A SIMPLE PROLINE CONTAINING PEPTIDE MIMETIC: THE CONFORMATIONAL STRUCTURE OF N-FORMYLPROLINAMIDE

R. J. LAVRICH,R. D. SUENRAM and D. F. PLUSQUELLIC, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; J. BRYK and M. J. TUBERGEN, *Department of Chemistry, Kent State University, Kent, OH 44242*.

Proline is unique among the amino acids: its amino nitrogen forms a covalent bond with the side chain terminal carbon. The resulting five-membered ring imparts distinctive properties to proline containing peptides including greatly restricted conformational freedom, a reduced barrier for cis-trans isomerization about the peptide bond, and a loss of the imino nitrogen's hydrogen bonding capacity. These properties play critical roles in secondary structure, protein folding and signal transduction mechanisms.

N-formylprolinamide, with its two peptide linkages, is the simplest peptide mimetic containing a proline residue. A Fourier-transform microwave spectrometer has been used to investigate the conformational structure of this biochemically important system. N-formylprolinamide was heated to 190 C in a glass coated reservoir nozzle to prevent thermal decomposition. Twenty nine b-type transitions were measured for the most abundant isotopomer. The resulting rotational transitions appeared as broad clusters of partially resolved lines, typically spanning 50 kHz to 100 kHz, due to the presence of two ^{14}N nuclei. Approximate line centers estimated near the center of the resulting hyperfine clusters were fit using the graphical interface fitting program JB95 yielding the following rotational constants; A = 1619.061(4) MHz, B = 1504.920(4) MHz and C = 894.010(1) MHz. The experimental rotational constants are consistent with a seven-membered ring structure having an intramolecular hydrogen bond between an amide proton and the formyl oxygen. Further conformational flexibility exists in the form of ring puckering of the five-membered proline ring. Current progress in the determination of these structural parameters will be discussed.