

Anhydrides of Real and Hypothetical [Hydroxy(R–O)iodo]benzenes

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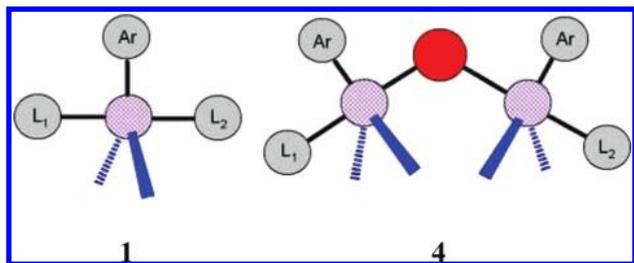
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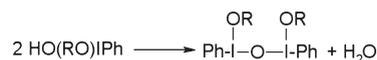
The anhydrides of [hydroxy(methanesulfonato–O)]iodobenzene (HMIB) and [hydroxy(toluenesulfonato–O)]iodobenzene (HTIB) were prepared by drying acetonitrile solutions of the compounds. The anhydrides of the hypothetical compounds [hydroxy(chloroacetato–O)]iodobenzene and [hydroxy(iodoacetato–O)]iodobenzene were obtained from aqueous solutions. Crystallographic structures were obtained for the anhydrides, except that of HTIB. The electron-domain geometries of the I atoms vis-à-vis secondary I···O bonds were explored. The presence of delocalized bonding in groupings of O and I atoms was suggested. A linear relationship between the C–I–O angles and the I–O bond orders was observed.

Introduction

Aryl λ^3 -iodanes (**1**) can support a variety of O-centered ligands such as water molecules, hydroxide ions, alkyl and aryl sulfonate ions, and carboxylate ions.^{1–3} The asymmetric species [hydroxy(methanesulfonato–O)]iodobenzene (HMIB, **2**)² and [hydroxy(toluenesulfonato–O)]iodobenzene (HTIB, **3**) are useful synthetic reagents.^{4,5} The nature of the bonding in these compounds has been examined.⁶



It is easy to visualize formation of the anhydrides of [hydroxy(R–O)iodo]benzenes:



Several of these μ -oxodiiiodanes (**4**) have been isolated (L_1 and L_2 defined in structures **1** and **4**). In 1972, Merkushev and co-workers reported the preparation of μ -oxobis[trichloroacetato–O(phenyl)iodine(III)],⁷ μ -oxobis[chloroacetato–O(phenyl)iodine(III)],⁷ and μ -oxobis[bromoacetato–O(phenyl)iodine(III)] with characterization via elemental analysis and molecular weight determinations. Structures have been determined via X-ray crystallography for μ -oxobis[nitrato–O(phenyl)iodine(III)],⁸ μ -oxobis[trifluoroacetato–O(phenyl)iodine(III)],⁹ μ -oxobis[trifluoroacetato–O(*m*-methylphenyl)iodine(III)],¹⁰ μ -oxo[nitrato–O(phenyl)iodine(III)][phenyl(trifluoroacetato–O)iodine(III)],¹¹ and the

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(1) Ochiai, M.; Miyamoto, K.; Yokota, Y.; Suefuji, T.; Shiro, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 75–78.

(2) Richter, H. W.; Cherry, B. R.; Zook, T. Z.; Koser, G. F. *J. Am. Chem. Soc.* **1997**, *119*, 9614–9623.

(3) Richter, H. W.; Koser, G. F.; Incarvito, C. D.; Rheingold, A. L. *Inorg. Chem.* **2007**, *46*, 5555–5561.

(4) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 4988–4989.

(5) Koser, G. F.; Wettach, R. H.; Troup, J. M.; Frenz, B. A. *J. Org. Chem.* **1976**, *41*, 3609–3611.

(6) Koser, G. F. Hypervalent halogen compounds. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1983; Chapter 18; pp 734–740.

(7) Merkushev, A. N.; Novikov, A. N.; Kogai, T. I.; Glushkova, V. V. *Zh. Org. Khim.* **1972**, *8*, 436.

(8) Alcock, N. W.; Countryman, R. M. *J. Chem. Soc., Dalton Trans.* **1979**, 851–853.

(9) Gallos, J.; Varvoglis, A.; Alcock, H. W. *J. Chem. Soc., Perkin Trans. 1* **1985**, 757–764.

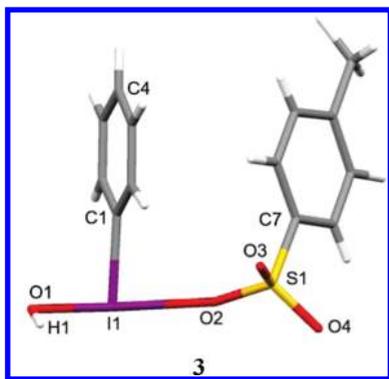
(10) Kokkou, S. C.; Cheer, C. J. *Acta Crystallogr., Sect. C* **1986**, *C42*, 1748–1750.

(11) Bushnell, G. W.; Fischer, A.; Ibrahim, P. N. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1281–1285.

methanesulfonate has an angle less than 90° . The plane of the phenyl ring is nearly normal to the T-shaped bond plane (83.3° between planes). The O–H bond distance in the hydroxide ligand is $0.809(1)$ Å, where the sum of the covalent radii is 1.10 Å, showing the robust nature of the ligand.

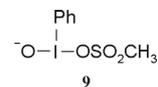
Secondary bonds are important in the solid-state structure of HMIB (Figures 2 and 3 and Table 1). The I atom has a weak intramolecular interaction with an O atom in the MsO^- ligand. Dimers form when two O–I–O segments assume an antiparallel alignment, stabilized by a pair of very strong intermolecular $\text{I}\cdots\text{O}$ bonds ($\text{I1}\cdots\text{O3}'$ and $\text{I1}'\cdots\text{O3}$, 2.820 Å). Pairs of dimers align with O–I–O segments end-to-end and offset, producing a stair-like structure where “risers” are produced when the dimer steps are joined by hydrogen bonds between the H atoms in the hydroxides and the O atoms in the methanesulfonate ligands ($\text{H1}\cdots\text{O4A}$ and $\text{H1A}'\cdots\text{O4}'$, 1.860 Å) and by weak $\text{I}\cdots\text{O}$ bonds ($\text{I1}\cdots\text{O4A}$ and $\text{I1A}'\cdots\text{O4}'$, 3.505 Å). The hydrogen bonds are strong, well below the van der Waals (vdw) sum of 2.50 Å.

Structure of HTIB. The structure of HTIB (**3**) was determined in 1976 (Table 1),⁵ and it mirrors that of HMIB. While the O–I–O segment in HTIB is virtually linear, the same droop-and-shrug motif in the C–I–O angles appears. The plane of the T-shaped bond is virtually planar; no atom is displaced by more than 0.001 Å from the plane. The intramolecular $\text{I1}\cdots\text{O3}$ bond approaches the vdw limit. Dimers form when two O–I–O segments assume an antiparallel alignment and are held in position by hydrogen bonds ($\text{H1}\cdots\text{O3A}'$ and $\text{O3}\cdots\text{H1A}'$, 2.004 Å; Figure 2). Pairs of dimers with O–I–O segments aligned in an opposite sense produce a stairlike structure stabilized by hydrogen bonds, much like that in HMIB.



Structure of HMIBA. The methanesulfonate ligands in this μ -oxo- λ^3 -iodane are robust, with the expected tetrahedral geometry about the S atoms (Figure 1 and Table 2). Each molecule has two nearly linear O–I–O bond segments, and each segment is unsymmetrically polarized; the interior I1–Oii and I2–Oii bond lengths are “short”, while I1–O1 and I2–O2 are “long”. The ligands on I1 are methanesulfonate and the conjugate base of HMIB (**9**); the bond lengths indicate that **9** is more basic than methanesulfonate, which should have a negligible base strength. The droop-and-shrug motif in the C–I–O angles appears with the phenyl ring slightly tilted away from the I–**9** bond and slightly toward the I–methanesulfonate bond. I2 has a good intramolecular secondary bond ($\text{I2}\cdots\text{O23}$, 3.165 Å), but I1 has only a marginal interac-

tion ($\text{I1}\cdots\text{O13}$, 3.622 Å). Dimers form when Oii–I2–O2 segments from two molecules align, held together by three pairs of $\text{I}\cdots\text{O}$ bonds [$\text{I1}\cdots\text{O22}'$ and $\text{I1}'\cdots\text{O22}$, $3.361(6)$ Å; $\text{I1}\cdots\text{O23}'$ and $\text{I1}'\cdots\text{O23}$, $3.089(7)$ Å; $\text{I2}\cdots\text{O23}'$ and $\text{I2}'\cdots\text{O23}$, $3.3672(5)$ Å; Figure 2].



Structure of HCIBA. The structure of HCIBA parallels that of HMIBA (Figures 1 and 2 and Table 2). The O–I–O segments are slightly bent, and the droop-and-shrug motif in the C–I–O angles becomes a “straight-and-shrug” motif, where the bonds to the bridging O atom give nearly normal angles but the bonds to methanesulfonate are 10° smaller. Both I1 and I2 have strong intramolecular $\text{I}\cdots\text{O}$ bonds. An antiparallel alignment of the Oii–I1–O1 segments in two HCIBA molecules produces a dimer by virtue of two intermolecular $\text{I}\cdots\text{O}$ bonds [$\text{I1}\cdots\text{O12}'$ and $\text{I1}'\cdots\text{O12}$, $3.020(1)$ Å]. The dimers stack in a stairlike array, with no $\text{I}\cdots\text{O}$ bonds between them. However, the segment containing I2 dangles from one of the Oii vertices of the O–I–O–O–I–O hexagon and places H27 directly above the hexagon in dimer A (Figures 3 and 4); the chloromethyl group rotates so that H27 points to the center of the hexagon, forming a rectangular pyramid with H27 at the apex, 2.183 Å above plane $\text{Oii–O1–Oii'–O1}'$ (distances from H27: Oii , 4.155 Å; O1 , 4.010 Å; Oii' , 4.647 Å; $\text{O1}'$, 3.634 Å).

Structure of HIIBA. The preparation of HIIBA yielded two crystallographically different forms with similar bond distances and angles (Table 2); only one form is discussed here. As in HCIBA, the O–I–O segments are slightly bent. Likewise, the C–I–O angles have a straight-and-shrug motif where the bonds to oxide give nearly normal angles but the bonds with the iodoacetate are 10° smaller. An antiparallel alignment of Oii–I2–O2 segments in two HIIBA molecules produces a dimer held together by two pairs of $\text{I}\cdots\text{O}$ bonds ($\text{I2}\cdots\text{O22}'$ and $\text{I2}'\cdots\text{O22}$, 3.004 Å; $\text{I1}\cdots\text{O22}'$ and $\text{I1}'\cdots\text{O22}$, 3.217 Å; Figure 2). The dimer is further stabilized by strong intramolecular $\text{I}\cdots\text{O}$ bonds for both I1 and I2 ($\text{I1}\cdots\text{O12}$ and $\text{I1}'\cdots\text{O12}'$, 2.993 Å; $\text{I2}\cdots\text{O22}$ and $\text{I2}'\cdots\text{O22}'$, 3.058 Å).

O–C–O–O–C–O Hexagons. In the reported compounds and in HTIB, dimers form when O–I–O segments from two molecules assume an antiparallel alignment. These dimers contain a hexagonal grouping with a flat “seat” formed by A–B–A'–B' and triangular “flaps” formed by A–C–B and A'–C'–B' (Figure 4 and Table 3). The seats are parallelograms; in all cases, a chair conformation is adopted with flap/seat angles from 2° to 84° . In the worst case (HIIBA), the I atoms are displaced from the planar seat by only 0.077 Å. In addition, each dimer contains a flat “diamond” structure (I–D–I'–D') formed by $\text{I}\cdots\text{O}$ bonds, where D and D' are tethered to the seat, one above and one below the plane. The seat and diamond are not coplanar: the angle between the planes ranges from 7° to 42° . Perhaps delocalized bonding arises in the four-atom “diamond” grouping (I–D–I'–D') that might stabilize the hexagonal groupings.

EDG of the I Atoms in HMIB and HTIB. The I atom in HMIB is CN 7 owing to three primary bonds, two

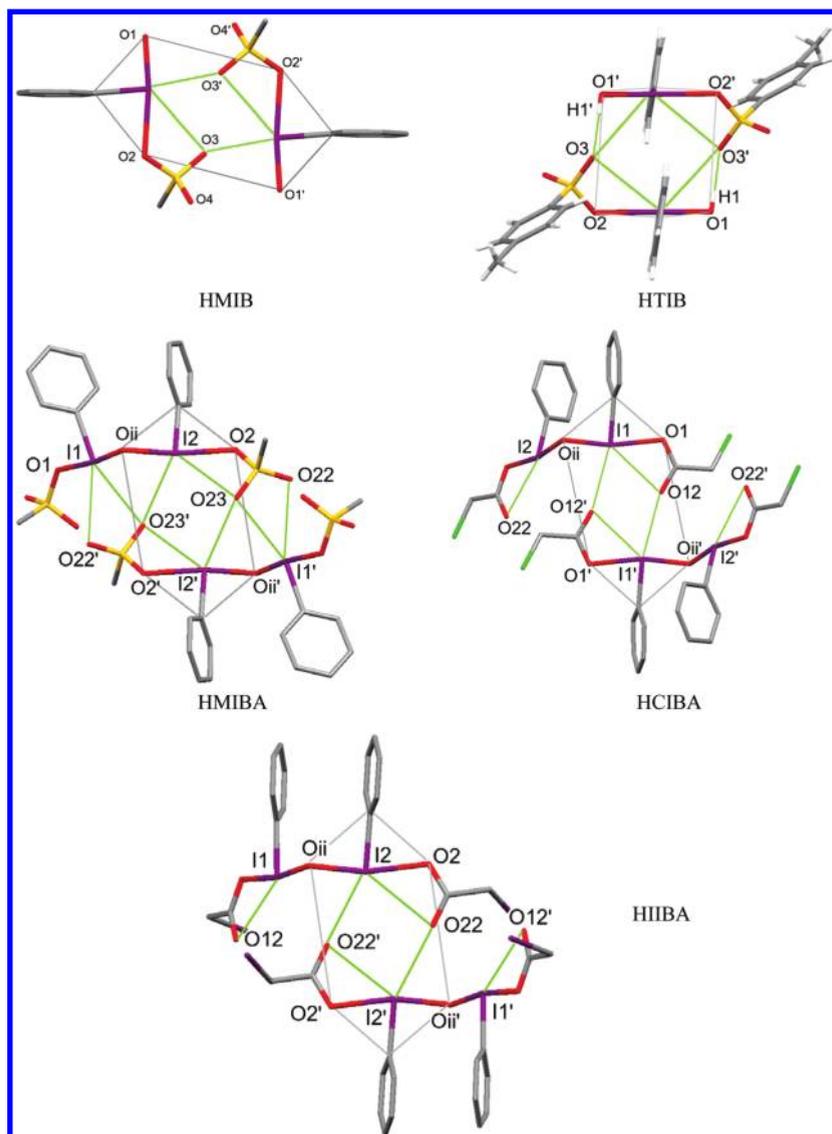


Figure 2. Structures of dimers of the reported compounds and HTIB. The green lines denote secondary bonds, and the light-gray line indicates the hexagonal structure. H atoms are omitted in some structures. Structures are generated by *Mercury 2.2* and annotated using *ArcSoft PhotoStudio 5.5.0.72*.

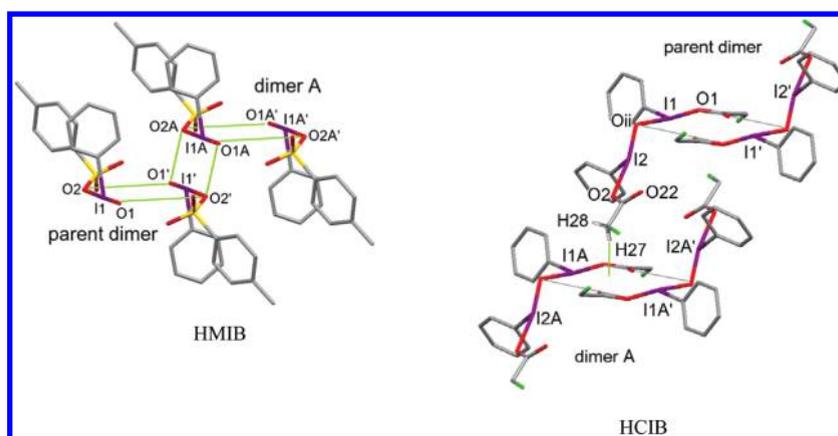


Figure 3. Packing of dimers into stair structures for HMIB and HCIB. H atoms are omitted. Green lines signify secondary bonds. Gray lines serve to clarify structures. Structures are generated by *Mercury 2.2* and annotated using *ArcSoft PhotoStudio 5.5.0.72*.

unshared pairs of electrons, an intramolecular bond ($I1 \cdots O3$, 3.388 Å), and a strong intermolecular bond ($I1 \cdots O3'$, 2.820 Å). The EDG is capped octahedral,

where $O3$ is the capping atom and the unshared pairs are assigned to the axial vertices (Figure 5). The equatorial plane defined by $C1$, $I1$, $O1$, $O2$, and $O3'$ is excellent, with

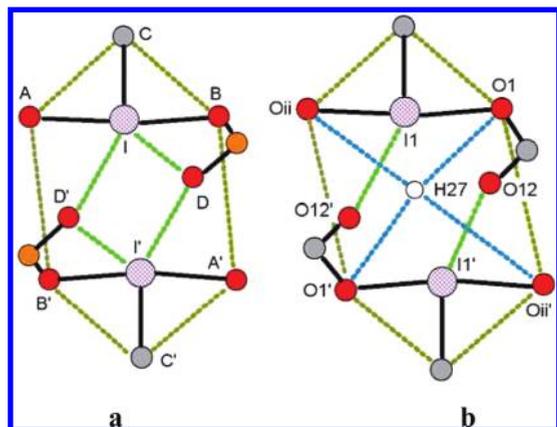


Figure 4. Structures of the O–C–O–O–C–O hexagons where solid black lines denote primary bonds, green lines denote secondary I···O bonds, blue lines denote hydrogen-bonding interactions, and brown lines outline the hexagon: (a) general labeling used for Table 3; (b) structure of the hexagon in HCIBA showing the position of H27 above the seat of the hexagonal grouping of a neighboring dimer.

Table 2. Structures of μ -Oxo Dimers

atom/segment	HMIBA	HCIBA	HIIBA	HIIBA'
Bond Distances (Å)				
Oii–I1	2.022(6)	2.048	2.042	2.036
I1–O1	2.315(6)	2.270	2.251	2.256
I1–C11	2.083(8)	2.102	2.104	2.130
O1–(S1 or C1)	1.502	1.292	1.281	1.308
Oii–I2	2.009(6)	2.027	2.040	2.045
I2–O2	2.342(6)	2.234	2.261	2.237
I2–C21	2.098(8)	2.099	2.104	2.106
O2–(S2 or C2)	1.502	1.280	1.315	1.300
Bond Angles (deg)				
Oii–I1–O1	173.7(3)	167.73	169.93	169.10
C11–I1–Oii	94.7(3)	88.23	89.91	89.56
C11–I1–O1	79.0(3)	79.51	80.03	79.60
I1–C11–C14	174.14	176.16	176.59	177.03
I1–O1–(S1 or C1)	126.2(3)	108.92	111.20	110.54
I1–Oii–I2	117.7(3)	122.21	117.64	116.33
Oii–I2–O2	172.4(2)	168.25	166.10	166.58
C21–I2–Oii	92.5(3)	90.58	88.23	88.69
C21–I2–O2	79.9(2)	80.71	78.46	77.95
I2–C21–C24	177.66	175.91	178.82	177.85
I2–O2–(S2 or C2)	115.0(3)	113.24	113.39	112.96
Angle of Segment w/I1–Oii–I2 Plane (deg)				
I1–C11	67.8	54.8	84.4	83.4
I2–C21	80.3	85.7	71.5	60.2
Angle of Segment w/Average Phenyl Plane (deg)				
I1–Oii	74.6	73.7	46.9	48.5
I2–Oii	64.4	69.6	90.0	71.4

an average atomic displacement of 0.034(22) Å. The I atom in HTIB is CN 8 owing to an intramolecular bond (I1···O3, 3.535 Å) and two intermolecular bonds (I1···O4', 3.003 Å; I1···O2', 3.351 Å). Atoms O1, C1, O2, and O2' give a plane with average atomic displacement of 0.032(6) Å; I1 is only 0.033 Å from the plane. Atoms O3 and O4' complete a hexagon, giving a hexagonal bonding-domain geometry in a chair conformation. The placement of the unshared electron pairs, as in Figure 5, produces a triangular dodecahedral EDG.

EDG of the I Atoms in HMIBA. I1 has two intermolecular bonds with its dimer partner [I1···O23', 3.089(1) Å;

I1···O22', 3.361(1) Å] for CN 7 and pentagonal-bipyramidal EDG (Figure 5). The pentagonal plane contains C11, O23', and O22' and the two unshared pairs; I1 is 0.022 Å out of this plane. The axial positions are occupied by Oii and O1, where the nearly linear axis [173.7(2)°] is slightly tipped. I2 is CN 8, with one intramolecular bond [I2···O23', 3.1650(1) Å], one bond with its dimer partner [I2···O23', 3.367(7) Å], and one bond with a neighboring dimer [I2···OiiA', 3.372(6) Å]. The EDG is best described as triangular dodecahedral,¹⁴ with the vertices occupied by C21, Oii, O2, O23, O23', and OiiA' and the two unshared pairs, with I2 at the center. Atoms Oii, C21, O2, and O23 are in a plane with an average atomic displacement of 0.094(25) Å; I2 is 0.411 Å out of the plane.

EDG of the I Atoms in HCIBA. Both I atoms in HCIBA are CN 7. I1 has an intramolecular bond [I1···O12, 2.971(7) Å] and one bond with its dimer partner [I1···O12', 3.020(1) Å], giving pentagonal-bipyramidal EDG. In contrast to I1 in HMIBA, all five pentagonal vertices are occupied by atoms, while the unshared pairs occupy the axial positions (Figure 5). The plane is lightly puckered, with an average atomic displacement of 0.088(49) Å; I1 is displaced by 0.012 Å. The pentagonal angles approach the ideal value of 72°, where O1–I1–O12 is constrained to a small value by the tether to C1. I2 has one intramolecular bond [I2···O22, 3.072(1) Å] and one very weak bond with its dimer partner [I2···O12', 3.534(7) Å]. The EDG is best described as capped octahedral, with the unshared pairs assigned to the axial positions and O12' as the capping atom (Figure 5); O12' lies 2.096 Å from the square plane (Oii–C21–O2–O22). The ideal 90° angles are not realized all around because O2–I2···O22 is constrained to a smaller angle by the tether to C2, and the capping atom opens angle Oii–I2···O22.

EDG of the I Atoms in HIIBA. HIIBA has four I atoms per molecule; I1 and I2 participate in three-center four-electron [3c–4e] bonds, while I12 and I22 have ordinary covalent bonds. I1 is CN 7, with one intramolecular bond [I1···O12, 2.989(1) Å] and one bond with its dimer partner [I1···O22', 3.217(6) Å]. The EDG is best described as capped octahedral, where the unshared pairs occupy the axial vertices and O22' is the capping atom (Figure 5). The average atomic displacement from the square plane (C12–Oii–O12–O1) is 0.031(11) Å, and I1 is only 0.043 Å out of the plane. I2 is CN 7, with one intramolecular bond [I2···O22, 3.089(1) Å] and one bond with its dimer partner [I2···O22', 3.004(7) Å]; the EDG is pentagonal bipyramidal, with the unshared pairs in the axial positions. The pentagonal plane is puckered with an average atomic displacement of 0.209(74) Å; I2 is displaced by only 0.040 Å. The pentagonal angles approach the ideal 72°, where O2–I2···O22 is small because of tethering. I12 and I22 are in the haloacetate ligands; I12 has no secondary bonds and exhibits bond distances and angles expected for I sp³.¹⁵ In contrast, I22 is the I atom in the I···O bond [I22···OiiB, 3.017(6) Å] that makes dimers (Figure 3)

(14) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984.

(15) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1992.

Table 3. Atomic Distances and Angles in the Hexagon and Diamond Structures^a

	I, A, B, D	distance (Å)				angle (deg)			
		I-□	D-□	I-D	I-D'	Δ-□	◇-□	A-B-A'	D-I-D'
HTIB	I1, O1, O2, O3	0.024	1.179	3.535	3.564	83.53	25.48	86.13	101.12
HMIB	I1, O1, O2, O3	0.021	0.876	3.388	2.820	16.8	29.44	104.12	71.26
HMIBA	I2, Oii, O2, O23	0.049	1.541	3.165	3.367	26.7	42.04	99.48	89.60
HCIBA	I1, Oii, O1, O12	0.000	0.201	2.971	3.020	2.37	7.28	101.75	64.13
HIIBA	I2, Oii, O2, O22	0.077	0.467	3.089	3.004	1.82	13.88	98.12	79.93
34	I1, O1, O3, O4	0.093	0.379	3.000	3.038	4.21	12.53	101.24	71.87
21	I1, O1, O3, O4	0.037	0.050	2.935	2.936	9.19	1.94	101.89	68.87
23	I2, O7, O5, O4	0.016	0.094	3.020	3.096	0.00	2.96	98.52	74.20
35	I2, O1, O2, O3	0.053	0.936	3.124	3.623	35.56	22.87	91.23	91.22

^a Refer to Figure 4 for atom labeling. □ denotes the seat of the hexagon, A-B-A'-B'; Δ denotes the flap on the hexagon, A-C-B; ◇ denotes the diamond, I-D-I'-D'.

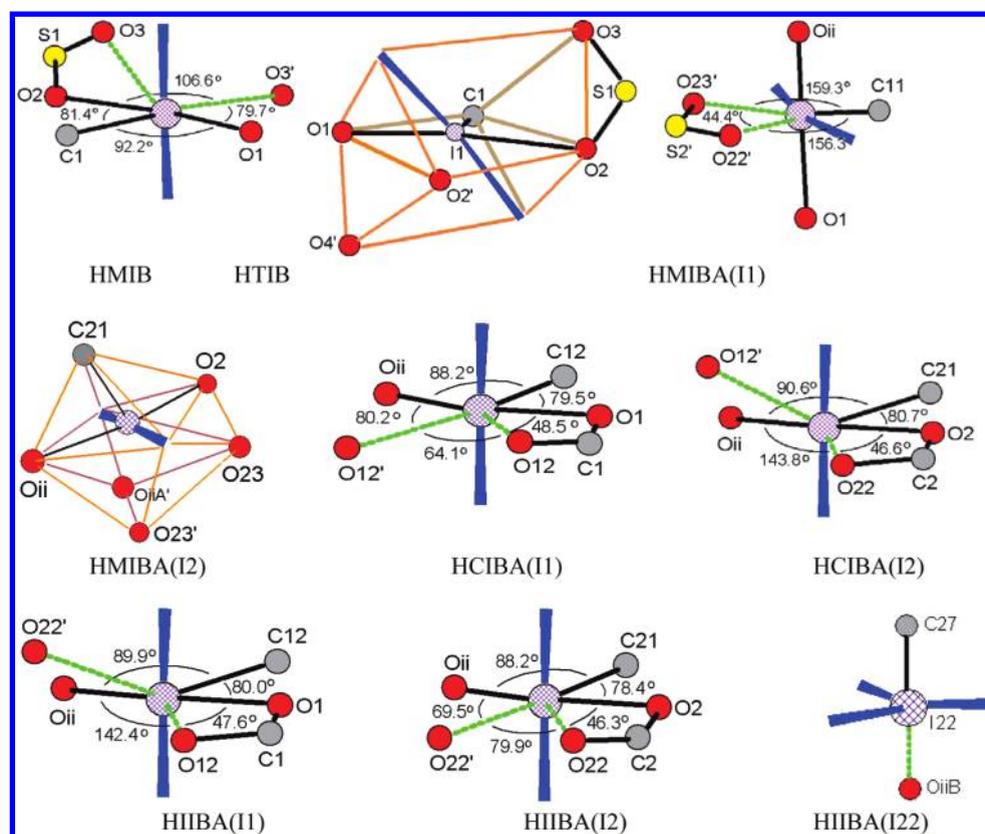
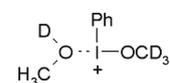


Figure 5. EDGs of the I atoms in the reported compounds and HTIB. Black lines denote primary bonds, green lines denote secondary bonds, bright-blue wedges denote unshared electron pairs, and orange/brown lines serve to visualize geometric structures. Secondary bonds in HTIB and HMIBA(I2) are not shown. The figures were prepared using MDL ISIS/Draw 2.5 from structures generated by Mercury 2.2.

so that it is CN 5. The molecular geometry is nearly linear ($\angle C27-I22 \cdots OiiB$, 170.58°), and the EDG is trigonal-bipyramidal.

NMR Spectroscopy. The 1H NMR spectra of CD_3OD solutions of HMIB, HMIBA, HTIB and HTIBA are virtually identical (Table 4), consistent with solvolysis of each compound to $PhI(OCD_3)_2$ and CH_3SO_3D . [Dimethoxy(iodo)]benzene has been isolated,¹⁶ though it is unstable probably because of the unfavorable influence of two strong trans-influencing ligands on I^{III} .¹² Consequently, the species in these acidic methanolic solutions is more likely the protonated form that circumvents this problem

(this species can be solvated with additional CD_3OD molecules):



In contrast, the aromatic δ for HCIBA and HIIBA are significantly shifted, suggesting that the haloacetate ligands successfully compete with methoxide in methanol solutions. Spectra of HMIBA and HTIBA in a $CDCl_3$ solution were obtained. In the driest HMIBA solutions prepared, the o - 1H appeared as a doublet with no fine structure; both the p - and m - 1H presented as triplets of triplets. The

(16) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563–1565.

Table 4. Chemical Shifts in the ^1H NMR Spectra of CD_3OD and CDCl_3 Solutions^a

sample	^1H NMR chemical shifts (ppm)			
	<i>o</i> -PhI	<i>p</i> -PhI	<i>m</i> -PhI	CH_3- or XCH_2-
CD ₃ OD Solutions				
HMIB	8.38	7.86	7.72	2.69
HMIBA	8.38	7.86	7.72	2.68
HTIB	8.35	7.83	7.69	2.38
HTIBA	8.35	7.84	7.70	2.37
HCIBA	8.12	7.65	7.57	4.00
HIIBA	8.11	7.64	7.57	3.61
CDCl ₃ Solutions				
HMIBA	8.12	7.58	7.48	2.72
HTIBA	8.09	7.51	7.41	2.33

^a For CD_3OD , δ are referenced to CHD_2OD at 3.31 ppm; in CDCl_3 , δ are referenced to CHCl_3 at 7.240 ppm. The tabulated δ are multiplet centers. All samples are prepared with 10 mg of solid per 1 mL of solvent. Spectra were taken at room temperature.

protons from the MsO^- ligands appeared as a sharp singlet at 2.71 ppm, far from that of free $\text{CH}_3\text{SO}_3\text{H}$ at 3.14 ppm, suggesting that the $\text{CH}_3\text{SO}_2\text{O}-\text{I}$ bonds remain intact in a chloroform solution. The aromatic ^1H shifts for HTIBA were slightly removed from those of HMIBA, again consistent with retention of the ligands by the I atoms.

Discussion

EDG of the I Atoms. Of the five compounds reported here, one has CN 5 with trigonal-bipyramidal EDG (HIIBA, I22), six have CN 7 with pentagonal-bipyramidal (HMIBA, I1; HCIBA, I1; HIIBA, I2) or capped octahedral (HMIB; HCIBA, I2; HIIBA, I1) EDG, and two have CN 8 with triangular dodecahedral EDG (HTIB; HMIBA, I2). These geometries and others can be found in literature compounds (Figure 6).¹⁷

There are examples in the literature of organoiodine species with CN 5 and trigonal-bipyramidal EDG; the I atom in $[(p\text{-toluenesulfonyl}(\text{imino})\text{i}(\text{odo})\text{-}o\text{-toluene}(\text{10})); \text{Figure 6}]^{18}$ is CN 5, with two unshared electron pairs and one strong $\text{I}\cdots\text{O}$ bond ($\text{I1}\cdots\text{O2}'$, 2.826 Å). The axial segment is bent ($\angle\text{N1}-\text{I1}\cdots\text{O2}'$, 168.8°), virtually matching the axial segment containing I22 in HIIBA.

None of the I atoms here has CN 6, but iodine frequently achieves CN6 and octahedral EDG. The tetra- μ -oxopentaidanyl dication repeat units in the phenyl-iodine(III) perchlorate polymer prepared earlier³ has five distinct I atoms: of these, I1 and I5 have octahedral EDG (I1; Figure 6). I1 has a secondary bond to a perchlorate counterion ($\text{I1}\cdots\text{O10}'$, 3.140 Å) and two unshared pairs. The four-atom equatorial plane is puckered [average atomic displacements of 0.215(40) Å], with the I atom 0.197 Å from the plane. The λ^5 -iodane (2-iodylphenyl)-diphenylphosphine oxide (I2; Figure 6)¹⁹ uses a strong intermolecular bond ($\text{I1}\cdots\text{O2}'$, 2.571 Å) and a strong intramolecular bond ($\text{I1}\cdots\text{O3}$, 2.612 Å) to yield an octahedral

EDG with atoms in the axial positions. The one lone pair resides in the equatorial plane. The phenyl C atom and an O atom from the intermolecular bond form the nearly linear axis ($\angle\text{C1}-\text{I1}\cdots\text{O2}'$, 168.2°). Other CN 6 species with octahedral EDG¹⁷ include [dichloro(iodo)]-trifluoromethane (I3),²⁰ [dichloro(iodo)]benzene (I4),²¹ 1-(*tert*-butylsulfonyl)-2-iodosylbenzene (I5),²² [dichloro(iodo)]-2,4,6-triisopropylbenzene (I6),²³ and 1-dichloro-iodo-2,6-bis(3,5-dichloro-2,4,6-trimethylphenyl)benzene (I7).²⁴

The pentagonal-bipyramidal EDG shown by three of the present CN 7 I atoms is favored by iodine in several oxidation states. The I-centered IOF_6^- anion (I8; Figure 6)²⁵ has oxide and fluoride in the axial vertices. The pentagonal equatorial plane is puckered with $\text{O}-\text{I}-\text{F}_{\text{eq}}$ angles from 92° to 102° [95.5(2)°] such that the I atom lies slightly out of the plane toward the oxide ligand. Both the EDG and molecular geometry is unambiguously pentagonal-bipyramidal. Christe, Schrobilgen, and co-workers²⁶ present a detailed treatment of the geometry. *p*-(Dichloroiodo)nitrobenzene (I9; Figure 6)²⁷ uses two intermolecular bonds ($\text{I1}\cdots\text{O1}'$, 3.286 Å; $\text{I1}\cdots\text{O2}'$, 3.164 Å) to achieve pentagonal-bipyramidal EDG. The $\text{Cl}-\text{I}-\text{Cl}$ axis is linear ($\angle\text{Cl1}-\text{I1}-\text{Cl2}$, 176.17°), and the two lone pairs lie in the equatorial plane. The axis is tilted with respect to the plane as the angle of segment $\text{Cl2}-\text{I1}$ to plane $\text{Cl1}-\text{O1}'-\text{O2}' = 74.3^\circ$. Other CN 7 species with pentagonal-bipyramidal EDG¹⁷ include the λ^3 -iodanes [bis(acetato-O)iodo]benzene (I20),²⁸ [bis(dichloroacetato-O)iodo]benzene (I21),²⁸ $[(p\text{-toluenesulfonyl}(\text{imino})\text{i}(\text{odo})\text{-}p\text{-toluene}(\text{22})); \text{I2}$ in μ -oxobis[acetato-O(phenyl)iodine(III)] (I23),¹³ and I1 in μ -oxobis[nitrato-O(phenyl)iodine(III)] (I24);⁸ the λ^5 -iodane 1-(*tert*-butylsulfonyl)-2-(dioxoiodo)benzene (I25),²² and the λ^7 -iodane anion *trans*- $\text{IO}_2\text{F}_5^{2-}$ (I26).

Three of the I atoms in this study displayed CN 7 with capped octahedral EDG. Literature examples of this geometry¹⁷ are provided by I1 in μ -oxobis[acetato-O(phenyl)iodine(III)] (I23),¹³ I2 in μ -oxobis[trifluoroacetato-O(phenyl)iodine(III)] (I27),⁹ and the (arylsulfonylimino)iodoarene *m*-tolylINTs (I28).³⁰ The capped octahedron evolves to a capped triangular prism if the capping atom and one of the axial occupants migrate somewhat, and the assignment

(20) Minkwitz, R.; Berkei, M. *Inorg. Chem.* **1999**, *38*, 5041–5044.

(21) Archer, E. M.; van Schalkwyk, T. G. D. *Acta Crystallogr.* **1953**, *6*, 88–92. Carey, J. V.; Chaloner, P. A.; Hitchcock, P. B.; Neugebauer, T.; Seddon, K. R. *J. Chem. Res., Miniprint* **1996**, 2031–2054. *J. Chem. Res., Synop.* **1996**, 358–359. Montanari, V.; Des Marteau, D. D.; Pennington, W. T. *J. Mol. Struct.* **2000**, *550*, 337–348.

(22) Macikenas, D.; Skrzypczak-Jankun, E.; Protasiewicz, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 2007–2010.

(23) Mishra, A. K.; Olmstead, M. M.; Ellison, J. J.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 3210–3214.

(24) Protasiewicz, J. D. *Chem. Commun.* **1995**, 1115–1116.

(25) Christe, K. O.; Dixon, D. A.; Mahjoub, A. R.; Mercier, H. P. A.; Sanders, J. C. P.; Seppelt, K.; Schrobilgen, G. J.; Wilson, W. W. *J. Am. Chem. Soc.* **1993**, *115*, 2696–2706.

(26) Boatz, J. A.; Christe, K. O.; Dixon, D. A.; Fir, B. A.; Gerken, M.; Gnann, R. Z.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **2003**, *42*, 5282–5292.

(27) Nikiforov, V. A.; Karavan, V. S.; Miltsov, S. A.; Selivanov, S. I.; Kolehmainen, E.; Wegelius, E.; Nissinen, M. *ARKIVOC* **2003**, *4*, 191–196.

(28) Alcock, N. W.; Countryman, R. M.; Esperas, S.; Sawyer, J. F. *J. Chem. Soc., Dalton Trans.* **1979**, 854–860.

(29) Boucher, M.; Macikenas, D.; Ren, T.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 9366–9376.

(30) Boucher, M.; Macikenas, D.; Ren, T.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 9366–9376.

(17) Coordinates from the CCDC files are used to construct these figures and additional figures in the Supporting Information.

(18) Cicero, R. L.; Zhao, D.; Protasiewicz, J. D. *Inorg. Chem.* **1996**, *35*, 275–276.

(19) Mepathu, B. V.; Justik, M. W.; Protasiewicz, J. D. *Tetrahedron Lett.* **2005**, *46*, 5187–5190.

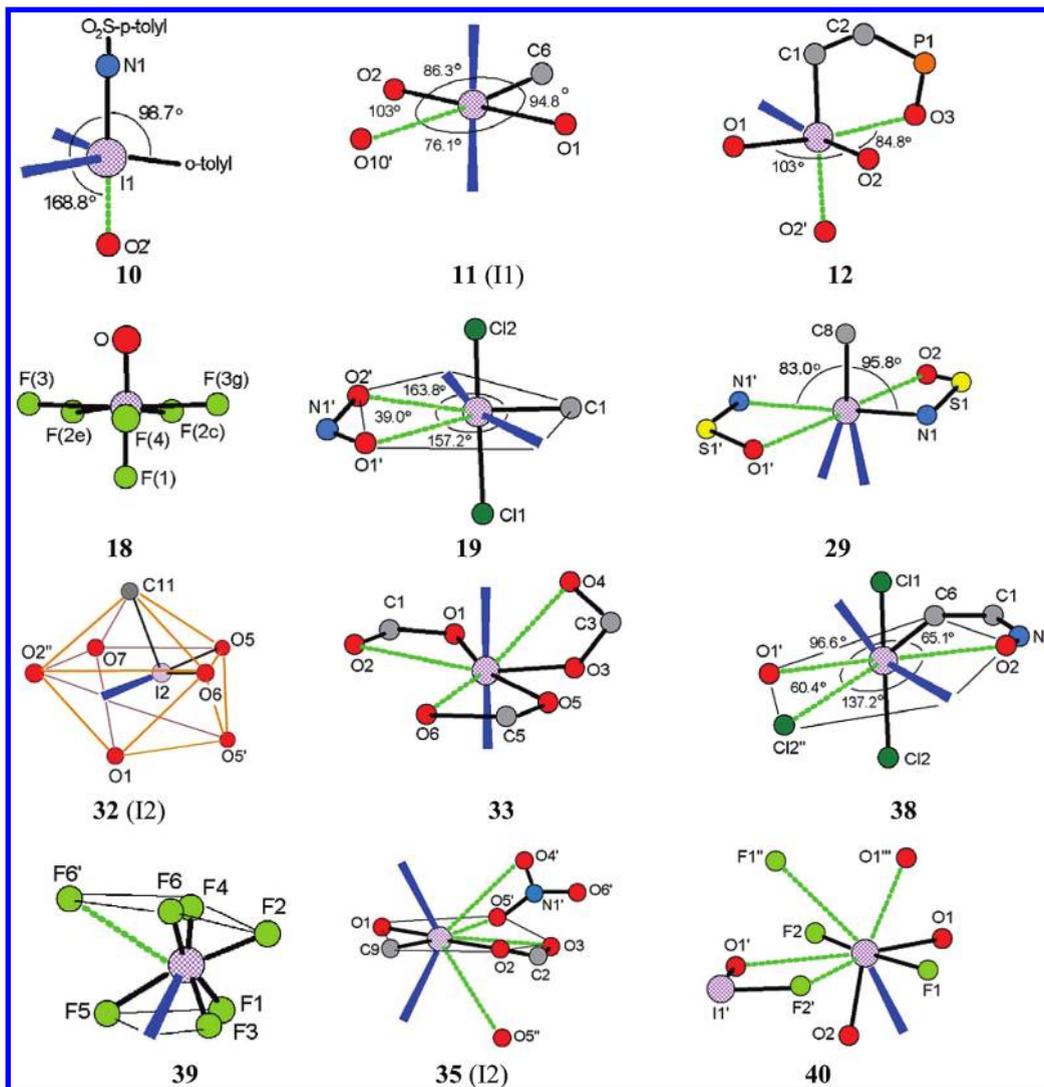


Figure 6. EDGs of the I atoms in literature sources. Primary bonds are given in black; secondary bonds are given in green; unshared electron pairs are given as blue wedges. Fine black lines are used to clarify geometric features. The figures were prepared using MDL ISIS/Draw 2.5 from structures generated by *Mercury 2.2*, using CCDC data, except for **18**, which was produced from drawings in the original publication.

of a capped octahedral or capped triangular prism to an EDG sometimes may be ambiguous. The (arylsulfonylimino)iodoarene PhINTs (**29**; Figure 6)²³ has three secondary bonds ($I1 \cdots O2$, 3.144 Å; $I1 \cdots O1'$, 3.271 Å; $I1-N1'$, 2.482 Å) that combine with two primary bonds to produce a planar bow-tie-shaped base to give a “square”-pyramidal molecular shape; the I atom is only 0.004 Å from the $O2-N1-O1'-N1'$ plane (maximum atomic displacement of 0.03 Å in the plane). The most likely location of the two equivalent unshared pairs is below the bow-tie plane, opposite to the C atom, providing the cross-bar for a capped triangular prismatic EDG. Similar examples¹⁷ are provided by the (arylsulfonylimino)iodoarene MesINTs (**30**)²³ and [difluoro(iodo)]trifluoromethane (**31**).³¹

The two instances of CN 8 in this study display triangular dodecahedral EDG. I2 in the λ^5 -iodane 2-iodoxybenzoic acid isopropyl ester (**32**; Figure 6)³² has three intermolecular $I \cdots O$ bonds ($I2 \cdots O2''$, 3.051 Å; $I2 \cdots O1$,

3.191 Å; $I2 \cdots O5'$, 2.560 Å) and one intramolecular bond ($I2 \cdots O7$, 2.698 Å) that likewise produce triangular dodecahedral EDG. Numerous examples of CN 8 with capped pentagonal-bipyramidal EDG appear,¹⁷ including I atoms in tris(acetato-O)iodine(III) (**33**; Figure 6),³³ [bis(trifluoroacetato-O)iodo]benzene (**34**),³⁴ I1 in μ -oxo[nitrato-O(phenyl)iodine(III)][phenyl(trifluoroacetato-O)iodine(III)] (**35**),¹¹ the (arylsulfonylimino)iodoarenes *m*-tolylINSO₂Ph (**36**)³⁰ and *m*-tolylINSO₂-*p*-NO₂C₆H₄ (**37**),³⁰ I1 in μ -oxobis[trifluoroacetato-O(phenyl)iodine(III)] (**27**),⁹ and *o*-[dichloro(iodo)]nitrobenzene (**38**; Figure 6).²⁷ A third CN 8 geometry is exhibited by the λ^5 -iodane IF₆⁻ (**39**; Figure 6).³⁵ Six primary bonds with F atoms, one intermolecular secondary bond ($I \cdots F6'$, 2.817 Å), and one unshared pair of electrons are arrayed in a cubic antiprismatic EDG.

(33) Birchall, T.; Frampton, C. S.; Kapoor, P. *Inorg. Chem.* **1989**, *28*, 636–639.

(34) Alcock, N.; Harrison, W. D.; Howes, C. *J. Chem. Soc., Dalton Trans.* **1984**, 1709–1716.

(35) Mahjoub, A. R.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 323–324.

(31) Minkwitz, R.; Berkei, M. *Inorg. Chem.* **1998**, *37*, 5247–5250.

(32) Zhdankin, V. V.; Litvinov, D. N.; Kuposov, A. Y.; Luu, T.; Ferguson, M. J.; McDonald, R.; Tykwinski, R. R. *Chem. Commun.* **2004**, 106–107.

Though not seen in the presented compounds, I atoms with CN 9 are to be found in the literature.¹⁷ I2 in **35** (Figure 6)¹¹ achieves CN 9 using four secondary bonds (I2···O3, 3.124 Å; I2···O5', 3.191 Å; I2···O4', 3.379 Å; I2···O5'', 3.381 Å) and produces a bicapped pentagonal-bipyramidal EDG. The pentagonal plane O1–C9–O2–O3–O5' is well formed and only lightly puckered with an average atomic displacement of 0.118(64) Å, and I2 is only 0.020 Å out of the plane. The I-centered angles approach the ideal 72°, where O3···I2–O2 is constrained to be small (45.36°) owing to tethering. A second example of an I atom with CN 9 and bicapped pentagonal-bipyramidal EDG is provided by the λ^5 -iodane IF₂(O)OCH₃ (**40**; Figure 6).³⁶ With one unshared pair of electrons and four secondary bonds (I1···O1', 3.413 Å; I1···F2', 2.876 Å; I1···F1'', 3.278 Å; I1···O1''', 2.645 Å), a lightly puckered pentagonal plane is produced with an average atomic displacement of 0.102(49) Å, where I1 is displaced by 0.129 Å.

T-Shaped Bond. An enduring point of interest in aryl λ^3 -iodanes and μ -oxodiodanes is the predicted T-shaped bond formed by the I atoms with three ligands, where one ligand is an aryl group. When the possible influence of secondary bonds is excluded, the EDG about the iodine is trigonal-bipyramidal, where the equatorial aryl ligand bonds to iodine by ordinary covalent overlap, while the two axial ligands join in a 3c-4e bond with the central I atom.⁶ The delocalized apical unit (L¹–I–L²) can be symmetrically or unsymmetrically polarized, depending on the relative electronegativities of the ligands. Symmetrical polarization gives fractional and equivalent I–L bond orders; unsymmetrical polarization produces nonequivalent bond orders. The I–O bond distances of aryl λ^3 -iodanes with two oxyanion ligands can be grouped into three categories. If the ligands are identical, the I–O bonds are about the same length and longer than the sum of the covalent radii (2.06 Å); when the ligands are not identical and differ substantially in electronegativity, the more basic ligand gives a short I–O bond (< 2.06 Å), while the other is “extra” long. This pattern is seen in the present compounds where the bond orders (*n*) can be calculated from the Pauling equation, $D(n) = D(l) - 0.6 \log n$, where $D(n)$ = observed I–O bond distance and $D(l)$ = I–O distance computed from I and O covalent radii.⁶ For both symmetrical and unsymmetrical polarization, C–I–O angles of 90° are expected; however, a droop-and-shrug motif is generally seen, where one angle is larger and the other smaller than 90°. When the C–I–O angles are plotted against the bond order for the reported compounds, polymer **11**, and a group of literature λ^3 -iodanes,¹⁷ a linear relationship appears (Figure 7). The I–sulfonate bonds in HMIB and HTIB, as well as the terminal I···O bonds in polymer **11** (all with very small bond orders), seem to be outliers; with these four I–O bonds excluded, a regression fit of 44 I–O bonds gives $\angle \text{C–I–O}(\text{deg}) = 74.6(20) + 17.7(11)n$. Figure 7 also shows data for cyclic λ^3 -iodanes (×), iodoxybenzene analogues (*), and additional λ^5 -iodanes (○). The linear correlation fails for $n > 1.5.0$

O–C–O–O–C–O Hexagons. Not all aryl λ^3 -iodanes and μ -oxodiodanes form the chair-conformation O–C–

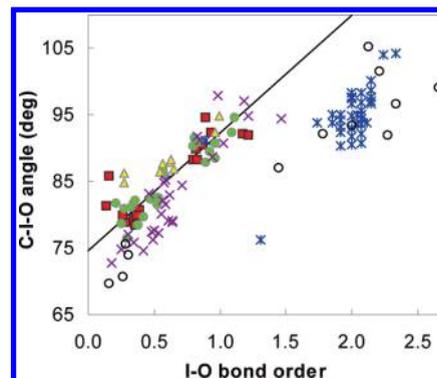


Figure 7. Dependence of the C–I–O angles on the I–O bond order (*n*): (■, filled in red) data from the reported compounds; (Δ, filled in yellow) data from polymer **11**; (●, filled in green) data from literature λ^3 -iodanes; (×) data from literature cyclic λ^3 -iodanes; (*) data from literature iodoxybenzene analogues; (○) literature benziodoxazoles, etc. Data for the plot are given in the Supporting Information.¹⁷ Bond orders are calculated using $D(l) = 1.99 \text{ \AA}$. The line in the linear regression fit to data for reported compounds, polymer **11**, and literature λ^3 -iodanes.

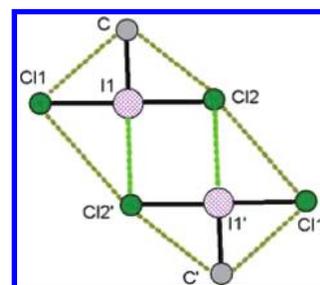


Figure 8. Diagram of hexagons formed in [dichloro(iodo)]benzene analogues.

Table 5. Hexagons in [Dichloro(iodo)]benzene Analogues^a

	distance (Å) ^b				angle (deg)	
	I–□	I1···Cl2'	Δ–□	◇–□	I1–Cl2···I1'	Cl1–Cl2–Cl1'
38	0.019	3.383	20.84	0.51	94.75	131.23
16	0.058	3.490	0.60	1.56	95.20	128.82
17	0.033	3.816	54.14	0.90	92.69	124.89

^a Refer to Figure 8 for atom labels: (□) plane Cl1–Cl2–Cl1'–Cl2'; (Δ) plane Cl1–C–Cl2; (◇) plane I1–Cl2–I1'–Cl2'. ^b The $\sum \text{vdw}$ limit for I–Cl is 3.95 Å.

O–O–C–O hexagons seen in the reported compounds. However, there are numerous examples of compounds that do give this structure: [bis(trifluoroacetato–O)iodo]benzene (**34**),³⁴ [bis(dichloroacetato–O)iodo]benzene (**21**),²⁸ μ -oxo-bis[acetato–O(phenyl)iodine] (**23**),¹³ and the mixed μ -oxodiodane **35**¹¹ all produce similar hexagons (Figure 4 and Table 3).

Analogues of dichloro(iodo)benzene also produce chair-conformation hexagons, where the structure arises from alignment of the Cl–I–Cl segments from neighboring molecules; the bonds supporting the structure are intramolecular I···Cl secondary bonds (Figure 8 and Table 5). Examples are provided by *o*-[dichloro(iodo)]nitrobenzene (**38**),²⁷ [dichloro(iodo)]-2,4,6-triisopropylbenzene (**16**),²³ and **1-17**.²⁴ The Cl1–Cl2–Cl1'–Cl2' seats are flat (0.000 Å atomic displacement), and the I atoms are nearly in the plane in each case. In all three compounds, the seat contains a flat (0.000 Å atomic displacement), nearly

(36) Minkwitz, R.; Berkei, M.; Studentkowski, M.; Ludwig, R. *Inorg. Chem.* **2000**, *39*, 4766–4768.

Table 6. Crystallographic Data for HMIB, HMIBA, HCIBA, and HIIBA^a

	HMIB	HMIBA	HCIBA	HIIBA
empirical formula	C ₇ H ₉ IO ₄ S	C ₁₄ H ₁₆ I ₂ O ₇ S ₂	C ₁₆ H ₁₄ Cl ₂ I ₂ O ₅	C ₁₆ H ₁₄ I ₄ O ₅
fw (g/mol)	316.11	614.20	610.99	793.89
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
cryst color, habit	colorless block	bright yellow, thin blade	faint yellow, needles	colorless needles
cell lengths (Å)	<i>a</i> = 6.1902(2) <i>b</i> = 7.4487(2) <i>c</i> = 21.8864(4)	<i>a</i> = 5.8908(2) <i>b</i> = 11.5575(5) <i>c</i> = 14.5665(6)	<i>a</i> = 9.7488(2) <i>b</i> = 22.0264(3) <i>c</i> = 18.2010(2)	<i>a</i> = 9.7924(2) <i>b</i> = 13.6145(2) <i>c</i> = 16.6725(2)
cell angles (deg)	α = 90.00 β = 94.8237(4) γ = 90.00	α = 102.5504(10) β = 98.2055(10) γ = 101.3640(12)	α = 90.00 β = 90.5158(6) γ = 90.00	α = 75.2793(2) β = 82.2582(9) γ = 80.5734(3)
volume (Å ³), <i>Z</i>	1005.70(3), 4	931.05(6), 2	3908.16, 8	2110.65, 4
density(calcd) (g/cm ³)	2.088	2.191	2.077	2.498
μ (Mo K α) (cm ⁻¹)	33.72	36.35	35.15	59.27
<i>R</i> (<i>F</i>) (%) ^b	2.91	4.96	4.27	4.95
<i>R</i> (<i>wF</i> ²) (%) ^b	8.25	13.52	14.51	16.65

^a In all cases, temperature = 173(2) K and wavelength = 0.7103 Å. ^b Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]^{1/2}$; $R = \sum\Delta / \sum(F_o)$, $\Delta = |F_o - F_c|/I$.

rectangular I1–Cl2···I1'–Cl2' "diamond"; the covalent I–Cl sides are between 2.45 and 2.53 Å, while the intermolecular I···Cl sides are in each case less than the \sum vdw limit (3.95 Å). In all of these examples, the diamond (I–D–I'–D') structure appears, and this may exhibit delocalized bonding that stabilizes the hexagon.

Physical Properties and Hydrogen Bonding. The solubility of HMIBA and HTIBA in chloroform is remarkable given the complete insolubility of HMIB and HTIB in this solvent. This difference likely arises from the strong hydrogen bonds (O···H, 1.860 and 2.004 Å) that bind the dimers in HMIB and HTIB that are absent in the anhydrides. This hydrogen bonding may likewise be the source of the higher melting point of HTIB relative to that of HMIB. Also noteworthy is that the melting point of HCIBA is much higher than that of HIIBA, which has the higher molar mass. In both HCIBA and HIIBA, dimers are joined into stair structures by similar strong I···O bonds. The HCIBA stairs are stabilized by the "tail" containing I2 that dangles from the vertex of the O–C–O–C–O hexagon and places the chloromethyl group directly above the hexagon/diamond groupings in the neighboring dimer; the chloromethyl group rotates so that H27 points to the center of that hexagon, forming a rectangular pyramid with H27 at the apex, 2.183 Å above the seat of the hexagon (Figures 3 and 4). Possibly, delocalized bonding in the hexagon/diamond grouping provides the electron density that is shared with H27, which is electron-deficient because of the Cl atom on the chloromethyl group; this explanation of the elevated melting point of HCIBA presents an example where hydrogen-bonding forces outweigh those in the I···O secondary bonding.³⁷

Conclusions

In a survey of the reported compounds and literature compounds, coordination numbers used by iodine include 5–9. The I-centered EDGs found include the trigonal bipyramid, octahedron, pentagonal bipyramid, capped octahedron, capped triangular prism, capped pentagonal bipyramid, dodecahedron, and bicapped pentagonal bipyramid.

These geometries are achieved using primary bonds, unshared pairs of electrons, and secondary bonds between I and O, N, Cl, and F atoms. There is no correlation between the oxidation state of iodine and the coordination number or EDG. For both aryl λ^3 - and λ^5 -iodanes with two or more O-centered ligands, the C–I–O angle increased correspondingly with the I–O bond order; this relationship and the EDG geometries seen bear on the 3c-4e view of the predicted T-shaped bond in these compounds. The possible presence of delocalized bonding in the hexagonal/diamond groupings arising from the antiparallel alignment of O–I–O segments from two molecules is supported by elevation of the melting point in HCIBA that can be attributed to hydrogen bonding to the ring.

Experimental Section

Analytical Methods. All NMR spectra were obtained on a Varian VXR 300 MHz spectrometer equipped with a broadband probe. Elemental analyses were performed either at Micro-Tech Laboratories, Skokie, IL, or Galbraith Laboratories, Knoxville, TN.

Crystal, data collection, and refinement parameters are given in Table 6. A suitable crystal was selected, mounted in a N₂-flushed, thin-walled capillary, and flame-sealed. All data were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector. The structure was solved using direct methods completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. An empirical absorption correction was applied, based on a Fourier series in the polar angles of the incident and diffracted beam paths, and was used to model an absorption surface for the difference between the observed and calculated structure factors.³⁸ All software and sources of the scattering factors are contained in the *SHELXTL* (5.10) program library (Sheldrick, G. *SHELXTL*; Bruker AXS: Madison, WI).

Preparation of HMIBA and HTIBA. (Diacetoxyiodo)benzene and toluenesulfonic acid monohydrate were purchased from Aldrich Chemical Co. and used directly. HTIB and HMIB were prepared as described previously.² HMIBA was prepared from acetonitrile solutions of HMIB by stripping away water with a continuous CH₃CN distillation; HTIBA was similarly prepared from HTIB. HMIBA was stable for long periods when stored under N₂ at –70 °C. HMIBA mp 149–150 °C (dec); HTIBA mp 123–125 °C (dec). HMIBA and HTIBA are soluble in CHCl₃, 33 and 16 mg/mL.

(37) Batchelor, R. J.; Birchall, T.; Sawyer, J. F. *Inorg. Chem.* **1986**, *25*, 1415–1420.

(38) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.

Preparation of HCIBA and HIIBA. HMIB (1.00 g, 3.16 mmol) dissolved in 10 mL of water was placed in a 25-mL graduated cylinder. Aqueous chloroacetic acid (0.32 g, 3.16 mmol) neutralized with 1 M NaOH for a total volume of 7.0 mL was layered on top of the HMIB solution, yielding a clear solution on top of the lemon-yellow HMIB solution. After 24 h, two types of solid were observed: (a) well-formed very-pale-yellow, long and flat or needle-shaped crystals and (b) yellowish "mold" mounds. The very-pale-yellow crystals (yield = 0.71 g) were subjected to X-ray structure analysis. Anal. Obsd (calcd for $C_{16}H_{14}Cl_2I_2O_5$): C, 31.26 (31.45); H, 2.45 (2.31); I, 43.05 (41.54).

Similarly for HIIBA, HMIB (1.00 g, 3.16 mmol) in 10 mL of water was placed in a 25-mL graduated cylinder. Iodoacetic acid (0.59 g, 3.16 mmol) was neutralized with 3.1 mL of 1 M NaOH (3.1 mmol) and diluted with water to 10 mL; this solution was layered on top of the lemon-yellow HMIB solution for a total volume \approx 20 mL. After 1 day, long white needles grew from the interface into the HMIB solution phase. The very white needles were collected by gentle swirling of the cylinder contents

followed by vacuum filtration and washing with ether (yield = 0.38 g).

Acknowledgment. Our thanks go to Prof. Ann D. Bolek of Science and Technology Library of The University of Akron for her support of this research. Financial support was given by The University of Akron, the University of Delaware, and Remington Products (Wadsworth, OH). Figures and structures were prepared using MDL ISIS/Draw 2.5, *Mercury 2.2* from the Cambridge Crystallographic Data Centre, and ArcSoft PhotoStudio 5.5.0.72.

Supporting Information Available: Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients for HMIB, HMIBA, HCIBA, and HIIBA in CIF files, table of values of the bond orders for the reported compounds and for literature compounds used for Figure 7, structures of literature I atoms referenced in the article. This material is available free of charge via the Internet at <http://pubs.acs.org>.