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Molecular tectonics

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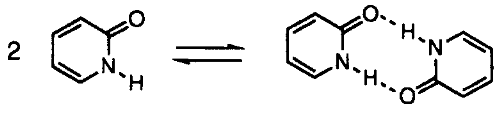
Tectons are defined as molecules whose interactions are dominated by specific attractive forces that induce the assembly of aggregates with controlled geometries; *molecular tectonics* is the art and science of supramolecular construction using tectonic subunits. Intermolecular hydrogen bonds offer a particularly effective force for promoting controlled tectonic aggregation, and tectons able to participate in extensive networks of hydrogen bonds can be constructed by the simple expedient of attaching multiple 2-pyridone subunits to carefully chosen molecular frameworks. For example, tectons that incorporate four tetrahedrally oriented 2-pyridone subunits are predisposed to generate diamondoid networks or related three-dimensional lattices. As expected, crystallization of nominally tetrahedral tectons 8, 10, and 11 produces diamondoid hydrogen-bonded networks with distances between the centers of adjoining tectons varying from approximately 12 to 20 Å. These networks define large internal volumes that are filled by a combination of independent interpenetrating diamond networks and enclathrated guests. Such networks are porous enough to permit the exchange of guests and robust enough to remain intact, even though their structural integrity is maintained only by hydrogen bonding. Three-dimensional hydrogen-bonded networks not based on diamond can be generated by the association of related tectons, including stannane 13, that incorporate features designed to make them more deformable. These observations are important because they suggest that clever application of the strategy of molecular tectonics can be used to build an unlimited range of ordered three-dimensional organic networks with some of the desirable properties of zeolites and related inorganic materials, including high structural integrity, potentially large void volumes, and adjustable microporosity.

INTRODUCTION

An important subject of contemporary research in chemistry is the study of molecules that are predisposed to participate in strong, specific intermolecular interactions.[3,4] Sticky molecules of this type are interesting because they can be designed so that their association produces complex supramolecular aggregates with well-defined and predictable structures. Furthermore, the aggregation occurs by a process of spontaneous self-assembly, thereby allowing chemists to avoid the tedious bond-by-bond syntheses normally used to build complex structures. We call these sticky molecules *tectons*.[3d] This name is derived from the Greek word *τεκτων*, which means "builder" and is the root of such words as architect. It is an appropriate name for molecules predisposed to associate in specific ways, because they serve as the fundamental building blocks for supramolecular construction; in addition, chemical information incorporated in the tectonic subunits provides the blueprint that governs how the individual blocks are joined together and determines what architecture will ultimately emerge. *Molecular tectonics* is the science, as well as the art, of supramolecular construction using tectonic subunits.

Of the various intermolecular interactions that can be used to regulate tectonic aggregation, one of the most suitable is the hydrogen bond. It is strong enough to ensure a high degree of association, but not so strong that the association becomes effectively irreversible. In addition, the hydrogen bond is directional, and the normal collinear orientation of donor atom, hydrogen, and acceptor makes the geometry of simple hydrogen-bonded aggregates relatively easy to predict without resorting to extensive computation. A suitable strategy for making tectons sticky is therefore to endow them with the ability to participate in multiple intermolecular hydrogen bonds. This requires that each tecton incorporate a particular pattern of hydrogen-bond donors and acceptors. In principle, it would be possible to devise a new type of tecton with a unique pattern of hydrogen-bonding sites for each application. In practice, however, it is more sensible to use a modular approach in which the patterns are constructed from repetitive use of simple, well-known hydrogen-bonding motifs that have been carefully studied and shown to be particularly strong and reliable. Of the many motifs with these characteristics, one of the most suitable is the cyclic hydrogen-bonded array defined by dimers of 2-pyridone and related heterocycles



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(eq. 1). Despite its simplicity, this motif has proven to be very effective for the regulation of tectonic association.[3]

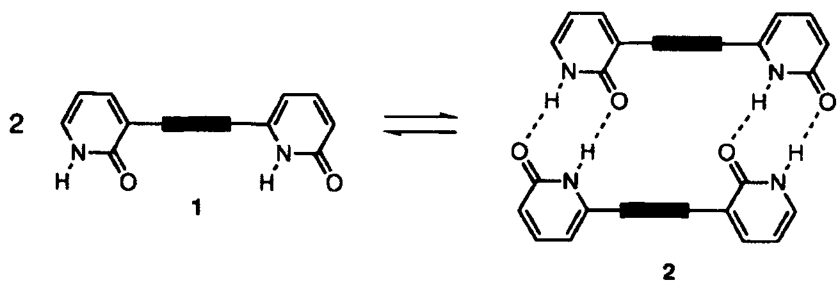
Use of Pyridone Subunits to Regulate Simple Tectonic Assembly

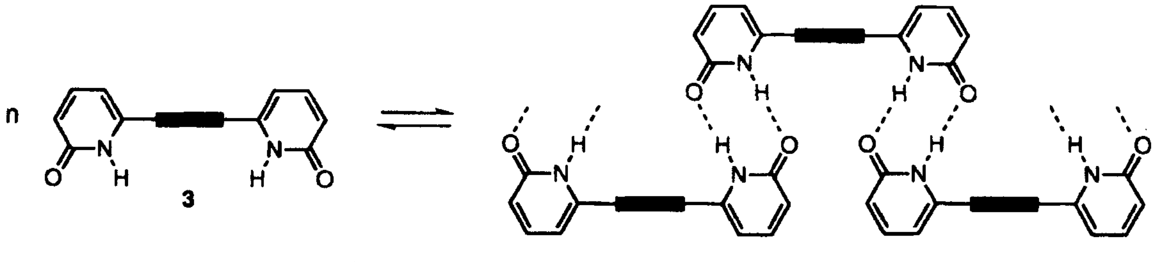
Extensive thermodynamic studies of the dimerization of 2-pyridone by Hammes and Beak[5] have established that $\Delta H°$ for the association of eq. 1 is -5.9 kcal/mol in $CHCl_3$, $\Delta S°$ is -10.7 eu, and $\Delta G°$ is -2.7 kcal/mol at 25°C. Under these conditions, approximately 80% of the molecules in a nominally 0.1 M solution of 2-pyridone are associated as dimers. Despite the notable strength of the pyridone dimer, it is naive to expect that effective tectons can be constructed by the simple expedient of attaching single pyridone subunits to various molecular frameworks. This is because the pyridone dimer is not strong enough to dominate aggregation by overriding all other intermolecular interactions that are likely to be present in a complex assembly. Fortunately, simultaneous attachment of multiple pyridone subunits to carefully chosen frameworks can produce tectons more highly predisposed to associate in particular ways.

An extremely simple example is provided by molecules in which two pyridones are linked to a rigid linear spacer. If the pyridones are linked at the 3 and 6 positions only, three isomeric dipyridones are possible. One of them, the 3,6′-dipyridone **1**, incorporates a self-complementary pattern of hydrogen-bond donors and acceptors. As a result, dipyridone **1** can form an antiparallel duplex **2** joined by four nearly ideal hydrogen bonds. In contrast, the 6,6′-dipyridone **3** and the corresponding 3,3′-isomer are not fully self-complementary and will be forced to form oligomeric chains (eq. 2). To test these generalizations, we synthesized a series of rigidly linked dipyridones, including the self-complementary acetylenic dipyridone **4** and the non-self-complementary isomer **5**.[3f] As expected, compound **4** forms an antiparallel duplex in the solid state and favors a similar structure in solution, whereas compound **5** forms an oligomeric chain. These examples confirm that multiple pyridone subunits can be attached to suitable frameworks to create molecules predisposed to associate in specific ways, both in the solid state and in solution.

Self-Assembly of Diamondoid Networks by Tectonic Aggregation

Although dipyridones **4** and **5** have interesting structures and striking properties of recognition and self-association, they nevertheless closely resemble the simple pyridone subunits from which they are constructed. It is not obvious that they offer the chemist any dramatic new opportunities. For this reason, use of the new terms *tecton* and *molecular tectonics* to identify molecules of this type and to define the study of their aggregation could reasonably be considered premature, unnecessary, or even pretentious. However, when more complex tectons are created by attaching multiple sticky subunits to large rigid frameworks, the power and elegance of the strategy of molecular tectonics become evident. Hypothetical tecton **6**, for example, which is created by using rigid arms to connect four sticky sites (·) to a tetrahedral core, is designed to generate the diamon-





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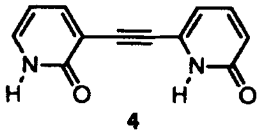

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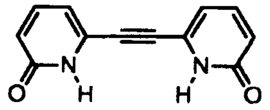

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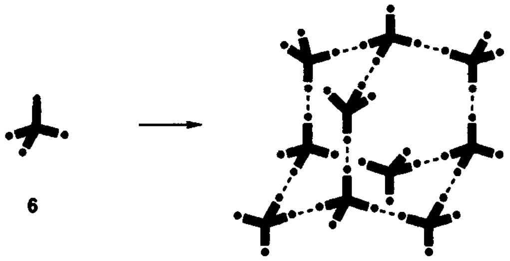
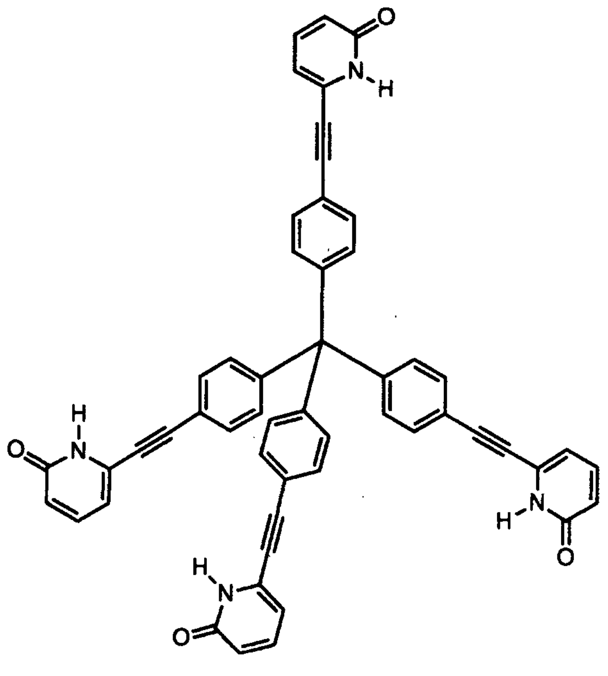


6 **7** (3)

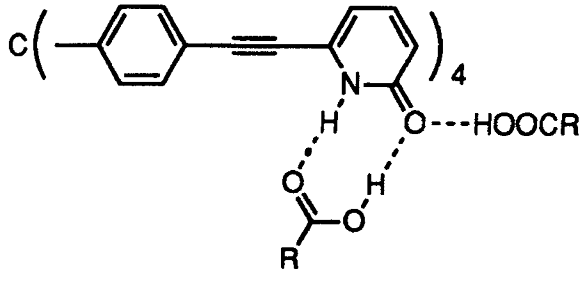
doid network **7** or a related three-dimensional lattice by a process of self-assembly (eq. 3). This concept is not new; indeed, structures as simple as H_2O and KH_2PO_4 are known to associate in this manner to form diamondoid networks held together by hydrogen bonds.[6] Moreover, in an influential paper published in 1988,[7] Ermer established that diamondoid networks can be formed by the self-association of complex organic molecules; for example, such a network is generated by intermolecular hydrogen bonding of the tetrahedrally-oriented acid groups in 1,3,5,7-adamantanetetracarboxylic acid. However, these studies of tectonic assembly had not demonstrated that it is possible 1) to make expanded or contracted diamondoid networks by systematically varying the structure of the tectonic subunits; 2) to make diamondoid networks with significant open spaces for the inclusion of guest molecules; 3) to endow these networks with properties more commonly associated with zeolites and related inorganic materials, including high structural integrity, selective microporosity, and catalytic activity; and 4) to use the strategy of molecular tectonics to construct a wide variety of three-dimensional networks not based on diamond. These were among the goals we set out to achieve in our own work.

We began by synthesizing tecton **8**, which incorporates four sticky pyridone subunits linked by acetylenic spacers to a core derived from tetraphenylmethane.[3d] Tecton **8** is large, rigid, and polar, so its solubility in organic solvents is low; nevertheless, it can be crystallized effectively from mixtures containing carboxylic acids. The use of acetic or propionic acid in hexane or in mixtures of hexane and methanol consistently produced extremely long needles of composition **8** · 8RCOOH (R = CH_3, C_2H_5). The morphology of these crystals was surprising, since we did not expect an essentially isotropic diamondoid network to permit such exaggerated growth along a single axis. In fact, diamondoid networks are not formed under these conditions of crystallization. Instead, an X-ray crystallographic study of complex **8** · 8 C_2H_5COOH revealed that self-assembly of a diamondoid network is thwarted by association of each of the four pyridone subunits with two molecules of carboxylic acid, thereby producing adduct **9**.



8

This was unexpected and disappointing, since we had already shown that the strong tendency of pyridones to dimerize can be used reliably to control tectonic aggregation in simpler systems. We were therefore tempted to treat the undesired mode of crystallization as an abnormality, and we reexamined the structure of the hypothetical diamondoid network **7** derived from tecton **8** in order to understand the origins of the abnormal crystallization. The intertectonic separation in this structure, defined by the distance between adjoining tetrahedral centers, should be approximately 20 Å. The resulting diamondoid network therefore defines enormous voids that must be filled by interpenetrating networks, molecules of solvent, or other guests. Since acetic and propionic acids are relatively small molecules, a correspondingly large number will be required to fill the voids, and the entropy of enclathration will be particularly unfavorable. For this reason, we turned to larger carboxylic acids for the crystallization of tecton **8**, and we found that the use of



9 (R = C_2H_5)

butyric acid/hexane/methanol produced high yields of prisms of approximate composition **8** · 2 $CH_3CH_2CH_2COOH$. The change in morphology and composition immediately suggested that a completely different structure had been formed. An X-ray crystallographic study confirmed that the pyridone subunits of tecton **8** interact in the expected way to induce self-assembly of the remarkable diamondoid network shown in Figure 1a.

The enormous voids in this structure, which has a measured average intertectonic separation of 19.7(1) Å, are filled by a combination of interpenetrating independent diamondoid networks and enclathrated molecules of butyric acid. The interpenetration occurs in the following manner. The upper drawing in Figure 2 shows hypothetical diamondoid network **7** when viewed at an angle of 45° with respect to the *b* axis. This view reveals conspicuous parallel hexagonal channels. If a second network is introduced by translating the first by a distance of $\frac{1}{2}b$ along the *b* axis, then the hexagonal channels defined by one network become at least partly filled by the second network (Figure 2, lower drawing). In principle, increasingly higher levels *n* of interpenetration can be achieved by translations of $1/n$ *b* along the *b* axis until adjacent tectons in independent networks become close-packed. In the case of tecton **8**, the intertectonic separation within each independent network is so large that seven-fold interpenetration can occur, and no significant spaces for inclusion remain in the hexagonal channels. Nevertheless, the interpenetrating diamondoid network retains a very high degree of openness. The upper drawing in Figure 3 views hypothetical non-interpenetrating diamondoid network **7** along the *b* axis and reveals conspicuous square channels. Interpenetration by one or more additional networks (Figure 3, lower drawing) occurs in a way that leaves these channels open and available for enclathration.

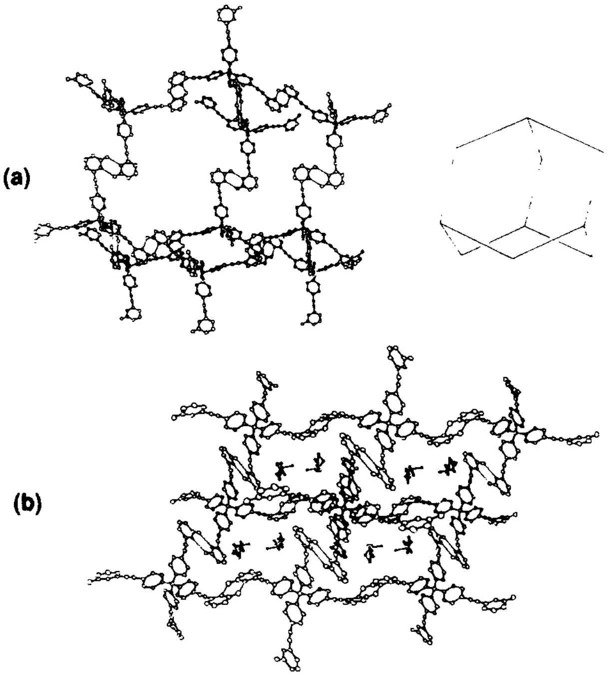


Figure 1 a) ORTEP drawing of part of the diamondoid network present in crystals of clathrate **8** · 2 $CH_3CH_2CH_2COOH$. The tetrahedral centers of the ten tectons shown in the drawing define a distorted adamantane, shown at the right at one-half scale. Non-hydrogen atoms are represented by ellipsoids corresponding to 50% probability. Butyric acid and all hydrogen atoms are omitted for clarity. Hydrogen bonds are represented by narrow lines. b) View along the *b* axis showing cross sections of the channels containing parallel columns of butyric acid.

The diamondoid network defined by clathrate **8** · 2 $CH_3CH_2CH_2COOH$ is distorted in a way that makes these channels rectangular rather than square (Figure 1b). They define openings approximately 4 × 8 Å in diameter,[8] making them even larger than those found in urea clathrates and similar to the pore sizes in typical zeo-

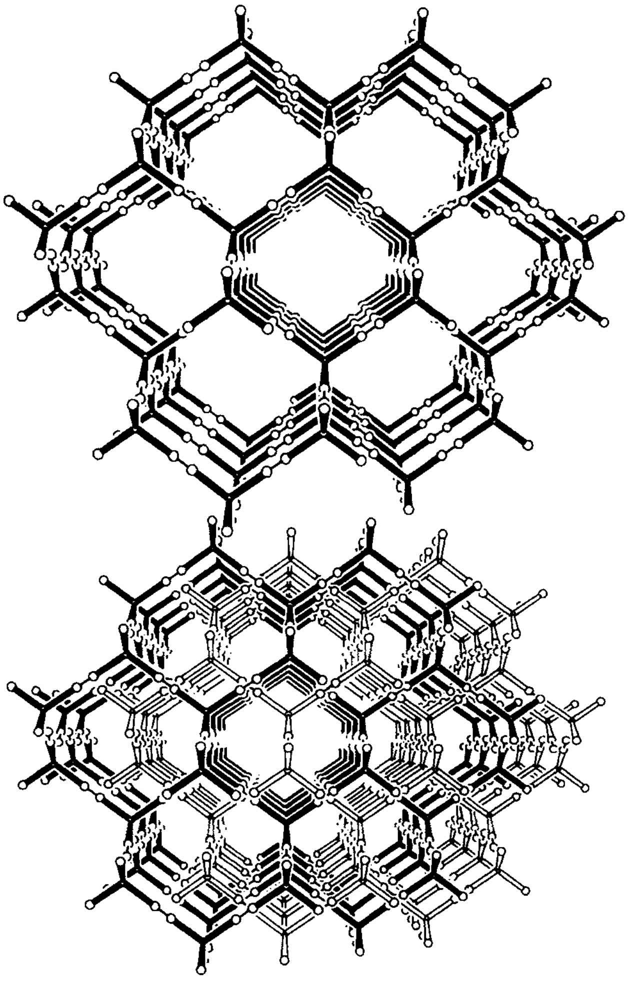


Figure 2 The upper drawing shows hypothetical non-interpenetrating diamondoid network **7** when viewed at an angle of 45° with respect to the *b* axis. This view reveals conspicuous parallel hexagonal channels. The lower drawing provides a similar view of two independent interpenetrating networks, one shown in black and the other in white, that result when the original network is translated by a distance of $\frac{1}{2}b$ along the *b* axis.

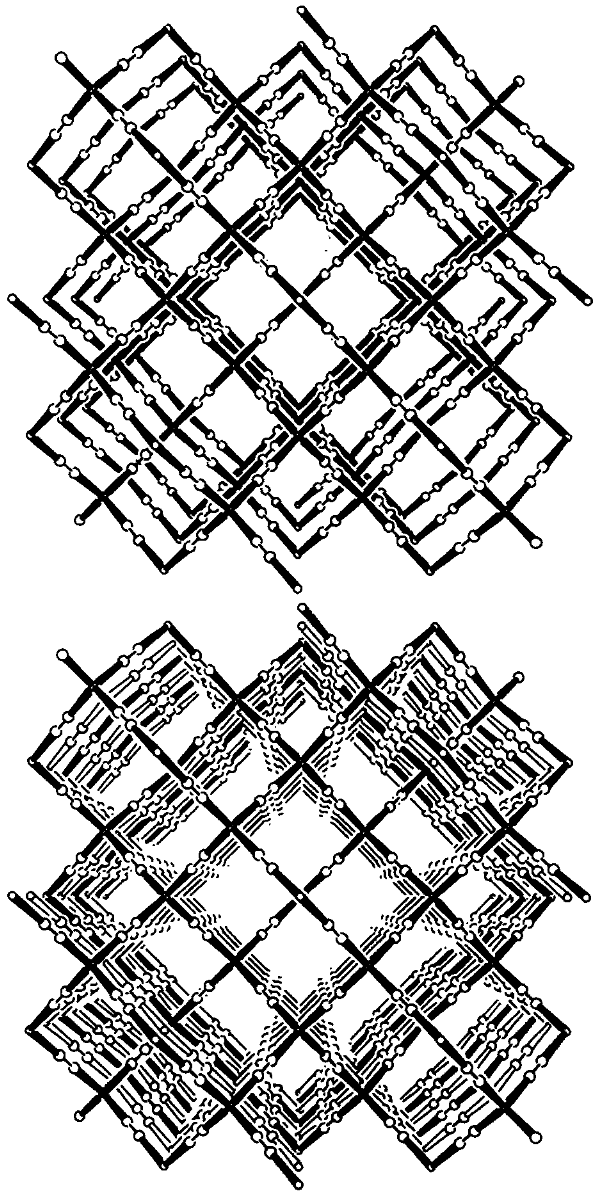


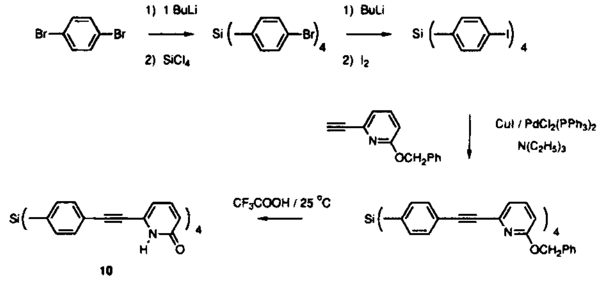
Figure 3 The upper drawing shows a view of hypothetical noninterpenetrating diamondoid network **7** parallel to the *b* axis. The lower drawing provides a similar view of two independent interpenetrating networks, one shown in black and the other in white, that result when the original network is translated by a distance of $\frac{1}{2}b$ along the *b* axis.

lites.[9] The channels are spacious enough to accommodate two parallel columns of butyric acid, which occupy approximately 24% of the volume of the crystals.[12] The enclathrated molecules are surprisingly well-ordered, even though they do not appear to have specific interactions with the walls of the channels; instead, they are joined to one another by hydrogen bonding of the carboxylic acid groups and by van der Waals interactions at the other termini.

If diamondoid assembly is entropically unfavorable when tecton **8** is crystallized from acetic and propionic acids but becomes feasible when butyric acid is used, then larger carboxylic acids should also promote diamondoid assembly. In fact, crystallizations in the presence of valeric acid, isovaleric acid, and isobutyric acid all appear to produce diamondoid clathrates. Even though the crystallizations take place in mixed solvents containing hexane and methanol, carboxylic acids are enclathrated with high selectivity, presumably because their polarity and hydrogen-bonding ability make them more complementary to the faces of growing crystals.

The large channels characteristic of diamondoid networks derived from tecton **8** suggest that the crystals should be porous and that it should be possible to remove enclathrated guests from the interior. Indeed, loss of butyric acid occurs when crystals of clathrate **8** · 2 $CH_3CH_2CH_2COOH$ are heated or placed under vacuum. Although samples do not change substantially in appearance during these experiments, they do not remain crystalline, nor can crystallinity be restored by brief exposure of the product to vapors of butyric acid. We conclude that the array of hydrogen bonds supporting the diamondoid network is not strong enough to resist the forces of close packing that are exerted when butyric acid is removed from the interior of the crystals.

Our observations show that the strategy of molecular tectonics can be used to build predictably ordered diamondoid networks with large intertectonic separations. In addition, the resulting structures have some of the desirable properties of zeolites and related inorganic materials, including potentially large void volumes, selective enclathration, and microporosity. We were eager to test the limits of this strategy by studying the association of tectons designed to generate expanded and contracted diamondoid networks with larger and smaller intertectonic separations. Although we have synthesized a large number of potentially suitable tectons, only a few have so far yielded crystals suitable for study by X-ray diffraction. One of these successful cases is tecton **10**, which was synthesized by the route summarized in Scheme 1.[13] The Si-C bonds at the tetrahedral core should be approximately 1.87 Å in length,[14] whereas the corresponding C-C bonds in tecton **8** are 1.54 Å in



Scheme 1

length. This means that the intertectonic separation in a diamondoid network derived from tecton **10** should increase by nearly 0.7 Å. Crystallization of tecton **10** from mixtures of valeric acid and ether produced a clathrate of approximate composition **10** · 2 $CH_3CH_2CH_2CH_2COOH$. An X-ray crystallographic study confirmed that the tectons aggregate in the expected way to form a diamondoid network despite the increased intertectonic separation (Figure 4a). In this case, the larger intertectonic separation accommodates an 8-fold interpenetration of diamondoid networks, whereas interpenetration of the networks derived from tecton **8** is only 7-fold. Despite the high degree of interpenetration, the network generated from tecton **10** again defines conspicuous channels that are parallel to the direction of translation of the interpenetrating networks (Figure 4b). In this case, the channels are approximately square and 5 Å in diameter.[8,15] The channels enclathrate valeric acid but do not enforce an ordered arrangement of the guests, and their precise location could not be determined.

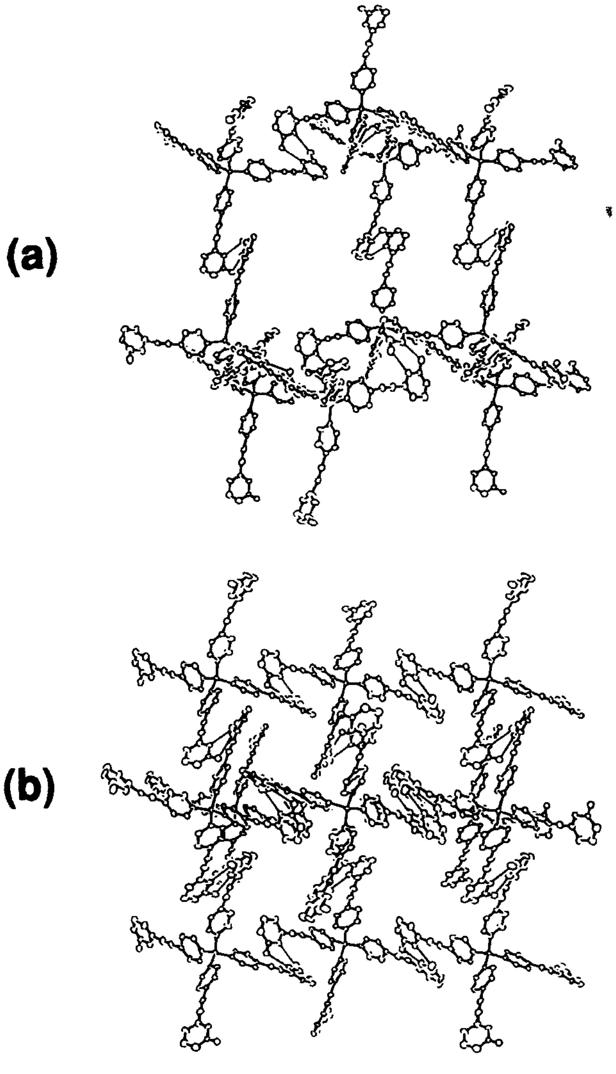
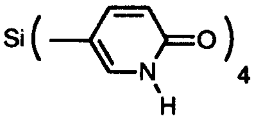


Figure 4 (a) ORTEP drawing of part of the diamondoid network present in crystals of clathrate **10** · 2 $CH_3CH_2CH_2CH_2COOH$. Nonhydrogen atoms are represented by ellipsoids corresponding to 40% probability. Valeric acid and all hydrogen atoms are omitted for clarity. Hydrogen bonds are represented by narrow lines. (b) View parallel to the channel axes showing the cross sections of adjacent channels.

To construct contracted diamondoid networks with shorter intertectonic spacings, we then synthesized tecton **11**.[3a] Compound **11** could be prepared conveniently in 52% overall yield from 5-bromo-2-(phenylmethoxy)-pyridine by bromine-lithium exchange and subsequent addition of $SiCl_4$, followed by treatment of the intermediate tetrapyridylsilane **12** with trifluoroacetic acid to effect deprotection. Crystallization of tecton **11** from mixtures of carboxylic acids and ether or hexane yielded a series of clathrates of approximate compositions **11** · 4 CH_3COOH, **11** · 4 CH_3CH_2COOH, **11** · $CH_3CH_2CH_2CH_2COOH$, and **11** · 0.5 $CH_3CH_2CH_2CH_2COOH$ · 1 CH_3COOH, and their structures were determined by X-ray crystallography. Clathrate **11** · 4 CH_3COOH forms an abnormal heterotectonic diamondoid network in which each molecule of silane **11** is joined to two neighbors by direct hydrogen bonding of pyridone rings, but the remaining pyridone rings in the resulting chains are linked indirectly by bridging molecules of acetic acid. The failure of tecton **11** to form a normal homotectonic diamondoid network when crystallized from acetic acid resembles the behavior of tecton **8** in the presence of small carboxylic acids and can be similarly attributed to a particularly unfavorable entropy of enclathration.



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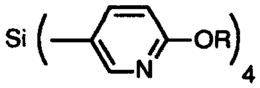


12 (R = CH_2Ph)

In contrast, crystallization of tecton **11** from propionic acid yielded a normal diamondoid clathrate **11** · 4 CH_3CH_2COOH with an average intertectonic separation of 11.7(1) Å (Figure 5a). Because the separation is smaller, the network is only doubly interpenetrating. Even though the separation is smaller, however, the network is perforated by very conspicuous square channels, approximately 6 Å in diameter,[8] which selectively enclathrate propionic acid (Figure 5b). In this case, the guests are well-ordered because they are joined by hydrogen bonds to the carbonyl groups of pyridone rings lining the channels. The low degree of interpenetration gives clathrate **11** · 4 CH_3CH_2COOH exceptional porosity, and fully 53% of the volume of the crystal is occupied by propionic acid.[12] The guest volume is significantly larger than those in clathrates **8** · 2 $CH_3CH_2CH_2COOH$ (24%) and **10** · 2

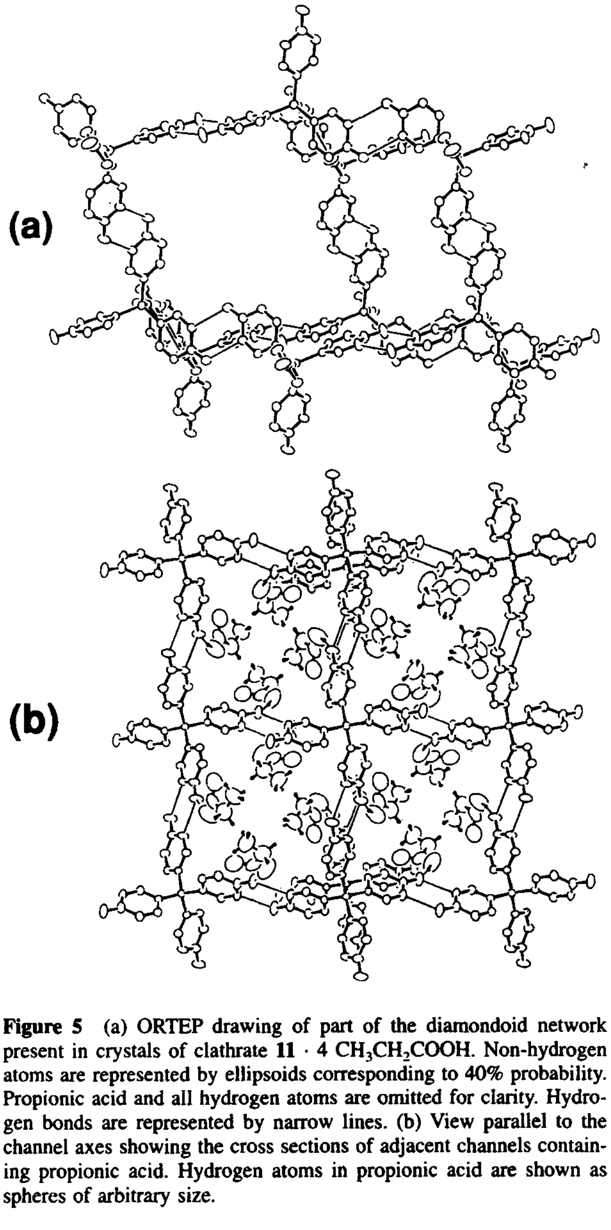


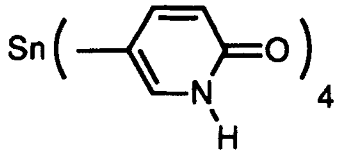
Figure 5 (a) ORTEP drawing of part of the diamondoid network present in crystals of clathrate **11** · 4 CH_3CH_2COOH. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability. Propionic acid and all hydrogen atoms are omitted for clarity. Hydrogen bonds are represented by narrow lines. (b) View parallel to the channel axes showing the cross sections of adjacent channels containing propionic acid. Hydrogen atoms in propionic acid are shown as spheres of arbitrary size.

$CH_3CH_2CH_2CH_2COOH$ (29%), primarily because the diamondoid network derived from tecton **11** is doubly interpenetrating whereas those generated from larger tectons **8** and **10** are much more highly interpenetrating.

Unlike zeolites, hydrogen-bonded diamondoid assemblies derived from tectons **8**, **10**, and **11** cannot be freed of guests to produce ordered networks with large voids. However, the following experiment demonstrates that our hydrogen-bonded networks are porous enough to permit the exchange of guests and robust enough to remain intact. Suspending crystals of clathrate **11** · 0.5 $CH_3CH_2CH_2CH_2COOH$ · CH_3COOH in acetic acid/ether (25°C, 30 min) causes essentially complete internal replacement of valeric acid by acetic acid as measured by ^1H NMR spectroscopy; moreover, subsequent study by X-ray crystallography shows that the space group remains the same and the cell dimensions do not change substantially. Because crystallization of tecton **11** from valeric acid/ether and acetic acid/ether produces distinctly different structures, this experiment establishes that exchange occurs not by recrystallization, with significant movement of tectonic subunits, but rather by replacement of guests within an intact microporous network.

Self-Assembly of Non-Diamondoid Three-Dimensional Networks by Tectonic Aggregation

In the cases of three-dimensional tectonic assembly that we have described so far, diamondoid networks tend to be favored because they accommodate nominally tetrahedral tectons and permit efficient interpenetration. Other lattices are undoubtedly feasible, however, particularly when the tecton or its intermolecular interactions are designed to be susceptible to deformations. In a similar way, small variations in the metal-oxygen-metal angles in zeolites allow nominally tetrahedral SiO_4 and AlO_4 subunits to generate a rich variety of three-dimensional networks.[16] We therefore decided to replace the central atom of silicon in tecton **11** by tin, which produces a tecton **13** with a core that is more susceptible to angular deformations.[3a,17] Tecton **13** was synthesized from 5-iodo-2-pyridone in 33% overall yield by O-silylation (TBDMS-Cl, $N(C_2H_5)_3$), followed by iodine-lithium exchange (BuLi), addition of $SnCl_4$, and desilylation (CH_3COOH, 25°C) of the resulting tetrapyridylstannane. Crystallization of tecton **13** from butyric acid/ether yielded a clathrate of approximate composition **13** · 2 $CH_3CH_2CH_2COOH$, and its structure was determined by X-ray crystallography. Each tecton is joined to three neighbors by normal hydrogen bonding of three of its pyridone rings, but the fourth pyridone is associated with butyric acid only, resulting in disruption of the diamondoid network. We then turned to a larger carboxylic acid and found that the use of valeric acid/hexane yielded a clathrate of approximate composition **13** $CH_3CH_2CH_2CH_2COOH$. An X-ray crystallographic study established that each tecton is linked to four neighbors by direct hydrogen bonding of pyridone rings to create cyclic quartets, which then interlock to build a



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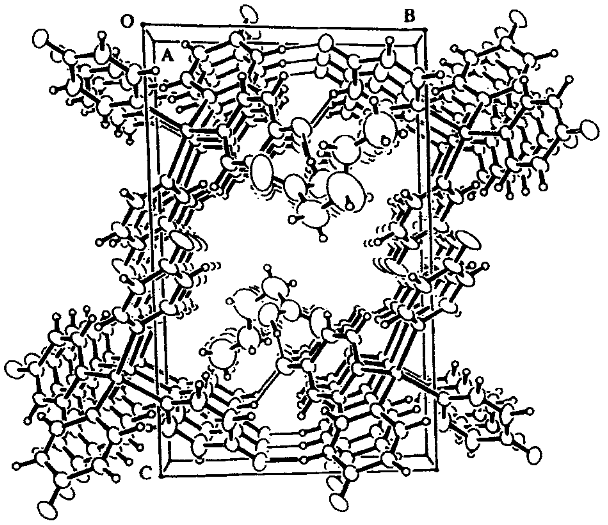

Figure 6 ORTEP view of superimposed unit cells of clathrate **13** · $CH_3CH_2CH_2CH_2COOH$ showing a single channel defined by stacked quartets. Pyridones lying in the *ac* plane are doubly hydrogen-bonded, while those lying in the *ab* plane are singly hydrogen-bonded. Each channel is surrounded by eight parallel channels, all filled with valeric acid. Hydrogen atoms are shown as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 40% probability. Hydrogen bonds are indicated by narrow lines.

novel network of parallel four-sided stacks (Figure 6). Each stack has an open diameter of approximately 2 × 9 Å[8,18], creating channels selectively filled with well-ordered molecules of valeric acid. Two features permit nominally tetrahedral tecton **13** to form cyclic quartets instead of the cyclic hextets characteristic of diamondoid networks: 1) Two of the four pyridone-pyridone interactions that link tecton **13** into quartets involve only a single hydrogen bond, so the pyridone rings do not need to be coplanar; and 2) bond angles at the central atom of tin in tecton **13** accept substantial deformations. For example, the C-Si-C angles in diamondoid clathrate **11** · 4 CH_3CH_3COOH range only from 108 to 110°, while the C-Sn-C angles in non-diamondoid clathrate **13** · $CH_3CH_2CH_2CH_2COOH$ vary from 102.99(16) to 119.66(16)°.

CONCLUSIONS

Our observations are important because they suggest that clever application of the strategy of molecular tectonics can be used to build an unlimited range of ordered three-dimensional organic networks. Furthermore, these networks can be designed to have a variety of useful properties similar to those of zeolites and related inorganic materials, including high structural integrity, potentially large void volumes, and adjustable microporosity.

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NOTES AND REFERENCES

1 Laboratoire de Diffraction des Rayons-X, Département de Chimie, Université de Montréal.

2 Killam Research Fellow, 1992–1994.

3 a) Wang, X.; Simard, M.; Wuest, J.D. *J. Am. Chem. Soc.*, **1994**, *116*, 12119. b) Wuest, J.D. In *Mesomolecules: From Molecules to Materials*; Mendenhall, G.D.; Greenberg, A.; Liebman, J.F., Eds.; Chapman & Hall: New York, 1995. c) Persico, F.; Wuest, J.D. *J. Org. Chem.* **1993**, *58*, 95. d) Simard, M.; Su, D.; Wuest, J.D. *J. Am. Chem. Soc.* **1991**, *113*, 4696. e) Gallant, M.; Phan Viet, M.T.; Wuest, J.D. *J. Org. Chem.* **1991**, *56*, 2284. f) Ducharme, Y.; Wuest, J.D. *J. Org. Chem.* **1988**, *53*, 5787.

4 For example, the following recent references describe molecules designed to participate in complex networks of hydrogen bonds: Hanessian, S.; Gomtsyan, A.; Simard, M.; Roelens, S. *J. Am. Chem. Soc.* **1994**, *116*, 4495. Zerkowski, J.A.; Mathias, J.P.; Whitesides, G.M. *J. Am. Chem. Soc.* **1994**, *116*, 4305. Zerkowski, J.A.; Whitesides, G.M. *J. Am. Chem. Soc.* **1994**, *116*, 4298. Russell, V.A.; Etter, M.C.; Ward, M.D. *J. Am. Chem. Soc.* **1994**, *116*, 1941. Kotera, M.; Lehn, J.-M.; Vigneron, J.-P. *J. Chem. Soc., Chem. Commun.* **1994**, 197. Ung, A.T.; Bishop, R.; Craig, D.C.; Dance, I.G.; Scudder, M.L. *J. Chem. Soc., Chem. Commun.* **1993**, 322. Copp, S.B.; Subramanian, S.; Zaworotko, M.J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 706. Geib, S.J.; Vicent, C.; Fan, E.; Hamilton, A.D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 119. Chang, Y.-L.; West, M.-A.; Fowler, F.W.; Lauher, J.W. *J. Am. Chem. Soc.* **1993**, *115*, 5991. Aakeröy, C.B.; Seddon, K.R. *Chem. Soc. Rev.* **1993**, 397.

5 Beak, P.; Covington, J.B.; Smith, S.G.; White, J.M.; Zeigler, J.M. *J. Org. Chem.* **1980**, *45*, 1354. Hammes, G.G.; Park, A.C. *J. Am. Chem. Soc.* **1969**, *91*, 956.

6 Endo, S.; Chino, T.; Tsuboi, S.; Koto, K. *Nature* **1989**, *340*, 452.

7 Ermer, O. *J. Am. Chem. Soc.* **1988**, *110*, 3747.

8 The estimated pore sizes correspond to distances between van der Waals surfaces of opposing walls defined by a projection along the channel axis.

9 For comparison, pore sizes in zeolites normally range from approximately 4 to 13 Å, and void volumes are typically less than 50%.[10] The cylindrical channels in urea clathrates are nearly 5 Å in diameter, and the void volumes are approximately 30%.[11]

10 For references, see: Davis, M.E.; Lobo, R.F. *Chem. Mater.* **1992**, *4*, 756.

11 Takemoto, K.; Sonoda, N. In *Inclusion Compounds*; Atwood, J.L.; Davies, J.E.D.; MacNicol, D.D., Eds.; Academic Press: London, 1984; Vol. 2, p 47. Smith, A.E. *Acta Crystallogr.* **1952**, *5*, 224.

12 Volumes occupied by guests were estimated by using the stoichiometry of the clathrate, its calculated density, and the density of the pure guest at 25°C.

13 Wang, X.; Simard, M.; Wuest, J.D., unpublished results.

14 Csákvári, E.; Shishkov, I.F.; Rozsondai, B.; Hargittai, I. *J. Mol. Struct.* **1990**, *239*, 291.

15 The interpenetrating networks in the expanded diamondoid lattice of clathrate **10** · 2 $CH_3CH_2CH_2CH_2COOH$ are slightly offset along the channel axis, so the pores are somewhat smaller than those in clathrate **8** · 2 $CH_3CH_2CH_2COOH$.

16 a) Smith, J.V. *Chem. Rev.* **1988**, *88*, 149. b) For a general discussion of three-dimensional four-connected networks, see: Wells, A.F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, 1984; p 63.

17 Horner, J.H.; Newcomb, M. *Organometallics* **1991**, *10*, 1732.

18 Periodic enlargements in the channels provide additional space for the enclathration of valeric acid.