A RELATIONSHIP BETWEEN THE COTTON EFFECT AND THE CONFORMATIONS OF LACTAMS

-STUDIES ON MO CALCULATION-

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There are many reports of the Cotton effect in relation to the conformations of peptides, amides and lactams. Schellman *et al.* published the quadrant rule for the peptide bond. However the rule cannot explain the Cotton effect of lactam rings, and Ogura *et al.* enunciated a lactam rule, linking the sign of the n-π^* carbonyl Cotton effect with the conformations of the lactam ring.

In this report, the origin of the Cotton effect of lactams was studied from the quantum chemical point of views by using the LCAO molecular orbitals obtained from the CNDO/2 method, on the basis of the atomic coordinates of amides and lactams from X-ray diffraction analysis. The results are as follows.

(1) The results of the calculations of optical rotational strength for ε-caprolactam and D-gluconic-δ-lactam are in accordance with those of the experiments.

(2) The sign of the n-π^* carbonyl Cotton effect for seven-membered ε-caprolactam is due to the methylene group covalently-bonded to the neighboring carbon of the carbonyl group.

(3) The sign of the n-π^* carbonyl Cotton effect for six-membered D-gluconic-δ-lactam is due to the hydroxyl group covalently-bonded to the neighboring carbon of the carbonyl group.

(4) From the calculation of the methyl substitution, the significance of the group covalently-bonded to the neighboring carbon of the carbonyl group was shown.