

P06.06.17

Acta Cryst. (2008). A64, C388**Guest-induced topological polymorphism of pseudo-cubic hydrogen bond networks**

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Polymorphism has been the focus of constant attention, especially in the area of crystal engineering and pharmaceutical chemistry. Most of the polymorphic crystals were found by chance and still remain uninterpreted in detail, despite lengthy research. On the other hand, guest-inclusion and co-crystallization are recognized as standard tactics for obtaining different molecular arrangements. In fact, a great deal of inclusion crystals exhibit a wide variety of the guest-dependent arrangements of the host molecules. For control of the molecular arrangements, the concept of supramolecular synthon has been employed as one of the most influential concepts in the field of crystal engineering during the past decade. Up to now, many supramolecular synthons have been reported and applied to crystal design. Among them, finite and closed hydrogen bonds have been under intense study. An interesting supramolecular synthon involves a robust pseudo-cubic network due to twelve charge-assisted hydrogen bonds. In this report, we demonstrate the first example of the guest-induced topological polymorphism of the pseudo-cubic supramolecular synthons composed of primary ammonium carboxylates. The guest-inclusion caused a change in their crystal systems and a topological change of only one hydrogen bond of the synthons.

Keywords: topology, polymorphism, clusters

P06.06.18

Acta Cryst. (2008). A64, C388**Supramolecular clusters composed of triphenylmethylamine and various sulfonic acids**

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Organic nanoparticles have attracted considerable research interest in molecular biology and life sciences as well as nanotechnology and materials science because of their unique properties. However, the preparation of nanoparticles with a uniform size has remained an important area of study. Furthermore, we can prepare homogeneously sized particles more efficiently and in greater amounts by borrowing techniques from supramolecular chemistry. With respect to supramolecular clusters, we have studied [4+4]-type clusters, which consist of eight organic components of two types connected through hydrogen bonds. We recently described the self-assembly of four ammonium and four triphenylacetate ions into a [4+4] ion-pair cluster through a cubic network of hydrogen bonds. However, these clusters are obtained only in a few combinations of amines and triphenylacetate. In this report, we describe that [4+4] ion-pair clusters composed of triphenylmethylammonium and sulfonate ions can be obtained easily and efficiently in the solid state and in solution with many different sulfonic acid derivatives. The universality of sulfonate-containing clusters, as observed in these experiments, contributes to their potential utility. These novel clusters have

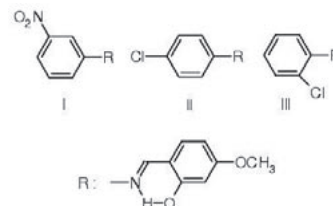
inherent shapes and sizes that are controlled by the substituent on the sulfonic acid. Their preparation is based on the specificity of the combination of the ammonium and sulfonate ions; this system is potentially useful for synthesizing organic nanoparticles.

Keywords: supramolecular cluster, cubic network, hydrogen bond

P06.10.19

Acta Cryst. (2008). A64, C388**Crystal structure and *ab initio* calculations of three 4-methoxy salicylaldehyde derivatives**Orhan Buyukgungor¹, Basak Kosar¹, Cigdem Albayrak², Mustafa Odabasoglu²¹Ondokuz Mayıs University, Physics Department, Kurupelit, Samsun, TR-55139, Turkey, ²Ondokuz Mayıs University, Chemistry Department, Kurupelit, Samsun, TR-55139, Turkey, E-mail: orhanb@omu.edu.tr

Schiff bases are widely used as ligands in the field of coordination chemistry and they play an important role in various field of chemistry due to their biological activities [1]. Here we report the molecular and crystal structures of (*E*)-5-Methoxy-2-[(3-nitrophenylimino) methyl]phenol, (*E*)-2-[(4-chlorophenyl imino) methyl]-5-methoxyphenol and (*E*)-2-[(2-chlorophenylimino) methyl]-5-methoxyphenol labeled as I, II and III, respectively. The optimized molecular geometries and energies of I, II and III were calculated using the restricted Hartree-Fock with 6-31+G(d,p) basis set. In the solid state, compounds adopt the enol-imine tautomeric form with the H atom located on O rather than N. In the optimized geometry, the total energies of molecules are -945.41, -1200.83 and -1200.82 Hartrees for I, II and III, respectively.

[1] Lozier, R.; Bogomolni, R. A.; Stoekenius, W. J. *Biophys.* 1975, 15, 955.Keywords: schiff bases, enol-imine, *ab initio*

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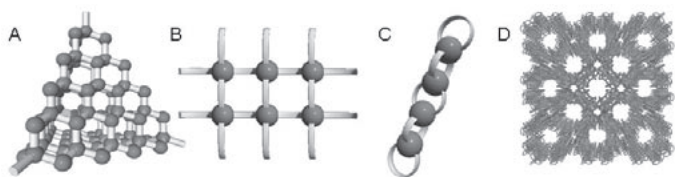
Acta Cryst. (2008). A64, C388-389**Constructions of higher order architectures by connecting of 4+4 supramolecular clusters**

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Hydrogen-bonded supramolecular synthons represent effective tools for crystal engineering. Recently, we have reported that organic salts composed of four triphenylacetic acids and four amines construct a cluster like a cubane through hydrogen bonds. Moreover, we succeeded in forming clusters with triphenylmethylammonium monosulfonates (Fig.1), which possess discrete hydrogen-bonded networks, and shape such as a tetrapod. Surprisingly, a wide range of sulfonic acids yield the clusters without exception. Here we show a connection of the supramolecular clusters with ammonium disulfonates. The connection has three kinds of networks. The first is 4-fold diamondoid network. The crystals have large channel-type spaces where various organic molecules are included. The next is

interwoven network. The disulfonic acid molecules in latter network are considerably bent by packing force. The last is a 1-dimensional supramolecular chain.



Keywords: supramolecular cluster, hydrogen-bond, higher order architecture

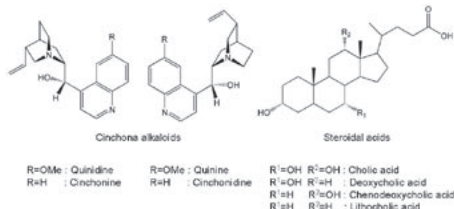
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Acta Cryst. (2008). A64, C389

Supramolecular structures in co-crystals composed of steroidal acids and cinchona alkaloids

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Organic crystals of steroids and alkaloids are very interesting, since these crystals involve diverse molecular assemblies with supramolecular chirality. We so far investigated inclusion crystals of steroidal acids, such as cholic acid and its derivatives, as well as brucine, one of alkaloids. Moreover, cinchona alkaloids, such as cinchonine and quinidine, are well known to form bicomponent crystals with various organic acids. To our knowledge, however, there are no systematic investigations of co-crystals composed of the steroidal acids and the alkaloids. Here we present the first study on preparation of such co-crystals as well as their supramolecular structures. The resulting co-crystals consist of hierarchical structures with hydrogen-bonded helical assemblies. The helices have right- or left-handedness on the basis of supramolecular three-axial and tilt chirality and form chiral bundles with different combinations of their directions. Moreover, we searched such supramolecular structures of the steroids and alkaloids on the basis of the Cambridge Structural Database.



Keywords: supramolecular assemblies, cocrystals, hydrogen bonds in organic crystals

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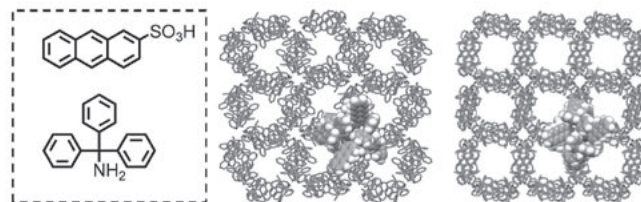
Acta Cryst. (2008). A64, C389

Functional porous crystals with supramolecular clusters of triphenylmethylammonium sulfonates

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Recently, organic porous materials are studied to develop more functional porous materials. In this work, functional porous crystals were constructed by triphenylmethylammonium 2-anthracene sulfonates. Four sulfonic acids and four triphenylmethylamines were assembled by hydrogen bonding to create cubic-like hydrogen-bonding networks. As a result, they formed supramolecular clusters.

And then clusters were integrated to construct porous structures. Surprisingly, different type porous structures were built up with same clusters due to a distinction of their integration patterns. These structures were obtained by recrystallization using same solvents. Although they are composed of same host and guest molecules, they had different size inclusion spaces and different host-guest ratio. Moreover, they had guest-depending fluorescent properties. When guest molecules were desorbed by vacuum, inclusion spaces were shrunk and fluorescent colors were changed. But, porous structures were recovered by intercalation of organic solvents. At the same time, fluorescent colors were turned again. They can be said to be guest-depending functional porous structures.



Keywords: porous materials, fluorescence, organic molecular crystal structures

P06.06.23

Acta Cryst. (2008). A64, C389

Designed supramolecular assembly of novel rosette layers

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In contrast to the classical design of hydrogen-bonded supramolecular rosette motifs based on the self-assembly of two kinds of C_3 -symmetric molecular components,[1] e.g. guanidinium/organic sulfonate, trimesate/ammonium, or cyanuric acid/melamine, a novel three-component guanidinium-boric acid-carbonate rosette layer has been constructed and characterized by X-ray crystallography (Fig. 1a). In addition, deviating from the conventional topological design, the generation of new rosette motifs without the restriction of exactly matched C_3 -symmetric building blocks has been explored. Herein, the 1,2-dithiosquarate dianion and 1,1'-biphenyl-2,2',6,6'-tetracarboxylate dianion are employed in place of C_3 -symmetric anionic components to generate two-component supramolecular quasi rosette layers by varying the symmetry, shapes, and sizes of the hub moieties (Fig. 1b and 1c).

References

[1] C.-K. Lam, F. Xue, J.-P. Zhang, X.-M. Chen, T. C. W. Mak, *J. Am. Chem. Soc.* 2005, 127, 11536; A. V. Ranganathan, R. Pedireddi, C. N. R. Rao, *J. Am. Chem. Soc.* 1999, 121, 1752; J. A. Zerkowski, C. T. Seto, G. M. Whitesides, *J. Am. Chem. Soc.* 1992, 114, 5473.

This work is supported by Hong Kong Research Grants Council Earmarked Grant CUHK 402003.

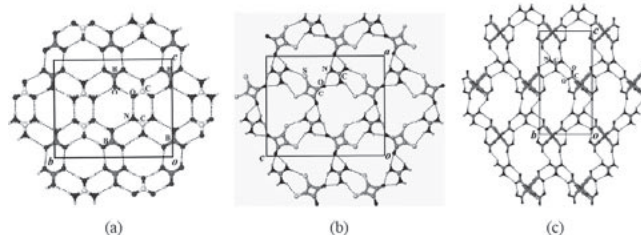


Fig. 1 Supramolecular rosette layers composed of (a) guanidinium, boric acid and carbonate; (b) guanidinium and 1,2-dithiosquarate dianion; (c) guanidinium and 2,2',6,6'-tetracarboxylate dianion.

Keywords: hydrogen bonding, rosette motif, supramolecular assemblies