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Self-Assembly of Hydroxy(phenyl)iodonium Ions in Acidic Aqueous Solution: Preparation, and X-ray Crystal Structures of Oligomeric Phenyliodine(III) Sulfates

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The treatment of [(diacetoxy)iodo]benzene with sodium bisulfate leads to the formation of oligomeric cationic species resulting from self-assembly of hydroxy(phenyl)iodonium ions, $[PhIOH]^+$, in an aqueous acidic media. Depending on the $PhI(OAc)_2$:$NaHSO_4$ ratio, three new oligomeric products have been isolated and characterized by X-ray crystallography. The treatment of 5 equiv of $PhI(OAc)_2$ with 1 equiv of $NaHSO_4 \cdot H_2O$ affords the previously unknown μ-oxo-[bis(acetoxy)iodo]benzene, PhI(OAc)OI(OAc)Ph, which was structurally characterized by X-ray crystallography. In the solid-state, this μ-oxo product forms an isolated diamond-core dimeric structure with pentagonal-planar iodine centers. The interaction of $PhI(OAc)_2$ with 1 equiv of $NaHSO_4 \cdot H_2O$ affords a solid-state polymeric phenyliodine(III) sulfate, $[(PhIO)_3 \cdot SO_3]_n$, in which bis(μ-oxo)triiodanyl dication repeat units are linked by sulfate anions. Three of these neighboring polymeric chains form pseudo triple-helix supramolecular structure, which translates along crystallographic *b*-axis. The reaction of $PhI(OAc)_2$ with 3 equiv of $NaHSO_4 \cdot H_2O$ results in the formation of a tetrameric phenyliodine(III) sulfate, $PhI(OH)OSO_2O(Ph)IOI(Ph)OSO_2OI(OH)Ph$, the solid state structure of which consists of μ-oxodiiodanyl dicationic species linked by sulfate anions to the terminal hydroxy(phenyl)iodonium groups. The pseudo double-helix structure of this compound formed by the strong intermolecular interactions between two neighbor μ-oxodiiodanyl dicationic fragments and four (per pseudo helix dimer) areas of sulfate anions to the terminal hydroxy(phenyl)iodonium groups interactions.

Introduction

Hypervalent iodine compounds are used extensively in organic synthesis as highly selective and environmentally friendly oxidizing reagents.[1] Among these reagents, iodosylbenzene, $(PhIO)_n$, is particularly important as an oxygen transfer agent that has found widespread application in catalytic oxygenation reactions after the discovery of its supreme efficacy as a source of oxygen atoms for oxidations catalyzed by cytochrome P-450 and by discrete transition metal complexes.[2,3] Despite its usefulness as an oxidant, practical applications of iodosylbenzene are hampered by its low solubility in nonreactive media,[3] as well as low thermal stability and explosive properties upon moderate heating.[4] The low solubility of iodosylbenzene is explained by a zigzag polymeric, asymmetrically bridged structure, in which monomeric units of PhIO are linked by intermolecular I···O secondary bonds. The polymeric structure of iodosylbenzene was also theoretically analyzed by density functional theory computations at the B3LYP level and, in particular, the importance of the presence of a terminal hydration water in its zigzag polymeric structure $HO-I(Ph)(PhIO)_n(Ph)I-OH$ was established[5] confirming an earlier suggestion.[6] The explanation of the oxo-bridged zigzag

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polymer structure of $(PhIO)_n$ on the basis of ligands' trans influences was recently provided.[7]

Iodosylbenzene can be depolymerized by protonation or by treatment with a Lewis acid. Ochiai and co-workers have reported the preparation, X-ray crystal structures, and useful oxidizing reactions of activated iodosylbenzene monomer complexes with 18C6 crown ether, such as complex **1**.[8] X-ray analysis of complex **1** revealed a structure in which hydroxy(phenyl)iodonium ions are stabilized by intramolecular coordination with the crown ether oxygen atoms.[8] The depolymerized, protonated iodosylbenzene **1** is an efficient oxidizing agent that has a moderate solubility and excellent stability in water.

[Hydroxy(tosyloxy)iodo]benzene (HTIB, **2**, Figure 1) and similar phenyliodine(III) organosulfonates $PhI(OH)OSO_2R$ represent an important class of hypervalent iodine reagents commonly used as versatile, mild oxidants and electrophiles in organic synthesis.[1,9] X-ray analysis of HTIB **2** has shown that the I−OTs bond distance (2.473 Å) is significantly longer than the I−OH bond of 1.940 Å, which is indicative of the ionic character of the structure of this compound in solid state.[10] It was shown by spectroscopic measurements and potentiometric titrations that in water solutions, HTIB is completely ionized to hydroxy(phenyl)iodonium ions (PhI^+OH in hydrated form) and tosylate anions. The hydroxy(phenyl)iodonium ion can combine with [oxo(aquo)iodo]benzene $PhI^+(OH_2)O^-$, a hydrated form of iodosylbenzene that is also observed in the solution, producing the dimeric μ-oxodiiodine cation $Ph(HO)I{-}O{-}I^+(OH_2)Ph$ and dication $Ph(H_2O)I^+{-}O{-}I^+(OH_2)Ph$.[6] Recently, Richter, Koser, and coauthors reported the preparation and structure of the oligomeric perchlorate **3**, which precipitated from dilute aqueous solutions of HTIB **2** and $Mg(ClO_4)_2$.[11] Single crystal X-ray study of the perchlorate **3** revealed a complex structure consisting of pentaiodanyl dicationic units joined by secondary I···O bonds into an infinite linear structure of 12-atom hexagonal rings. The formation of product **3** can be explained by self-assembly of the hydroxy(phenyl)iodonium ions (PhI^+OH in hydrated form) and [oxo(aquo)iodo]benzene $PhI^+(OH_2)O^-$ in aqueous solution under reaction conditions.[11]

In contrast to phenyliodine(III) organosulfonates $PhI(OH)OSO_2R$, the similar derivatives of sulfuric acid have not been extensively investigated. The formation of a highly hygroscopic sulfate **4** in the reaction of $PhICl_2$ and Ag_2SO_4 was briefly described by Alcock and Waddington in 1963,[12] and the unstable and extremely hygroscopic sulfates **5** ($PhIO \cdot SO_3$) and **6** [$(PhIO)_2 \cdot SO_3$] were generated from PhIO and SO_3 or Me_3SiOSO_2Cl under absolutely dry conditions.[13] The crystal structure of phenyliodine(III) sulfates **4**−**6** has never been reported, and their characterization is unreliable because of the low stability of these compounds. In our preliminary communication,[14] we have reported the X-ray structure of a new, stable, and water-soluble oligomeric iodosylbenzene sulfate, $[(PhIO)_3 \cdot SO_3]_n$ (product **8** in Scheme 1) which can be considered as a partially depolymerized and activated form of iodosylbenzene. Interestingly, structure **8** is very different from the solid-state polymeric perchlorate **3** reported by Richter, Koser, and coauthors.[11] In the present paper, further details on compound **8**, as well as the isolation and X-ray structures of two additional products resulting from the self-assembly of hydroxy(phenyl)iodonium ions, are presented.

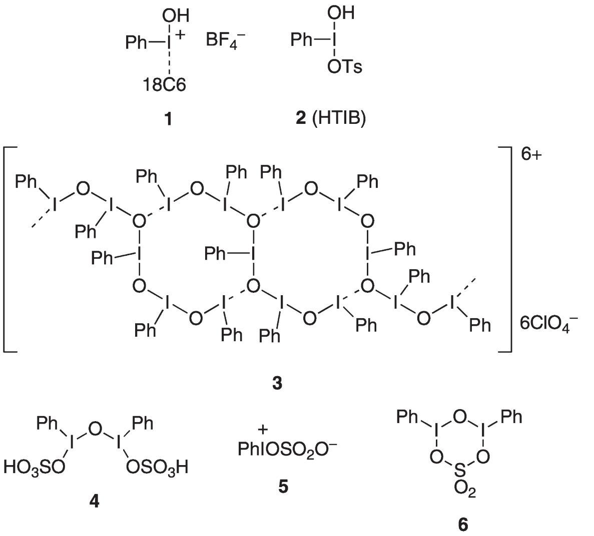
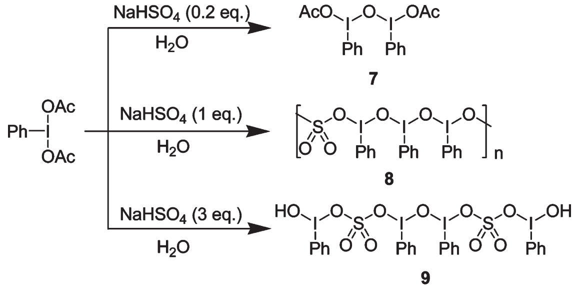


Figure 1. Representative examples of the key structural motifs of iodonium compounds.

Scheme 1. Reactions of [(Diacetoxy)iodo]benzene with Sodium Hydrogen Sulfate in the Presence of Water



Results

We have found that the reaction of [(diacetoxy)iodo]benzene with sodium hydrogen sulfate in the presence of water leads to the formation of several different products (Scheme 1). Depending on the $PhI(OAc)_2$:$NaHSO_4$ ratio, three new iodonium species **7**−**9** have been isolated and characterized by X-ray crystallography. The key feature in all three isolated products is the formation of the I−O−I μ-oxo bond, which connects phenyl iodonium fragments.

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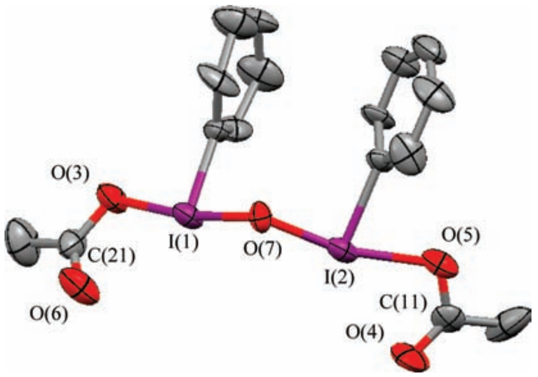

Figure 2. X-ray crystal structure of μ-oxodiiodanyl diacetate **7** (ellipses are shown at 50% probability; hydrogen atoms are omitted for clarity).

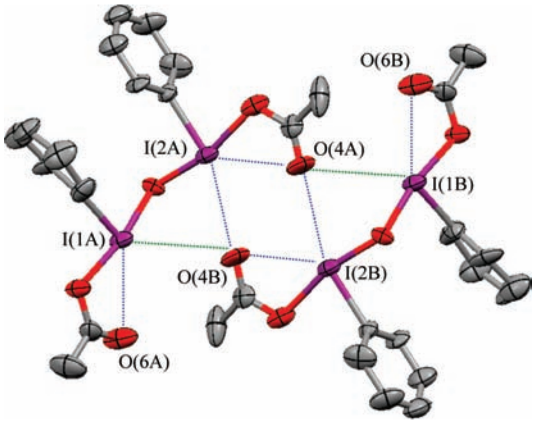

Figure 3. Dimeric structure of μ-oxodiiodanyl diacetate **7**. Short intra- (inter-) molecular bonds are shown as blue dotted lines, while long one as green lines (ellipses are shown at 50% probability; hydrogen atoms are omitted for clarity).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) in μ-Oxodiiodanyl Diacetate **7**[a]

atoms	length	atoms	angle
I(1)−C(13)	2.089(18)	O(3)−I(1)−C(13)	79.8(7)
I(1)−O(3)	2.214(15)	O(7)−I(1)−C(13)	91.5(7)
I(1)−O(6)	2.857(18)	O(5)−I(2)−C(16)	78.5(7)
I(1)−O(7)	2.045(13)	O(7)−I(2)−C(16)	87.9(7)
I(2)−C(16)	2.13(2)	O(3)−I(1)−O(7)	170.9(6)
I(2)−O(4)	3.02(2)	O(5)−I(2)−O(7)	166.4(6)
I(2)−O(5)	2.245(17)	I(1)−O(7)−I(2)	117.7(7)
I(2)−O(7)	2.020(13)	C(13)−I(1)−O(6)	129.6(8)
I(1A)−O(4B)	3.38(2)	C(13)−I(1)−O(4B)	137.9(7)
I(2A)−O(4B)	3.10(2)	C(16)−I(2)−O(4)	125.2(7)
		C(16)−I(2)−O(4B)	160.6(7)

[a] Numbered according to Figures 2 and 3.

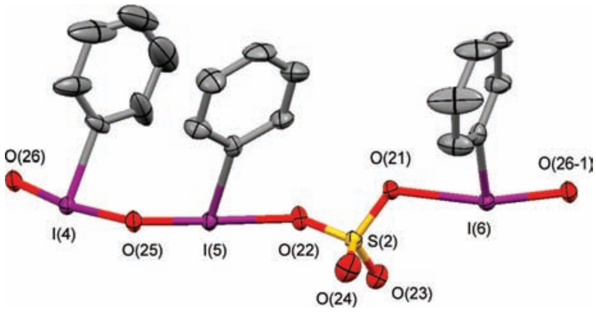

Figure 4. X-ray crystal structure of one out of three unique μ-oxotriiodanyl sulfate fragments of **8** (173 K structure, ellipses are shown at 50% probability; hydrogen atoms are omitted for clarity).

Expectedly, the number of sulfate fragments incorporated into oligomeric or polymeric backbone depends on the $PhI(OAc)_2$:$NaHSO_4$ ratio and increases with the increase of $NaHSO_4$ introduced in the reaction. Indeed, no sulfate moiety was observed when the $PhI(OAc)_2$:$NaHSO_4$ ratio was high (5:1), while it is 3:1 (phenyl iodonium:sulfate) in the case of polymer **8**, and 2:1 (phenyl iodonium:sulfate) in the case of oligomer **9**. Despite the isolation of target compounds **7**−**9** from water, it is interesting to see that the dimer **7** and polymer **8** have no terminal hydroxy groups, while these are present in oligomer **9** (similar to terminal hydroxy groups found in iodosyl benzene).

The interaction of a large excess (5 equiv) of [(diacetoxy)iodo]benzene with 1 equiv of sodium hydrogen sulfate followed by aqueous workup and removal of the unreacted solid $PhI(OAc)_2$ leads to formation of previously unknown μ-oxodiiodanyl diacetate **7**, PhI(OAc)−O-I(OAc)Ph. Slow evaporation of aqueous solution afforded colorless block-shaped crystals suitable for characterization by X-ray diffraction (Figures 2 and 3, Table 1). In the structure of **7**, both iodine centers have pentagonal planar coordination with three short covalent and two long secondary bonds similar to that observed in the case of the previously reported μ-oxo-[bis(trifluoroacetoxy)iodo]benzene.[15] The I(1)−O(7)−I(2) μ-oxo bridge is bent and consists of two short (2.03 Å, average) I−O bonds (Figure 2), which are close to those observed in μ-oxodiiodanyl ditrifluoroacetate (2.02 Å),[15] μ-oxodiiodanyl trifluoroacetate nitrate (2.01 Å),[16] and μ-oxodiiodanyl dinitrate (2.00 Å).[17] The degree of deviation of I(1)−O(7)−I(2) μ-oxo bridge angle (117.7°) from that expected for sp^3 hybridization of oxygen atom is significant, but close to that observed in the recently reported polymeric tetra-μ-oxopentaiodanyl dication[11] and other μ-oxodiiodane analogues including those with μ-oxodiiodanyl fragment (118.0−123.7°).[15−17] As discussed earlier, such deviation most likely originates from the nature of [3c-4e] I−O−I bond. Similar to the other μ-oxodiiodanyl compounds,[15−17] the acetate fragments are coordinated to iodine centers of the same molecule in η^2-manner with one short (2.23 Å, average) and one long (2.94 Å, average) nonequivalent I−O bonds. Interestingly, both of these bonds are shorter than those in η^2-fragments of the other μ-oxodiiodanyl compounds suggesting larger degree of covalency in **7**.[15−17] Both acetate fragments are almost coplanar with respective iodine atoms with I(1)−O(3)−C(21)−O(6) and I(2)−O(5)−C(11)−O(4) torsion angles being 1.64° and 8.12°, respectively. The I−C (phenyl) bond distances (2.11 Å, average) are in the typical for aryl-λ^3-iodanes range.[15−18] The tetraatomic O−I(C)−O fragment, which has three shortest I−X bonds in **7** (I−O and I−C bonds) reflects a T-shape around iodine atoms with O−I−O angles close to linear (168.6°, average for two angles) and perpendicular (84.4°, average for four angles) geometries

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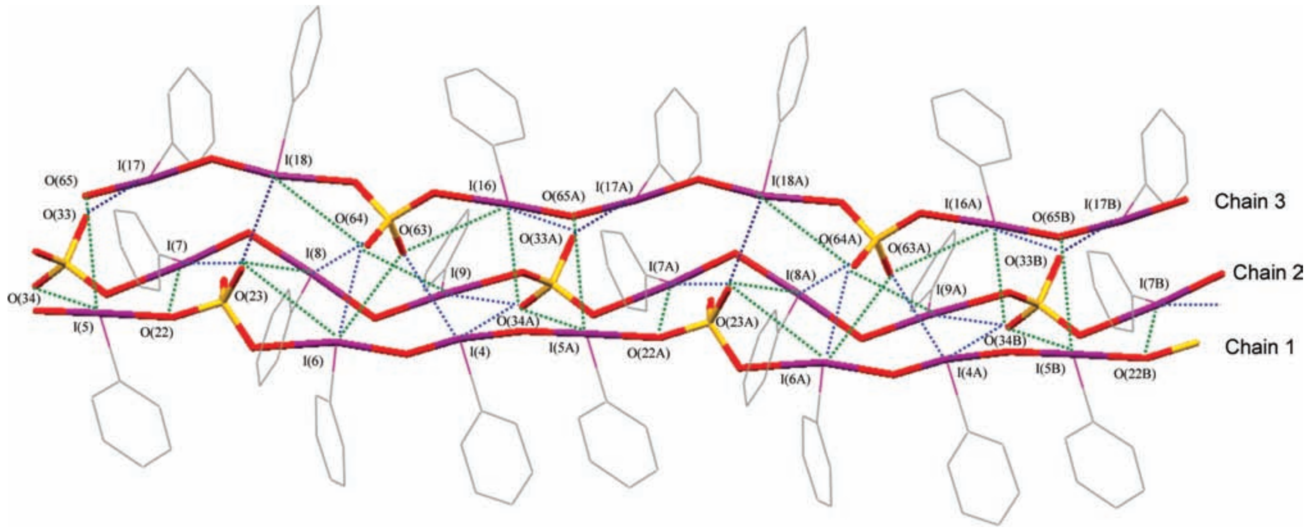

Figure 5. Supramolecular triple-helix structure of μ-oxotriiodanyl sulfate **8**. Short intra- (inter-) molecular interactions are shown as blue dotted lines, while long ones as green lines.

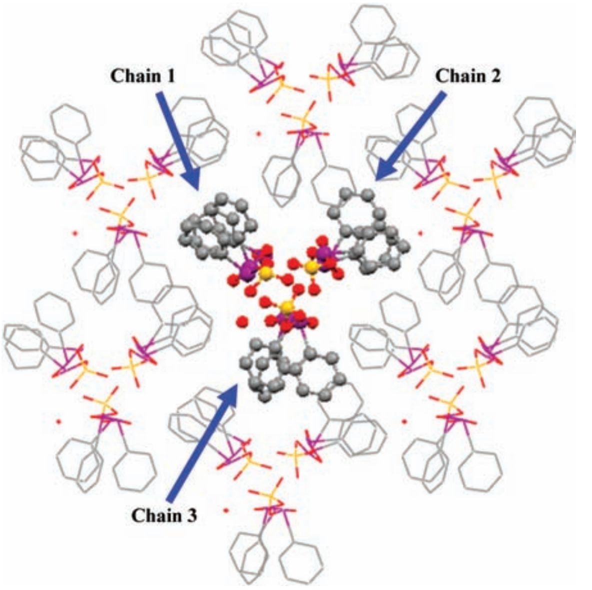

Figure 6. Triple-helix supramolecular motif of polymer **8** shown along crystallographic *b* axis.

very similar to those observed in the other μ-oxodiiodanyl compounds.[15-17]

The presence of secondary intermolecular bonds in **7** results in formation of dimeric units of **7** (formed between molecule located at the origin and that located at the $1-x$, $-y$, $-z$ position) with short (3.096 Å) intermolecular I(2A)−O(4B) and I(2B)−O(4A) contacts (Figure 3). This pair of relatively short intermolecular bonds along with I(2)−O(4) intramolecular bonds form I(2A)−O(4A)−I(2B)−O(4B) "diamond" core in dimer of **7**, which completes an overall pentagonal planar coordination around I(2) centers (Figure 3). Another pair of weak secondary bonds (3.381 Å) originates from I(1A)−O(4B) and I(1B)−O(4A) interactions and close to the sum of van der Waals radii of iodine and oxygen (3.55 Å). This pair of secondary bonds completes an overall pentagonal planar geometry around I(1) atoms of **7**.

The reaction between [(diacetoxy)iodo]benzene and 1 equiv of sodium hydrogen sulfate results in the formation of a yellow polymeric compound **8**, which can be purified by crystallization from hot water. Taking into account the low solubility of $NaHSO_4$ in organic solvents and the insolubility of $PhI(OAc)_2$ in water, the reaction was initially conducted under solvent-free conditions similarly to the recently reported synthesis of HTIB.[19] The polymeric compound **8** can also be prepared by the direct interaction of $PhI(OAc)_2$ with 1 equiv of $NaHSO_4$ in water without preliminary grinding in the solid state, but in this case the yield is relatively low (56%). The analytical and spectroscopic (IR, NMR, and MS) data are suggestive of the molecular formula of $(PhIO)_3 \cdot SO_3$ (**8**), (Scheme 1).

X-ray quality, yellow block shape crystals of polymeric **8** were obtained from aqueous solutions. X-ray analysis of polymeric **8** conducted at room and −100 °C clearly suggests phase transition in the structure. Indeed, high-temperature unit cell is twice smaller than that found at −100 °C. Polymeric chains of **8** are assembled from the monomeric units, which consist of one $-OSO_2-$ fragment per three PhIO moieties (Figure 4).[14] There are three and six slightly different polymeric chains in the high- and low-temperature structures of **8**, respectively. An intermolecular interaction between these polymeric chains results in a unique triple pseudohelix structural motif formed by three polymeric chains translated along crystallographic *b* axis (Figures 5 and 6). All three polymeric chains in triple-helix structure are connected by a number of intermolecular interactions primarily between oxygen atoms of the sulfate group and the hypervalent iodine centers. The low temperature unit cell of polymer **8** consists of two of such triple-helix motifs (six unique polymeric chains), while only one triple-helix supramolecular structure (three unique polymeric chains) survives in the room temperature unit cell because of the thermal averaging process. In each triple-helix, the position of the sulfate group in each unique polymeric chain is shifted on one-third of the length as compared to those on other two subunits providing specific coordination within a polymer chain (Figure 5). Unlike, in the case of μ-oxodiiodanyl diacetate **7**, the large intensity decay was observed during data collection in the case of the room-temperature experiment for polymer **8**. Because of this, the only structural

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Polymer **8**[a]

chain 1	chain 2	chain 3	chain 4	chain 5	chain 6
Intramolecular Covalent Bonds					
I(1)−C(11) 2.116(7)	I(4)−C(41) 2.082(8)	I(7)−C(71) 2.105(8)	I(10)−C(101) 2.150(8)	I(13)−C(131) 2.142(8)	I(16)−C(161) 2.147(8)
I(1)−O(12) 2.380(5)	I(4)−O(25) 2.193(5)	I(7)−O(31) 2.361(6)	I(10)−O(41) 2.415(5)	I(13)−O(51) 2.310(6)	I(16)−O(61) 2.318(5)
I(1)−O(16) 1.973(5)	I(4)−O(26) 2.082(5)	I(7)−O(35) 1.974(5)	I(10)−O(45) 1.950(5)	I(13)−O(55) 1.951(5)	I(16)−O(65) 1.974(5)
I(2)−C(21) 2.096(8)	I(5)−C(51) 2.143(8)	I(8)−C(81) 2.092(9)	I(11)−C(111) 2.091(8)	I(14)−C(141) 2.094(8)	I(17)−C(171) 2.085(8)
I(2)−O(15) 2.124(5)	I(5)−O(22) 2.419(5)	I(8)−O(35) 2.104(5)	I(11)−O(45) 2.183(5)	I(14)−O(55) 2.139(5)	I(17)−O(65) 2.119(5)
I(2)−O(16) 2.088(5)	I(5)−O(25) 1.959(5)	I(8)−O(36) 2.116(6)	I(11)−O(46) 2.083(6)	I(14)−O(56) 2.079(5)	I(17)−O(66) 2.101(5)
I(3)−C(31) 2.100(9)	I(6)−C(61) 2.088(8)	I(9)−C(91) 2.114(8)	I(12)−C(121) 2.031(11)	I(15)−C(151) 2.102(8)	I(18)−C(181) 2.098(8)
I(3)−O(11) 2.348(5)	I(6)−O(21) 2.317(5)	I(9)−O(32) 2.333(6)	I(12)−O(42) 2.319(6)	I(15)−O(52) 2.351(5)	I(18)−O(62) 2.385(6)
I(3)−O(15) 1.953(5)	I(6)−O(26) 1.985(5)	I(9)−O(36) 1.946(5)	I(12)−O(46) 1.975(6)	I(15)−O(56) 1.983(5)	I(18)−O(66) 1.962(5)
S(1)−O(11) 1.502(6)	S(2)−O(21) 1.510(6)	S(3)−O(31) 1.481(8)	S(4)−O(41) 1.492(6)	S(5)−O(51) 1.504(6)	S(6)−O(61) 1.507(6)
S(1)−O(12) 1.505(6)	S(2)−O(22) 1.490(5)	S(3)−O(32) 1.471(7)	S(4)−O(42) 1.506(6)	S(5)−O(52) 1.497(6)	S(6)−O(62) 1.490(6)
S(1)−O(13) 1.452(6)	S(2)−O(23) 1.463(6)	S(3)−O(33) 1.461(12)	S(4)−O(43) 1.431(6)	S(5)−O(53) 1.464(6)	S(6)−O(63) 1.465(6)
S(1)−O(14) 1.468(6)	S(2)−O(24) 1.440(6)	S(3)−O(34) 1.373(10)	S(4)−O(44) 1.466(5)	S(5)−O(54) 1.438(6)	S(6)−O(64) 1.461(6)
Most Important Intra- and Intermolecular Contacts					
I(1)-(44)[b] 2.903(6)	I(4)−O(63)[e] 2.849(7)	I(7)−O(23)[f] 2.889(6)	I(10)−O(55)[g] 3.202(7)	I(13)−O(14)[i] 2.944(7)	I(16)−O(33) 3.091(15)
I(1)−O(13) 3.232(7)	I(4)−O(34) 3.103(12)	I(7)−O(33) 3.231(13)	I(10)−O(14)[h] 3.300(6)	I(13)−O(53) 3.271(6)	I(16)−O(63)[e] 3.243(6)
I(1)−O(41)[b] 3.357(6)	I(5)−O(65) 3.244(7)	I(7)−O(22) 3.447(6)	I(11)−O(53)[g] 2.821(7)	I(13)−O(13)[i] 3.343(7)	I(16)−O(34) 3.430(2)
I(2)−O(54)[c] 3.032(6)	I(5)−O(34) 3.417(10)	I(8)−O(64) 3.002(6)	I(11)−O(14)[h] 3.137(6)	I(14)−O(13)[j] 2.951(6)	I(17)−O(33) 2.841(13)
I(2)−O(44)[d] 3.246(7)	I(6)−O(64)[e] 2.979(6)	I(8)−O(23)[f] 3.351(7)	I(12)−O(54)[g] 3.157(7)	I(15)−O(44)[k] 2.830(6)	I(18)−O(23)[f] 2.777(7)
I(3)−O(14) 3.123(6)	I(6)−O(63)[e] 3.316(6)	I(9)−O(34)[f] 3.036(11)	I(12)−O(53)[g] 3.303(6)	I(15)−O(54) 3.288(7)	I(18)−O(64) 3.258(7)
I(3)−O(54)[c] 3.281(7)	I(6)−O(23) 3.381(7)	I(9)−O(64) 3.328(7)	I(12)−O(15)[h] 3.338(7)		
Angles					
O(12)−I(1)−C(11) 81.8(2)	O(25)−I(4)−C(41) 84.5(3)	O(35)−I(7)−C(71) 92.2(3)	O(41)−I(10)−C(101) 88.3(3)	O(51)−I(13)−C(131) 88.2(3)	O(61)−I(16)−C(161) 89.5(3)
O(16)−I(1)−C(11) 90.5(3)	O(26)−I(4)−C(41) 87.5(3)	O(31)−I(7)−C(71) 79.4(3)	O(45)−I(10)−C(101) 93.8(3)	O(55)−I(13)−C(131) 93.3(3)	O(65)−I(16)−C(161) 92.4(3)
O(15)−I(2)−C(21) 85.7(3)	O(22)−I(5)−C(51) 88.1(2)	O(35)−I(8)−C(81) 87.8(3)	O(45)−I(11)−C(111) 86.6(3)	O(55)−I(14)−C(141) 84.5(3)	O(65)−I(17)−C(171) 85.6(3)
O(16)−I(2)−C(21) 87.8(3)	O(25)−I(5)−C(51) 94.1(3)	O(36)−I(8)−C(81) 84.4(3)	O(46)−I(11)−C(111) 83.4(3)	O(56)−I(14)−C(141) 88.6(3)	O(66)−I(17)−C(171) 88.0(3)
O(11)−I(3)−C(31) 79.3(3)	O(21)−I(6)−C(61) 78.4(3)	O(32)−I(9)−C(91) 80.0(3)	O(42)−I(12)−C(121) 82.4(3)	O(52)−I(15)−C(151) 79.9(3)	O(62)−I(18)−C(181) 79.2(3)
O(15)−I(3)−C(31) 92.2(3)	O(26)−I(6)−C(61) 91.1(3)	O(36)−I(9)−C(91) 92.0(3)	O(46)−I(12)−C(121) 91.6(3)	O(56)−I(15)−C(151) 92.0(3)	O(66)−I(18)−C(181) 91.7(3)
O(12)−I(1)−O(16) 171.5(2)	O(25)−I(4)−O(26) 170.2(2)	O(31)−I(7)−O(35) 171.3(2)	O(41)−I(10)−O(45) 174.3(2)	O(51)−I(13)−O(55) 178.3(2)	O(61)−I(16)−O(65) 178.0(2)
O(15)−I(2)−O(16) 173.4(2)	O(22)−I(5)−O(25) 174.4(2)	O(35)−I(8)−O(36) 171.9(2)	O(45)−I(11)−O(46) 169.3(2)	O(55)−I(14)−O(56) 173.1(2)	O(65)−I(17)−O(66) 173.5(2)
O(11)−I(3)−O(15) 170.4(2)	O(21)−I(6)−O(26) 166.6(2)	O(32)−I(9)−O(36) 169.5(3)	O(42)−I(12)−O(46) 169.9(2)	O(52)−I(15)−O(56) 171.0(2)	O(62)−I(18)−O(66) 170.9(2)
I(1)−O(16)−I(2) 120.5(3)	I(4)−O(25)−I(5) 115.7(2)	I(7)−O(35)−I(8) 119.2(3)	I(10)−O(45)−I(11) 116.3(3)	I(13)−O(55)−I(14) 119.6(3)	I(16)−O(65)−I(17) 117.1(3)
I(2)−O(15)−I(3) 122.4(3)	I(4)−O(26)−I(6) 124.7(3)	I(8)−O(36)−I(9) 124.4(3)	I(11)−O(46)−I(12) 126.3(3)	I(14)−O(56)−I(15) 120.4(3)	I(17)−O(66)−I(18) 121.3(3)

[a] Numbered according to Figures 4 and 5. [b] At $x, y, -1+z$ position. [c] At $1+x, y, -1+z$ position. [d] At $x, 1+y, -1+z$ position. [e] At $x, 1+y, z$ position. [f] At $x, -1+y, z$ position. [g] At $1+x, y, z$ position. [h] At $x, y, 1+z$ position. [i] At $-1+x, y, 1+z$ position. [j] At $-1+x, 1+y, 1+z$ position. [k] At $-1+x, 1+y, z$ position.

parameters observed for the low-temperature structure of **8** will be discussed below.

The most important bond lengths and angles of six unique polymeric chains observed in the low-temperature structure of **8** are listed in Table 2. All I−C(Ph) bond distances in polymer **8** (2.10 Å, average) are within the expected range for iodine(III) iodosylaryl structures. Sulfate groups in polymeric chains of **8** retain tetrahedral geometry characteristic for the sp^3 hybridization of sulfur atom. As expected, S═O terminal double bonds are significantly shorter (1.45 Å, average) as compared to S−O bonds involved in the formation of polymeric chains (1.50 Å, average). Similarly, I−O bonds in S−O−I fragments are significantly longer (2.36 Å, average) as compared to those in I−O−I fragments (2.04 Å, average). Such significant elongation of I−O bonds in S−O−I fragments indicate that polymer chain fragmentation of **8**, observed experimentally by mass spectrometry in solution, can start from the dissociation of the relatively weak I−O bond in this fragment. The iodine atoms in the −O−I(Ph)−O− fragment of **8** exhibit a typical of trivalent iodine T-shaped intramolecular geometry. Indeed, all O−I−C(Ph) angles are close to the expected ~90° values although it is interesting to note that the observed values for O(I)−I−C(Ph) angles (89.2°, average) are significantly larger compared to those observed for O(S)−I−C(Ph) fragments (82.9°, average). As expected for T-shaped iodosylarenes, all O−I−O angles are close to 180° (172.1°, average). The degree of deviation of the I−O−I μ-oxo bridge angle (120.7°) from expected for sp^3 hybridization of oxygen atom is similar to that found in the μ-oxo dimer **7**, polymeric tetra-μ-oxopentaiodanyl dication, and other *μ*-oxodiiodane analogues (118.0−123.7°), which reflect the [3c-4e] nature of the I−O−I bond.[11,14−17]

The supramolecular triple-helix structure of **8** is formed by the set of intra- and intermolecular iodine−oxygen interactions. Taking into consideration the zigzag nature of the polymeric chains of **8**, it is not surprising that only terminal S=O oxygen atoms are involved into intramolecular I−O interactions. On the other hand, although terminal sulfate oxygen atoms provide the dominant contribution to the intermolecular contacts, several I−O intermolecular bonds form as a result of *μ*-oxo oxygen atom-iodine interactions (see for instance I(7)−O(22) and I(5)−O(65) contacts, Figure 5). All observed intermolecular contacts with the participation of the terminal oxygen atoms in the sulfate unit are unique for each polymeric chain. For instance, in one out of two independent triple-helixes (Figure 5) both of O(33) and O(34) atoms form intermolecular and one intramolecular contacts with I(7), I(16), I(17) and I(4), I(9), I(16), respectively. In the second sulfate unit, the O(63) atom forms two intermolecular and one intramolecular contacts with I(4), I(6), and I(16), while the O64 atom participates in four close contacts with I(6), I(8), I(9), and I(18). Finally, out of two terminal oxygen atoms in the third chain, only O(23) is involved in the formation of three close contacts with I(7), I(8), and I(18). On the other hand, one of the non-terminal oxygen atoms of this group, O(22), forms an additional intermolecular contact with the I(7) atom. Since very similar oxygen−iodine contacts were also observed in the second triple-helix structure, these will not be discussed.

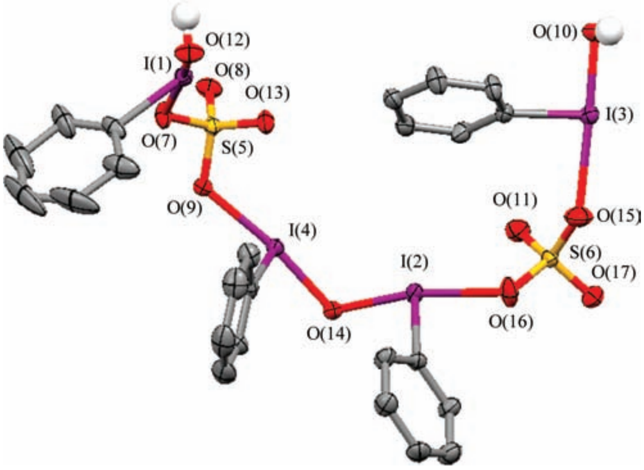

Figure 7. X-ray crystal structure of tetrameric phenyliodine(III) sulfate **9** (low-temperature structure, ellipses are shown at 50% probability; hydrogen atoms except in OH groups are omitted for clarity).

In general, iodine centers can be grouped into three categories: (i) the iodine centers with a single secondary bond (I(14) and I(17) atoms); (ii) the iodine atoms with two secondary contacts (I(2), I(3), I(4), I(5), (8), I(9), I(10), I(11), I(15), and I(18) centers); and (iii) the iodine centers with three secondary bonds (I(1), I(6), I(7), I(12), I(13), and I(16) atoms). The intermolecular contacts, which form the triple-helix structure of **8** can be tentatively described as relatively short (> 3.1 Å, blue dotted lines, Figure 5) and relatively long (3.1 to 3.5 Å, green dotted lines, Figure 5) contacts. Out of eighteen iodine centers present in low-temperature structure of **8**, fourteen have short intermolecular I−O contacts, which strengthen the triple-helix structure. In addition to the triple-helix formation, terminal oxo-groups of sulfate fragments participate in hydrogen-bond formation with the solvent molecule of water. In particular, O(24) and O(62) atoms form a strong intermolecular bond with the water molecule observed in the unit cell, although the presence of eighteen iodine and six sulfur heavy atoms does not allow to refine positions of water hydrogen atoms accurately.

The reaction of $PhI(OAc)_2$ with a 3-fold excess of $NaHSO_4$ afforded, after crystallization from water, a light-yellow crystalline product **9** (Scheme 1). Elemental analysis is consistent with the structure in which sulfate fragments are connected to the iodozobenzene groups in 1:2 ratio. In addition, NMR and IR spectra of compound **9** show the absence of the initially present acetate ions. Single crystal X-ray analysis of product **9** revealed a solid state structure of a tetrameric phenyliodine(III) sulfate, which consists of *μ*-oxodiiodanyl dicationic species linked by sulfate anions to the terminal hydroxy(phenyl)iodonium groups (Figure 7).

X-ray crystal structure determination of tetrameric product **9** was performed at room temperature as well as at −100 °C to investigate the potential phase transition, which was clearly observed in the structure of **8**. However, in the case of tetramer **9** no phase transition was observed. In particular, the crystal of **9** at both temperatures revealed the same space group (triclinic $P\overline{1}$) with the same unit cell parameters. Because of the large crystal decay of the tetramer **9** under X-ray radiation at room temperature, only the low-temperature structure is discussed here. The most important projections of tetramer **9** are shown in Figures 7−10, while

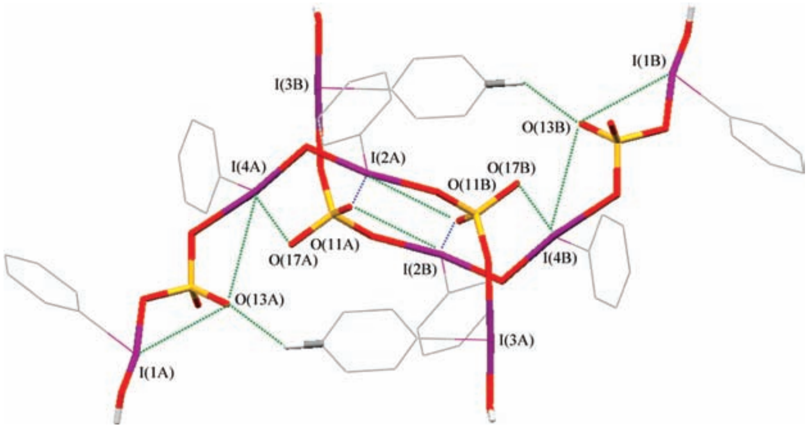

Figure 8. Intra- and intermolecular secondary bonding in two molecules of the tetramer **9**.

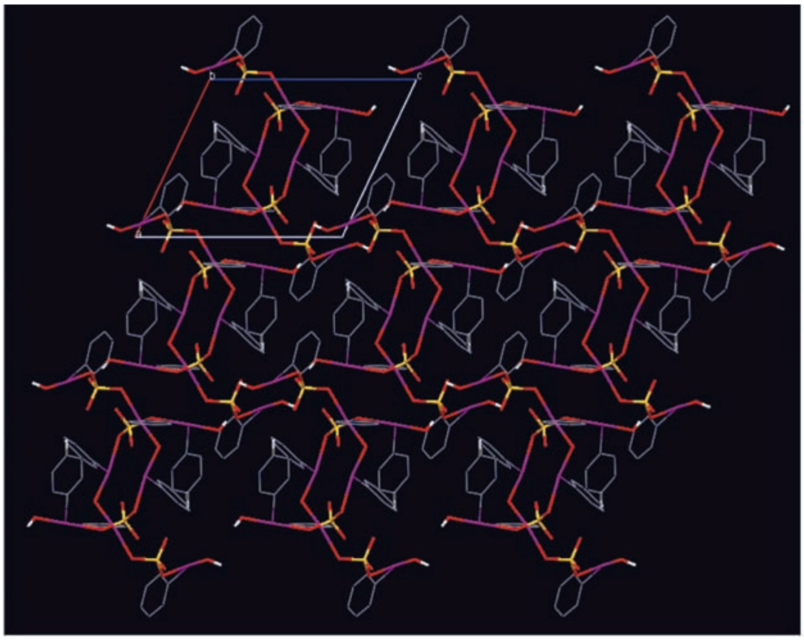

Figure 9. Packing diagram of tetramer **9** along crystallographic *b* axis.

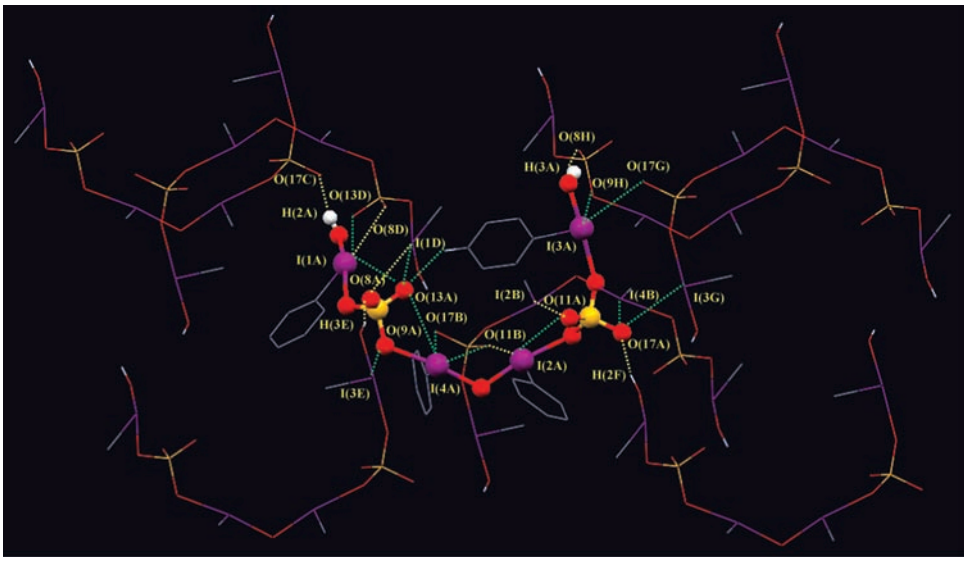

Figure 10. Complete set of intra- and intermolecular interactions observed in the tetramer **9**. Only phenyl groups of "parent" tetramer **9** are shown. Yellow lines indicate "short" (>3.1 Å) and green lines indicate "long" (3.5 Å $> x >$ 3.1 Å) intermolecular contacts. Locations of the nonparent molecules: B = $-1-x, -1-y, -1-z$; C = $-1-x, -y, -z$; D = $-x, -y, -z$; E = $1+x, y, z$; F = $-1+x, -1+y, -1+z$; G = $-2-x, -1-y, -1-z$; H = $-1+x, y, z$.

metric parameters for this compound are listed in Table 3. The low-temperature structure of **9** is shown in Figure 7. Again, the I$-$C(Ph) bond distances in tetramer **9** (2.10 Å, average) are within expected range for iodine(III) iodosylarene structures. Sulfate groups in **9** have tetrahedral geometry characteristic for sp^3 hybridization of sulfur atom with metric parameters close to those observed in polymer **8**. In particular, S$=$O terminal double bonds are short (1.46 Å, average), while S$-$O bonds are significantly longer (1.50 Å, average). I$-$O(S) bonds are quite long (2.34 Å, average) as compared to those in I$-$O(I) fragments (2.01 Å, average). Similar to X-ray crystal structure of PhI(OTs)OH, I$-$OH bonds are very short (1.96 Å, average), which can be explained by the trans-effect discussed earlier.[7] Taking into account the significant elongation of the I$-$O bonds in the S$-$O$-$I fragments, it is expected that tetramer **9** can be even more soluble as compared to polymer **8**. The iodine atoms in the $-$O$-$I(Ph)$-$O$-$ fragment of tetramer **9** have a typical trivalent iodine T-shaped intramolecular geometry. Indeed, all O$-$I$-$C(Ph) angles are close to expected ~90° (86.4°, average), while all O$-$I$-$O angles are close to 180° (171.7°, average). The degree of deviation of I$-$O$-$I μ-oxo bridge angle (118.56°) from that expected for sp^3 hybridization of oxygen atom is similar to that found in μ-oxo dimer **7**, polymeric **8**, polymeric tetra-μ-oxopentaiodanyl dication,[11] and other μ-oxodiiodane analogues[15−17] (118.0$-$123.7°), which reflect the [3c-4e] nature of the I$-$O$-$I bond. In addition, the intramolecular hydrogen bonding between O(13) and H(351) (2.34(2) Å) has been observed in the crystal structure of **9**.

The secondary bonding in the tetramer **9** is quite complex (Figures 8$-$10, Table 3). First, two of the tetramers **9** form

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Tetramer Compound **9**[a]

Intramolecular Covalent Bond Distances and Angles

iodine center 1	iodine center 2	iodine center 3	iodine center 4	sulfate 1	sulfate 2	μ-oxo-bridge
I(1)−C(29) 2.093(3)	I(2)−C(23) 2.086(3)	I(3)−C(22) 2.099(3)	I(4)−C(24) 2.116(3)	S(5)−O(7) 1.485(2)	S(6)−O(11) 1.460(2)	I(2)−O(14)−I(4) 118.56(10)
I(1)−O(7) 2.413(2)	I(2)−O(14) 1.999(2)	I(3)−O(10) 1.953(2)	I(4)−O(9) 2.237(2)	S(5)−O(8) 1.466(2)	S(6)−O(15) 1.480(2)	
I(1)−O(12) 1.961(2)	I(2)−O(16) 2.315(2)	I(3)−O(15) 2.407(2)	I(4)−O(14) 2.024(2)	S(5)−O(9) 1.527(2)	S(6)−O(16) 1.500(2)	
O(7)−I(1)−O(12) 170.32(9)	O(14)−I(2)−O(16) 167.84(8)	O(10)−I(3)−O(15) 176.46(9)	O(9)−I(4)−O(14) 172.35(8)	S(5)−O(13) 1.447(2)	S(6)−O(17) 1.460(2)	
O(7)−I(1)−C(29) 80.08(10)	O(14)−I(2)−C(23) 88.83(10)	O(10)−I(3)−C(22) 91.03(10)	O(9)−I(4)−C(24) 86.07(10)			
O(12)−I(1)−C(29) 90.25(11)	O(16)−I(2)−C(23) 79.31(9)	O(15)−I(3)−C(22) 86.18(10)	O(14)−I(4)−C(24) 89.05(10)			

Most Important Intra- And Intermolecular Contacts

iodine center 1	iodine center 2	iodine center 3	iodine center 4	hydrogen bonds
I(1)−O(8D)^{b} 2.963(3)	I(2)−O(11B)^{c} 2.940(3)	I(3)−O(17G)^{d} 3.128(4)	I(4)−O(11B)^{c} 3.122(3)	S(5)−H(331) 2.34(2)
I(1)−O(13)^{b} 3.261(3)	I(2)−O(11) 3.134(3)	I(3)−O(9H)^{e} 3.434(3)	I(4)−O(13) 3.327(2)	H(2)−O(17C)^{c} 1.79(2)
I(1)−O(13D) 457(3)			I(4)−O(17B)^{c} 3.452(3)	H(3)−O(8H)^{e} 1.72(4)

[a] Numbered according to Figure 7. [b] At $-x, -y, -z$ position. [c] At $-1-x, -1-y, -1-z$ position. [d] At $-2-x, -1-y, -1-z$ position. [e] At $-1+x, y, z$ position.

the "slipped"-dimer structure presented in Figure 8, which involves eight intermolecular contacts between terminal oxygen atoms of sulfate fragments and iodine centers of neighboring molecule (6 contacts) in addition to two hydrogen bonds. Terminal oxygen atoms of sulfate fragments are also involved in the formation of three intramolecular O−I contacts. The packing diagram of tetramer **9** along crystallographic *b* axis (Figure 9) reveals two major characteristic areas. One consists of "slipped−stacked" dimeric subunits similar to those shown in Figure 8, and another area formed by I−O secondary bonds, as well as strong hydrogen bonds. Overall, every tetrameric molecule of **9** involved in the intermolecular secondary interactions with seven (!) other tetramers (Figure 10). First, the terminal hydrogen atom H(2A) ("A" designates a "parent" molecule) forms a strong (1.79 Å) hydrogen bond with the O(17) atom of molecule C (Figure 10). First iodine center of parent molecule (I(1A), Figure 10) is involved in one intra- and two intermolecular interactions. The intramolecular contact (3.26 Å) originates from the I(1)−O(13) sulfate group interaction, while both intermolecular contacts belong to the iodine−sulfate group interactions with molecule D (I(1A)−O(8D) and I(1A−O(13D)). One of the latter is relatively short (2.96 Å) and one is long (3.46 Å). Similarly, the O(8A) atom provides a single short-range (2.96 Å) secondary bond to the I(1D) atom of molecule D in addition to the hydrogen bond formed with the H(3E) atom of molecule E. The O(13A) atom forms three relatively long intramolecular contacts with the I(1A), I(4A), and H(351) atoms, as well as a single intermolecular contact with the I(1D) atom located in molecule D (Figure 10). The O(9A) atom forms a single, relatively long intermolecular bond with the I(3E) atom of molecule E. The I(4A) atom has three relatively long secondary bonds with O(13A) (intramolecular), O(17B) (intermolecular), and O(11B) (intermolecular). The I(2A) atom is involved in a short secondary bond with the O(11B) atom and a long secondary intramolecular interaction with O(11A). In addition to the latter, O(11A) forms a relatively short intermolecular contact with the I(2B) atom of molecule B (Figure 10). The O(17A) atom forms a short hydrogen bond with H(2F) and two relatively long contacts with the I(4B) and I(3G) atoms of neighboring molecules. The I(3A) atom is pentacoordinated with two relatively long contacts formed with the O(9H) and O(17G) atoms. Finally, the H(3A) hydrogen is involved in a short hydrogen bond with the O(8H) atom of molecule H (Figure 10). Overall, the parent molecule A is connected to the other 7 neighboring molecules B−H by 17 intermolecular contacts, which include 13 I−O secondary bonds and 4 hydrogen bonds.

Discussion

The formation of oligomeric products **7**−**9** in the solid state can be explained by the interaction of species present in the acidic aqueous solution of the initial (diacetoxyiodo)benzene. First, the molecule of μ-oxo-[bis(diacetoxy)iodo]benzene **7** is formed by condensation of two molecules of PhI(OAc)$_2$ under slightly acidic conditions, similarly to the formation of μ-oxo-[bis(trifluoroacetoxy)iodo]benzene.[15] The low PhI(OAc)$_2$:NaHSO$_4$ ratio (1:0.2) makes it difficult to incorporate any of the sulfate anions into the dimeric structure of **7**. The gradual increase of the NaHSO$_4$ concentration with respect of PhI(OAc)$_2$ leads to incorporation of sulfate anions into polymeric (**8**) or oligomeric (**9**) structures. Thus, the formation of oligomeric sulfates **8** and **9** is best explained by the self-assembly of hydroxy(phenyl)iodonium ions, PhI$^+$OH, which are generated from PhI(OAc)$_2$ in the acidic aqueous solution, and the sulfate anions. This process is similar to the condensation of species observed in aqueous solutions of phenyliodine(III) organosulfonates PhI(OH)OSO$_2$R.[6,11] It has been shown by spectroscopic measurements and potentiometric titrations that phenyliodine(III) organosulfonates upon solution in water undergo complete ionization to give the hydroxy(phenyl)iodonium ion (PhI^+OH in hydrated form) and the corresponding sulfonate ions.[6] The hydroxy(phenyl)iodonium ion can combine with [oxo(aquo)iodo]benzene $PhI^+(OH_2)O^-$, a hydrated form of iodosylbenzene that is also observed in the solution, producing the dimeric μ-oxodiiodine cation $Ph(HO)I-O-I^+Ph$ and the dication PhI^+-O-I^+Ph in hydrated form.[6] Further condensation of μ-oxodiiodine dimeric species with [oxo(aquo)iodo]benzene may produce the trimeric dicationic species observed in polymeric sulfate **8**. In agreement with this mechanistic consideration, the ESI mass spectrum of a solution **8** in aqueous acetonitrile displayed intense peaks corresponding to the hydroxy(phenyl)iodonium ion $[PhIOH]^+$, μ-oxodiiodine cation $[Ph(HO)I-O-I^+Ph]$, and the protonated molecular ion of **6** $[M+H]^+$. Likewise, the formation of the tetrameric phenyliodine(III) sulfate **9** is explained by the self-assembly of two hydroxy(phenyl)iodonium ions ($2PhI^+OH$), two sulfate anions ($2SO_4^{2-}$), and one μ-oxodiiodine dication (PhI^+-O-I^+Ph). A similar self-assembly of hydroxy(phenyl)iodonium ions and [oxo(aquo)iodo]benzene explains the formation of a complex supramolecular solid state structure **3** consisting of pentaiodanyl dicationic units and perchlorate anions.[11] However, in contrast to the perchlorate **3**, the bidentate sulfate anions are incorporated into the polymeric or oligomeric chain in structures **8** and **9** as the links between iodanyl dicationic species.

The analysis of structural parameters of the $(PhIO)_n$ fragment in polymer **8** and tetramer **9** provides a new insight into the structure of iodosylbenzene, which is the parent representative of λ^3-iodanes and one of the most important oxygenating reagents.[1–3] Although known for over 100 years, structural details of iodosylbenzene are still limited. On the basis of spectroscopic studies, it was suggested that in the solid state iodosylbenzene exists as a zigzag polymeric, asymmetrically bridged structure, in which monomeric units of PhIO are linked by intermolecular $I\cdots O$ secondary bonds (Figure 2).[20] Within PhIO units, the I–O bond distance (2.04 Å) and C–I–O bond angle near 90° have been deduced from EXAFS analysis.[20]

Our results directly confirm that iodosylbenzene does indeed have the expected T-shaped geometry around the trivalent iodine center, and that it can exist in a polymeric structure. Our analysis, however, shows significantly different O–I–O bond distances from what was reported based on the EXAFS analysis of iodosobenzene. Specifically, the longer I–O bond in $(PhIO)_n$ was estimated as 2.37 Å and the shorter one was estimated at 2.04 Å.[20] In the polymeric structure **7** both I–O distances around the middle iodine atom (I2) are approximately equal. The I–O bond distances around other iodine atoms (I1 and I3) are alternating because of the presence of the electron-withdrawing sulfate group.

From a practical viewpoint, the solid-state polymeric phenyliodine(III) sulfate **8** and tetramer **9**, which can be formally considered as a partially depolymerized, activated iodosylbenzene, are potentially interesting as a readily available, stable, and water-soluble hypervalent iodine reagent. Representative reactions of polymeric reagent **8** were described in our preliminary communications.[14,21] The reactivity pattern of compound **8** has been tested using a set of representative oxidation reactions that are typical of hypervalent iodine reagents: the oxidation of sulfides,[1,3,22] alcohols,[1,3,22,22] and alkenes.[1,3,23,24] In particular, the oxidation of an aryl alkyl sulfide proceeds at room temperature within 10 min, which demonstrates the high oxidizing ability of reagent **8**. The oxidation leads to the formation of the corresponding sulfoxide in high yield without overoxidation to sulfone.[14] A similar oxidation with iodosylbenzene proceeds under the same conditions (water, room temperature), but only in the presence of a catalytic bromide anion, which is required for the depolymerization of $(PhIO)_n$.[22] Alcohols could also be oxidized at room temperature in short reaction times. For example, the oxidation of benzyl alcohol with reagent **8** affords benzaldehyde **11** in 92% isolated yield without overoxidation to benzoic acid. In contrast, iodosylbenzene reacts with benzyl alcohol in 30 h giving benzoic acid as the main product.[22] The oxidation of cyclohexene with reagent **8** results in ring contraction with the formation of cyclopentanecarbaldehyde (cf. ref 23). Likewise, the oxidation of 1,1-diphenylethylene leads to the oxidative rearrangement forming a corresponding ketone (cf. ref 24). This reactivity pattern is similar to the reactivity of iodosylbenzene activated by a Bronsted or Lewis acid. The reactivity of polymeric **8** can also be greatly enhanced by catalytic amounts of transition-metal complexes as recently demonstrated by us for oxidations of alcohols and C–H bond activation reactions.[21,22] The reactivity of tetramer **9** is expected to be similar to that of polymer **8** and is currently under investigation in our laboratories.

Conclusions

In conclusion, treatment of [(diacetoxy)iodo]benzene with sodium bisulfate leads to the formation of oligomeric cationic species resulting from the self-assembly of hydroxy(phenyl)iodonium ions, $[PhIOH]^+$, and [oxo(aquo)iodo]benzene in an aqueous acidic solution. Depending on the $PhI(OAc)_2$:$NaHSO_4$ ratio, three new oligomeric products **7**–**9** have been isolated and characterized by X-ray crystallography. Particularly interesting is the new phenyliodine(III) sulfate **8**, which has a complex solid-state polymeric structure of the oligomeric iodosylbenzene units connected together by SO_3 links, $[(PhIO)_3\cdot SO_3]_n$. Sulfate **8** can find practical application as a readily available, stable, and water-soluble reagent with reactivity pattern similar to activated iodosylbenzene.

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Experimental Section

General Experimental Information. 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 and are uncorrected. Infrared spectra were recorded as a KBr pellet on a Perkin-Elmer 1600 series FT-IR spectrophotometer. NMR spectra were recorded on a Varian $^{\text{UNITY}}$ INOVA 500 MHz NMR spectrometer at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to the tetramethylsilane. GC-MS analysis was carried out with a HP 5890A Gas Chromatograph using a 5970 Series mass selective detector. Mass-spectra were obtained with a Micromass Zabspec oaTOF or PE Biosystems Mariner TOF instrument. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, Georgia.

Synthesis and Characterization of PhI(OAc)OI(OAc)Ph (7). Solid (diacetoxyiodo)benzene (1.61 g, 5.0 mmol) was added to $NaHSO_4 \cdot H_2O$ (138 mg, 1.0 mmol) in a mortar. The mixture was ground for 10 min, and the resulting mass was transferred to a beaker and mixed with water (3 mL). The resulting suspension was filtered to remove the unreacted solid (diacetoxyiodo)benzene. Slow evaporation of the filtered aqueous solution afforded 100 mg of white crystals, mp 132−134 °C (dec). IR (KBr): 3051, 1573 (br), 1409, 1013, 994, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.85 (d, J = 6.3 Hz, 2H), 7.50 (m, 1H) 7.37 (m, 2H), 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 176.75, 135.06, 133.42, 131.84, 131.42, 130.98, 123.78, 21.71. Anal. Calcd for $C_{16}H_{16}I_2O_5$: C, 35.45; H, 2.97; I, 46.82. Found: C, 35.35; H, 2.98; I, 46.61.

Single crystals of product **7** suitable for X-ray crystallographic analysis were obtained by slow evaporation of water solution of **7**. X-ray diffraction data were collected on Rigaku AFC-7R diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Psi-scan absorption corrections were applied to the data using TeXsan 10.3b program (Rigaku Inc. 1997). The structure was solved by direct methods (SIR-92) and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **7** $C_{16}H_{16}I_2O_5$: M 542.09, monoclinic, space group *P*21/*c*, a = 11.946(4), b = 9.383(3), c = 17.097(4) Å, β = 107.36(2)°, V = 1829.1(10) Å^3, Z = 4, μ = 3.459 mm^{-1}, 2538 reflections measured, 2532 unique; final R_1 = 0.1249, R_w = 0.3041. CCDC-693032 contains the supplementary crystallographic data for compound **7**. 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 UK; fax: (+44) 1223−336−033, or deposit@ccdc.cam.ac.uk).

Synthesis and Characterization of $[(PhIO)_3 \cdot SO_3]_n$ (8). Method A. Solid (diacetoxyiodo)benzene (322 mg, 1.00 mmol) was added to $NaHSO_4 \cdot H_2O$ (142 mg, 1.03 mmol) in an agate mortar. The mixture was ground for 5 min, and the resulting yellowish mass was transferred to a beaker and mixed with water (3 mL). A clear yellow solution was formed after 1 min of stirring and then yellow crystals started to precipitate. After 1 h, the precipitate was filtered, washed with cold water, and dried to afford 127 mg of yellow crystalline solid. Additional product (71 mg) was obtained by a slow evaporation of mother liquor; overall combined yield 198 mg (80%), mp 143−145 °C. ^{1}H NMR (D_2O): δ 8.18 (d, J = 8.4 Hz, 2H), 7.7 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 2H); ^{13}C NMR (D_2O): δ 135.26, 134.49, 134.22, 133.84, 133.12, 132.78, 132.02, 131.62, 130.88. High resolution ESI-MS m/z 740.8025 (10%) ($[M+H]^+$ $C_{18}H_{16}I_3O_6S$ requires 740.7802), 440.8806 (30%) ($[Ph(HO)IOIPh]^+$ $C_{12}H_{11}I_2O_2$ requires 440.8843), 220.9424 (100%) ($[PhIOH]^+$ C_6H_6IO requires 220.9458). Anal. Calcd for $C_{18}H_{15}I_3O_6S$: C, 29.21; H, 2.04; I, 51.44; S, 4.33. Found: C, 29.22; H, 2.08; I, 51.06; S, 4.32.

Method B. Solid (diacetoxyiodo)benzene (161 mg, 0.50 mmol) was mixed with $NaHSO_4 \cdot H_2O$ (71 mg, 0.51 mmol) in water (1 mL) under stirring at room temperature. The mixture was stirred overnight, and the resulting yellow precipitate was filtered, washed with cold water (2 × 5 mL), and dried in vacuum to afford 69 mg (56%) of product **8** as a yellow crystalline solid. X-ray crystal structure analysis of product **7** was reported in our preliminary communication.[14]

Synthesis and Characterization of $PhI(OH)OSO_2O(Ph)IOI(Ph)OSO_2OI(OH)Ph$ (9). Solid (diacetoxyiodo)benzene (322 mg, 1.00 mmol) was added to solid $NaHSO_4 \cdot H_2O$ (414 mg, 3.00 mmol) in a mortar. The mixture was ground for 10 min, and then dissolved in water (3 mL). Slow evaporation from water solution yielded clear light-yellow crystals, yield 214 mg (81%), mp 122−123.5 °C. IR (KBr): 3054, 1206, 1107, 1010, 991, 895, 733, 615, 574 cm^{-1}; ^{1}H NMR (D_2O): δ 8.23 (d, J = 8.4 Hz, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.5 Hz, 2H). Anal. Calcd for $C_{24}H_{22}I_4O_{11}S_2$: C, 27.24; H, 2.10; S, 6.06. Found: C, 27.11; H, 1.96; S, 6.02.

Single crystals of product **9** suitable for X-ray crystallographic analysis were obtained by slow evaporation of water solution of **9**. X-ray diffraction data were collected on Rigaku AFC-7R diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at −100 °C. Psi-scan absorption corrections were applied to the data using TeXsan 10.3b program (Rigaku Inc. 1997). The structure was solved by direct methods (SIR-92) and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **9** $C_{24}H_{22}I_4O_{11}S_2$: M 1058.16, triclinic, space group $P\bar{1}$, a = 10.707(3), b = 12.529(4), c = 13.899(4) Å, α = 114.221(4), β = 111.995(4), γ = 91.960(4)°, V = 1537.2(8) Å^3, Z = 2, μ = 4.246 mm^{-1}, 5906 reflections measured, 5809 unique; final R_1 = 0.0170, R_w = 0.0376. CCDC-631619 contains the supplementary crystallographic data for compound **9**. 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 UK; fax: (+44) 1223−336−033, or deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic information files (CIF) for compounds **7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.