SPECTROSCOPIC INVESTIGATION OF β-PEPTIDES: Ac-β^3-Phe-NHMe, Ac-β^3-Phe-β^3-Ala-NHMe AND Ac-β^3-Ala-β^3-Phe-NHMe

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Recently, there has been much interest in developing biomimetic polymers that are analogous to natural proteins. These polymers have great potential as models for understanding structure and stabilization in proteins. β-peptides are particularly interesting for structural studies because they represent the smallest step away from α-peptides and the potential energy surface should contain a diversity of low energy minima. The conformational preferences and spectroscopic signatures of β-peptides have received little attention. In this study three small β-peptides were investigated in the isolated environment of a supersonic molecular beam. The molecules contain one or two β residues and a UV chromophore that enables their study via double resonance spectroscopy. Resonant two photon ionization (R2PI) and UV-UV holeburning spectroscopies were used to resolve the number of conformations in each molecule. The simplest β-peptide analog contains two methyl-capped amides separating a single β-peptide linkage, (Ac-β^3-Phe-NHMe). Two conformations of this molecule were resolved and resonant ion dip infrared (RIDIR) spectra in the N-H and alkyl C-H stretch regions indicate that the two conformers represent distinct intramolecular hydrogen bonded configurations. One exhibits a 6-membered H-bonded ring (C6) and the other an 8-membered ring (C8). The dominant conformer in the expansion is the C6 ring, consistent with the predictions of theory that this conformation is energetically more stable than C8. Ac-β^3-Phe-β^3-Ala-NHMe and Ac-β^3-Ala-β^3-Phe-NHMe each contain three amide groups and two β-peptide linkages. UV-UV holeburning spectroscopy resolves 5 conformers of each molecule and the RIDIR spectra exhibit NH stretch patterns consistent with classification of the structures into either singly or doubly hydrogen bound conformations. Calculations predict single ring structures as C10 or C12 member rings, while double ring combinations contain C8/C8 or C8/C6 arrangements. The frequency shifts observed experimentally in comparison to calculations aid in a qualitative assignment of the observed structures. These assignments and the consequences for β-peptide conformational preferences will be discussed.