Inorganic Chemistry

Victor N. Nemykin,^{*,†} Andrey V. Maskaev,[†] Margarita R. Geraskina,[†] Mekhman S. Yusubov,^{*,‡} and Viktor V. Zhdankin^{*,†}

⁺Department of Chemistry and Biochemistry, University of Minnesota Duluth, 1039 University Dr., Duluth, Minnesota 55812, United States

[‡]The Siberian State Medical University and The Tomsk Polytechnic University, 634050 Tomsk, Russian Federation

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*-1 λ^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 iodo-dichloride with water. 1-Acetoxy-4-fluoro-1*H*-1 λ^3 -benzo[*d*][1,2,3]iodoxoborol-3-ol, 1-acetoxy-1*H*-1 λ^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 NaHCO₃. 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*-1 λ^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*-1 λ^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. $^{\rm 2a}$

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*-ClC₆H₄CO₂)^{Si} 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

Received:September 1, 2011Published:October 11, 2011

ARTICLE





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-chlorobenziodoxoles⁷ (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)





Figure 1. (a) CAMERON view of 1-chloro-4-fluoro- $1H-1\lambda^3$ -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) Intraand intermolecular secondary bonding in 13.

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).

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

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)		

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

Scheme 2. Preparation of 1-Acetoxybenziodoxaboroles 15 and 16







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



Figure 2. (a) CAMERON view of 4-fluoro-1-trifluoroacetoxy- $1H-1\lambda^3$ 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-1H- $1\lambda^3$ -benzo-[d][1,2,3]iodoxoborol-3-ol 18 (ellipses are shown at 50% probability). (b) Intra- and intermolecular secondary bonding in 18.

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).

Selected Bond Distances for Compound 17 (A)						
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)	I2-07 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)	07-12-05 168.71(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)			

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

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-OCOCF₃ (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)

Scheme 5. Preparation of 1-Hydroxybenziodoxaborole 19



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).

A mild, basic hydrolysis of 1-acetoxy- or 1-trifluoroacetoxybenziodoxaborole affords 1-hydroxybenziodoxaborole **19** (Scheme 5) as a white powder, which was characterized by ¹H 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 sp² hybrid boron atoms into tetrahedral sp³ hybridized atoms. Indeed, each boron atom in tetramer 21 forms one covalent bond with carbon and three covalent bonds with oxygen atoms. Interestingly, boronoxygen 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 sp³ hybridized boron atoms. The change in hybridization of the boron atoms in tetramer 21 also leads to a significant elongation of boroncarbon 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-acetoxy-benziodoxoles 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 sp² hybridized boron atom (compounds 13, 17, and 18) compared to those observed in tetramer 21, which has a tetrahedral sp³ 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 character⁹ in the new boron-containing heterocycles, which should be eliminated upon transformation of the boron atom from trigonal-planar (sp²) to tetrahedral (sp³) 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 fivemembered 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, sixelectron [5c,6e] -C-C-B-O-I- and -C-C-C-O-Iheterocyclic 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

ARTICLE



Figure 4. (a) Perspective view of tetrameric 4-fluoro-1,3-dimethoxy- $1H-1\lambda^3$ -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 Crystallograph	graphy
--	--------

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)	07-I3-08 170.04(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*-1 λ^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*-1 λ^3 -benzo[*d*][1,2,3]iodoxoborol-3-ol, 1-acetoxy-1*H*-1 λ^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 NaHCO₃. X-ray structural studies of 1-chloro- and 1-trifluoroacetoxy substituted



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

benziodoxaboroles have shown the presence of a planar fivemembered 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*-1 λ^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*-1 λ^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.

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 (¹H NMR), 125 MHz (¹³C NMR), and 160 MHz (¹¹B NMR). Chemical shifts are reported in parts per million (ppm). ¹H and ¹³C chemical shifts are referenced relative to tetramethylsilane, and ¹¹B chemical shifts are referenced relative to BF₃-etherate. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, Georgia.

Synthesis and Characterization of 1-Chloro-4-fluoro-1H- $1\lambda^3$ -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 CHCl₃ (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 CHCl₃, 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 CHCl₃; mp 135-137 °C (dec). ¹H NMR (CDCl₃): 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); ¹³C NMR (CDCl₃): δ 168.6 (d, J_{CF} = 255 Hz), 135.4 (d, ${}^{3}J_{CF}$ = 8.3 Hz), 129.9 (d, ${}^{3}J_{CF} = 8.8 \text{ Hz}$), 123.8 (d, ${}^{4}J_{CF} = 3.8 \text{ Hz}$), 117.6 (d, ${}^{2}J_{CF} = 23.8 \text{ Hz}$); ¹¹B NMR (CDCl₃): δ 31.01 (br s) and 19.74 (s). Anal. Calcd. for C₆H₄BClFIO₂: 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 MoK α radiation ($\lambda =$ 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 Crystal-Structure 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 $P\overline{1}$, a = 7.4745(4), b = 10.5487(6), c = 11.7411(8) Å, $\alpha = 109.722(8)^\circ$, $\beta = 99.391(7)^\circ$, $\gamma =$ 97.560(7)°, V = 842.22(11) Å³, Z = 4, $\mu = 4.086$ 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*-1λ³-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). ¹H NMR (D₂O): δ 7.72 (m, 2H), 7.32 (m, 1H), 2.10 (s, 3H); ¹¹B NMR (D₂O): δ 19.80 (s). Anal. Calcd. for C₈H₇BFIO₄: C, 29.67; H, 2.18; I, 39.19. Found: 29.62; H, 2.11; I, 38.93.

1-Acetoxy-1*H*-1 λ^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). ¹H NMR (D₂O): δ 7.85 (m, 3H), 7.65 (m, 1H), 2.10 (s, 3H); ¹¹B NMR (CDCl₃): δ 19.86 (s). Anal. Calcd. for C₈H₈BIO₄: 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*-1 λ^3 -benzo[*d*][1,2,3]iodoxoborol-3-ol (17) and 1-Trifluoroacetoxy-1*H*-1 λ^3 -benzo[*d*][1,2,3]iodoxoborol-3-ol (18). To a stirred mixture of acetate 15 (0.650 g, 2.0 mmol) in CH₂Cl₂ (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 CH₂Cl₂ to give analytically pure trifluoroacetate 17 as colorless needles; yield 0.720 g (95%); mp 139–140 °C (dec). ¹H NMR (CDCl₃): δ 7.83–7.76 (m, 2H), 7.33 (ddd, *J* = 8.0, 8.0, and 0.5 Hz, 1H); ¹³C NMR (CDCl₃): δ 169.61 (d, *J*_{CF} = 257.3 Hz), 162.1 (q, ²*J*_{CF} = 4.1 Hz), 118.4 (d, ²*J*_{CF} = 22.9 Hz), 114.6 (q, *J*_{CF} = 283 Hz); ¹¹B NMR (CDCl₃): δ 19.75 (s). Anal. Calcd. for C₈H₄BF₄IO₄: 25.43; H, 10.7; 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 MoK α radiation ($\lambda = 0.71073$ 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 C₈H₄B₁F₄I₁O₄: M 377.82, triclinic, space group $P\overline{1}$, a = 9.0868(4), b = 10.3720(5), c =12.5120(8) Å, $\alpha = 77.436(6)^{\circ}$, $\beta = 81.887(6)^{\circ}$, $\gamma = 71.565(5)^{\circ}$, V =1088.59(11) Å³, Z = 4, μ = 3.001 mm⁻¹, 28579 reflections measured, 4988 unique; final R₁ = 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***-**1 λ^3 **-benzo**[*d*][1,2,3]iodoxoborol-3ol (18). Compound 18 was prepared by a similar procedure in 91% yield starting from 1-acetoxy-1*H*-1 λ^3 -benzo[*d*][1,2,3]iodoxoborol-3-ol 16; mp 123–125 °C (dec). ¹H NMR (CDCl₃–CF₃CO₂D, 20:1): δ 8.01 (d, *J* = 6.5 Hz, 1H), 7.95 (m, 2H) 7.72 (m, 1H); ¹³C NMR (CDCl₃): δ 162.9 (q, ²*J*_{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_3BF_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 MoK α radiation ($\lambda = 0.71073$ 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 C₈H₅B₁F₃I₁O₄: M 359.83, triclinic, space group $P\overline{1}$, a = 5.1165(3), b = 7.9571(5), c =13.7918(9) Å, $\alpha = 90.851(6)^{\circ}$, $\beta = 90.094(6)^{\circ}$, $\gamma = 105.522(7)^{\circ}$, V =540.95(6) Å³, 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*-1 λ^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*-1 λ^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 NaHCO₃ (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). ¹H NMR (CDCl₃): δ 7.81 (m, 2H), 7.33 (ddd, *J* = 8.5 Hz, 7.5 Hz, 1.0 Hz, 1H); ¹¹B NMR (CDCl₃): δ 19.86 (s). Anal. Calcd. for C₆H₅BFIO₃: 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*-1 λ^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 MoK α 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 C₃₂H₃₆B₄F₄I₄O₁₂: M 1239.45, monoclinic, space group C2/c, a = 15.3210(3), b = 13.6647(2), c = 37.391(3) Å, $\beta = 99.240(7)^{\circ}$, V = 7726.5(7) Å³, Z = 8, $\mu = 3.306$ mm⁻¹, 24417 reflections measured, 8610 unique; final R₁ = 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.

AUTHOR INFORMATION

Corresponding Author

*E-mail: vnemykin@d.umn.edu (V.N.N.), yusubov@mail.ru (M.S.Y.), vzhdanki@d.umn.edu (V.V.Z.).

ACKNOWLEDGMENT

This work was supported by a research grant from the National Science Foundation (CHE-1009038) and by NSF-MRI award (MRI-0922366). V.V.Z. and M.S.Y. are also thankful to the Government of Russia for support of their cooperative research program on hypervalent iodine chemistry (FCP, GK 02.740.11.5211; Zayavka 2010-1.5-000-010-044 and FCP, GK 11.519.11.5010, Zayavka 2011-1.9-519-024-070).

REFERENCES

(1) For books and selected reviews on hypervalent iodine chemistry, see: (a) Varvoglis, A. Hypervalent Iodine in Organic Synthesis; Academic Press: London, U.K., 1997. (b) Hypervalent Iodine Chemistry; Wirth, T., Ed.; Springer-Verlag: Berlin, Germany, 2003. (c) Koser, G. F. Aldrichimica Acta 2001, 34, 89-102. (d) Koser, G. F. Adv. Heterocycl. Chem. 2004, 86, 225-292. (e) Moriarty, R. M. J. Org. Chem. 2005, 70, 2893-2903. (f) Quideau, S.; Pouysegu, L.; Deffieux, D. Synlett 2008, 467-495. (g) Ladziata, U.; Zhdankin, V. V. ARKIVOC 2006, No. ix, 26-58. (h) Ciufolini, M. A.; Braun, N. A.; Canesi, S.; Ousmer, M.; Chang, J.; Chai, D. Synthesis 2007, 3759-3772.(i) Zhdankin, V. V. In Science of Synthesis; Thieme: Stuttgart, Germany, 2007, Vol. 31a, Chapter 31.4.1, pp 161-234. (j) Zhdankin, V. V.; Stang, P. J. Chem. Rev. 2008, 108, 5299-5358. (k) Ladziata, U.; Zhdankin, V. V. Synlett 2007, 527-537. (1) Dohi, T.; Kita, Y. Chem. Commun. 2009, 2073-2085. (m) Ochiai, M.; Miyamoto, K. Eur. J. Org. Chem. 2008, 4229-4239. (n) Yusubov, M. S.; Zhdankin, V. V. Mendeleev Commun. 2010, 20, 185-191. (o) Zhdankin, V. V. ARKIVOC 2009, No. i, 1-62. (p) Uyanik, M.; Ishihara, K. Chem. Commun. 2009, 2086-2099. (q) Ngatimin, M.; Lupton, D. W. Aust. J. Chem. 2010, 63, 653-658. (r) Yusubov, M. S.; Nemykin, V. N.; Zhdankin, V. V. Tetrahedron 2010, 66, 5745-5752. (s) Quideau, S.; Wirth, T. Tetrahedron 2010, 66, 5737-5738. (t) Uyanik, M.; Ishihara, K. Aldrichimica Acta 2010, 43, 83-91. (u) Merritt, E. A.; Olofsson, B. Angew. Chem., Int. Ed. 2009, 48, 9052–9070. (v) Merritt, E. A.; Olofsson, B. Synthesis 2011, 517-538. (w) Zhdankin, V. V. J. Org. Chem. 2011, 76, 1185-1197. (x) Silva, J. L. F.; Olofsson, B. Nat. Prod. Rep. 2011, 28, 1722-1754.

(2) For reviews on benziodoxole-based hypervalent iodine reagents, see: (a) Brand, J. P.; Gonzalez, D. F.; Nicolai, S.; Waser, J. Chem. Commun. 2011, 47, 102–115. (b) Duschek, A.; Kirsch, S. F. Angew. Chem., Int. Ed. 2011, 50, 1524–1552. (c) Satam, V.; Harad, A.; Rajule, R.; Pati, H. Tetrahedron 2010, 66, 7659–7706. (d) Zhdankin, V. V. Rev. Heteroat. Chem. 1997, 17, 133–151. (e) Zhdankin, V. V. Curr. Org. Synth. 2005, 2, 121–145. (f) Morales-Rojas, H.; Moss, R. A. Chem. Rev. 2002, 102, 2497–2521.

(3) (a) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Formaneck, M. S.; Bolz, J. T. *Tetrahedron Lett.* **1994**, 35, 9677–9680. (b) Zhdankin, V. V.; McSherry, M.; Mismash, B.; Bolz, J. T.; Woodward, J. K.; Arbit, R. M.; Erickson, S. *Tetrahedron Lett.* **1997**, 38, 21–24. (c) Zhdankin, V. V.; Kuehl, C. J.; Bolz, J. T.; Formaneck, M. S.; Simonsen, A. J. *Tetrahedron Lett.* **1994**, 35, 7323–7326. (d) Zhdankin, V. V.; Koposov, A. Y.; Litvinov, D. N.; Ferguson, M. J.; McDonald, R.; Luu, T.; Tykwinski, R. R. J. Org. Chem. **2005**, 70, 6484–6491. (e) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T.; Mismash, B.; Woodward, J. K.; Simonsen, A. J.

Tetrahedron Lett. **1995**, *36*, 7975–7978. (f) Eisenberger, P.; Gischig, S.; Togni, A. *Chem.—Eur. J.* **2006**, *12*, 2579–2586. (g) Kieltsch, I.; Eisenberger, P.; Stanek, K.; Togni, A. *Chimia* **2008**, *62*, 260–263.

(4) (a) Balthazor, T. M.; Godar, D. E.; Stults, B. R. J. Org. Chem.
1979, 44, 1447–1449. (b) Moss, R. A.; Chatterjee, S.; Wilk, B. J. Org. Chem. 1986, 51, 4303–4307. (c) Zhdankin, V. V.; Arbit, R. M.; Lynch, B. J.; Kiprof, P.; Young, V. G. J. Org. Chem. 1998, 63, 6590–6596.
(d) Zhdankin, V. V.; Koposov, A. Y.; Su, L. S.; Boyarskikh, V. V.; Netzel, B. C.; Young, V. G. Org. Lett. 2003, 5, 1583–1586. (e) Zhdankin, V. V.; Koposov, A. E.; Smart, J. T.; Tykwinski, R. R.; McDonald, R.; Morales-Izquierdo, A. J. Am. Chem. Soc. 2001, 123, 4095–4096. (f) Zhdankin, V. V.; Nemykin, V. N.; Karimov, R. R.; Kazhkenov, Z.-G. Chem. Commun. 2008, 6131–6133. (g) Koser, G. F.; Sun, G.; Porter, C. W.; Youngs, W. J. J. Org. Chem. 1993, 58, 7310–7312. (h) Koposov, A. Y.; Litvinov, D. N.; Zhdankin, V. V.; Ferguson, M. J.; McDonald, R.; Tykwinski, R. R. Eur. J. Org. Chem. 2006, 4791–4795. (i) Jaffe, H.; Leffler, J. E. J. Org. Chem. 1975, 40, 797–799. (j) Balthazor, T. M.; Miles, J. A.; Stults, B. R. J. Org. Chem. 1978, 43, 4538–4540.

(5) (a) Batchelor, R. J.; Birchall, T.; Sawyer, J. F. Inorg. Chem. 1986, 25, 1415-1420. (b) Zhdankin, V. V.; Maydanovych, O.; Herschbach, J.; McDonald, R.; Tykwinski, R. R. J. Am. Chem. Soc. 2002, 124, 11614-11615. (c) Zhdankin, V. V.; Krasutsky, A. P.; Kuehl, C. J.; Simonsen, A. J.; Woodward, J. K.; Mismash, B.; Bolz, J. T. J. Am. Chem. Soc. 1996, 118, 5192-5197. (d) Amey, R. L.; Martin, J. C. J. Org. Chem. 1979, 44, 1779-1784. (e) Ochiai, M.; Masaki, Y.; Shiro, M. J. Org. Chem. 1991, 56, 5511-5513. (f) Shefter, E.; Wolf, W. J. Pharm. Sci. 1965, 54, 104-107. (g) Etter, M. C. J. Am. Chem. Soc. 1976, 98, 5326-5331. (h) Etter, M. C. J. Am. Chem. Soc. 1976, 98, 5331-5339. (i) Gougoutas, J. Z.; Lessinger, L. J. Solid State Chem. 1974, 9, 155-164. (j) Ochiai, M.; Ito, T.; Masaki, Y.; Shiro, M. J. Am. Chem. Soc. 1992, 114, 6269-6270. (k) Ochiai, M.; Ito, T.; Shiro, M. J. Chem. Soc., Chem. Commun. 1993, 218-220. (l) Zhdankin, V. V.; Kuehl, C. J.; Arif, A. M.; Stang, P. J. Mendeleev Commun. 1996, 50-51. (m) Akai, S.; Okuno, T.; Takada, T.; Tohma, H.; Kita, Y. Heterocycles 1996, 42, 47-51. (n) Braddock, D. C.; Cansell, G.; Hermitage, S. A.; White, A. J. P. Chem. Commun 2006, 1442-1444. (o) Kieltsch, I.; Eisenberger, P.; Togni, A. Angew. Chem., Int. Ed. 2007, 46, 754-757.

(6) Zhdankin, V. V.; Arbit, R. M.; McSherry, M.; Mismash, B.; Young, V. G. J. Am. Chem. Soc. **1997**, 119, 7408–7409.

(7) Amey, R. L.; Martin, J. C. J. Org. Chem. 1979, 44, 1779.

(8) For representative examples of self-assembly of hypervalent iodine species into supramolecular cyclic or polymeric structures, see: (a) Richter, H. W.; Koser, G. F.; Incarvito, C. D.; Rheingold, A. L. *Inorg. Chem.* **2007**, *46*, 5555–5561. (b) Nemykin, V. N.; Koposov, A. Y.; Netzel, B. C.; Yusubov, M. S.; Zhdankin, V. V. *Inorg. Chem.* **2009**, *48*, 4908–4917. (c) Koposov, A. Y.; Netzel, B. C.; Yusubov, M. S.; Nemykin, V. N.; Nazarenko, A. Y.; Zhdankin, V. V. *Eur. J. Org. Chem.* **2007**, 4475–4478.

(9) Planar geometry and bond shortening in a heterocyclic ring are commonly accepted criteria of aromaticity; see: (a) Balaban, A. T.; Oniciu, D. C.; Katritzky, A. R. *Chem. Rev.* 2004, *104*, 2777–2812.
(b) Katritzky, A. R.; Jug, K.; Oniciu, D. C. *Chem. Rev.* 2001, *101*, 1421–1449. (c) Krygowski, T. M.; Cyranski, M. K.; Czarnocki, Z.; Hafelinger, G.; Katritzky, A. R. *Tetrahedron* 2000, *56*, 1783–1796.

(10) Vidovic, D.; Moore, J. A.; Jones, J. N.; Cowley, A. H. J. Am. Chem. Soc. 2005, 127, 4566–4567.