5-METHOXY-N-ACETYL TRYPTOPHAN METHYL AMIDE: THE DRAMATIC EFFECTS OF A REMOTE SUBSTITUTION AND A SINGLE WATER MOLECULE ON ITS CONFORMATIONAL PREFERENCES

JASPER R. CLARKSON, BRIAN C. DIAN, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*.

Following earlier studies in our group on the conformational preferences of N- acetyl tryptophan methyl amide (NATMA) and N-acetyl tryptophan amide (NATA), we have modified NATMA by substitution of a methoxy group for hydrogen in the 5- position on the indole ring. We present results from a variety of techniques, including LIF, fluorescence-dip infrared spectroscopy (FDIRS), UV-UV hole-burning spectroscopy, and resonant two-photon ionization (R2PI) which characterize the infrared and ultraviolet spectra of this molecule and its water-containing complexes. While NATMA and NATA have three and two significantly populated conformations, respectively, the LIF spectrum of 5- methoxy-NATMA can be accounted for in its entirety by a single conformation. The infrared spectrum of this conformer is consistent with a C5 conformation, in which the dipeptide backbone is in an extended conformation, with no intramolecular H-bond present. *Ab initio* and density functional theory calculations are used to assign the structure observed, and to understand how the methoxy group restricts the conformations of the dipeptide backbone. When a single water molecule is attached to 5-methoxy-NATMA, a single conformation is observed once again, with water bound to the carboxy amide carbonyl group. However, in this case, the 5-methoxy-NATMA 'solute' is a $C7_{eq}$ conformation, in which the dipeptide backbone has an intramolecular H-bond. The reasons for this change in conformational preference will be discussed, as will preliminary studies of larger 5-methoxy NATMA-$(water)_n$ clusters.