JET-COOLED ROTATIONAL STUDIES AT THE VALLADOLID LABORATORY

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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. The first observation of axial and equatorial hydrogen-bonded complexes has been reported for tetrahydropyran and pentamethylene sulphide complexes with HCl and HF.[a] 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$\cdots$HCl.[b] For isolated trimethylene sulphide the ring-puckering tunnellig 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$\cdots$HF complexes.

An unsubstituted alkane such as methane might act as a proton donor only in certain extraordinary circunstances. However alkanes appear capable of forming hydrogen bonds when sufficiently activated by neighboring electronegative substituents. In this context, the C-H$\cdots$O interaction between the substituted alkane trifluoromethane and oxirane has been analyzed by MB-FTMW spectroscopy for the parent and ^{13}C isotopomers. A r_o-like 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 ^{o}C) has been observed. The sensitivity of the instrument proved to be high enough to observe ^{33}S isotopic species in natural abundance.

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[a] S. Antolínez, J.C. López and J.L. Alonso, Angew. Chem. Int. Ed., 1999, 38,1772-1774. M.E. Sanz, J. C. López and J.L. Alonso, Chem. Eur. J., 1999, 5, 3293-3298. S. Antolínez, J.C. López and J.L. Alonso, ChemPhysChem, 2001, 2, 114-117.

[b] M.E. Sanz, A. Lesarri, J.C. López and J.L. Alonso, Angew. Chem. Int. Ed., 2001,(in press).