

PS06.05.15 NON-COVALENT SYNTHESIS OF HOST GUEST ASSEMBLIES THROUGH MOLECULAR RECOGNITION. V. R. Pedireddi, W. Jones, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

The creation of supramolecular structures requires an appreciation of the types of intermolecular interactions which can be reliably used to create ordered arrays. The nature of the assemblies thus formed also depends upon the position of the substituents on the molecule(s) under consideration.

It is interesting that within certain crystals potential cavities for guest inclusion may exist but because of catenation or interpenetration of the adjacent layers (for reasons of efficient close packing) guests are not incorporated. The crystal structures of trimesic acid and adamantanetetra-carboxylic acid are representative examples.

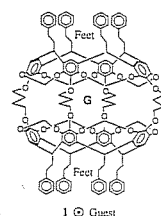
Another example of a system which contains potential guest cavities is 3,5 dinitro-4-methylbenzoic acid, **1**. It adopts a layered structure such that in every layer, six molecules are connected through O-H...O and C-H...O Hydrogen bonds to create $7 \times 13 \text{ \AA}$ voids. The voids are subsequently filled by groups from adjacent layers. We wished to discover whether these cavities could be filled by guests of appropriate dimension. When **1** is co-crystallised with 2,6-dimethylnaphthalene, **2**, the molecules of **2** in fact fit into the cavity through the formation of C-H...O H-bonds. The structure of the complex, the underlying supramolecular chemistry and further implications will be discussed with respect to **2** and other guest molecules.

PS06.05.16 NEW CLASSES OF MOLECULES FOR DESIGNING STRUCTURES IN THE ORGANIC SOLID STATE. John C. MacDonald, Northern Arizona University; Kathy E. Schwiebert, G. Tayhas, R. Palmore, Jon A. Zerkowski, Serge Palacin, and George M. Whitesides, Harvard University.

This talk will describe our efforts to design molecules that crystallize in well-defined structures, to rationalize the structures of crystals based on the structures of their component molecules, and to predict the structures of new molecular crystals. Our approach attempts to simplify the packing of molecules by constraining them to form tapes—that is, flat linear aggregates—that pack with their long axes parallel, an arrangement likely to minimize free volume in a crystal. We have based our design for tapes on the network of hydrogen bonds present in three separate classes of molecules: (1) 1:1 complexes between N,N'-diphenylmelamines and 5,5-diethylbarbituric acid (mel•bar complexes); (2) 4,5-disubstituted 2-benzimidazolones (cyclic ureas); (3) diketopiperazines. Series of derivatives from each of these classes of molecules have been synthesized and their structures determined in the solid state. These molecules crystallized in several different structural motifs that can be rationalized using familiar concepts such as steric repulsion and principles of closest packing. In several cases, mel•bar complexes formed tapes that crystallized in different crystalline forms; this polymorphism complicates our efforts at understanding the relationship between molecular and crystal structure. Cyclic ureas and diketopiperazines have not exhibited polymorphism under normal conditions of crystallization.

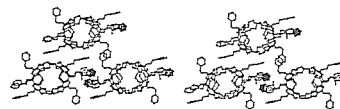
Inclusion Compounds and Complexes

PS06.06.01 AN ADAPTABLE HOST FOR ORGANIC GUESTS AND THEIR REACTIONS. E. F. Maverick, C. B. Knobler and D. J. Cram, Dept. of Chemistry and Biochemistry, UCLA, Los Angeles, CA 90095.*



'Hemicarcerand' host **1** forms stable complexes with guests ranging in size from xenon to phenyl allyl ether. The inner phase provided by the container is a favorable location for selected chemical reactions.¹

Crystals of **1** ⊙ Guest ⊙ 2PhNO₂ grow from solutions containing nitrobenzene. The phenethyl 'feet' of the host are organized so that six feet from neighboring complexes encapsulate two nitrobenzene molecules, while the remaining two feet 'shake hands'. (PhNO₂ is darkened in the stereoview below; guests are omitted.) Twenty-four structures with different guests, 23 of them isostructural, have the same general features for the hemicarcerand moiety. Many are low resolution structures with poorly determined guests. Even so, the orientation of the guest can be deduced and the inter-hemispheric distance is reasonably well determined, allowing conclusions to be drawn about the guest's influence on the host.

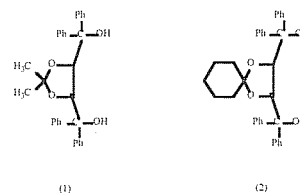


¹ Robbins, T. A., Knobler, C. B., Bellew, D. R. and Cram, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 111-122; Kurdistani, S. K., Helgeson, R. C. and Cram, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 1659-1660.

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PS06.06.02 STRUCTURE AND DECOMPOSITION KINETICS OF INCLUSION COMPOUNDS OF A DIOL HOST. Susan A. Bourne, Chemistry Department, University of Cape Town, Rondebosch 7700, South Africa

Inclusion chemistry offers wide scope for carrying out selective separation reactions. Considerable effort has gone into trying to improve the applications offered by naturally occurring resolving agents such as tartaric acid or brucine. An example is the class of compounds derived from a tartaric acid, such as (1) or (2).



The crystal structures of (1) (4,5-bis(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxolane) with methanol and ethanol have been elucidated. These two compounds are isostructural, with the alcohol trapped in a cavity and held in place in a cyclic hydrogen-bonded network.

On heating, the alcohol is released in a single step. The kinetics of this decomposition reaction were studied using isothermal thermogravimetry. In both cases, desorption occurred by a diffusion-controlled mechanism. Kinetic parameters for the desorption reactions have been determined and compared.