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Influence of Fluorination and Boronic Group Synergy on the Acidity and Structural Behavior of *o*-Phenylenediboronic Acids

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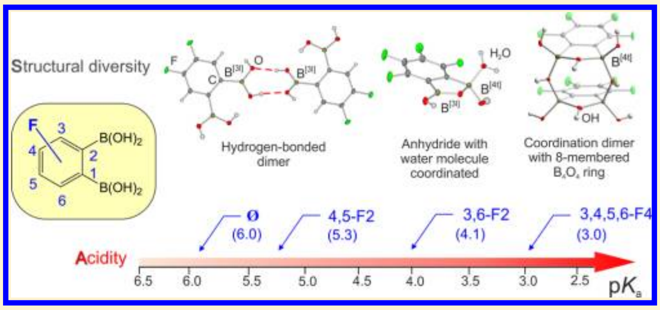
Supporting Information



ABSTRACT: The solid-state and solution structural properties and acidity of a series of fluorinated 1,2-phenylenediboronic acids were investigated. Solution NMR studies indicate that these compounds equilibrate with their dehydrated forms, in the simplest case presumably possessing the cyclic benzoxadiborole structure. Ab initio calculations showed that the stability of such cyclic semianhydrides is improved by fluorination of the aromatic ring and complexation of one of the boron centers with water. This was demonstrated by the crystal structure determination of tetrafluoro-1,2-phenylenediboronic acid. The coordinated water molecule participates in very strong intermolecular hydrogen bonding with the OH group bonded to the four-coordinate boron center ($d_{O\cdots O}$ = 2.423(2) Å, E_{int} = −87 kJ mol^{-1}). This indicates that in fact this compound is an oxonium, i.e., Brønsted acid, which is exceptional for boronic acids. Under different crystallization conditions, tetrafluoro-1,2-phenylenediboronic acid dimerizes by aggregation of boronic groups, which leads to the formation of an uncommon eight-membered B_4O_4 ring. Such a coordination dimer exists as the boat conformer, featuring $\pi-\pi$ interactions of fluorinated aromatic rings. The enhanced acidity of 1,2-phenylenediboronic acids can be rationalized in terms of a synergic effect of two adjacent boronic groups and is manifested by relatively low pK_a values ranging from 6.0 (1,2-phenylenediboronic acid) to only 3.0 for the perfluorinated derivative.

INTRODUCTION

Interest in arylboronic acids is stimulated by their increasing application in organic synthesis, medicine, materials science, and analytical chemistry.[1] Fluorinated boranes, due to their Lewis acidic properties, were used in the field of catalysis for organic transformations,[2] polymerization processes,[3] and chemical sensing.[4] In the case of 1,2-bifunctional diboranes the bidentate Lewis acid chelation effect from two boron-containing groups was crucial for catalytic (polymerization of olefins,[5] activation of group 4 metallocene dialkyls,[6] or reduction of CO_2 with H_2[7]) and F^-/CN^- anion sensing properties.[8] It was also shown that such compounds can chelate a variety of anions to form new classes of weakly coordinating anions.[5e,9] The related 9,10-dihydro-9,10-diboraanthracenes have found application in the fields of catalysis (bidentate Lewis acid for the activation of 1,2-diazines in the inverse-electron-demand Diels−Alder reaction,[10] chelate ditopic Lewis bases,[11] polymerization of olefins[12]), crystal engineering,[13] and materials chemistry (construction of semiconductors[14] and organic light emitting devices[15]).

Organoboron Lewis acidity should also be reflected by the solid-state properties of the compounds presented here. However, compounds bearing boron−oxygen bonds such as arylboronic acids are not strong Lewis acids, due to the so-called back-bonding effect, leading to the partial electronic saturation of the boron atom. Thus, unlike their aluminum counterparts, boron−oxygen compounds exist typically as monomers. A rare example is tetramethyldiboroxane $(Me_2B)_2O$, which dimerizes in the solid state by forming a four-membered B_2O_2 ring.[16] A useful method for tuning the Lewis acidity of arylboronic acids is fluorination of the aromatic ring. Fluorine atoms are structurally comparable to hydrogen atoms (similar atomic radii), and they do not participate in strong intermolecular interactions, although, weak contacts with fluorine atoms are very desirable in supramolecular chemistry.[17] This is often beneficial from the point of view of crystal engineering. Recently, we have shown that the boron atom in fluorinated 1,4-phenylenediboronic acids becomes a stronger Lewis acid, attracting more electronegative partners such as oxygen and fluorine atoms as well as π-electron density from aromatic rings, which affects molecular organization in the crystal.[18] To extend the chemistry in this area, we turned our attention to fluorinated 1,2-phenylenediboronic acids (Chart 1). In this paper we show that the specific structural behavior of these compounds in the solid state and solution is dictated by the superposition of two major factors: the vicinity of two boronic groups and the strong effect of fluorine substituents. This observation was also supported by theoretical calculations and additionally discussed in terms of varying the acidity of the

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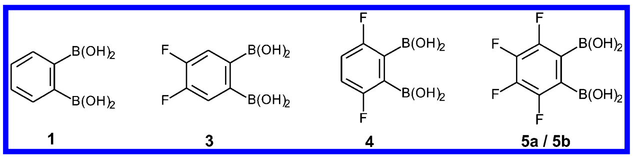
Chart 1. Studied 1,2-Phenylenediboronic Acids



studied compounds, which was evaluated using experimental pK_a measurements.

RESULTS AND DISCUSSION

Synthesis. 1,2-Phenylenediboronic acid (**1**)[19] and its perfluorinated analogue **5**[20] were synthesized according to published procedures. 4,5-Difluoro-1,2-phenylenediboronic acid (**3**) was synthesized by protecting 2-bromo-4,5-difluorophenylboronic acid with *N*-butyldiethanolamine (BDEA) to give 2-(2′-bromo-4′,5′-difluorophenyl)-6-butyl[1,3,6,2]-dioxazaborocan (**2a**). This kind of protection of the $B(OH)_2$ group was used previously for the generation of various aromatic[21] and heteroaromatic boron−lithium reagents.[15d,22] Thus, **2a** was subjected to Br/Li exchange in the mixed solvent Et_2O/THF, resulting in the intermediate **2a-Li.** The reaction was performed at low temperature (−90 °C) to avoid the risk of degradation or isomerization of **2a-Li** due to the basicity-gradient driven migration of lithium to one of the positions ortho to fluorine atoms. Finally, **2a-Li** was treated with $B(OMe)_3$. The synthesis of the 3,6-difluoro derivative **4** started from 1,4-difluoro-2-iodobenzene. It was subjected to lithiation/silylation, and the intermediate arylsilane was ipso-iododesilylated with ICl to give 1,4-difluoro-2,3-diiodobenzene (**2c**). The key step was accomplished by a double iodine/lithium exchange reaction using an excess of *n*-BuLi at low temperature (−110 °C), as it was suspected that at higher temperatures the dilithio intermediate may readily decompose via an aryne mechanism or undergo coupling with the byproduct *n*-BuI. Subsequent boronation with $B(OMe)_3$ and quench with ethereal HCl afforded diboronate **2d**. Free acids **3** and **4** were obtained by the aqueous hydrolysis of the corresponding 1,2-phenylenediboronate precursors. It should noted that the obtained 1,2-phenylenediboronic acids are readily soluble in water, which should be taken into account during their isolation. All reactions are shown in Scheme 1.

Crystal Structure Description. The asymmetric part of the unit cell of **3** comprises the two independent molecules **3-A** and **3-B** (Figure 1a), whose geometrical parameters differ only marginally. They are linked via dimeric $B(OH)_2\cdots{}_2(HO)B$

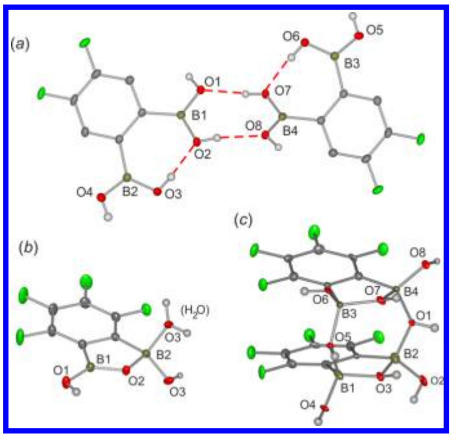
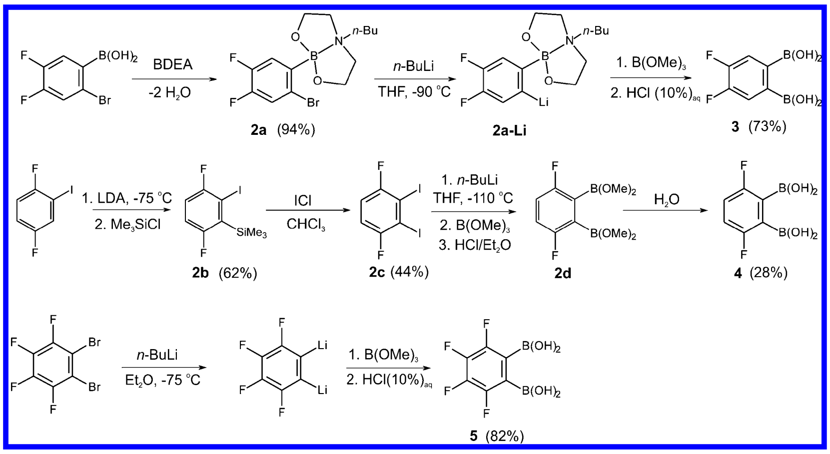


Figure 1. Molecular structures of (a) **3**, (b) **5a**, and (c) **5b** together with atom-labeling schemes. Thermal ellipsoids were generated at the 50% level of probability. Hydrogen bonds are shown as red dashed lines. Selected bond distances (Å) and angles (deg) for **3**: C(1)−B(1) = 1.579(2), C(2)−B(2) = 1.582(2), C(7)−B(3) = 1.583(2), C(8)−B(4) = 1.588(2), B(1)−O(1) = 1.371(2), B(1)−O(2) = 1.364(2), B(2)−O(3) = 1.370(2), B(2)−O(4) = 1.366(2), B(3)−O(5) = 1.364(2), B(3)−O(6) = 1.373(2), B(4)−O(7) = 1.373(2), B(4)−O(8) = 1.353(2); C(1)−C(2)−B(1) = 124.9(1), C(2)−C(1)−B(2) = 125.5(1), C(8)−C(7)−B(3) = 127.0(1), C(7)−C(8)−B(4) = 127.9(1), C(6)−C(1)−B(1)−O(1) = 27.3(1), C(3)−C(2)−B(2)−O(4) = −45.1(1), C(12)−C(7)−B(3)−O(5) = 23.5(1), C(9)−C(8)−B(4)−O(8) = −10.8(1). Selected bond distances (Å) and angles (deg) for **5a**: C(1)−B(1) = 1.572(2), C(2)−B(2) = 1.628(1), B(1)−O(1) = 1.353(1), B(1)−O(2) = 1.372(1), B(2)−O(2) = 1.491(1), B(2)−O(3) = 1.492(1), B(2)−O(4) = 1.452(1); C(6)−C(1)−B(1) = 136.7(1), C(3)−C(2)−B(2) = 133.1(1), C(1)−B(1)−O(2) = 109.8(1), C(2)−B(2)−O(2) = 103.3(1), B(1)−O(2)−B(2) = 112.1(1), C(1)−B(1)−O(1) = 125.9(1), C(2)−B(2)−O(3) = 109.2(1), C(2)−B(2)−O(4) = 118.4(1). Selected bond distances (Å) and angles (deg) for **5b**: C(1)−B(1) = 1.58(2), C(2)−B(2) = 1.62(1), C(7)−B(3) = 1.61(1), C(8)−B(4) = 1.60(1), B(1)−O(1) = 1.45(1), B(1)−O(2) = 1.53(1), B(1)−O(4) = 1.50(1), B(2)−O(3) = 1.44(1), B(2)−O(5) = 1.47(1), B(2)−O(2) = 1.54(1), B(2)−O(4) = 1.366(2), B(3)−O(4) = 1.53(1), B(3)−O(6) = 1.44(1), B(3)−O(7) = 1.57(1), B(4)−O(7) = 1.52(1), B(4)−O(8) = 1.41(1), B(4)−O(5) = 1.52(1); B(1)−O(2)−B(2) = 116.1(7), B(2)−O(5)−B(4) = 130.5(7), B(4)−O(7)−B(3) = 116.1(7), B(3)−O(4)−B(1) = 127.9(7).

Scheme 1. Synthesis of Fluorinated 1,2-Phenylenediboronic Acids



hydrogen-bonded interactions, forming [010] chains (Figure 2a) typical of diboronic acids.[23] The geometrical parameters of hydrogen bonds are given in Table S2 in Supporting Information. The chains are linked by lateral H bonds derived from molecules **3-A**, resulting in a double-chain motif. The further propagation of these motifs into 2D layers is hampered, as molecules **3-B** participate in H-bonding interactions with acetone molecules, which resembles the situation observed for 1,2-ethynediylbis(4,1-phenylene)diboronic acid solvated with THF molecules.[24]

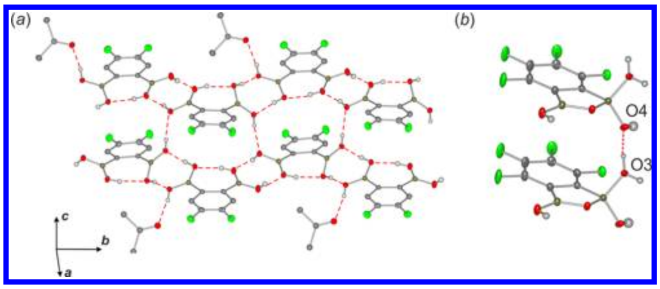


Figure 2. Hydrogen-bonded motifs in (a) **3** and (b) **5a**. Hydrogen bonds are shown as red dashed lines.

Tetrafluoro-1,2-phenylenediboronic acid crystallizes in two completely different forms. The first one is the semianhydride **5a** with one water molecule coordinated to one of the boron atoms (Figure 1b). It crystallized from the aqueous solution. One of the boron atoms in **5a** is three-coordinate (B1) and the other is four-coordinate (B2). The geometry of the three-coordinate boron atom is flat with a C1−B1−O2 endocyclic angle close to 110° and C1−B1−O1 and O1−B1−O1 angles both close to 125°. The geometry of the four-coordinate boron atom is tetrahedral, and all B−O bonds are of a comparable length. It should be noted that the formally dative B(2)−O(3) bond length in **5a** is much shorter in comparison to the values found for the analogous distance in the crystal structures comprising molecules of the related species $(C_6F_5)_3BOH_2$ (1.55−1.63 Å).[25] Hence, it seems that the molecular structure of **5a** can be properly interpreted as the oxonium acid—a cyclic tautomer of the classical open form of **5**, which would possess two $B(OH)_2$ groups, as observed for acids **1**[19] and **3**. The tautomerization would involve the formation of the B−O bond due to the strong donor−acceptor interaction of the Lewis acidic B atom with the O atom of the neighboring $B(OH)_2$ followed by proton transfer to one of the O atoms bonded to the tetracoordinate B atom. It should be noted that the related heterocyclic systems featuring the B−(*μ*-OR)−B moiety (R = H, Me) were isolated as products of hydrolysis or alcoholysis of perfluorinated diborane (o-$C_6F_4[9\text{-}BC_{12}F_8]_2$).[5d] Another notable example constitutes 1*H*,3*H*-naphth[1,8-*cd*][1,2,6]-oxadiborin,[26] which is an anhydride of 1,8-naphthalenediboronic acid featuring a six-membered heterocyclic ring with a B−O−B moiety. The O(3)−H(3B)···O(4) H bond with the very short intermolecular contact of $d_{O\cdots O}$ = 2.423(2) Å occurs between the coordinated water molecule (proton donor) and the OH group bonded to the four-coordinate boron center of the adjacent molecule. This distance is close to the lower limit observed for strong anion-supported H bonds in adducts formed by the strong Brønsted acid $(C_6F_5)_3BOH_2$ and its conjugated base $(C_6F_5)_3BOH^-$, as the corresponding O···O contacts vary in the range 2.40−2.52 Å, depending on the given crystal structure.[27] The short H bridge in **5a** is in fact close to the symmetrical one, as the O(3)−H(3B) bond is significantly lengthened (d_{O-H} = 1.01(1) Å) while the H(3B)···O(4) contact is very short ($d_{H\cdots O}$ = 1.42(1) Å). The position of the H(3B) proton was visible on the difference density map and was refined without any constraints (Figure S2a in the Supporting Information). The calculated energy profile (MP2[28]/6-31g(d,p)[29] level of theory) for linear proton motion across the O(3)−H(3B)···O(4) hydrogen bond gives one broad minimum (Figure S2b in the Supporting Information). Presumably, the H(3B) proton can easily migrate from one oxygen to another, which is characteristic for very strong H bonds.[30] The estimated interaction energy of this H bond is very high at −87 kJ mol^{-1}. This also indicates that **5a** can effectively act as a Brønsted acid, which should readily lose the proton in solution to give the corresponding anionic species. This is not common for boronic acids, which are generally weak Lewis acids accepting OH^- anions to a small extent by the heterolytic cleavage of water molecules.[31] A notable exception is the cyclic hemiester of 2′-hydroxybiphenyl-2-boronic acid, where the proton abstraction is favored, as it retains the aromaticity of the boraheterocycle.[32] Weaker H-bonding interactions link molecules of **5a** to form hydrogen-bonded dimers resembling the structural motif typical of benzoxaboroles.[33] Within this motif the endocyclic oxygen atoms (O2) act as acceptors, whereas external OH groups bonded to the three-coordinate boron center are donors of H bonding (O1−H1···O2). Under different crystallization conditions (slow evaporation of 1/2 acetone/toluene solution), the process of aggregation of boronic groups in **5** goes further, involving two molecules and leading to the formation of the unique eight-membered B_4O_4 ring (Figure 1c). Thus, the aggregation in **5b** is not based on H bonding but, primarily, on Lewis acid−base interactions between boron and oxygen atoms. It should be noted that the only other reported example of a structure comprising the related B_4O_4 ring is a tetramer resulting from the self-assembly of the initially formed 4-fluoro-1,3-dimethoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborole.[34]

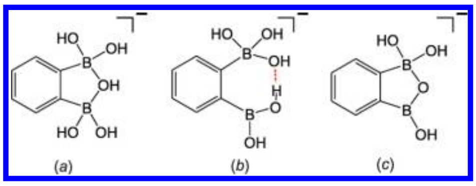
In the molecular structure of **5b**, all four boron atoms are four-coordinate, linked with four bridging hydroxyl groups. The B−O bond lengths within the eight-membered boron−oxygen skeleton show a wide range of lengths (d_{B-O} = 1.47−1.54 Å) and are slightly shorter between monomers in comparison to those within the same monomeric unit. For comparison, the B−O bond distances in previously reported compounds possessing the B−(*μ*−OH)−B moiety also fall in the range 1.47−1.54 Å.[35] As expected, bond distances between boron atoms and the corresponding terminal OH groups are shorter, ranging from 1.41 to 1.46 Å. The molecule **5b** features a boat conformation, which means that the aromatic rings are located above each another. The interplanar angle between aromatic ring planes is equal to 14.4°, and the distance between centroids of the two rings is 3.42(1) Å, which indicates a weak *π*−*π* stacking interaction. It seems that the strength of this intramolecular interaction depends on the number of fluorine substituents. According to the computations, the hypothetical chair conformer (see Computational Studies) is less stable than the boat form by about 60 kJ mol^{-1}. However, when the number of fluorine substituents decreases, these differences are less pronounced and, for the nonfluorinated derivative **1**, both hypothetical forms, i.e., chair and boat, have comparable stabilities.

Acidity of *o*-Phenylenediboronic Acids. To quantitatively describe the cooperative effect of two adjacent boronic groups and the additional influence of fluorination on the acidity, we have measured the pK_a values of all studied 1,2-phenylenediboronic acids. We have also compared them with those obtained for phenylboronic (PhBA), 1,4-phenylenediboronic (1,4-dBA), and thiophene-2,3-diboronic acids (2,3-ThdBA) (Table 1). The measurements were done by a potentiometric titration with 0.1 M aqueous NaOH in H_2O/MeOH (1/1) or by conductometry in the case of **4** and **5**. For **1** and **3**, pK_a values were estimated to be 6.0 and 5.3, respectively, which means that these compounds are significantly stronger acids than phenylboronic acid and its many functionalized derivatives, where typical pK_a values are about 9.[36] The pK_a value for 1,4-phenylenediboronic acid (1,4-dBA) is 7.9; i.e., it is a much weaker acid than the isomeric compound **1**. The stronger acidity of **1** can be attributed to the increased stabilization of its anion resulting from the proximity of two boronic groups. However, the rationale for this stabilization remains debatable, as it depends on the structural formulation of the anionic form of **1**. Proposed structures can include the symmetrical arrangement with the bridging OH^- binded simultaneously to two boron atoms (Chart 2a), the unsymmetrical form, where neutral $B(OH)_2$ and the anionic $B(OH)_3^-$ are linked by an intramolecular H-bond (Chart 2b), and the cyclic semianhydride complexed with OH^- (Chart 2c). The stability of all these forms was confirmed by theoretical calculations (see the Supporting Information). The vicinity of two boronic groups apparently accounts for the acidity of thiophene-2,3-diboronic acid (pK_a = 7.0). However, in this case the anion stabilization is less effective in comparison to that for **1**. This can be simply understood by considering that two Lewis acidic boron atoms are more separated in thiophene-2,3-diboronic acid than in **1** (by ca. 0.15 Å according to X-ray structure measurements).[19,22] This is due to a wider angle between the two B−C vectors in the former compound. For compound **4**, pK_a = 4.1, i.e., it is stronger acid than the parent compound **1** and also the isomeric derivative **3**, which reflects the potent acidifying effect of two fluoro substituents at the position ortho to two boronic groups. For compound **5**, pK_a = 3.0, which makes it the most acidic boronic acid known to date, with an acidity comparable to that of a related aromatic dicarboxylic acid: namely, phthalic acid (pK_{a1} = 2.9).[37] It should be noted that the differential titration curve for **3** shows a distinct maximum close to the expected half-neutralization point. This means that the pK_a obtained for this compound is rather a rough approximation and may not correspond to the behavior of **3** in solution. We suppose that this may be due to the formation of a fairly stable 1:1 adduct between the anionic and neutral forms of **3**. The details concerning the pK_a value estimations are given in the Supporting Information.

Table 1. pK_a Values of Studied Boronic Acids

	PhBA[36]	1,4-dBA	2,3-ThdBA	**1**	**3**	**4**	**5**
pK_a	9.0	7.9	7.0	6.0	5.3	4.1	3.0

Chart 2. Proposed Structures of 1,2-Phenylenediboronate Anions



Solution NMR Studies. In our recent study on the structure of 1,2-phenylenediboronic acid (**1**), we have concluded that this compound undergoes partial dehydration when dissolved in deuterated acetone, THF, or DMSO.[38] The respective ^{1}H NMR spectra indicate the formation of additional species. For instance, in acetone-d_6 signals of **1** (a sample was obtained by dissolving the crystalline dihydrate) appear at 7.88 and 7.36 ppm. The less abundant component (ca. 50% in comparison to **1**) features resonances of aromatic protons at 7.69 and 7.44 ppm and a strongly deshielded broadened singlet at 8.73 ppm, which can be assigned to the OH group. The addition of D_2O to solutions of **1** resulted in the simplification of the spectra, showing only resonances of **1** irrespective of the kind of deuterated solvent used. The ^{11}B NMR spectrum of **1** in acetone-d_6 comprises the signal at 34 ppm partially overlapping with the major peak at 30 ppm. The former peak can be assigned to a dehydrated form of **1**, as it disappears after addition of D_2O. On the basis of these observations, we proposed that in solution **1** coexists in equilibrium with its cyclic semianhydride form, possessing the structure of benzoxadiborole and featuring an increased ^{11}B NMR chemical shift with respect to that of **1** (Table 2). In addition, the ^{1}H NMR spectrum of crystalline anhydrous **1** in acetone-d_6 showed that the proportions of **1** and its dehydrated form are comparable. However, additional signals are observed at 8.12 and 7.53 ppm. They become much stronger when a sample of **1** was subjected to dehydration in vacuo at 100 °C. This indicates that additional dehydration processes occur already in solutions of anhydrous acid **1**.

The results obtained for **1** have prompted us to study the solution behavior of its fluorinated analogues **3**−**5**. The ^{1}H NMR spectrum of **3** in acetone-d_6 exhibits a broad resonance at 7.72 ppm as a major signal. In the ^{19}F NMR spectrum, the major broadened signal at −139.0 ppm is accompanied by a set of four smaller broad resonances in the range −140 to −135

Table 2. Summary of ^{11}B NMR Data for Studied Systems

	^{11}B chem shift (ppm)					
compd	acetone-d_6	acetone-d_6 + D_2O	D_2O	D_2O + K_2CO_3[b]	D_2O + NaOH[c]	D_2O + NaOH[d]
1[a]	34.0, 29.7 (20:80)[e]	29.9	30.1	18.0, 7.6 (50:50)	7.8, 1.5 (85:15)	9.0, 1.8 (80:20)
3	28.9	28.6	32.9	17.8, 6.5 (85:15)	10.1, 5,6 (85:15)	8.7, 4,6 (60:40)
4	28.6	28.5	27.5	16.6, 6.8 (90:10)	9.7, 5.6 (85:15)	8.7, 4.6 (70:30)
5	23.7, 16.3, 2.3 (20:20:60)	23.5, 16.4, 2.2 (30:30:40)	23.4	13.8, 6.9 (60:40)	9.3, 5.6 (85:15)	9.2, 5.4 (5:95)

[a] See ref 19. [b] 0.05 M solutions of **1** and **3**−**5** in 0.15 M K_2CO_3/D_2O. [c] 0.05 M solutions in 0.10 M NaOH/D_2O. [d] 0.05 M solutions in 0.30 M NaOH/D_2O. [e] Approximate integral ratios are given in parentheses; however, they may not represent the relative proportions of species due to strongly varying peak half-widths.

ppm. The ^{13}C NMR spectrum also features broadened signals. However, at lower temperatures (below 0 °C) a well-resolved triplet at 7.72 ppm and other minor resonances in the range 7.8−7.4 ppm appear in the ^{1}H NMR spectrum of **3**. This is also reflected by significant changes in the VT ^{19}F NMR spectra recorded in the range +25 to −30 °C. On the basis of the results obtained previously for **1**,[19] the distinctive labile behavior of **3** can be attributed to the equilibrium with its dehydrated forms. This is supported by the fact that the ^{1}H and ^{19}F NMR spectra of a solution of **3** in wet acetone-d_6 (i.e., containing a drop of D_2O) exhibit triplets instead of the aforementioned broad resonances. The dehydration could be simply interpreted as the formation of a cyclic semianhydride, but an analysis of the spectra (e.g., the number of peaks in the ^{19}F NMR spectra) indicates that the situation is more complicated, presumably due to other processes involving aggregation of dehydrated forms of **3**. However, the observed processes are not reflected by the ^{11}B NMR spectrum, which shows only one signal in the range typical of a three-coordinate boron atom in arylboronic acids[39] (Table 2).

The ^{1}H NMR analysis of **4** indicates that this acid is also labile in acetone-d_6 but gives a well-resolved multiplet at 6.84 ppm in D_2O. Thus, it seems that **4** also undergoes reversible dehydration, in acetone. As found for **3**, the ^{11}B NMR spectrum in acetone-d_6 is not a good probe of the observed equilibrium and shows only a single resonance at 28.6 ppm. For **5**, the situation was more complicated, as the NMR spectra strongly differ depending on the solvent used. Thus, the ^{19}F NMR of a sample of **5** in acetone-d_6 shows two complex sets of signals at −130 to −138 ppm and −153 to −163 ppm. However, in D_2O one observes only two relatively narrow resonances (albeit still lacking the multiplet structure resulting from expected F−F couplings) at −136.8 and −156.8 ppm. Accordingly the ^{11}B NMR spectrum in acetone-d_6 shows three signals at 23.7, 16.3, and 2.3 ppm. We suppose that this may be due to the occurrence of species bearing a tetracoordinate boron atom such as the cyclic tautomer **5a** or the dimeric species **5b**, which should clearly give rise to an upfield shift (with respect to the classical form of boronic acid). In contrast, a solution of **5** in D_2O shows one signal at 23 ppm. A significant upfield shift with respect to the values typical of arylboronic acids (ca. 30 ppm) may suggest coordination of water to the boron atoms, as observed in the crystal structure of **5a**. However, two separate resonances expected for three- and four-coordinate boron atoms in **5a** are averaged for the solution spectrum. Thus, it is clear that **5** is fluxional in D_2O. The situation is complicated by the low pK_a of **5** consistent with a significant ionization in D_2O, which results in the formation of its anionic form, presumably by proton abstraction from the coordinated water molecule (see structure c in Chart 2). Interestingly, upon addition of 1 drop of concentrated aqueous HCl two broad resonances at 20 and 13 ppm of approximately equal intensities appear, which may suggest that some aggregation of **5** occurs under these conditions.

Further work was performed to study the behavior of acids **3**−**5** under aqueous alkaline conditions. Approximately 0.05 M solutions in 0.1 M NaOH/D_2O were studied by ^{11}B NMR spectroscopy. In all cases we observed the major broad resonance at ca. 9−10 ppm accompanied by a smaller but more narrow peak at ca. 5−6 ppm (Table 2). When the concentration of base is higher (0.3 M), the former resonance becomes less abundant and almost disappears for **5**. We suppose that it can be assigned to a monoanionic form possessing one of the structures proposed in Chart 2. The second peak can be attributed to the dianionic form 1,2-$Ph[B(OH)_3^-]_2$, which is in agreement with the ^{11}B NMR chemical shift of the $PhB(OH)_3^-$ anion in D_2O (2.9 ppm). It should be noted that the proportions of mono- vs dianionic species depend on the base concentration but even in the presence of a large excess of base the dianion is not formed quantitatively. When K_2CO_3 was used as the base, the ^{11}B NMR spectra of **3** and **4** showed a broad resonance at ca. 17 ppm and a less intense and more narrow peak at ca. 7 ppm. In the case of **5** one observes two peaks possessing comparable intensities at 13 and 7 ppm. These results may point to the formation of complexes of acids **3**−**5** with carbonate anion. It should be noted that, despite the presence of two anionic forms in solution, the ^{1}H NMR spectra of **3** and **4** show only one signal with a well-resolved multiplet structure. On the other hand, the broad ^{19}F NMR resonance of **3** indicates that some dynamic process still persists. In the case of **3** the triplet at 7.22 ppm observed in D_2O is shifted to 7.06 ppm in K_2CO_3/D_2O and 7.02 ppm in NaOH/D_2O. For **4**, the triplet at 6.84 ppm in D_2O is shifted to 6.65 ppm in K_2CO_3/D_2O and 6.46 ppm in NaOH/D_2O. The different values of ^{1}H NMR chemical shifts point again to a different nature of boronate anions generated upon addition of hydroxide vs carbonate anion.

Computational Studies. In order to get more information about the relative stability of different conformers of diboronic acids and their dimers and anhydrides, we performed ab initio calculations at the MP2[28] level of theory with a 6-31G(d,p)[29] basis set using Gaussian09.[40] To get more details about the role of the fluorination on the formation of cyclic semianhydrides and coordination dimers, all appropriate species derived from **1** and **3**−**5** were studied. The studied transfomations are depicted in Figure 3, and the results of appropriate calculations are given in Table 3. The theoretical calculation on single molecules of **1** and **3**−**5** revealed that *o*-diboronic acid displays two stable conformations. The basic form found in the crystal structures of **1** and **3** is stabilized by an intramolecular H bond. In the second form, the boronic groups are significantly twisted along the B−C bonds and a B···O dative interaction between them occurs. The O−H···O conformer for **1** and **3** is more stable by $\Delta E_c \approx 15$ kJ mol^{-1}, but electron-withdrawing fluoro substituents in the positions ortho to boronic groups increase the boron Lewis acidity, which results in the relative stabilization of the B···O conformer. Thus, for derivatives **4** and **5** both forms have similar stability. One can expect that the occurrence of a B···O conformation should facilitate the formation of an oxadiborole heterocycle featuring the B−O−

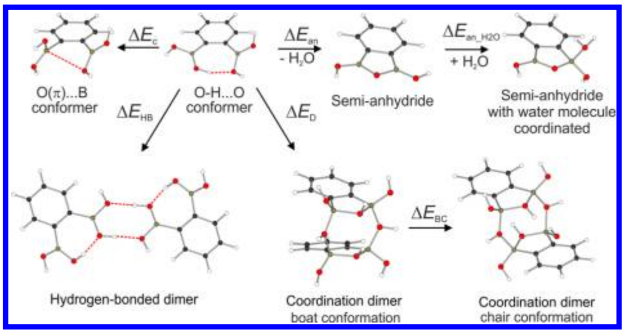


Figure 3. Schematic representation of equilibria between various forms of *o*-phenylenediboronic acids.

Table 3. Results of Quantum-Chemical Calculations at the MP2/6-31G(d,p) Level of Theory[a]

	ΔE_c	ΔE_{an}	ΔE_{an_H2O}	ΔE_{HB}[b]	ΔE_D[b]	ΔE_{BC}
1	16.6	50.1	14.2	−49.3	43.4	4.6
3	15.4	56.8	10.9	−48.4	44.5	1.7
4	−1.2	43.9	−9.7	−51.0	−13.9	48.0
5	−2.3	37.0	−15.5	−53.0	−33.4	65.9

[a] All energy values are given in kJ mol^{-1}. Definitions: ΔE_c = energy difference between H-bonded and B···O-bonded conformers of monomeric diboronic acids; ΔE_{an} = dehydration energy; ΔE_{an_H2O} = energy of the coordination of water molecule to semianhydride; ΔE_{HB} = energy of the formation of the hydrogen-bonded dimer; ΔE_D = energy of the formation of the coordination dimer; ΔE_{BC} = energy difference between boat and chair conformations of the coordination dimer. [b] Energy of the formation of a dimer from two monomeric molecules.

B linkage. Nevertheless, the dehydration process is energetically disfavored, as evidenced by positive ΔE_{an} values (Table 3). However, in the case of **4** and **5**, the coordination of H_2O to one of the boron atoms in oxadiborole is energetically favorable (negative ΔE_{an_H2O} values for these two compounds). It is notable that a significant stabilization through Lewis base coordination was also observed for the boroxine complexes, where N-donor ligands, such as pyridine, facilitate the trimerization of arylboronic acids under mild conditions.[41] However, as already mentioned, the formation of the structure of oxonium acid occurs rather through cyclic tautomerization of the classical open form of diboronic acid than by the simple coordination of water molecules to one of the boron center.

We have also performed ab initio calculations on coordination dimers possessing either a boat conformation similar to that of **5b** or the hypothetical chair structure and referenced the results to the energy of independent molecules and H-bonded dimers. It appears that the coordination dimers (in both conformations) are much less stable than classical H-bonded forms and, for molecules **1** and **3**, are even less stable than two noninteracting independent molecules of 1,2-diboronic acid. As observed for semianhydrides, fluorine substituents in the ortho positions significantly increase the stabilities of coordination dimers, as for **5** the energy difference between the dimer **5b** and the classical H-bonded form does not exceed 20 kJ mol^{-1}. We also suppose that the stability of the coordination dimer is strongly enhanced by the crystal field. It is notable that crystals composed of the monomeric species **5a** were obtained by crystallization from water, while the structure **5b** came from acetone/toluene (1/2). However, the crystallization mechanism and the role of the solvent are still unclear. The chair conformation is unstable for the **4** and **5** derivatives (positive ΔE_{BC} values), which may suggest the contribution of $\pi-\pi$ stacking interactions of aromatic rings to the stabilization of the boat conformer.

CONCLUSIONS

The relatively high acidity of *o*-phenylenediboronic acids is due to the proximity of two boronic acid groups. Hence, they can be regarded as bidentate Lewis acids and their acidity increases continuously in the order **1** < **3** < **4** < **5**, reaching the upper limit for boronic acids (for **5** pK_a = 3.0). Regarding solution NMR studies, it should be stressed that the spectra of **1** and **3**−**5** vary significantly depending on the water content in a sample. This is consistent with the nature of the observed labile behavior of studied compounds. It is based on their reversible dehydration, presumably resulting in the formation of cyclic semianhydrides and other species. Quantum chemical calculations show that the dehydration process is rather disfavored, but the formed semianhydride is stabilized by a coordinated water molecule. This was confirmed by the X-ray structure of **5a**, which can be described as a semianhydride with a water molecule coordinated to one of the boron atoms. The very strong hydrogen bond between the coordinated water molecule and the OH group bonded to the four-coordinate boron center ($d_{O\cdots O}$ = 2.423(2) Å, E_{int} = 87 kJ mol^{-1}) together with the low pK_a value and high proton mobility across the O3−H3···O4 bond indicate that **5** can act effectively as a Brønsted oxonium acid which readily loses a proton to give the corresponding anionic species. The enhanced Lewis acidic properties of boron atoms in **5** are also responsible for the formation of the unique dimeric self-aggregate featuring a rare eight-membered B_4O_4 ring stabilized by the intramolecular $\pi-\pi$ interaction of two aryl rings. Unlike the case for **5**, the molecular structure of **3** is typical of boronic acids and similar to that observed in **1**, as it features two $B(OH)_2$ groups linked by an intramolecular O−H···O bond. This indicates that two fluorine atoms remote from both boronic groups are not sufficient to affect any significant structural changes, as the Lewis acidity of the boron atoms in **3** is only slightly higher than that in **1**. An extension to this work currently in progress in our laboratory is the utilization of *o*-phenylenediboronic acids as effective Lewis acid catalysts in selected organic transformations.

EXPERIMENTAL SECTION

General Comments. All reactions involving air- and moisture-sensitive reagents were carried out under an argon atmosphere. Organic solvents were stored over sodium wire before use. Key reagents, including 2-bromo-4,5-difluorophenylboronic acid, 1,4-difluoro-2-iodobenzene, 1,2-dibromotetrafluorobenzene, *n*-BuLi (10 M solution in hexanes), trimethyl borate, *N*-butyldiethanolamine, diisopropylamine, chlorotrimethylsilane, and iodine chloride, were received from Aldrich and used without additional purification. Phenylboronic acid and 1,4-phenylenediboronic acid were also received from Aldrich. Thiophene-2,3-diboronic acid,[22] 1,2-phenylenediboronic acid,[19] and tetrafluoro-1,2-phenylenediboronic acid[20] were obtained according to the literature procedures.

The NMR chemical shifts are given relative to TMS using known chemical shifts of residual proton (^{1}H) or carbon (^{13}C) solvent resonances. In the ^{13}C NMR spectra the resonances of boron-bound carbon atoms were not observed in most cases due to their broadening caused by partially relaxed B−C couplings. ^{19}F NMR chemical shifts are given relative to $Et_2O{\cdot}BF_3$ and $CFCl_3$, respectively.

Synthesis. *2-(2′-Bromo-4′,5′-difluorophenyl)-6-butyl[1,3,6,2]-dioxazaborocan (**2a**).* A mixture of 2-bromo-4,5-difluorophenylboronic acid (11.9 g, 0.05 mol), *N*-butyldiethanolamine (8.5 g, 0.052 mol), anhydrous $MgSO_4$ (5 g), and acetone (50 mL) was stirred for 1 h at 35 °C. The mixture was filtered and concentrated under reduced pressure. To the remaining solid residue was added hexane (25 mL) followed by filtration of the resultant slurry. The crystalline product was washed with hexane (2 × 20 mL) and dried in vacuo at 50 °C to give the title compound. Yield: 17.0 g (94%). Mp: 115−117 °C. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.62 (dd, *J* = 11.0, 10.0 Hz, 1 H, Ph), 7.32 (dd, *J* = 9.5, 7.0 Hz, 1 H, Ph), 4.19−4.10 (m, 4 H, CH_2O), 3.32−3.24 (m, 2 H, CH_2N), 3.04−3.11 (m, 2 H, CH_2N), 2.63−2.58 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.62−1.52 (m, 2 H, $NCH_2\mathit{CH_2}CH_2CH_3$), 1.27−1.16 (m, 2 H, $NCH_2CH_2\mathit{CH_2}CH_3$), 0.87 (t, *J* = 7.0 Hz, 3 H, $NCH_2CH_2CH_2\mathit{CH_3}$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 149.7 (dd, *J* = 250.0, 10.5 Hz), 148.5 (dd, J = 247.0 Hz, 11.0 Hz), 129.3 (dd, *J* = 19.0 Hz, 4.0 Hz), 121.2, 115.1 (dd, *J* = 19.0, 4.0 Hz), 63.1, 59.8, 57.4, 26.8, 20.0, 13.7 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ 12.1

ppm. Anal. Calcd for $C_{14}H_{18}BBrF_2NO_2$ (362.02): C, 46.45; H, 5.29; N, 3.87. Found: C, 46.31; H, 5.39; N, 3.80.

*4,5-Difluoro-1,2-phenylenediboronic Acid (**3**).* A solution of **2** (9.05 g, 0.025 mol) in 1/2 THF/Et_2O (50 mL) was added to a previously prepared solution of *n*-BuLi (10 M solution in hexane, 2.60 mL, 0.026 mol) in Et_2O (80 mL) at −90 °C. The lithiated intermediate precipitated gradually to give a brown slurry. It was stirred for ca. 30 min at −90 °C followed by the dropwise addition of $B(OMe)_3$ (3.2 mL, 0.026 mol). The mixture was stirred for ca. 30 min at −75 °C and hydrolyzed with 10 wt % aqueous HCl (30 mL). The water phase was separated, followed by extraction with Et_2O (2 × 15 mL). The extracts were added to the organic phase, which was concentrated under reduced pressure. The solid residue was filtered and washed with toluene (5 mL) and hexane (5 mL). Drying in vacuo afforded the title compound as a white powder, which was recrystallized from toluene. Yield: 3.67 g (73%). Mp: 123−125 °C. ^{1}H NMR (acetone-d_6, 499.9 MHz): δ 7.67 (broad, 2H, Ph) ppm. ^{1}H NMR (acetone-d_6 + D_2O, 400.1 MHz) δ 7.71 (t, J = 10.5 Hz, 2H, Ph) ppm. ^{1}H NMR (D_2O, 400.1 MHz): δ 7.22 (t, J = 10.0 Hz, 2H, Ph) ppm. ^{1}H NMR (D_2O + K_2CO_3, 400.1 MHz): δ 7.07 (dd, J = 12.0, 8 Hz, 2H, Ph) ppm. ^{1}H NMR (D_2O + NaOH, 200.0 MHz): δ 7.02 (t, J = 8.5 Hz, 2H, Ph) ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ 151.7 (d, J = 240.0 Hz), 138.9 (broad), 123.8 (broad) ppm. ^{13}C NMR (acetone-d_6 + D_2O, 100.6 MHz): δ 151.7 (dd, J = 249.0, 13.6 Hz), 138.4 (broad), 124.3 (t, J = 249.0, 5.5 Hz) ppm. ^{13}C NMR (D_2O + K_2CO_3, 100.6 MHz): δ 168.4, 154.0 (d, J = 240 Hz), 119.6 ppm. ^{19}F NMR (acetone-d_6, 470.4 MHz): δ −135.5 (broad), −136.5 (broad), −138.0 (broad), −139.0 (broad), −140.0 (broad) ppm. ^{19}F NMR (acetone-d_6 + D_2O, 376.5 MHz): δ −138.7 (t, J = 10.5 Hz) ppm. ^{19}F NMR (D_2O + K_2CO_3, 376.5 MHz): δ −143.0 (broad) ppm. ^{11}B NMR (acetone-d_6, 64.16 MHz): δ 28.9 ppm. ^{11}B NMR (acetone-d_6 + D_2O, 64.16 MHz): δ 28.6 ppm. ^{11}B NMR (D_2O, 64.16 MHz): δ 32.9 ppm. ^{11}B NMR (D_2O + K_2CO_3, 64.16 MHz): δ 17.8, 6.5 ppm. ^{11}B NMR (D_2O + NaOH, 64.16 MHz): δ 10.1, 5.6 ppm. Anal. Calcd for $C_6H_6B_2F_2O_4$ (201.73): C, 35.72; H, 3.00. Found: C, 35.55; H, 3.10.

*1,4-Difluoro-2,3-diiodobenzene (**2c**).* A solution of 1,4-difluoro-2-iodobenzene (24.0 g, 0.10 mol) in THF (20 mL) was added to a stirred solution of LDA freshly prepared from *n*-BuLi (10 M, 10 mL, 0.10 mol) in THF (100 mL) at −75 °C. The resulting white slurry was stirred for 15 min, followed by the dropwise addition of Me_3SiCl (12.5 mL, 0.10 mol). Then the reaction mixture was warmed slowly to ca. −30 °C and quenched with 2 M aqueous H_2SO_4 (2 M solution in Et_2O, 18 mL, 0.036 mol). The mixture was concentrated in vacuo. The residue was subjected to fractional distillation to give crude 1,4-difluoro-2-iodo-3-(trimethylsilyl)benzene (**2b**; 19.3 g, 62%) as a colorless oil. Bp: 90−95 °C (1 Torr). It was added dropwise to a solution of ICl (11.5 g, 0.07 mol) in $CHCl_3$ (100 mL). The resulting dark solution was refluxed for 1 h, and then it was quenched with 10 wt % aqueous $NaHSO_3$ (50 mL). The organic layer was separated, washed with water, and concentrated in vacuo. The residue was subjected to fractional distillation to give crude **2c** as a pale yellow oil. Bp: 110−115 °C (1 Torr). The product solidified when it was cooled to room temperature. It was purified by crystallization from hexane (50 mL). Yield: 16.0 g (44%). Mp: 67−69 °C. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.11 (t, J = 11.2 Hz, 2H, Ph) ppm. ^{1}H NMR (D_2O, 400.1 MHz): δ 6.84 (td, J = 6.5, 2.0 Hz, 2H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 158.1 (dd, J = 244.0, 4.0 Hz), 115.7 (m), 97.5 (m) ppm. Anal. Calcd for $C_6H_2F_2I_2$ (365.89): C, 19.70; H, 0.55. Found: C, 19.5; H, 0.52.

*3,6-Difluoro-1,2-phenylenediboronic Acid (**4**).* A solution of **2c** (5.5 g, 0.015 mol) in Et_2O (20 mL) was added to a stirred solution of *n*-BuLi (10 M, 3.5 mL, 0.035 mol) in THF/Et_2O (50 mL, 4/1) at −110 °C. The resulting white slurry was stirred for 15 min followed by the dropwise addition of $B(OMe)_3$ (5.5 mL, 0.050 mol). Then the reaction mixture was warmed slowly to ca. −100 °C, which resulted in the formation of a white gelatinous mixture. It was warmed to −10 °C and quenched with anhydrous HCl (2 M solution in Et_2O, 18 mL, 0.036 mol). The mixture was concentrated in vacuo. The residue was subjected to fractional distillation to give crude 1,4-difluoro-2,3-bis(dimethoxyboryl)benzene (**2d**; 1.25 g) as a pale yellow oil. It was hydrolyzed by the addition of water (0.3 g) to the solution in Et_2O (18 mL). The resulting mixture was evaporated to dryness, and the remaining solid was washed with Et_2O (2 × 3 mL) and dried in vacuo to give the title compound. Yield: 0.85 g (28%). Mp: 132−135 °C dec. ^{1}H NMR (acetone-d_6, 499.9 MHz): δ 7.05 (broad, 2H, Ph) ppm. ^{1}H NMR (acetone-d_6 + D_2O, 400.1 MHz): δ 7.73 (t, J = 6.0 Hz, 2H, Ph) ppm. ^{1}H NMR (D_2O, 200.0 MHz): δ 6.87 (t, J = 5.5 Hz, 2H, Ph) ppm. ^{1}H NMR (D_2O + K_2CO_3, 200.0 MHz): δ 6.65 (t, J = 5.5 Hz, 2H, Ph) ppm. ^{1}H NMR (D_2O + NaOH, 200.0 MHz): δ 6.48 (t, J = 5.0 Hz, 2H, Ph) ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ 161.8 (d, J = 213.0 Hz), 117.7 ppm. ^{13}C NMR (acetone-d_6 + D_2O, 100.6 MHz): δ 161.9 (d, J = 222.0 Hz), 117.7 ppm. ^{19}F NMR (acetone-d_6, 470.4 MHz): δ −114.1 ppm (broad). ^{19}F NMR (acetone-d_6 + D_2O, 376.5 MHz): δ −112.8 ppm (t, J = 6.0). ^{11}B NMR (acetone-d_6, 64.16 MHz): δ 28.6 ppm. ^{11}B NMR (acetone-d_6 + D_2O, 64.16 MHz): δ 28.5 ppm. ^{11}B NMR (D_2O, 64.16 MHz): δ 31.3 ppm. ^{11}B NMR (D_2O + K_2CO_3, 64.16 MHz): δ 16.6, 6.8 ppm. ^{11}B NMR (D_2O + NaOH, 64.16 MHz): δ 9.7, 5.6 ppm. Anal. Calcd for $C_6H_6B_2F_2O_4$ (201.73): C, 35.72; H, 3.00. Found: C, 35.42; H, 3.21.

*Tetrafluoro-1,2-phenylenediboronic Acid (**5**).* ^{13}C NMR (acetone-d_6, 100.6 MHz): δ 149.5 (d, J = 236.0 Hz), 140.8 (d, J = 251.5 Hz) ppm. ^{13}C NMR (D_2O + K_2CO_3, 100.6 MHz): δ 151.7 (d, J = 241.0 Hz), 144.6 (d, J = 240.0 Hz) ppm. ^{19}F NMR (acetone-d_6, 376.5 MHz): δ −130 − −138 (broad), −153 − −157 (broad),−157 − −163 (broad) ppm. ^{19}F NMR (acetone-d_6 + D_2O, 376.5 MHz): δ −132.8 (2F), −156.8 (2F) ppm. ^{19}F NMR (D_2O, 376.5 MHz): δ −138.7 (broad, 2F), −160.2 (broad, 2F) ppm. ^{19}F NMR (1 M HCl in D_2O, 471.0 MHz): δ −136.8 (2F), −156.8 (2F) ppm. ^{11}B NMR (acetone-d_6, 64.16 MHz): δ 23.7, 16.3, 2.3 ppm. ^{11}B NMR (acetone-d_6 + D_2O, 64.16 MHz): δ 23.5, 16.4, 2.2 ppm. ^{11}B NMR (D_2O, 64.16 MHz): δ 23,4 ppm. ^{11}B NMR (D_2O + K_2CO_3, 64.16 MHz): δ 13.8, 6.9 ppm. ^{11}B NMR (D_2O + NaOH, 64.16 MHz): δ 9.3, 5.6 ppm. ^{11}B NMR (1 M HCl in D_2O, 64.16 MHz): δ 19.3, 13.4 ppm. Anal. Calcd for $C_6H_4B_2F_4O_4$ (237.71): C, 30.32; H, 1.70. Found: C, 30.45; H, 1.72.

Crystallization and Structural Measurement Details. Single crystals of **3** were obtained upon crystallization from acetone solution. The crystallization of **5** from water solution results in the formation of the semianhydride **5a**. In turn, by slow evaporation of a 1/2 acetone/toluene solution the dimeric form **5b** was obtained. All attempts to grow crystals of **4** were unsuccessful. Despite numerous solvent and temperature conditions tested, we always obtained amorphous powders or glasses. The crystal structure of **5a** contains three H_2O molecules per one molecule of **5a** incorporated into the lattice during crystallization. In the case of **5b** there are two H_2O molecules and one acetone molecule per one molecule of **5b**. A detailed discussion of supramolecular networks is given in the Supporting Information.

Single-crystal X-ray measurements were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The crystals were positioned at 45 mm from the KM4CCD camera. The data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the Oxford Diffraction Ltd. suit of programs.[42] All structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97.[43] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of C−H bonds were placed in idealized positions. The position of the H(3B) proton in **5a** was refined without any constraints. The structure of **5b** is of moderate quality, due to the fact that this compound crystallizes as tiny, small needles. The problem with crystallization is ascribed to the labile behavior of this compound in solution. During the refinement several atoms were restrained so that their displacement parameters approximate isotropic behavior (ISOR instruction with SHELXL). Selected crystal data and geometry of hydrogen bonds for all crystals are summarized in Tables S1 and S2 of the Supporting Information.

Computational Methods. All geometry optimizations and frequency calculations were carried out with the GAUSSIAN 09 suite of programs,[40] and the MP2 method was applied[28] using 6-31G(d,p)[29] basis sets. The minima were confirmed by vibrational frequency calculations within the harmonic approximation (no imaginary frequencies). The computations were performed with Tomasi's polarized continuum model,[44] using the polarizable conductor calculation model (SCRF(CPCM, solvent = H_2O)). In optimization processes no symmetry constraints were applied. The hydrogen-bonded dimer interaction energies as well as the energy of the O(3)−H(3B)···O(4) bond in **5a** were calculated using supramolecular methods including basis set superposition error (BSSE), and the B97D[45] functional with a 6-31G(d,p) basis set was applied. However, due to significant contribution of π stacking and other types of weak interactions to the total interaction energy between molecules of **5a**, the O(3)−H(3B)···O(4) hydrogen bond energy could not be directly estimated. Therefore, the coordinated water molecule together with a second molecule of **5a** was rotated by 180° along the B(2)−O(3) bond, preserving the geometry of the hydrogen bond (Figure S3, Supporting Information). Under these circumstances the interaction energy decreased from −104 to −87 kJ mol^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving details of X-ray crystallographic, computational, and solution multinuclear NMR studies and acidity constant measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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