VALINAMIDE BACKBONE STRUCTURE AND SIDE CHAIN ORIENTATION FROM ROTATIONAL SPECTROSCOPY

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Rotational spectra have been recorded for five isotopic species of valinamide, the amide derivative of the amino acid valine. The rotational constants for the normal species are A = 3019.242 (1) MHz, B = 1473.0587 (7) MHz, and C = 1252.5350 (8) MHz. Ab initio calculations at the MP2/6-31G** level identify six conformational minima with three different orientations of the isopropyl side chain and two different intramolecular hydrogen bonding interactions. None of the theoretical structures reproduces the fifteen experimental moments of inertia derived from the rotational constants. Least squares fits of the theoretical structure with χ_1 = 300° and an amide-to-amine intramolecular hydrogen bond find that the amino amide backbone torsional angle Ψ increases from -9.3° to +10(3)°. The nitrogen atomic coordinates of the least-squares-fit structure were found to be in agreement with the coordinates calculated using Kraitchman's equations for single isotopic substitution, but the nitrogen coordinates of the theoretical structures were significantly different from the Kraitchman coordinates.