FLUORINE SUBSTITUTION AND COMPLEXATION EFFECTS ON FLEXIBILITY AND TUNNELING PATHWAYS: THE ROTATIONAL SPECTRUM 2-FLUOROBENZYLAMINE AND BENZYLAMINE-WATER

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Complex organic molecules are characterized by a high number of low energy conformations and the presence of large amplitude motions. Non-bonding interactions compete to shape their conformational space and potential energy surfaces and these interactions can be changed drastically through substitution of atoms and complexation. We report the effect of ring fluorination and water complexation on the structural and dynamical properties of the flexible model molecule benzylamine.[a] 2-fluorobenzylamine was studied by rotational spectroscopy in free jet expansion and quantum chemical methods. The complete potential energy surface originating from the flexibility of the aminic side chain, has been calculated at the B3LYP/6-311++G** level of theory and the stable geometries have been characterized also with MP2/6-311++G** obtaining a significant variation of the energy differences among conformers. The rotational spectra show the presence of two stable conformers analogous to those of benzylamine, but while in benzylamine the two conformations are isoenergetic the energy difference is increased 2-fluorobenzylamine. One of the observed conformers is characterized by a tunnelling motion between two equivalent positions of the amino group with respect to the phenyl plane which splits the rotational transition. The *ortho* fluorination increased, with respect to benzylamine, the tunnelling splitting of this motion by four orders of magnitude. The motion was analyzed with a one-dimensional flexible model which allowed to estimate the energy barrier for the transition state. The rotational spectra of the complex of water with benzylamine also recorded in free jet expansion shows the presence of only one conformation with the water molecule hydrogen bound to the nitrogen atom. The formation of the complex does not disrupt the initial conformation of the benzylamine monomer which is very close to that of conformer II of benzylamine while the tunneling motion is quenched.

[a] S. Melandri, A. Maris, P. G. Favero and W. Caminati *Chem. Phys. Chem.* **3** 172 2001