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# Solid-State Supramolecular Structures of Resorcinol–Arylboronic Acid Compounds

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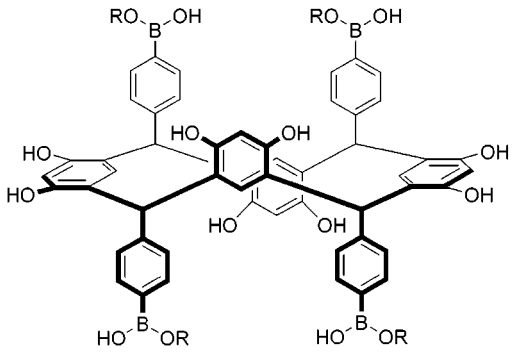
## ABSTRACT




**1** R = H
**2** R = $CH_3$

**An X-ray crystallographic study of unique hydrogen-bonded supramolecular solid-state networks comprised of a tetraarylboronic acid resorcinarene is described. When 1 is recrystallized from 9:1 MeOH:EtOH, partial esterification takes place to give compound 2, the corresponding half methyl ester, which forms an infinite two-dimensional array. Each molecule participates in 12 hydrogen bonds with other macrocycles. These hydrogen bonds are both B–OH- - - OH (phenolic) and OH (phenolic)- - -OH (phenolic).**

Resorcinol-derived supramolecular synthons[1] have attracted much recent attention in promoting the formation of unique resorcinarene (cyclic tetramers of resorcinol)[2] solid-state architectures.[3] We have been investigating the solution-phase properties of resorcinarene macrocycles (e.g., $C_{2h}$-symmetric **1**[4]) (Figure 1) embodying arylboronic acid substituents. We have employed boronic acid-derived resorcinarenes as both chiral and achiral molecular hosts[4] and as substrates for the creation of deep-cavity oligoaromatic molecules.[5] We have reported the discovery that these materials can function as visual indicators for saccharides.[6] In light of the solid-state properties of related resorcinarenes[3] and the well-known role of arylboronic acids in molecular recognition and catalysis, we herein report the use of an arylboronic acid resorcinarene toward the creation of a unique solid-state supramolecular array.

The "chair" $C_{2h}$ stereoisomeric resorcinarenes have been less studied as functional[2] and solid-state materials[3] relative to their all-*cis* crown ($C_{4v}$) or boat ($C_{2v}$) counterparts. Our current findings complement those of Böhmer et al. who described the only prior solid-state structures of an underivatized $C_{2h}$ resorcinarene.[7] The macrocycle used in their studies, a congener of **1** which contains tetraarylhydroxyl moieties rather than tetraarylboronic acids, was either completely solvated (when recrystallized from DMSO) or formed two pairs of intermacrocycle hydrogen bonds (when recrystallized from pyridine) mediated by pyridine, resulting in infinite

(1) Review: Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.
(2) Review: Timmerman, P.; Reinhoudt, D. N. *Tetrahedron* **1996**, *52*, 2263.

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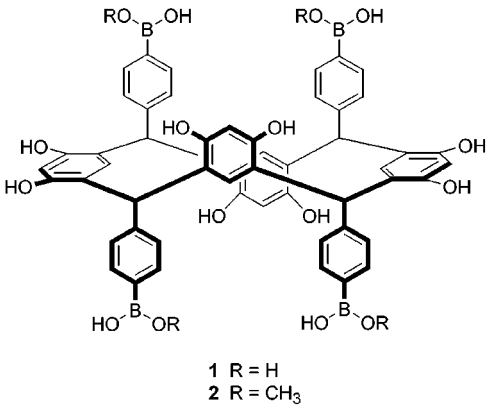


**Figure 1.** Compounds **1** and **2**.

columns wrapped by layers of solvent.[8] We find that **1** crystallizes from 9:1 MeOH:EtOH as the corresponding half methyl boronate ester **2**. This results in the formation of infinite, antiparallel two-dimensional hydrogen-bonded columns with a single macrocycle at the focal point. Each molecule participates in 12 hydrogen bonds with other macrocycles. The present study demonstrates that the incorporation of divergent hydrogen-bonding moieties in a single resorcinarene framework leads to unique architectures with enhanced intermacrocycle contacts.

A slow recrystallization of **1** from 9:1 MeOH:EtOH at room temperature for 7 days yielded colorless crystals of **2** of sufficient quality for X-ray structure analysis. The crystals survived for several minutes in ambient conditions. X-ray structure analysis at 150 K ($R = 0.084$) shows **2** to be a resorcinarene incorporating four half-phenylboronic acid/half-methyl boronate ester moieties. The molecule has crystallographic inversion symmetry and approximate $C_{2h}$ symmetry, with the chair conformation (Figure 2).

This is an example of a potential half-boronate ester prototype. Two opposite resorcinol rings of the macrocyclic framework are nearly coplanar with the resorcinarene best plane, and the two remaining resorcinol rings are almost perpendicular to this plane, with their hydroxyl groups pointing in opposite directions. Due to the presence of the crystallographic inversion center, the opposite resorcinol units are rigorously parallel. The C1−C6 resorcinol ring forms a dihedral angle of 89.0(1)° with the C8−C13 ring.

The phenylboronic acid moieties at the methylene bridges assume the axial position, with two units pointing up and two of them down, roughly perpendicular to the coplanar resorcinol units (dihedral angles 75.2(2) and 86.1(2)°). The phenyl rings of the phenylboronic moieties are not parallel, forming a dihedral angle of 40.0(1)°. No intramolecular hydrogen bonding exists; however, all potential donors are involved in intermolecular hydrogen bonds. Each molecule of **2** forms 18 intermolecular hydrogen bonds, including 12 to four other molecules of **2** and 6 to solvent molecules (Figure 3). Central macrocyclic unit **2** is hydrogen bonded about an inversion center to a unit of **2** (right side) via phenolic OH groups (O4- - -O2, 2.821 (4) Å) and also to the molecule of **2** on the left by the same interactions. The central macrocyclic unit **2** is connected to a third unit of **2** (top) via four phenolic/boronic acid interactions (O1- - -O5, 2.753(4) Å, O2- - -O7′, 2.698(4) Å, and their equivalents). A fourth unit of **2** (bottom) is connected to the central unit **2** by the same phenolic/boronic acid interactions (O1- - -O5 and O2- - -O7). Each molecule of **2** also donates two hydrogen bonds to solvent molecules via phenolic OH (O3- - -O 2.677 (5) Å) and four hydrogen bonds via B−OH units to solvent (O5- - -O 2.748(6), O7- - -O 2.669(5) Å).

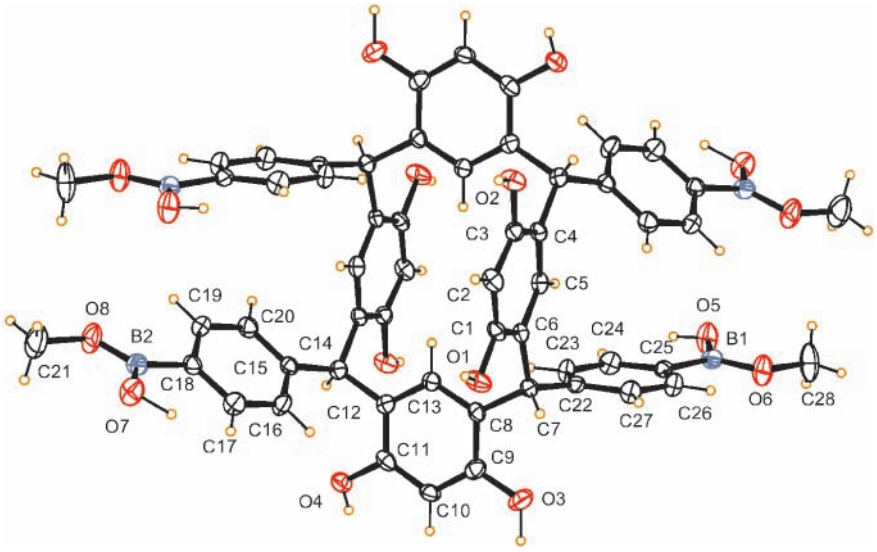


**Figure 2.** Conformation and numbering scheme for compound **2**. Oxygen atoms are in red and boron atoms are shown in blue.

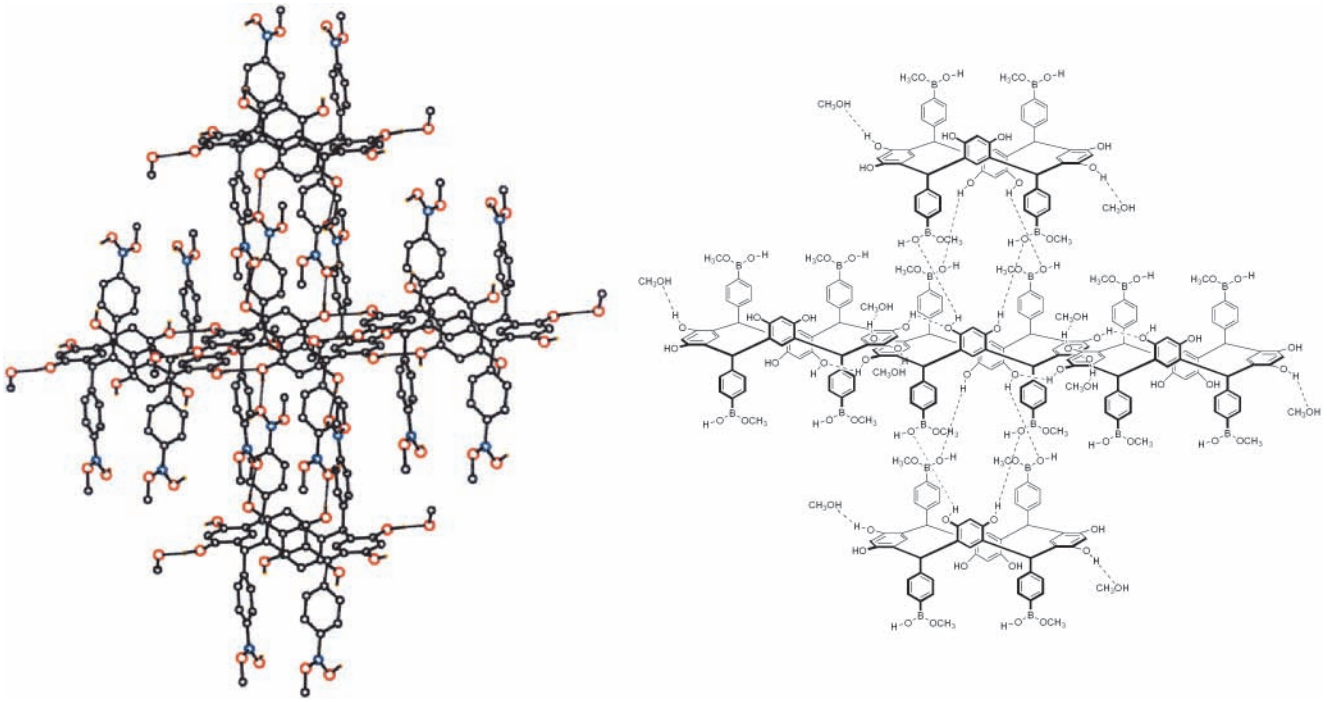

**Figure 3.** Hydrogen bonding in the unit cell of **2**. The macrocyclic units form a complex network of hydrogen bonds to each other and to solvent molecules. They extend infinitely in two dimensions.

Two other independent solvent molecules are disordered and do not hydrogen bond to **2**.

In conclusion, resorcinol/arylboronic acid macrocycles form unique hydrogen-bonded supramolecular arrays. These findings suggest a potential for using these compounds in designing and tailoring solid-state materials for molecular recognition and catalysis. Currently we are synthesizing and studying guest-bound supramolecular structures based on **1**, **2**, and congeners.

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**Supporting Information Available:** X-ray structural information for **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) Most of the prior work leading to solid-state architectures employing resorcinarenes with free resorcinol hydroxyl moieties involved crown ($C_{4v}$) or boat ($C_{2v}$) stereoisomeric macrocycles with appended alkyl rather than boronic acid or other divergent polar groups, for example: (a) MacGillivray, L. R.; Atwood, J. L. *Nature* **1997**, *369*, 469. (b) Murayama, K.; Aoki, K. *J. Chem. Soc., Chem. Commun.* **1997**, 119. (c) MacGillivray, L. R.; Atwood, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 6931. (d) Rose, K. N.; Barbour, L. J.; Orr, G. W.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1998**, 407. (e) Murayama, K.; Aoki, K. *J. Chem. Soc., Chem. Commun.* **1998**, 607. (f) MacGillivray, L. R.; Diamente, P. R.; Reid, J. L.; Ripmeester, J. A. *J. Chem. Soc., Chem. Commun.* **2000**, 359. (g) Shivanyuk, A.; Rissanen, K.; Kolehmainen, E. *J. Chem. Soc., Chem. Commun.* **2000**, 1107. (h) Zhang, Y.; Kim, C. D.; Coppens, P. J. *J. Chem. Soc., Chem. Commun.* **2000**, 2299.

(4) Lewis, P. T.; Davis, C. J.; Saraiva, M. C.; Treleaven, W. D.; McCarley, T. D.; Strongin, R. M. *J. Org. Chem.* **1997**, *62*, 6110.

(5) Lewis, P. T.; Strongin, R. M. *J. Org. Chem.* **1998**, *63*, 6065.

(6) (a) Davis, C. J.; Lewis, P. T.; McCarroll, M. E.; Read, M. W.; Cueto, R.; Strongin, R. M. *Org. Lett.* **1999**, *1*, 331. (b) Lewis, P. T.; Davis, C. J.; Cabell, L. A.; He, M.; Read, M. W.; McCarroll, M. E.; Strongin, R. M. *Org. Lett.* **2000**, *2*, 589.

(7) Shivanyuk, A.; Paulus, E. F.; Böhmer, V.; Vogt, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1301.

(8) Both MeOH and EtOH are involved in hydrogen bonding. It appears that each molecule accepts two hydrogen bonds from EtOH molecules (O3S- - -O1 2.742(13) Å), but we were not able to locate the EtOH hydroxyl hydrogen atom, and these interactions are not illustrated in Figure 3.