THE EFFECT OF DEUTERIUM SUBSTITUTION IN THE AMINO/IMINO GROUP ON THE DYNAMICAL MOLECULAR STRUCTURE OF PEPTIDE MOLECULES:ACETAMIDE AND N-METHYL FORMAMIDE

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Peptide molecules XCO-NYY′ are characterized by the low potential barrier V_3 to internal rotation of CH_3 substituted for X and/or Y. A most conspicuous example is acetamide, for which V_3 was previously reported to be 25.043857(19)cm^{-1}. The present study intended to clarify why V_3 is so low in peptide molecules, by examining the effect of the out-of-plane bending or inversion of the amino/imino group on the molecular structure through deuterium substitution for amino/imino hydrogens. The potential barrier V_3 in acetamide was found to decrease by 2.509, 2.958, and 5.422cm^{-1}, when H's at cis, $trans$, and both positions in the amino group were replaced by deuterium atoms, respectively. The reduction was proportional to the effective mass of the amino inversion, which was in turn ascribed to the change in electronic resonance character of the peptide linkage. The amino inversion is coupled with the CH_3 internal rotation, producing an interaction term proportional to $\tau sin3\alpha$ (τ: amino inversion, α: methyl internal rotation). This coupling term, when the inversion is treated by second order perturbation, yields a V_6 term, in agreement with Ilyushin $etal.$, who derived an unusually large V_6 term of -10.044874(73) cm^{-1}. Deuteration for the imino hydrogen reduces V_3 by 11.40$\mathrm{cm}^{-1}$for the N-methyl formamide $trans$ form, whereas for the cis form it increases V_3 by 8.09cm^{-1}. It is interesting that even a small perturbation like deuterium substitution causes a substantial change in electronic structure of the peptide systems.