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Preparation and X-ray Crystal Study of Benziodoxaborole Derivatives: New Hypervalent Iodine Heterocycles

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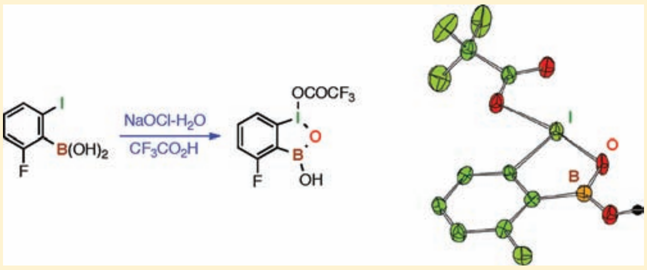
Supporting Information

ABSTRACT: A series of heterocyclic compounds containing trivalent iodine, oxygen, and boron in a five-membered ring were prepared and structurally investigated by X-ray crystallography. 1-Chloro-4-fluoro-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol was synthesized by chlorination of 2-fluoro-6-iodophenylboronic acid followed by treatment of the intermediate iododichloride with water. 1-Acetoxy-4-fluoro-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol, 1-acetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol, and similar 1-substituted trifluoroacetate derivatives of benziodoxaborole were prepared the hypochlorite oxidation of 2-fluoro-6-iodophenylboronic acid or 2-iodophenylboronic acid in acetic or trifluoroacetic acid, respectively. 1-Acetoxy substituted benziodoxaborole can be further converted to the respective trifluoroacetate by treatment with trifluoroacetic acid or to the 1-hydroxy derivative by basic hydrolysis with aqueous $NaHCO_3$. X-ray structural studies of 1-chloro- and 1-trifluoroacetoxy substituted benziodoxaboroles **13**, **17**, and **18** have shown the presence of a planar five-membered heterocyclic ring with unusually short endocyclic I−O bond distance of 2.04−2.09 Å. Slow crystallization of 4-fluoro-1-trifluoroacetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol from methanol resulted in the formation of a tetrameric macrocyclic structure **21** resulting from self-assembly of the initially formed 4-fluoro-1,3-dimethoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol. Structural parameters of the five-membered iodoxoborol ring, such as the planar geometry and the short B−O and O−I bonds lengths in **13**, **17**, and **18** compared to those in **21** and known benziodoxoles are indicative of partially aromatic character of this ring. Density functional theory (DFT) predicted NIST (0) and NIST (1) indexes for 1-chloro- and 1-trifluoroacetoxy substituted benziodoxaboroles, however, are indicative of significantly lower aromaticity compared to the classic aromatic systems.



INTRODUCTION

Hypervalent iodine compounds are extensively employed in organic synthesis as highly selective and environmentally friendly oxidizing reagents.[1,2] Especially important are the heterocyclic iodine(III) and iodine(V) derivatives in which iodine and oxygen are incorporated in a five-membered ring, known under the common name of benziodoxoles (structures **1**−**3**).[2] Benziodoxoles have higher thermal stability and a useful reactivity pattern compared to that of the analogous noncyclic derivatives.[2] Particularly important benziodoxole-based oxidizing reagents are represented by 2-iodosylbenzoic acid (**1**, 2X = O, Y = OH), 2-iodylbenzoic acid (**2**, IBX), and Dess−Martin periodinane (**3**, DMP).[2] Since the early 1990s, numerous other iodine-substituted benziodoxols **1** have been prepared, including: azidobenziodoxoles (**1**, Y = N_3),[3a] amidobenziodoxoles (**1**, Y = NHCOR),[3b] organosulfonyloxybenziodoxoles (**1**, Y = OSO_2R),[3c,d] cyanobenziodoxoles (**1**, Y = CN),[3e] and trifluoromethylbenziodoxoles (**1**, Y = CF_3).[3f,g] All these iodine-substituted benziodoxoles have found synthetic application as the reagents for various atom-transfer reactions.[2a]

Besides benziodoxoles, the other known five-membered heterocyclic systems incorporating hypervalent iodine (Chart 1) are represented by benziodazoles **4**,[4a−d] **5**,[4e] benziodoxazoles **6**,[4f] benziodoxathioles **7**,[4g,h] **8**,[4h] benziodathiazoles **9**,[4i] and cyclic phosphonate **10**.[4j] X-ray molecular structures were reported for numerous benziodoxole derivatives **1**,[3d,f,5] benziodazoles **4**,[4a,c,d,6] benziodoxathioles **7**,[4g,h] and cyclic phosphonate **10**.[4j] In general, the five-membered ring in benziodoxole is highly distorted with almost linear alignment of the two electronegative ligands. The I−O bond length in benziodoxolones (**1**, 2X = O) varies in a wide range from 2.11 Å in carboxylates (**1**; Y = *m*-$ClC_6H_4CO_2$)[5i] to 2.48 Å in the phenyl derivative (**1**, Y = Ph),[5a] which indicates considerable changes in the ionic character of this bond. The endocyclic C−I−O bond angle is typically around 80°, which is a

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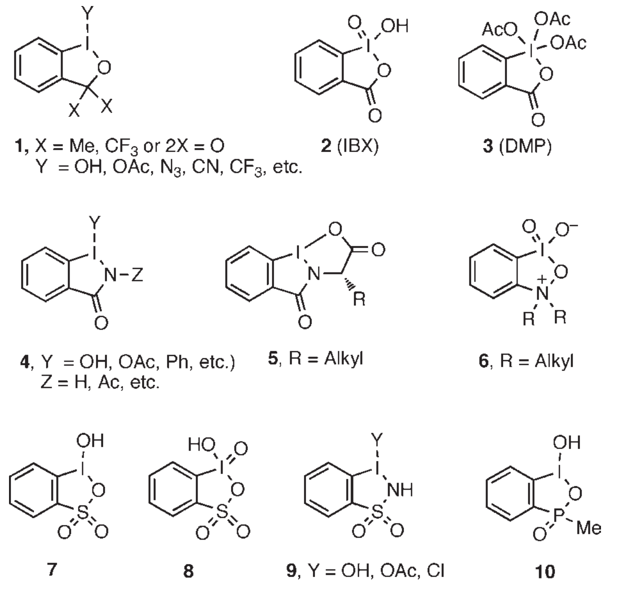
Chart 1. Known Hypervalent Iodine Heterocyclic Systems


1, X = Me, CF_3 or 2X = O
Y = OH, OAc, N_3, CN, CF_3, etc.
2 (IBX)
3 (DMP)
4, Y = OH, OAc, Ph, etc.)
Z = H, Ac, etc.
5, R = Alkyl
6, R = Alkyl
7
8
9, Y = OH, OAc, Cl
10

significant deviation from the expected angle of 90° for the normal T-shaped geometry of hypervalent iodine. The structural parameters of benziodazoles (**4**, Y = OAc or Ph) in general are similar to those of benziodoxoles.[4a,c,d,6]

In this article we report the first preparation and X-ray crystal study of several cyclic derivatives incorporating hypervalent iodine, oxygen, and boron in a five-membered ring, representing the new hypervalent iodine heterocyclic system of benziodoxaborole.

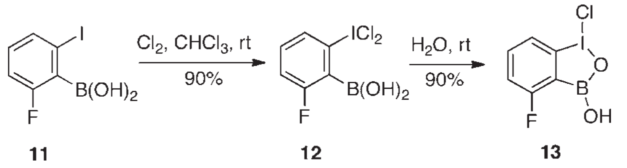
■ RESULTS

Our approach to the heterocyclic system of benziodoxaborole is based on the oxidative cyclization of the commercially available *ortho*-iodophenylboronic acids **11** and **14**. 1-Chlorobenziodoxaborole derivative **13** was synthesized in two simple steps analogously to the known procedure for the preparation of 1-chlorobenziodoxoles[7] (Scheme 1). At the first step, the chlorination of 2-fluoro-6-iodophenylboronic acid **11** in chloroform afforded a yellow, crystalline precipitate of the unstable dichloride **12**. The precipitate of **12** was filtered, washed with cold chloroform, and then was immediately converted to the final chloride **13** by treatment with excess of water (Scheme 1). An attempt to prepare a similar chlorobenziodoxaborole derivative from 2-iodophenylboronic acid **14** resulted in the formation of unstable products.

Compound **13** is relatively stable at room temperature and can be stored for several weeks in a refrigerator in the absence of light. It was identified by NMR, elemental analysis, and single crystal X-ray crystallography (Figure 1).

Iodine centers in both independent molecules observed in the unit cell of compound **13** have characteristic iodine(III) compounds' T-shape geometry with an almost linear Cl—I—O fragment (174.7°, average, Table 1). Observed I—Cl (2.49 Å, average) as well as I—C (2.13 Å, average) bond distances are in the normal range for the aryl-containing iodine(III) molecules, while corresponding I—O bonds (2.08 Å, average) are among the shortest ever observed for the five-membered iodine(III) heterocycles. Another interesting feature of the new five-membered iodine-containing heterocycle is that the B—C (1.57 Å, average) and B—O (1.36 Å, average) bond distances in compound **13** are significantly shorter compared to the usual B—C(aryl) and B—O(alkyl/aryl) bond distances. Such short bond distances along with the very short I—O bond distance are indicative of some additional conjugation in the five-membered heterocycle, which is in agreement with its planarity (the largest deviation for C8—B2—O3—I2 torsion angle is 3.59°). The presence of the OH group in compound **13** dictates its packing motif (Figure 1b). Indeed, two pairs of two independent molecules form the hydrogen-bonded tetramer assembly. Specifically, hydrogen atoms of the O2(A)H and O2(D)H fragments form strong (H---O distance of 2.004 Å) hydrogen bonds with the O4(C) and O4(B) oxygen atoms, respectively, while hydrogen atoms of the O4(B)H and O4(C)H fragments form strong (H---O distance of 1.841 Å) hydrogen bonds with the O3(C) and O3(B) oxygen atoms, respectively (Figure 1b). In addition, several other very weak intermolecular contacts between fluorine and oxygen, oxygen and iodine, and chlorine and iodine atoms have been observed in the tetrameric assembly (Figure 1b).

Scheme 1. Preparation of 1-Chlorobenziodoxaborole 13



11 **12** **13**

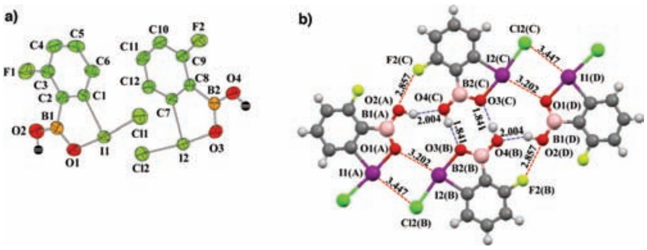


Figure 1. (**a**) CAMERON view of 1-chloro-4-fluoro-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol **13** (ellipses are shown at 50% probability; two independent molecules present in the unit cell are shown). (**b**) Intra- and intermolecular secondary bonding in **13**.

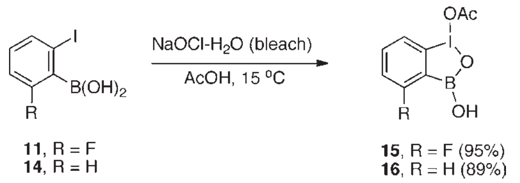
The acetoxy and trifluoroacetoxy derivatives represent the most practically important class of polyvalent iodine compounds.[1] A well-known, general approach to the hypervalent iodine acetates is based on the oxidation of an appropriate iodoarene by an oxidant in acetic acid.[10] We have found that the oxidation of *ortho*-iodophenylboronic acids **11** and **14** with bleach (~5% aqueous sodium hypochlorite) in acetic acid results in the formation of the respective 1-acetoxybenziodoxaboroles **15** and **16** in high yields (Scheme 2).

Products **15** and **16** were isolated as white, stable microcrystalline solids and were identified by ^1H NMR and elemental analysis. Both acetates **15** and **16** have very low solubility in organic solvents and in water, which makes difficult their advanced structural analysis. In search for the more soluble benziodoxaborole carboxylates, we have investigated the preparation of the trifluoroacetoxy derivatives (Schemes 3 and 4). Our initial approach to 1-trifluoroacetoxybenziodoxaborole **17** was based on the oxidation of 2-fluoro-6-iodophenylboronic acid **11** with bleach in

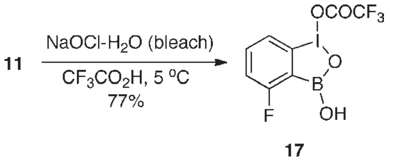
Table 1. Selected Bond Distances and Angles of Compound 13 Determined by the X-ray Crystallography

Selected Bond Distances (Å)			
I1−O1 2.070(3)	I2−O3 2.090(3)	I1−C1 2.124(4)	I2−C7 2.132(4)
I1−Cl1 2.5080(11)	I2−Cl2 2.4770(10)	B1−C2 1.572(6)	B2−C8 1.571(5)
O1−B1 1.359(5)	O3−B2 1.356(5)	B1−O2 1.345(5)	B2−O4 1.357(5)
Selected Angles (deg)			
O1−I1−Cl1 175.38(8)	O3−I2−Cl2 174.06(8)	O1−I1−C1 83.05(13)	O3−I2−C7 82.00(12)
I1−O1−B1 114.5(2)	I2−O3−B2 114.9(2)	O1−B1−C2 114.5(3)	O3−B2−C8 114.8(3)

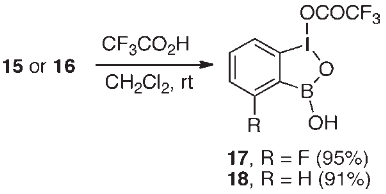
Scheme 2. Preparation of 1-Acetoxybenziodoxaboroles 15 and 16



Scheme 3. Preparation of 1-Trifluoroacetoxybenziodoxaborole 17 by the Oxidation of 2-Fluoro-6-iodophenylboronic Acid 11 with Bleach in Trifluoroacetic Acid



Scheme 4. Preparation of 1-Trifluoroacetoxybenziodoxaboroles 17 and 18 from Acetates 15 and 16



trifluoroacetic acid (Scheme 3); however, the yield of the trifluoroacetate **17** was relatively low compared to the yield of the acetate **15**.

We have found that a better procedure for the preparation of trifluoroacetoxybenziodoxaboroles is based on the reaction of readily available acetates **15** and **16** with trifluoroacetic acid (Scheme 4). Treatment of acetate **15** with excess trifluoroacetic acid in dichloromethane at room temperature results in quick formation of 1-trifluoroacetoxybenziodoxaborole **17**, which was isolated in excellent yield by evaporation of solvent and volatile byproducts followed by recrystallization from dichloromethane. 1-Trifluoroacetoxybenziodoxaborole **18** was prepared by a similar procedure from the acetate **16** (Scheme 4).

Both trifluoroacetoxybenziodoxaboroles **17** and **18** were isolated in the form of stable microcrystalline products and were identified by multinuclear NMR, elemental analysis, and single crystal X-ray crystallography (Figures 2 and 3).

Both trifluoroacetates **17** and **18** have many similarities in their X-ray determined structures (Figures 2 and 3, Table 2).

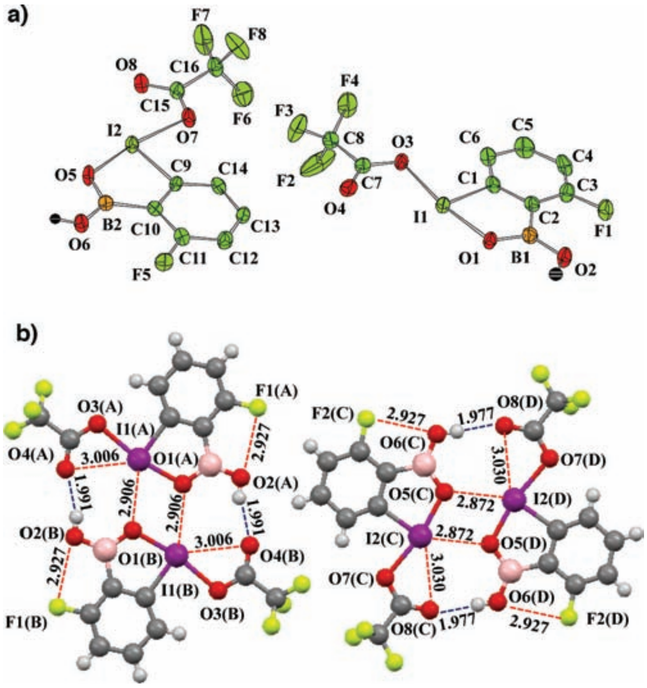


Figure 2. (**a**) CAMERON view of 4-fluoro-1-trifluoroacetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol **17** (ellipses are shown at 50% probability; two independent molecules observed in the unit cell of **17** are shown). (**b**) Intra- and intermolecular secondary bonding in **17**.

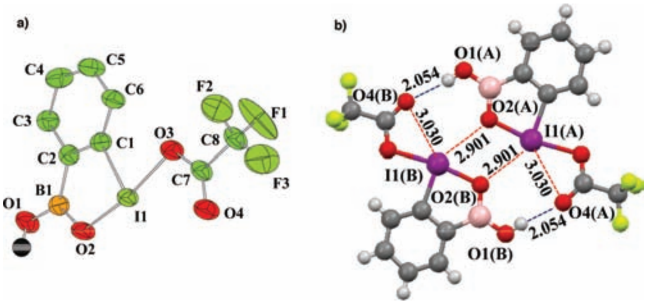


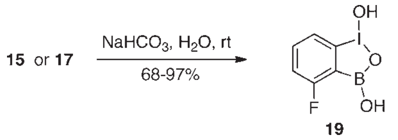
Figure 3. (**a**) CAMERON view of 1-trifluoroacetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol **18** (ellipses are shown at 50% probability). (**b**) Intra- and intermolecular secondary bonding in **18**.

Table 2. Selected Bond Distances and Angles for Compounds **17** and **18** Determined by X-ray Crystallography

Selected Bond Distances for Compound **17** (Å)			
I1−O1 2.038(4)	I2−O5 2.047(4)	I1−C1 2.119(6)	I2−C9 2.114(6)
I1−O3 2.221(4)	I2−O7 2.223(4)	C2−B1 1.565(9)	C10−B2 1.559(9)
O2−B1 1.352(8)	O6−B2 1.348(8)	O1−B1 1.365(8)	O5−B2 1.373(8)
O3−C7 1.275(7)	O7−C15 1.289(7)	O4−C7 1.224(7)	O8−C15 1.211(7)
Selected Angles for Compound **17** (deg)			
O1−I1−O3 169.13(16)	O7−I2−O5 168.71(16)	I1−O1−B1 115.3(4)	I2−O5−B2 115.0(4)
C2−B1−O1 114.8(6)	C10−B2−O5 114.5(5)	C2−B1−O2 123.2(6)	C10−B2−O6 123.8(6)
Selected Bond Distances for Compound **18** (Å)			
I1−O3 2.231(3)	I1−O2 2.036(3)	I1−C1 2.116(4)	O3−C7 1.265(6)
C7−O4 1.206(6)	O2−B1 1.369(6)	B1−O1 1.348(6)	B1−C2 1.563(7)
Selected Angles for Compound **18** (deg)			
O3−I1−O2 169.69(13)	O3−I1−O2 169.69(13)	O2−B1−C6 114.8(4)	I1−O2−B1 114.5(3)

First, iodine centers in both independent molecules observed in the unit cell of compound **17** as well as the iodine atom in **18** have the usual T-shape geometry for iodine(III) compounds. Iodine atoms in compound **17** and **18** form, as is very typical for iodine(III) acetates and trifluoroacetates, one short (2.22−2.23 Å) covalent bond and one relatively long (3.01−3.03 Å) secondary intramolecular interaction with the trifluoroacetate anion. Such pseudo-η^2 iodine-trifluoroacetate interactions result in elongation of the formally double C═O bonds and shortening of the formally single C−O bonds in the trifluoroacetate group (Table 2). Because of the presence of the additional relatively weak secondary intramolecular interaction with trifluoroacetate anion, the O−I−O angle in compounds **17** (168.9°, average, Table 2) and **18** (169.7°, Table 2) is significantly smaller compared to the Cl−I−O angle observed in compound **13** (174.7°, average, Table 1). Observed I−OCOCF$_3$ (2.22 Å, average) as well as I−C (2.12 Å, average) bond distances are in the normal range for the aryl-containing iodine(III) acetates or trifluoroacetates, while the corresponding I−O(B) bonds (2.04 Å, average) are again very short compared to similar bond distances observed in the other five-membered iodine(III) heterocycles. Similar to compound **13**, the B−C (1.56 Å, average) and B−O (1.37 Å, average) bond distances in compounds **17** and **18** are significantly shorter compared to the usual B−C(aryl) and B−O(alkyl/aryl) bond distances. Again, the iodine-containing five-membered heterocycle is almost planar (the largest deviation for the B1−O2−I1−C1 torsion angle in compound **18** is 2.09°) suggesting additional conjugation between six- and five-membered rings in the target compounds. Packing diagrams for compounds **17** and **18** (Figure 2b and 3b) resemble dimeric motifs very typical for iodine(III) acetates and trifluoroacetates. Compared to the earlier published iodine(III) acetates and trifluoroacetates results, dimeric structures in compounds **17** and **18** are additionally stabilized by strong hydrogen bonds. Specifically, in the case of **17**, hydrogen atoms of O2(A)H and O2(B)H fragments form strong (H---O distance of 1.99 Å) hydrogen bonds with the O4(B) and O4(A) oxygen atoms of trifluoroacetate groups, respectively, while hydrogen atoms of the O6(C)H and O6(D)H fragments form strong (H---O distance of 1.98 Å) hydrogen bonds with the O8(D) and O8(C) oxygen atoms of the trifluoroacetate group, respectively (Figure 2b). Similarly, hydrogen atoms of the O1(A)H and O1(B)H fragments of **18** form strong (H---O distance of 2.05 Å) hydrogen bonds with the O4(B) and O4(A) oxygen atoms of the trifluoroacetate groups, respectively. Interestingly, the presence of the strong electron-withdrawing fluorine atom in the phenyl group of **17** results in shorter hydrogen bonds compared to those observed in **18**. In addition, several other intra- and intermolecular contacts between fluorine and oxygen as well as oxygen and iodine atoms have been observed in the dimeric motifs of compounds **17** and **18** (Figure 2b and 3b). In particular, in addition to the above mentioned I−OCOCF$_3$ secondary interactions, oxygen atoms of the iodine-containing five-membered heterocycle form short (2.87−2.91 Å for **17** and 2.90 Å for **18**) intermolecular I−O contacts resulting in pentacoordinated iodine(III) centers in **17** and **18**. Finally, fluorine atoms of **17** are involved in additional intramolecular contacts with corresponding oxygen atoms of the OH groups (Figure 2b and 3b).

Scheme 5. Preparation of 1-Hydroxybenziodoxaborole **19**

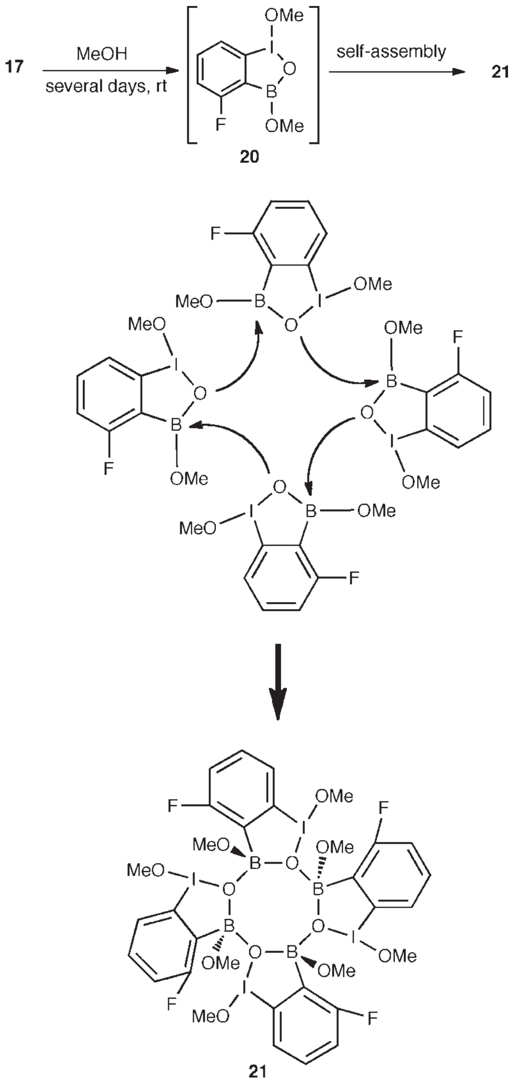


A mild, basic hydrolysis of 1-acetoxy- or 1-trifluoroacetoxybenziodoxaborole affords 1-hydroxybenziodoxaborole **19** (Scheme 5) as a white powder, which was characterized by ^{1}H NMR and elemental analysis. The hydroxy derivative **19** has a low solubility in organic solvents and in water, which hampers its advanced structural study. It is possible that the low solubility of this product is explaned by its oligomeric structure analogous to that of the methoxy derivative (see below).

A slow crystallization of 1-trifluoroacetoxybenziodoxaborole **17** from methanol at room temperature during 10 days resulted in the formation of white crystals, which were investigated by X-ray diffraction analysis. The X-ray diffraction study revealed an unusual macrocyclic structure **21**, the formation of which can be explained by self-assembly of four molecules of the dimethoxy derivative **20** as shown in Scheme 6.

The X-ray structure of compound **21** represents an interesting addition to the rich collection of highly unusual supramolecular iodine(III) assemblies.[4e,8] The inner cyclic system of the tetramer **21** is formed by four boron and four oxygen atoms (Figure 4). The driving force for formation of such eight-membered cyclic

Scheme 6. Self-Assembly of Benziodoxaborole into the Tetrameric Structure 21



system is the transformation of initial trigonal-planar sp^2 hybrid boron atoms into tetrahedral sp^3 hybridized atoms. Indeed, each boron atom in tetramer **21** forms one covalent bond with carbon and three covalent bonds with oxygen atoms. Interestingly, boron−oxygen bonds, which form the eight-membered cycle (1.48−1.50 Å), are significantly longer compared to the B−OMe bond distances (1.43−1.44 Å). The eight-membered cycle in **21** is nonplanar with alternating larger B−O(I)−B bond angles (126.2°, average) and smaller O−B−O bond angles (110.7°, average) with the latter being close to the expected for the sp^3 hybridized boron atoms. The change in hybridization of the boron atoms in tetramer **21** also leads to a significant elongation of boron−carbon and heterocyclic iodine−oxygen bonds (Table 3) compared to those observed in compounds **13**, **17**, and **18** (Table 1 and 2). For instance, boron−carbon distances in **13**, **17**, and **18** are ~0.07 Å shorter compared to those in tetramer **21**, while iodine−oxygen bond distances in **13**, **17**, and **18** are ~0.1 Å shorter compared to those in tetramer **21**. Similarly to compounds **13**, **17**, and **18**, iodine centers have the usual T-shape geometry for iodine(III) compounds with O−I−OMe bond angles varying between 167.2 and 170.5°. Another interesting feature of tetramer **21** is its packing diagram (Figure 4d). Indeed, all tetrameric units are almost isolated from each other except the very weak (3.47 Å) O1---I4 contacts, which results in the formation of linear polymeric chains of **21**.

Preliminary studies of the reactions of benziodoxaboroles **15**−**18** with organic substrates have shown a generally lower reactivity compared to that of the known 1-hydroxy- and 1-acetoxybenziodoxoles **1**−**3**.[2] In particular, benziodoxaboroles **15**−**18** do not oxidize alcohols even in the presence of such catalysts as BF_3-etherate.

DISCUSSION

The synthesized compounds represent a new type of iodine(III) five-membered heterocycles containing the −C−C−B−O−I− fragment. One of the most striking features of these new heterocycles is the presence of the shorter carbon−boron and oxygen−iodine bonds in a cyclic system with the trigonal-planar sp^2 hybridized boron atom (compounds **13**, **17**, and **18**) compared to those observed in tetramer **21**, which has a tetrahedral sp^3 hybridized boron atom. Indeed, the Cambridge Structural Database analysis of oxygen−iodine bond lengths in iodine(III) five-membered heterocycles (Figure 5) indicates that the most typical oxygen−iodine(III) bond length should be observed between 2.10 and 2.15 Å, which is significantly longer compared to the same bond distance observed in compounds **13**, **17**, and **18** (2.04−2.09 Å).

Such bond shortening could potentially reflect a partial aromatic character[9] in the new boron-containing heterocycles, which should be eliminated upon transformation of the boron atom from trigonal-planar (sp^2) to tetrahedral (sp^3) configuration. To probe a possible partial aromatic character in new heterocyclic systems, we used the well-known computational NIST approach.[9] Specifically, NIST (0) and (1) indexes were calculated at the geometric centers of the six-membered and five-membered rings for the set of test compounds shown in Figure 6. As expected, density functional theory (DFT) predicted NIST (1) indexes for the six-membered cyclic fragments became more negative compared to respective NIST (0) indexes proving aromaticity in six-center, six electron [6c,6e] benzene rings. DFT predicted NIST (0) indexes for the supposedly five-center, six-electron [5c,6e] −C−C−B−O−I− and −C−C−C−O−I− heterocyclic fragments are also negative (indicative of aromaticity), but the respective NIST(1) indexes are all less negative (indicative of smaller aromaticity) for the same fragments. Thus, five-membered heterocyclic fragments in new boron-containing heterocycles as well as the well-known benzoiodoxoles cannot be considered among the classic aromatic [5c,6e] systems, and such electron delocalization scheme cannot completely explain the presence of short oxygen−iodine bonds observed in compounds **13**, **17**, and **18**.

To understand the presence of the short oxygen−iodine bond distance in compounds **13**, **17**, and **18**, the following hypothesis could be proposed (Figure 7). In the case of the well-known iodine(III)-containing five-membered heterocycles such as benziodoxoles (Figure 7a), the two-center, two-electron [2c,2e] conjugated to the benzene ring C═O bond is located on the periphery of the five-membered ring with the two other possible resonance structures playing insignificant role. As a result, the −C−O−I− fragment of this five-membered heterocycle should consist of the classic single bonds and cannot provide additional

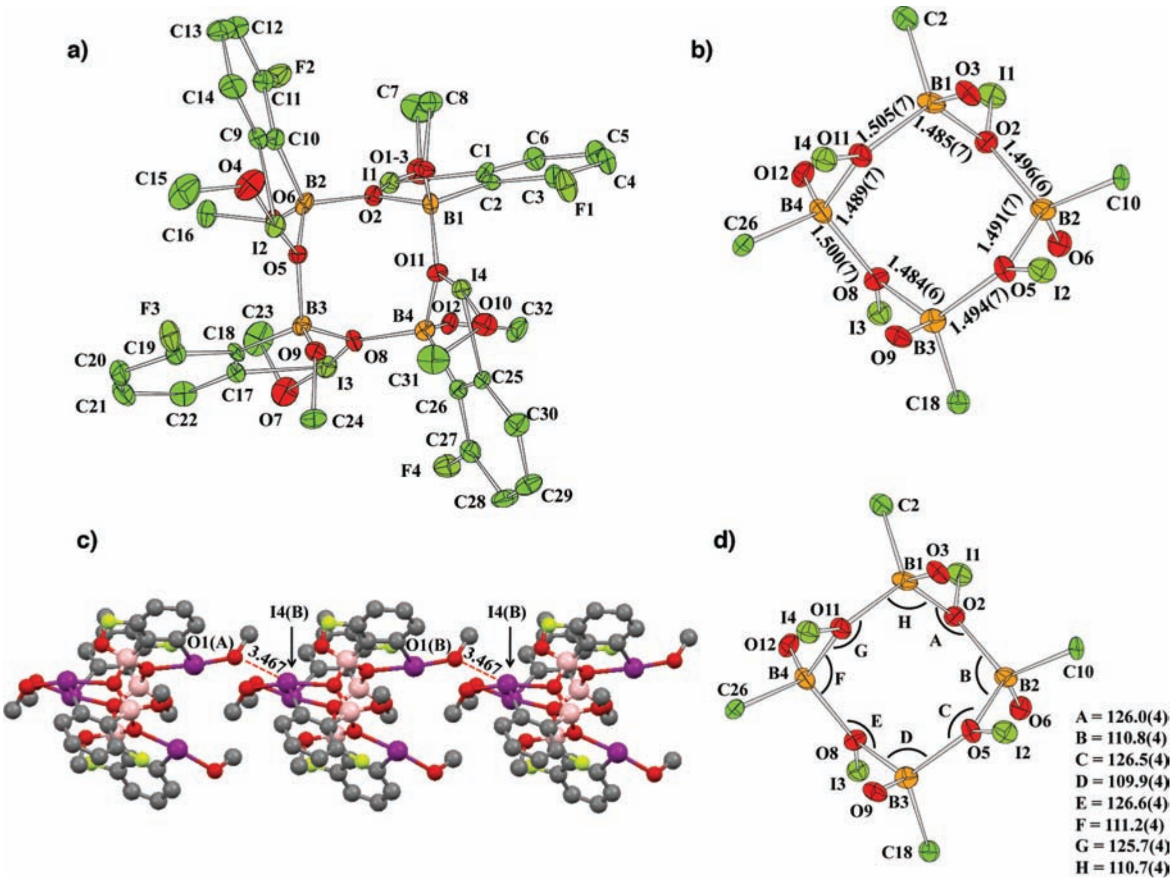


Figure 4. (**a**) Perspective view of tetrameric 4-fluoro-1,3-dimethoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol **21** (ellipses are shown at 50% probability). (**b**) Bond distances [Å] in the macrocyclic fragment of **21**. (**c**) Intermolecular secondary bonding in **21** showing O1(A)---I4(B) and O1(B)---I4(C) contacts. (**d**) Angles [deg] in the macrocyclic fragment of **21**.

Table 3. Selected Bond Distances and Angles for Tetramer 21 Determined by X-ray Crystallography

Selected Bond Distances (Å)			
I1−O2 2.227(3)	I2−O5 2.193(3)	I3−O8 2.200(3)	I4−O11 2.229(3)
I1−C1 2.125(5)	I2−C9 2.131(6)	I3−C17 2.117(5)	I4−C25 2.117(5)
I1−O1 2.019(4)	I2−O4 2.036(4)	I3−O7 2.045(4)	I4−O10 2.009(4)
B1−C2 1.640(7)	B2−C10 1.641(8)	B3−C18 1.630(8)	B4−C26 1.642(8)
O2−B1 1.485(7)	O2−B2 1.496(6)	B2−O5 1.491(7)	O5−B3 1.494(7)
B3−O8 1.484(6)	O8−B4 1.500(7)	B4−O11 1.489(7)	O11−B1 1.505(7)
B1−O3 1.441(7)	B2−O6 1.443(7)	B3−O9 1.442(7)	B4−O12 1.431(7)
Selected Angles (deg)			
O1−I1−O2 170.49(14)	O4−I2−O5 170.29(16)	O7−I3−O8 170.04(15)	O10−I4−O11 167.20(14)
B1−O2−B2 126.0(4)	B2−O5−B3 126.5(4)	B3−O8−B4 126.6(4)	B4−O11−B1 125.7(4)
O2−B1−O11 110.7(4)	O2−B2−O5 110.8(4)	O5−B3−O8 109.9(4)	O8−B4−O11 111.2(4)
I1−O2−B1 118.8(3)	I2−O5−B2 119.1(3)	I3−O8−B3 118.2(3)	I4−O11−B4 117.9(3)

electron delocalization, which would shorten the oxygen−iodine bond. In the case of iodoxoborol-containing compounds **13**, **17**, and **18**, [2c,2e] conjugation with the benzene ring is provided by the *inner* boron−oxygen fragment (Figure 7b). Moreover, the B−O−I fragment of the five-membered ring could potentially provide four electrons to form a nonclassic [5c,6e] aromatic system. A possible contribution of the resonance structure involving boron−oxygen double bonds (Figure 7b) is supported by a recent experimental characterization of a coordinated oxoborane.[10] Because of the large size mismatch between iodine p-orbitals and p-orbitals of carbon and oxygen atoms, the contribution of such aromatic resonance structure (Figure 7b) should be minor. Having such a minor contribution, however, will bring some degree of delocalization in the five-membered heterocyclic fragment and thus will shorten carbon−boron, boron−oxygen, and iodine−oxygen bonds, which was observed experimentally in compounds **13**, **17**, and **18**.

■ CONCLUSIONS

In conclusion, we have reported the preparation and X-ray structural investigation of new heterocyclic compounds containing trivalent iodine, oxygen, and boron in a five-membered ring. 1-Chloro-4-fluoro-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol was synthesized by chlorination of 2-fluoro-6-iodophenylboronic acid followed by treatment of the intermediate iododichloride with water. 1-Acetoxy-4-fluoro-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol, 1-acetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol, and similar 1-substituted trifluoroacetate derivatives of benziodoxaborole were prepared the hypochlorite oxidation of 2-fluoro-6-iodophenylboronic acid or 2-iodophenylboronic acid in acetic or trifluoroacetic acid, respectively. 1-Acetoxy substituted benziodoxaborole can be further converted to the respective trifluoroacetate by treatment with trifluoroacetic acid or to the 1-hydroxy derivative by basic hydrolysis with aqueous $NaHCO_3$. X-ray structural studies of 1-chloro- and 1-trifluoroacetoxy substituted benziodoxaboroles have shown the presence of a planar five-membered heterocyclic ring with unusually short endocyclic I—O bond distance of 2.04—2.09 Å. Slow crystallization of 4-fluoro-1-trifluoroacetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol from methanol resulted in the formation of a tetrameric macrocyclic structure resulting from self-assembly of the initially formed 4-fluoro-1,3-dimethoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol. Structural parameters of the five-membered iodoxoborol ring, such as the planar geometry and the short B—O and O—I bonds lengths in **13**, **17**, and **18** compared to those in **21** and the known benziodoxoles, are indicative of partially aromatic character of this ring. DFT predicted NIST (0) and NIST (1) indexes for 1-chloro- and 1-trifluoroacetoxy substituted benziodoxaboroles, however, are indicative of significantly lower aromaticity compared to the classic aromatic systems.

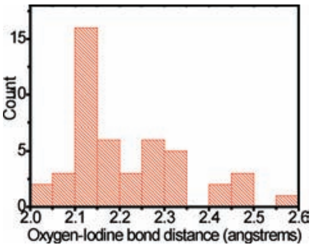


Figure 5. CSD histogram analysis of the oxygen—iodine bond length in five-membered iodine heterocycles.

■ EXPERIMENTAL SECTION

General Experimental Procedures. All commercial reagents were ACS reagent grade and used without further purification. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. Infrared spectra were recorded as a KBr pellet on a Perkin-Elmer 1600 series FT-IR spectrophotometer. NMR spectra were recorded on a Varian UNITY/INOVA 500 MHz NMR spectrometer at 500 MHz (^{1}H NMR), 125 MHz (^{13}C NMR), and 160 MHz (^{11}B NMR). Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to tetramethylsilane, and ^{11}B chemical shifts are referenced relative to BF_3-etherate. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, Georgia.

Synthesis and Characterization of 1-Chloro-4-fluoro-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol (13). Excess of chlorine gas

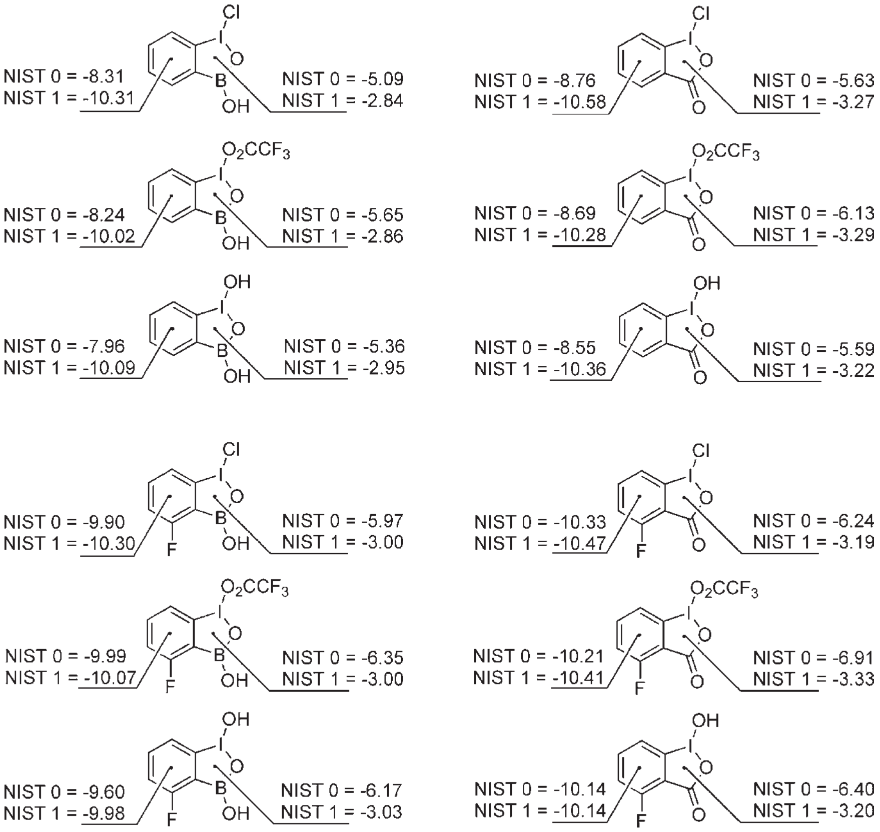


Figure 6. DFT predicted NIST (0) and (1) indexes for model iodine(III) compounds.

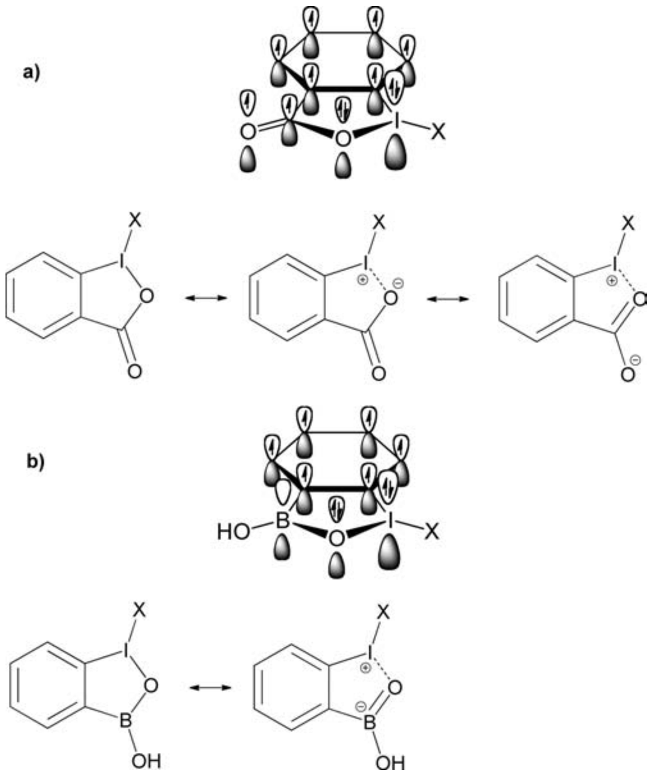


Figure 7. Resonance structures and π-orbital systems in benziodoxoles (**a**) and benziodoboroxoles (**b**).

was passed through a solution of 2-fluoro-6-iodophenylboronic acid **11** (0.266 g, 1.0 mmol) in $CHCl_3$ (25 mL) until complete disappearance of starting material according to TLC. The formation of yellow, crystalline precipitate of the dichloride **12** was observed. The precipitate was filtered, washed with cold $CHCl_3$, and dried in vacuum to afford 0.340 g (90%) of the unstable product **12**, mp 100−100.5 °C (dec). Product **12** is unstable and should be immediately converted to the final chloride **13** by treatment with water. In a typical procedure, the dichloride **12** (0.169 g, 0.5 mmol) was stirred with water (2 mL) for 10 min at room temperature. The resulting light yellow solid was filtered, washed with water and dried in vacuum to give 0.135 g (90%) of crude product **13**, which can be additionally purified by recrystallization from $CHCl_3$; mp 135−137 °C (dec). ^{1}H NMR ($CDCl_3$): δ 8.12 (dd, J = 8.0, 1.5 Hz, 1H), 7.72 (m, 1H), 7.34 (ddd, J = 8.5, 8.0, and 2.0 Hz, 1H), 4.97 (br s, OH); ^{13}C NMR ($CDCl_3$): δ 168.6 (d, J_{CF} = 255 Hz), 135.4 (d, $^3J_{CF}$ = 8.3 Hz), 129.9 (d, $^3J_{CF}$ = 8.8 Hz), 123.8 (d, $^4J_{CF}$ = 3.8 Hz), 117.6 (d, $^2J_{CF}$ = 23.8 Hz); ^{11}B NMR ($CDCl_3$): δ 31.01 (br s) and 19.74 (s). Anal. Calcd. for $C_6H_4BClFIO_2$: C, 24.00; H, 1.34; Cl, 11.81; I, 42.26. Found: C, 23.89; H, 1.27; Cl, 11.60; I, 41.99.

Single crystals of product **13** suitable for X-ray crystallographic analysis were obtained by slow evaporation of the chloroform solution of **13**. X-ray diffraction data were collected on a Rigaku RAPID II diffractometer using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) at 123 K. Multiscan absorption correction was applied to the data using the CrystalClear 2.0 program (Rigaku Inc. 2010). The structure was solved by the Patterson method (PATTY) using the CrystalStructure 4.0 program and refined by full-matrix least-squares refinement on F^2 using the Crystals for Windows program. Crystal data for **13** $C_6H_4B_1Cl_1F_1I_1O_2$: M 300.26, triclinic, space group $P\bar{1}$, a = 7.4745(4), b = 10.5487(6), c = 11.7411(8) Å, α = 109.722(8)°, β = 99.391(7)°, γ = 97.560(7)°, V = 842.22(11) Å^3, Z = 4, μ = 4.086 mm^{-1}, 22003 reflections measured, 3861 unique; final R_1 = 0.0272, R_w = 0.0667. CCDC-836131 contains the supplementary crystallographic data for compound **13**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ U.K.; fax: (+44) 1223−336−033, or deposit@ccdc.cam.ac.uk).

Preparation of 1-Acetoxy-4-fluoro-1*H*-1λ^3-benzo[*d*][1,2,3]-iodoxoborol-3-ol (15). A solution of 2-fluoro-6-iodophenylboronic acid **11** (1.330 g, 5.0 mmol) in acetic acid (6 mL) was cooled to 15 °C, and the commercial bleach solution (6.5 mL of ∼5% aqueous NaOCl) was added by small portions (about 0.1 mL each) under stirring. The stirring was continued at 15 °C for additional 30 min until complete disappearance of starting material according to thin layer chromatography (TLC). If starting material was still present, additional amount of bleach was added. Then water (20 mL) was added, and the resulting white, crystalline precipitate was filtered, washed with water, and dried in vacuum to afford 1.540 g (95%) of product **15**, mp 154−155 °C (dec). ^{1}H NMR (D_2O): δ 7.72 (m, 2H), 7.32 (m, 1H), 2.10 (s, 3H); ^{11}B NMR (D_2O): δ 19.80 (s). Anal. Calcd. for $C_8H_7BFIO_4$: C, 29.67; H, 2.18; I, 39.19. Found: 29.62; H, 2.11; I, 38.93.

1-Acetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol (16). Compound **16** was prepared by a similar procedure in 89% yield starting from 2-iodophenylboronic acid **14**; mp 110.5−111.5 °C (dec). ^{1}H NMR (D_2O): δ 7.85 (m, 3H), 7.65 (m, 1H), 2.10 (s, 3H); ^{11}B NMR ($CDCl_3$): δ 19.86 (s). Anal. Calcd. for $C_8H_8BIO_4$: C, 31.41; H, 2.64; I, 41.49. Found: C, 31.32; H, 2.51; I, 41.40.

Synthesis and Characterization of 4-Fluoro-1-trifluoroacetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol (17) and 1-Trifluoroacetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol (18). To a stirred mixture of acetate **15** (0.650 g, 2.0 mmol) in CH_2Cl_2 (6 mL) was added trifluoroacetic acid (2.0−2.5 mL) at room temperature until formation of a homogeneous solution. Stirring of the solution was continued for additional 30 min, and then the solvent and volatile products were evaporated in vacuum to afford an off-white solid, which was recrystallized from CH_2Cl_2 to give analytically pure trifluoroacetate **17** as colorless needles; yield 0.720 g (95%); mp 139−140 °C (dec). ^{1}H NMR ($CDCl_3$): δ 7.83−7.76 (m, 2H), 7.33 (ddd, J = 8.0, 8.0, and 0.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 169.61 (d, J_{CF} = 257.3 Hz), 162.1 (q, $^2J_{CF}$ = 43.0 Hz), 137.6 (d, $^3J_{CF}$ = 8.3 Hz), 130.7 (d, $^3J_{CF}$ = 8.8 Hz), 125.6 (d, $^4J_{CF}$ = 4.1 Hz), 118.4 (d, $^2J_{CF}$ = 22.9 Hz), 114.6 (q, J_{CF} = 283 Hz); ^{11}B NMR ($CDCl_3$): δ 19.75 (s). Anal. Calcd. for $C_8H_4BF_4IO_4$: 25.43; H, 1.07; I, 33.59. Found: C, 25.31; H, 0.92; I, 33.37.

Single crystals of product **17** suitable for X-ray crystallographic analysis were obtained by slow evaporation of the chloroform solution of **17**. X-ray diffraction data were collected on a Rigaku RAPID II diffractometer using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) at 123 K. Multiscan absorption correction was applied to the data using the CrystalClear 2.0 program (Rigaku Inc. 2010). The structure was solved by the Patterson method (PATTY) using the CrystalStructure 4.0 program and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **17** $C_8H_4B_1F_4I_1O_4$: M 377.82, triclinic, space group $P\bar{1}$, a = 9.0868(4), b = 10.3720(5), c = 12.5120(8) Å, α = 77.436(6)°, β = 81.887(6)°, γ = 71.565(5)°, V = 1088.59(11) Å^3, Z = 4, μ = 3.001 mm^{-1}, 28579 reflections measured, 4988 unique; final R_1 = 0.0419, R_w = 0.0941. CCDC-836132 contains the supplementary crystallographic data for compound **17**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44) 1223−336−033, or deposit@ccdc.cam.ac.uk).

1-Trifluoroacetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol (18). Compound **18** was prepared by a similar procedure in 91% yield starting from 1-acetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol **16**; mp 123−125 °C (dec). ^{1}H NMR ($CDCl_3$−CF_3CO_2D, 20:1): δ 8.01 (d, J = 6.5 Hz, 1H), 7.95 (m, 2H) 7.72 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 162.9 (q, $^2J_{CF}$ = 41 Hz), 138.3, 137.1, 131.9, 129.3, 114.5 (q, J_{CF} = 286 Hz);

^{11}B NMR (CDCl$_3$): δ 19.75 (s). Anal. Calcd. for $C_8H_5BF_3IO_4$: C, 26.70; H, 1.40; I, 35.27. Found: C, 26.55; H, 1.31; I, 34.99.

Single crystals of product **18** suitable for X-ray crystallographic analysis were obtained by slow evaporation of the chloroform solution of **18**. X-ray diffraction data were collected on a Rigaku RAPID II diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 298 K. Multiscan absorption correction was applied to the data using the CrystalClear 2.0 program (Rigaku Inc. 2010). The structure was solved by the Patterson method (PATTY) using the CrystalStructure 4.0 program and refined by full-matrix least-squares refinement on F^2 using the Crystals for Windows program. Crystal data for **18** $C_8H_5B_1F_3I_1O_4$: M 359.83, triclinic, space group $P\overline{1}$, a = 5.1165(3), b = 7.9571(5), c = 13.7918(9) Å, α = 90.851(6)°, β = 90.094(6)°, γ = 105.522(7)°, V = 540.95(6) Å^3, Z = 2, μ = 3.001 mm^{-1}, 13990 reflections measured, 2482 unique; final R_1 = 0.0317, R_w = 0.0821. CCDC-836130 contains the supplementary crystallographic data for compound **18**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44) 1223−336−033, or deposit@ccdc.cam.ac.uk).

Preparation of 4-Fluoro-1-trifluoroacetoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol (17) by Direct Oxidation of 2-Fluoro-6-iodophenylboronic Acid in Trifluoroacetic Acid. A solution of 2-fluoro-6-iodophenylboronic acid **11** (0.266 g, 1.0 mmol) in trifluoroacetic acid (2 mL) was cooled to 5 °C, and the commercial bleach solution (2.0 mL of ~5% aqueous NaOCl) was added in 0.1 mL portions under stirring. The stirring was continued at 5 °C for additional 30 min until complete disappearance of starting material according to TLC. Then water (5 mL) was added, and the resulting white, crystalline precipitate was filtered, washed with water, and dried in vacuum to afford 0.292 g (77%) of product **17**, mp 139−140 °C (dec), identical to the sample of **17** prepared by the previous procedure.

Synthesis and Characterization of 4-Fluoro-1-hydroxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol-3-ol (19). Solid acetate **15** (0.097 g, 0.3 mmol) was mixed with water (2 mL) and $NaHCO_3$ (50 mg) at room temperature. The resulting suspension was stirred overnight, then the solid was filtered, washed with water, and dried in vacuum to give 0.057 g (68%) of product **19**; mp 138−138.5 °C (dec). ^{1}H NMR (CDCl$_3$): δ 7.81 (m, 2H), 7.33 (ddd, J = 8.5 Hz, 7.5 Hz, 1.0 Hz, 1H); ^{11}B NMR (CDCl$_3$): δ 19.86 (s). Anal. Calcd. for $C_6H_5BFIO_3$: C, 25.57; H, 1.79; I, 45.03. Found: C, 25.97; H, 1.32; I, 45.40. Product **19** can be prepared using a similar procedure starting from trifluoroacetate **17** in 97% yield.

X-ray Crystal Structure of Tetrameric 4-Fluoro-1,3-dimethoxy-1*H*-1λ^3-benzo[*d*][1,2,3]iodoxoborol (21). Single crystals of product **21** suitable for X-ray crystallographic analysis were prepared by slow crystallization from a solution of the trifluoroacetate **17** in methanol at room temprature in the dark during 10 days. X-ray diffraction data were collected on a Rigaku RAPID II diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 123 K. Multiscan absorption correction was applied to the data using the CrystalClear 2.0 program (Rigaku Inc. 2010). The structure was solved by the Patterson method (PATTY) using the CrystalStructure 4.0 program and refined by full-matrix least-squares refinement on F^2 using the Crystals for Windows program. Crystal data for **21** $C_{32}H_{36}B_4F_4I_4O_{12}$: M 1239.45, monoclinic, space group $C2/c$, a = 15.3210(3), b = 13.6647(2), c = 37.391(3) Å, β = 99.240(7)°, V = 7726.5(7) Å^3, Z = 8, μ = 3.306 mm^{-1}, 24417 reflections measured, 8610 unique; final R_1 = 0.0393, R_w = 0.0753. CCDC-836133 contains the supplementary crystallographic data for compound **21**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44) 1223−336−033, or deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic information files (CIF) for compounds **13**, **17**, **18**, and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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