

## Engineering crystals built from molecules containing boron\*

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*Abstract:* The study of compounds containing boron continues to have an important impact on virtually every area of chemistry. One of the few areas in which compounds of boron have been neglected is crystal engineering, which seeks to develop and exploit an understanding of how the structure and properties of crystals are related to the individual atomic or molecular components. Although detailed predictions of crystal structures are not yet reliable, crystal engineers have developed a sound qualitative strategy for anticipating and controlling structural preferences. This strategy is based on the design of special molecules, called tectons, which feature carefully selected cores and multiple peripheral functional groups that can direct association and thereby place neighboring molecules in predetermined positions. Recent work has demonstrated that molecular crystals with unique properties can be constructed logically from tectons with boron in their cores or sticky sites of association. In particular, the  $-\text{B}(\text{OH})_2$  group of boronic acids engages in reliable patterns of hydrogen bonding, and its use as a sticky site in tectons has emerged as an effective tool for controlling association predictably. In addition, replacement of tetraphenylsilyl or tetraphenylmethyl cores in tectons by tetraphenylborate leaves the overall molecular geometry little changed, but it has the profound effect of introducing charge. Tectons derived from tetraphenylborate can be used rationally to construct porous charged molecular networks that resemble zeolites and undergo selective ion exchange. In such ways, boron offers chemists exciting new ways to engineer molecular crystals with predetermined structures and properties.

*Keywords:* crystal engineering; supramolecular chemistry; hydrogen bonding; boronic acids; materials science.

### INTRODUCTION: CRYSTAL ENGINEERING AND THE ROLE OF BORON

The study of compounds containing boron continues to have an impact that touches virtually every area of chemistry. In particular, our general understanding of structure and bonding has been greatly enriched, and reagents containing boron have become essential tools in molecular synthesis. There are few major areas of chemistry in which compounds of boron are not actively examined and exploited.

Until recently, one of these areas was crystal engineering, which seeks to develop and exploit an understanding of how the structure and properties of crystals are related to the individual atomic or molecular components [1–4]. These relationships can be exceedingly subtle, making crystal engineering

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an inherently challenging endeavor. Indeed, it remains impossible to predict the detailed structure of crystals of even simple molecular substances with a high level of confidence [5–7]. These intrinsic difficulties have tended to limit crystal engineering to molecules of modest complexity containing only the most frequently encountered elements, and compounds of boron have been neglected.

Although detailed predictions are not yet reliable, crystal engineers have developed a sound qualitative strategy for anticipating and controlling structural preferences. In part, this strategy relies on an analysis of molecular geometry and on an understanding of the ability of certain functional groups to direct association and thereby place neighboring molecules in predetermined positions. The growing importance of this strategy in crystal engineering has recently been underscored by Dunitz in the following way [7]:

...Computational methods for predicting crystal structures of organic compounds cannot yet be regarded as reliable. From a more qualitative and descriptive viewpoint has come the notion that certain groupings in organic molecules exercise attractive intermolecular interactions and so guide the molecules into distinctive patterns in their crystal structures.... This has indeed become one of the tenets of crystal engineering.

The potential of this strategy to generate predictably organized crystalline materials with novel properties has spurred crystal engineers to identify particular interactions that can be used dependably to control molecular association. The search for such interactions has focused on hydrogen bonds and coordinative interactions with metals, both of which have directional preferences that help position neighboring molecules predictably. Molecules that have proven to be especially suitable for engineering crystals can be constructed by choosing suitable cores and linking them to multiple groups able to engage reliably in hydrogen bonding, coordination to metals, or other well-defined intermolecular interactions. Such molecules, which have been called tectons from the Greek word for builder [8–10], are programmed to associate and to serve as subunits for the purposeful construction of ordered materials.

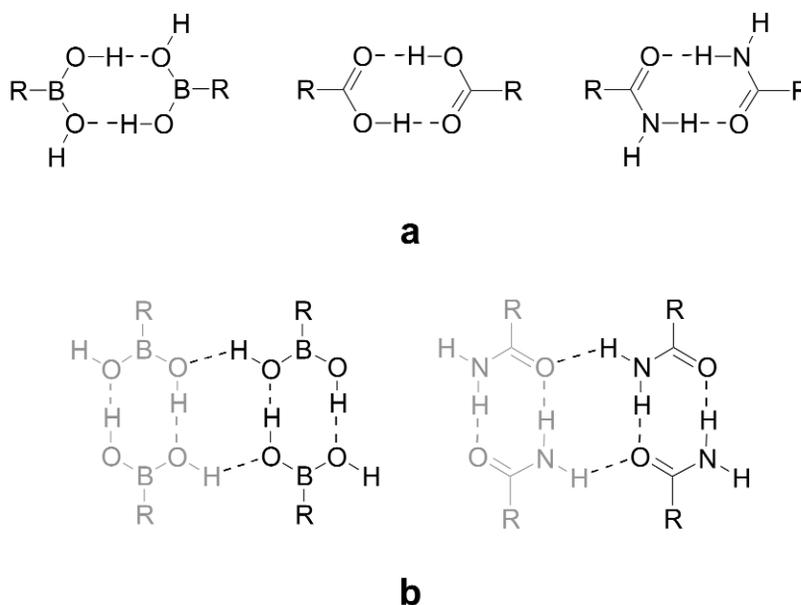
Recent research in molecular tectonics has helped end crystal engineering's long neglect of boron. As summarized below, various unique properties can be introduced rationally by incorporating boron in the cores of tectons, as well as in the sticky sites that ensure their directional interactions with neighboring molecules.

## **BORON IN CRYSTAL ENGINEERING: USE OF THE $-B(OH)_2$ GROUP OF BORONIC ACIDS TO DIRECT MOLECULAR ASSOCIATION**

### **Introduction to the association of boronic acids**

Many sticky functional groups that engage in reliable hydrogen-bonding motifs have been identified and exploited in crystal engineering, but the field remains rich in undeveloped potential, particularly for researchers willing to undertake complex molecular syntheses, examine more exotic functional groups, or explore parts of the periodic table previously ignored by crystal engineers. The  $-B(OH)_2$  group illustrates this undeveloped potential. The crystallization of boronic acids typically produces cyclic hydrogen-bonded pairs similar to those formed by carboxylic acids and amides (Fig. 1a), yet the  $-B(OH)_2$  group has only recently been used to control supramolecular assembly [11–19], despite widespread application of derivatives of boronic acids in other areas of molecular recognition [20].

Unlike cyclic dimers of carboxylic acids, analogous dimers formed by boronic acids and amides have unused capacity for donating hydrogen bonds and can associate further to create tapes held together by lateral hydrogen bonds (Fig. 1b). The effect of these lateral interactions is to add hydrogen bonds and extend them in a new direction, thereby producing a reinforced structure. By combining the characteristic cyclic hydrogen-bonding motif shown in Fig. 1a with the supplementary lateral motif il-

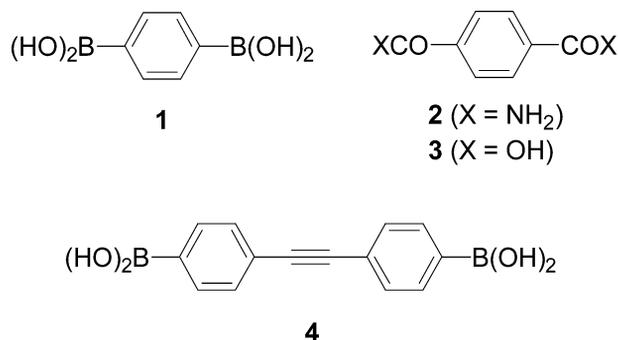


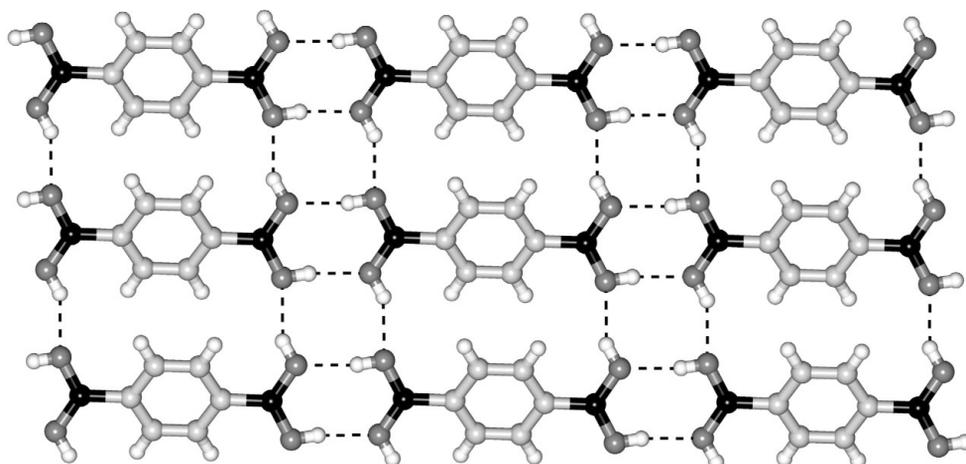
**Fig. 1** (a) Cyclic hydrogen-bonded dimers of boronic acids, carboxylic acids, and amides. (b) Lateral hydrogen bonding of cyclic dimers of boronic acids and amides, with one dimer shown in contrasting gray.

illustrated in Fig. 1b, the  $-\text{B}(\text{OH})_2$  group gives crystal engineers a potent tool for producing predictable structures.

### Engineering two-dimensional networks using boronic acids

The special potential of the  $-\text{B}(\text{OH})_2$  group is revealed by the structure of crystals of 1,4-benzenediboronic acid (**1**) grown from water (Fig. 2) [13]. As expected, the cyclic hydrogen-bonding motif characteristic of boronic acids (Fig. 1a) joins the molecules into chains, which then associate predictably by forming additional lateral hydrogen bonds (Fig. 1b), thereby producing a fully hydrogen-bonded sheet. Hydrogen bonds within the chains are shorter ( $d_{\text{O}\dots\text{O}} = 2.761(2) \text{ \AA}$ ) than those between the chains ( $d_{\text{O}\dots\text{O}} = 2.781(2) \text{ \AA}$ ), so the chains can be considered to be the primary structural motif. The observed structure results logically from (1) the presence of two  $-\text{B}(\text{OH})_2$  groups in tecton **1**; (2) the predictable hydrogen-bonding motifs characteristic of these groups; and (3) the well-defined divergent linear orientation of the groups, fixed by the rigid 1,4-phenylene core. An analogous two-dimensional network is formed by the corresponding amide, terephthalamide (**2**) [21], whereas terephthalic acid (**3**) can only produce hydrogen-bonded chains [22].



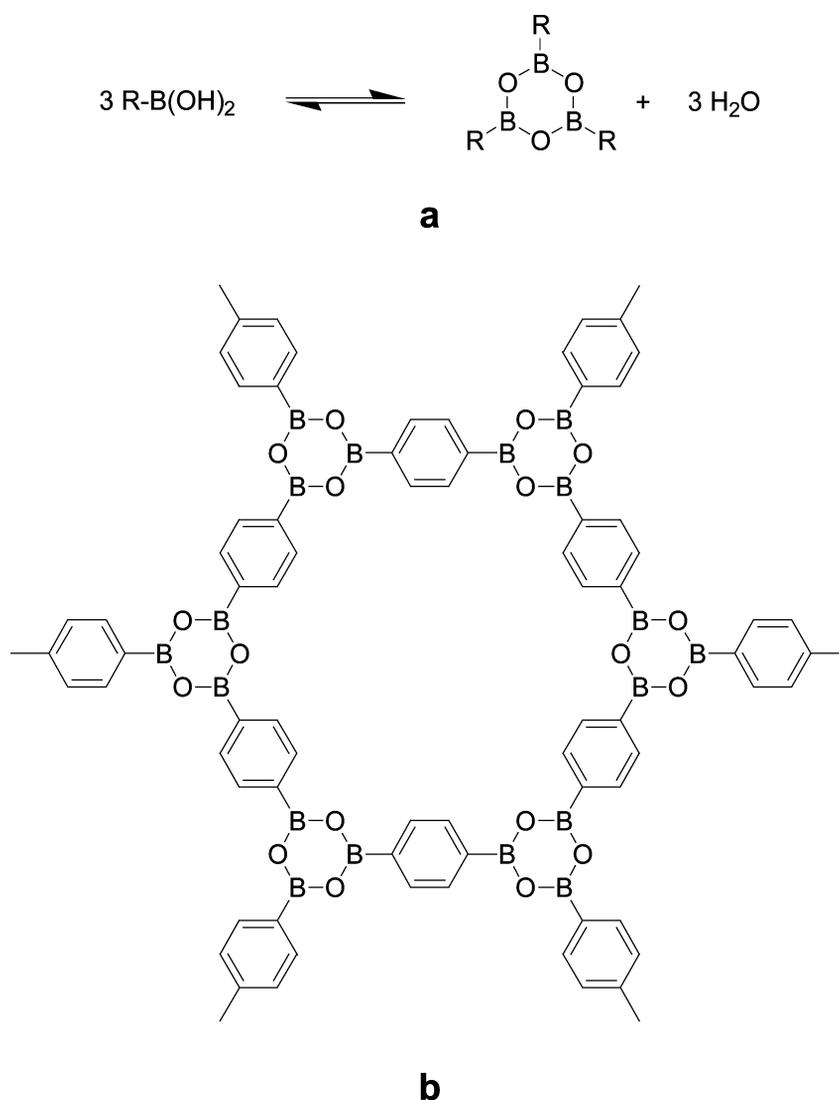


**Fig. 2** View of the structure of crystals of 1,4-phenylenediboronic acid (**1**) grown from water, showing a hydrogen-bonded sheet that combines a primary hydrogen-bonded chain (Fig. 1a) with secondary lateral hydrogen bonds between the chains (Fig. 1b). Atoms of hydrogen appear in white, atoms of carbon in light gray, atoms of oxygen in dark gray, and atoms of boron in black. Hydrogen bonds are represented by broken lines.

Although the observed network is logical, it does not result from the molecular structure of 1,4-phenylenediboronic acid (**1**) with total inevitability. Compound **1** also crystallizes as a tetrahydrate in which the characteristic hydrogen-bonded chains are retained, but their normal association to give sheets does not occur [18]. Instead, the chains use their latent capacity for hydrogen bonding to interact with included molecules of water. This shows that suitable guests can divert boronic acids from their usual preference for laterally paired dimers.

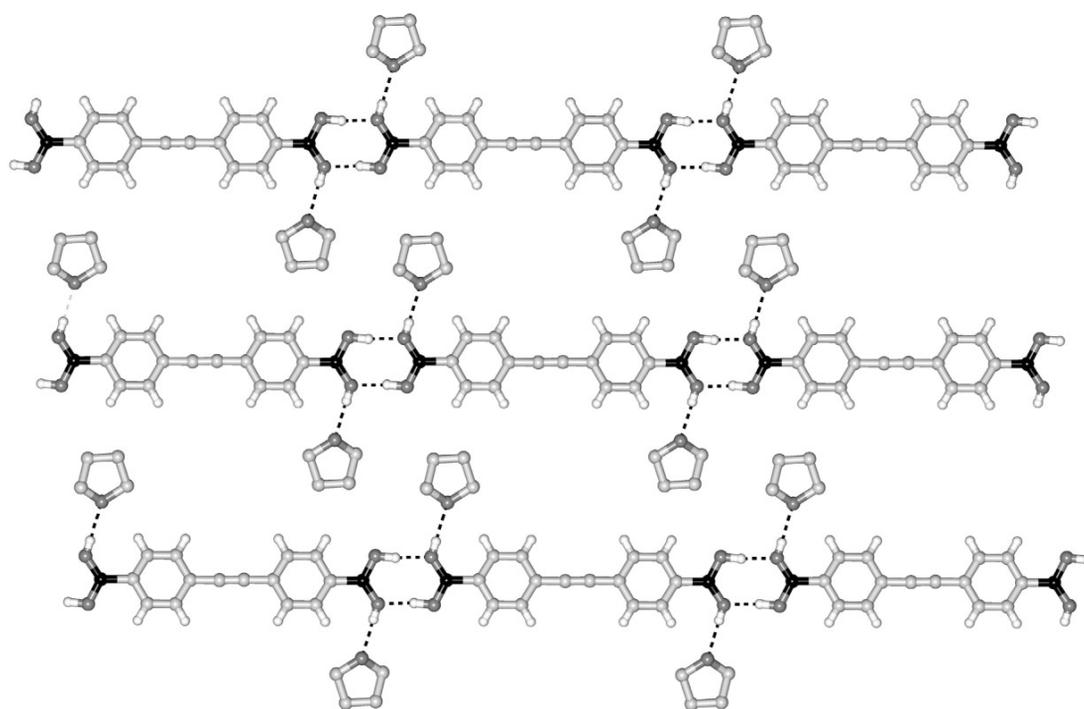
Boronic acids undergo reversible cyclodehydration to form boroxines (Fig. 3a), and crystallization of boronic acids is often carried out in the presence of water to disfavor this reaction. Thermal dehydration of 1,4-phenylenediboronic acid (**1**) at 120 °C has recently been observed to produce a microcrystalline solid consisting of open hexagonal sheets (Fig. 3b) [23]. The resulting material is porous, and it is held together by robust covalent bonds between boron, carbon, and oxygen. In this way, molecules with multiple diverging  $\text{-B(OH)}_2$  groups promise to serve a dual role (1) as subunits for engineering predictably ordered supramolecular networks held together by hydrogen bonds and (2) as precursors for the logical construction of ordered covalent materials.

Crystallization of 1,4-phenylenediboronic acid (**1**) does not occur in precisely the same way under all conditions examined, but the two reported structures nevertheless show deep underlying similarity [13,18]. In particular, both are built from the same hydrogen-bonded chains, which either associate directly or are bridged by intervening guests. This shows that even if molecular tectonics does not yet allow crystal engineers to make rigorous structural predictions, it nevertheless provides very valuable guidance.

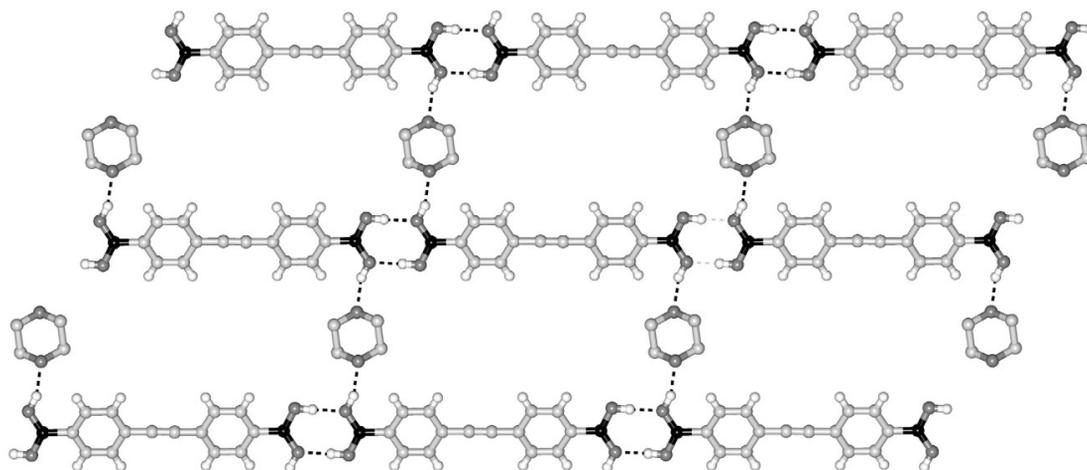


**Fig. 3** (a) Cyclodehydration of boronic acids to give boroxines. (b) Open hexagonal sheets produced by thermal dehydration of 1,4-phenylenediboronic acid (**1**) at 120 °C [23].

To further test the ability of molecular tectonics to serve as a reliable strategy for engineering crystals, we examined the consequences of lengthening the linear spacer joining the two  $-\text{B(OH)}_2$  groups in tecton **1**. The corresponding diphenylacetylene **4** was synthesized and crystallized from tetrahydrofuran (THF)/hexane, dioxane, and ethyl acetate to give three related structures [11]. Crystals of tecton **4** grown in the presence of THF or dioxane proved to incorporate the expected hydrogen-bonded chains, previously observed as primary features in both structures of analog **1** (Figs. 4–5). The repeating distance between the centers of the hydrogen-bonded rings is thereby extended rationally from 10 Å in shorter tecton **1** to 17 Å in longer tecton **4**. Included molecules of THF or dioxane are basic enough to accept hydrogen bonds from the chains and to disrupt their lateral association to form sheets (Figs. 4–5). In the case of dioxane, both atoms of oxygen act simultaneously as acceptors and bridge the chains, leading to the formation of a fully hydrogen-bonded sheet co-assembled from tecton **4** and dioxane. These sheets are closely related to those constructed from shorter tecton **1** (Fig. 2), but they have been extended logi-



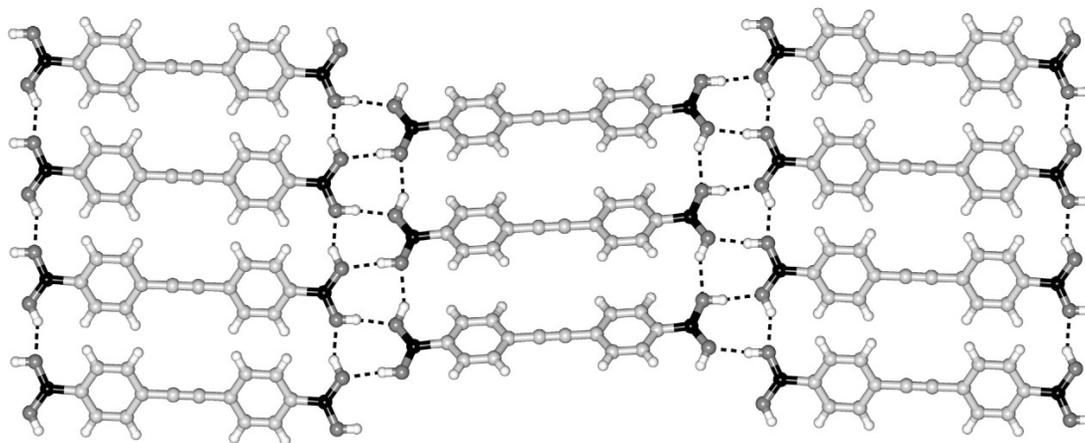
**Fig. 4** View of the hydrogen-bonded chains in crystals of lengthened diboronic acid **4** grown from THF/hexane. The chains are separated by intervening molecules of THF, which accept lateral hydrogen bonds donated by the chains. Atoms of hydrogen appear in white, atoms of carbon in light gray, atoms of oxygen in dark gray, and atoms of boron in black. Hydrogen bonds are represented by broken lines. Atoms of hydrogen in THF are omitted, as are included molecules of THF not involved in hydrogen bonding.



**Fig. 5** View of the structure of crystals of lengthened diboronic acid **4** grown from dioxane, showing how the characteristic chains are bridged by dioxane to create a hydrogen-bonded sheet that has been extended in two directions. Atoms of hydrogen appear in white, atoms of carbon in light gray, atoms of oxygen in dark gray, and atoms of boron in black. Hydrogen bonds are represented by broken lines. Atoms of hydrogen in dioxane are omitted, as are included molecules of dioxane not involved in hydrogen bonding.

cally in two directions, both along the chains (by lengthening the linear spacer between the  $-\text{B}(\text{OH})_2$  groups) and perpendicular to the chains (by inserting intervening molecules of dioxane).

In contrast, crystallization of diboronic acid **4** from ethyl acetate proved to give hydrogen-bonded sheets with no included solvent (Fig. 6), possibly because ethyl acetate is less able than THF and dioxane to disrupt lateral hydrogen bonding. Unexpectedly, the sheets are not built from chains of the type observed in the structure of shorter analog **1** (Fig. 2); instead, alternating columns are formally displaced, leading to a network in which each molecule forms eight single hydrogen bonds with a total of six neighbors (Fig. 6).

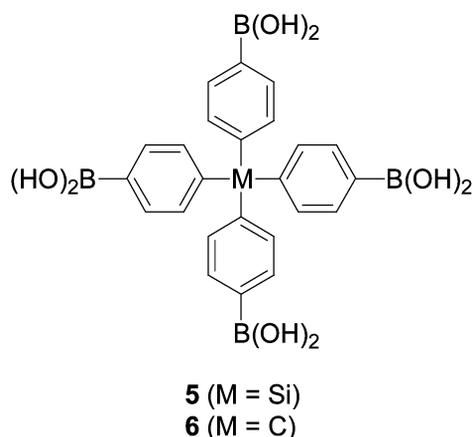


**Fig. 6** View of part of a single hydrogen-bonded sheet in close-packed crystals of diboronic acid **4** grown from ethyl acetate. Atoms of hydrogen appear in white, atoms of carbon in light gray, atoms of oxygen in dark gray, and atoms of boron in black. Hydrogen bonds are represented by broken lines.

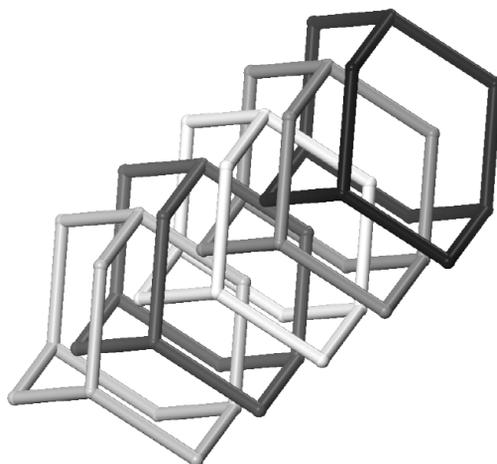
Together, the structures of crystals of 1,4-phenylenediboronic acid (**1**) and its extended analog **4** reveal some of the strengths and limitations of molecular tectonics. Despite the close structural similarity of tectons **1** and **4**, their crystallization under diverse conditions yields networks that are not rigorously analogous. The differences observed are noteworthy, and their origins are subtle. Clearly, molecular tectonics does not yet permit strict predetermination of the resulting structures, at least when the goal is to engineer two-dimensional networks built from linear diboronic acids. Nevertheless, certain key features appear in all of the observed structures and can be considered to be introduced by design. In particular, the presence of two divergent  $-\text{B}(\text{OH})_2$  groups connected by a linear spacer ensures the formation of extensively hydrogen-bonded networks, with a strong predisposition for sheets constructed from chains.

### Engineering three-dimensional networks using boronic acids

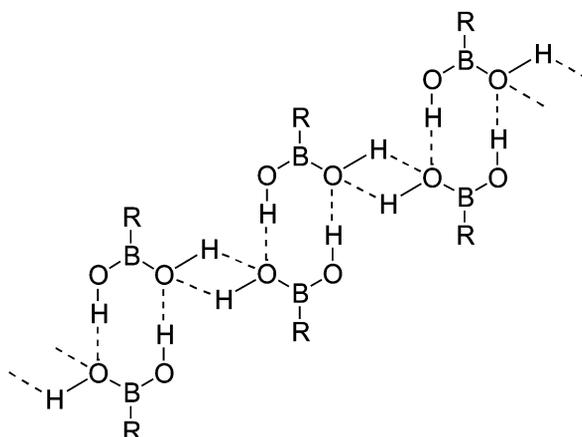
The tectons most likely to yield crystals with fully predictable structures are presumably those with rigid cores and multiple sticky sites that can position every neighboring molecule according to strong directional preferences. Tectons designed to associate to form one- or two-dimensional motifs do not normally meet these exacting prerequisites because the ultimate three-dimensional structures require further assembly of chains or sheets, governed by interactions that are not typically directional and subject to rational control [24]. Together, these considerations led us to synthesize tetraboronic acid **5**, in the expectation that its relatively rigid tetraphenylsilyl core and four tetrahedrally oriented  $-\text{B}(\text{OH})_2$  groups would reliably generate a three-dimensional hydrogen-bonded network with a predictable diamondoid architecture [14,25].



Crystallization of tecton **5** from wet ethyl acetate proceeded as planned to give a diamondoid hydrogen-bonded network held together in part by the characteristic self-association of  $\text{-B(OH)}_2$  groups (Fig. 1a). In this network, the average intertectonic distance between the tetrahedral centers of hydrogen-bonded neighbors is 16.63 Å. As a result, the network is open enough to permit interpenetration by four independent diamondoid networks (Fig. 7) [26,27]. Each network is linked to two adjacent interpenetrating networks by supplementary lateral hydrogen bonds closely similar to those formed between cyclic pairs of  $\text{-B(OH)}_2$  groups in the crystal structures of other boronic acids (Fig. 8).



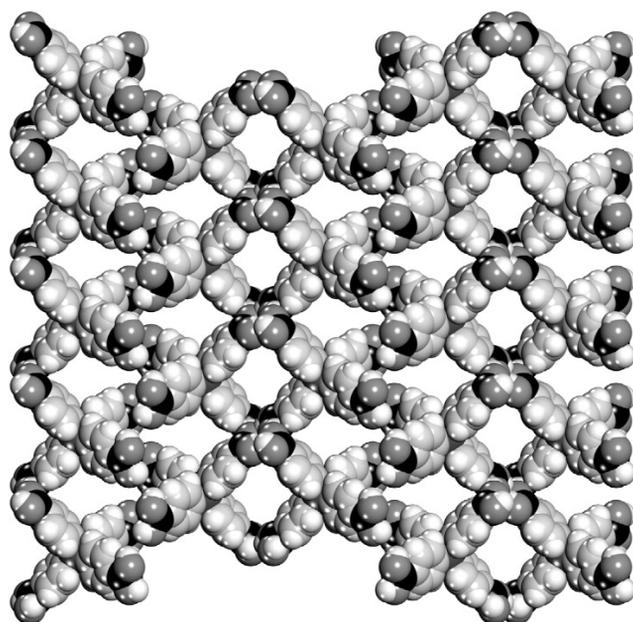
**Fig. 7** View of the five-fold interpenetration of diamondoid hydrogen-bonded networks generated by self-association of tetraboronic acid **5**. Each tecton lies at the intersection of solid lines that represent its interactions with the four neighbors to which it is linked by characteristic cyclic hydrogen-bonded pairs of  $\text{-B(OH)}_2$  groups (Fig. 1a). The independent networks are shown in different shades of gray.



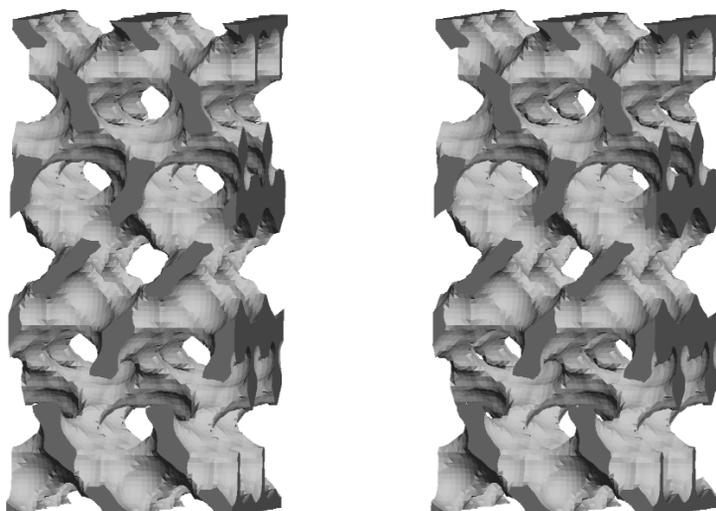
**Fig. 8** Representation of the structure of tetraboronic acid **5**, showing the interaction of adjacent interpenetrating diamondoid networks by the formation of lateral hydrogen bonds between cyclic pairs of  $-B(OH)_2$  groups.

Despite five-fold interpenetration, about 64 % of the volume of crystals of tecton **5** is available for including guests, as measured by standard methods [28]. This value is notable because it far exceeds the fraction of unfilled space (roughly 30 %) that is considered to be present in normal molecular crystals as a consequence of inefficient packing [29]. Moreover, tecton **5** has a simple symmetric shape that should not by itself prevent packing with normal efficiency; indeed, tetraphenylsilane, tetraphenylmethane, and simple substituted derivatives do not typically form inclusion compounds with guests [14]. By failing to act like a normal molecule, tetraboronic acid **5** shows behavior that warrants treating tectons as a special class of compounds. In particular, it demonstrates that packing and the directional interactions involved in tectonic association cannot usually be optimized at the same time. Directional interactions dominate, leading to the assembly of porous networks with significant volume for the inclusion of guests.

Available volume inside the interpenetrated diamondoid networks in crystals of tecton **5** is filled initially by disordered molecules of ethyl acetate. The available volume defines two types of interconnected channels aligned with the  $a$  and  $b$  axes, with cross-sections of approximate dimensions  $6.4 \times 6.4 \text{ \AA}^2$  and  $6.4 \times 9.0 \text{ \AA}^2$  at the narrowest points (Fig. 9). The channels themselves and their connectivity can be represented by the surface shown in Fig. 10. Each molecule of tetraboronic acid **5** is linked to 4 neighbors within the same network by a total of 8 hydrogen bonds. Furthermore, each tecton is joined to neighbors in the two adjacent networks by a total of 8 additional lateral hydrogen bonds (Fig. 8). Overall, each tecton is held in place by 16 hydrogen bonds, ensuring that the network is robust. In contrast, the guest molecules are weakly bonded and are located in large channels that in principle offer easy escape from the network by diffusion along redundant pathways. Not surprisingly, exposure of single crystals of tecton **5** to other suitable guests allows exchange to occur without loss of crystallinity. In this way, crystals of tecton **5** display a permeability that justifies describing them as molecular analogs of zeolites.



**Fig. 9** View along the  $a$  axis of the network constructed from tetraboronic acid **5**, showing the cross-sections of channels. All atoms are shown as spheres of van der Waals radii, with atoms of hydrogen appearing in white, atoms of carbon in light gray, atoms of oxygen in dark gray, and atoms of boron in black. Disordered guests are omitted for clarity.



**Fig. 10** Stereoscopic representation of the interconnected channels defined by the network constructed from tetraboronic acid **5**. The image shows a  $2 \times 2 \times 1$  array of unit cells viewed with the  $c$  axis vertical. The outsides of the channels appear in light gray, and dark gray is used to show where the channels are cut by the boundaries of the array. The surface of the channels is defined by the possible loci of the center of a sphere of diameter 3 Å as it rolls over the surface of the ordered tectonic network [30].

To further probe the ability of molecular tectonics to engineer crystals with sub-nanometer precision, we synthesized and crystallized analogous tetraboronic acid **6**, which replaces the tetraphenylsilyl core of tecton **5** with a slightly more compact tetraphenylmethyl core. As planned, crystals of analog **6** proved to be isostructural, with key parameters reduced logically in size in response to the changed dimensions of the core. In particular, the intertectonic distance between the tetrahedral centers of neighboring tectons within a single diamondoid network was reduced from 16.63 to 15.79 Å. In addition, the porosity (as measured by the percentage of the volume of the crystals accessible to guests [28]) was decreased from 64 to 60 %, and the cross-sections of the channels were reduced from  $6.4 \times 6.4 \text{ \AA}^2$  and  $6.4 \times 9.0 \text{ \AA}^2$  at the narrowest points to  $5.9 \times 5.9 \text{ \AA}^2$  and  $5.2 \times 8.6 \text{ \AA}^2$ .

The structures of crystals of tetraboronic acids **5** and **6** provide an impressive illustration of the ability of molecular tectonics to engineer materials by design. Tectons **5** and **6** behave according to plan because (1) they incorporate sticky sites with reliable patterns of association, (2) the sticky sites are grafted to cores that are structurally well defined, and (3) every tecton is held in place by specific directional interactions with each of its neighbors. In these ways, the molecular structures of tectons **5** and **6** provide clear blueprints that direct the compounds to form a particular architecture with predictable dimensions.

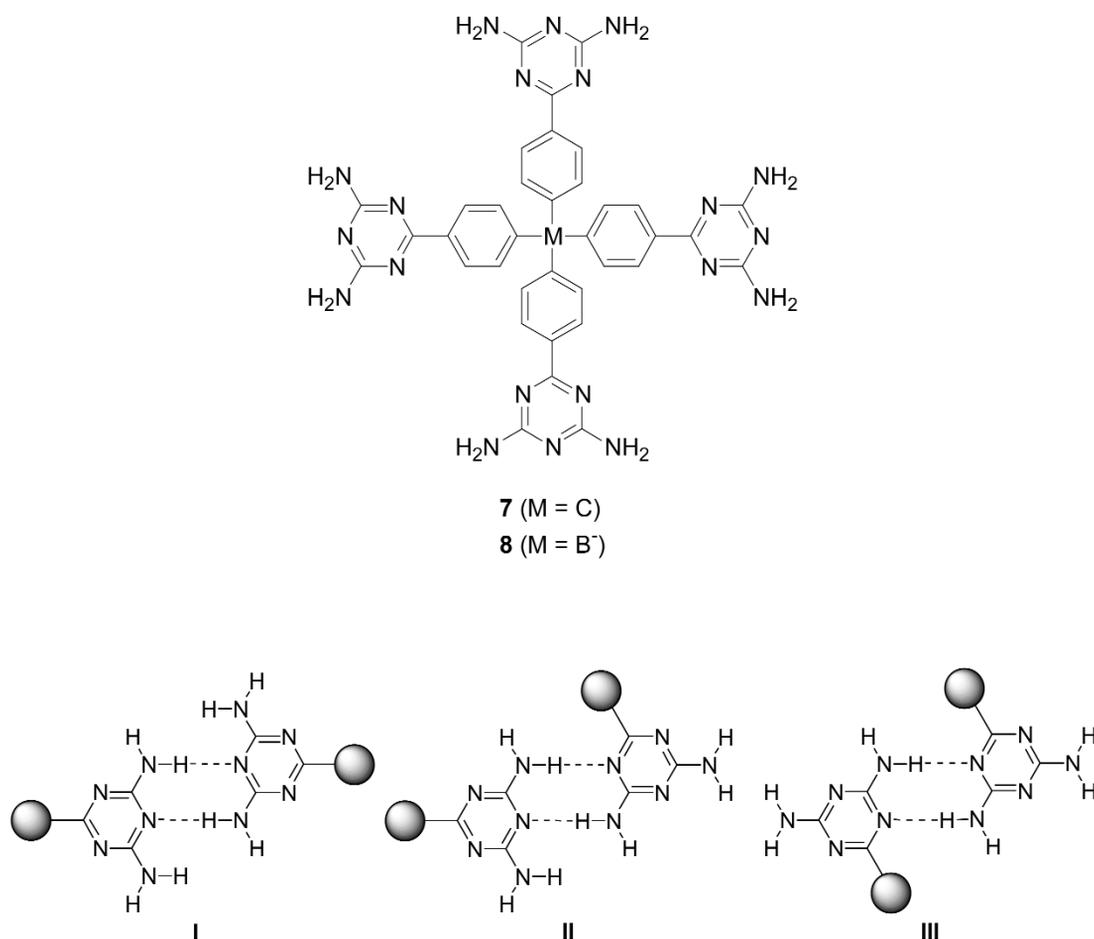
## **BORON IN CRYSTAL ENGINEERING: USE OF TECTONS DERIVED FROM TETRAPHENYLBORATE**

### **Engineering porous charged hydrogen-bonded networks for use in ion exchange**

Valuable information about the generality of the strategy of molecular tectonics is provided by comparative experiments in which the same sticky sites are attached to different cores, such as the studies of tectons **5** and **6** summarized above, and experiments in which different sticky sites are attached to the same core. In such comparisons, derivatives of tetraphenylmethane have been widely used as cores and derivatives of aminotriazines as sticky sites. These sites offer the dual advantages of easy synthesis and reliable participation in multiple hydrogen bonds according to the standard motifs **I–III** (Fig. 11). These factors led us to synthesize and crystallize tecton **7** [31].

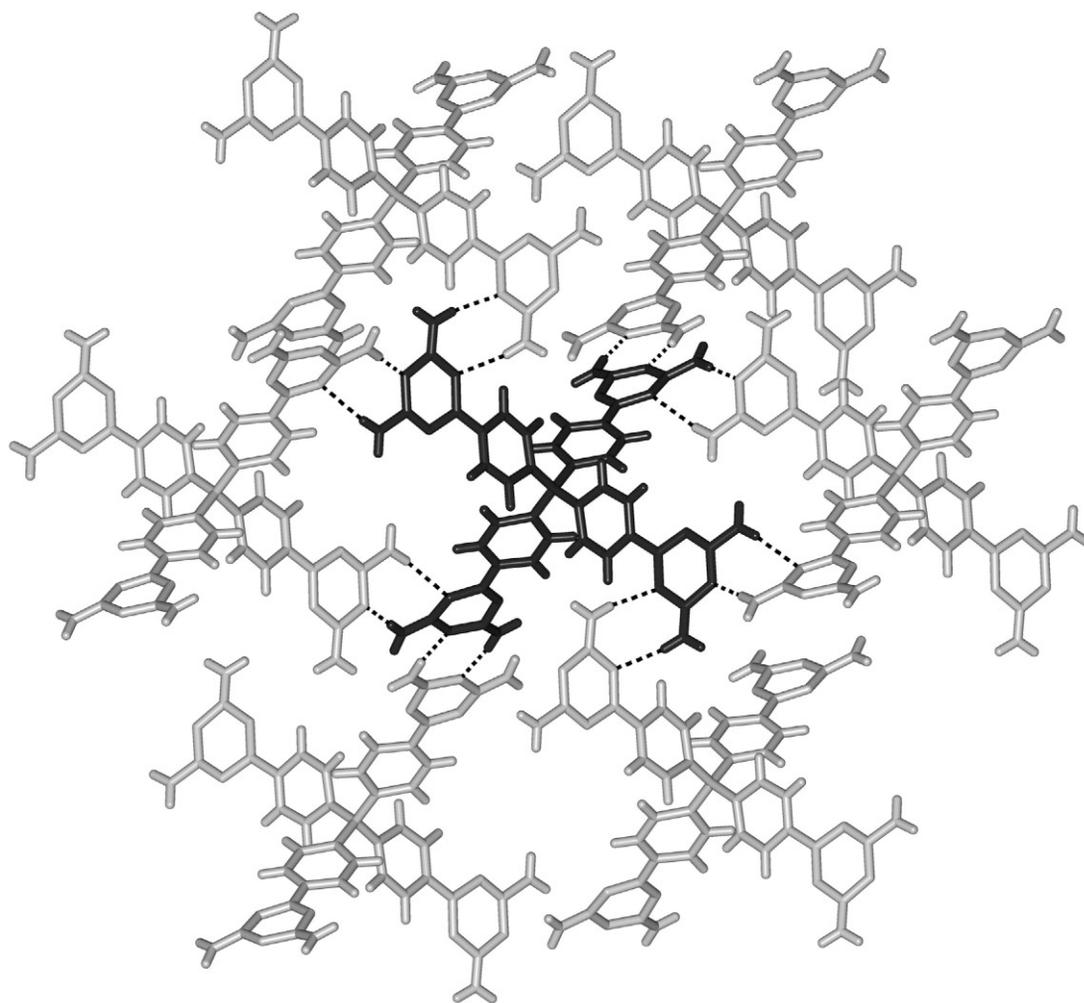
Crystals of tecton **7** grown from HCOOH/dioxane proved to form a non-interpenetrated three-dimensional network in which each tecton participates in a total of 16 hydrogen bonds, all according to motif **II** (Fig. 11). Each tecton has 8 hydrogen-bonded neighbors, and their central carbon atoms are separated by an intertectonic distance of 14.91 Å. About 45 % of the volume is accessible to guests, which occupy parallel channels and can be exchanged selectively in single crystals or even partly removed without loss of crystallinity.

Crystals of tecton **7** therefore provide an ordered permeable molecular material with properties closely similar to those of zeolites and other microporous inorganic substances. In one important respect, however, the materials are distinctly different: The porous molecular network built from tecton **7** is neutral, whereas the porous aluminosilicate frameworks of zeolites are charged. This difference has two significant consequences: (1) Porous neutral molecular networks are unsuitable for ion exchange, and (2) coulombic attraction provides a strong driving force for including guests of opposite charge in ionic networks, but no comparable effect propels inclusion in neutral networks, making the introduction of particular guests a challenging and often unsuccessful endeavor.

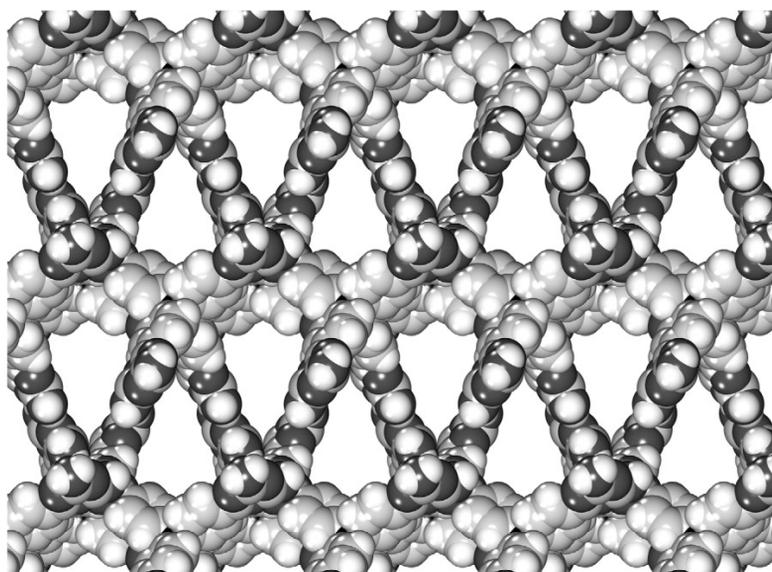


**Fig. 11** Cyclic hydrogen-bonding motifs characteristic of aminotriazines.

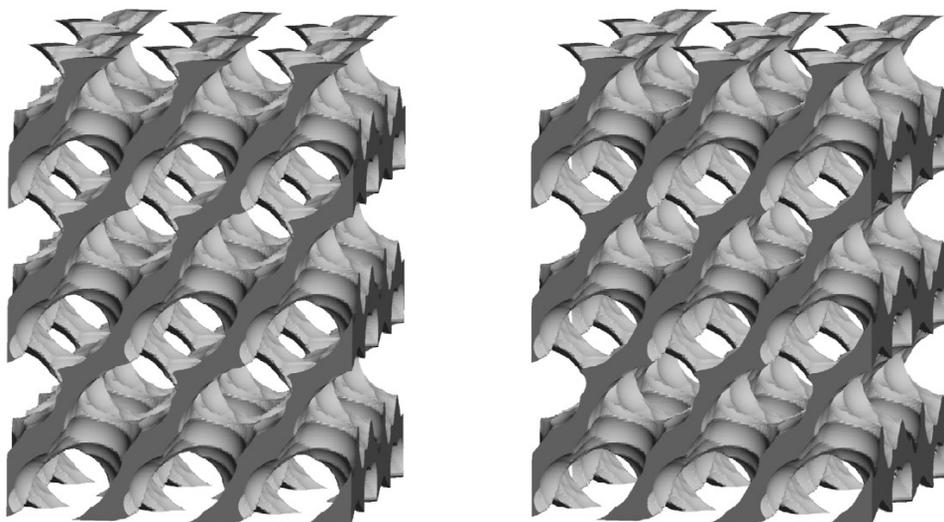
The chemistry of boron helped us meet this challenge by providing tetraphenylborate **8** [12], an anion closely analogous to neutral tecton **7**. Like neutral analog **7**, tetraphenylborate **8** crystallized as its  $\text{PPh}_4^+$  salt to give a porous non-interpenetrated three-dimensional network in which each tecton participates in a total of 16 hydrogen bonds (Fig. 12). However, the networks formed by neutral tecton **7** and anionic analog **8** are not identical, presumably because the need to accommodate cations and to minimize coulombic repulsion requires a significantly different arrangement of the tectons. In particular, the number of hydrogen-bonded neighbors is reduced from eight in the case of neutral tecton **7** to six in the case of anionic tecton **8**, and the average intertectonic separation is increased from 14.91 to 15.64 Å. Moreover, 74 % of the volume of the crystals of anionic tecton **8** is available for including cations and guests, whereas the corresponding value for crystals of neutral analog **7** is only 45 %. Cations and guests included in the anionic network built from tecton **8** are disordered and occupy large interconnected channels. The most impressive channels are aligned with the *c* axis and have triangular cross-sections of approximate dimensions  $8 \times 12 \text{ \AA}^2$  (Fig. 13). The channels themselves can be represented by the surface shown in Fig. 14. Together, these observations suggest that modifying tectons by introducing charge may be a generally effective way to increase their separation and thereby increase the porosity of the resulting molecular networks.



**Fig. 12** View of the structure of crystals of tetraphenylborate **8** •  $\text{PPh}_4^+$  grown from dimethyl sulfoxide (DMSO)/toluene, showing a central tecton (dark gray) surrounded by its six hydrogen-bonded neighbors (light gray). Hydrogen bonds appear as broken lines, and all guests and cations are omitted for clarity. The four diamino-triazine groups of the central tecton form a total of 16 hydrogen bonds according to all three standard motifs **I–III** (Fig. 11).

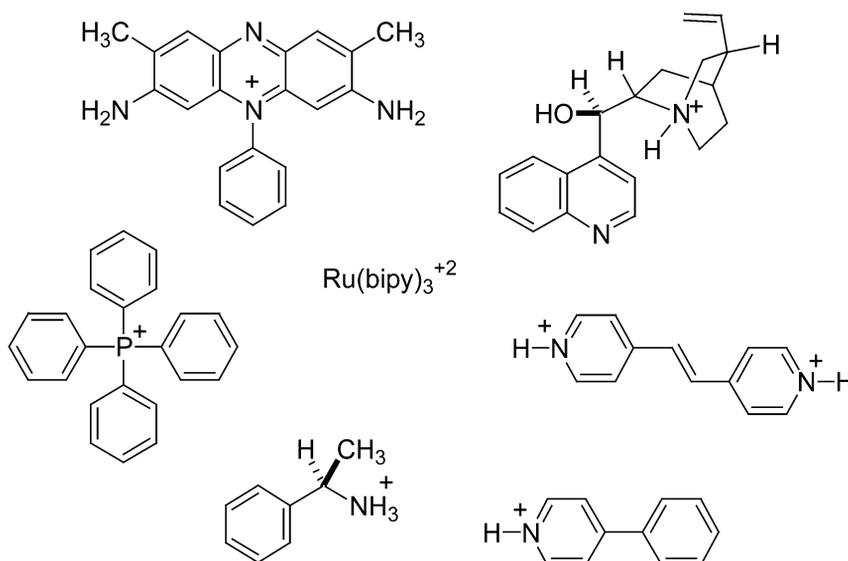


**Fig. 13** View along the  $c$  axis of the network formed by crystallizing anionic tecton  $\mathbf{8} \bullet \text{PPh}_4^+$  from DMSO/toluene. The view shows a  $4 \times 2 \times 4$  array of unit cells, with guests omitted and atoms represented by spheres of van der Waals radii to reveal the cross-sections of the channels. Atoms of hydrogen appear in white, atoms of carbon in light gray, atoms of nitrogen in dark gray, and atoms of boron in black.



**Fig. 14** Stereoscopic representation of interconnected channels within the network constructed from anionic tecton  $\mathbf{8} \bullet \text{PPh}_4^+$ . The image shows a  $3 \times 3 \times 2$  array of unit cells viewed along the  $c$  axis. The outsides of the channels appear in light gray, and dark gray is used to show where the channels are cut by the boundaries of the array. The surface of the channels is defined by the possible loci of the center of a sphere of diameter 5 Å as it rolls over the surface of the ordered network [30].

Salts of anionic tecton **8** with all the cations shown in Scheme 1 proved to crystallize as the same hydrogen-bonded network, with unit-cell parameters closely similar ( $\pm 6\%$ ) to those of the  $\text{PPh}_4^+$  salt. We were also able to crystallize the  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $[\text{CH}_3(\text{CH}_2)_3]_4\text{N}^+$  salts under similar conditions, but so far we have not been able to determine their structures. Because the salts are different compounds, and because the size and structural complexity of some of the cations in Scheme 1 rival those of anion **8** itself, consistent formation of the same network is a significant observation. It confirms that the oriented arrays of sticky sites in tectons are programmed to generate specific networks and to disfavor alternatives. The effect of charge and the multiplicity of potential hydrogen-bonding patterns adopted by aminotriazines (Fig. 11) make it exceedingly difficult to foresee what particular structure will result from association of tecton **8**; once revealed, however, the favored architecture is persistent and can be used dependably to accommodate a wide variety of cations, at least within geometric limits imposed by the surrounding anionic network.



Scheme 1

In this way, materials with specific properties can be made by design. For example, Scheme 1 shows how judicious choice of the cations can introduce chirality, catalytic activity, and luminescence within a single porous framework. Insertion of these cations is controlled reliably by coulombic attraction to the anionic network, whereas there is no particular driving force for introducing comparable neutral guests within neutral frameworks. It is noteworthy that the largest cations accommodated by the anionic network built from tecton **8** are much too big to enter classical natural or synthetic zeolites.

Like tetraphenylsilane **5** and tetraphenylmethanes **6–7**, tetraphenylborate **8** generates a network that is highly porous and robust, as measured by the number of hydrogen bonds per tecton. As expected, single crystals of salts of anion **8** can undergo cation exchange without loss of crystallinity. This process of exchange is notable because it provides a reliable source of single crystals of new salts of tecton **8** with the specific structure shown in Figs. 12–14, even when direct crystallization is impossible or favors a different structure. Competitive exchanges of tetraalkylammonium cations showed selectivity similar to that observed in natural zeolites and their synthetic analogs. Together, these observations underscore the high degree of robustness and porosity that can be attained in molecular networks, and they show that the performance of such materials can equal or even surpass that of classical zeolitic analogs.

## CONCLUSIONS

Molecular crystals with unique properties can be constructed logically from tectons with boron in their cores or sticky sites of association. In particular, the  $-B(OH)_2$  group of boronic acids engages in reliable patterns of hydrogen bonding, and its use as a sticky site in tectons has emerged as an effective tool for controlling association predictably. In addition, replacement of tetraphenylsilyl or tetraphenylmethyl cores in tectons by tetraphenylborate leaves the overall molecular geometry little changed, but it has the profound effect of introducing charge. Tectons derived from tetraphenylborate can be used rationally to construct porous charged molecular networks that resemble zeolites and undergo selective ion exchange. In such ways, boron offers chemists exciting new ways to engineer molecular crystals with predetermined structures and properties.

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