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PROPOSAL OF A SYMMETRY RULE FOR β,γ-UNSATURATED KETONES

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Summary: A symmetry rule for the sign of Cotton effect of β,γ-unsaturated ketnoes in n→π* region has been proposed and this rule can correctly predict the sign of c.d. even for the ketones to which the generalized octant rule could not be applied.

The Extended Octant Rule or Generalized Octant Rule proposed by Mislow$^{1)}$ for the c.d. of β,γ-unsaturated ketones has been effectively utilized for the determination of absolute configuration and, in some cases, for the assignment of rotomeric conformations in situation where free rotation may occur. However, as has been pointed out,$^{2)}$ the application of the rule should be restricted to the one case of array of the carbonyl group and double bond as in Figure 1A, since the rule was inferred from the results of only three special cases of arrays (Figure 1A, B, and C).$^{1)}$ Because of the insufficient knowledge about the chiroptical properties in other possible arrangement of the two chromophores, the configurations of some β,γ-unsaturated ketones were erroneously assigned on the basis of the generalized octant rule.$^{3)}$

Recently we have studied on two β,γ-unsaturated ketones **1** and **2** (Figure 2) to inquire into the novel types of arrays and reported that, in spite of the same octant disposition of C=C in both ketones, **1** and **2** showed oppositely signed Cotton effect to each other in the n→π* region.$^{4)}$ Hence we concluded that the direction of double bond as well as the position are important for the sign of Cotton effect of β,γ-unsaturated ketones, as has already been noted by Moscowitz.$^{1b)}$

For the theoretical explanation of these results,$^{3,4)}$ we have calculated the optical activity of **1** and **2** based on μ-m coupling mechanism$^{5)}$ (point-quadrupole-point-dipole approximation for the interaction between n→π* of carbonyl and π→π* of ethylenic bond). We computed for many possible arrays of chromophores by rotating the single bonds C_1-C_5 and C_5-C_6 in **1** and **2**, and could successfully elucidate the sign and magnitude of their c.d.s. The most characteristic feature of the results of calculation is that the coupling mode for the magnetic moment ($\vec{\mu}_m$) of

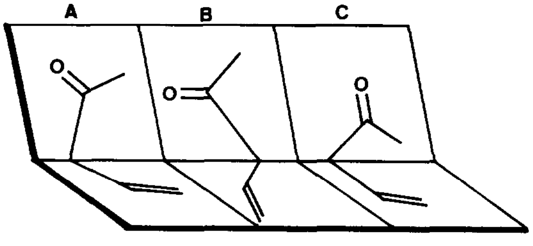
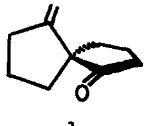
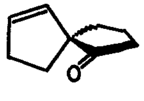


Figure 1



1

ε_{301} 66.1
$\Delta\varepsilon_{301}$ +1.47



2

ε_{306} 86.8
$\Delta\varepsilon_{306}$ -3.14

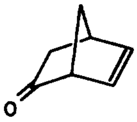
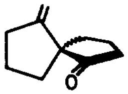
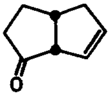
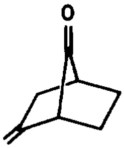
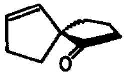
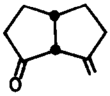
Figure 2

carbonyl n→π* and the electric moment ($\vec{\mu}_e$) of olefin π→π* is always the same in any arrangement of chromophores studied unless the spiro configuration is changed. In other words, the coupling mode in n→π* region is such that $\vec{\mu}_m$ in C→O direction always couples with $\vec{\mu}_e$ in $C_\gamma \rightarrow C_\beta$ direction when the C=C is placed at the positive region of carbonyl octant (Figure 2).6) From the symmetry nature of μ-m interaction,5) it is easily deduced that, when the C=C is reflected by σ-plane of carbonyl (that is, disposed at the negative octant region), $\vec{\mu}_m$ in C→O direction couples with $\vec{\mu}_e$ in $C_\beta \rightarrow C_\gamma$ direction. Since the rotational strength is the scalar product of $\vec{\mu}_m$ and $\vec{\mu}_e$, the sign of Cotton effect by μ-m coupling is expressed as follows,

$$\text{(sign of Cotton effect in } n \rightarrow \pi^* \text{ region)} = (\text{sign of } XYZ\cos\theta) \qquad (1)$$

where X, Y, and Z are the position of C=C in carbonyl rear octant (sign of XYZ presents the sign of the region of C=C in carbonyl rear octant) and θ is the angle between C→O and $C_\gamma \rightarrow C_\beta$ vectors. The equation (1) constitutes the symmetry rule for β,γ-unsaturated ketones, clearly showing that the dominant factor for the sign of c.d. in n→π* region is the angle between two chromophores besides the octant disposition of the C=C double bond.

This new symmetry rule can nicely explain the c.d. of β,γ-unsaturated ketones not only of cisoid type2) so far studied, but also of transoid type2) which is not covered by the Generalized Octant Rule (see Table below).

	cisoid2)			transoid2)		
						
sign of XYZ	+	+	+	+	+	+
sign of $\cos\theta$	+	+	+	+	−	−
predicted sign	+	+6)	+	+	−	−
observed sign	+1)	+4)	+7)	+2)	−4)	−7)

References and Notes

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6) The temperature dependent c.d. of $\underset{\sim}{1}$2) can be well explained as the overlap of a small negative c.d. of preferred conformer and a large positive c.d. of the unpreferred one. The details of calculation will be reported in the near future.
7) These bicyclooctanone derivatives have been synthesized recently. The details will be reported elsewhere.

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