Rotational spectra of Gly-Pro and Pro-Gly dipeptides have been examined with laser ablation molecular beam Fourier transform microwave (LA-MB-FTMW) spectroscopy. Three conformers for Gly-Pro and one for Pro-Gly have been unequivocally identified in the supersonic expansion by the comparison of the experimental rotational and $^{14}$N (I=1) nuclear quadrupole coupling constants with those predicted by ab initio methods. The quadrupole hyperfine structure of two $^{14}$N nuclei has been totally resolved and it allows to experimentally characterize the main intramolecular forces which stabilize the assigned conformers. The biomimetic molecule Ac-Ala-NH$_2$ has been also studied. The C$_7$ and C$_5$ peptide conformations (intramolecularly hydrogen-bonded seven- or five-membered cycle, respectively) have been unequivocally identified in the supersonic expansion. The ability to identify peptide conformations suggest that it soon may be possible to explore the structures of larger peptides using LA-MB-FTMW spectroscopy.

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