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Calculation of the Rotational Strength of β, γ-Unsaturated Ketones Based on a Non-empirical Molecular Orbital Method

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The values of rotational strength for β, γ-unsaturated ketones arising from the coupling between n-π* and π-π* transitions were calculated based on a non-empirical molecular orbital method and the results were compared with the experimentally observed values.

Circular dichroism (CD) spectroscopy and optical rotatory dispersion (ORD) are important methods to determine absolute configuration or conformation of natural products. The CD of β, γ-unsaturated ketones has been explained by the generalized octant rule,[1-2] in which the geometries of n-π* and π-π* chromophores are important. Contribution of the coupling between the two chromophores to the rotational strengths for β, γ-unsaturated ketones was calculated by a non-empirical molecular orbital method and the results were found to agree reasonably well with experimentally observed values.

Conventional perturbation approximation was employed to derive the π-π* transition rotational strengths using the n-π* chromophore as a single perturber in the previous paper.[3] Similarly the n-π* transition

$$R_A = \frac{2\nu_a \ \mathrm{Im}\, V_{i0a;jb0} \ \boldsymbol{\mu}_{i0a} \cdot \mathbf{m}_{jb0}}{h(\nu_b^2 - \nu_a^2)} + \frac{\mathrm{Im}\, V_{i00;j0b} \ (\boldsymbol{\mu}_{j00} - \boldsymbol{\mu}_{jbb}) \cdot \mathbf{m}_{jb0}}{h\nu_b} \qquad (1)$$

rotational strengths with the π-π^* chromophore as a perturber is given by Eq. 1. Notations are the same as the previous paper.[3] It should be noted that the origin of the coordinate should be chosen at the center of the π-π^* chromophore.

In order to estimate the importance of couling between n-π^* and π-π^* transtions, we calculated the rotational strength from Eq. 1 based on simple molecular orbitals and compared the results with the experiment. The following atomic and molecular orbitals were assumed. As an atomic orbital, only p-orbitals were employed: one p-orbital was approximated by the linear combination of six Gaussian lobe wavefunctions, where parameters reported by Whitten[4] were used. The molecular orbital for the ethylene group was assumed to be the linear combination of two $2p_z$ orbitals of carbons, whereas the molecular orbital for the carbonyl group be the single $2p_y$ orbital of oxygen for the ground state[1] and two $2p_z$ orbitals of carbon and oxygen for the excited state. We ignored the

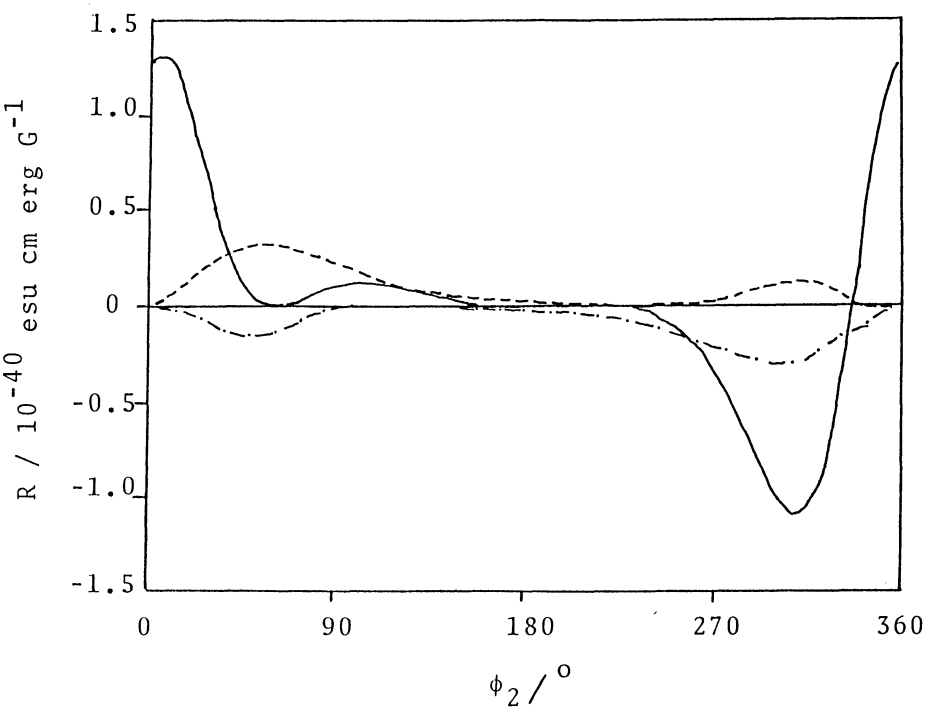
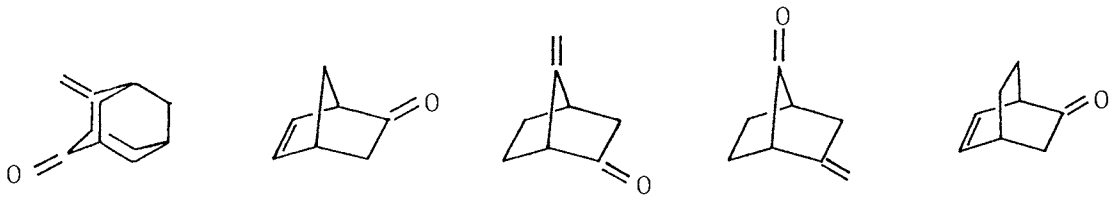


Fig. 1. Rotational strength for β, γ-unsaturated ketones. ———— ϕ_1 = 45 °; - - - - - - - - - - - 135 °; —·—·—·— 225 °. The absorption maximum for the ethylene group was assumed to be 190 nm and that for the carbonyl group be 290 nm according to the experimental observations.[7,8] Other parameters needed for the calculation were taken from Whitten's paper.[4]



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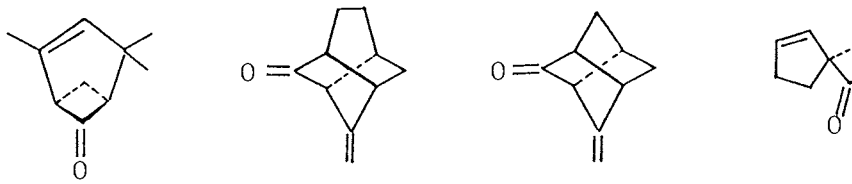

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second term in Eq. 1 in the calculation because it is considered to be minor.[5] The dihedral angle ϕ_1 and ϕ_2 were varied and bond lengths and bond angles were fixed to the standard values. The results for ϕ_1 = 45°, 135°, and 225° were shown in Fig. 1. The definition of the dihedral angles ϕ_1 and ϕ_2 is shown in Fig. 2. It was confirmed

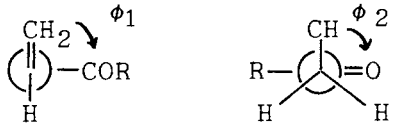

Fig. 2. The dihedral angles ϕ_1 and ϕ_2.

Table 1. Calculated and observed rotational strength (R) for β, γ-unsaturated ketones

Ketones	R(calcd)[a]	R(obsd)[a,b]	ϕ_1[c]	ϕ_2[c]
1	0.0066	6.2	235	120
2	0.1152	51.1	75	120
3	-0.0089	20.5	235	140
4	0.0034	-15.2	135	235
5	0.1045	29.0	55	120
6	0.1317	12.4	50	100
7	0.0043	-14.5	130	230
8	-0.0134	-13.8	120	240
9	-0.3713	-8.0	245	35

a) x 10^{-40} esu cm erg G^{-1}. b) Ref. 7. c) Degree.

that the values of rotational strength followed the relation: R_A (ϕ_1 , ϕ_2) = $-R_A$ ($360^o - \phi_1$, $360^o - \phi_2$), which should be valid based on the enantiomeric relation between the two geometries.

The calculated and observed values of rotational strength for β,γ-unsaturated ketones **1-9** were summarized in Table 1.[6] The dihedral angles ϕ_1 and ϕ_2 were estimated based on a molecular model. Qualitatively, agreement between the calculated values and observed ones was generally good, taking into account the simple molecular orbitals were used in the calculation. For compounds **1**, **2**, **5**, **6**, **8**, and **9**, the calculated signs of the Cotton effect agreed with the observed ones. These observations suggest that the coupling of n-π^* and π-π^* transitions gives rise to the major contribution to CD of these compounds. For compounds **3**, **4**, and **7**, discrepancy between the calculated and observed signs of the Cotton effect was found. However, for these compounds, the calculated values were small (less than 0.01×10^{-40} esu cm erg G^{-1}). Disagreement between the calculation and the experiment implies that the other interaction is the major factor determining the observed sign of the Cotton effect for compounds **3**, **4**, and **7**.

It should be noted that this treatment of the rotational strength is non-empirical. The only empirical parameters we used were absorption maxima for both π-π^* and n-π^* transitions, which could be replaced by the calculated values if an accurate molecular orbital is known. Moreover, the treatment is quite general and can be extended to the calculation of the coupling between groups, at least one of which exhibits electrically allowed transition.

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6) 1 esu = 3.33×10^{-10} C, 1 erg = 10^{-7}J, and 1 G = 10^{-4}T.
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