Accurate structures of amino acids in the gas phase have been obtained by joint microwave and quantum-chemical investigations. However, the structure and conformational behavior of \(\alpha\)-aminoacids once incorporated into peptide chains are completely different and have not yet been characterized with the same accuracy. To fill this gap, we present here an accurate characterization of the simplest dipeptide analogue (N-acetylglycinamide) involving peptidic bonds. State-of-the-art quantum-chemical computations are complemented by a comprehensive study of the rotational spectrum using a combination of Fourier transform microwave spectroscopy with laser ablation. The coexistence of the \(C_7\) and \(C_5\) conformers has been proved and energetically as well as spectroscopically characterized. This joint theoretical-experimental investigation demonstrated the feasibility of obtaining accurate structures for flexible small biomolecules, thus paving the route to the elucidation of the inherent behavior of peptides.