

CONFORMATIONAL LANDSCAPE OF 3-MERCAPTOPROPIONIC ACID AND METHYL 3-MERCAPTOPROPIONATE REVEALED BY MICROWAVE SPECTROSCOPY AND THEORETICAL CALCULATIONS

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The structures of 3-mercaptopropionic acid (mpa) [HS-CH₂-CH₂-C(O)-OH] and methyl 3-mercaptopropionate (mp) [HS-CH₂-CH₂-C(O)-O-CH₃] were investigated in the range of 8-18 GHz using both chirped pulse and cavity-based Fourier transform microwave spectrometers. One (mpa1) and two (mp1 and mp2) stable conformers were assigned in the rotational spectra for the acid and the ester compound, respectively. Despite our efforts, no other energy minima predicted by theory was experimentally observed in the spectra which could be a result of their high relative energies and/or small barriers to rearrangement (relaxation to lower energy conformers). Splitting due to the presence of the methyl internal rotor in the ester species were observed in the rotational transitions of both mp1 and mp2. The latter also presents an additional splitting related to the torsional motion of the SH group around the C-C-S-H dihedral angle that allows the interconversion between two enantiomers of mp2. The observed rotational transitions for the acid and the ester were fit using the Pickett's SPFIT and the XIAM programs, respectively. The derived rotational parameters are well-determined and consistent with the quantum mechanical calculations performed at both DFT B3LYP-D3BJ and ab initio MP2 methods with the aug-cc-pVTZ basis set. The higher stability of conformers mpa1 and mp1 is explained by the presence of an intramolecular SH \cdots O=C interaction, investigated on the basis of the quantum theory of atoms in molecules (QTAIM) and the non-covalent interaction (NCI) analyses.