

THE ROLE OF THE LOCAL CONFORMATION OF A CYCLICALLY CONSTRAINED β -AMINO ACID IN THE SECONDARY STRUCTURES OF A MIXED α/β DIASTEREOMER PAIR

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Synthetic foldamers are non-natural polymers designed to fold into unique secondary structures that either mimic nature's preferred secondary structures, or expand their possibilities. Among the most studied synthetic foldamers are β -peptides, which lengthen the distance between amide groups from the single substituted carbon spacer in α -peptides by one (β) additional carbon. Cyclically constrained β -amino acids can impart rigidity to the secondary structure of oligomers by locking in a particular conformation. The β -residue *cis*-2-aminocyclohexanecarboxylic acid (*cis*-ACHC) is one such amino acid which has been shown to drive vastly different secondary structures as a function of the local conformation of the cyclohexane ring. We present data on two diastereomers of the mixed α/β tri-peptide Ac-Ala- β_{ACHC} -Ala-NHBn which differ from one another by the chirality along the ACHC residue (SRSS vs. SSRS). The first oligomer is known to crystallize to a 9/11 mixed helix while the second forms no intramolecular hydrogen bonds in the crystal state. This talk will describe the conformation-specific IR and UV spectroscopy of the above two diastereomers under jet cooled conditions in the gas phase. Assignments based on comparison with calculations show the presence of incipient 9/11 mixed helices and competing structures containing more tightly folded hydrogen-bonded networks. The calculated global minimum structures are observed in each case, and in each case these folded structures are reminiscent of a β -turn.