CONFORMATIONAL STUDIES IN FORMIC ACID OLIGIMERS

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Hydrogen bonding in organic acid oligimers can give rise to a number of conformational possibilities. This is due to the ability of the acids to form multiple hydrogen bonds in the dimerization process. The most stable dimer between two organic acids is one in which the two acid functionalities form an eight membered ring where the hydroxyl hydrogens of the monomer units form hydrogen bonds to the keto oxygens of the opposing monomers. For microwave work, one is normally forced to study mixed acid dimers in order that the dimer possess a permanent electric dipole moment.[abc] Here we revisit the conformational opportunities using the simplest organic acid, formic acid. In this work, we were guided by density functional calculations at the B3LYP/6-311+G(d) level. These calculations indicated that there should be a stable six membered ring dimer in the system. This dimer would be polar and should be observable using microwave techniques. Broad banded searches from 12 to 20 GHz were carried out with neat formic acid samples using FTMW spectroscopy. These scans yielded a plethora of rotational transitions. Eventually these were assigned to a formic acid trimer consisting of the standard symmetric eight membered ring dimer plus a third formic acid monomer unit forming a third hydroxyl-keto linkage. Details of the experimental work will be presented along with a comparison of density functional calculations for a number of other oligimer possibilities

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