Detailed Structural Characterization of the Polyvalent Iminoiodinanes ArINTs (Ar = C_6H_5 or 2,4,6-$Me_3C_6H_2$; Ts = $SO_2C_6H_4$-4-Me) and the Aryldichloroiodinane 2,4,6-*i*-$Pr_3C_6H_2ICl_2$

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The growth of crystals suitable for X-ray crystallography has resulted in the first complete structural characterizations of two iminoiodinanes PhINTs, **1**, and MesINTs, **2** (Mes = 2,4,6-$Me_3C_6H_2$; Ts = $SO_2C_6H_4$-4-Me). Two different types of structures were observed. They consist of monomeric ArINTs units, bridged either by I- - -N interactions 2.482(2) Å in length in the case of **1** or by long (2.857(4) Å) I- - -O interactions in the case of **2**. The structural parameters of **1** and **2** show that the intramolecular I−N distance is consistent with a single bond and that the structures are probably best represented by resonance forms that feature negative charge at the oxygens and positive charge at iodine. Compounds **1** and **2** are closely related to the iodosylaryls, ArIO, and their structures lend further weight to the proposed associated structures of these oxygen derivatives which are thought to have a backbone composed of an -I−O- - -I−O- bridging array. The structure of $TripICl_2$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$), **3**, shows that the iodine center has T-shaped geometry and that the molecules are very weakly associated in the solid state through a long I- - -Cl interaction of 3.490(2) Å. Crystal data at 130 K with Mo Kα (λ = 0.710 73 Å) radiation: **1**, $C_{13}H_{12}INO_2S$, a = 11.519(2) Å, b = 7.687(2) Å, c = 15.181(4) Å, β = 104.88(2)°, Z = 4, monoclinic, space group $P2_1/c$, R = 0.021, for 2537 ($I > 2\sigma(I)$) data; **2**, $C_{16}H_{18}INO_2S$, a = 9.203(2) Å, b = 17.010(7) Å, c = 19.888(5) Å, Z = 8, orthorhombic, space group *Pbca*, R = 0.033 for 2642 ($I > 2\sigma(I)$) data; **3**, $C_{16}H_{23}Cl_2I$, a = 8.485(2) Å, b = 17.308(3) Å, c = 11.880(3) Å, β = 101.75(2)°, Z = 4, monoclinic, space group $P2_1/c$, R = 0.046 for 3314 ($I > 2\sigma(I)$) data.

Introduction

Polycoordinated iodine compounds, both inorganic and organic, have proven to be useful reagents in organic synthesis.[1] Their major applications are in oxidation or oxygen transfer reactions.[2] One of the most important families of compounds are the hypervalent organodihaloiodinanes $RICl_2$ (R = alkyl or aryl group) which are trivalent and have the formal iodine oxidation state of +3.[3] These compounds, which have low toxicity, can be conveniently prepared and easily handled. A key starting material in this area is (dichloroiodo)benzene, $PhICl_2$,[4] which is an important chlorinating agent that can also be used to make a variety or other derivatives such as the iodosylarenes, PhIO,[5] its tosylated imino analogue PhINTs[6] (Ts = tosylate, i.e. $O_2SC_6H_4$-4-Me), and other halogen derivatives such as $ArIX_2$ (X = F or Br).[7] In spite of the wide use of such compounds, their physical and structural characteristics are often incompletely understood. An example of this is the frequently used iodosylbenzene (PhIO) itself, whose exact structure is unknown. Spectroscopic studies have pointed to a polymeric structure with a backbone composed of alternating iodine and oxygen atoms in the solid.[8] Recent investigations using EXAFS and X-ray powder diffraction techniques are indeed consistent with the presence of the - - -I−O- - -I−O- - - backbone.[9] The closely related (tosylimino)iodinanes (e.g. PhINTs) are thought to have polymeric structures similar to those of the iodosylarenes, and a partial structure determination (also based on EXAFS and X-ray powder data) is in agreement with this view.[9] In this paper full X-ray crystal structural studies of (tosylimino)phenyliodinane, PhINTs, **1**, and its mesityl analogue (tosylimino)mesityliodinane, MesINTs (Mes = 2,4,6-$Me_3C_6H_2$), **2**, are reported. Synthetic routes to **2** and its precursor $MesI(OAc)_2$ and the related species $TripI(OAc)_2$ are also described. In addition, the synthesis and X-ray crystal structure of the sterically encumbered aryl dihalide species $TripICl_2$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$), **3**, are provided.

Experimental Section

General Procedures. All experiments, unless otherwise noted, were performed either by modified Schlenk techniques or in a Vacuum Atmospheres HE 43-2 drybox under a nitrogen atmosphere. Solvents used in the recording of NMR data were dried by standard methods. NMR data were recorded on a General Electric QE-300 spectrometer operating near 300 (^1H) or 75.44 (^{13}C) MHz.

Starting Materials. PhI (Aldrich), Cl_2 (Matheson), acetic anhydride, hydrogen peroxide, and *p*-toluenesulfonamide (Aldrich) were used as received. The iodides MesI and TripI were synthesized by standard procedures.[10]

(Tosylimino)phenyliodinane, 1. This compound was prepared as described in ref 6 except that crystallization was effected from a 4:1

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1995.

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mixture of warm (50 °C) methanol and water to yield the product as yellow crystals in 75% yield. Mp: 110−112 °C (lit.[6] 102−104 °C). The ^{1}H NMR spectrum was as described in the literature. $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 142.6 (*i*-C, C_6H_4-4-Me), 140.1 (*p*-C, C_6H_4-4-Me), 137.5 (*o*-C, Ph), 130.8 (*m*-C, Ph), 130.5 (*m*-C, C_6H_4-4-Me), 129.0 (*p*-C, Ph), 117.8 (*i*-C, Ph), 126.5 (*o*-C, C_6H_4-4-Me), 25.7 (4-Me).

(Tosylimino)mesityliodinane, 2. This compound was prepared similarly to **1** except that the appropriate quantity of MesI$(OAc)_2$ (vide infra) was used instead of PhI$(OAc)_2$.[5c] The yield was 80%. Mp: 107−109 °C. ^{1}H NMR (DMSO-d_6): δ 7.10 (d, *o*-H, C_6H_4-4-Me), 6.80 (d, *m*-H, C_6H_4-4-Me), 6.73 (s, *m*, H, Mes), 2.29 (*p*-CH_3, C_6H_4-4-Me), 2.11 (s, *p*-CH_3, Mes) 2.09 (s, *o*-CH_3, Mes). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 142.5 (*o*-C, Mes), 142.0 (*p*-C, Mes), 141.5 (*i*-C, C_6H_4-4-Me), 141.3 (*p*-C, C_6H_4-4-Me), 139.9 (*m*-C, C_6H_4-4-Me) 128.4 (*m*-C, Mes), 125.8 (*o*-C, C_8H_4-4-Me), 122.8 (*i*-C, Mes).

MesI(OAc)$_2$. To a three-necked flask cooled in an ice bath and equipped with magnetic stirrer, condenser, and thermometer were added acetic anhydride (65 mL) and H_2O_2 (35%, 14 mL). The mixture was stirred for 30 min and heated at 40 °C for 4 h. Iodomesitylene 4.0 g (28 mmol) was added, and the reaction mixture was stirred for an additional 2 h. It was allowed to stand at room temperature overnight (12 h) and then diluted with water (80 mL). The precipitate was collected by filtration, washed with water, and allowed to air-dry. Yield: 81%. Mp: 161−163 °C. ^{1}H NMR ($CDCl_3$): δ 6.97 (s, *m*-H), 2.57 (s, *p*-CH_3), 2.24 (s-*o*-CH_3), 1.84 (s, Ac CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.4 (Ac CO), 143.1 (*o*-C), 141.2 (*p*-C), 128.8 (*m*-C), 128.7 (*i*-C), 26.5 (*p*-CH_3), 21.02 (*o*-CH_3), 20.12 (Ac C).

TripI(OAc)$_2$. This compound was synthesized in a similar manner to that for its mesityl analogue in 85% yield by using TripI[10] (1.26 g, 3.8 mmol), acetic anhydride (14 mL), and 4 mL of 35% H_2O_2. ^{1}H NMR ($CDCl_3$): δ 7.06 (s, *m*-H), 3.25 (sept, *p*-$CHMe_2$), 2.85 (sept, *o*-$CHMe_2$), 1.22 (d, *o*-$CHMe_2$), 1.20 (d, *p*-$CHMe_2$), 1.85 (Ac CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.24 (Ac CO), 153.6 (*o*-C), 150.5 (*p*-C), 130.8 (*i*-C), 123.4 (*m*-C), 39.3 (*o*-$CHMe_2$), 34.1 (*p*-$CHMe_2$), 24.2 (*p*-$CHMe_2$), 23.63 (*o*-$CHMe_2$), 20.26 (Ac CH_3).

TripICl$_2$, 3. (Triisopropylphenyl)dichloroiodinane was prepared by a modification of the literature procedure.[4] At −10 °C iodotriisopropylbenzene (2.3 g, 7.0 mmol)[10] and dry chloroform (10 mL) were placed in a three-necked flask wrapped in aluminum foil and equipped with an outlet tube containing $CaCl_2$. Dry chlorine gas was bubbled through this solution for 1 h with vigorous stirring. The solvent was removed under reduced pressure to afford a crude product which was dissolved in warm diethyl ether (25 mL). The solution was allowed to cool to room temperature, whereupon yellow crystals of the product (triisopropylphenyl)dichloroiodinane started to appear. The reaction mixture was then stored in a 4 °C refrigerator to afford crystals suitable for X-ray diffraction. The mother liquor was decanted, and the product was dried under reduced pressure. Yield: 2.3 g (86%). ^{1}H NMR ($CDCl_3$): δ 7.14 (s, *m*-H), 3.64 (sept, *p*-C*H*Me$_2$), 3.07 (sept, *o*-C*H*Me$_2$), 1.39 (d, *o*-CH*Me*$_2$), 1.37 (d, *p*-CH*Me*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.0 (*o*-C), 148.9 (*p*-C), 124.1 (*m*-C), 121.9 (*i*-C), 40.0 (*o*-$CHMe_2$), 34.1 (*p*-$CHMe_2$), 24.2 (*p*-$CHMe_2$), 23.6 (*o*-$CHMe_2$).

X-ray Data Collection and Solution and Refinement of Structures. The crystals of **1−3** were placed on a glass plate and covered with a layer of hydrocarbon oil. Single crystals were selected, mounted on a glass fiber, and immediately placed in the low-temperature N_2 stream as described in ref 11. The X-ray data were collected on a Siemens R3m/V diffractometer. Calculations were performed on a MicroVax 3200 using the SHELXTL PLUS program system. The atomic form factors including anomalous scattering factors were taken from the usual sources.[12a] An absorption correction was applied by using the method described in ref 12b. In **1** and **2**, the hydrogen atoms of the *p*-methyl group of the tosylated substituent are disordered into two sets. These were refined as two rigid groups of idealized hydrogen positions (initially set from difference map positions) and their occupancies converged with relative values of 0.74/0.26 for **1** and 0.73/0.27 for **2**. The remaining hydrogen atoms were added geometrically, assuming a C−H distance of 0.96 Å, and refined by use of a riding model and fixed isotropic thermal parameters equal to 0.030 Å^2. Refinement of **1−3** was by full-matrix least-squares methods, based on *F*, with anisotropic thermal parameters for all non-hydrogen atoms except for the disordered carbons. The final difference map shows only minor features of no chemical significance.

Table 1. Selected Crystallographic Data[a] for **1−3**

	1	**2**	**3**
formula	$C_{13}H_{12}INO_2S$	$C_{16}H_{18}INO_2S$	$C_{16}H_{23}Cl_2I$
fw	373.2	415.3	401.1
cryst syst	monoclinic	orthorhombic	monoclinic
color, habit	colorless prisms	pale yellow needles	colorless prisms
space group	$P2_1/c$	*Pbca*	$P2_1/c$
a, Å	11.519(2)	9.203(2)	8.485(2)
b, Å	7.687(2)	17.010(7)	17.308(3)
c, Å	15.181(4)	19.888(5)	11.880(3)
β, deg	104.88(2)		101.75(2)
V, Å^3	1299.2(5)	3113.4(17)	1708.1(7)
Z	4	8	4
d(calc), g cm^{-3}	1.908	1.772	1.560
linear abs coeff, mm^{-1}	2.618	2.195	2.171
2θ range, deg	0−55	0−55	0−55
no. of obsd rflcns	2537 ($I > 2\sigma(I)$)	2642 ($I > 2\sigma(I)$)	3314 ($I > 2\sigma(I)$)
no. of variables	164	191	163
$R(F)$; $R_w(F)$	0.021; 0.024	0.033; 0.031	0.046; 0.064

[a] All data were collected with Mo Kα (λ = 0.710 73 Å) radiation at 130 K.

Table 2. Atom Coordinates (×10^4) for Selected Atoms in **1−3**

atom	*x*	*y*	*z*
	Compound **1**		
I	118.8(1)	4740.5(2)	2531.1(1)
S	2425.8(6)	7047.3(8)	3098.3(4)
N	1040(2)	7003(3)	2523.7(14)
C(1)	3285(2)	7017(3)	2284(2)
C(2)	2908(3)	8001(4)	1489(2)
C(6)	4343(3)	6093(4)	2450(2)
C(8)	728(2)	3522(3)	1487(2)
C(9)	1938(3)	3114(4)	1665(2)
C(13)	-79(3)	3225(4)	650(2)
O(1)	2634(2)	8716(3)	3552.1(12)
O(2)	2763(2)	5513(3)	3660.5(12)
	Compound **2**		
I	801.0(3)	2081.4(1)	436.7(1)
S	3125.2(12)	2932.5(6)	1240.5(5)
N	2081(4)	2184(2)	1249(2)
C(1)	2123(5)	3755(3)	1532(2)
C(2)	2440(5)	4498(2)	1292(2)
C(6)	1072(5)	3663(2)	2025(2)
C(8)	−704(5)	3009(2)	579(2)
C(9)	−592(5)	3641(2)	135(2)
C(13)	−1719(5)	2955(3)	1103(2)
O(1)	3658(4)	3166.6(18)	580.8(14)
O(2)	4224(4)	2765(2)	1739.6(15)
	Compound **3**		
I	1420.4(3)	4860.4(2)	1802.8(2)
Cl(1)	1374(2)	5601.4(8)	3559.8(12)
Cl(2)	1424(2)	4031.3(8)	49.1(9)
C(1)	3059(5)	4082(2)	2816(3)
C(2)	4657(5)	4322(2)	3172(3)
C(6)	2432(5)	3386(2)	3124(3)

Results

Syntheses. The syntheses of **2** and **3** were adapted from published procedures[5,6] and proceeded smoothly. Attempts to synthesize TripIO by standard methods[5] from TripI$(OAc)_2$ led to mixtures of products of which TripI constituted the largest fraction.

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(10) These syntheses were accomplished by quenching the corresponding arylmagnesium bromides (generated from Mg and the commercially available ArBr) with an excess of I_2.

(11) This method is described by: Hope, H. A Practicum in Synthesis and Characterization. In *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

(12) (a) *International Tables for Crystallography*; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1993; Vol. C. (b) Moezzi, B. Ph.D. Dissertation, University of California, Davis, CA, 1993.

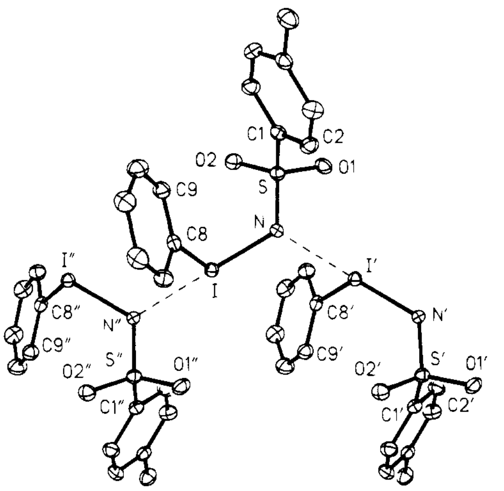


Figure 1. Computer-generated thermal ellipsoid plot of **1**. Hydrogen atoms are omitted for clarity.

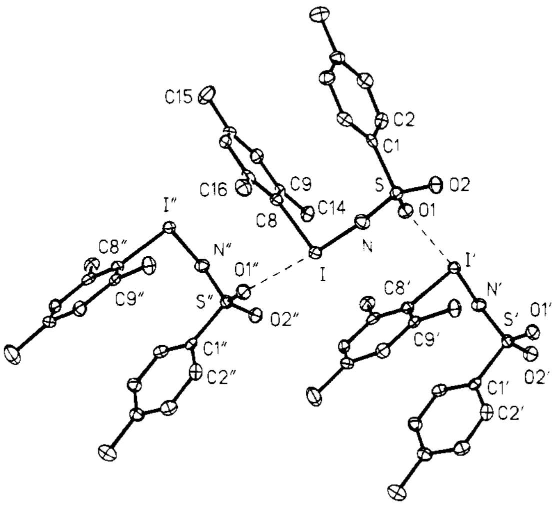


Figure 2. Computer-generated thermal ellipsoid plot of **2**. Hydrogen atoms are omitted for clarity.

Structural Descriptions. PhINTs, 1. This structure is illustrated in Figure 1. The basic motif consists of monomeric PhINTs units which are associated (along the *b* axis) through I′- - -N bridges. The structure can thus be regarded as a zigzag chain of alternating PhI and $NSO_2C_6H_4$-4-Me groups with each nitrogen asymmetrically bridging the iodine centers. The I−N, I−C, and N−S bond distances within the monomer are 2.039(2), 2.110(3), and 1.611(2) Å. In contrast, the I′- - -N bridging distance is 2.482(2) Å. The N−I- - -N″ angle, 177.8(1)°, is almost linear and the N−I−C(8) and C(8)−I- - -N″ angles are 95.8(1) and 83.0(1)°, respectively. Thus, each iodine has a distorted T-shaped coordination with some deviation from planar geometry (Σ°I = 356.6(2)°. The nitrogen centers are coordinated in a flattened trigonal, pyramidal manner with almost equal I−N- - -I′, I−N−S, and S−N−I angles of 116.6(1), 117.4(1), and 116.7(1)°. The I- - -I′ separation is 3.853(1) Å, and the torsion angle between the I−C(8) and S−N vectors is 83.2°. The other closest interatomic contacts involving I are I- - -O(1)″ and I- - -O(2) which have distances of 3.144(2) and 3.271(2) Å. Distances and angles surrounding the sulfur center in the tosylate unit are provided in Table 3.

MesINTs, 2. The structure (Figure 2) is composed of monomeric units of **2** which are weakly associated through interactions between the iodine and an oxygen from the tosylate substituent of an adjacent molecule, I- - -O(1)″ = 2.857(4) Å. Within the monomer, the I−N and N−S distances are 2.008(4) and 1.595(4) Å. The nitrogen has a bent (I−N−S = 114.5(2)°) two-coordinate geometry. The iodine is quasi-two-coordinate with an N−I−C(8) angle of 102.2(1)° and an I−C(8) distance of 2.119(4) Å. The I- - -I′ separation is 5.120(1) Å and the torsion angle between the S−N and I−C(8) vectors is 71.2°.

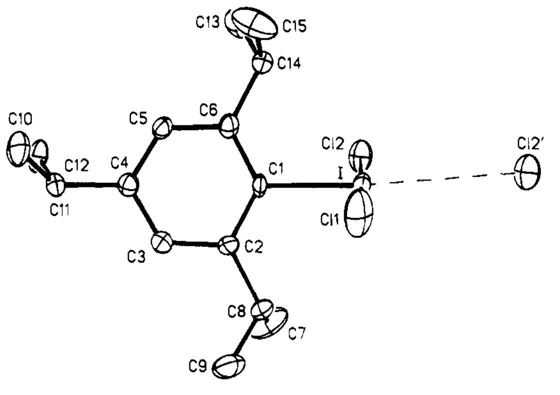


Figure 3. Computer-generated thermal ellipsoid plot of **3**. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) in **1**−**3**

Compound **1**			
I−N	2.039(2)	N−I- - -N″	177.8(1)
I- - -N(1)″	2.482(2)	N−I−C(8)	95.8(1)
I−C(8)	2.110(3)	C(8)−I- - -N″	83.0(1)
S−O(1)	1.447(2)	I−N- - -I′	116.6(1)
S−O(2)	1.449(2)	I−N−S	117.4(1)
S−N	1.611(2)	S−N- - -I′	116.7(1)
S−C(1)	1.771(3)	O(1)−S−O(2)	117.1(1)
I- - -I′	3.853(1)	O(1)−S−N	107.2(1)
		O(2)−S−N	112.3(1)
		O(1)−S−C(1)	106.9(1)
		O(2)−S−C(1)	106.7(1)
		N−S−C(1)	106.0(1)
Compound **2**			
I−N	2.008(4)	O(1)″- - -I−C(8)	75.7(1)
I−C(8)	2.119(4)	N−I- - -O(1)″	171.2(1)
S−O(1)	1.456(3)	N−I−C(8)	102.2(1)
S−O(2)	1.445(3)	I−N−S	114.5(2)
S−N	1.595(4)	O(1)−S−O(2)	115.9(2)
S−C(1)	1.774(4)	O(1)−S−N	115.6(2)
I- - -O(1)″	2.857(4)	O(2)−S−N	104.9(2)
I- - -I′	5.120(1)	O(1)−S−C(1)	104.7(2)
		O(2)−S−C(1)	107.1(2)
Compound **3**			
I−Cl(1)	2.457(2)	Cl(1)−I−Cl(2)	176.8(1)
I−Cl(2)	2.530(1)	Cl(1)−I−C(1)	88.4(1)
I−C(1)	2.125(4)	Cl(2)−I−C(2)	89.8(1)

TripICl$_2$, 3. This molecule (Figure 3) crystallizes as essentially discrete monomers with no imposed symmetry. The geometry at iodine is close to perfectly T-shaped with a Cl(1)−I−Cl(2) angle of 176.8(1)° and Cl(1)−I−C(1) and Cl(2)−I−C(1) angles of 88.4(1) and 89.8(1)°. There is also some pyramidal distortion of the iodine coordination (Σ°I = 355.0(1)°) from planarity. The I−Cl distances 2.457(2) and 2.530(1) Å show slight asymmetry, and there is also a longer intermolecular contact of 3.490(2) Å involving a chlorine from a neighboring molecule. The I−C(1) bond length is 2.125(4) Å, and there is an angle of 76.2(2)° between the averaged perpendiculars to the $ClCl_2$ plane and the plane of the aromatic ring. A summary of the essential structural details is given in Table 3.

Discussion

The X-ray crystal structures of **1** and **2** represent the first complete structural determinations for compounds of the formula ArINR. Previous spectroscopic studies[8] (i.e. IR−Raman and Mössbauer spectroscopy) of their oxygen analogues, the iodo-

Table 4. Comparison of Selected Single-Crystal X-ray Bond Distances (Å) and Angles (deg) for **1** with Those from X-ray Powder and EXAFS Studies[9]

	crystallographic data	X-ray powder data	EXAFS data
I−N	2.039(2)		2.06
I- - -N′	2.482(2)	2.77	2.49
I- - -S	3.127(1)	2.94	3.14
I- - -I′	3.853(1)	3.95	3.8
N−S	1.611(2)	1.62[a]	
I−N- - -I′	116.6(1)	109[a]	
I−N−S	117.4(1)	105[a]	
I′- - -N−S	116.7(1)	146[a]	
N−I- - -N′	177.8(1)	171[a]	

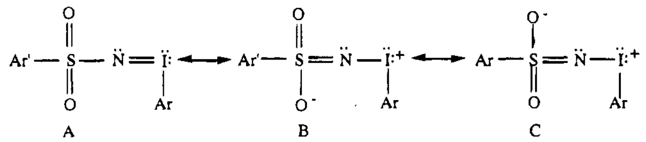
[a] Assumed distance and estimated angles.

sylbenzenes, ArIO, were consistent with the existence of a polymeric structure with an - - -I−O- - -I−O- - - backbone in the solid state. Although IR data were recorded for PhINTs, **1**, and related species, no structural conclusions regarding the degree of association in these molecules were made.[6] It was, however, concluded that **1** existed in the "ylide" form featuring positive charge at iodine (vide infra; structures **B** and **C**). Recent X-ray powder diffraction data have led to the opinion that polymeric chains composed of iodine and nitrogen atoms are also the main structural feature of the iminoiodinane PhINTs in the solid state.[9] The polymeric chain is proposed to be derived from the association of the monomeric PhINTs units through I- - -N bridging. Only the iodine and sulfur atoms were located from the X-ray powder data, however, and the position of the nitrogen atom was deduced from EXAFS data.[9] An N−S distance of 1.62 Å and sp^2 hybridization at the nitrogen center were also assumed. A comparison of these data with those derived from the X-ray crystal diffraction study is provided in Table 4. Although it can be seen that there is good agreement for the I−N, I- -S, and I- - -I interactions, there is significant disagreement between the X-ray powder and the EXAFS and crystallographic data on the question of the key I- - -N′ distance. The crystal structure unequivocally establishes that this distance is 2.482(2) Å (cf. EXAFS 2.49 Å) and not 2.77 Å as suggested by the powder data. This affords an intermolecular I- - -N bond order of 0.16 according to the Pauling formula.[13] In addition, the EXAFS distances for the I- -S are and I- -I′ interactions are closer than the X-ray powder diffraction values to those measured by single-crystal X-ray diffraction. The inferred values for the angle surrounding nitrogen are partly based on the assumption of planar geometry at this atom. The single-crystal structure shows that the nitrogen has instead a flattened pyramidal coordination. The main disagreement concerning the nitrogen coordination geometry is in the predicted value of the I′- - -N−S angle which differs by about 30° from the experimental crystallographic value.

Compound **2** differs from **1** in that the phenyl group at iodine has been replaced by the somewhat bulkier mesityl substituent. This difference, however, results in a large change in the way the MesINTs molecules are associated. Although the basic structural motif, the monomeric MesINTs moiety, remains similar in many details to the corresponding unit in **1**, association results from bridging between the iodine and one of the oxygens of the tosylate group. The atoms that constitute the backbone are thus - - -I−N−S−O- - -I′- and not - - -I−N- - -I′ as in **1**. Moreover, the length of the associative interaction between I and O is 2.857(1) Å (intermolecular I- - -O bond order 0.024[13]). This is significantly longer (by about 0.38 Å) and weaker than the corresponding I′- - -N distance in **1**, especially when it is recalled that the covalent radius of oxygen is less than that of nitrogen. By the same token, the I- - -I′ separation in **2**, 5.120(1) Å, is over 1.26 Å longer than that it is in **1**. It is also notable that the bridging I- - -O interaction in **2** is considerably (0.52 Å) longer than the 2.377(12) Å distance derived from EXAFS data for PhIO.[9]

There are also other smaller differences between the two structures. The I−N and S−N distances are slightly (two to three hundredths of an angstrom) longer in **1** than they are in **2**. This can be attributed to the stronger association involving the bridging nitrogen in the case of **1**. The I−C, S−C, and S−O distances in the two molecules are essentially equal, being within three standard deviations of each other. The near equality of the S−O bond lengths in the two molecules is consistent with the weakness of the association in **2**. Presumably, a stronger association interaction between I and O would have led to a more noticeable effect on the length of the S−O bond in the bridging I′- - -O(1)−S moiety.

What do the crystal structures of **1** and **2** reveal regarding the nature of the I−N bond? The simplest representation of the monomeric unit (the neutral representation **A**) implies the



presence of an I−N double bond, but resonance forms **B** and **C**, which feature I−N single bonds, may also be easily written. In weakly associated **2**, which presumably has structural parameters that are very close to those that would be observed in an unassociated ArINTs species, the I−N distance is 2.008(4) Å. The covalent radii[14] for I and N are 1.33 and 0.73 Å, respectively, which, when added together, afford a predicted I−N single-bond distance of 2.06 Å. Since the I−N bond has a polar component (owing to the difference in electronegativity between I and N), the 2.06 Å distance may be adjusted for ionic effects by the Schomaker−Stevenson method[15] to afford a corrected value of 1.99 Å. This predicted distance for an I−N single bond is thus very close to what is observed experimentally. On the other hand, the sulfur−nitrogen distance in **2**, 1.593(4) Å, is suggestive of substantial multiple character[16] since it is about 0.1 Å shorter than the predicted value (1.69 Å) of an S−N single bond even when allowance is made for ionic effects. The S−N distance in **2** is in fact almost identical to the value of 1.590(2) Å observed in the structure of chloramine-T hydrate,[17] where it was concluded that the resonance form involving the S−N double bond was more consistent with the structural data. The S−C and S−O distances observed in chloramine-T are also very similar to those in **1**. It appears therefore that resonance forms **B** and **C**, which feature an S−N double bond and positive and negative charges located on the iodine and oxygens, respectively, represent the bonding in both **1** and **2** more closely than does the neutral form **A**. Given the greater electronegativity of N in comparison to iodine there must also be substantial negative charge density at N although a resonance form of this type would not normally be considered likely as it involves adjacent positive and negative charges on I and N.

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[13] Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 54. Single I−N and I−O bond distances of 1.99 and 1.88 Å were assumed. See also refs 14 and 15.

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[16] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: New York, 1984; pp 854−881.

[17] Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 4057.

What are the major reasons for the difference in structure between **1** and **2**? The answer to this question is at present unclear. It could be that the higher steric requirements of the mesityl substituent at I imposes a more open structure that features a weaker association mode involving the S−O- - -I interaction. But why should association through I- - -N interactions take place in **1**, given the nature of the resonance forms **B** and **C**, which suggest more likely association between I and O owing to the positive and negative charges on these atoms. It has already been stated that the nitrogen must have significant negative charge density since it is bound to the less electronegative atoms S and I. Bearing in mind that oxygen itself is more electronegative[3] than nitrogen and is, in consequence, less likely to be a good donor of electron density, it is possible that nitrogen can serve as a better bridging atom. In addition, nitrogen, since it is larger than oxygen, is a softer base and therefore better matched to the rather large iodine acceptor.

The compound TripICl$_2$ was isolated during the investigation of possible synthetic routes to the, as yet unreported, species TripINTs. It is a straightforward example of a T-shaped molecule whose iodine coordination geometry is determined primarily by interelectronic repulsion. The Cl−I−C angles are marginally less than 90°, and the Cl−I−Cl angle deviates from strict linearity by about 3°. The sum of the angles at iodine is 355° so that there is a slight distortion in its coordination toward pyramidal. These distortions and the slight asymmetry (0.06 Å) in the I−Cl bond distances may be a result of the long interaction between the iodine and a chlorine from a neighboring molecule. The structure of **3** bears quite a close resemblance to the classic structure determined from PhICl$_2$[18], which was the only structurally characterized molecule of this type previously reported. The more modern equipment and data recording methods that are currently available have allowed the observation of the slight difference in the I−Cl distances resulting from the long-range I- - -Cl(2)′ interactions in the case of **3**. It is notable that the replacement of the phenyl group by the bulkier Trip substituent increases the intermolecular I- - -Cl distance from 3.40 to 3.49 Å (intermolecular bond order[13] = 0.02). In the unsubstituted parent ICl$_3$ species, the structure becomes dimeric with a bridging I−Cl distance of 2.70 Å.[19]

Conclusions

The X-ray crystal structures of ArINTs (Ar = Ph or Mes) have shown that they have I−N single bonds and are associated by different types of bridging, one involving I- - -N and the other involving I- - -O interactions—the latter being much weaker than the former. The structure of TripICl$_2$ is essentially the same as that observed for PhICl$_2$ but with an even weaker intermolecular associative interaction between iodine and a chlorine from a neighboring molecule.

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Supplementary Material Available: Text describing the X-ray experimental work, full tables of data collection parameters and further details of refinement, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, and hydrogen coordinates and isotropic thermal parameters, and additional structural diagrams (21 pages). Ordering information is given on any current masthead page.

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