

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.

[1] A. Parkin, S. Harte, A. Goeta, C.C. Wilson, *New J. Chem.* **2004**, 28, 718-721

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

## MS73.P16

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### 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

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### 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

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### 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

primary hydrogen bond backbone; **Fpm<sub>N</sub>** with N-H...N and **Fpm<sub>O</sub>** with N-H...O=C as primary interaction. The **Fom** isomer was unexpectedly found highly disordered with  $Z' = 6$ .

The most significant structural characteristic of the **Fxo** triad was formation of twisted dimmers through double N...H-N hydrogen bonding creating centrosymmetric  $R^2_2(8)$  rings. Formation of dimmers when pyridine nitrogen is in *ortho* position is already seen in analogue **Mxo** [2] isomers.

Computational modelling and conformational analyses of the **Fxx** isomers and their comparison with solid state structures showed that modelled structures generally comply with solid state conformations except in the **Fxm** isomers. Modelling of the **Fox** isomer triad suggested existence of intramolecular F...H-N bonding. Spectroscopic and crystallographic data supported this prediction.

This work represents the final step in the investigation of the four benzamide/carboxamide isomer grids with methyl/fluorine substituents (**Mxx** [1], **NxxF** [2], **NxxM** [3] and **Fxx**), by both solid state methods and computational modelling, with innovative approach in bridging two powerful structural methods together. The comparison of the four isomer grids revealed high degree of similarity regarding solid state aggregation and physicochemical properties, while correlated melting point values indicated significance of the substituent position on thermal behaviour, rather than the nature of substituent.

[1] P. Mocilac, M. Tallon, A.J. Lough, J.F. Gallagher, *CrystEngComm*, **2010**, *12*, 3080-3090. [2] P. Mocilac, A.J. Lough, J.F. Gallagher, *CrystEngComm*, **2011**, *13*, 1899-1909. [3] P. Mocilac, J.F. Gallagher, *CrystEngComm*, **2011**, (DOI:10.1039/c1ce05169e).

**Keywords:** benzamides, solid-state, modelling

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### Analysis of Ethyl (2E)-3-(4-hydroxy-3,5-dimethoxyphenyl) prop-2-enoate

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In recent decades it has been discovered a wide range of biological activities for the derivatives of cinnamic acid. There are reports that the derivatives trans-cinnamic acid possess hepatoprotective activity, antimalarial, antimicrobial antioxidant and  $\alpha$ -glucosidase. Furthermore, *in vitro* tests showed regression of malignant cells in human tumors. The single crystal of Ethyl (2E)-3-(4-hydroxy-3,5-dimethoxyphenyl) prop-2-enoate ( $C_{13}H_{16}O_5$ ) was obtained by slow evaporation technique using as solvent ethyl ether. The structure was solved by Direct Methods and refined by full matrix Least Square methods on  $F^2$  using WINGX package [1]. Non H atoms were refined anisotropically and all H atoms were placed geometrically except the hydrogen of the water molecule and of the hydrogen of the hydroxyl that were placed by D.W. Smith method [2], where the hydrogen are placed by estimating atomic charges by electronegativity equilibration. The compound crystallizes in the C2/c monoclinic space group and the cell dimensions are:  $a = 21.273(5)$  Å,  $b = 7.391(3)$  Å,  $c = 17.898(7)$  Å,  $\alpha = \gamma = 90^\circ$  and  $\beta = 92.64(3)^\circ$ ,  $Z = 8$  and  $V = 2811(2)$  Å<sup>3</sup>. 23018 measured reflections with 4279 unique and 2587 observed [ $I > 2\sigma(I)$ ]. The final residual factor  $R_1$  is 0.0607 for 181 refined parameters using 25 restraints. In the asymmetric unit there is a disordered water molecule that causes a partial disorder at the ester molecule, the disorder may be caused by a repulsive interaction between the hydrogen of the water molecule and of the hydroxyl of the ester molecule.

[1] S. L. Farrugia, *J. Journal Appl. Cryst.*, **1999**, *32*, 837. [2] M. Nardelli, *J. Appl. Cryst.*, **1999**, *32*, 563-571.

**Keywords:** cinnamic acid, X-ray diffraction, hydrogen bonds

## MS73.P20

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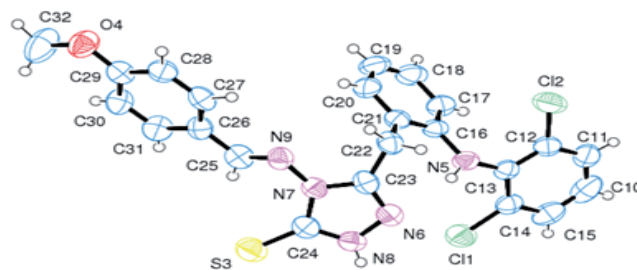
### X-ray structure of 4-methoxybenzylideneamino-5-substituted triazole derivative

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The crystal structure of the title derivative, 5-[2-[(2',6'-dichlorophenyl) amino] benzyl]-4-(4-methoxybenzylideneamino)-2H-1,2,4-triazole-3(4H)-thione ( $C_{23}H_{19}N_3OSCl_2$ ) is determined by X-ray diffraction method and crystallizes in the Triclinic space group *P-1* with cell parameters  $a = 7.9438(4)$  Å,  $b = 10.9163(7)$  Å,  $c = 14.0384(8)$  Å,  $V = 1140.98(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{calc} = 1.410$  mg/m<sup>3</sup>,  $\mu = 0.402$  mm<sup>-1</sup>,  $F_{000} = 500$ ,  $\lambda(MoK_{\alpha}) = 0.71073$  Å and the structure was refined to  $R = 0.0561$ .

Schiff bases are condensation products of primary amines with carbonyl compounds. The presence of lone pair of electrons in the  $sp^2$  hybridised orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Schiff bases are some of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis and polymer stabilisers. They have also been shown to exhibit broad range of biological activities including antimalarial, antibacterial, antifungal, antiviral and antitubercular/Imine or azomethine groups are present in various natural, natural-derived and non-natural compounds. The imine group present in such compounds has been shown to be critical to their biological activities.

The structure of 5-[2-[(2',6'-dichlorophenyl) amino] benzyl]-4-(4-methoxybenzylidene amino) -2H-1,2,4-triazole-3 (4H)-thione contains just one molecule in the asymmetric unit. The triazole ring makes dihedral angles of 24.81 (18)°, 69.94(19)° and 35.68(18)° with the three aromatic rings, respectively. The structure of the molecules is stabilized by intermolecular N-H...S and intramolecular C-H...S & N-H...N hydrogen bonds. In the crystal, molecules are stacked along *a* axis.



[1]. L.J. Farrugia, *J. Appl. Cryst.*, **1997**, *30*, 565. [2]. M.S. Karthikeyan, D.J. Parsad, K. Boja Poojary, S. Bhat, B.S. Holla, N.S. Kumari, *Bioorg. Med. Chem.* **2006**, *14*, 7482-7489. [3]. S.N. Pandeya, D. Sriram, G. Nath, E. Declercq, *Eur. J. Pharmacol.* **1999**, *9*, 25-31. [4]. P. Panneerselvam, R.R. Nair, G. Vijayalakshmi, E.H. Subramanian, S.K. Sridhar, *Eur. J. Med. Chem.* **2005**, *40*, 225-229. [5]. K. Singh, M.S. Barwa, P. Tyagi, *Eur. J. Med. Chem.* **2006**, *41*, 1-9. [6]. G.M. Sheldrick, *Acta Cryst. A*, **2008**, *64*, 112-122.

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