EXPERIMENTAL STUDIES OF PEPTIDE BONDS: THE C_7^{eq} CONFORMATION OF THE ALANINE DIPEPTIDE ANALOGUE N-ACETYL-ALANINE $N' - METHYLAMIDE$

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The alanine dipeptide analogue, N-Acetyl-alanine $N' - methylamide$, serves as a model of protein conformation due to its two peptide bonds. A Fourier-transform microwave spectrometer is used to obtain the first gas phase spectroscopic evidence of the amide hydrogen-to-carbonyl oxygen intramolecular hydrogen bonding interaction in this important bio-memetic. Spectra of the normal, one ^{13}C and double ^{15}N isotopomers have been obtained using a glass coated reservoir nozzle to prevent thermal decomposition. The structure of the dipeptide contains three methyl tops. Two of them, the acetyl methyl and amide methyl groups, have low methyl torsional barriers (100 cm^{-1}) which give rise to additional splittings in the spectra. The AA- and AE-states have been well-fit using "high barrier" Hamiltonians. The rotational constants assigned to the AA-state are: A = 1717.383(22) MHz, B = 992.9221(23) MHz, and C = 716.4911(18) MHz. The perturbation parameters derived from the AE-state fits have been used to accurately determine the rotor axis orientation angles and V_3 barriers. The geometric parameters lead to a unique determination of the conformational structure. The rotational constants, rotor angles and V_3 barriers are in good agreement with the lowest energy C_7^{eq} structure calculated from theory. A similar analysis has been performed for six isotopomers of a decomposition product of alanine dipeptide, a five-membered heteroatom ring structure resulting from loss of H_2O and will also be discussed.