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Article

Preparation and Structure of a Solid-State Hypervalent-Iodine Polymer Containing Iodine and Oxygen Atoms in Fused 12-Atom Hexagonal Rings

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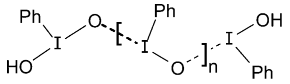
The treatment of dilute aqueous solutions of [hydroxy(tosyloxy)iodo]benzene with aqueous $Mg(ClO_4)_2$ produced thin elongated-hexagonal plates exhibiting a supramolecular structure in which tetra-μ-oxopentaiodanyl dication repeat units are joined to each other by significantly ionic bonds and each unit is associated with two perchlorate ions. The linearly extended cationic structure is formed from the 12-atom hexagonal rings of alternating iodine and oxygen atoms, a novel structure. Each 12-membered ring forms a nearly planar hexagonal shape with sides defined by almost linear O–I–O segments (175.7 ± 1.6)°. The apexes are occupied by bridging oxide ligands where the I–O–I angles deviate only slightly from an ideal 120° hexagonal angle (116.8 ± 1.2) °, consistent with sp^2 hybridization of the bridging oxygen atoms that participate in three-center four-electron bonds with iodine. These 12-atom hexagons are slightly "chair" distorted at the oxygen atoms. The planes of the rings are separated by layers containing the phenyl rings. The perchlorate ions reside in void spaces created by the three-up, three-down arrangement of the phenyl rings around each 12-membered I–O ring and are positioned directly above and below the I–O rings.

Introduction

Iodosylbenzene (**1**) was first described by Willgerodt in 1892,[1] and it is among the oldest known examples of hypervalent organoiodine compounds. In the solid state, iodosylbenzene is an amorphous powder and a polymer of **1**.[2] It seems likely that each polymer chain is "hydrated" with one molecule of water so that the chain possesses terminal hydroxide ligands (structure **2**).[3,4]



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Iodosylbenzene is a valuable synthetic reagent with the limitation of near insolubility in nonreactive media;[5] insertion of an *o*-*tert*-butylsulfonyl in the phenyl group of **1** (giving structure **3**) introduces an intramolecular secondary I···O bond that produces a reagent soluble in media such as chloroform.[6,7] A single-crystal X-ray analysis of **3**·$CDCl_3$ revealed the polymeric structure in Chart 1 (where the compound is shown in "short-hand") in which the units of **3** are joined by secondary I···O bonds in a square-planar configuration, giving this polymer an $-(I-O)_n-$ backbone.[7]

A variety of aryl-λ^3-iodanes formally derived from the iodobenzene dication (PhI^{2+}) and two oxygen-centered anionic ligands are known (structure **4**, Chart **2**). The most prominent examples are [bis(acetoxy)iodo]benzene (**4a**, BAIB) and [hydroxy(tosyloxy)iodo]benzene (**4b**, HTIB). Compounds possessing two PhI^{2+} units with a bridging oxide

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Chart 1

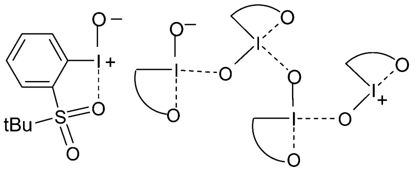

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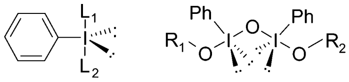
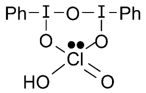
Chart 2



4a, $L_1 = L_2 = CH_3CO_2$ **5a**, $R_1=R_2=ClO_3$
4b, $L_1=OH$, $L_2=TsO$
4c, $L_1=L_2=ClO_4$

ligand are also known; in these μ-oxodiiodanes (structure **5**, Chart 2), the iodine atoms are also bound to weakly basic oxygen-centered anionic ligands.

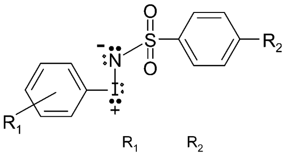
The perchlorate analogues of **4** and **5** (**4c** and **5a)** have been reported. **4c** was prepared from **4a** (BAIB) and 1 equiv of $Mg(ClO_4)_2$ in ethyl acetate;[8] this iodane detonates at ca. 100 °C but is stable for weeks at room temperature. The μ-oxodiiodane **5a** was made from BAIB and perchloric acid (decomposition at 116−118 °C).[9,10] To our knowledge, single-crystal X-ray studies of **4c** and **5a** have not been reported. Wettach[11] reported that treatment of aqueous solutions of HTIB with sodium, lithium, or magnesium perchlorate yielded minute yellow crystalline plates, where the product structure was assigned to the cyclic μ-oxodiiodane **5b** based on the elemental analysis and production of an unidentified oxidant. None of these compounds has a reported supramolecular structure that is polymeric in nature.



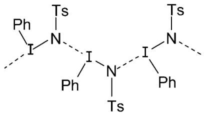
5b

Single-crystal X-ray studies of several (sulfonylimino)iodanes (structure **6**, Chart 3), iodine(III)−nitrogen ylides generally regarded as analogues of iodosylbenzene, have been reported.[2,6,7,12−15] Except for **6h**, these (sulfonylimino)iodanes are polymeric in the solid state. The supramolecular solid-state structure of compound **6a** (PhINTs) closely resembles that assumed for solid-state iodosylbenzene where the bridging oxide ligands in **2** are replaced by nitrene ylide ligands, as shown in Chart 3. Linear N−I···N segments (177.8°) are joined into infinite zigzag polymer chains by means of unsymmetrical I−N···I contacts (2.039 and 2.482 Å, 116.6°), giving a polymer with an $-(\text{I}-\text{N})_n-$ backbone.[2,12] The N···I bond length is sufficiently long that this might be considered a secondary bond. The polymeric character of (sulfonylimino)iodanes **6b**−**g** results from networks of I···N and I···O secondary bonds that produce a variety of supramolecular structures, none as simple as that for the parent compound **6a**.[6,7,12,14] The introduction of an *o-tert*-butylsulfonyl group in **6h** disrupts much of this networking via an *intramolecular* I···O secondary bond finally producing a "loosely associated" dimeric structure;[6,7] in addition, there was a 50-fold increase in the solubility of **6h** in chloroform over that of the parent **6a**.

Chart 3



	R_1	R_2
6a	H	Me
6b	2,4,6-Me_3	Me
6c	2-Me	Me
6d	3-Me	Me
6e	3-Me	NO_2
6f	3-Me	H
6g	4-Me	Me
6h	2-$SO_2{}^tBu$	Me



6a

The electron-domain geometry about the iodine center in aryl-λ^3-iodanes is pseudo-trigonal-bipyramidal (structure **4**) with the essentially T-shaped molecular geometry stabilized by the presence of the electronegative ligands at the apical sites. Bonding in these compounds is successfully described by a model in which the equatorial aryl ligand is attached to iodine by ordinary covalent overlap, while the apical ligands are connected to iodine via a three-center four-electron [3c-4e] bond, generated by the σ overlap of a 5p orbital on iodine with the orbitals of each of the apical ligands.[16] At 178.8°, the O−I−O angle in HTIB (**4b**) is virtually linear.[17] On the basis of this molecular orbital picture, the delocalized apical ligands in aryl-λ^3-iodanes can be symmetrically (**4s**) or unsymmetrically (**4u**) polarized, depending on the pairwise combinations and relative electronegativities of the apical ligands. In the former case, fractional and equivalent I−L bond orders are predicted, but in the latter, a spectrum of unsymmetrically polarized structures up to the iodonium limit can be envisioned.

The I−O bond distances in reported structures with two oxygen-centered anionic ligands can generally be grouped into three categories. When the ligands are either identical

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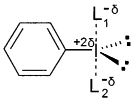
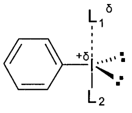


4s



4u

or of comparable basicity, the bonds are about the same length and are longer than the sum (2.06 Å) of the covalent radii. When the ligands are not identical and exhibit substantially different basicities, one I−O bond is short (<2.06 Å) and the other is "extra" long.

In this paper, we report the preparation and structure of a compound with the supramolecular structure **7** (Figure 1) in which tetra-μ-oxopentaiodanyl dication repeat units (**8**, Figure 2) are fused together to give 12-atom hexagonal rings; each repeat unit is associated with two perchlorate ions. The linearly extended cationic structure is formed from 12-atom hexagonal rings of alternating iodine and oxygen atoms. This compound exhibits all of the structural elements discussed above for aryl-λ^3-iodanes. In addition, the structure of the compound confirms an unusual electron-domain geometry about oxygen atoms that are directly bonded to iodine atoms in aryl-λ^3-iodanes.

Results and Discussion

Polymer **7** self-assembles in dilute aqueous solutions of HTIB and $Mg(ClO_4)_2$ over a period of hours

$$\text{HTIB} \xrightarrow{Mg(ClO_4)_2,\ H_2O} \mathbf{7}$$

The crystals are elongated-hexagonal plates that are intense yellow with a green hue, which are stable in air at room temperature for at least three weeks. The compound detonates at 112−113 °C. The single-crystal X-ray structure of **7** reveals a linearly extended cationic structure, formed from nearly planar 12-atom hexagonal rings of alternating iodine and oxygen atoms; oxygen atoms occupy the vertices and the sides are O−I−O segments (Figures 1 and 3). The repeat unit in **7** is the tetra-μ-oxopentaiodanyl dication **8** (pentaiodanyl dication, Figure 2). Each unit of **8** is locked into the conformation depicted in Figure 3 and is associated with two perchlorate ions. The pentaiodanyl dication **8** is essentially hydrated pentameric iodosylbenzene (structure **2** with $n = 3$) with the terminal hydroxide ligands removed.

To see how the hexagonal rings form, consider the three pentaiodanyl dications shown in Figure 3. The O−I−O segment angles are nearly linear, as expected for aryl-λ^3-iodanes, while the I−O−I segment angles are almost trigonal (≤115.0° to 118.5°); this combination allows the dicationic repeat units to interlock, forming the 12-atom hexagonal rings. A lone pair on O(2B) allows the B unit to become a ligand on the positively charged I(1A) in the A unit; O(2B) is then a ligand on three iodine atoms, I(1A), I(2B), and I(3B). A lone pair on O(3A) allows the A unit to become a ligand on the positively charged I(5B); O(3A) is thus a ligand on three iodine atoms, I(5B), I(3A), and I(4A). Thus, the hexagonal structure is formed from two pentaiodanyl dications, which then interlock with succeeding units to produce the extended structure **7.** In each ring, the fused side is the nearly linear O(2)−I(3)−O(3) segment. An ORTEP diagram with a detailed view of a hexagon is given in Figure 4.

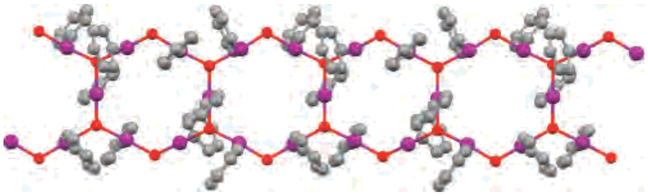


Figure 1. Extended solid-state diagram of polymer **7** with the perchlorate counterions and hydrogen atoms omitted for clarity.

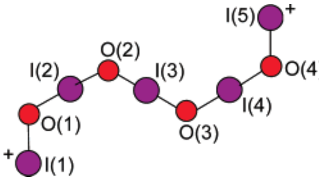


Figure 2. Diagram of the pentaiodanyl dicationic repeat unit, **8.** Purple circles denote an iodine atom with an attached phenyl ligand where the phenyl ligands are omitted for clarity. Red circles denote an oxygen atom.

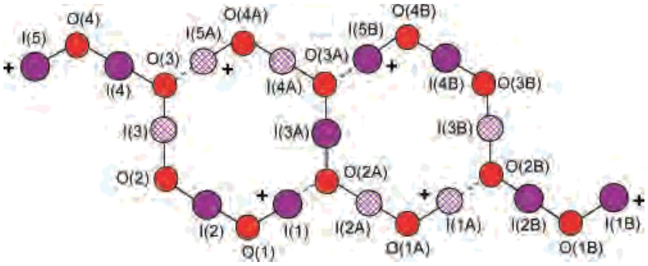


Figure 3. Diagram of three of the repeat units in **7**, showing the interlocking of the dication units. Cross-hatched circles denote an iodine atom with the attached phenyl ligand oriented above the plane; filled purple circles denote an iodine atom with the attached phenyl ligand below the plane. Filled red circles denote an oxygen atom. Solid lines denote covalent bonds, while dashed lines indicate more ionic bonds.

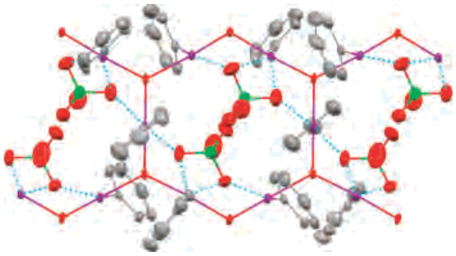


Figure 4. *ORTEP* diagram of one of the rings in **7**, with parts of two other rings. H atoms are omitted for clarity. The thermal ellipsoids are at 50% probability. Secondary bonds between perchlorate O atoms and I atoms are shown as dashed blue lines.

The three-atom sides vary in length by less than 3% (4.21−4.33 Å, or a difference of 0.06 Å per I−O bond) even though the individual I−O bonds vary from 2.10 to 2.33 Å, a range of about 10% (Table 1). This results from the pairing of each of the shortened terminal I−O bonds in the repeat unit with an elongated I−O ion-dipole bond in the ring, sides O(2B)−I(1A)−O(1A) and O(3A)−I(5B)−O(4B) (Figure 3). The extended structure of **7** is nearly planar (Figure 5). The 12-membered rings, edge-fused along the O(2)−I(3) −O(3) segments, are infinitely extended along the *a* crystallographic axis. The least-squares planes for the rings are slightly zigzagged with a 17.2° angle between planes. The rings are in the *ab* plane. The hexagons are very slightly "chair"

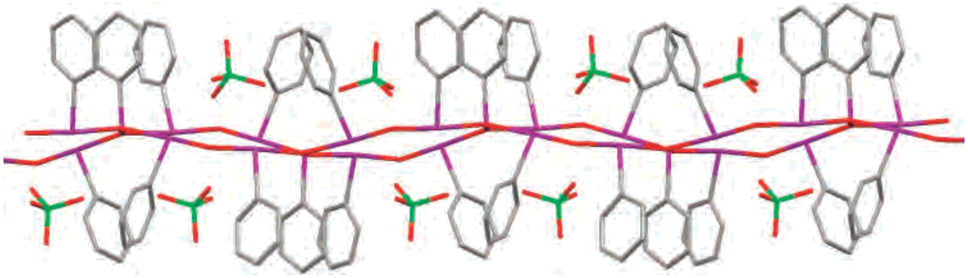


Figure 5. Side view of polymer **7** showing the near planarity of the extended ring structure. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths and Bond Angles[a]

atoms	angle (deg)	atoms	length (Å)
O(2B)−I(1A)−O(1A)	178.63(19)	I(1)−O(1)	1.992(4)
O(1A)−I(2A)−O(2A)	173.76(17)	I(1A)−O(2B)	2.330(3)
O(2A)−I(3A)−O(3A)	175.1(2)	I(2)−O(1)	2.115(3)
O(4B)−I(4B)−O(3B)	175.10(17)	I(2)−O(2)	2.147(4)
O(3A)−I(5B)−O(4B)	175.86(15)	I(3)−O(2)	2.101(3)
five O−I−O avg (std dev)	175.69(1.62)	I(3)−O(3)	2.113(4)
I(1)−O(1)−I(2)	118.5(2)	I(4)−O(3)	2.129(4)
I(2)−O(2)−I(3)	115.03(15)	I(4)−O(4)	2.112(3)
I(3)−O(3)−I(5A)	116.21(15)	I(5)−O(4)	2.000(4)
I(5)−O(4)−I(4)	118.0(2)	I(5B)−O(3A)	2.326(3)
I(4)−O(3)−I(3)	116.16(16)	I(1)−C	2.074(7)
I(3A)−O(2A)−I(1)	117.04(16)	I(2)−C	2.104(7)
six I−O−I avg (std dev)	116.8(1.2)	I(3)−C	2.108(8)
I(1)−O(2A)−I(2A)	124.57(19)	I(4)−C	2.086(7)
I(4)−O(3)−I(5A)	123.96(19)	I(5)−C	2.085(7)
O(1)−I(1)−C	94.7(2)	I−C avg (std dev)	2.091(0.013)
O(1)−I(2)−C	87.8(2)	linear three-atom segments	
O(2)−I(2)−C	86.44(19)	O(2B)−I(1A)−O(1A)	4.322(7)
O(2)−I(3)−C	86.8(2)	O(1A)−I(2A)−O(2A)	4.262(7)
O(3)−I(3)−C	88.2(2)	O(2A)−I(3A)−O(3A)	4.214(7)
O(3)−I(4)−C	87.68(19)	O(3A)−I(5B)−O(4B)	4.326(7)
O(4)−I(4)−C	88.35(19)	O(4B)−I(4B)−O(3B)	4.241(7)
O(4)−I(5)−C	92.4(2)		

[a] Numbered according to Figure 3.

distorted at the oxygen atoms: the average deviation from planarity for all ring atoms is 0.11 Å, while for the oxygen atoms, the average deviation is slightly greater, at 0.17 Å.

The planes of the extended structure are separated by layers containing the phenyl groups attached to the iodine atoms. The planes of the phenyl rings are all nearly perpendicular to the plane of the hexagonal I−O rings, with O−I−C bond angles ranging from 81.5° (phenyl groups on I(1) and I(5)) to 94.9° (phenyl group on I(2)). The I−C (ipso) bonds form angles to the plane of the I−O rings that are also nearly perpendicular and are slightly tilted away from the plane at 95.2° (I(3)−C) to 116.3° (I(2)−C) and appear above or below the plane in a regular pattern that is reversed in adjacent pentaiodanyl dication units (Figures 1 and 3).

The tetrahedral perchlorate ions reside in void spaces created by the three-up, three-down arrangement of the phenyl rings around each 12-atom ring and are positioned directly above and below the 12-atom rings (Figures 4 and 5) where the O_3Cl−O••centroid distance is ca. 1.9 Å. Each I atom has secondary bonds with one or two perchlorate O atoms (Figure 4). I(1) and I(5) each have one bond with respective lengths of 3.14 and 3.02 Å. The remaining I atoms each have two secondary bonds with an average length of (3.25 ± 0.11) Å, compared with a sum of van der Waals radii of 3.55 Å.

The O−I−O Bond Angles. Beginning with the nearly T-shaped geometry at each of the iodine atoms in **8**, the structural characteristics of symmetrical and unsymmetrical aryl-λ^3-iodanes are all manifest in the hexagonal iodine polymer (Table 1). The O−I−O angles at I(1), I(2), I(3), I(4), and I(5) are 178.6°, 173.8°, 175.1°, 175.1°, and 175.9°, respectively, an average of 175.7 ± 1.6°. The largest O−I−O angles (175.9° and 178.6°) in the hexagonal polymer belong to the unsymmetrically polarized triads that join repeat units in the extended structure; these approach the virtual linearity of the O−I−O angle in HTIB.

The I−O Bond Lengths. The I−O bond distances in **7** can be assigned to the three categories already described. The six I−O bonds to the “interior” iodine atoms in the repeating unit **8**, i.e., I(2), I(3), and I(4), are all longer than 2.06 Å and are nearly equal with an average length of 2.120 ± 0.015 Å. These bond lengths fall in the intermediate range and reflect the near equivalence of the apical ligands attached to these iodine atoms, namely, a bridging oxide ligand shared by two iodine atoms. The “terminal” I−O bonds (1.99 and 2.00 Å) in the repeat unit are relatively short and are coaxial with the long I−O bonds (2.33 Å) that bind the pentaiodanyl dications together. The apical ligands attached to these terminal iodines are of significantly different character. On one side, iodine shares an oxide ligand with one other iodine atom, but the other side binds to an oxygen that is already shared by two iodine atoms and is clearly a weaker base. Significantly, all these I−O bonds are essentially covalent bonds.

Secondary I···O Bonds. The only secondary I···O bonds in **7** arise from interactions with the perchlorate O atoms. As illustrated in Figure 4, I(5) and I(1) each have one I···O bond, while I(2), I(3), and I(4) each have two I···O bonds. With an average bond length of 3.25 ± 0.11 Å, these differ vastly from the long I−O bonds (2.33 Å) that bind the pentaiodanyl dications.

The I−C Bonds. The I−C_{Ar} bond distances (2.074−2.108-Å) to the equatorial phenyl ligands in **7** are typical of aryl-λ^3-iodanes and, for that matter, of the iodoarenes, ArI. The average I−C_{Ar} distance in **7** is 2.091 ± 0.013 Å, where the sum of the covalent radii is 2.10 Å.

The I−O−I Bond Angles. The I−O−I bond angles deserve a close examination: the electron-domain geometry of the oxygen is not tetrahedral (Table 1). The oxide ligands at the “free” apexes, O(1) and O(4), have I−O−I bond angles of 118.5° and 118.0°, respectively. The oxide ligands at the apexes where the rings fuse, O(2) and O(3), each have three I−O−I angles to consider and none is close to the tetrahedral ideal of 109.5°. For O(2), the interior angles of I(1)−O(2A)−I(3A) and I(2)−O(2)−I(3) are 117° and 115°, respectively. For O(3), the interior angles of I(3)−O(3)−I(4) and I(3)−O(3)−I(5A) are both 116°. The “exterior” angles for O(2) and O(3), i.e., I(1)−O(2A)−I(2A) and I(4)−O(3)−I(5A), are 124.6° and 124.0°, respectively. In summary, the four interior I−O−I angles for O(2) and O(3) are all virtually the same at 116°, while the two exterior angles are the same at 124°.

The bridging oxide ligands O(2) and O(3) have three bonding and one nonbonding electron domains; simple VSEPR considerations predict a trigonal-pyramidal molecular geometry for the oxygen atoms. However, the three I−O−I bond angles sum to 357° and 356° for O(2) and O(3), respectively, a mere 3−4° deviation from the 360° of an ideal trigonal-planar geometry. What is apparent is that the participation of one of the orbitals on oxygen in the [3c-4e] bond centered on I strongly affects the character of the oxygen atom. A valence-bond view of O(2) and O(3) consistent with the observed bond angles is that as a result of participation in the [3c-4e] bond, the three shared electron pairs reside in three sp^2 hybrid orbitals (one devoted to the [3c-4e] bond) while the unshared electron pair remains in an unhybridized p orbital. Thence, the observed trigonal-planar molecular geometry about the oxygen atoms is produced for a species with four electron domains.

The novel structure of polymer **7** in which there are three bonds each to O(2) and O(3) opens a window that lets us see that three of the four electron domains on each oxygen lie in a plane in an unusual geometry. The oxide ligands on the free apexes have two unshared pairs and only two ligands each, so we cannot ascertain the electron-domain geometry; however, at 118.5° and 118.0°, the I−O−I bond angles for O(1) and O(4) are consistent with the type of bonding observed for O(2) and O(3), resulting from participation in the [3c-4e] bond centered on iodine.

Table 2. ^1H NMR Chemical Shifts of Aromatic Protons in CD_3OD Solution[a]

solute	o-^1H	p-^1H	m-^1H
7	8.11	7.70	7.61
HTIB (**4b**)	8.35	7.83	7.69

[a] All δ are referenced to CHD_2OD at 3.31 ppm.

Reported bond angles for oxide ligands in μ-oxodiiodanes also exhibit this departure from sp^3 hydridization for the O atom. For the bistriflouroacetato- (**5b**), the dinitrato- (**5c**), and the trifluoroacetato-nitrato- (**5d**) μ-oxodiiodane analogues, the I−O−I angles are 123.7°, 121.2°, and 120.8°, respectively.[18−20]

NMR Spectra and Solubilities. Compound **7** is insoluble in $CHCl_3$ and water but is soluble in methanol (>10 mg/mL). The ^1H NMR spectrum in CD_3OD is simple, consisting of a somewhat-broadened doublet of quartets for the o-^1H, a well-resolved triplet of triplets for the p-^1H, and a less-resolved triplet of quartets for the m-^1H (Table 2). This simple spectrum is consistent with a single solution-phase species or multiple species in a rapid equilibrium. HTIB (**4b**) likewise gives a simple, well-resolved ^1H NMR spectrum in CD_3OD, which is nearly identical to that from **7**. The slight downfield shifts in the HTIB spectrum probably arise from differing acidities of the methanolic solutions.

The First Polymer: Iodosylbenzene. Comparison of the structure of the present polymer **7** to another well-known hypervalent organoiodine polymer is clearly of interest. Solid-state iodosylbenzene (**2**) is not monomeric; early suggestions that iodosylbenzene is polymeric, based on spectroscopic studies,[21,22] have been confirmed by extended x-ray absorption fine structure studies. The I−O−I angles in **2** are 114°, closer to the 109.5° tetrahedral angle than those seen in **7** for oxide ligands at the free apexes (118.5° and 118.0° for O(1) and O(4)). The length of the I−O bond joining the PhIO monomers is 2.38 Å. The average of the I−O and I−C bond distances in PhIO is 2.04 Å; since the I−C bond length is probably about 2.10 Å, the I−O bond is probably about 1.98 Å. If we think of **2** as an infinite strand of iodobenzene dications joined by bridging oxide ligands, we would expect **2** to exhibit essentially equal I−O bond lengths, just as we see in the interior iodine atoms of the pentaiodanyl dication **7**, where the average length is 2.12 ± 0.02 Å. However, polymer **2** exhibits a pairing of long and short bonds (2.38 and 1.98 Å), which is consistent with a [3c-4e] bond where the ligands *differ substantially* in basicity.

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Clearly, the I−O bonding in **2** differs in some substantial way from that in **7**.

In the polymer given by the substituted iodosylbenzene **3** (Chart 1), the polymer is built using intermolecular secondary I⋯O bonds. Interestingly, these bonds lie in the *equatorial* plane of the molecule contributing the I atom, nearly collinear with the C−I segment, and not in the apical plane as is seen in **2**. With an I⋯O bond length of 2.665(6) Å, the supramolecular polymeric structure of **3** is considerably weaker than that of polymers **6a** and **7**.

Polymeric PhINTs. As described earlier, the supramolecular structure of solid-state PhINTs (**6a**, Chart 3) is polymeric, and the contrasts with **7** are significant. Solid-state **6a** has a zigzag linear structure with the bridging oxide ligands in **7** replaced by nitrene ylide ligands.[12] In compound **7**, the I atoms that have identical apical ligands (i.e., oxide ions) give linear O−I−O segments with equal I−O bond lengths (2.12 Å) as expected for [3c-4e] bonds with identical apical ligands. In compound **6a**, the observed backbone structure presents linear (177.8°) N−I−N segments, where the two apical ligands would appear to be identical; however, the I atom clearly does not see them this way, as the two I−N bond lengths are far from equal at 2.04 and 2.48 Å. These bond lengths are reminiscent of those (2.00 and 2.33 Å) for the terminal iodines in **7** where the basicity of the apical ligands is very different. This short−long I−X bond length combination is expected for apical ligands with substantial differences in basicity. Thus, the PhINTs polymer presents the same conundrum as the iodosylbenzene polymer: the structure of **2** suggests that the iodine has two equivalent apical ligands (both oxide ions), but the bond lengths (1.98 and 2.38 Å) indicate asymmetrical ligands. The reason (or reasons) for the divergence of the behavior of **2** and **6a** from that of **7** is not immediately apparent, and all three polymers have similar long−short bond values.

Conclusions

The solid-state hypervalent-iodine polymer (**7**) described in this paper contains alternating iodine and oxygen atoms in fused 12-atom hexagonal rings, a novel structure. Beginning with the nearly T-shaped geometry at each of the iodine atoms in **7**, the structural characteristics of symmetrical and unsymmetrical aryl-λ^3-iodanes are all manifest in this polymer. The apical ligands attached to the interior iodine atoms in the repeating unit, i.e., I(2), I(3), and I(4), are of comparable basicity, giving nearly equal I−O bond lengths that are longer than the 2.06 Å sum of the covalent radii. The apical ligands attached to the terminal iodine atoms in the repeat unit, i.e., I(1) and I(5), are of very different basicity and this is reflected in the presence of a short ($<$2.06 Å) and an elongated I−O bond on each iodine atom. The observed I−O−I bond angles establish that the hybridization on the oxygen atoms is not the tetrahedral electron-domain structure expected from simple VSEPR considerations. Rather, it appears that the participation of one of the orbitals on the oxygen atom in the [3c-4e] bond with iodine results in three shared electron pairs residing in three sp^2 hybrid orbitals (one devoted to the [3c-4e] bond), while the unshared electron pair remains in an unhybridized p orbital. Thence, the observed trigonal-planar molecular geometry about the oxygen atoms is produced for a species with four electron domains. Compound **7** provides a unique window into the hybridization of the oxygen atoms, since the two bridging oxygens, O(2) and O(3), each have three bonds, allowing the determination of the electron-domain angles in this unusual geometry.

Table 3. Crystal Data and Structure Refinement for Compound **7**

empirical formula	$C_{30}H_{25}Cl_2I_5O_{12}$
fw	1282.90
T (K)	173(2)
wavelength (Å)	0.71073
unit cell dimensions (Å, deg)	*a* = 14.8422(2), 90 *b* = 21.3463(2), 90 *c* = 23.7846(2), 90
volume (Å^3), *Z*	7535.58(11), 4
density (calculated) (g/cm^3)	2.262
abs coeff	4.327/mm
F(000)	4800
cryst size (mm^3)	0.40 × 0.30 × 0.10
cryst color	yellow plate
θ range for data collection (deg)	1.71−25.99
limiting indices	$0 \leq h \leq 18$ $0 \leq k \leq 26$ $0 \leq l \leq 26$
reflns collected	9751
independent reflns	6790 (R_{int} = 0.0486)
abs cor	empirical from *DIFABS*
max and min trans	1.00 and 0.434
refinement method	full-matrix least-squares on F^2
data/restraints/params	6790/0/442
GOF on F^2	1.598
final *R* indices [$I > 2\sigma(I)$]	Rl = 0.0406, wR2 = 0.1121
R indices (all data)	Rl = 0.0515, wR2 = 0.1222
largest diff peak and hole (e/Å^3)	0.828 and −1.246

This compound is able to self-assemble into the hexagonal rings because (i) the O−I−O segments are nearly linear as a result of the [3c-4e] bonding between I and O, and (ii) the I−O−I angles are very nearly the hexagonal ideal of 120° owing to the influence of the [3c-4e] bond on the hybridization of the oxygen atom.

Experimental Section

Materials. HTIB (**4b**) was prepared from BAIB **(4a)** (10.0 g, 31.0 mmol) dissolved in CH_3CN (30 mL) treated with *p*-toluenesulfonic acid monohydrate (6.50 g, 34.2 mmol) in CH_3CN (20 mL) and gentle heating. Recrystallization from CH_3CN gave a 91% yield (mp 135−138 °C).[17]

Preparation of Polymer 7. HTIB (1.02 g, 2.60 mmol) was dissolved in water (200 mL). Aqueous $Mg(ClO_4)_2{\cdot}6H_2O$ (0.90 g, 2.72 mmol, 30 mL H_2O) was added at once. After 10−12 h, thin elongated-hexagonal plates began to appear. The color was intense yellow, with a green hue. The yields varied from 78 to 100%. The compound was stable in air at room temperature for at least three weeks.

Caution! *Compound* ***7*** *does not melt; instead, it detonates at 112−113 °C. It is not shock sensitive.*

NMR Spectroscopy. All NMR spectra were obtained on a Varian VXR 300 MHz spectrometer equipped with a broad-band probe.

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters for **7** are given in Table 3. A suitable crystal was selected and mounted in a nitrogen-flushed, thin-walled capillary and flame-sealed. All data were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector. The data show that **7** is orthorhombic. The systematic absences in the diffraction data are uniquely consistent with the space group *Pbca*. 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.[23] The molecule lies on a crystallographic inversion center and forms an extended solid-state structure of repeating $(C_6H_5I)_5O_4$ units locked into hexagonal rings. The asymmetric unit contains half of one ring and two perchlorate counterions. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the *SHELXTL* (5.10) program library (G. Sheldrick; Siemens XRD: Madison, WI).

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Supporting Information Available: Crystal data and structure refinement, atomic coordinates, bond lengths and bond angles, anisotropic displacement coefficients, and H-atom coordinates for compound **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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