CHARACTERIZING PEPTIDE β-HAIRPIN LOOPS VIA COLD ION SPECTROSCOPY OF MODEL COMPOUNDS

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The introduction of non-native D-amino acids into peptides is known to reduce conformational entropy in peptides. D-proline has been shown to promote the formation of β-hairpin loops when paired with Gly, providing a framework for building these loops with different lengths of anti-parallel beta-sheet. This study seeks to characterize and compare the conformational preferences of a model protonated pentapeptide containing DPG, [YAP^{D}GA+H]$^+$, with its L-Pro counterpart via conformation specific cold ion spectroscopy as a foundation for future consideration of larger beta-hairpin models.

The UV spectrum of YAP^{D}GA of the Tyr chromophore is beautifully sharp, but contains a complicated set of transitions that could arise from the presence of more than one conformer. To assess this possibility, we recorded non-conformation specific IR "gain" spectra in the hydride stretch region. The IR spectrum so obtained displays a set of five strong IR transitions that bear a close resemblance to those found in one of the conformers of its close analog, [YAP^{D}AA+H]$^+$, signaling that a single conformer dominates the population. Two transitions at 3392 and 3464 cm-1 are slightly shifted versions of the C10 and C14 hydrogen bonds found in one of the conformers of [YAP^{D}AA+H]$^+$, and are characteristic of formation of a β-hairpin loop. Notably, in [YAP^{D}GA+H]$^+$, there is at most a minor second conformer with a free carboxylic acid OH, appearing weakly in the IR "gain" spectrum. As expected, the UV spectrum of YAP^{L}GA is more congested, which suggests the presence of multiple conformers. Further investigation into this peptide will reveal the conformational preferences of the L-pro containing molecule. Preliminary data affirms that D-proline containing peptides show reduced conformational states when compared to their natural counterparts.