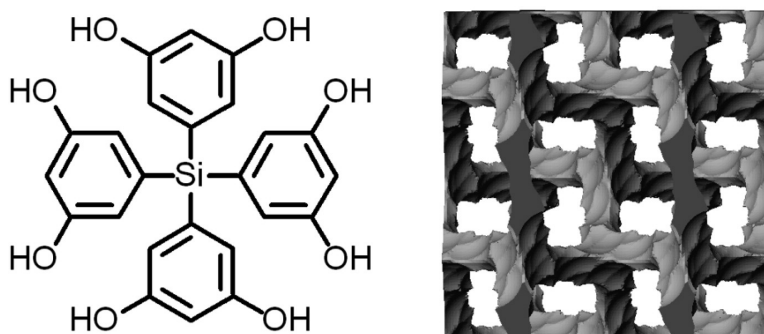


## Submaximal Interpenetration and Bicontinuous Three-Dimensional Channels in Porous Molecular Networks

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## Submaximal Interpenetration and Bicontinuous Three-Dimensional Channels in Porous Molecular Networks

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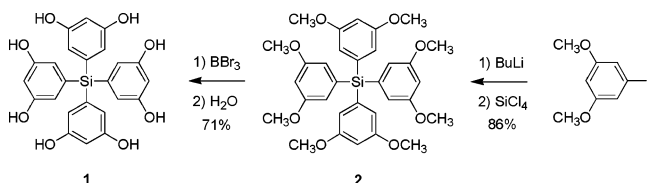
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Our current inability to predict the structure and properties of molecular crystals impedes progress in many areas of science and technology.<sup>1</sup> An emerging strategy for controlling crystallization relies on building networks from molecules that are positioned predictably by strong directional interactions. Such molecules have been called tectons from the Greek word for builder.<sup>2</sup> Tectons tend to crystallize according to directional preferences even when the result is not a normal close-packed structure, but rather a porous network analogous to zeolites.<sup>3</sup>

Systematic efforts to increase porosity have yielded molecular crystals in which at least 75% of the volume is available for including guests.<sup>3</sup> Unfortunately, space in open networks can also be filled by independent interpenetrating networks,<sup>4</sup> thereby reducing the volume accessible to guests. In fact, nearly every previous study of open molecular networks has shown that the degree of interpenetration is as high as the porosity permits.<sup>5,6</sup> Attempts to increase porosity should therefore target structures in which interpenetration is disfavored or impossible. In searching for such structures, we have found that tetrakis(3,5-dihydroxyphenyl)silane (**1**) crystallizes as a porous hydrogen-bonded network with submaximal interpenetration and novel bicontinuous systems of channels.

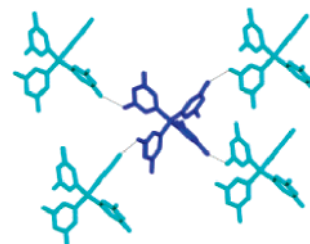
Tetraresorcinol **1** was synthesized in 61% overall yield from 1-iodo-3,5-dimethoxybenzene (Scheme 1).<sup>7</sup> Intermediate octamethyl

### Scheme 1

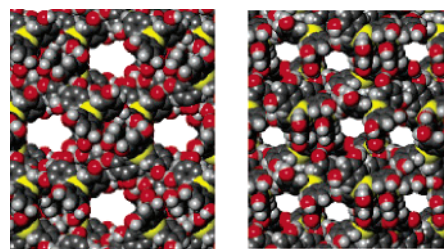


ether **2** crystallized from CH<sub>2</sub>Cl<sub>2</sub> as a close-packed structure,<sup>8</sup> whereas tetraresorcinol **1** tended to crystallize as an open network. This underscores how typical tectons differ from normal molecules. Compound **1** was initially crystallized from hexane containing ethyl acrylate, ethyl acetate, THF, or dioxolane. In the first two cases, the crystals are isomorphous, belong to the tetragonal space group *I*4<sub>2</sub>*d*, and correspond to inclusion compounds of approximate composition **1**·2.0 ethyl acrylate and **1**·2.7 ethyl acetate.<sup>9</sup> In the other cases, the crystals are also isomorphous, belong to the tetragonal space group *I*4<sub>1</sub>/*a*, and have the approximate composition **1**·3.3 THF and **1**·3.3 dioxolane.<sup>9</sup> The inclusion compounds are closely similar, and only those of ethyl acrylate and THF are discussed in detail.

In crystals grown from hexane/ethyl acrylate, two symmetry-independent molecules of tetraresorcinol **1** are present (T<sub>1</sub> and T<sub>2</sub>). Each T<sub>2</sub> molecule forms O—H···O hydrogen bonds characteristic of phenols with four neighboring T<sub>2</sub> molecules (Figure 1),<sup>10,11</sup> thereby defining an open diamondoid network in which the central Si2 atoms are separated by 12.62(1) Å.<sup>12</sup> The T<sub>1</sub> molecules define a second diamondoid network, which interpenetrates and contacts



**Figure 1.** Partial view of the structure of crystals of tetraresorcinol **1** grown from hexane/ethyl acrylate, showing a central T<sub>2</sub> tecton (dark blue) and four hydrogen-bonded T<sub>2</sub> neighbors (light blue) that define a single diamondoid network. Hydrogen atoms are omitted, and hydrogen bonds appear as broken lines.

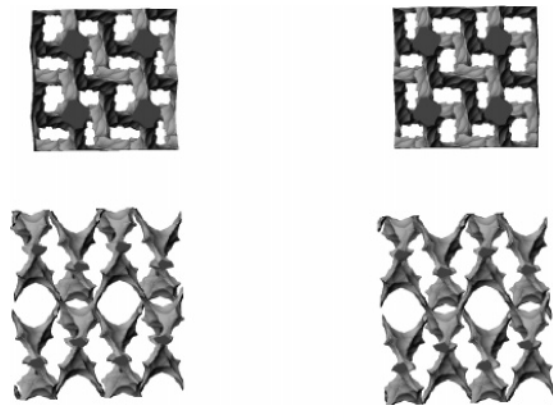


**Figure 2.** Channels in the networks constructed by crystallizing tetraresorcinol **1** from hexane/ethyl acrylate (left) and hexane/THF (right), viewed along the *abc* diagonals with guests omitted.

the one built from T<sub>2</sub>. All C—Si—C angles are close to the tetrahedral ideal. The central Si1 atoms in the T<sub>1</sub> network are separated from their closest neighbors in the T<sub>2</sub> network by a distance Si1—Si2 of 7.40(1) Å. The initial T<sub>2</sub> network is also interpenetrated by a symmetry-equivalent T<sub>2</sub> network, which contacts the T<sub>1</sub> network and thereby creates a closely packed T<sub>2</sub>T<sub>1</sub>T<sub>2</sub> triad. The structural integrity of this triad is ensured by T<sub>2</sub>—T<sub>2</sub> and T<sub>1</sub>—T<sub>1</sub> hydrogen bonds within each network (Figure 1), as well as by additional T<sub>1</sub>—T<sub>2</sub> and T<sub>2</sub>—T<sub>2</sub> hydrogen bonds between different networks in each triad.<sup>13</sup>

Despite interpenetration, space remains for guests, and the T<sub>2</sub>T<sub>1</sub>T<sub>2</sub> triads are separated by a continuous volume of diamondoid topology filled with disordered ethyl acrylate. Approximately 45% of the volume of the crystals is accessible to guests, which occupy interconnected channels 8 × 6 Å<sup>2</sup> in cross section along the *abc* diagonal (Figures 2 and 3). The closest central Si2 atoms of adjacent triads are separated by 22.55(1) Å, which is approximately 3 times the Si1—Si2 distance (7.40(1) Å) separating adjacent T<sub>1</sub> and T<sub>2</sub> networks within an individual triad.

The initial diamondoid T<sub>2</sub> network is therefore open enough to accommodate four similar networks, yet only two are actually present. The feasibility of further interpenetration was subsequently proved by finding that compound **1** crystallizes from hexane/methyl propiolate in the same *I*4<sub>2</sub>*d* space group, but as a 5-fold interpenetrated network with no included guests. The overall structure of crystals grown from hexane/ethyl acrylate can therefore be repre-



**Figure 3.** Stereoviews of channels within networks formed by crystallizing tetraresorcinol **1** from hexane/ethyl acrylate (upper) and hexane/THF (lower). The surfaces of the channels (light gray) are defined by the possible loci of the center of a sphere of diameter  $d$  as it rolls over the surface of the ordered network. The upper pair is viewed along the  $c$  axis with  $d = 5 \text{ \AA}$ , and the lower is viewed along the  $b$  axis with  $d = 4 \text{ \AA}$ .

sented by an repeating TTTSS pattern of interpenetrated diamondoid topologies, three composed of tetraresorcinol **1** (T) and two in which missing tectons are replaced by solvent (S).

Crystals of tetraresorcinol **1** grown from hexane/THF differ in a subtle and intriguing way. Again, two symmetry-independent molecules ( $T_1$  and  $T_2$ ) are present and define three interpenetrated hydrogen-bonded diamondoid networks. In this case, however, the two  $T_2$  networks lie in close contact to form  $T_2T_2$  diads, which are separated from the  $T_1$  networks by diamondoid volumes of solvent, thereby defining a TTSTS pattern of interpenetration. The included THF is partially ordered, and tracing the centers of gravity of the guests confirms that they occupy different diamondoid volumes. The central Si2 atoms in one  $T_2$  network are separated from those of their closest neighbors in the adjacent  $T_2$  network by an Si2–Si2 distance of  $7.43(1) \text{ \AA}$ , which is closely similar to the related Si1–Si2 distance ( $7.40(1) \text{ \AA}$ ) in crystals grown from hexane/ethyl acrylate. The corresponding distance between the central Si atoms of the separated  $T_1$  and  $T_2$  networks is more than 2 times larger ( $15.60(1) \text{ \AA}$ ). This offers enough space for 5-fold interpenetration, but again only submaximal 3-fold interpenetration is observed. Approximately 52% of the volume of the crystals is accessible to THF, which occupies bicontinuous interpenetrated channels approximately  $4 \times 3 \text{ \AA}^2$  in cross section (Figures 2 and 3). In principle, a guest in one system of channels can diffuse in three dimensions throughout 26% of the volume of the crystal, but it cannot enter the other system of channels without first exiting the crystal.

The structures of the inclusion compounds of tetraresorcinol **1** are strikingly similar to complex topologies adopted by block copolymers and amphiphilic assemblies to optimize interfacial contact.<sup>14,15</sup> Specifically, the structures mimic double-diamond cubic  $Pn\bar{3}m$  phases and thereby provide detailed models, characterized unambiguously by single-crystal X-ray diffraction, of architectures previously inferred from less direct evidence. Closely similar solvents cause tetraresorcinol **1** to crystallize with different degrees and modes of interpenetration, suggesting that the observed structures result from a delicate balance of thermodynamic or kinetic effects. In probing these effects, we found that crystals of tetraresorcinol **1** grown from hexane containing 1:1 ethyl acetate/

THF include only THF and have the same TTSTS structure as crystals grown from hexane/THF. Selective inclusion of THF, partial ordering of THF, and greater T–S contact in TTSTS structures than in alternative TTTSS and TTTTT architectures all suggest that hydrogen bonding between tetraresorcinol **1** and suitable guests, particularly THF, may be more effective than self-association of compound **1**, thereby making submaximally interpenetrated structures more stable than close-packed alternatives.

The concepts that underlie the strategy of molecular tectonics are simple and qualitative, but they have led repeatedly to the discovery of molecular crystals with new properties. The present study establishes the feasibility of engineering networks with high porosity, incomplete interpenetration, and channels with complex topologies not previously noted in any crystalline materials, including zeolites. Close structural analogies with block copolymers and surfactant assemblies show that crystal engineers and scientists studying softer materials can both draw inspiration from the same sources.

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**Supporting Information Available:** Detailed crystallographic analyses of all structures of tetraresorcinol **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Dunitz, J. D. *Chem. Commun.* **2003**, 545–548. (b) Desiraju, G. R. *Nat. Mater.* **2002**, *1*, 77–79. (c) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309–314. (d) Maddox, J. *Nature* **1988**, *335*, 201.
- (2) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696–4698.
- (3) For references to related work, see: (a) Malek, N.; Maris, T.; Perron, M.-E.; Wuest, J. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4021–4025. (b) Malek, N.; Maris, T.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **2005**, *127*, 5910–5916. (c) Fournier, J.-H.; Maris, T.; Wuest, J. D. *J. Org. Chem.* **2004**, *69*, 1762–1775.
- (4) (a) Batten, S. R. *Cryst. Eng. Commun.* **2001**, *18*, 1–7. (b) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494.
- (5) For a rare exception, see: Boldog, I.; Rusanov, E. B.; Sieler, J.; Blaurock, S.; Domasevitch, K. V. *Chem. Commun.* **2003**, 740–741.
- (6) Submaximal interpenetration is somewhat more common in networks joined by coordination to metals. For example, see: Chae, H. K.; Siberio-Pérez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523–527.
- (7) Dol, G. C.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Org. Chem.* **1998**, 359–364.
- (8) Saied, O.; Maris, T.; Simard, M.; Wuest, J. D., manuscript in preparation.
- (9) Compositions were estimated by X-ray crystallography and  $^1\text{H}$  NMR spectroscopy of dissolved samples.
- (10) For recent references to the hydrogen bonding of phenols, see: Fournier, J.-H.; Maris, T.; Simard, M.; Wuest, J. D. *Cryst. Growth Des.* **2003**, *3*, 535–540.
- (11) For other recent uses of resorcinols in crystal engineering, see the Supporting Information.
- (12) For a review of diamondoid hydrogen-bonded networks, see: Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, *23*, 283–288.
- (13) Average hydrogen bonds within the networks are shorter than those between them (Supporting Information), so the overall structure is properly viewed as the result of interpenetration, rather than as a single network.
- (14) For related analogies, see: (a) Lee, S.; Mallik, A. B.; Xu, Z.; Lobkovsky, E. B.; Tran, L. *Acc. Chem. Res.* **2005**, *38*, 251–261. (b) Ward, M. D.; Horner, M. J. *Cryst. Eng. Commun.* **2004**, *6*, 401–407.
- (15) Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: Oxford, 1998.

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