; i.e., the molecule is rigid with respect to the mutual orientation of the C=C and C=O functional groups. To best ensure this, we have chosen only those β,γ-enones where the mutual orientation of both groups is fixed by a bridged ring system.



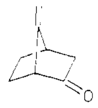
1



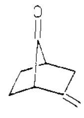
1a



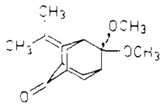
2



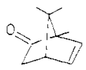
3



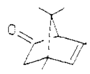
4



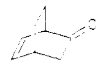
1b



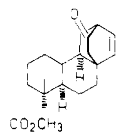
2a



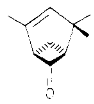
2b



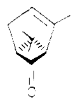
5a



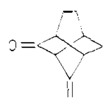
5b



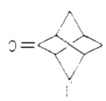
6a



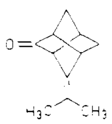
6b



7



8a



8b

9

The resulting compounds and their chiroptical data are contained in Table I. For convenience, the data in the table all refer to the same absolute configuration, i.e., that for which the product of coordinates xy of the C_β atom (Figure 1) is negative. In case the measurements pertain to the enantiomer, this is indicated by an E in the first column of the table. Where possible, we have cited data obtained in paraffinic solvents. For a few compounds data were available in various solvents; they appeared not to differ essentially. For compounds **1**, **1a**, **2**, **3**, and **4**, the values of R and D were determined by integrating the CD and absorption spectra available from our own measurements.[9] The literature data of the other compounds usually include $\Delta\epsilon_{max}$ and ϵ_{max} values only, and in those cases we have followed another procedure to obtain R and D. Guided by the experience that the bandwidths of the n → π^* absorption and circular dichroism are rather constant in the series of saturated ketones, we have assumed a

---

[9] Schippers, P. H.; van der Ploeg, J. P. M.; Dekkers, H. P. J. M. *J. Am. Chem. Soc.*, following paper in this issue.

[10] Lightner, D. A.; Jackman, D. E.; Christiansen, G. D. *Tetrahedron Lett.* **1978**, 4467-4470.

Table I. Absorption and CD Data and Values of the Spectroscopic (θ) and Geometric (ξ) Angles for β,γ-Enones

enone	$\Delta\epsilon$, L mol^{-1} cm^{-1} (λ_{max}, nm)	ϵ_{max}, L mol^{-1} cm^{-1} (λ_{max}, nm)	solvent	$R \times 10^{40}$,[a] cgs	$D \times 10^{38}$,[b] cgs	cos θ[c]	θ, deg	ξ, deg	cos ξ	ref
1	2.55 (305)	110 (295)	*n*-heptane	6.22	14.0	0.13	83	90	0	9
1a	2.58 (306)	401 (306.5)	*n*-heptane	6.29	50.9	0.07	86	90	0	9
1b	3.25 (302)	380 (298)	ethanol	8.3	49	0.09	85	90	0	32
2	18.8 (306)	277 (308)	*n*-heptane	51.1	36.0	0.67	48	55	0.57	33
2a, E	18.5 (309)	303 (307)	cyclohexane	50.0	39	0.63	51	55	0.57	34
2b	19.9 (309)	325 (310)	cyclohexane	53.7	42	0.65	49	55	0.57	34
3	7.55 (307)	140 (295)	*n*-heptane	20.5	17.9	0.38	68	70	0.34	9
4, E	5.69 (303)	143 (298)	*n*-heptane	15.2	18.7	0.28	74	70	0.34	9
5a	12.0 (298)	122 (296)	isooctane	29.0	16	0.57	55	60	0.50	7
5b	9.25 (306)	131 (296)	cyclohexane	23.6	17	0.45	63	60	0.50	34
6a	4.87[d] (293)	102 (293)	chloroform	12.4	13	0.27	74	75	0.26	35
6b, E	4.71[d] (296)	126 (295)	chloroform	12.0	16	0.24	76	75	0.26	35
7, E	5.7 (302.5)	278 (303)	isooctane	14.5	36	0.19	79	85	0.09	37
8a, E	5.4 (301)	445 (300.5)	isooctane	13.8	57	0.14	82	90	0	37
8b, E	4.1 (298.5)	616 (298)	isooctane	10.5	79	0.09	85	90	0	38
9	−3.14 (306)	86.8 (306)	isooctane	−8.0	11	−0.19	101	105	−0.26	16

[a] Values were obtained as follows: **1**, **1a**, and **2–4** by integrating the experimental CD (cf. ref 9); **5a**, from ref 7; all other compounds except **2a** and **2b** by multiplying $\Delta\epsilon_{max}$ by 2.55×10^{-40} (see text); **2a** and **2b**, because of the close resemblance with **2**, we have used the factor found for **2** (2.70×10^{-40}). [b] **1**, **1a**, and **2–4** from integrated absorption curves (cf. ref 9); all other compounds by multiplying ϵ_{max} with the conversion factor 12.9×10^{-40} (see text). [c] Calculated with eq 4 after correcting R and D for solvent effects with the Lorentz factor, taken equal to $^4/_3$.[12,13] The value of $|\vec{\mu}|$ is taken to be 1.10×10^{-20} cgs.[14,15] [d] The CD values from ref 35 were corrected for incomplete optical purity (**6a**, 27.7%; **6b**, 24.6%) according to the α_D values given in ref 36.

similar regularity with the β,γ-enones. Accordingly, we have converted ϵ_{max} ($\Delta\epsilon_{max}$) values into D (R) values by multiplying with 12.9×10^{-40} (2.55×10^{-40}),[11] the latter factors holding within 2% (5%) for **1–4**. The resultant values of R and D are given in columns 5 and 6 of the table.

The quantity of main interest here, cos θ, is obtained by application of eq 4 to the R and D values, corrected for solvent effects by means of a Lorentz factor, taken equal to $^4/_3$,[12,13] using 1.10×10^{-20} cgs as the numerical value for $|\vec{\mu}|$. The latter value is found from an analysis of the spectra of the model ketone *trans*-β-hydrindanone.[14,15] Table I also gives the angle ξ between the direction of the C→O bond and the $C\gamma \rightarrow C_\beta$ bond in the various enones (cf. Figure 1). Since no experimental structural data were available, we have measured this angle from Dreiding molecular models. The results from the table are reproduced in Figure 2, where the cosine of the spectroscopic angle θ is plotted against that of the geometric angle ξ, to facilitate the discussion.

The discussion of the results from the figure may best proceed in two stages.

(i) Since cos θ equals $R/(D^{1/2} \cdot |\vec{\mu}|)$, where only the numerator is a signed quantity, the various points in the figure relate the sign of R with cos ξ. Hence we conclude that all enones having cos $\xi \geq 0$ possess a positive rotational strength. As mentioned above, we have chosen the enantiomers with negative xy for C_β, which in practice implies that the data refer to that absolute configuration where the product of the x and y coordinates of the midpoint of the C=C bond is also negative; i.e., all these enones satisfy the generalized octant rule.

Though not strictly rigid, we have included in the series of enones also **9**. Its value of ξ, as listed in the table and figure, is obtained from the conformation where both rings are flat. Although the numerical value of cos ξ contains a large uncertainty, it appears from the Dreiding model that the sign of cos ξ is negative for all feasible conformations ($115° \leq \xi \leq 95°$). The reason for including **9** is apparent from its position in the figure: although the C=C group is in a positive octant, the rotational strength is negative, and the compound thus violates the GOR. In this, it is the only well-documented molecule of its kind that we are aware of.

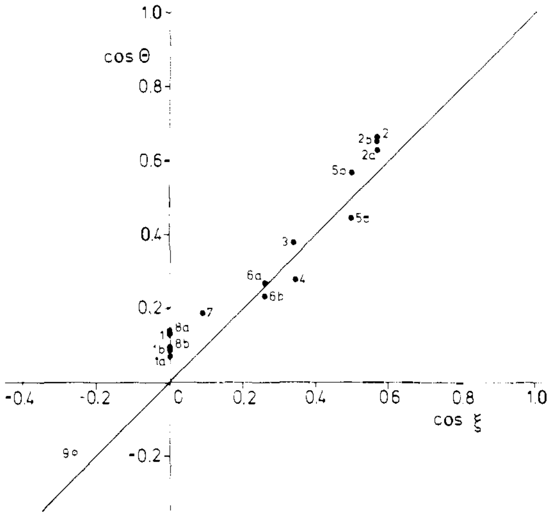


Figure 2. Plot of the spectroscopic quantity cos θ against the cosine of the angle ξ between C=O and C_γ=C_β bond for the enones **1–8b** (●) and **9** (○).

Thus all data in the figure are consistent with the conclusion that the sign of the circular dichroism of the n → π* band in β,γ-enones is governed by the contribution of the C=C group and is consignate with the octant rule when cos ξ is positive and dissignate when cos ξ is negative. This in fact is the symmetry rule for β,γ-enones recently put forward by Kuritani et al.[8] to explain the anomalous behavior of the CD of **9**. They substantiated their rule from model calculations on **9**[8,16] that were based on the assumption that only the ethylenic $\pi_{CC} \rightarrow \pi^*_{CC}$ transition is mixed in the carbonyl $n_{CO} \rightarrow \pi^*_{CO}$ transition. With their explanation of the anomalous sign of the CD of **9**, Kuritani et al.[8] took a different view than Lightner et al.,[10] who suggested that it might be explained from a consignate contribution of C=C that is overruled, however, by opposite contributions from other perturbing groups in the molecule.

(ii) Turning to a quantitative interpretation, we note a significant correlation between the points in the figure. For a more demanding comparison, the figure also contains the line cos ξ = cos θ, which should hold exactly when both n → π* absorption

---

(11) See, however, footnote *a* to Table I.

(12) Weigang, O. E. *J. Chem. Phys.* **1964**, *41*, 1435–1441.

(13) Höhn, E. G.; Weigang, O. E. *J. Chem. Phys.* **1968**, *48*, 1127–1137.

(14) (a) Emeis, C. A.; Oosterhoff, L. J. *J. Chem. Phys.* **1971**, *54*, 4809–4819. (b) Emeis, C. A. Ph.D. Thesis, Leiden, 1968.

(15) The same value was found for dimethyldibenzsuberone; cf.: Robinson, G. M.; Weigang, O. E. *J. Am. Chem. Soc.* **1969**, *91*, 3709–3714.

(16) Kuritani, H.; Iwata, F.; Sumiyoshi, M.; Shingu, K. *J. Chem. Soc., Chem. Commun.* **1977**, 542–543.

and circular dichroism are exclusively due to the ethylenic $\pi_{CC} \rightarrow \pi^*_{CC}$ transition or, more precisely, to z'-polarized (Figure 1) transitions. Although the points in Figure 2 show a tendency to lie above this line, a significant correlation of the set of points with the theoretical line is unmistakable. This leads to several conclusions. To the extent that the correlation holds, there exists for the β,γ-enones a simple empirical sector rule relating not only sign but also magnitude of $R/D^{1/2}$ to molecular geometry (cos ξ). The nature of this sector rule implies that the radiative properties of the n → π^* transition in β,γ-enones are to a surprisingly large extent determined by the admixture of z'-polarized transitions. This justifies the extension of the relationship into the lower left quadrant of the figure and underlines the relevance of cos ξ as a principal factor in determining R.

In constructing Figure 2, we have selected the enantiomers with $xy < 0$. If we had included both enantiomers, the figure would have contained a second set of points along the extra line $\cos\theta = -\cos\xi$. Such an extension of Figure 2 leads to a more general formulation of the chirality rule:

$$\cos\theta = -(\text{sign } xy)\cdot(\cos\xi) \qquad (5)$$

where x and y are the cartesian coordinates of C_β in the reference frame of Figure 1. We note that eq 5 implies quadrant (and not octant) behavior; with the molecules studied there is no indication that a third nodal plane, i.e., the sign of a z coordinate, should come into play. Apart from the latter aspect, eq 5 is the quantitative version of the symmetry rule of Kuritani et al.[8]

Discussion of the Chirality Rule

Even when disregarding the errors made in evaluating ξ and $R/(D^{1/2}\cdot|\vec{\mu}|)$ (apart from those mentioned before, these include in particular the neglect of effects due to conformational and vibrational freedom), there are several reasons why one simply cannot expect all points in Figure 2 to coincide with the theoretical line. This, namely, would imply that the radiative properties of the $^1n\pi^*$ state of β,γ-enones result from interaction of the carbonyl $^1n\pi^*$ state solely with z'-polarized states of only the ethylenic group. The situation of course is not as simple as that.

To illustrate this, we consider the enone as the result from the replacement in a saturated parent ketone of a $-H_2C_\beta{-}C_\gamma H_2-$ fragment by a $-HC_\beta{=}C_\gamma H-$ group (endocyclic enone) or of a $>C_\beta H_2$ moiety by a $>C_\beta{=}C_\gamma H_2$ group (exocyclic enone). It is convenient to describe the optical activity of ketones as arising from an interaction between the achiral carbonyl chromophore with chirally disposed and mutually not interacting extrachromophoric groups. More specifically, as interaction we choose that between the electric quadrupole moment associated with the $n_{CO} \rightarrow \pi^*_{CO}$ transition in the chromophore and electric dipole transition moments (or, what amounts to the same, polarizabilities) in the various extrachromophoric groups.[13] When the parent compound in our example is achiral, e.g., because it has a symmetry plane σ, the resultant enone has a rotational strength always consisting of two terms. The first is due to the $>C_\beta{=}C_\gamma H_2$ group and the second to the $>C_{\beta'}H_2$ group. Moreover, even if the first term in R dominates the second one, all transitions in the C=CH$_2$ group may contribute to R and not only the z'-polarized ones. Speaking in terms of polarizabilities, not only the component $\alpha_{z'z'}$ but also $\alpha_{x'x'}$ and $\alpha_{x'y'}$ may play their part. Since in the theory the contribution of an isotropic polarizability leads to a rotational strength that shows octant behavior,[13] this might explain why in Figure 2 the points tend to cluster above the line that holds if only z' polarization were in question.

With enones constructed from a chiral parent ketone, the situation is more complex. Here all chirally disposed groups contribute to the optical activity, and the observed rotational strength contains a portion not arising from the C=C moiety (background rotational strength). As a first approximation, this background may be assumed to equal the rotational strength of the parent ketone.

For the majority of the enones contained in Figure 2, the parent ketone is either achiral (**1**, **1a**, **1b**, **4**, **5a**, **9**), or has a small CD, as known from experiment (**2**,[17] **2a**,[18] **2b**,[18], **3**[17]) or estimated from the octant rule (**6a**, **6b**). Accordingly, in these enones the contribution of background to R probably is low. For the parent ketones of **7** and **8a,b**, $\Delta\epsilon$ values of -4.5[19] and -3.2[20] have been reported. Correction for the background CD, i.e., subtraction of these $\Delta\epsilon$ values from the actual $\Delta\epsilon$ values of **7** and **8a,b** prior to calculating cos θ, would result in somewhat lower cos θ values: +0.04 (**7**), +0.06 (**8a**), and +0.02 (**8b**), all quite close to the theoretical line $\cos\theta = \cos\xi$. The octant rule predicting a positive CD for the parent of **5b**, an explanation of the discrepancy between **5a** and **5b** in terms of a background effect appears less adequate. A similar discrepancy arises with **3** and **4**. Since these compounds are even more rigid than the bicyclo[2.2.2]octenones, here an effect of substitution on ξ seems highly unlikely. Therefore the different positions of **3** and **4** in the figure underline the approximate nature of the simple $\cos\theta = \cos\xi$ relationship. Anyhow, since the spread in cos θ for enones with identical ξ does not exceed the average deviation from the theoretical line for enones with different ξ, we accept it as it is.

Although the enones we have studied include but a restricted number of possible C=O···C=C arrays, Figure 2 contains examples from all classes defined earlier[3,10] in the discussion of the chiroptical properties of β,γ-enones. We take this as an indication that eq 5 may be generalized as to enone geometry.

In conclusion, for simple β,γ-enones, where n → π^* intensity is enhanced and where background rotational strength is small or can be corrected for, the chirality rule offers a tool for the quantitative study of their stereochemistry. Since eq 5 is derived for ketones with a homoconjugated carbon–carbon double bond, its application to other systems is not warranted. For example, eq 5 probably is not adequate for cases where the double bond is heterosubstituted or forms part of a larger π system. However, in view of the close resemblence of the n → π^* transition in aldehydes and ketones, we are confident that eq 5 applies to aldehydes as well.

Comparison with Dynamic Coupling Model

The chirality rule (eq 5) implies that the n → π^* transition in β,γ-enones essentially has z' polarization, and this in turn strongly suggests that the carbonyl $n_{CO}\pi^*_{CO}$ state is contaminated by the ethylenic $\pi_{CC}\pi^*_{CC}$ state. This means that the wave function for the enone excited state is given by

$$\psi = n_{CO}\pi^*_{CO} + \lambda\pi_{CC}\pi^*_{CC} \qquad (6)$$

With the wave function 6, the chirality rule requires[21] that λ is positive for all structures shown in Figure 2. We have examined whether the obvious dynamic coupling model,[22] which quite successfully explains the chiroptical properties of bicyclo[2.2.2]octenone,[7] can account for this.

In this model, λ has the form

$$\lambda = \frac{\langle n_{CO}\pi^*_{CO}|V|\pi_{CC}\pi^*_{CC}\rangle}{\Delta E} \qquad (7)$$

where ΔE is the energy separation of the locally excited $n_{CO}\pi^*_{CO}$ and $\pi_{CC}\pi^*_{CC}$ states and the matrix element represents the electrostatic interaction of the transition charge densities. In evaluating the matrix element, we have used a method due to London[24]

---

(17) Thomas, H. T. T.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 6292–6298.

(18) Cookson, R. C. *Proc. R. Soc. London, Ser. A* **1967**, *297*, 27–39.

(19) Naemura, K.; Nakazaki, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 888–892.

(20) Nakazaki, M.; Naemura, K.; Arashiba, N. *J. Chem. Soc., Chem. Commun.* **1976**, 678–679.

(21) As discussed, θ is the angle between magnetic ($\vec{\mu}$) and electric ($\vec{r}$) dipole moments in the enone's n → π^* transition, i.e.; $\cos\theta = \vec{e}_\mu\cdot\vec{e}_r$, where $\vec{e}$ denotes a unit vector. With the wave function 6 and the choice of axes given in Figure 1, the dot product can be rewritten as $\pm\vec{e}_z\cdot\vec{e}_{z'}$, which from definition equals $\pm\cos\xi$. Here the + sign, applying for λ positive, gives rise to the line drawn in Figure 2, the − sign, applying for λ negative, to the extra line mentioned before. Since it is the enantiomers with $xy < 0$ that correlate with the line $\cos\xi = +\cos\theta$, it follows that they all must have positive λ.

(22) For a recent discussion, see ref 23.

(23) Hansen, A. E.; Bouman, T. D. *Adv. Chem. Phys.* **1980**, *44*, 545–644.

(24) London, F. *J. Phys. Chem.* **1942**, *46*, 305–316.

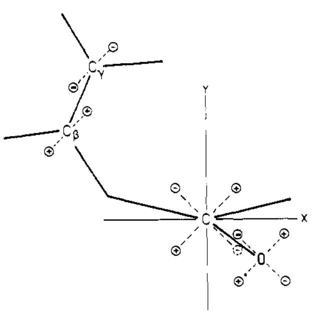


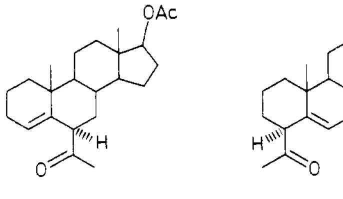
Figure 3. Point charges taken to represent the carbonyl nπ* and ethylenic ππ* charge densities. The component charges of the quadrupoles at the carbonyl C and O atoms lie in the planes $x = \pm y$. The line connecting the negative (positive) charges around the ethylenic group is perpendicular to the plane of that group.

as used before.[14b],[25] It amounts to representing each transition charge density by a set of point charges and calculating the coulombic interaction between the two sets, which in our case is the interaction of the pair of quadrupoles around the C and O atoms of the C=O bond with the pair of dipoles around the $C_\beta{=}C_\gamma$ bond (Figure 3). The interaction λ consists of two parts: a part λ_β, involving the interaction of the charges around the carbonyl and the charges at C_β, and a part λ_γ, defined analogously. Already from a qualitative inspection of Figure 3 it appears that the sign of λ_β follows a quadrant rule, i.e., it is equal to that of $-xy$. In many β,γ-enones, the sign of λ will be determined by the of λ_β because the interaction falls off rapidly with distance. Obvious exceptions include C=O···C=C arrays having approximately C_s symmetry, arrays with C_β situated near the xz plane ($\lambda_\beta \simeq 0$),[26] or arrays with large values of ξ ($\xi \rightarrow 180°$). Then, however, one expects λ, and thus the enhancement of intensity, to be inherently small, and this situation can readily be recognized from experiment. Excluding such cases, the electrostatic model satisfies the requirement set by Figure 2[27] and it suggests simple quandrant rule behavior for the sign of λ. Further work, however, is required for a more detailed study of the scope and limitations of the dynamic coupling scheme as a function of β,γ-enone geometry. In this respect, semiempirical[7] or ab initio calculations[23] that make use of the localized MO's of the olefinic and carbonyl chromophores seem most promising. First, such calculations are better at taking into account the spatial distribution of the interacting transition charge densities.[27] More importantly, they also allow for an evaluation of the importance of interchromophoric electron exchange and overlap effects.[23]

Some Applications

To illustrate the use of the chirality rule in conformational studies, we mention two examples.

(i) UV and CD data of some steroidal β,γ-unsaturated ketones were used by Gorodetsky et al.[28] to establish their conformations. For **10** they found a large negative CD ($\Delta\epsilon = -11.71$) and a strongly enhanced n → π* absorption ($\epsilon = 137$), whereas **11** showed a large positive CD ($\Delta\epsilon = +11.32$; $\epsilon = 105$), which points to an enantiomeric relationship of the β,γ-enone moieties in these compounds.[28] However, the conformations proposed by the authors, having almost perpendicularly oriented C=O and C=C bonds, do not account for the large CD as already noted by Houk.[1] In his comprehensive review on β,γ-unsaturated ketones, Houk[1] mentions for **10** a conformation in which the carbonyl group points away from the B ring, situating the double bond in the upper-left back octant but close to the third octant plane. In our notation, this conformation would have $xy < 0$ and $\cos \xi < 0$. Interestingly, Houk[1] recognized a possible negative CD for this conformation by anticipating an inversion of sign in the GOR in case the double bond were in a front octant.[29]



10 11

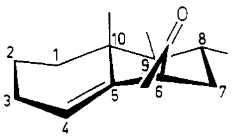
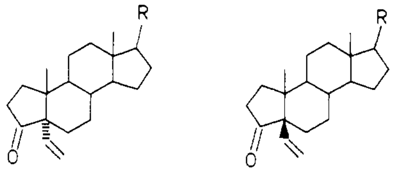


Figure 4. Preferred conformation of the A/B ring system of **10**; see text.

Our correlation enables a more detailed specification of the molecular conformation. With the observed absorption and CD data, ignoring possible background effects, we find $\cos \theta = -0.56$. As a result of rotational freedom of the acetyl group, this yields two feasible solutions: (a) $xy < 0$ and $\xi \simeq 125°$ and (b) $xy > 0$ and $\xi \simeq 55°$. Due to steric hindrance between the acetylic methyl group, which in (a) is above the B ring, and the methyl group at C_{10}, we judge conformation (b) to be more favorable. In this structure, the carbonyl group is above the ring and its orientation is such that the plane of the carbonyl approximately bisects the C_8–C_9 bond (Figure 4). For **11**, a similar reasoning leads to a preferred conformation that has $\xi \simeq 50°$ and is, when disregarding rings C and D, virtually enantiomeric to that of **10**.

(ii) A second example refers to the β,γ-enones **12** and **13**, which differ in their configuration at C_5. This configuration was originally assigned[30] on the basis of the GOR but appeared to be erroneous from an X-ray study on **12**,[31] which showed that despite the GOR, it is the C_5 epimer **12** that has the negative CD ($\Delta\epsilon = -4.1$, $\epsilon \simeq 100$; **13** has $\Delta\epsilon = +3.1$ and $\epsilon \simeq 100$). As noted by Kuritani et al.,[8] this is an example that cannot be handled by the GOR.



12 13

From the spectral data for **12** we find $\cos \theta \simeq -0.23$, implying an angle $\xi \simeq 105°$ ($xy < 0$). It is interesting to compare this with the experimental angle found from the X-ray analysis: $\xi \simeq 130°$. The rather large difference cannot be accounted for by a

---

[25] Dezentje, R. F. R.; Dekkers, H. P. J. M. *Chem. Phys.* **1976**, *18*, 189–197.

[26] When the interaction is dominated by λ_γ, the model predicts an inversion of sign; cf. Figure 3.

[27] For all structures in Figure 2, the explicitly calculated values of λ confirm this picture but always underrate dipole and rotational strength. Probably this is a systematic error due to the use of the London approximation,[24] since the effect does not occur when the interaction is calculated by the procedure of Moscowitz et al.[7]

[28] Gorodetsky, M.; Amar, D.; Mazur, Y. *J. Am. Chem. Soc.* **1964**, *86*, 5218–5224.

[29] However, also for **10** the dynamic coupling model predicts quadrant-rule behavior: for all rotamers, λ appears to be positive.

[30] Fischer, M.; Zeeh, B. *Chem. Ber.* **1968**, *101*, 2360–2364.

[31] Akiyama, T.; Pedder, D.; Silverton, J. V.; Seeman, J. I.; Ziffer, H. *J. Org. Chem.* **1975**, *40*, 3675–3680.

[32] Snatzke, G.; Klein, H. *Chem. Ber.* **1972**, *105*, 244–256.

[33] Lightner, D. A.; Beavers, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 2677–2684.

[34] Bays, D. E.; Cookson, R. C.; MacKenzie, S. *J. Chem. Soc. B* **1967**, 215–226.

[35] Erman, W. F.; Treptow, R. S.; Bakuzis, P.; Wenkert, E. *J. Am. Chem. Soc.* **1971**, *93*, 657–665.

[36] Erman, W. F. *J. Am. Chem. Soc.* **1967**, *89*, 3828–3841.

[37] Nakazaki, M.; Naemura, K.; Harita, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1907–1933.

[38] Nakazaki, M.; Naemura, K.; Kondo, Y. *J. Org. Chem.* **1976**, *44*, 1229–1233.

background effect as measured by the CD of the corresponding hydrogenated structure ($\Delta\epsilon = -1.3$), for this works in the opposite direction. We suspect that the difference is, at least in part, due to a larger amplitude of the rotation around the vinyl bond in solution. Inspection of Dreiding models shows that rotation of the vinyl moiety out of the position, as determined by the X-ray analysis, almost invariably results in a decrease of the angle ξ. Hence, the X-ray structure having the maximum $|R|/D^{1/2}$ value, all contributions of other rotamers will result in a lower $|R|/D^{1/2}$ value. Although the rather low $|\cos \theta|$ value in solution suggests a large amplitude of rotation, contributions of rotamers with positive $\cos \xi$ values, which would arise when the double bond is under the steroid skeleton, seem unlikely.

Acknowledgment. It is a pleasure to acknowledge Dr. H. J. C. Jacobs for stimulating discussion and helpful suggestions.

Registry No. **1**, 73586-29-5; **1a**, 30979-67-0; **1b**, 83780-96-5; **2**, 694-98-4; **2a**, 22516-10-5; **2b**, 66088-27-5; **3**, 61207-62-3; **4**, 74183-81-6; **5a**, 2220-40-8; **5b**, 83731-99-1; **6a**, 50585-71-2; **6b**, 473-06-3; **7**, 57226-88-7; **8a**, 57969-20-7; **8b**, 57969-21-8; **9**, 61765-61-5.

Circular Polarization in the Fluorescence of β,γ-Enones: Distortion in the $^1n\pi^*$ State

P. H. Schippers, J. P. M. van der Ploeg, and H. P. J. M. Dekkers*

Contribution from the Department of Theoretical Organic Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands. *Received March 15, 1982*

Abstract: The circular dichroism (CD) and the circular polarization of the luminescence (CPL) in the n–π^* transition were measured for a series of five rigid β,γ-unsaturated ketones: (1*S*,3*R*)-4-methyleneadamantan-2-one (**1**), (1*S*,3*R*)-4-adamantylideneadamantan-2-one (**1a**), (1*R*,4*R*)-bicyclo[2.2.1]hept-5-en-2-one (**2**), (1*R*)-7-methylenebicyclo[2.2.1]heptan-2-one (**3**), and (1*S*)-2-methylenebicyclo[2.2.1]heptan-7-one (**4**). All compounds exhibit marked differences between the degree of circular polarization in absorption and in fluorescence, giving evidence of important changes in molecular geometry upon excitation. The nature of these distortions is tentatively analyzed by using the previously found quantitative chirality rule for β,γ-enones (preceding paper in this issue). In the $^1n\pi^*$ state of β,γ-enones, the carbonyl group no longer is planar but is pyramidal due to an out-of-plane displacement of the oxygen atom (local symmetry C_s instead of C_{2v}). The out-of-plane angle is large, and its direction is such that the oxygen approaches the double bond, pointing to a bonding interaction in the excited state, which is briefly discussed.

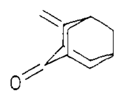
Chiral molecules exhibit circular dichroism (CD): they absorb left and right circularly polarized light to a different extent. Analogously, in the spontaneous emission of such molecules, the left and right circularly polarized photons are unequal in number: circular polarization of the luminescence (CPL).[1,2] Whereas circular dichroism provides information on the chirality of the molecule in its ground state, CPL probes the molecular structure of the excited species.

We were inspired by the interesting photophysics[3,4] and photochemistry[3,5] of the $^1n\pi^*$ state of β,γ-enones to study the circular polarization in the n–π^* absorption and fluorescence of some of these compounds. From the results (next section), it appears that frequently the optical activity in emission differs drastically from that in absorption, pointing to severe distortions in the $^1n\pi^*$ state. These are analyzed and discussed in the last part of this paper.

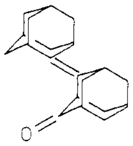
Discussion of the Spectra

We have studied the CD and CPL of five β,γ-unsaturated ketones: (1*S*,3*R*)-4-methyleneadamantan-2-one (**1**), (1*S*,3*R*)-4-adamantylideneadamantan-2-one (**1a**), (1*R*,4*R*)-bicyclo[2.2.1]hept-5-en-2-one (**2**), (1*R*)-7-methylenebicyclo[2.2.1]heptan-2-one (**3**), and (1*S*)-2-methylenebicyclo[2.2.1]heptan-7-one (**4**).

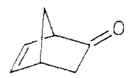
In the absorption spectra of the β,γ-enones, two main regions can be distinguished. First, the usually well-structured absorption around 33 000 cm^{-1} (Figures 1–5), which is due to the carbonyl n $\rightarrow$ π^* transition. Compared with saturated ketones ($\epsilon_{max} \sim$ 20–40), its intensity is strongly enhanced, a common phenomenon with many β,γ-enones.[6-9] The circular dichroism shows a fine structure coinciding with that in the unpolarized absorption. For the adamantanone derivatives **1** and **1a**, shape and magnitude of the CD are almost identical (Figures 1 and 2). Whereas the intensity of the Cotton effect of these compounds ($\Delta\epsilon_{max} \simeq 2, 5$) is not much larger than that found for saturated ketones, the intensity of the CD of **2** ($\Delta\epsilon_{max} = 18.8$) is greatly enhanced (Figure 3) relative to its saturated counterpart, and a similar observation is made for **3** ($\Delta\epsilon_{max} = 7.6$) and **4** ($\Delta\epsilon_{max} = -5.7$) (Figures 4 and 5). The opposite and roughly equal CD values in the n $\rightarrow$ π^* transitions of **3** and **4**, compounds that differ only by interchanged carbonyl and methylene groupings, suggest an approximately enantiomeric relationship of the chromophoric systems involved.



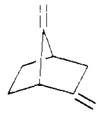
1



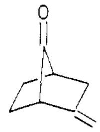
1a



2



3



4

---

[1] (a) Emeis, C. A.; Oosterhoff, L. J. *Chem. Phys. Lett.* **1967**, *1*, 129–132, 268. (b) Emeis, C. A.; Oosterhoff, L. J. *J. Chem. Phys.* **1971**, *54*, 4809–4819. (c) Emeis, C. A. Ph.D. Thesis, University of Leiden, The Netherlands, 1968.

[2] Richardson, F. S.; Riehl, J. P. *Chem. Rev.* **1977**, *77*, 773–792.

[3] Houk, K. N. *Chem. Rev.* **1976**, *76*, 1–74.

[4] Schuster, D. I. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 232–279.

[5] (a) Dauben, W. G.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73–114. (b) Hixson, S. S.; Mariano, P. S.; Zimmermann, H. E. *Chem. Rev.* **1973**, *73*, 531–551.

[6] Cookson, R. C.; Wariyar, N. S. *J. Chem. Soc.* **1956**, 2302–2311.

[7] Labhart, H.; Wagnière, G. *Helv. Chim. Acta* **1959**, *42*, 2219–2227.

[8] Murrell, J. N. "The Theory of the Electronic Spectra of Organic Molecules"; Methuen: London, 1963; pp 164–168.

[9] (a) Ballard, R. E.; Mason, S. F.; Vane, G. W. *Trans. Faraday Soc.* **1963**, *59*, 775–782. (b) Grinter, R.; Mason, S. F.; Vane, G. W. *Ibid.* **1964**, *60*, 285–290.