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X-ray diffraction and microscopy study of supramolecular networks of amido functionalized compounds

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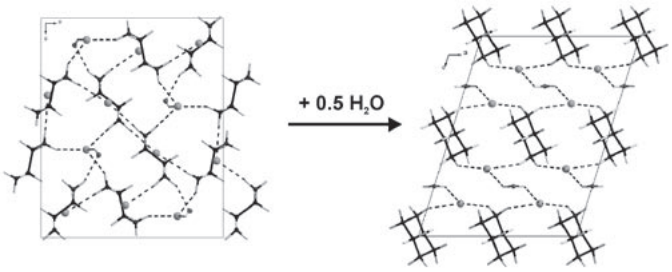
Crystalline amido functionalized organic compounds have been investigated towards the forming of solvates, halogenides and their reactivity towards various metal salts at different temperatures and under variable recrystallization conditions. Crystal structure determination, temperature-dependant X-ray powder diffraction as well as hot-stage microscopy experiments have been carried out successfully and revealed new aspects for a crystal engineering of isotypical but not isomorphous co-crystals or supramolecular compounds. Even though the crystal structure of co-crystals of melamine and EDTA (ethylenediaminetetracetic acid) contains water molecules, the two components form a solvent-less stable supramolecular network. In contrast to this, the inclusion of different solvents into the structure of 1,4-diaminocyclohexane chloride and 1,4-piperazine chloride (see Fig.) causes significant structural changes as demonstrated by hot-stage microscopy and X-ray diffraction experiments at various temperatures. We investigate the reasons for these structural changes due to solvent inclusion.



Keywords: crystal engineering, hydrogen bonding, supramolecular amides

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Systematic mutation study toward the engineering of protein crystals

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It is well-known that the protein crystallizability is influenced by a site-directed mutagenesis on the molecular surface of proteins, indicating that the intermolecular interactions at crystal packing regions might have a crucial role on the structural regularity at atomic resolution of protein crystals. Here we systematically examined the improvement of the resolution of protein crystals by introducing a single mutation to the crystal packing residue so as to provide more favourable packing interactions, using a model system of diphthine synthase from *Pyrococcus horikoshii* OT3. All the designed 21 mutants in total at 13 different crystal packing residues yielded nearly isomorphous crystals from the same crystallization condition to that for the wild-type crystals which diffracts X-rays at 2.1 Å resolution. Of the 21 mutants, eight have provided crystals with improved resolutions of 1.8 Å or better. Thus it has been clarified that the crystal quality can be improved by introducing a proper single mutation to the crystal packing residue. In the improved crystals, more intimate crystal packing interactions than those in the wild-type crystal are seen. Notably, the mutants K49R and T146R yielded crystals with outstandingly improved resolutions of 1.5 and 1.6 Å, respectively, in which a large-scale rearrangement of packing interactions is unexpectedly observed in spite of retaining the same isomorphous crystal form. On the other hand, the mutants that provided results in good agreement with the designed putative structures tend to achieve only moderate improvements in resolution up to 1.75 Å. These results suggest a difficulty in the rational prediction of highly effective mutations in the crystal engineering.

Keywords: protein crystallography, crystal engineering, crystal packing

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Crystal engineering of materials with potential NLO properties using barbituric acid as component

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The barbituric acid and urea addition compound have been considered in crystal engineering of materials with potential NLO properties. Using different crystallization conditions three polymorphs have already been obtained and their crystal structures were determined. Two polymorphs belong to monoclinic space groups $P2_1/c$ and Cc, whereas the third one is triclinic P-1. Due to complementarity of the donor and acceptor functional groups of the barbituric acid and urea molecules, the moderate hydrogen bonds were formed. The interactions dominate in the structures. The recognized tautomers of barbituric acid [1] seems to be responsible for different hydrogen-bond systems observed in the polymorphs and for different packing topology. The polymorphic forms have been easily differenciated already at the first-level graph-set analysis [2] of their hydrogen bond systems, newertheless the higher-level approach enabled to reveal significant features of the spacial mutual arragement of the structural components. Only one polymorph of polar space group *Cc* could be considered as a potential non-linear material and the appropriate measurements are in progress.

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[2] Bernstein J., Davis R.E., Shimoni L., Chang Ning-Leh (1995). *Angew. Chem. -Int. Edition in English* 34, 1555-1573.

Keywords: polymorphism, barbituric acid and urea addition compound, graph-set analysis

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Energy versus 3D geometry - A study of intermolecular interactions using theory and experiment

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Crystal structures are in general held together by “a combination of intermolecular pair interactions that, taken separately, are less

than optimal" [1]. Nevertheless, it is important to appreciate the preferred arrangement of functional groups within a non-covalent interaction if a crystal is to be engineered. An understanding of the relative energetics of different interaction motifs as well as the effect of changes in the geometry on the interaction energy is also crucial when designing or analysing crystal structures. Towards this goal a number of intermolecular interaction types have been investigated based on energy and geometry, including cyano...cyano contacts and hydrogen bonds to C=S acceptors. A combination of approaches has been used in this study to investigate the changes in the non-covalent interactions. Firstly, a study of structures available in the Cambridge Structural Database [2] has been performed to determine the relative directionalities of the interactions and their preferred geometries in the solid state. Intermolecular interaction energy calculations have then been carried out using intermolecular perturbation theory as implemented in the CADPAC 6.5 program package [3].

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[2] Allen, F. H. (2002). Acta Crystallographica, Section B58, 380-388.
[3] Amos, R. D. et al. (1998). CADPAC 6.5, The Cambridge Analytic Derivatives Package.

Keywords: intermolecular interactions, energy calculations, cambridge structural database

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Controlling the formation of co-crystal polymorphs

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Crystal engineering as a concept is approaching its 20th birthday, since first defined by Desiraju[1] in 1989. This area of chemistry has been of increasing importance, as our knowledge of the solid-state has developed. Crystal engineers have tended to focus solely on the single crystal products of their co-crystallisation experiments, although increasingly polymorphism is being observed in these products grown under different conditions[2]. It seems, therefore, that as with traditional chemical synthesis and the crystallization of single-component systems, the method of synthesis can greatly affect the observed product. Polymorphism adds a new level to the challenge facing crystal engineers; not only is it necessary to understand the co-crystal (we use the term here in its broadest sense, encompassing all "multi-component" crystals) in terms of the supramolecular synthon, but to successfully predict and synthesise new co-crystal complexes it is also necessary to investigate the method of co-crystal formation. Our aim has been to prepare, characterise and control new co-crystal complexes by varying the physical conditions under which they are grown. This poster will present some results of our investigations into the control of polymorphism in co-crystals by using a range of solvents, and will illustrate how the combined use of a number of analytical techniques − including single crystal diffraction, powder diffraction, Differential Scanning Calorimetry and Infra-Red Spectroscopy − is necessary to fully investigate the compounds observed.

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2. Sreekanth,B.R.,Vishweshwar,P and Vyas,K. (2007).Chem. Comm.2375-2377.

Keywords: polymorphs, solvent effects, crystal engineering

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Comparing entire crystal structures: Structural genetic fingerprinting

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A method is described that is both robust and generally applicable, which allows the calculation of a similarity index between whole molecular crystal structures [1]. It is based on the use of fingerprint plots derived from Hirshfeld surfaces coupled with cluster analysis and associated multivariate statistics. Using this formalism, it is possible to show quantitatively that naphthalene is more similar to anthracene than to benzene, and moreover that benzodicoronene is more similar to anthrabenzonaphthopentacene than naphthalene is to anthracene. Whereas the correlation coefficients themselves obtained say nothing about the ways in which the patterns of intermolecular interactions are similar or different for two different structures, the fingerprint plots do contain such information. For the first time structural analysts have a robust method for quantifying structural similarities of whole molecular crystal structures; this has been termed 'Structural Genetic Fingerprinting'. Developments of this method, including the use of partial fingerprints, will be presented. A number of examples will be used to illustrate the broad applicability of the method, including a comparison of predicted crystal structures and a comparison of intermolecular interactions in apparently dissimilar structures. The method will be shown to be suitable for large datasets of hundreds or even thousands of structures.

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Keywords: structure comparison, hirshfeld surface, structural genetic fingerprinting

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Mixed crystal of bidentate and tridentate perfluoro-phenylmercury Lewis acids with organic molecules

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At present a number of studied organic/organic mixed crystals (co-crystals) is quite significant, however not many mixed organic/organometallic crystals have been synthesised and described till now. Our group collected a large array of experimental data that have shown affinity of Lewis acids, such as cyclic tridentate perfluoro-o-phenylmercury, o-$C_6F_4Hg)_3$ (I) and bidentate 1,2-bis(chloromercurio) tetrafluorobenzene o-$(C_6F_4)(HgCl)_2$ (II), to formation of mixed crystals with numerous neutral and ionic organic molecules. Formation of mixed crystals can influence catalytic activity, solid state polymerization, prevent decomposition of unstable guest-molecules, transform spectral behaviour of guest,