

CONFORMATIONAL EQUILIBRIUM OF THE CHALCOGEN-BRIDGED COMPOUNDS ALLYL ETHYL ETHER AND ALLYL ETHYL SULFIDE REVEALED BY MICROWAVE SPECTROSCOPY AND COMPUTATIONAL CHEMISTRY

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The conformational landscapes of allyl ethyl ether (AEE) and allyl ethyl sulfide (AES) were investigated using Fourier transform microwave spectroscopy in the frequency range of 5-23 GHz aided by the density functional theory (DFT) B3LYP-D3(BJ)-aug-cc-pVTZ calculations. The quantum chemical calculations identified a rich conformational equilibrium with 14 stable conformers for AEE and 13 for AES within 14 kJ/mol. Experimentally, rotational transitions corresponding to three low energy conformers of AEE and two forms of AES were assigned. Interconversion pathways were modelled to understand the relaxation of the higher energy conformers to the more stable forms in the supersonic jet expansion and to explain the observed tunneling splitting in one conformer of AEE. To better understand the stereoelectronic effects and topology of the interactions governing the conformational preferences of AEE and AES, natural bond orbital (NBO) and non-covalent interaction (NCI) analyses were performed. For the lowest energy conformers of AEE and AES, ground state effective (r_0) and substitution (r_s) structures were derived using the spectral data collected for the ^{13}C and ^{34}S isotopologues in natural abundance. The results confirm the theoretical predictions that the lowest energy geometries are surprisingly different depending on the identity of the bridging chalcogen atom.