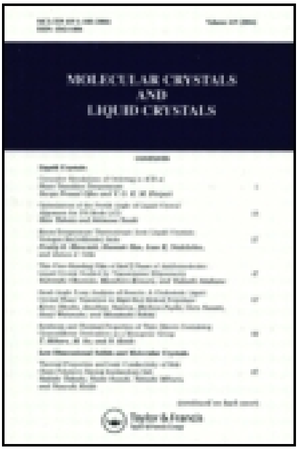

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The Host Guest Co-Crystal Approach to Supramolecular Structure

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The Host Guest Co-Crystal Approach to Supramolecular Structure

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A host-guest co-crystal approach to supramolecular structure has been developed. Molecular functionalities have been identified that will self assemble via hydrogen bonds to give one dimensional α-networks with defined intermolecular distances. Host molecules based on these functionalites can be co-crystallized with guest molecules, the characteristic distance defined by the host is thus imposed on the guest. Using this strategy, functional supramolecular solids can be prepared. One molecule, the host determines the structure, while a second molecule, the guest, provides the function.

Keywords: supramolecular structure; hydrogen bonding

Introduction

Supramolecular chemistry has been one of the most rapidly developing fields of science in the 1990s. This development is due to the now recognized importance of intermolecular interactions, structure, and cooperativity in most all aspects of molecular science and many technological endeavors. From biology to pharmacology to materials science the challenges are to understand existing supramolecular constructs and to design and build new supramolecular entities for function and application.

Supramolecular chemistry has often been referred to as the chemistry of the non-covalent bond. The forces involved in non-covalent bonds are relatively weak, non-directional and occur over the entire van der Waals surface of a molecule. The preparation of a supramolecular structure requires controlling these weak, non-directional forces in three dimensions. This is a formidable problem beyond our current abilities. Therefore, our approach to the preparation of designed supramolecular structures has been to develop methods to control certain elements of supramolecular structure such as molecular spacing by constructing networks in one or two dimensions. This reduces the supramolecular synthesis of designed structures to a more a tractable problem. Fortunately, many applications, such as the development of advanced materials, do not require the complete control of supramolecular structure just the control of the supramolecular feature of interest.

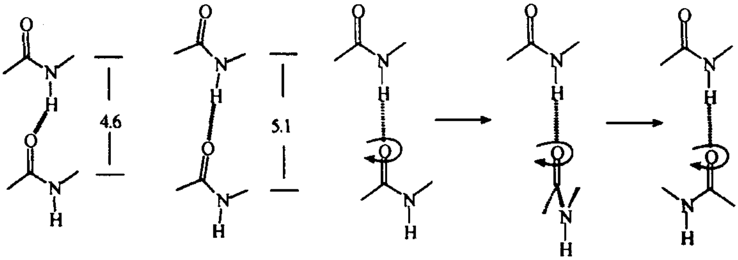
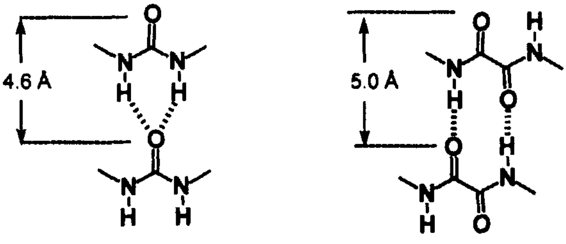


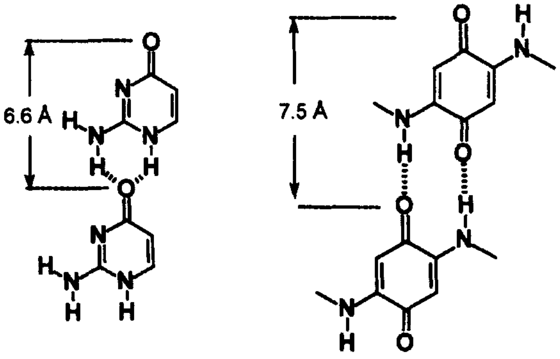
Figure 1. Simple amides will self-assemble into one-dimensional a-networks, but they can show considerable variation.

We focussed on the identification of molecular functionalities that would reliably yield networks with predictable intermolecular distances. We began by considering simple amides. Amides form one-dimensional α-networks. The repeat distance can vary from about 4.6Å to 5.1Å depending on the position of the hydrogen atom above the oxygen of the carbonyl. The repeat is shorter if the hydrogen approaches the classic "lone pair" position, longer if it takes a position co-linear with the carbonyl. Amides also have a free torsion angle about their hydrogen bond leading to a range of possible structures, with no obvious predictability. Thus, a simple amide will always form a hydrogen bond, but one with a considerable amount of structural freedom and structural uncertainty. Furthermore in the presence of other functional groups a simple amide is not reliably self complementary. For more reliability, we focused on amides and amide analogues that will form two hydrogen bonds to each neighbor, a more specific interaction.

Two such groups are the urea and oxalamide functionalities Figure 2. The two hydrogen bonds "lock in" predictable distances and eliminate the free torsion angle of a simple amide. In addition, the crystallographic symmetry is reproducible, symmetrical ureas tend to have a two-fold axis; oxalamides, an inversion center. [1] One can take either of these functional groups, add side substituents with additional hydrogen bond capability and reliably form layered β-network structures such as the one shown in Figure 3.



ureas **oxalamides**



aminopyrimidones **diaminoquinones**

Figure 2. A selection of host molecules, each gives a different characteristic distance.

In our initial work, we focused on the study of molecules that formed self-complimentary hydrogen bonds in the solid state. Although the approach is quite sound, it becomes much more limited as we move forward to applications. The problem with a strategy based on one molecule is that it is difficult to combine into one molecule those features needed to control a supramolecular structure with those structural features needed for function. If such a sophisticated molecule can be designed, it is likely that a complex molecular synthesis will be required. Once the molecule has been synthesized it is then allowed to self-assemble. Either the desired supramolecular structure is formed or it is not. If it is, one celebrates and moves on, but if some alternate structure is found, one unsuitable for the application, there is little one can do to change the supramolecular structure of a single molecule. One must go back, design and synthesize a new, perhaps more sophisticated molecule for another "one shot" experiment. This linear approach is tedious and not very efficient.

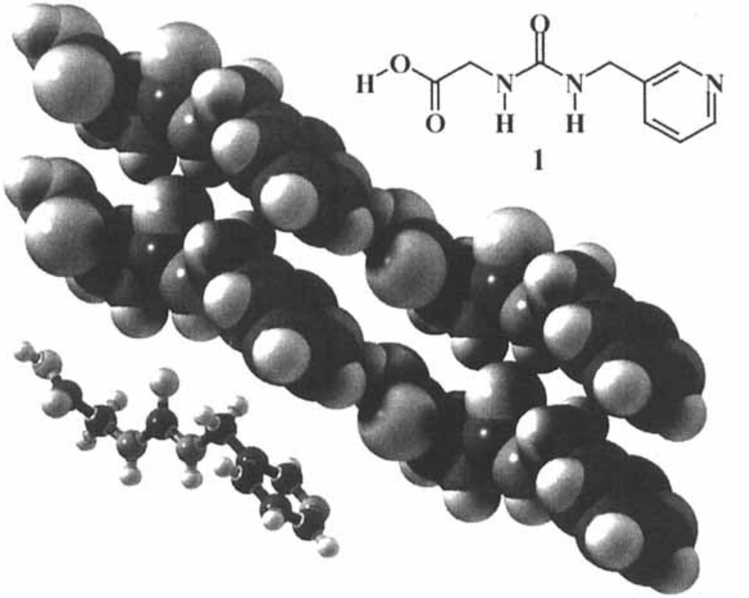


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FIGURE 3 Molecule **1** forms two independent α-networks, the first via urea hydrogen bonds, the second by a strong carboxylic acid pyridine hydrogen bond. Together these two interaction bring the molecules together to form a two dimensional β-network.

A binary system using two molecules to prepare a desired supramolecular structure is an attractive alternative. In a binary system, one molecule can serve as a host and provides the functionality necessary for the controlling the supramolecular structure. A second molecule provides the functionality with the property of interest, such as a photochemical chromophore, a magnetic center, or a monomeric unit for a solid state polymerization reaction.

Reliable Intermolecular Interactions.

For the co-crystal strategy to work, the forces between unlike molecules must be greater than the forces between like molecules. Figure 4. Otherwise, the molecules will crystallize separately. The simplest interactions of this type are acid-base interactions. The pyridine-carboxylic acid hydrogen bond has proven to be very useful. It is relatively strong and has been used for molecular organization of liquid crystals and polymers. We have prepared a large number of co-crystals based upon this motif.

We have also investigated some less conventional alkyne interactions with pyridines. The alkyne *sp* CH bond is relatively acidic and forms C-H hydrogen bonds in a reliable manner. Interestingly, we have discovered that bromo alkynes form persistent and reliable intermolecular interactions with pyridines. Finally pyridine is known to coordinate to many metals yielding a wide variety of bond strengths.

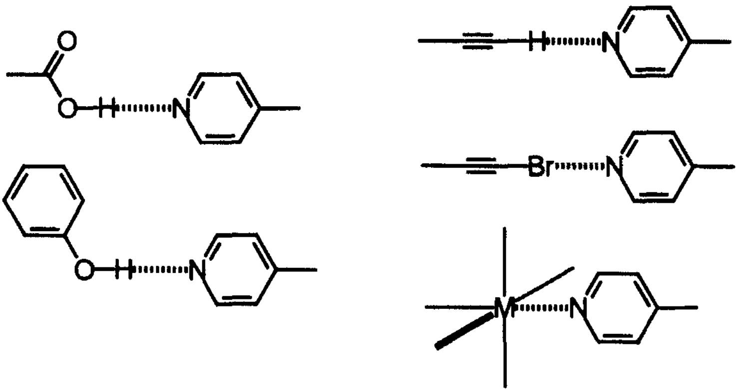


FIGURE 4. Pyridines form a variety of intermolecular interactions.

Distance control.

Functional supramolecular structures may have a variety of structural requirements. The desired function may require a specific molecular orientation, a polar environment, or close proximity between a pair of molecules. As we mentioned earlier we have focussed on the identification of molecular functionalities that will reliably yield networks

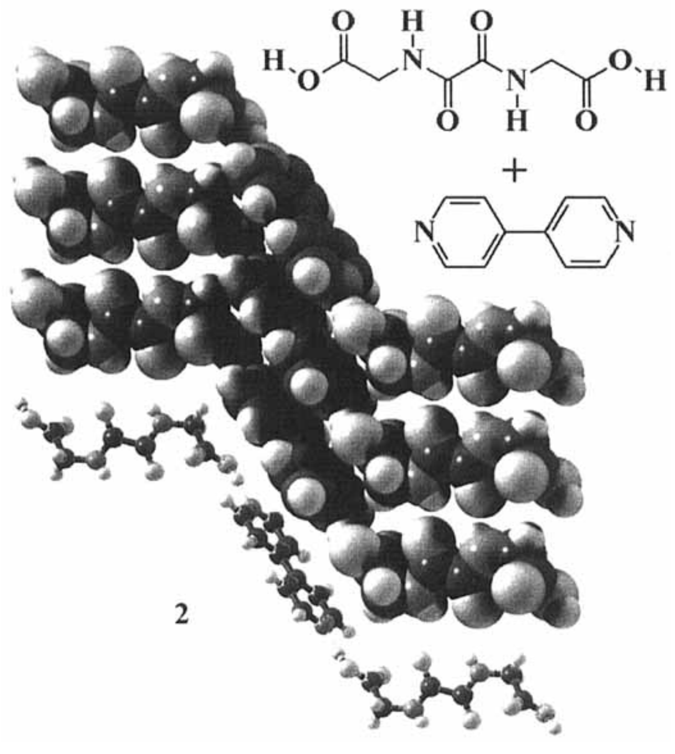


FIGURE 5. Host-guest complex **2**..

with predictable intermolecular distances. Once such functionalites are discovered they can be used to build host molecules to control the intermolecular distances between designated guest molecules. We have demonstrated such distance control in a variety of molecular systems including a series transition metal complexes [2], a variety of designed diacetylene topochemical polymerizations [3,4], and a butadiene polymerization study [5].

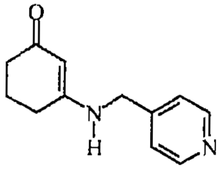
Consider the host-guest complex, **2**, shown in Figure 5. It was prepared simply by co-crystallizing bipyridine with the oxalamide of glycine. The fundamental intermolecular interactions within the crystal are the same as those found in the structure of molecule **1** in Figure 3. The significance of structure **2** is that the intermolecular distance of 5.0Å defined by the oxalamide hydrogen bonds is imposed upon the bipyridine in a completely predictable manner. In a similar manner the co-crystal of the urea of glycine shows a short repeat distance of 4.6Å imposed by the shorter urea hydrogen bond network.[3]

Longer Distances.

In our diacetylene studies we used urea and oxalamide hosts to align various diacetylene monomers at the distances needed for the topochemical diacetylene polymerization to take place. [3, 4] The diacetylene co-crystals polymerized upon heating. The next higher congeners of the polyacetylene series would be the polytriacetylenes. The 1-6 polymerization of a polytriacetylene is an unknown reaction, although polytriacetylene oligomers have been made by other means. [6] Enkelmann investigated the requirements for a 1-6 topochemical triacetylene polymerization and he calculated that an intermolecular spacing of about 7.5Å and an "tilt" angle of 27° is needed.[7] We would like to use our host-guest co-crystal approach to organize a triacetylene in accordance with these structural parameters. To do this we need to develop host molecules that will self-assemble near the 7.5Å value.

Two candidate host functionalities are shown in Figure 2. The aminopyrimidones have been shown to form co-crystals, but because of tautomerism they are not very reliable. Their characteristic distance of 6.6Å is also a little short. The diaminoquinones give an ideal distance, but they have proven to be very insoluble, a fatal characteristic if one wants to use a molecule to form a co-crystal with a second molecule.

Recently we have turned to a much simpler system of vinylogous amides such as compounds **3** and **4**. They are relatively easy to make via a condensation of 1,3-hexanedione with the corresponding amine.



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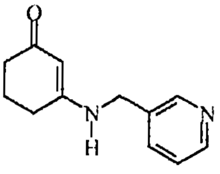

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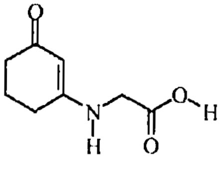

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Like a simple amide, Figure 1. they can self assemble into an α-network using a single hydrogen bond. Unfortunately like the simple amides this means that a variety of structures are possible. Functionalities with two hydrogen bonds, such as the diaminoquinones would be expected to give networks in more reliable manner. Due to this uncertainty we thought it was important to test the vinylogous amides as hosts before going on to prepare an actual triacetylene cocrystal.

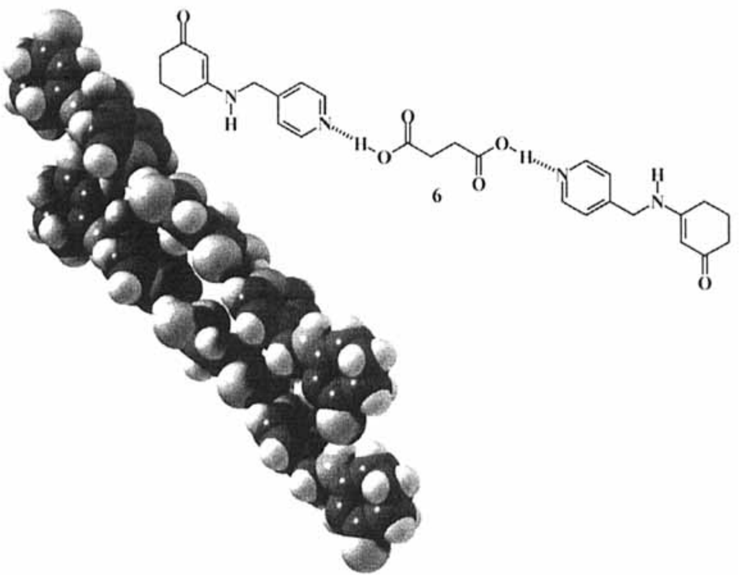
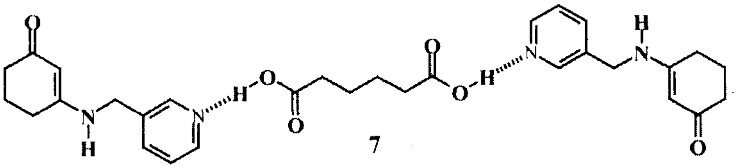


Figure 6. Crystal structure, **6**, formed by co-crystallizing vinylogous amide 3 with succinic acid in a 2:1 ratio.

Vinylogous Amide Test Structures.

Figure 6 illustrates the co-crystal of vinylogous amide **3** and succinic acid. In this case the supramolecular structure, **6**, has formed in accordance with our design, yielding a intermolecular spacing of 7.2Å. This intermolecular spacing is determined by the host, and imposed upon the guest dicarboxylic acid. It is serves as a encouraging test structure for the triacetylene polymerization.

The second test structure was not so encouraging. Vinylogous amide **4**, was co-crystallized with adipic acid in a 2:1 ratio. As can be seen in Figure 7A the acid and pyridine molecules assemble as anticipated. However the vinylogous amides do not self-assemble via translation. Instead they assemble in twisted manner via a glide plane, Figure 7b. Thus adjacent adipic acid molecules are not aligned.



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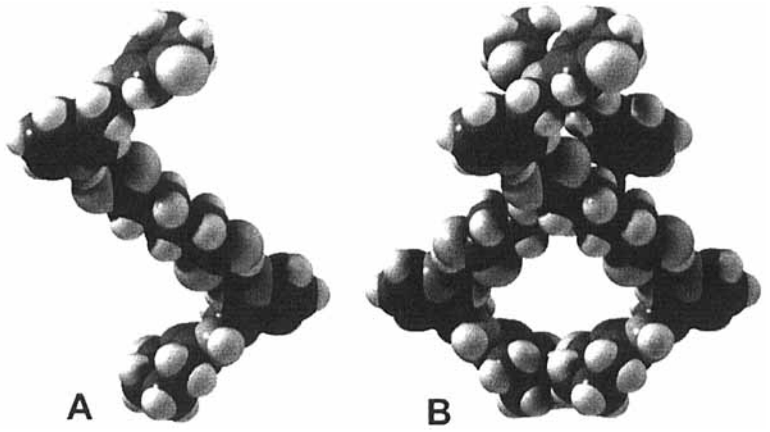

Figure 7. Crystal structure 7, the 2:1 co-crystal of 4 with adipic acid. In **A** it can be seen that the pyridine rings associate with the adipic acid molecules as anticipated. However neighboring molecules assemble with glide plane symmetry, **B**, instead of simple translation as they do in structure **6**.

These test structures confirm what we knew already. A vinylogous amide with a single hydrogen bond *may* assemble to give the structure we would like as in structure **6**, but the rotational freedom of a vinylogous amide, which is analogous to the rotational freedom of a simple amide, Figure 1, can lead to difficulties. Applications of this host-guest co-crystal strategy to the designed synthesis of a polytriacetylene are underway.

Crystallographic Data

Crystallographic data for structures, 1, **2**, **6**, and **7** have been deposited with the Cambridge Structural Database.

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