

formula  $C_{19}H_{22}FN_3O_3 \cdot 6(H_2O)$  which crystallizes in a triclinic crystal system with space group  $P-1$ . Water molecules of the network array of hydrogen bonding interactions of the type O-H...H with distances that are within the range of 1.93 a 2.23 Å and as a few examples, in this case shows that some water molecules have three hydrogen bonds at the same time, which favors a two-dimensional crystal growth with the *motif*  $R^6_6(12)$ , giving rise to the supramolecular arrangement in a lamina.

In the dimeric complex of copper acetate (II) with molecular formula  $C_8H_{16}Cu_2O_{10}$ , have a monoclinic crystal system with space group  $C2/c$ , in this compound the water molecules establish three hydrogen bonds in the range of 2.03 to 2.58 Å, giving rise to *motif*  $R^2_2(8)$  mainly. While for crystals of  $[Fe(H_2O)_6]SO_4 \cdot 2(H_2O)$  (II) with molecular formula  $FeH_{12}O_6 \cdot 2(SO_4) \cdot 2(H_2O)$  crystallizing in a monoclinic crystal system with space group  $P2_1/n$ ; the large number of water molecules present in this complex supports a large number of such interactions O-H...H with hydrogen bond lengths are in the range of 1.85 to 2.19 Å.

In a global analysis of data from X-ray diffraction, is that the magnitude of the hydrogen bonds are present in the energy range of 4 to 15 Kcal, being strong bonds with weak covalence and dominant electrostatic contribution, these properties are required for the design and application engineering of crystals and / or molecular devices

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**Keywords:** hydrogen-bond, motif, engineering-crystals

## MS73.P14

*Acta Cryst.* (2011) **A67**, C666

### Structural analysis of aziridine-2-methanol derivatives

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Aziridines are widely used as versatile building blocks for the synthesis of a variety of biologically and pharmaceutically important molecules [1]. Among the available methodologies for the preparation of functionalised aziridines, the lithiation/trapping sequence of simple parent aziridines is growing in importance [2]. Present work reports the results concerning the structural study of aziridine-2-methanol derivatives by dynamic nuclear magnetic resonance (DMNR) [3] and single crystal X-ray diffraction. A careful examination of the aziridine 2 (see figure 1) by NMR data, shows that at room temperature the meta protons and the protons of the two ortho methyl groups of the mesityl ring gives featureless lumps, likely as consequence of a restricted rotation around the  $Csp^3-Csp^2$  bond between the carbinolic carbon and the ipso carbon of the mesityl ring. Also in the solid state, an almost identical arrangement of the mesityl ring, with respect to the other two phenyl rings, has been observed. In this case, the aziridine nitrogen substituent was found in a syn relationship with respect to the carbinolic group so preventing the possibility of forming a hydrogen bond with the hydroxyl group. This evidence underlines a slow rotation of the mesityl group instead of a nitrogen inversion as usually is expected. By X-ray analysis of 3 and *diast-3* (figure 1), it is estimated that the nitrogen substituents set on the opposite side with respect the carbinolic carbon. *Via* study of crystal structures, the presence of hydrogen bonds between the hydroxyl group and the aziridine nitrogen lone pair was ascertained for aziridine 3 but not for *diast-3* (figure 1). Such

a hydrogen bond, which is persistent also in solution, could prevent the formation of conformational diastereoisomers by rotation around the bond between the carbinolic carbon and the aziridine quaternary carbon. This hypothesis has been demonstrated by

NMR experiments. This investigation allowed us to calculate some  $Csp^2-Csp^3$  and  $Csp^3-Csp^3$  rotational barriers and highlight a sort of “geared” rotation between aryl and alkyl substituents; this is possible if the structure is not in a locked conformation by an hydrogen bond as demonstrated by NMR and X-ray diffraction.

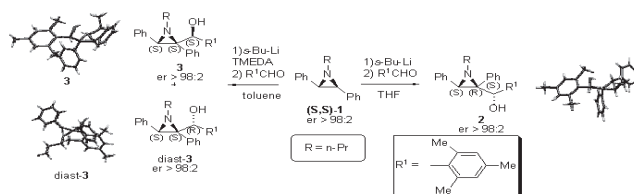


Figure 1

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**Keywords:** NMR, organic synthesis, structural solution.

## MS73.P15

*Acta Cryst.* (2011) **A67**, C666–C667

### Proton migration in molecular complexes of urea and its derivatives

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Systems showing proton disorder, transfer and migration are an area of much interest in recent times with widespread implications for areas such as ferroelectrics and enzyme action. These often subtle processes can affect the properties of systems and are often observed in materials containing short strong hydrogen bonds. They can be probed using variable temperature diffraction experiments. We aim to identify and characterise systems that show such effects, with a view to predicting and controlling this potentially “tunable” behaviour. These processes have previously been observed in complexes of urea [1].

Single crystal X-ray and neutron diffraction have been used to study molecular complexes of urea and its derivatives with a particular focus on characterising the hydrogen atom behaviour. The proton behaviour is monitored over variable temperatures, with the aim of observing movement of the proton with changing temperature. A limited number of such mobile proton effects have been observed using variable temperature diffraction measurements, and this project aims to build on these observations by extending these investigations to further, related, systems. The instrument used for the neutron studies is the single crystal Laue diffractometer VIVALDI at the ILL in Grenoble which is ideal for use here due to its potential for high throughput single crystal diffraction of small samples.

Temperature dependent proton migration in the 2:1 complex of N,N-dimethylurea and oxalic acid has been observed by single crystal X-ray and neutron diffraction data confirming the existence of this phenomenon. Accurate determination of the hydrogen atom parameters in this system is vital in understanding this phenomenon and also in explaining a single-crystal to single-crystal phase transition

at ~120-130 K observed using X-ray powder diffraction. Unusual thermal properties have been observed in the 2:1 complex of urea and fumaric acid in which hydrogen ADP trends may play a role in potential negative thermal expansion along one of the crystallographic axes. Proton transfer has also been observed in a series of complexes of urea with bromanilic acid. All of these studies have benefited from our approach of multiple condition diffraction studies of structural evolution.

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**Keywords:** hydrogen-bonding, neutron, laue

## MS73.P16

*Acta Cryst.* (2011) **A67**, C667

### Design and control of hydrogen bonding in DMAN proton sponge complexes

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1,8-bis(dimethylamino)naphthalene (DMAN) is commonly known as a proton sponge and is often observed to accept a proton from acidic materials into an N-H...N intramolecular hydrogen bond. We have been using co-crystallisation with a series of benzoic acid derivatives to explore the charge assisted hydrogen bonding induced both within the DMAN and between benzoic acid molecules. X-ray diffraction has been used extensively to determine the resulting crystal structures, with a particular emphasis on attempting to determine accurate hydrogen atom parameters and to define the hydrogen bonding schemes.

In general, DMAN and halogen substituted benzoic acid co-crystals form in a 1:2 ratio where the DMAN molecule deprotonates one benzoic acid molecule taking the hydrogen into a short strong intramolecular hydrogen bond. To compensate for this, the two halogen substituted benzoic acid molecules then form a short, strong, charge assisted hydrogen bond between themselves to stabilise this loss of a proton by forming a single hydrogen bonded dimer motif and with the protonated DMAN molecule acting as building blocks of the complex. This dimer motif is present across almost the entire series of halogen substituted benzoic acid and DMAN molecular complexes with divergence present between the benzoic acids relative position to each other caused mainly by the halogen-halogen interactions occurring in these complexes. Increasing the competition for hydrogen bonds by using hydroxybenzoic acids as the co-molecule induces a different composition ratio and behaviour of the benzoic acid in the complex formed. The 3-hydroxy and 4-hydroxy benzoic acids co-crystallise with DMAN in a hydrated 2:2:1 ratio where the stabilisation of charge takes place through two medium strength intermolecular hydrogen bonds – one to a hydroxy group of a neighbouring molecule and one to a water molecule. The single hydrogen bonded dimer motif is no longer present in the complex hence there are no distinctive building blocks in the structure. The benzoic acid molecules instead form extended chain like structures where the water molecules take part in the interactions both within the chains and between the layers of benzoic acids creating a framework between which DMAN molecules are sandwiched. The water thus plays an important role in the structure as a whole.

The effect of hydration has been studied further by introducing water as a third component in DMAN and halogen-substituted benzoic acid molecular complexes; the DMAN to benzoic acid ratio is reversed in this case (2:1, DMAN to BA) and the single hydrogen bonded benzoic acid dimer motifs are not present. Stabilisation of the lost hydrogen on the benzoic acid is achieved in this case through two water

molecules creating a hydrogen bonded ring involving four molecules. The DMAN and the ring of two water and two benzoic acid molecules thus become the building units of this molecular complex. Unusually, in this case DMAN appears in both its protonated and unprotonated forms, a consequence of the crystallization ratio and the resulting molecular complex stoichiometry.

**Keywords:** hydrogen bonding, proton transfer, proton sponge

## MS73.P17

*Acta Cryst.* (2011) **A67**, C667

### Organic and inorganic halogens as HB acceptors in halopyridine complexes of Cu<sup>II</sup>

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Although interactions involving halogen acceptors have been reported from the early years of hydrogen bonding (HB) research, the primary attention was paid on the oxygen and nitrogen acceptors [1]. Furthermore, due to large partial negative charges in their complexes, fluorine and chlorine are more frequently observed as HB acceptors than less electronegative heavier halogens, e.g. bromine and iodine. The information retrieved from X-ray studies on hydrogen bonding are geometry details of the D—H...A—Y moiety. While the linear D—H...A angles are statistically favoured over bent ones, the preference for the bent angles at accepting halogen atoms originates in the highly anisotropic electron density around the halogen nucleus known as 'polar flattening' [2].

Here we report the preparation and characterization of a series of halopyridine complexes of copper(II) with intention to examine the geometry details of weak hydrogen bonding involving organic and inorganic halogens as HB acceptors. In addition to thermal and spectroscopic techniques, the complexes have been characterized using single crystal X-ray diffraction as well.

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**Keywords:** Cu(II) complexes, weak H-bonds, supramolecular synthons

## MS73.P18

*Acta Cryst.* (2011) **A67**, C667-C668

### Structural systematics of fluoro-N-(pyridyl)benzamides and related isomer grids

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A 3x3 isomer grid of nine fluoro-N-(pyridyl)benzamides (C<sub>12</sub>H<sub>9</sub>N<sub>2</sub>O<sub>F</sub>) as **Fxx** (x = *para*-/*meta*-/*ortho*-) was studied to evaluate and correlate structural relationships from both *ab initio* calculations and the solid-state. The effect of fluoro (**Fx**) and pyridine N atom (**x**) substitution patterns on molecular conformations from calculations and in terms of molecular organization was evaluated.

Eight isomers are forming N-H...N hydrogen bonds and only one isomer (**Fom**) is found to have exclusively N-H...O=C interactions. However, the **Fpm** isomer was found in two polymorphs, **Fpm\_N** and **Fpm\_O**, both in the same space group (P2<sub>1</sub>/n) but with different