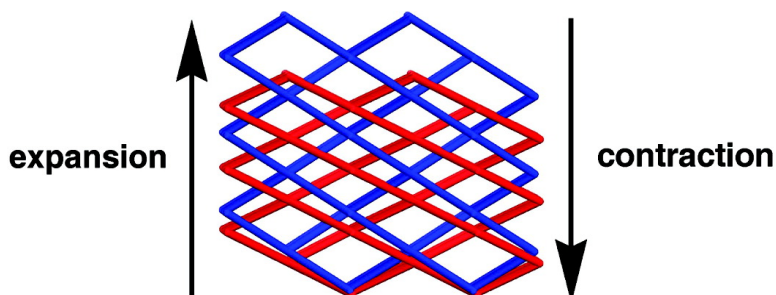


## Deformation of Porous Molecular Networks Induced by the Exchange of Guests in Single Crystals

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## Deformation of Porous Molecular Networks Induced by the Exchange of Guests in Single Crystals

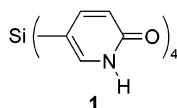
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The detailed structure of molecular crystals cannot be deduced from their composition alone.<sup>1</sup> Increasingly, however, crystal engineers are able to devise compounds predisposed to crystallize in particular ways.<sup>2</sup> One effective strategy uses molecules that form strong directional interactions with neighbors according to well-established motifs.<sup>3</sup> Such molecules, which have been called tectons,<sup>4</sup> do not typically form normal close-packed crystals; instead, they tend to create open networks filled with potentially mobile guests. We have now found that single crystals of this type, when built from suitably flexible molecules linked by hydrogen bonds, can undergo substantial deformations without losing crystallinity.

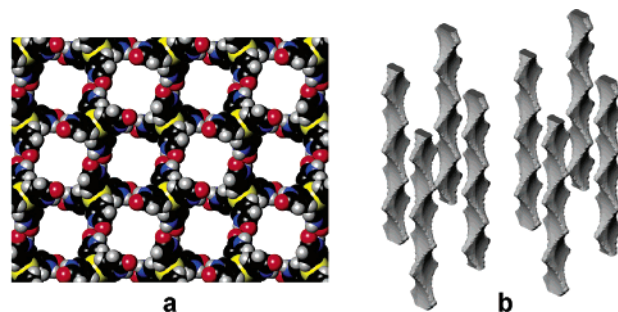
In tecton **1**, a nominally tetrahedral core is attached to four pyridone groups, which associate predictably by hydrogen bonding. Tetrapyrindone **1** is known to crystallize from CH<sub>3</sub>CH<sub>2</sub>COOH/hexane in the tetragonal space group *P*4<sub>2</sub>/*n* as a doubly interpenetrated diamondoid network.<sup>5,6</sup> Each tecton forms a total of eight hydrogen bonds with four neighbors. Nearly 60% of the volume of the crystals is available for including guests,<sup>7</sup> and the composition is 1·4 CH<sub>3</sub>CH<sub>2</sub>COOH.<sup>8</sup> The guests occupy separate parallel channels that measure approximately 6.3 × 6.3 Å<sup>2</sup> in cross section and lie along the *c* axis (Figure 1).<sup>9</sup>



Tecton **1** crystallizes consistently from other carboxylic acids to give similar inclusion compounds belonging to the *P*4<sub>2</sub>/*n* space group, with a stoichiometry of 1·4 RCOOH.<sup>8</sup> Table 1 shows unit cell parameters and other data for crystals of tecton **1** grown from various carboxylic acids, shown in order of increasing size. Comparison reveals that *a* and *b* remain nearly constant (increase of <2% from smallest to largest values), but *c* varies markedly (increase of >30%). Despite these large structural differences, single crystals of tecton **1** can withstand the exchange of guests and concomitant changes of dimensions without shattering or losing crystallinity. For example, when single crystals grown from isovaleric acid (0.5 mm × 0.5 mm × 0.5 mm) were exposed to CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH/hexane at 25 °C, complete exchange occurred (≥98%) without loss of crystallinity.<sup>8</sup> The resulting single crystals remained transparent, and they continued to diffract and exhibit uniform extinction between crossed polarizers.

Similarly large differences in unit cell parameters, although unusual, have nevertheless been observed in other molecular inclusion compounds when crystals grown with different guests have been compared.<sup>11</sup> However, only in the case of tecton **1** have such different structures been interconverted directly by exchange in single-crystal to single-crystal transformations.<sup>12</sup>

The special resilience of crystals of tecton **1** appears to be due in part to the incorporation of highly flexible Si nodes in an otherwise robust network maintained by multiple hydrogen bonds.



**Figure 1.** (a) View along the *c* axis showing the cross sections of adjacent parallel channels in crystals of tecton 1·4 CH<sub>3</sub>CH<sub>2</sub>COOH, with guests removed for clarity. (b) View of the channels in a 2 × 2 × 3 array of unit cells with the *c* axis vertical. The surface of the channels is defined by the possible loci of the center of a sphere of diameter 6 Å as it rolls over the surface of the ordered network.<sup>9</sup>

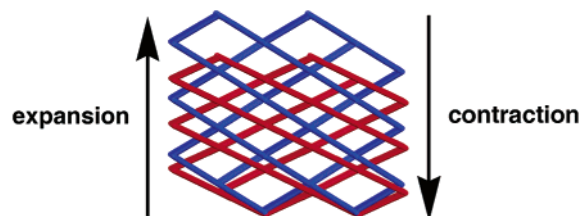
**Table 1.** Structural Parameters (220 K) for Crystals of Tecton 1·4 RCOOH Grown from Various Carboxylic Acids

guest <sup>a</sup> (% volume) <sup>7</sup>	<i>a</i> = <i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	O···Si···O angle <sup>10</sup> (deg)
A (56%)	15.655(2)	7.360(2)	1804(1)	114.2
P (58%)	15.647(1)	7.66(2)	1875(1)	113.4
M (59%)	15.656(7)	7.885(7)	1933(2)	111.4
B (61%)	15.460(1)	8.799(1)	2103(1)	107.7
I (65%)	15.413(2)	9.584(2)	2277(1)	104.9
B (65%, from I by exchange)	15.465(9)	9.578(6)	2291(2)	104.4

<sup>a</sup> A = acrylic acid, P = propionic acid, M = methacrylic acid, B = butyric acid, I = isovaleric acid.

Surprisingly, no major changes occur in the hydrogen bonds themselves;<sup>13</sup> in particular, the N···O distances in crystals obtained from the acids shown in Table 1 vary only in the range 2.754(4)–2.776(5) Å. In contrast, the O···Si···O angles<sup>10</sup> deviate significantly from tetrahedral values (104–114°). These deformations (1) arise primarily from flexibility of the Si core, (2) are correlated monotonically with *c*, which corresponds to the distance separating adjacent interpenetrating networks, and (3) lengthen or shorten the structure in the direction of the channels (Figure 2). This occurs without changing the cross sections substantially. Deformation in the *c* direction appears to be favored by subtle factors that optimize the packing of guests.

Remarkably, these deformations can be slower than exchange itself. For example, replacement of isovaleric acid by butyric acid in single crystals (5 h, 25 °C) is initially isomorphous, giving exchanged crystals (≥98%) with nearly unchanged unit cell parameters (*a* = *b* = 15.465(9) Å and *c* = 9.578(6) Å). These crystals are different from those obtained when tecton **1** is crystallized directly from CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH/hexane. Keeping the exchanged crystals in further contact with CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH/hexane (24 h, 25 °C) resulted in their contraction to give single crystals identical to those obtained by direct crystallization.



**Figure 2.** Superimposed representations of the diamondoid networks formed when tecton **1** crystallizes from isovaleric acid (blue) and propionic acid (red), showing how the structure distorts significantly in the *c* direction (vertical) but changes little in the *a* and *b* directions.

Together, these observations show that (1) the kinetic product of exchange is a metastable polymorph and (2) exchange cannot occur by a mechanism involving free movement of the tectons themselves, which would presumably lead to recrystallization and direct formation of the stable polymorph.<sup>14</sup>

Similar replacement of isovaleric acid by propionic acid in single crystals (1.5 h, 25 °C) was again complete ( $\geq 98\%$ ),<sup>8</sup> but contraction occurred without detectable hysteresis, and the resulting single crystals had unit cell parameters essentially identical to those of crystals grown directly from  $\text{CH}_3\text{CH}_2\text{COOH}$ /hexane. It is possible that smaller guests are more mobile and permit more rapid structural adjustment of the surrounding network. Pairwise competitive exchanges showed that smaller carboxylic acids are normally preferred as guests, perhaps because they offer better solvation of the polar network. For this reason, expansion of single crystals (in which a smaller acid is replaced by a larger acid) appears to be somewhat more difficult than contraction but is nevertheless feasible.

Our observations underscore the potential of using well-designed tectons to create new materials with unusual properties, including porosity and deformability in the crystalline state. Single-crystal deformations of the type we have observed promise to be useful. For example, the demonstrated ability of the network derived from tecton **1** to adjust to guests ensures that porosity is adaptive, with guests always placed in close contact with each other and with the walls of the channels. This enforced proximity may facilitate the transfer of information between host and guest, thereby helping to increase the selectivity of inclusion. Initial studies of competitive crystallizations and exchanges using two carboxylic acids have yielded crystals of mixed composition with unit cell parameters intermediate between those of crystals obtained from the two pure acids. This creates an exciting opportunity to use single-crystal deformability as a strategy for engineering structures on a subnanometric scale and for making fine adjustments of properties, simply by systematically varying the identity and ratio of guests.

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**Supporting Information Available:** X-ray experimental details (CIF) and descriptions of selected procedures (PDF). 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. (b) Desiraju, G. R. *Nat. Mater.* **2002**, *1*, 77. (c) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309. (d) Maddox, J. *Nature* **1988**, 335, 201.
- (2) For general references, see: (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107. (c) *Crystal Engineering: From Molecules and Crystals to Materials*; Braga, D., Grepioni, F., Orpen, A. G., Eds.; Kluwer: Dordrecht, The Netherlands, 1999. (d) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.
- (3) For recent references, see: Fournier, J.-H.; Maris, T.; Wuest, J. D.; Guo, W.; Galoppini, E. *J. Am. Chem. Soc.* **2003**, *125*, 1002.
- (4) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696.
- (5) Wang, X.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12119.
- (6) (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (b) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, *23*, 283.
- (7) Volume accessible to guests was estimated according to: (a) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001. (b) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.
- (8) Compositions were determined by X-ray crystallography, <sup>1</sup>H NMR spectroscopy of dissolved samples, and thermogravimetry.
- (9) Representations of channels were generated by the Cavities option in the program ATOMS (ATOMS, version 5.1; Shape Software: Kingsport, TN).
- (10) The O···Si···O angles are defined by pairs of pyridone O atoms and the Si core of tecton **1**. Comparison of O···Si···O angles rather than C–Si–C angles takes into account the distortion of Si–C–C angles and other effects as well. Table 1 shows the value of the two O···Si···O angles that have bisectors parallel to the *c* axis. See the Supporting Information for further discussion.
- (11) For example, see: Byrn, M. P.; Curtis, C. J.; Hsiou, Y.; Khan, S. I.; Sawin, P. A.; Tendick, S. K.; Terzis, A.; Strouse, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 9480.
- (12) For related single-crystal dynamics in networks joined by coordination to metals, see: (a) Suh, M. P.; Ko, J. W.; Choi, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 10976. (b) Cusson, E. J.; Claridge, J. B.; Rosseinsky, M. J.; Kepert, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 9574. (c) Biradha, K.; Hongo, Y.; Fujita, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3395. (d) Biradha, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3392. (e) Kepert, C. J.; Hesek, D.; Beer, P. D.; Rosseinsky, M. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 3158.
- (13) Deformations of other molecular networks have been attributed to the weakness of the connecting interactions. (a) Thaimattam, R.; Xue, F.; Sarma, J. A. R. P.; Mak, T. C. W.; Desiraju, G. R. *J. Am. Chem. Soc.* **2001**, *123*, 4432. (b) Dewa, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1998**, *120*, 8933.
- (14) We are currently studying the detailed mechanism of guest exchange in crystals of tecton **1**. In cases where the guests are ordered, X-ray crystallography has established that they are not packed in a single file<sup>5</sup> so that two-way diffusion is permitted. We cannot rule out the possibility that exchange is further accelerated by fractures or other crystalline defects.

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