The low-temperature environment of a free jet expansion provides an excellent laboratory for probing the conformational behaviour of hydrogen bonding. The first observation of axial and equatorial hydrogen-bonded complexes has been reported for tetrahydrofuran and pentamethylene sulphide complexes with HCl and HF. Both six-membered rings present two nonequivalent lone pairs at the O or S atoms and the formation of hydrogen bonds gives rise to two different axial and equatorial conformers. Recently, we have also reported axial and equatorial hydrogen bonds for trimethylene sulphide—HCl. For isolated trimethylene sulphide the ring-puckering tumbling motion makes equivalent the nonbonding electron pairs at the S atom. This equivalence is broken by effect of complexation, giving rise to axial and equatorial conformers. In this contribution we present the results on the related pentamethylene and trimethylene sulphide—HF complexes.

An unsubstituted alkane such as methane might act as a proton donor only in certain extraordinary circumstances. However alkanes appear capable of forming hydrogen bonds when sufficiently activated by neighboring electronegative substituents. In this context, the C-H–O interaction between the substituted alkane trifluoromethane and oxirane has been analyzed by MB-FTMW spectroscopy for the parent and $^{13}$C isotopomers. A $\eta_2$-$\eta_3$ structure has been derived and the barrier to internal rotation of the CF$_3$ group has been determined from the observed A-E splittings.

A MB-FTMW Spectrometer incorporating a laser ablation source has been constructed in our lab which avoids the use of high temperature techniques commonly used for vaporising low-volatility compounds. As a preliminary test, the rotational spectrum of 1,3,5-trithiane (m.p. 216°C) has been observed. The sensitivity of the instrument proved to be high enough to observe $^{34}$S isotopic species in natural abundance.

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