CONFORMATIONAL BEHAVIOR OF HYDROGEN BOND COMPLEXES

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The low-temperature environment of a free jet expansion provides an excellent laboratory for probing the conformational behaviour of hydrogen bonding. We have reported the first observation of axial and equatorial hydrogen-bonded complexes in the jet-cooled rotational studies of tetrahydropyran, pentamethylene sulphide and trimethylene sulphide complexes with HCl and HF.[a b c d e] The six-membered rings present two nonbonding electron pairs at the O or S atoms that turn out to be nonequivalent due to the chair conformation of the ring. Consequently, the formation of hydrogen bonds give rise to two different axial and equatorial conformers. The four-membered rings of trimethylene sulphide and 3,3-dimethyl oxetane execute a ring-puckering large amplitude motion which interconverts via tunneling the two C_s puckered conformations making equivalent the nonbonding electron pairs at the O or S atoms. In this case, this equivalence is broken by effect of complexation giving rise to axial and equatorial conformers. In this context we present our last results on the trimethylene sulphide···HF, 3,3-dimethyl oxetane···HF and 3,3-dimethyl oxetane···HCl complexes.

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