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A Molecular Orbital Study on the n-π^* Cotton Effect of ε-Caprolactam[1]

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In order to elucidate origin of the Cotton effect of ε-caprolactam, the molecular orbital studies were performed by using the MO's obtained from the CNDO/2 method. It was shown that the sign of the n-π^* carbonyl Cotton effect for ε-caprolactam is due to the electronic structure of the neighboring carbon of the carbonyl group and the delocalization energy between -CONH- group and the two methylene groups of $C(3)H_2$ and $C(5)H_2$.

Keywords——CNDO/2 method; circular dichroism; calculation of rotational strength; n-π^* Cotton effect; ε-caprolactam; lactam rule

Introduction

Many experimental studies on Cotton effect of lactam rings have been carried out and the Cotton effect due to the transition moment of n-π^* of amide group was observed around 200—230 nm.[3] Schellman and Oriel[4] proposed the quadrant rule for a sign of the Cotton effects of the amide group.

On the other hand, Ogura *et al.*[5] reported the conformation of lactam ring having *cis* amide structure significant in order to determine the sign of the Cotton effect on circular dichroism (CD). The purpose of the present paper is to elucidate the relation between the sign of the Cotton effect and the stereochemistry of lactams by the molecular orbital (MO) studies of ε-caprolactam.

Method

Rotational strength was calculated as follows.[6]

$$\boldsymbol{R} = \mathrm{Im}\{\langle\Psi_o|\boldsymbol{\mu}|\Psi_e\rangle\cdot\langle\Psi_e|\boldsymbol{m}|\Psi_o\rangle\}$$

where Ψ_o and Ψ_e are wave functions of ground and excited states, respectively, $\boldsymbol{\mu}$ electric dipole moment operator and $\boldsymbol{m}$ magnetic dipole moment operator. The molecular orbitals employed were calculated by the CNDO/2 method.[7] This method has been known to give fairly good results as far as the rotational strength is concerned.[8] In order to avoid the origin dependency, the following equation was used.[9]

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$$\langle \phi_i | \boldsymbol{r} | \phi_j \rangle = \frac{\hbar^2}{m} \langle \phi_i | \boldsymbol{\nabla} | \phi_j \rangle / \Delta E_{ji}$$

where ϕ_i is *i*-th molecular orbit, and ΔEji the relevant transition energy.

Accordingly, rotational strength is given by the following equation,

$$[\boldsymbol{R}_{ij}] = -7313 \langle \phi_i | \boldsymbol{\nabla} | \phi_j \rangle \cdot \langle \phi_j | \boldsymbol{r} \times \boldsymbol{\nabla} | \phi_i \rangle / \Delta E_{ji}$$

where $(Ej-Ei)$ is represented in eV. Since the denominator of the above equation is nearly constant from molecule to molecule in the present study, the value of the numerator only will be given in the following.

During the calculations of the rotational strength, configuration interaction (CI) was not considered, because it was thought to be unnesessary to include CI calculations to discuss the sign of the Cotton effect.

Molecular structure of ε-caprolactam was obtained from X-ray analysis.[10]

Calculations were carried out by using a HITAC 8700 and 8800 Computer of Tokyo University Computer Center.

Results and Discussion

Table I shows the results of calculations of ε-caprolactam. The rotational strength of n-π* for ε-caprolactam (Fig. 1) was calculated to be −229.1 (Fig. 1, 2, Table I). This negative

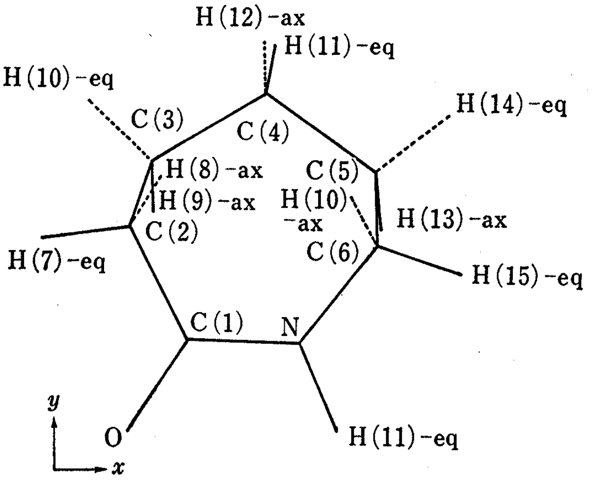


Fig. 1

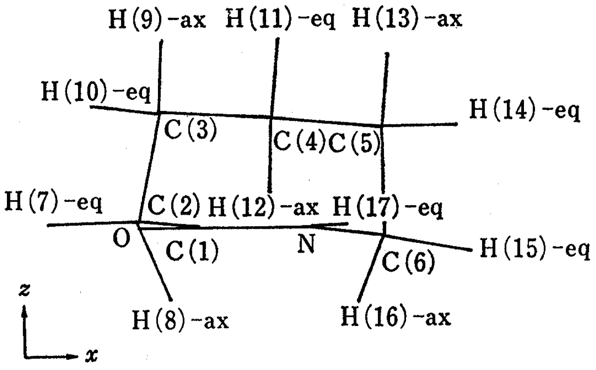
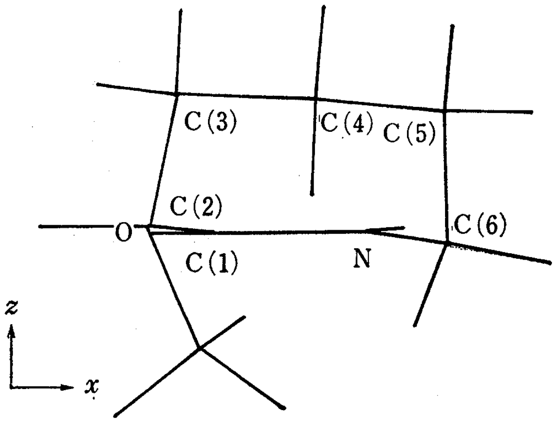


Fig. 2

Table I. Calculated Optical Rotational Strength for ε-Caprolactam and Monomethyl Substituted Derives in eV

	n-π*
ε-Caprolactam	−229.1
C(2)-eq-CH_3	−406.6
C(2)-ax-CH_3	2.8
C(3)-ax-CH_3	−233.5
C(3)-eq-CH_3	−691.5
C(4)-eq-CH_3	−176.3
C(4)-ax-CH_3	−332.6
C(5)-ax-CH_3	−302.9
C(5)-eq-CH_3	−98.4
C(6)-eq-CH_3	−257.6
C(6)-ax-CH_3	−159.5
N-CH_3	−179.1



C(2)-ax-methyl-ε-caprolactam

Fig. 3

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[10] I. Nitta, M. Haisa, N. Yasuoka, K. Kasami, Y. Tomii, and Y. Okaya, *Ann. Reports Fiber. Res, Inst, Osaka Univ.*, **1**, 17 (1965).

sign is in agreement with the empirical rule (lactam rule) which were proposed by Ogura *et al.*[5] In order to elucidate the origin of the negative sign, the effects of methyl substitution for each hydrogen were calculated (Table I). No influence except for the methyl substitution of H(8) was observed on the Cotton effect. The rotational strength of C(2)-ax-methyl-ε-caprolactam was almost zero. Its structure is shown in Fig. 3. The substituted methyl group is bound to the carbon which is on the amide plane and neighboring to the carbonyl group. The change of the rotational strength from -229.1 to 2.8 may be explained by the fact that the bond between C(2) and this methyl group is almost symmetry for amide plane with C(2)—C(3) bond. This means that C(3) atom of ε-caprolactam is the main origin of the negative sign of the Cotton effect. Rotational strength of C(2)-eq-methyl-ε-caprolactam has a negative sign in accordance with that of ε-caprolactam.

The results of the calculation revealed that σ-atomic orbital of C(2) interacts with the lone pair of the carbonyl oxygen through C(1)–C(2) bond. The unoccupied π^* MO of n-π^* localizes electronic population between C(2) and the carbonyl carbon. Through these two effects, therefore, the electronic structure of C(2) may influence the rotational strength. On the other hand, the methyl substituted structure for H(15) which is on the amide plane and covalently bound to the carbon neighboring to the amide nitrogen increases the absolute value by 28.5. In comparison with the H(7) methyl substituted structure, the change of the rotational strength is small. By the methyl substitution of H(16) which is axial for amide plane, the absolute value of the rotational strength decreases by 69.6. In comparison with substituent effect of C(2)-axial position, however, that of C(6)-axial position is small. Therefore the effects of the electronic structure of C(2) on the sign of the Cotton effect is more predominant than that of C(6). The methyl substitution of H(9) which is bound to C(3) increases extremely the absolute value, but that of H(13) which is binding to C(5) decreases it largely. Since C(3) and C(5) atom are over the amide plane, the significance of the conformation of lactam rings is shown by the effects of those atoms.

Inorder to elucidate the conformation effects on the rotational strength, morever, calculations without interatomic delocalization energies were performed by using the method described in the paper by Umeyama *et al.*[11] The calculated results is collected in Table II.

Table II. Calculated Optical Rotational Strengths without Interatomic Delocalization Energies for ε-Caprolactam in eV

			n-π^*
1	H (9) H (10) C (3) H (11) H (12) C (4) H (13) H (14) C (5)	CONH	55.2
2	H (9) H (10) C (3)	CONH	-167.7
3	H (11) H (12) C (4)	CONH	-200.9
4	H (13) H (14) C (5)	CONH	-586.7
5	H (9) H (10) C (3) H (11) H (12) C (4)	CONH	-200.0
6	H (9) H (10) C (3) H (13) H (14) C (5)	CONH	77.1
7	H (11) H (12) C (4) H (13) H (14) C (5)	CONH	-448.9

Calculated rotational strength without delocalization energies among -CONH- group, $C(3)H_2$, $C(4)H_2$ and $C(5)H_2$ was 55.2. Next, calculations without the delocalization energy between -CONH- group and $C(3)H_2$, $C(4)H_2$ or $C(5)H_2$ were carried out to explain the change of the sign. The increase of the absolute value was large without delocalization energies

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11) H. Umeyama, A. Imamura, C. Nagata, and M. Hanano, *J. Theor. Biol.*, **41**, 485 (1973).

for $C(5)H_2$ and without delocalization energies for $C(4)H_2$ or $C(3)H_2$ the effects were small. However these results did not explain the change of the sign of the Cotton effect. Whitout delocalization energies for $C(3)H_2$ and $C(4)H_2$, $C(3)H_2$ and $C(5)H_2$ or $C(4)H_2$ and $C(5)H_2$, then, the calculations of rotational strength were performed.

As the results, the calculations without delocalization energies for $C(3)H_2$ and $C(5)H_2$ showed the positive value of 77.1. Therefore the delocalization energies among –CONH– group, $C(3)H_2$ and $C(5)H_2$ contribute to the sign of the Cotton effect as the conformation effect. Accordingly, the sign of the Cotton effects of ε-caprolactam are largely influenced by the electronic structure of the neighboring carbon of the carbonyl group and the delocalization energy between –CONH– group and the two methylene groups of $C(3)H_2$ and $C(5)H_2$.