Supramolecular Synthons in Crystal Engineering. 4. Structure Simplification and Synthon Interchangeability in Some Organic Diamondoid Solids[1]

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Abstract: *Any* organic crystal structure can be simplified to a network wherein the molecules are the nodes and the supramolecular synthons are the node connections. This approach to crystal engineering is illustrated in this paper with reference to organic structures based on the diamond network. By introducing N···Br synthons into this network, a 2-fold-catenated structure is obtained for the 1:1 complex between hexamethylenetetramine (HMT) and CBr_4. The use of C−H···N mediated synthons in the same network results in the 1:2 complex of 1,3,5,7-tetrabromoadamantane ($AdBr_4$) with HMT. Further structural flexibility is achieved by the interchange of molecular and supramolecular synthons. Accordingly, the diamond-based crystal structures of tetrakis-(4-bromophenyl)methane and the 1:1 molecular complex of tetraphenylmethane and CBr_4 are very similar. This near-identity arises because of the structural equivalence of the CBr_4 molecular synthon and the Br_4 supramolecular synthon and the ability of the CBr_4 molecule to participate in Br···phenyl interactions. In general, there is much topological correspondence between organic and inorganic crystal structures, and this can be utilized in the description of organic crystal structures as networks. Such a depiction is of much practical utility and is different from Kitaigorodskii's model which distinguishes fundamentally between molecular and crystal structure. In the network model, molecular and supramolecular synthons are interchangeable within the same network structure.

Introduction

Supramolecular synthons are the smallest structural units within which is encoded all the information inherent in the mutual recognition of molecules to yield solid state supermolecules, that is, crystals. A key aspect of crystal engineering is therefore the dissection of a target network into supramolecular synthons and the not so critical fragments (molecular synthons) which connect the supramolecular synthons.[2] Such a dissection simplifies the analysis of a target network and is important in crystal engineering because it recognizes the interchangeability of supramolecular synthons in a family of structures. From such interchangeability follows the well-known observation that molecules with widely differing functionalities can have rather similar crystal structures.[3] At a higher level, supramolecular synthons may be interchanged with *molecular* synthons so that even more widely dissimilar compounds can be predicted to have closely related crystal structures. These ideas are discussed in this paper with reference to diamondoid networks formed by some S_4-symmetry molecules.

Inorganic three-dimensional networks having large cavities have several applications in materials science. For example, such solids could act as organic zeolites. Among these, the supramolecular synthesis of organic diamondoid materials has received attention for the following reasons: (i) They represent a new family of organic hosts in which network assembly follows from molecular symmetry. (ii) Synthesis of such materials tests the robustness of several supramolecular synthons, particularly those constituted with the weaker intermolecular interactions. (iii) They are aesthetically appealing synthetic targets.

Organic diamondoid networks were first discussed by Ermer who showed that the crystal structures of adamantane-1,3,5,7-tetracarboxylic acid, **1**, and methanetetraacetic acid, **2**, are based on self-assembly via carboxylic acid dimer synthons **I**.[4] It is possible to substitute other synthons for **I** on adamantyl or other tetrahedral templates and generate similar diamondoid structures. Wuest and co-workers have used this concept and introduced the related *cis*-amide dimer synthon **II** instead of the carboxyl synthon **I** so that the anticipated diamondoid networks are achieved through centrosymmetric N−H···O hydrogen bonding.[5] Zaworotko and co-workers have used the O−H···N synthon **III** in a similar manner, with S_4-symmetry organometallic precursors defining the tetrahedral nodes and rigid, linear spacer molecules connecting these nodes (as in the SiO_2 or Cu_2O structures).[6] Robson and co-workers have reported on similar diamondoid structures based on the metal···N≡C synthon **IV**.[7] From these examples, it is clear that the synthesis of organic diamondoid networks is most conveniently achieved by the use of tetrahedral molecules. In all the above cases, the supramolecular synthons used are based on "strong" hydrogen bonds or coordinate covalent bonds. We have used a similar strategy

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(1) For Part 3 of this series, see: Reddy, D. S.; Ovchinnikov, Y. E.; Shishkin, O. V.; Struchkov, Y. T.; Desiraju, G. R. *J. Am. Chem. Soc.* **1996**, *118*, 4085.

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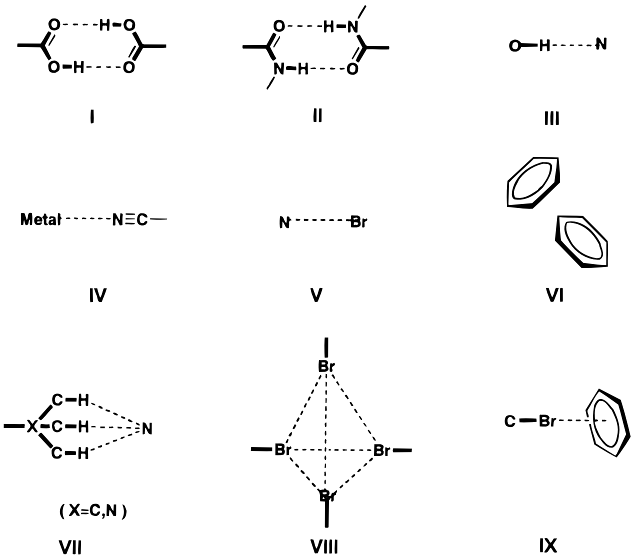
with weaker interactions. By replacing any of the synthons **I**−**IV** in the diamond network with the N···Br synthon **V**, one obtains the 1:1 molecular complex **3** of hexamethylenetetramine (HMT) with CBr_4. This complex has a network structure similar to that in the $Zn(CN)_2$ structure.[8]



Extending this strategy, synthon **V** in complex **3** may be replaced with an appropriate C−H···N synthon, **VII**, which is constituted with three equivalent C−H···N hydrogen bonds, as node connections.[9] This then is the structure of the 1:2 complex **4** of 1,3,5,7-tetrabromoadamantane, $AdBr_4$, and HMT and of the 1:1:1 complex **5** of $AdBr_4$, HMT, and CBr_4. It is relevant to note that in these ZnS-based structures, four $AdBr_4$ molecules converge tetrahedrally to give six identical Br···Br contacts of around 4.08 Å (Figure 1). This Br_4 cluster (synthon **VIII**) occupies face-centered cubic (FCC) octants at (3/4, 1/4, 1/4) leaving the alternate octants for the HMT (1/4, 1/4, 1/4) molecules, and one can connect these clusters with the adamantyl molecular synthons to obtain an alternative diamondoid network (Figure 2). The Br_4 cluster **VIII** is the starting point for the crystal engineering exercise described in this paper.

Experimental Section

Crystal data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer. The structures were solved with MULTAN80[10] and refined with BLOCKLS.[11] All non-H atoms were refined anisotropically.[12] The crystallographic information is deposited in the supporting information.

Results and Discussion

Diamondoid Networks Based on Br···Br and Br···Phenyl Interactions. It was noted that, in both complexes **4** and **5**, cluster **VIII** has a shape and size which matches well with those of HMT and, in particular, CBr_4. The occurrence of **VIII** in the crystal structures of **4** and **5** indicates its robustness and potential use as a design element in the crystal engineering of other diamondoid networks. Because of the size similarity between cluster **VIII** and the CBr_4 molecule, the possibility arises that these entities can be mutually exchanged with little change in the overall crystal packing. According to the well-known principle of structural mimicry, molecules of the same size and shape have similar crystal structures.[13] We have shown in the preceding paper in this issue that supramolecular fragments of the same size and shape confer similar effects on crystal structures. A powerful extension to these ideas is that *molecular and supramolecular synthons are interchangeable in a family of crystal structures.* The following example shows how this principle as applied to CBr_4 and synthon **VIII** may be used to generate new diamondoid networks.

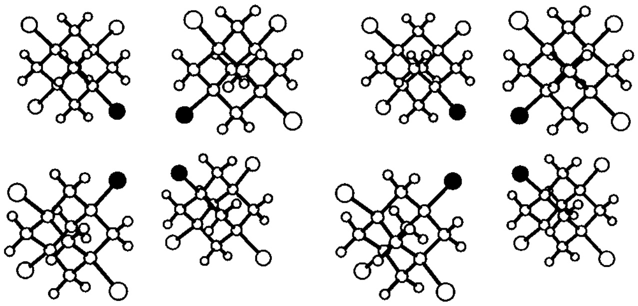


Figure 1. Formation of the Br_4 cluster in complexes **4** and **5** by the convergence of four $AdBr_4$ molecules. Notice the Br···Br interactions.

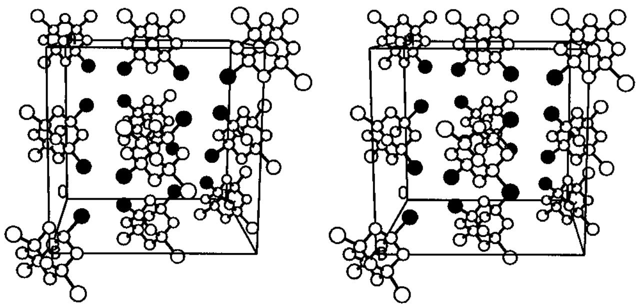


Figure 2. Networking of the Br_4 clusters **VIII** in complexes **4** and **5** via the adamantyl molecular synthons to generate a complementary superadamantoid cage. The Br_4 clusters are shaded.

With this background, we examined the crystal structure of tetrakis(4-bromophenyl)methane, **6**. From the molecular structure, it was anticipated that the crystal packing should be controlled by the Br···Br interactions. It was further expected that there could be two possibilities for the packing. The first is through the formation of a diamondoid network similar to acid **1** but with Br···Br interactions. The second possiblity is via the formation of the CBr_4 synthon **VIII** by the aggregation of four molecules of **6**.

In reality, it is the second possibility which is adopted. Compound **6** crystallizes in the tetragonal system, and the Br_4 cluster **VIII** is shown in Figure 3. In this cluster, four Br atoms are arranged in a tetrahedral fashion, and the distance between any two bromine atoms is 3.91 Å. If the empty centroid in **VIII** is considered as a phantom "carbon" atom, the cluster becomes a super-CBr_4 molecule. The C−Br bond distance in this super-CBr_4 is 2.146 Å, and Br−C−Br angles are 108.35° (four angles) and 110.04° (two angles). These parameters compare well with those of the CBr_4 molecule in complex **8** in which the C−Br distance is 1.926 Å and the Br−C−Br angles are 108.92° (two angles) and 110.58° (four angles). The structure of **6** is easily understood in terms of the combination

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(12) For all crystal structure data for **6** and **8**, see the supporting information. **6**: $I\bar{4}$, $a = 12.713(2)$ Å, $c = 7.114(2)$ Å. **8**: $I\bar{4}$, $a = 12.638(2)$ Å, $c = 7.298(2)$ Å.

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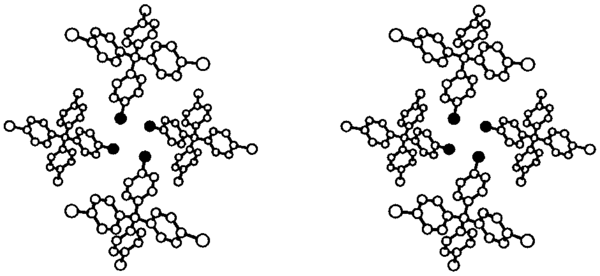

Figure 3. Formation of the Br_4 cluster **VIII** from four molecules of **6** in its crystal structure.

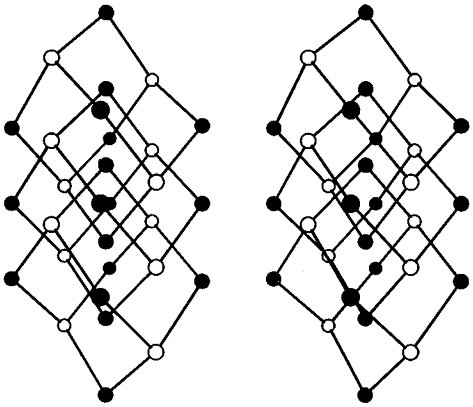

Figure 4. Three interpenetrating diamondoid networks in the crystal structure of **6**. Both super-CBr_4 and tetraphenyl moities are shown as alternating circles.

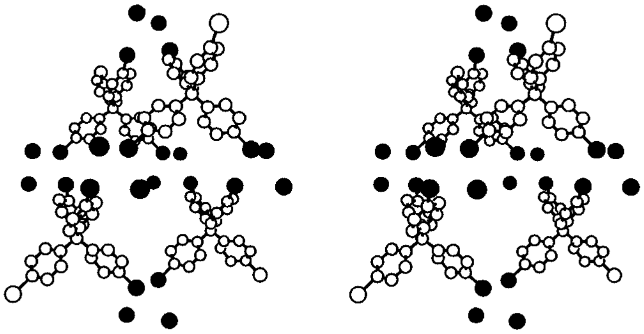

Figure 5. Stereoview of the structure of compound **6**. The super-CBr_4 molecules are shaded. Note that the tetrahedral topologies of the tetraphenyl and Br_4 moieties define a superadamantoid cage. The molecules in this figure define one out of the three diamondoid networks depicted schematically in Figure 4.

of the two tetrahedral moieties, the tetraphenylmethane molecular synthon and the Br_4 supramolecular synthon **VIII**. If these tetrahedral moieties are reduced to spheres lying at their centers and the spheres joined, distorted diamondoid networks are the result. Figure 4 is a schematic view of the structure, and Figure 5 is a stereoview of the actual structure.

We are now in a position to interchange molecular and supramolecular synthons. In **6**, the Br_4 clusters **VIII** are connected to the tetraphenyl moieties through C−Br covalent bonds. It was expected that these Ph−Br molecular synthons could be replaced with the supramolecular synthon **IX** which is based on the Br···phenyl interaction. In other words, the replacement of **VIII** with CBr_4 accompanied by the concomitant replacement of **6** by tetraphenylmethane, **7**, should lead to no major structural change. In practice, cocrystallization of CBr_4 and **7** led exclusively to the formation of complex **8** which is nearly isostructural with **6**.[12] In this structure (Figure 6), four molecules of **7** are linked to a CBr_4 molecule through synthon **IX** (Br···phenyl ring center 3.67 Å). With reference to the positions of the tetraphenyl moieties, the Br atom positions in structures **6** and **8** are nearly inverted about the centroid to take into account the different geometrical requirements of the C−Br covalent bond and the Br···phenyl intermolecular interaction. However, there are no major differences in these crystal structures, and in **8** too, the centroids of the CBr_4 and **7** molecules may be taken as spheres and joined to form a distorted diamondoid network.[12] The schematic view of such a network is shown in Figure 7, and the stereoview of the actual structure is shown in Figure 8.

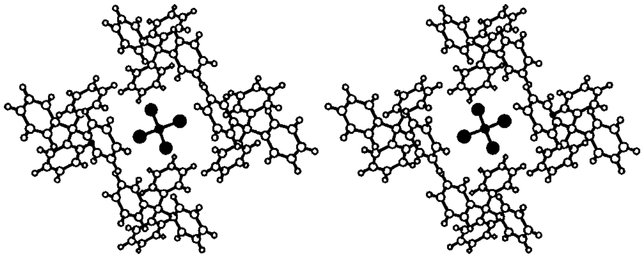

Figure 6. Br···phenyl interactions (synthon **IX**) in the crystal structure of complex **8**. Notice that the CBr_4 molecule (shaded) is surrounded by four tetraphenylmethane molecules.

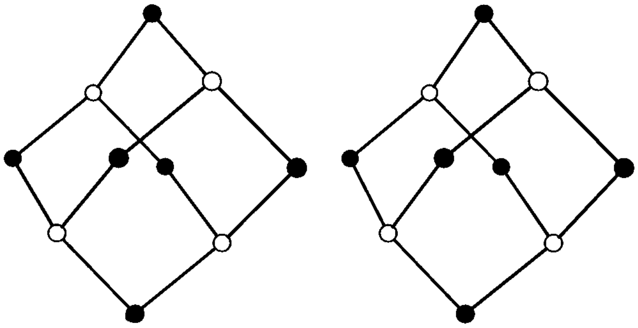

Figure 7. Schematic representation of the network structure in complex **8**. Shaded and unshaded circles represent CBr_4 and tetraphenylmethane molecules.

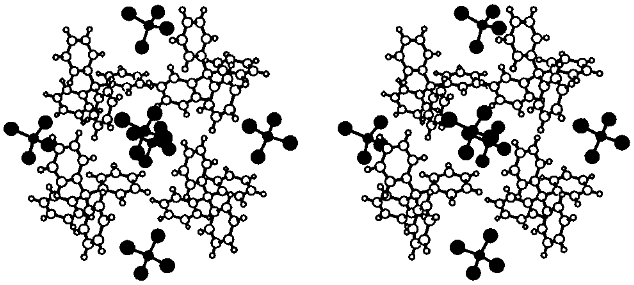

Figure 8. Stereoview of the structure of complex **8** with the same molecules that are depicted schematically in Figure 7. The CBr_4 molecules are shaded.

Though the crystal structures of **6** and **8** appear to be formed from widely different components (**6** is a one-component crystal while **8** is a two-component crystal), they have close similarities at the supramolecular level and identical distorted diamondoid networks mediated, respectively, by Br···Br and Br···phenyl supramolecular synthons. It is clear that synthon **VIII** in the structure of **6** is the supramolecular equivalent of the CBr_4 molecule in complex **8**, while synthon **IX** in **8** is the equivalent of the covalent Ph−Br bond in **6**. Finally, the intermolecular Br···Br interaction in **6** is equivalent to the covalent Br−C−Br connection in complex **8**.

A final common feature of interest in structures **6** and **8** is the phenyl···phenyl supramolecular synthons **VI**. These herringbone synthons are ubiquitous and are found in the crystal structure of the parent hydrocarbon **7** also.[14,15] The robustness of this synthon in this structural family is manifested by the constancy of the tetragonal axis length in **6**, **7**, and **8** with the phenyl···phenyl interactions operating along this direction. Indeed, the importance of this geometry results in an anisotropy of the interaction arrangement with the result that these tetrahedrally shaped molecules adopt tetragonal rather than cubic space groups. The crystal structures of **6**, **7**, and **8** are all tetragonal, with the *a* and *b* axes in **6** and **8** being enlarged to accommodate the Br groups, but in an overall sense, there are many similarities in these structures with regard to the phenyl···phenyl interactions.

Topological Equivalences between Organic and Inorganic Crystal Structures. Implicit in the supramolecular synthon approach to crystal engineering is the consideration of an organic crystal structure as a network[2,16] rather than as a collection of (molecular) objects assembled with forces which are much weaker than the forces within the object.[17] This earlier classical depiction owes mainly to Kitaigorodskii, and even as considerable advances were made in our understanding of molecular crystals based on this earlier model, it is becoming more evident that the network model for an organic crystal is of much utilitarian value in crystal engineering, especially if more complex crystal packings are to be constructed.[18] Such a conceptualization has been greatly facilitated by the development and growth of supramolecular chemistry which looks beyond the molecule in all senses.[19] Kitaigorodskii's model is essentially "molecular" in concept because it distinguishes fundamentally between a molecule and what is outside the molecule (the intermolecular interactions). In the network model, however, there need be no critical distinctions between molecular and supramolecular fragments. What is important here are nodes (notice that the molecules have been reduced to points!) and node connections, that is, the supramolecular synthons. With such a background, seeking similarities between structures such as **6** and **8** is intuitive.

Though the development of network theory to organic crystal chemistry is recent, this is hardly the case for inorganic crystal structures which have traditionally been viewed in this fashion.[20] Thus, the next logical step after depicting an organic crystal structure as a network is to search for its inorganic counterpart. These comparisons are not just chemical curiosities but play a very important part in the development of a proper theory of crystal engineering because one is able to draw from the very considerable literature which exists in the inorganic structural domain to choose new target networks. In this context, the structures described in this paper are especially interesting.

Conclusions

This paper shows that the simplification of an organic crystal structure as a network and the subsequent dissection of this network into nodes and node connections are helpful for the development of general strategies of crystal engineering. Node connections or supramolecular synthons are substructural units of the greatest importance in crystal structure design. Supramolecular synthons can be interchanged in a given network so that molecules with different functionalities can have very similar crystal structures. At a higher level, it is seen that molecular and supramolecular synthons with similar shapes and sizes have similar effects on crystal packing and may be interchanged so that substances with extremely different molecular functionalities can have similar, even isomorphous, packing arrangements in the crystal. The analysis of an organic crystal structure as a network leads to natural comparisons between organic and inorganic crystal structures. Such comparisons are expected to be of value in the establishment of general methods of crystal engineering of complex networks.

Acknowledgment. We thank the DST and UGC (Government of India) and the DITAC (Government of Australia) for financial assistance.

Supporting Information Available: Crystallographic data, fractional atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters for compound **6** and complex **8** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the Journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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