

## THE EFFECTS OF C-TERMINAL FLUOROPHORE CAPS ON THE STRUCTURE OF AMINOISOBUTYRIC ACID DIPEPTIDES

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Aminoisobutyric acid (Aib) is an achiral synthetic amino acid with a high propensity to form  $3_{10}$  helices, the second most biologically abundant helix. Aib is also known to induce helix formation in other peptides, and can persuade helix formation from a consecutive sequence of as little as three residues. Studying polyAib in the gas-phase provides a spectroscopic opportunity to examine the inherent hydrogen bonding that directs this helix formation. Since Aib is achiral, there is no infrared (IR) distinction between left- and right-handed helices, preventing powerful IR-based structural differentiation of left- and right-handed structures. However, the introduction of chirality through a cap offers a means by which the balance between the two can be tipped. However, it could also induce alterations to the structure. This talk describes conformation-specific IR and ultraviolet (UV) double-resonance spectroscopy of a series of three Aib dipeptides with three UV-active C-terminal caps: NH-benzyl (NHBn) as a reference structure due to its common use as a fluorophore in similar studies, NH-p-fluorobenzyl (NHBnF), and alpha-methylbenzylamine (AMBA), a chiral cap. These molecules are brought into the gas phase via laser desorption and cooled in a supersonic expansion, enabling us to probe the inherent conformational preferences of the isolated molecules. For both the NHBn and NHBnF cap, a single conformer is observed, with infrared spectra assignable to nearly identical type II  $\beta$ -turn structure. Additionally, the higher oscillator strength of the NHBnF cap enabled UV-UV holeburning, not readily accomplished with the NHBn cap. For AMBA, two unique conformers were found, one of which was a nearly identical type II  $\beta$ -turn, while the minor conformer possessed two sequential  $\gamma$ -turns formed between adjacent amide groups, stabilized by an NH- $\pi$  interaction.