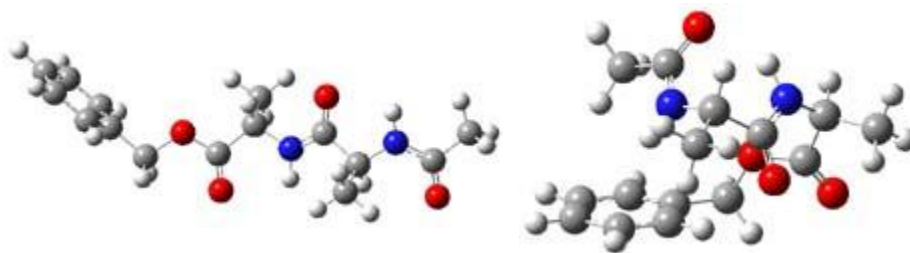


# DIPEPTIDE STRUCTURE: COMPUTATION AND EXPERIMENT

Here's a nice example of the productive interplay between experiment and computations.<sup>1</sup> The dipeptide N-Acyl-Ala-Ala-Benzyl was prepared and subjected to UV and IR/UV analysis. The IR showed two separate structures with distinctly different environments for the NH bonds: one structure showed intramolecular hydrogen bonding while the other did not.

B97/TZVPP computations revealed two structures. The first is a linear dipeptide with intramolecular hydrogen bonding occurring in a 5,5 relationship. (There are actually three conformers of this but all have similar energy, only one is shown in Figure 1.) The second structure displays a bent shape with a NH- $\pi$  interaction, also shown in Figure 1. The computed vibrational spectra for each structure matches up well with the NH region of the experimental IR.



**Figure 1.** B97-D/TZVPP optimized structures of N-Acyl-Ala-Ala-Benzyl.

The authors spend a great deal of time noting that the 0 K energies predict that the second structure, being  $4 \text{ kcal mol}^{-1}$  more stable, should be the only one observed. However, since the jet cooling will likely trap the structures at their 300 K distribution, this could account for the existence of two structures. However, when the computations include entropy corrections, so now we're looking at  $\Delta G(200 \text{ K})$ , B97-D and MO6-2x suggest that the two structures are very close in energy. But they caution that MP2 predicts a large energy gap unless atomic counterpoise corrections are used to account for intramolecular basis set superposition (see [this post](#)), a problem that appears to be much less severe with the DFT methods.

Source: <http://comporgchem.com/blog/?p=1134>