PROTON DONOR/ACCEPTOR PROPENSITIES OF AMMONIA: ROTATIONAL STUDIES OF ITS MOLECULAR COMPLEXES WITH ORGANIC MOLECULES

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We studied the rotational spectra of the adducts of ammonia with several organic molecules, namely *tert*-butanol,[a] glycidol,[b] ethyl alcohol, anisol and 1,4-difluorobenzene. The adducts with glycidol and ethanol have been observed for both conformers of the substrate molecule. Based on the rotational and ^{14}N quadrupole coupling constants of the various complexes, we found a considerably different behaviour of ammonia, with respect to water, in its proton donor/acceptor double role. In the interaction with the three alcohol molecules, NH_3 acts as a proton acceptor and the OH groups as a proton donor. However, in the case of glycidol-NH_3, a secundary N-H$\cdots$O interaction occurrs between ammonia and the ether oxygen. This interaction generates a sizable V_3 barrier to the internal rotation of the NH_3 moiety, while NH_3 undergoes a free rotation in *tert*-butanol-NH_3 and in ethanol-NH_3. As to the anisole-NH_3 and 1,4-difluorobenzene-NH_3 complexes, the NH_3 group explicits its double proton donor/acceptor role, although through two weak (C_{Me}-H$\cdots$N and N-H$\cdots\pi$) H-bonds. There is, however, an important difference between the two complexes, because in the first one NH_3 lies out of the aromatic plane, while in the second one it is in the plane of the aromatic ring.

[a] B. M. Giuliano, M. C. Castrovilli, A. Maris, S. Melandri, W. Caminati and E. A. Cohen, *Chem.Phys.Lett.*, 2008, 463, 330

[b] B. M. Giuliano, S. Melandri, A. Maris, L. B. Favero and W. Caminati, *Angew.Chem.Int.Ed.*, 2009, 48, 1102