DISPERSION-DRIVEN ISOMERISM IN THE GAS PHASE: THEORETICAL AND MICROWAVE SPECTROSCOPIC STUDY OF ALLYL ISOCYANATE

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The pure rotational spectrum of allyl isocyanate ($\mathrm{CH_2 = CHCH_2NCO}$) was studied using chirped pulse and Balle-Flygare Fourier Transform microwave (FTMW) spectroscopy. Besides the previously reported *gauche* conformer,[a] the lowest energy conformer was identified for the first time with the assistance of the quantum-chemical calculations performed at the B3LYP-D3(BJ) and MP2 levels of theory with Dunning's cc-pVQZ basis set. The assignments were confirmed by the resolved hyperfine structure due to the ^{14}N quadrupole moment and the spectra of the corresponding ^{13}C, ^{15}N and ^{18}O singly substituted isotopologues in natural abundance. Rotational transitions of the most stable conformer revealed a tunneling splitting due to the interconversion motion between its two mirror images, and the tunneling path was established theoretically. In addition, benchmark calculations of various density functionals with and without dispersion corrections were carried out to investigate the effect of the short-range dispersion energy on the conformational structures.

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[a] S. Maiti, A. I. Jaman, and R. N. Nandi, *J. Mol. Spectrosc.* **158**, 8-13 (1993)