Dipoles in Crystal Engineering

Molecular Tectonics: Porous Cleavable Networks Constructed by Dipole-Directed Stacking of Hydrogen-Bonded Sheets[**]

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An exciting challenge in contemporary science is learning how to make ordered molecular materials with predetermined structures and properties. The effort to reach this goal continues to yield new knowledge of both fundamental and practical value. Of particular interest are ordered molecular materials produced spontaneously by methods of self-assembly, such as crystallization. Although detailed predictions of the structure of molecular crystals remain unreliable,[1] crystal engineering provides increasingly effective strategies for identifying compounds predisposed to crystallize in particular ways.[2] One such strategy, which has been called molecular tectonics,[3,4] relies on special compounds that participate in multiple directional interactions. Such compounds, called tectons from the Greek word for builder, are programmed to associate and to form networks in which each molecule is placed in a predictable position with respect to its neighbors. Herein, we show how two different directional forces, hydrogen bonding and dipole-dipole interactions,[5] can be used in potent combination to engineer molecular networks with predictable cleavage and high porosity.[6]

Tetrahedral tectons **1** with peripheral sites of association (●) are predisposed to form three-dimensional four-connected networks, whereas trigonal analogues **2** favor sheets (Figure 1). In the first case, the entire three-dimensional structure is programmed by the tectons and maintained by strong interactions in all directions; in the second case, however, the ultimate structure must result from the stacking or interpenetration of sheets,[7] governed by forces that are not normally subject to rational control. Examples of structural polytypism resulting from subtle variations in the stacking of sheets are numerous in chemistry and include the diverse phases of graphite,[8] sheet silicates in which the layers have different offsets,[9] and various hydrogen-bonded molecular sheets.[10] For many applications, polytypism is undesirable because it makes full structural predictions unreliable, even when the positions of all the atoms in individual sheets are well established.

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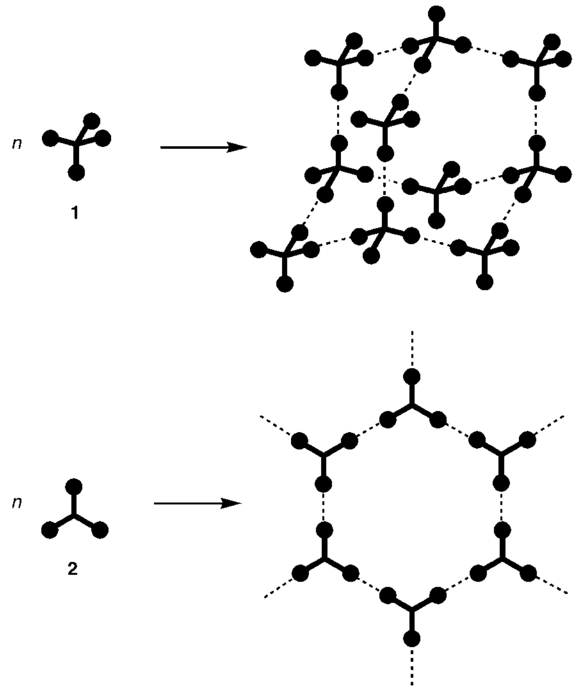


Figure 1. Representations of the hypothetical three-dimensional network built from tetrahedral tecton **1** and the two-dimensional network formed by trigonal tecton **2**.

A potentially effective element of control can be introduced by incorporating a dipole at each trigonal center to create tecton **3** (Figure 2). Assembly directed cooperatively by the normal association of the sticky sites (●) and by antiparallel orientation of neighboring dipoles should produce the sheet shown in Figure 2. Such sheets are then predisposed to create a hexagonal three-dimensional array by stacking in registry, directed by the formation of head-to-tail columns of dipoles that lie perpendicular to the sheets. An encouraging precedent for the dipole-directed assembly of sheets is provided by the structure of the most stable polymorph of phosphorus pentoxide.[11] In this structure, PO_4 tetrahedra share three corners to form covalently bonded sheets composed of 12-membered rings. Adjacent P=O bonds are oriented perpendicularly toward opposite faces of each sheet, and their alignment suggests that dipolar interactions control the stacking of the sheets.

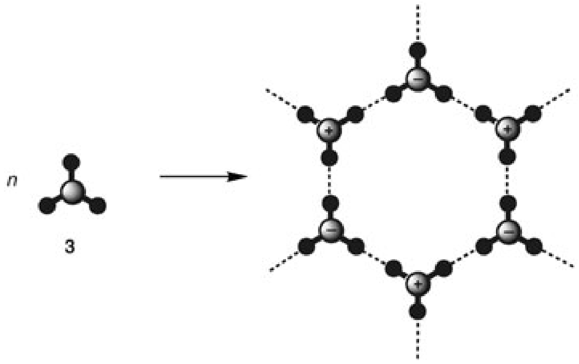
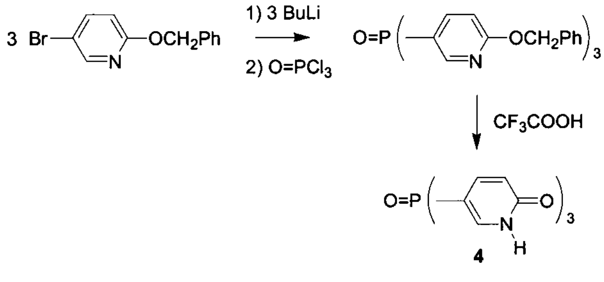


Figure 2. Hypothetical sheet resulting from trigonal tecton **3** with a dipolar core (white circle) showing the expected antiparallel alignment of adjacent dipoles (represented by inscribing + and − in the cores).

The feasibility of using dipoles to direct the stacking of hydrogen-bonded molecular sheets was tested by studying phosphine oxide **4** (Scheme 1). Three pyridinone groups are incorporated in compound **4** to ensure strong intermolecular hydrogen bonding through a reliable supramolecular synthon,[12–14] and the P=O bond introduces a large and unambiguous dipole, which is approximately 4.5 D in triphenylphosphine oxide.[15] Compound **4** was prepared in 89% overall yield from 5-bromo-2-(phenylmethoxy)pyridine[16] by the route summarized in Scheme 1. Crystallization was achieved by allowing hexane to diffuse into solutions of compound **4** in either CH_3COOH or CH_3CH_2COOH. Both crystallizations produced hexagonal prisms of composition **4**·3 RCOOH, as determined by X-ray crystallography, thermogravimetry, and ^{1}H NMR spectroscopy of dissolved samples. X-ray diffraction established that crystals grown under both conditions belong to the trigonal space group $P\bar{3}$ and are isomorphous, so only views of the structure containing CH_3COOH are shown (Figures 3 and 4).



Scheme 1. Synthesis of phosphine oxide **4**.

The structure produced by crystallizing tecton **4** can be interpreted as a direct consequence of the combined effects of hydrogen bonding and dipolar interactions. Characteristic intermolecular hydrogen bonding of the three pyridinone groups defines a porous sheet composed of cyclic hexamers (Figure 3). It is noteworthy that hydrogen bonding of carboxylic acid solvents with compound **4** does not prevent normal association of its pyridinone groups. Since the P atom is approximately tetrahedral (∢O-P-C 112.08(11)° in crystals grown from CH_3COOH/hexane), the pyridinone groups do not diverge from the core in a single plane, and the resulting sheet is corrugated (Figure 4). Each cyclic hexamer has a chair conformation with the P=O dipoles oriented axially, and adjacent dipoles are antiparallel and directed toward opposite faces of the sheet. Like other triarylphosphine oxides,[17–19] compound **4** adopts a chiral conformation in the crystalline state, and molecules with dipoles oriented in one direction are enantiomers of those with dipoles aligned in the opposite direction. The intertectonic distance between the P atoms of neighboring hydrogen-bonded molecules is 11.82 Å, and the pores in individual sheets are approximately 15.1 Å in diameter.[20]

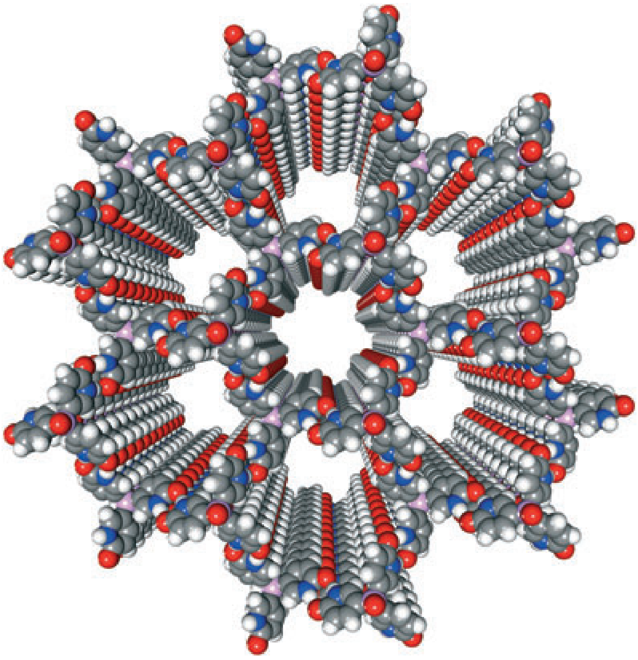


Figure 3. Perspective view along the *c* axis of the network constructed by crystallizing phosphine oxide **4** from CH_3COOH/hexane. Guests are omitted, and atoms are shown as spheres of van der Waals radii to reveal the cross-sections of the channels. Atoms of hydrogen are shown in white, carbon in gray, nitrogen in blue, oxygen in red, and phosphorus in pink.

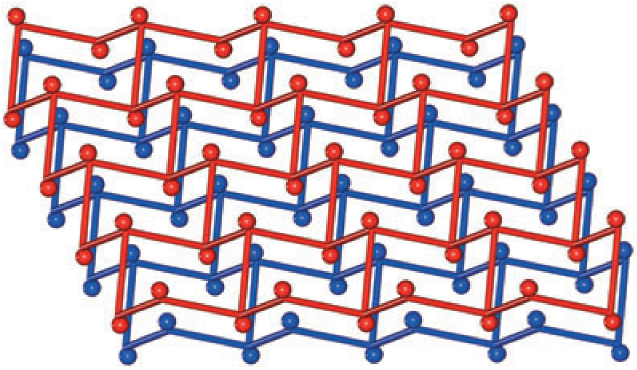


Figure 4. Representation of the dipole-directed stacking of corrugated sheets observed in crystals of phosphine oxide **4** grown from CH_3COOH/hexane, as viewed with the *c* axis approximately vertical. Two adjacent sheets are shown, one in red and the other in blue, and $P{=}O$ dipoles are represented by lobes of the same color. The sheets are defined by lines joining the central phosphorus atom of each tecton to the centers of the three hydrogen-bonded neighbors.

As planned, the sheets then stack in registry in a way that appears to be directed by head-to-tail alignment of $P{=}O$ dipoles in adjacent layers (Figure 4). In the resulting structure, the average intertectonic distance between the closest P atoms of neighboring sheets is 5.39 Å. As a result of the registry the pores in each sheet are aligned with those in adjacent sheets, thereby creating impressive parallel channels that run perpendicular to the sheets and contain partially ordered molecules of CH_3COOH and CH_3CH_2COOH. Approximately 50 % of the volume of the crystals of compound **4** is available for including guests.[21,22] This degree of porosity is impressive but somewhat smaller than that of the very best three-dimensional molecular networks,[23] perhaps because tecton **4** favors association in two dimensions to form sheets that can then pack closely. However, the channels are among the largest ever observed in molecular crystals. It is instructive to compare the network constructed from compound **4** with those of crystalline inorganic analogues that have similar parallel channels and have been cited repeatedly as benchmarks in the field of microporous materials. In particular, gross structural features of the network built from tecton **4** (porosity 50 %, 15-Å channels) resemble those of the synthetic aluminophosphate VPI-5 (porosity 43 %, 13-Å channels)[24] and the natural Fe^{III} phosphate cacoxenite (porosity 49 %, 17-Å channels).[25,26] These analogies underscore the potential of engineering porous networks from purely molecular precursors. Moreover, the network derived from compound **4** was built by design and can be assembled at 25 °C as large single crystals with a structure that can be solved by straightforward X-ray diffraction, unlike VPI-5, cacoxenite, and many related inorganic and metal–organic materials.[26]

The behavior of compound **4** differs significantly from that of structurally similar molecules lacking the same capacity to take part in directional interactions. For example, compound **4** yields isomorphous structures when crystallized from either CH_3COOH/hexane or CH_3CH_2COOH/hexane, whereas triphenylphosphine oxide crystallizes under different conditions as multiple polymorphs.[17,18] Some of these polymorphs do not incorporate the head-to-tail alignment of $P{=}O$ dipoles observed in crystals of compound **4**, which suggests that the contribution of dipolar interactions to the overall lattice energy is important but not dominant. In addition, compound **4** forms a highly porous network, whereas all known polymorphs of triphenylphosphine oxide are close-packed, and enclathration of guests is not observed.[17,18,27] Together, these comparisons show how the behavior of tectons differs markedly from that of models lacking oriented arrays of sticky sites, and they confirm that tectonic association normally reduces opportunities for polymorphism and favors the formation of networks that are not close-packed.

In the open network constructed from phosphine oxide **4**, each tecton forms a total of six hydrogen bonds with its three neighbors in the same sheet, and it participates in attractive dipole–dipole interactions with the two closest neighbors in adjacent sheets. In contrast, included guests are weakly bound to the network and are located in large channels that in principle offer easy escape from the network. As observed in other porous molecular networks held together by multiple hydrogen bonds, crystals of compound **4** are permeable, and guests can be exchanged in single crystals without loss of crystallinity. For example, crystals of composition **4**·3 CH_3COOH and approximate dimensions $0.5 \times 0.5 \times 2.0\ mm^3$ were suspended in $CH_2{=}CHCOOH$/hexane at 25 °C for 3 days.[28] The recovered sample remained transparent and morphologically unchanged. Furthermore, it continued to diffract and to show uniform extinction between crossed polarizers. Analysis of dissolved samples by ^1H NMR spectroscopy confirmed that CH_3COOH had been replaced completely to give new crystals of composition **4**·3 $CH_2{=}CHCOOH$. The quality of the exchanged crystals was high enough to allow their structure to be solved by single-crystal X-ray diffraction. The exchanged crystals proved to be isomorphous, with unit cell parameters essentially identical to those of the initial crystals (±4%). The close similarity of the structures of crystals containing CH_3COOH, CH_3CH_2COOH, or $CH_2{=}CHCOOH$ suggests that the network built from tecton **4** is resistant to deformation.[12]

The three-dimensional architecture generated by crystallizing compound **4** consists of sheets held together by a high density of strong hydrogen bonds, stacked in the perpendicular direction by a lower density of weaker dipolar interactions. As a result, we reasoned that the mechanical properties of the crystals would be highly anisotropic. In particular, we expected cleavage of the crystals to show marked directional preferences, perhaps similar to those observed in micas and other lamellar inorganic materials, and we hoped to be able to make thin sections by cleaving crystals perpendicular to the axes of the channels. Unlike sections cleaved from lamellar inorganic materials, which are typically dense and nonporous,[29] those split from crystals of compound **4** are expected to be selectively permeable and to have well-defined pores of nanometric dimensions.

Indexation of hexagonal prisms of compound **4** grown from CH_3COOH established that the long axis of the crystals corresponds to the crystallographic *c* axis, so the channels run from one end of the prisms to the other. Stress was induced in the crystals by removing them from their mother liquors and exposing them to air, thereby initiating slow loss of included guests. Close examination of a typical stressed crystal (Figure 5) reveals multiple planes of fracture, all lying perpendicular to the *c* axis. This fractographic analysis[30] confirmed that the crystals are mechanically fragile and susceptible to preferential basal cleavage between adjacent hydrogen-bonded sheets, as expected. Moreover, pressing gently on crystals with a microscalpel held perpendicular to the length of the prism readily cleaved sections as thin as 30 μm, such as the one shown in Figure 5. The prism faces in ideal prisms free of defects should not show significant permeability; instead, guests should enter or exit only at the terminations, then reach the core by diffusion.[31] In real crystals, however, fractures may provide additional surfaces for the exchange of guests. In a prism with N complete basal fractures of the type observed, the surface available for exchange will in principle be multiplied by a factor of $2N+2$, and the rate of exchange will increase accordingly. Similar phenomena may account in part for the high rate of exchange observed in other permeable molecular crystals.

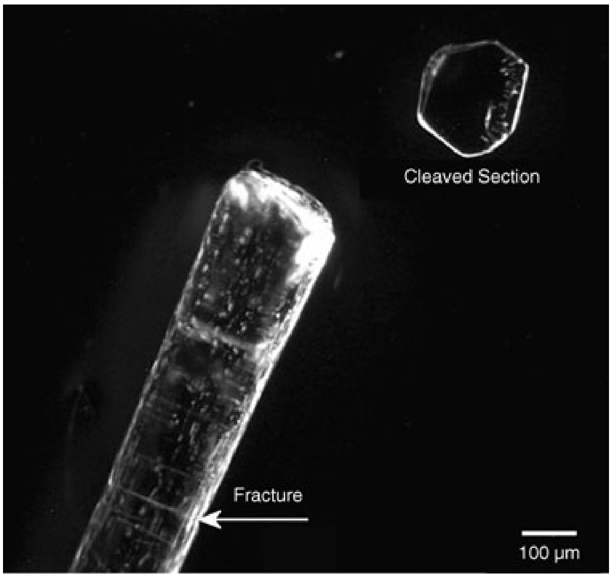


Figure 5. Optical micrograph showing 1) an intact single crystal of phosphine oxide **4** (lower left) grown from CH_3COOH/hexane, then stressed by partial evaporation of guests to induce the formation of basal fractures and 2) a thin section (upper right) cleaved from the same single crystal.

Together, these observations underscore the potential of molecular tectonics as a strategy for the purposeful construction of ordered materials with new properties, and they show how carefully selected combinations of directional forces can be used to engineer crystals with particular anisotropic features.

Experimental Section

For experimental details, see reference [32]. X-ray crystal structural analyses:[33] Data were collected at 223 K using a Bruker SMART 2000 CCD diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). Intensities were integrated using SAINT[34] and corrected for absorption and other effects using SADABS.[35] Structures were solved and refined using the SHELX suite of programs.[36]

Crystal data for tecton **4**·3 CH_3COOH: crystal size $0.40\times0.15\times0.15$ mm^3, trigonal, space group $P\bar{3}$, $a=b=16.9535(8)$, $c=5.2396(3)$ Å, $V=1304.21(11)$ Å^3, $Z=2$. Least-squares refinement of 137 parameters using 73 restraints for 1404 reflections with $I>2\sigma(I)$ out of 1659 reflections gave residual factors $R_1=0.0772$, $wR_2=0.2660$, and GOF = 1.086.

Crystal data for tecton **4**·3 CH_3CH_2COOH: crystal size $0.40\times0.40\times0.20$ mm^3, trigonal, space group $P\bar{3}$, $a=b=17.1474(4)$, $c=5.3885(2)$ Å, $V=1372.13(7)$ Å^3, $Z=2$. Least-squares refinement of 117 parameters using 2 restraints for 1403 reflections with $I>2\sigma(I)$ out of 1691 reflections led to residual factors $R_1=0.0682$, $wR_2=0.1984$, and GOF = 1.071.

Crystal data for tecton **4**·3 $CH_2{=}CHCOOH$: crystal size $0.60\times0.25\times0.25$ mm^3, trigonal, space group $P\bar{3}$, $a=b=17.4823(8)$, $c=5.0683(8)$ Å, $V=1341.5(2)$ Å^3, $Z=2$. Least-squares refinement of 115 parameters using 30 restraints for 699 reflections with $I>2\sigma(I)$ out of 1211 reflections gave residual factors $R_1=0.0956$, $wR_2=0.2542$, and GOF = 1.031.

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[21] The percentage of volume accessible to guests was estimated by the PLATON program.[22] PLATON calculates the accessible volume by allowing a spherical probe of variable radius to roll over the internal van der Waals surface of the crystal structure. PLATON uses a default value of 1.20 Å for the radius of the probe, which is an appropriate model for small guests such as water. The van der Waals radii used to define surfaces for these calculations are as follows: C: 1.70 Å, H: 1.20 Å, N: 1.55 Å, O: 1.52 Å, and P: 1.80 Å. If V is the volume of the unit cell and V_g is the guest-accessible volume as calculated by PLATON, then the porosity P in % is given by 100 V_g/V.

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