Molecular Tectonics. Use of the Hydrogen Bonding of Boronic Acids To Direct Supramolecular Construction

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Abstract: Tetraboronic acids 1 and 2 have four $-\text{B(OH)}_2$ groups oriented tetrahedrally by cores derived from tetraphenylmethane and tetraphenylsilane. Crystallization produces isostructural diamondoid networks held together by hydrogen bonding of the $-\text{B(OH)}_2$ groups, in accord with the tendency of simple arylboronic acids to form cyclic hydrogen-bonded dimers in the solid state. Five-fold interpenetration of the networks is observed, but 60% and 64% of the volumes of crystals of tetraboronic acids 1 and 2, respectively, remain available for the inclusion of disordered guests. Guests occupy two types of interconnected channels aligned with the a and b axes; those in crystals of tetraphenylmethane measure approximately $5.9 \times 5.9 \text{ Å}^2$ and $5.2 \times 8.6 \text{ Å}^2$ in cross section at the narrowest points, whereas those in crystals of tetraphenylsilane are approximately $6.4 \times 6.4 \text{ Å}^2$ and $6.4 \times 9.0 \text{ Å}^2$. These channels provide access to the interior and permit guests to be exchanged quantitatively without loss of crystallinity. Because the Si–C bonds at the core of tetraboronic acid 2 are longer (1.889(3) Å) than the C–C bonds at the core of tetraboronic acid 1 (1.519(6) Å), the resulting network is expanded rationally. By associating to form robust isostructural networks with predictable architectures and properties of porosity, compounds 1 and 2 underscore the usefulness of molecular tectonics as a strategy for making ordered materials.

Introduction

Molecular tectonics is a strategy for building predictably ordered networks from subunits called tectons, which are molecules designed to interact strongly with their neighbors in ways that are specific and directional. The strategy provides chemists with a useful tool for achieving the spontaneous assembly of new ordered materials with predetermined structures and properties. Of particular interest is the observation that tectons cannot typically form normal close-packed structures in which their ability to take part in specific intermolecular interactions is fully exploited at the same time; instead, they tend to form open networks in which significant volumes are available for the inclusion of guests.

In a conceptually simple method for making tectons, multiple functional groups that promote strong intermolecular interactions can be attached to geometrically suitable cores. Many sticky functional groups have now been tested and found useful as the principal sites of association, but the field remains rich in unexplored potential. For example, the crystallization of arylboronic acids typically produces cyclic hydrogen-bonded dimers (eq 1), but this interaction has not yet been exploited in supramolecular assembly, despite the extensive use of boronic acids in other areas of molecular recognition. In this paper, we describe the crystal structures of tetraboronic acids 1 and 2, and we confirm our expectation that they are predisposed to associate by hydrogen bonding according to eq 1 and to thereby form open three-dimensional, four-connected networks with significant internal volumes for the inclusion of guests.

Results and Discussion

Synthesis. Tetraboronic acid 1 was prepared by minor modifications of the known method. The analogous silane 2 was prepared in 84% overall yield by tetralithiation of tetrakis(4-bromophenyl)silane (BuLi), followed by the addition of B(O-i-Pr)$_3$ and subsequent hydrolysis. Tetraboronic acids 1 and
2 are both of intrinsic interest as substrates for Suzuki couplings and as precursors for the synthesis of a wide range of tetrahedral molecular building blocks derived from tetraphenylmethane and tetraphenylsilane.\textsuperscript{11}

**General Description of Structures.** Crystallization of compounds 1 and 2 was achieved by partial evaporation of solutions in wet ethyl acetate or by diffusion of hexane into solutions in wet ethyl acetate,\textsuperscript{12} and the structures were determined by X-ray crystallography. Both compounds crystallize in the tetragonal space group $I\bar{4}$/$a$ to give isostructural networks held together by hydrogen bonding of $\text{-BOH}$ groups, in accord with the

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**Figure 1.** ORTEP view of the structure of tetraboronic acid 2. Disordered guests are omitted, non-hydrogen atoms are represented by ellipsoids containing 30% probability, and hydrogen atoms are shown as spheres of arbitrary size.

**Figure 2.** Representation of the system of 5-fold interpenetrated diamondoid networks generated by tetraboronic acid 2. In this drawing, the tectons lie at the intersections of solid lines that represent their interactions with four neighbors by hydrogen bonding according to the motif shown in eq 1. The independent networks are shown in different shades of gray.

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Small amounts of H$_2$O may be included, but the quantity could not be determined accurately by $^1$H NMR spectroscopy of dissolved samples. In both cases, the guests are highly disordered, and their location within the networks cannot be determined precisely. However, the volume available for inclusion defines two types of interconnected channels aligned with the crystallographic $a$ and $b$ axes. In the network derived from tetr phenylmethane 1, these channels have cross sections of approximately 5.9 $\times$ 5.9 Å$^2$ and 5.2 $\times$ 8.6 Å$^2$ at the narrowest points, whereas those in the isostructural network derived from tetr phenylsilane 2 are 6.4 $\times$ 6.4 Å$^2$ and 6.4 $\times$ 9.0 Å$^2$. Both cross sections in the structure assembled from tecton 2 are clearly visible in the view along the $a$ axis shown in Figure 3.

The channels themselves and their connectivity are represented by the surface shown in Figure 4. This establishes that (1) the channels are highly interconnected, (2) their detailed shapes are much more complex than those suggested by the simple cross sections shown in Figure 3, and (3) guests that diffuse within the network can reach any point within the channels by multiple redundant pathways. In principle, the high connectivity should help ensure that diffusion is not prevented by occasional obstacles or defects in the system of channels.

Overall, nearly 60% and 64% of the volume of crystals of tectons 1 and 2, respectively, are available for including guests. These values are notably high and far exceed the unused space in normal molecular crystals, typically close to 30%, that is created by inefficient packing. In fact, the available volume in crystals of tectons 1 and 2 even exceeds that used to include water in many protein crystals, despite the characteristically large, complex, and irregular shapes of proteins. In principle, the very simple shapes of tectons 1 and 2 would allow them to be packed with normal efficiency to create relatively compact periodic structures; indeed, tetr phenylmethane, tetr phenylsilane, and simple substituted derivatives do not typically form inclusion compounds. By not acting like normal molecules, compounds 1 and 2 show special behavior that fully supports the emerging principles of molecular tectonics. In particular, the inherent tendency of tectons to form strong directional interactions disfavors efficient molecular packing and promotes the formation of structures in which significant volume is available for the inclusion of guests.

Exchange of Guests. In the structures derived from tetraboronic acids 1 and 2, each tecton participates in a total of eight hydrogen bonds with four neighbors to form a diamondoid network. Moreover, each diamondoid network is linked to the two adjacent interpenetrating diamondoid networks by supplementary hydrogen bonds between cyclic dimers, as shown in structure 3. Similar interdimeric hydrogen bonding has also been observed in the structures of simpler ary lboronic acids. As a result, each tecton participates in a total of 16 hydrogen bonds,
eight involving neighbors in the same diamondoid network and
eight involving tectons in the adjacent interpenetrating networks.
This extensive hydrogen bonding helps ensure that the structural
integrity of the ordered assembly is high.

In contrast, the guests are disordered, potentially mobile, and
located in channels that in principle provide multiple routes of
escape from inside the crystal. As observed in other tectonic
materials, the exchange of guests can take place without destroying
the ordered network. For example, single crystals of estimated composition
1·5CH$_2$COOC$_2$H$_5$·3H$_2$O and approximate dimensions 1 mm × 1 mm × 1 mm were suspended in tetrahydrofuran (THF)/hexane at 25 °C for 24 h. The recovered sample remained transparent and morphologically unchanged, continued to diffract and to exhibit uniform extinction
between crossed polarizers, and showed closely similar unit cell
parameters when studied by single-crystal X-ray diffraction.
However, analysis of dissolved samples by $^1$H NMR spectroscopy established that the initial guest, CH$_2$COOC$_2$H$_5$, had been
replaced quantitatively by THF to give new crystals of approximate composition 1·5THF·2H$_2$O. In similar single-crystal to single-crystal transformations, CH$_2$COOC$_2$H$_5$ was also
replaced quantitatively by two guests approximately twice as large,
diethyl malonate and diethyl methylmalonate. The exchange of
guests is feasible, at least within geometric limits imposed by the
channels, but the removal of guests by exposure of crystals to air or vacuum leads to a loss of crystallinity.

The unit cell parameters before replacement of CH$_2$COOC$_2$H$_5$
between THF were $a = b = 10.627(11)$ Å, $c = 41.608(6)$ Å, $\alpha = \beta = 90^\circ$, and $V = 4699(7)$ Å$^3$, whereas those after exchange
were $a = b = 10.794(17)$ Å, $c = 42.08(7)$ Å, $\alpha = \beta = 90^\circ$, and $V = 4902(5)$ Å$^3$ at the same temperature (226 K). This observation shows that the replacement of CH$_2$COOC$_2$H$_5$ by
THF induces a small expansion of the network, possibly associated with subtle changes in the conformation of tecton 1, differences in internal solvation of the network by the included guests, or an increase in the number of guests.

Together, our studies of exchange demonstrate that (1) the crystalline network is robust enough to remain insoluble and to retain its original ordered architecture during the exchange of
guests, yet (2) the network is deformable enough to accommodate
small structural changes. In general, tectonic networks may prove to offer a unique balance between structural integrity and
deformability that makes them distinctly different from both
normal soft organic materials and hard inorganic materials.

Channels in the structures derived from tectons 1 and 2 provide access to $\equiv$OH groups involved in intertectonic hydrogen bonding. Because arylboronic acids are moderately acidic (pK$_a$ 8.83 for benzeneboronic acid itself), porous crystals constructed by the association of boronic acids may prove to
be useful in heterogeneous acidic catalysis or in the separation of
bases according to size, shape, and other characteristics.

Detailed Analysis and Comparison of Structures. The bond
lengths and angles in the structures of tectons 1 and 2 are similar
to those of simpler arylboronic acids. For example, the O···O distances in the dimeric units defined by eq 1 are 2.693(5) and
2.713(3) Å in the networks derived from compounds 1 and 2, respectively, whereas they are 2.743(2) Å in the dimer of
phosphorylboronic acid itself. Similar values are also found for the
O···O angles (118.7(8)$^\circ$ and 119.5(4)$^\circ$ in the structures derived from tectons 1 and 2, respectively, and 116.2(2)$^\circ$ in the model dimer), the average values for the angle between the planes defined by the aryl groups and the $-\text{B(OH)}_2$ groups (13.2$^\circ$ and 1.6$^\circ$ in the structures derived from compounds 1 and 2, respectively, and 14.2$^\circ$ in the model dimer), and other parameters.

In both structures derived from tetraboronic acids 1 and 2, adjacent interpenetrating networks are related by a displacement
along the $a$ or $b$ axis equal to the unit cell parameters ($a = b = 10.627(11)$ Å for tetraphenylmethane 1 and $a = b = 10.8370(15)$ Å for tetraphenylsilane 2). The O···O distances for the interdimeric hydrogen bonds defined by structure 3 are 2.700(8) and
2.729(5) Å, respectively. These distances are slightly longer than those corresponding to the intradimeric hydrogen bonds, so it is appropriate to consider the cyclic arrangement shown in eq 1 as the primary hydrogen-bonding motif present in the structures of tectons 1 and 2. Nevertheless, the interdimeric hydrogen bonds also appear to make an important contribution.

Because the average Si···C distance at the core of tetraphenyl-
silane 1 (1.889(3) Å) is significantly greater than the average C···C distance at the core of tetraphenylmethane 2 (1.519(6) Å), the average intertectonic distances between the centers of hydrogen-bonded neighbors are correspondingly larger (15.79 vs 16.63 Å). As a result, the dimensions of the channels, the percentage of volume available for inclusion, and various unit cell parameters are increased predictably. Specifically, the values of $a = b = 10.627(11)$ Å, $c = 41.608(6)$ Å, and $V = 4699(7)$ Å$^3$ in the structure of tetraphenylmethane 1 are increased to $a = b = 10.8370(15)$ Å, $c = 45.602(9)$ Å, and $V = 5355.6(15)$ Å$^3$ in the structure of tetraphenylsilane 2.

Although the networks constructed from tectons 1 and 2 are predictably similar, several minor differences are noteworthy. In particular, the C···C angles at the core of tetraphenyl-
methane 1 have values of either 102.1(4)$^\circ$ or 113.3(2)$^\circ$, whereas the C···Si···C angles at the core of tetraphenylsilane 2 vary less
widely (106.0(2)$^\circ$ or 111.2(1)$^\circ$), despite the presumably greater
distance between the centers of the two silane cores. In either case, however, do deviations from ideal tetrahedral geometry give rise to nondiamondoid architectures.

Detailed prediction of the structures of molecular crystals remains impossible. However, our study of the behavior of tectons 1 and 2 shows that the strategy of molecular tectonics gives chemists an effective tool for engineering new crystalline structures with important elements of predictability. As their design intends, tectons 1 and 2 self-associate by hydrogen bonding of $\equiv$B(OH)$_2$ groups according to the standard motifs


suitable crystals of tetraboronic acid 1 or 2 could also be obtained by slow evaporation of solutions in wet CH3COOC2H5.

**X-ray Crystallographic Studies.** The structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.21 All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in ideal positions and refined as riding atoms. In both structures, the included guests were found to be highly disordered and could not be resolved. The SQUEEZE option of the PLATON program was used to eliminate the contribution of the guests and to give final models based only on the ordered part of the structures.21

**Structure of Tetraboronic Acid 1.** Data were collected using a Bruker SMART 2000 CCD diffractometer with Cu Kα radiation at 226 K. Crystals of compound 1 belong to the tetragonal space group I4_1/a (No. 88) with a = b = 10.627(11) Å, c = 41.608(6) Å, V = 4699(7) Å3, Dcalc (without solvent) = 0.701 g cm⁻³, and Z = 4. Full-matrix least-squares refinements on F² led to final residuals R₁ = 0.0938, Rₑ = 0.2759, and GOF = 0.699 for 358 reflections with I > 2σ(I).

**Structure of Tetraboronic Acid 2.** Data were collected using an Erraf-Nionius CAD-4 diffractometer with Cu Kα radiation at 210 K. Crystals of compound 2 belong to the tetragonal space group I4_1/a (No. 88) with a = b = 10.8370(15) Å, c = 5535.6(15) Å, V = 5355.6(15) Å³, Dcalc (without solvent) = 0.634 g cm⁻³, and Z = 4. Full-matrix least-squares refinements on F² led to final residuals R₁ = 0.0701, Rₑ = 0.1717, and GOF = 0.666 for 804 reflections with I > 2σ(I).

**Exchange of Guests in Crystals of Tetraboronic Acid 1.** Single crystals of estimated composition 1:5CH3COOC2H5·2H2O and approximate dimensions 1 mm × 1 mm × 1 mm were grown in the normal manner. The mother liquors were removed by pipet, and the crystals were immediately covered with a 1:9 mixture of THF/hexane and kept unstirred at 25 °C for 24 h. The liquid was removed by pipet, the recovered crystals were washed three times with hexane, and their content was determined by 1H NMR spectroscopy. Replacement of CH3COOC2H5 by diethyl malonate and methyl diethylmalonate was carried out under similar conditions.

**Acknowledgment.** We thank Dr. Richard Gilardi for preliminary crystallographic studies and helpful discussions. We are grateful to the Natural Sciences and Engineering Research Council of Canada, the Ministère de l’Éducation du Québec, Merck Frosst, the US National Science Foundation, and the Rutgers University Research Council for financial support. In addition, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

**Supporting Information Available:** ORTEP drawings and tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for tetraboronic acids 1 and 2. This information is available free of charge via the Internet at http://pubs.acs.org.

JA0276722