PROBING THE ELECTRONIC STRUCTURE OF PEPTIDE BONDS USING METHYL GROUPS: EXPERIMENTAL MEASURES OF RESONANCE WEIGHTS

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The observed V_3 torsional barriers reported for nine methyl groups attached alpha to peptide bond linkages in five gas phase biomimetics are interpreted at the HF/6-311++G(d,p) level of theory in terms of the natural bonding orbitals and the natural resonance structures of the peptide bond. This decomposition has revealed that delocalization of the nitrogen lone pair electrons into anti-bonding orbitals of the carbonyl group is principally responsible for the torsional barriers and lowest energy staggered or $anti$ conformations of the carbonyl methyl groups. In contrast, the minimum energy configuration and V_3 barriers of the amide methyl groups are dominated by Lewis-like steric interactions that lead to syn preferences. The Lewis vs non-Lewis energies are sufficiently well balanced that low barriers (<0.5 kcal/mole) result in both methyl group classes. These results reveal that a linear correlation exists between the barriers to internal rotation of attached methyl groups and the relative importance of the two principal resonance structures that contribute to the peptide bond. Predictions at the MP2 levels of theory are consistent with these trends but opposite to the conformational preferences calculated using popular force field models. The impact of the torsional state dependence of the resonance weights on internal rotation models also will be discussed.

[a]Work supported by NSF (CHE-015884)