

chemical groups (10 of donors and 14 of acceptors). It is shown that many HBs are *intrinsically weak* because of impossible pK_{AH}/pK_{BH} matching and that strong HBs can be obtained only by combining donor and acceptor molecules for which the $\Delta pK_a \approx 0$ condition is actually accessible.

Keywords: hydrogen bond, PA/pKa equalization, pKa slide rule

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Proton Migration in Hydrogen Bonded Donor-Acceptor Complexes

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Intermolecular hydrogen bonding plays an important role in forming anisotropic interactions in condensed systems, and subtle competition between H-bond acceptors/donors can lead to dramatically different solid-state structures. There is significant national and international research effort directed at the study of hydrogen bonding in the solid state. Much of this work has focussed on the *static* structures adopted by molecular hydrogen-bonded systems, but the importance of hydrogen atom migration through hydrogen bonds between molecules has also been identified. It is becoming increasingly apparent that the positions of the protons involved in hydrogen bonds are highly susceptible not only to chemical environment, but also to the effects of temperature and pressure.

A collaborative project has been set up with the aim of preparing molecular adducts in which a proton migrates between the donor and acceptor species as temperature and/or pressure is varied. In this poster we will describe our experimental techniques [1] and present results for some of our variable temperature studies of the 1:1 salt formed between 2-iodoaniline and picric acid [2].

[1] Parkin A., Harte S.M., Goeta A.E., Wilson C.C., *New J. Chem.*, 2004. [2] Tanaka M., Matsui H., Mizoguchi J., Kashino S., *Bull. Chem. Soc. Jpn*, 1994, **67**, 1572-1579.

Keywords: hydrogen bond, intermolecular interactions, variable temperature

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Multi-temperature Neutron & X-ray Studies of Hydrogen Bonded Molecular Complexes

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X-ray single crystal diffraction is a commonly used technique in many structural chemistry laboratories to find the structure of large and small molecules. However, neutron diffraction, although less readily accessible, is more sensitive to the determination of detailed hydrogen atom parameters, and this is of particular importance in hydrogen-bonded systems. By application of a multi-temperature approach to both these techniques, it is possible to study in detail the temperature-dependent behaviour of the hydrogen atoms within these hydrogen bonds. Features such as proton disorder and migration can be frequently observed.

Both X-ray and neutron multi-temperature single-crystal data has been collected on the molecular complex of isonicotinamidium formate. Neutron data were collected at four temperatures (40K, 100K, 150K, 200K) on the SXD instrument at ISIS, and X-ray data were collected on a laboratory diffractometer at 50K intervals from 100K-300K.

We will present the initial analysis of the neutron data, including some discussion of the inherent difficulties in processing such datasets and some of the early use in the chemical crystallography area of the new SXD2001 software developed for the instrument, which we are helping to test. We will also present how these initial neutron results compare with the X-ray data.

Keywords: neutron crystallography, hydrogen bonds, variable

temperature

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Proton Sponges of 1,2-bis(di-*R*-aminomethyl)benzene Type

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The pK_a values for 1,2-bis(di-*R*-aminomethyl)benzenes (DRAMB) are much higher than for DMAN, 1,8-bis(dimethylamino)naphthalene, the classic proton sponge. On protonation a strong intramolecular N-H...N H bond is formed. The molecule of DRAMB can adopt four idealized conformations with the following symmetries: (i) C_{2v} , (ii) C_2 , (iii) C_s -mirror plane in the benzene ring, (iv) C_s -mirror plane normal to the benzene ring. The C_{2v} symmetry is achieved by symmetric disposition of the alkyl groups above and below the benzene ring with the N atoms exactly in the ring plane, and with the lone pairs oriented away from or towards the aromatic ring. In both conformations, the monoprotonated DRAMB⁺ cation cannot form an intramolecular N...H...N bond. Conformation (ii) is characterized by location of the N atoms on the opposite sides of the benzene ring. Formation of a twofold-symmetric intramolecular N...H...N bonds is possible but the proximity of the N atoms in short bridges causes large steric effects even in simple system, such as DMAMB ($M=CH_3$). Form (iii) is compatible with intermolecular N-H...X hydrogen bonds. Form (iv), with the N atoms on one side of the aromatic system, is optimal for minimization of steric hindrance and for the formation of a short intramolecular H bond. A DMAMBH⁺ cation with exact C_s -symmetry (iv) is observed in the ClO_4^- salt. Pseudo C_s cations are found in the crystals of DMAMBH⁺·NO₃⁻ and DEAMBH⁺·ClO₄⁻ ($E=ethyl$). For bulkier substituents ($R=propyl$, butyl) the symmetry of the bis(aminomethyl)benzene moiety is closer to C_s .

Keywords: proton sponges, N-H...N hydrogen bond, conformation

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Ordering of Hydrogen Bonds in High-pressure Low-temperature Ices

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We have studied the near *K*-edge structure of oxygen in liquid water and ices III, II, and IX at 0.25 GPa and several low temperatures down to 4 K using inelastic x-ray scattering at 9884.7 eV with a total energy resolution of 305 and 175 meV [1]. It is found that the ordering of the oxygen network from the liquid phase to ice III causes only a small decrease of the preedge intensity, whereas the ordering of the hydrogen bonds in the proton-ordered lattice of ices II and IX dramatically reduces the preedge intensity, which is interpreted as a result of the diminishing number of uncoordinated hydrogen bonds in ices II and IX. Some preedge intensity remains, however, in the latter phases unexpectedly according to previous first principles calculations [2]. Our density functional theory calculations of the near-edge X-ray absorption spectrum for ice IX indicate that the remaining intensity may be due to the influence of the local electronic structure by the Madelung potential of the crystal lattice. Substantial changes of the near *K*-edge spectra from ice IX have also been observed below 50 K.

[1] Cai Y.Q., et al., *Phys. Rev. Lett.*, 2005, **94**, 025502. [2] Myneni S., et al., *J. Phys. : Condens. Matter*, 2002, **15**, L213.

Keywords: hydrogen bonds, electronic structure, X-ray inelastic scattering