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 $-B(OH)_2$ groups oriented tetrahedrally by cores derived from tetraphenylmethane and tetraphenylsilane. Crystallization produces isostructural diamondoid networks held together by hydrogen bonding of the $-B(OH)_2$ 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 **1** measure approximately 5.9×5.9 Å^2 and 5.2×8.6 Å^2 in cross section at the narrowest points, whereas those in crystals of tetraphenylsilane **2** are approximately 6.4×6.4 Å^2 and 6.4×9.0 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.[2,3] 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,[4] but the field remains rich in unexplored potential. For example, the crystallization of arylboronic acids typically produces cyclic hydrogen-bonded dimers (eq 1),[5,6] but this interaction has not yet been exploited in
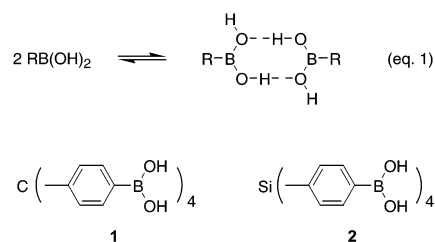
supramolecular assembly,[7,8] despite the extensive use of boronic acids in other areas of molecular recognition.[9] In this paper, we describe the crystal structures of tetraboronic acids **1** and **2**, and we confirm our expectation that they are predisposed to associate by hydrogen bonding according 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.[10] The analogous silane **2** was prepared in 84% overall yield by tetralithiation of tetrakis-(4-bromophenyl)silane (BuLi),[11] followed by the addition of B(O-*i*-Pr)$_3$ and subsequent hydrolysis. Tetraboronic acids **1** and

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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.[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,[12] and the structures were determined by X-ray crystallography. Both compounds crystallize in the tetragonal space group $I4_1/a$ to give isostructural networks held together by hydrogen bonding of $-B(OH)_2$ groups, in accord with the
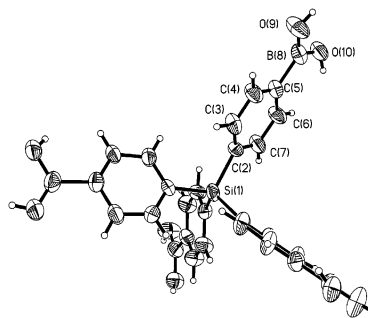
Figure 1. ORTEP view of the structure of tetraboronic acid **2**. Disordered guests are omitted, non-hydrogen atoms are represented by ellipsoids corresponding to 30% probability, and hydrogen atoms are shown as spheres of arbitrary size.
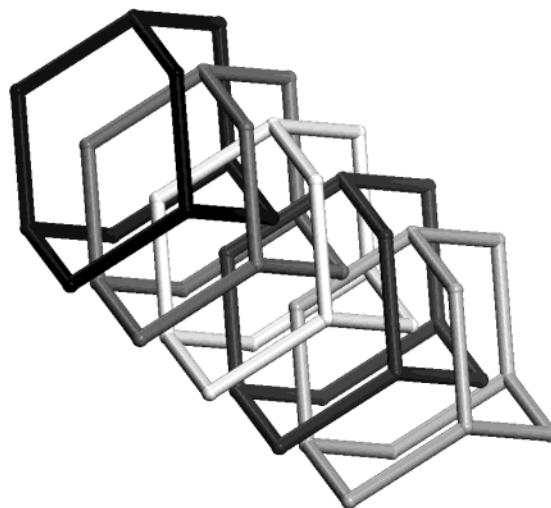
Figure 2. Representation of the system of 5-fold interpenetrated diamondoid networks generated by tetraboronic acid **2**. In this drawing, the tectons lie at the intersections of solid lines that represent their interactions with four neighbors by hydrogen bonding according to the motif shown in eq 1. The independent networks are shown in different shades of gray.

characteristic motif shown in eq 1.[13] Because the two structures are closely similar, only views of the network derived from tetraphenylsilane **2** are shown (Figures 1−4). The $-B(OH)_2$ groups are oriented tetrahedrally by the relatively rigid tetraphenylmethyl and tetraphenylsilyl cores to which they are attached, so both networks are predisposed to favor diamondoid connectivity,[14] which is observed, or a related three-dimensional, four-connected arrangement. The average intertectonic distances between the tetrahedral centers of neighboring hydrogen-bonded tetraboronic acids are 15.79 and 16.63 Å in the structures of compounds **1** and **2**, respectively. As a result, each diamondoid network is open enough to permit interpenetration by four independent diamondoid networks (Figure 2).[15]

Inclusion of Guests. Despite this 5-fold interpenetration, the structures of compounds **1** and **2** both retain very significant volume for the inclusion of guests. Specifically, crystallization produces inclusion compounds of approximate compositions **1·**

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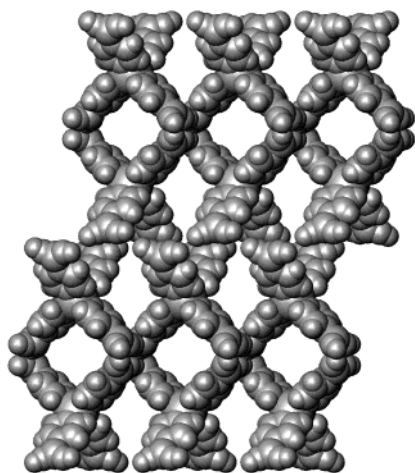
Figure 3. View along the *a* axis of the network constructed from tetraboronic acid **2** showing a 3 × 3 × 1 array of unit cells with disordered guests omitted.
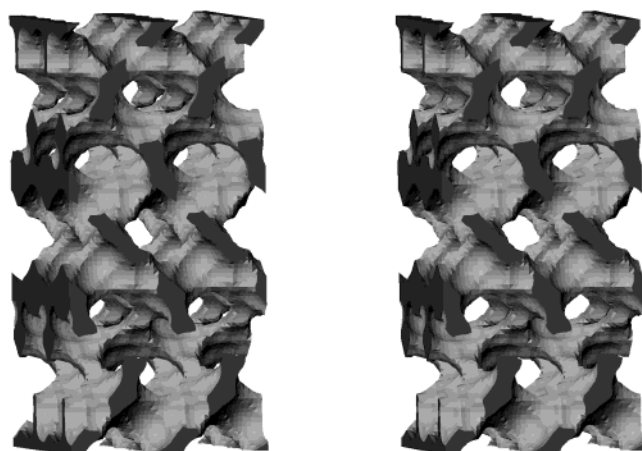

Figure 4. Stereoscopic representation of the interconnected channels defined by the network constructed from tetraboronic acid **2**. The image shows a 2 × 2 × 1 array of unit cells viewed with the *c* axis vertical. The outsides of the channels appear in light gray, and dark gray is used to show where 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.[18]
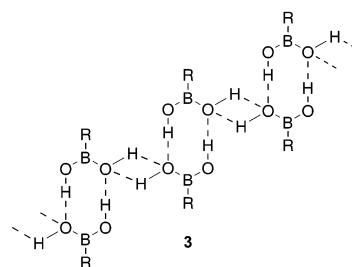
5CH$_3$COOC$_2$H$_5$·xH$_2$O and **2**·5CH$_3$COOC$_2$H$_5$·yH$_2$O, as estimated by ^{1}H NMR spectroscopy of dissolved samples.[16] In both cases, the guests are highly disordered, and their location within the networks cannot be determined precisely. However, the volume available for inclusion defines two types of interconnected channels aligned with the crystallographic *a* and *b* axes. In the network derived from tetraphenylmethane **1**, these channels have cross sections of approximately 5.9 × 5.9 Å^2 and 5.2 × 8.6 Å^2 at the narrowest points, whereas those in the isostructural network derived from tetraphenylsilane **2** are 6.4 × 6.4 Å^2 and 6.4 × 9.0 Å^2.[17] Both cross sections in the structure

(16) Small amounts of H$_2$O may be included, but the quantity could not be determined accurately by ^{1}H NMR spectroscopy. In addition, rapid loss of guests from crystals removed from their mother liquors prevented us from using thermogravimetric analysis to estimate the composition.

(17) The dimensions of a channel in a particular direction correspond to the cross section of an imaginary cylinder that could be passed through the hypothetical empty network in the given direction in contact with the van der Waals surface. Such values are inherently conservative because (1) they measure the cross section at the most narrow constriction and (2) they systematically underestimate the sizes of channels that are not uniform and linear.

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.[18] 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.[19] 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.[20,21] 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.[22] 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.[23] 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, tetraphenylmethane, tetraphenylsilane, and simple substituted derivatives do not typically form inclusion compounds.[24] 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 arylboronic acids.[5,6] As a result, each tecton participates in a total of 16 hydrogen bonds,

(18) Representations of channels were generated by the Cavities option in the program ATOMS Version 5.1 (Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663; www.shapesoftware.com). We are grateful to Eric Dowty of Shape Software for integrating this capacity in ATOMS at our suggestion.

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(20) The percentage of volume accessible to guests was estimated by the PLATON program.[21]

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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,[2] the exchange of guests can take place without destroying the ordered network. For example, single crystals of estimated composition **1**·5$CH_3COOC_2H_5$·xH_2O 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, $CH_3COOC_2H_5$, had been replaced quantitatively by THF to give new crystals of approximate composition **1**·5THF·zH_2O.[16] In similar single-crystal to single-crystal transformations, $CH_3COOC_2H_5$ 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 $CH_3COOC_2H_5$ by THF were $a = b = 10.627(11)$ Å, $c = 41.608(6)$ Å, $\alpha = \beta = \gamma = 90°$, and $V = 4699(7)$ Å^3, whereas those after exchange were $a = b = 10.794(17)$ Å, $c = 42.08(7)$ Å, $\alpha = \beta = \gamma = 90°$, and $V = 4902(5)$ Å^3 at the same temperature (226 K). This observation shows that the replacement of $CH_3COOC_2H_5$ 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.[25]

Channels in the structures derived from tectons **1** and **2** provide access to −OH groups involved in intertectonic hydrogen bonding. Because arylboronic acids are moderately acidic (pK_a 8.83 for benzeneboronic acid itself),[26] 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.[27]

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 phenylboronic acid itself.[5] Similar values are also found for the O−B−O angles (118.7(8)° and 119.5(4)° in the structures derived from tectons **1** and **2**, respectively, and 116.2(2)° in the model dimer[5]), the average values for the angle between the planes defined by the aryl groups and the −B(OH)$_2$ groups (13.2° and 1.6° in the structures derived from compounds **1** and **2**, respectively, and 14.2° in the model dimer[5]), 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 tetraphenylsilane **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−C angles at the core of tetraphenylmethane **1** have values of either 102.1(4)° or 113.3(2)°, whereas the C−Si−C angles at the core of tetraphenylsilane **2** vary less widely (106.0(2)° or 111.2(1)°), despite the presumably greater flexibility of the tetraphenylsilyl core. In neither case, however, do deviations from ideal tetrahedral geometry give rise to nondiamondoid architectures.

Detailed prediction of the structures of molecular crystals remains impossible.[28] 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 −B(OH)$_2$ groups according to the standard motif

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(eq 1), thereby forming isostructural three-dimensional, four-connected networks with significant degrees of openness that depend predictably on the size of the individual subunits.

Conclusions

Our studies of tetraboronic acids **1** and **2** are of broad chemical interest for the following reasons: (1) both compounds are promising precursors for synthesizing a range of tetrahedral molecular building blocks by Suzuki couplings; (2) their association establishes for the first time the usefulness of boronic acids in the self-assembly of supramolecular structures; and (3) their predictable behavior confirms that molecular tectonics is an effective strategy for making ordered supramolecular materials by design.

Experimental Section

Tetrahydrofuran (THF) was dried by distillation from the sodium ketyl of benzophenone. All other reagents were commercial products that were used without further purification.

(Methanetetrayltetra-4,1-phenylene)tetrakisboronic Acid (1).[10] A solution of tetrakis(4-bromophenyl)methane (1.27 g, 2.00 mmol)[29,30] in THF (125 mL) was stirred at −78 °C under dry N_2 and treated dropwise with a solution of butyllithium (6.4 mL, 2.5 M in hexane, 16 mmol). The resulting mixture was kept at −78 °C for 30 min, and then B(O-*i*-Pr)$_3$ (5.50 mL, 23.8 mmol) was added dropwise. The mixture was stirred at −78 °C for 20 min and then at 25 °C for 1 h. After acidification with 1 M aqueous HCl (25 mL), the mixture was concentrated by partial evaporation of volatiles under reduced pressure. The concentrate was treated with aqueous 1 M NaOH and filtered, and the filtrate was acidified with 1 M aqueous HCl. This yielded a precipitate, which was separated by filtration and dried in air to afford (methanetetrayltetra-4,1-phenylene)tetrakisboronic acid (**1**; 0.914 g, 1.84 mmol, 92%) as a colorless solid: mp >300 °C; IR (KBr) 3369 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (s, 8H), 7.66 (d, 8H, $^3J = 8.4$ Hz), 7.12 (d, 8H, $^3J = 8.4$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.3, 134.5, 132.3, 130.6, 65.9; MS (FAB, glycerol) *m/e* 721. Anal. Calcd for $C_{25}H_{24}B_4O_8\cdot4H_2O$: C, 52.89; H, 5.68. Found: C, 53.51; H, 5.93.

(Silanetetrayltetra-4,1-phenylene)tetrakisboronic Acid (2). An analogous procedure converted tetrakis(4-bromophenyl)silane (1.30 g, 1.99 mmol)[11] into (silanetetrayltetra-4,1-phenylene)tetrakisboronic acid (**2**; 0.860 g, 1.68 mmol, 84%), which was isolated as a colorless solid: mp >300 °C; IR (KBr) 3369 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (s, 8H), 7.79 (d, 8H, $^3J = 7.8$ Hz), 7.42 (d, 8H, $^3J = 7.8$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.9, 136.4, 135.9, 134.5; MS (FAB, glycerol) *m/e* 737. Anal. Calcd for $C_{24}H_{24}B_4O_8Si\cdot1H_2O$: C, 54.41; H, 4.95. Found: C, 53.66; H, 4.79.

Crystallization of Tetraboronic Acids 1 and 2. In typical crystallizations, tetraboronic acid **1** or **2** (0.2 mmol) was treated with CH$_3$COOC$_2$H$_5$ (15 mL), and the mixture was shaken with H$_2$O.[12] The organic phase was separated and exposed to vapors of hexane. Crystals suitable for X-ray diffraction were obtained after 2 days. Alternatively, suitable crystals of tetraboronic acid **1** or **2** could also be obtained by slow evaporation of solutions in wet CH$_3$COOC$_2$H$_5$.

X-ray Crystallographic Studies. The structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.[31] 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, $V = 4699(7)$ Å^3, D_{calcd} (without solvent) = 0.701 g cm^{-3}, and $Z = 4$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0938$, $R_w = 0.2759$, and GOF = 0.699 for 358 reflections with $I > 2\sigma(I)$.

Structure of Tetraboronic Acid 2. Data were collected using an Enraf-Nonius 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, $c = 45.602(9)$ Å, $V = 5355.6(15)$ Å^3, D_{calcd} (without solvent) = 0.634 g cm^{-3}, and $Z = 4$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0701$, $R_w = 0.1717$, and GOF = 0.666 for 804 reflections with $I > 2\sigma(I)$.

Exchange of Guests in Crystals of Tetraboronic Acid 1. Single crystals of estimated composition **1**·5CH$_3$COOC$_2$H$_5$·xH$_2$O 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 ^{1}H NMR spectroscopy. Replacement of CH$_3$COOC$_2$H$_5$ by diethyl malonate and methyl diethylmalonate was carried out under similar conditions.

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.

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