

chemical modifications of the molecular structures are very reliable and accessible, prediction of the supramolecular behavior is not always easy and in some cases can be very complex.

In this paper, examples of these new hosts will be presented as well as their design and synthesis procedures. Furthermore, the crystal structures of some of these new inclusion compounds will be described in detail.

[1] Alshahateet S. F., Bishop R., Scudder M. L., Hu C. Y., Lau E. H. E., Kooli F., Judeh Z. M. A., Chow P. S., *CrystEngComm.*, 2004, *submitted*. [2] Alshahateet S. F., Bishop R., Craig D. C., Scudder M. L., *Cryst. Growth Des.*, 2004, 4(4), 837-844. [3] Bishop R., Scudder M. L., Rahman A. M. M., Alshahateet S. F., Craig D. C., *Molecular Crystals & Liquid Crystals*, 2005, *accepted*.

Keywords: inclusion compounds, host, crystal structure

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Interactions of Supramolecular Synthons Formed by Secondary Propargylic Alcohols

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Chiral secondary propargylic alcohols are used in the enantioselective synthesis of natural products and as synthetic precursors of several optically active compounds. Secondary propargylic alcohols with aryl substituents possess three important functional groups: the hydroxyl group, the π system of the alkyne moiety, and a variety of aryl rings that can be involved in π - π stacking as well as other interactions. The combination of the three functional groups attached to one chiral carbon makes secondary propargylic alcohols well suited for applications in supramolecular chemistry and crystal engineering [1-3].

The competition between O-H...O hydrogen bonds and weaker interactions such as C-H... π and π - π stacking leads to the formation of a diverse set of synthons, including non-planar hexamers. The cooperativity between intermolecular forces is essential for the stabilization of these synthons.

[1] Desiraju G.R., *Angew. Chem. Int. Ed. Engl.*, 1995, 34, 2311. [2] Bilton C., Howard J.A.K., Madhavi N.N.L., Nangia A., Desiraju G.R., Allen F.H., Wilson C.C., *Acta Cryst.*, 2000, B56, 1071. [3] Madhavi N.N.L., Desiraju G.R., Bilton C., Howard J.A.K., Allen F.H., *Acta Cryst.*, 2000, C56, 1359.

Keywords: supramolecular chemistry, crystal engineering, organic molecule

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Stereochemistry in Crystal Engineering

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Molecular recognition by hydrogen bonding between organic molecules has been explored in supramolecular chemistry to a great extent.^{1,2} Most of the recognition motifs are however two-dimensional in nature. By employing organic compounds in the context of supramolecular chemistry and utilizing their chiral attributes the three-dimensional nature of intermolecular hydrogen bonding may be revealed.

This project, to date, has been focused on the design and synthesis of sulfides, sulfoxides and sulfones. Sulfoxides are ideally suited as a recognition motif as they are extremely polar and have the potential to participate in hydrogen bonding. The intrinsic chirality at sulfur introduces the three-dimensional nature of the study. The effect of the oxidation state of sulfur on the hydrogen bonding array is also investigated, along with other substituent effects.

[1] Desiraju G.R., *Angew. Chem. Int. Ed. Engl.*, 1995, 34, 2311. [2] Weiss H.C., Boese R., Smith H.L., Haley M.M., *Chem. Commun.*, 1997, 2403.

Keywords: hydrogen bonding, chirality, sulfur

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Ringling the Changes with Tetrazole: Hydrogen Bonding Studies

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Tetrazoles are acidic heterocycles and used in angiotensin II receptor antagonists for the treatment of high blood pressure. The binding mode is still controversial [1], as yet the only published crystal structure of a tetrazole-protein complex shows close contacts between two of the tetrazole nitrogen atoms and two lysine residues within the enzyme binding site. [2]

Tetrazoles are used as bioisosteric replacements for carboxylic acids in modern drug design. Transmembrane receptors are notoriously difficult to study, so model systems can provide further insight into non-covalent binding interactions.

This work describes the hydrogen-bonding patterns seen for readily available ionic model complexes, developing earlier studies of hydrogen-bonding tetrazolate anion [3] and illustrate how the tetrazole, or simple derivatives bind to acetamidine (arginine model), propranolol (an antihypertensive drug) and spermine (a natural hormone). These will be compared with analogous carboxylic acid complexes to provide insight into the hydrogen bonding interactions favoured by tetrazoles as well as difference in binding properties.

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Keywords: drug binding, hydrogen bonding, heterocyclic compounds

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Structure of N,N-dimethylaminopyridinium L-malate

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The crystal structure of a new L-malic acid salt, N,N-dimethylaminopyridinium L-malate has been determined at room temperature using single crystal X-ray diffraction techniques. The space group is orthorhombic $P2_12_12_1$ with lattice parameters $a = 7.461(1)$, $b = 7.945(1)$ and $c = 20.774(4)$ Å. Similarly to other L-malic salts, the malate anions form hydrogen-bonded head-to-tail (carboxylic and carboxylate groups) infinite chains parallel to the [100] crystal direction. On the other hand, the dimethylaminopyridinium cations are arranged with their mean plane approximately perpendicular to the [100] crystal direction. The N-H group of every cation forms two hydrogen bonds with oxygen atoms of different anion chains connecting L-malate chains along the [010] crystal direction. The whole crystal packing can be viewed as parallel two-dimensional hydrogen-bonded molecular arrangements perpendicular to the [001] direction. As in other L-malic salts, preliminary measurements show optical second-harmonic generation.

Keywords: nonlinear optical materials, molecular crystals, crystal engineering

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Complexes of Non-chiral Surfactant Molecules with Chiral and Racemic Compounds

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Understanding the interactions between two different types of molecules in the complex crystal become important in the study of molecular recognition and crystal engineering. Particularly, the molecular recognition in the complex crystal is a subject of considerable interest because of its applications to separation purposes. A few years ago, it was reported [1] that an interaction between a chiral onium salt (Cinchonidinium Chloride) and racemic compound (Bis- β -naphthol) accomplishes a successful enantiomeric resolution, but many researchers are interested in exploiting economical means of resolving racemic compounds such as probable useage of a non-chiral host molecule. This is a difficult task yet to be achieved.

As an initial approach in our investigations, the crystallization of non-chiral host compound (monoalkyltrimethylammonium halides) with (R)-(+)-1,1'-Bi-2-naphthol (RBNP) and Rac-1,1'-Bi-2-naphthol (BNP) were chosen to investigate the molecular recognition between non-chiral host compound and chiral as well as racemic compound from the viewpoint of crystal structure studies in order to know the feasible interactions, molecular packing structures and space groups of such complexes. The investigations revealed that the hexyltrimethylammonium bromide (6TAB) and octyltrimethylammonium bromide (8TAB) interact with RBNP and BNP to form molecular complexes (6TAB/RBNP, 6TAB/BNP, 8TAB/RBNP and 8TAB/BNP) by crystallization or mixing of powdered samples in a mortar. Both 6TAB/RBNP and 8TAB/RBNP molecules crystallize in monoclinic space group $P2_1$, whilst 6TAB/BNP and 8TAB/BNP crystallize in triclinic space group $P\bar{1}$ and monoclinic space group $P2_1/c$, respectively. Hydrogen bonds and C-H $\cdots\pi$ interactions stabilize the crystal structures and also contribute to the different packing modes observed in the complexes.

[1] Toda F., Tanaka T., *Chem. Commun.*, 1997, **12**, 1087.

Keywords: molecular recognition, crystal engineering, molecular compounds

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Spontaneous Resolution of *N*-sulfonylpyrimidine Compounds Induced by Chemical Modifications

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The title compounds belong to a novel series of pyrimidine nucleobase derivatives, some of which exhibit significant anticancer activity *in vitro*. [1] The crystal structures of 1-tosylthymine (**1**), 1-tosyluracil (**2**), α -naphthyl derivatives of thymine (**3**) and uracil (**4**) are presented. The conformational chirality was encountered in all compounds, as the consequence of the S-N single bond free rotation hindrance in solid state (*atropisomerism*). [2]

The spontaneous resolution (*à la Pasteur*) of *P* and *M* conformational enantiomers occurred during the crystallization of **2** and **4**, whereas their 5-methyl analogues, **1** and **3**, crystallized as racemic mixtures. Moreover, spontaneous resolution in the case of **2** was accompanied by a formation of racemically twinned crystals regardless of the solvent used. Obviously, substituents at C-5 position of pyrimidine base as well as in -SO₂-R group dictate the occurrence (or absence) of spontaneous resolution.

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Keywords: conformational chirality, racemic twinning, pyrimidine nucleobases

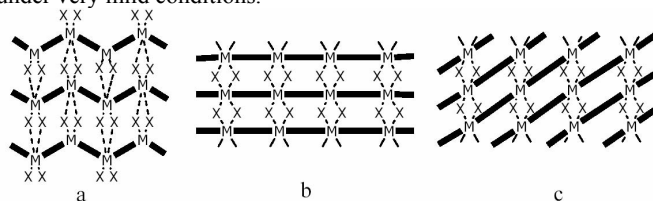
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Single-Crystal to Single-Crystal Reactions

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Single-crystal to single-crystal (SCSC) reaction represents the most fascinating field of solid-state chemistry [1-2], which in nature demands to make or break strong chemical bonds. Such transformation involves cooperative atomic movement between reactant and product (both are single crystals) in solids. In this contribution we wish to present two thermal-induced reversible SCSC reactions, in which unprecedented changes in network topology occur under very mild conditions.



1) Topotactic phase transformation between 1D tetrahedral chain polymers $[Zn(\mu-Cl)_2(4,4'-bpy)]_\infty^1$ (**1a** and **1b**, structure a) and 2D network $[Zn(\mu-Cl)_2(\mu-bpy)]_\infty^2$ (**2**, b) [3]; 2) between two 2D networks b and c on the polymer $[Pb(\mu-Cl)_2(\mu-bpy)]_\infty^2$ (**3**).

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Keywords: crystal engineering, topotactic phase transformations, crystal chemistry and reactions in solids

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Crystal Engineering of Metal-organic Frameworks Using 4,4'-Dipyridyl-N,N'-Dioxide

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Hybrid organic-inorganic materials provide the possibility of combining the advantages of organic and inorganic substances [1]. Schröder *et al* reported [2] that several terbium (III) coordination polymers of differing stoichiometry can be prepared by means of diffusion solvent mixtures using 4,4'-dipyridyl-N,N'-dioxide (dpdo). We have been investigating the coordination polymers of gadolinium (III) and thallium (III). Crystal structures acquired had either zigzag diamondoid or ladder shapes.

The study of metal-organic frameworks (MOF) has been extended to transition elements such as CuCl₂, ZnBr₂, Zn(NCS)₂ and PbCl₂. We have found that changing the metal geometry, while using the same spacer ligand (dpdo), has a significant effect on the type of MOF obtained. The effect of the metal salt anion is also examined. Crystal structures show that the materials we obtain are either polymeric or discrete molecules, which form a 2D or 3D network by means of supramolecular interactions.

Compounds synthesized were characterized by x-ray diffraction and thermal analysis {thermogravimetry (TG), differential scanning calorimetry (DSC) and hot stage microscopy}. Microanalysis was used to confirm the elemental composition.

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Keywords: crystal engineering, metal-organic framework, X-ray diffraction

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MOFs of Phenylamine and Pyridine Derivatives: Structure and Thermal Analysis

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