LETTER

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Intra- and intermolecular interactions in the solid state structure of 2-iodylbenzenesulfonamides: a heptacoordinated organic iodine(V) compound†

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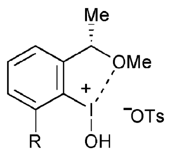
Single crystal X-ray structures of two 2-iodylbenzenesulfonamides reveal a combination of intra- and intermolecular I···O interactions leading to a typical hexacoordinated and a unique heptacoordinated iodine(V) center.

Structural aspects of hypervalent iodine chemistry have attracted significant recent interest and research activity.[1–5] Several research groups have demonstrated that variations in the complexation of the iodine(III) or iodine(V) center can lead to dramatic changes in the solubility and reactivity of hypervalent iodine reagents.[2–5] In a recent example, Ochiai reported the structure and reactivity of iodonium salt complexes with 1,10-phenanthroline[2a] and with 18-crown-6 ethers,[2b,c] and in particular, noted a "dramatic" improvement in stability and solubility of ethynyl(phenyl)iodonium tetrafluoroborate due to the complexation and, at the same time, preservation of the desired high reactivity.[2] Nicolaou and co-workers have reported that the reactivity of iodine(V) reagents can be modulated by complexation with various oxygen-based ligands.[3] A significant improvement in solubility, reactivity, and stability was observed in aryliodosyl and aryliodyl derivatives bearing an appropriate substituent in the *ortho*-position to the iodine (structures **1–3**).[4,5] These molecules are characterized by the presence of a planar, pseudo-cyclic structural moiety due to strong intramolecular secondary bonding between the hypervalent iodine center and the oxygen atom in the *ortho*-substituent.[4,5] Esters and amides of 2-iodylbenzoic acid **3** are particularly useful oxidizing reagents with reactivity similar to IBX and DMP,[5] but with significantly higher solubility in common organic solvents, which is explained by a partial disruption of their polymeric nature due to the redirection of secondary bonding from intermolecular to intramolecular mode.[4,5]



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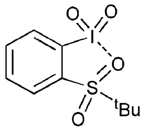

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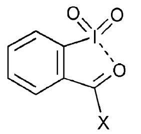

X = NHR or OR

3

In this communication, we report the crystal structures of two representatives of 2-iodylbenzenesulfonamides **5**,[6] which are also characterized by a significant coordination of the iodine(V) center with the *ortho*-substituent.

Compounds **5** were prepared by the dioxirane oxidation of the readily available 2-iodobenzenesulfonamides **4** (Scheme 1), in good yields, in the form of microcrystalline solids, which have a relatively low solubility in non-polar organic solvents.

The structures of **5a** and **5b** have been established by the combination of elemental analysis, spectroscopic data, ESI mass spectroscopy, and single crystal X-ray crystallography‡ (Fig. 1). The X-ray crystallographic analysis of compound **5a** shows two crystallographically independent molecules (**A** and **B**) in the unit cell with different arrangements of oxygen atoms around the hypervalent iodine center (Fig. 2). Thus, in the molecule **A**, the oxygen atom O(2) in the iodyl group is directed toward the sulfonamide substituent by the intramolecular hydrogen bond with an NH···O distance of 2.709 Å, while in the molecule **B** the oxygen atom O(39) forms a very strong intermolecular hydrogen bond with an NH···O distance of 1.575 Å.

These two types of arrangements lead to slightly different intramolecular distances between the iodine atom and the oxygen atom of the sulfonamide group in the five-membered pseudo-cycle, with the distances of 2.858 Å and 2.781 Å in molecules **A** and **B**, respectively. This intramolecular interaction is significantly weaker compared to the previously reported pseudo-benziodoxoles, in which the distance between the iodine and oxygen atoms in the pseudo-cyclic moiety varies in the range 2.47 Å to 2.7 Å.[1c,4,5] For comparison, the average covalent I–O bond length is 2.14 Å[7a] and the sum of iodine and oxygen van der Waals radii is about 3.5 Å.[7b] In contrast to the other pseudo-cyclic structures reported before,[4,5] the structure of **5a** shows strong intermolecular bonding interactions between the iodine atom and the O=I oxygen atom of the neighboring molecule, thus forming a polymeric three-dimensional network. It is interesting to note that the unique molecules **A** and **B** are forming polymer chains *only* with the same type of molecules. In both polymeric chains the driving force for their formation is strong intermolecular interactions between the IO_2 groups of the neighboring molecules: 2.549 Å in the case of molecules **A** and 2.827 Å for the chain formed by molecules **B**. In addition to these interactions, the coordination of iodine atoms to the carbonyl oxygens of the carboxyl groups of the amino acid fragments (2.896 Å for molecules **A** and 3.022 Å for molecules **B**, respectively) was also found, thus resulting in pseudo-octahedral geometry of the iodine center. A

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† Electronic supplementary information (ESI) available: Cambridge Crystallographic Database structural data on previously reported iodyl-containing compounds. See http://dx.doi.org/10.1039/b506573a

‡ CCDC reference numbers 268074–268075. See http://dx.doi.org/10.1039/b506573a for crystallographic data in CIF or other electronic format.

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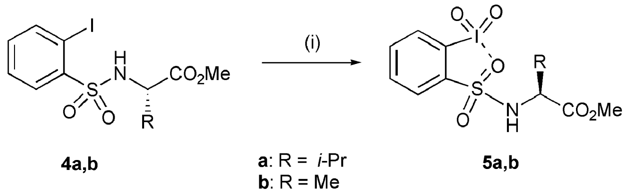

Scheme 1 Preparation of 2-iodylbenzenesulfonamides **5**. (i) Dimethyldioxirane, acetone, 0 °C to rt.

similar distorted octahedral geometry around the hexacoordinated hypervalent iodine center was observed in the previously reported iodine(v) structures.[4b,5–8]

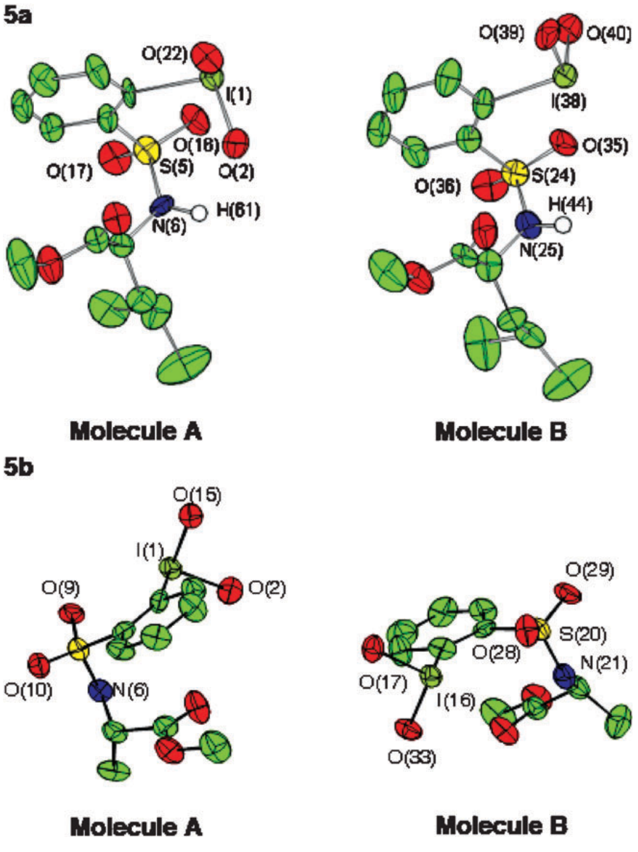

Fig. 1 CAMERON[14] drawing of **5a** and **5b** at the 50% probability level (hydrogens are omitted for clarity). Selected distances [Å]: for **5a** I(38)···O(35) 2.781; I(1)···O(16) 2.858; for **5b** I(16)···O(28) 3.084; I(1) ···O(9) 3.010.

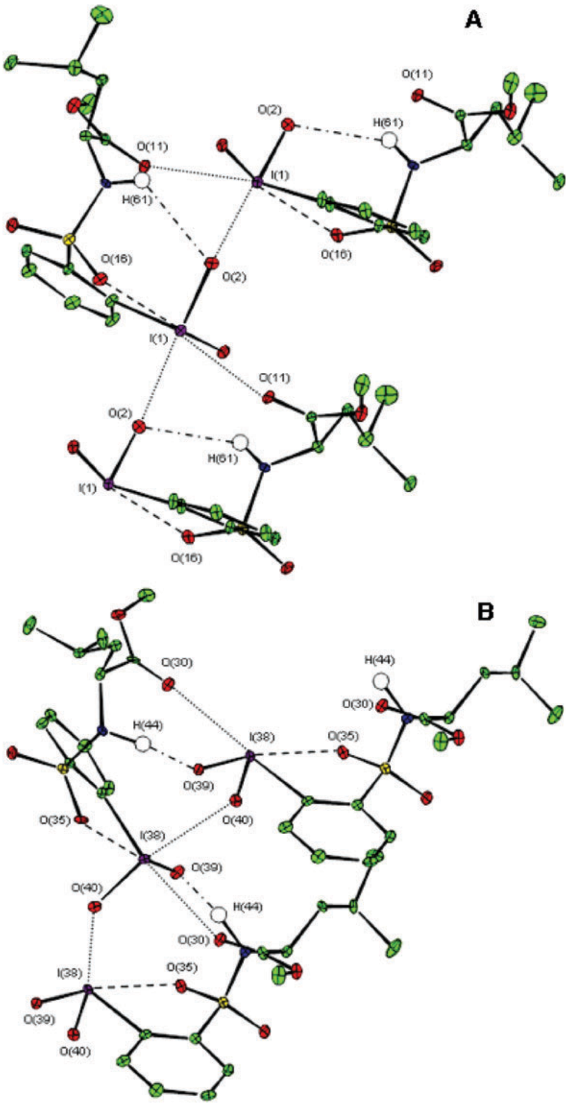

Fig. 2 CAMERON[14] drawing of polymeric chains of independent molecules of **A** and **B** observed in the solid state structure of **5a** at the 5% probability level (hydrogens are omitted for clarity). Selected distances [Å]: for molecules **A**: I(1)···O(2) 2.549; I(1)···O(11) 2.896, O(2)···H(61) 2.709; for molecules **B**: I(38)···O(40) 2.827; I(38)···O(30) 3.022, O(39)···H(44) 1.575.

In both cases **A** and **B**, such an octahedral configuration results from four intra- and two intermolecular interactions. The N–S–I–O torsion angles (θ) for the polymeric chains constructed by molecules **A** and **B**, however, show the major difference between these chains. Indeed, the "*cis*" orientation of the IO_2 group with respect to the SO_2NH fragment has been observed in the case of molecule **A** (θ = 14.97°), while it is "*trans*" in the case of molecule **B** (θ = 158.82°). The main structural motif of the solid state structure of **5b** is the polymeric chain formed by two crystallographically independent molecules, which can be characterized by two intermolecular I···O interactions (2.897 to 2.663 Å) between IO_2 groups (Fig. 3). This motif is different from that observed in the case of **5a**, where only single intermolecular interactions between two IO_2 groups of the neighbouring have been observed (Fig. 2). Moreover, the polymeric chain in the case of **5b** has an **A**–**B**–**A**–**B** motif, while in the case of compound **5a**, the polymeric chains consist of **A**–**A**–**A**–**A** and **B**–**B**–**B**–**B** motifs. In addition, the iodine atom exhibits a pseudo-cyclic environment, with an intramolecular I···O(S) distance of 3.010–3.084 Å within the pseudo five-membered ring. It should be noted that the "*trans*" orientation of the IO_2 group with respect to the SO_2NH fragment (θ = 157.31° and 160.14° for both independent molecules of **5b**) has been observed, similarly to that indicated for molecule **B** in the case of structure **5a**. As it was shown for structure **5a**, the additional intermolecular interactions of the iodine atoms and the carbonyl oxygens of the carboxyl groups of the amino acid fragments (2.876 and 2.991 Å) provide a greater stability to the polymeric arrangement of the molecules. In total, the coordination polyhedron for each of the iodine atoms consists of four intramolecular and three intermolecular bonds, with interatomic distances between 1.80 and 3.080 Å for the independent molecule **A** in structure **5b**, and between 1.793 to 3.010 Å for the independent molecule **B** in structure **5b**. To the best of our knowledge, **5b** represents the first example of a heptacoordinated iodine(v) molecule. According to the Cambridge Structural Database, all of the nine previously reported structures of iodyl-containing compounds have a hexacoordinated iodine(v) atom (see ESI for details†).[9] Previously, heptacoordinated iodine has been reported only for inorganic derivatives of iodine(vii).[10] The structural polyhedron proposed for these types of structures was pentagonal bipyramidal with D_{5h} symmetry. In the case of compound **5b** the geometry of the iodine coordination sphere could be represented as

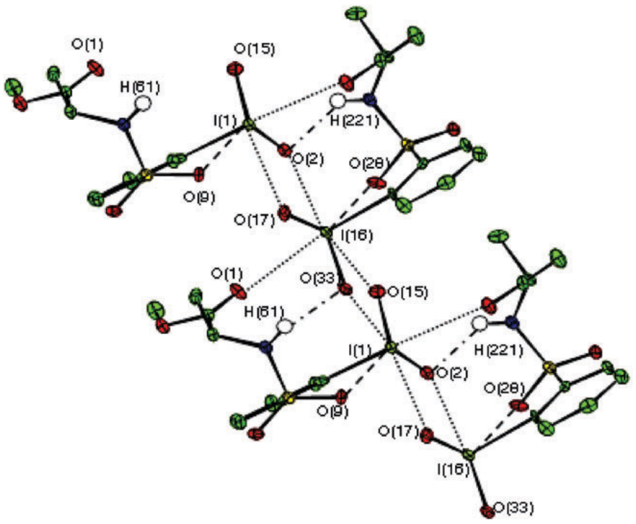

Fig. 3 CAMERON[14] drawing of polymeric chain of **5b** at the 10% probability level (hydrogens are omitted for clarity). Selected distances [Å]: I(1)···O(17) 2.663, I(1)···O(33) 2.897, I(16)···O (15) 2.764, I(16)···O(2) 2.745.

pentagonal bipyramidal, but with a significantly distorted equatorial plane, due to different types of bonding of the equatorial oxygen atoms [two atoms of O(1), two atoms of O(2) and O(3)] to the iodine as shown in Fig. 3.

In conclusion, X-ray crystallographic analysis of 2-iodylbenzenesulfonamides **5** reveals a complex network of intra- and intermolecular I···O interactions leading to a typical hexa-coordinated octahedral iodine geometry in compound **5a** and the unique heptacoordinated iodine(V) center in compound **5b**. The greater contribution of the intermolecular I···O interactions in compounds **5** compared to the previously reported pseudo-benziodoxoles[4,5] results in the observed polymeric structure of compounds **5a** and **5b**, which explains their relatively low solubility and reactivity in the oxidation reactions.[6]

Experimental

2-Iodylbenzenesulfonamides **5a** and **5b** were prepared by oxidation of 2-iodobenzenesulfonamides **4a** and **4b** with dimethyldioxirane according to the previously reported procedure.[6]

X-Ray crystallography

Single crystals of compounds **5a** and **5b** as colorless needles were grown from methanol over a four day period. The X-ray data for compounds **5a** and **5b** were collected on Rigaku AFC-7R diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Psi-scan absorption corrections were applied to the data using the TEXSAN 10.3b program.[11] The structures were solved by direct methods (SIR-92[12]) and refined by full-matrix least-squares on F^2 using the Crystals for Windows program.[13] All of the non-hydrogen atoms were refined anisotropically. Selected data:‡

5a: $C_{13}H_{18}INO_6S$, $M = 443.26$, monoclinic, space group $P2_1$, $a = 15.878(4)$, $b = 8.135(11)$, $c = 13.873(6)$ Å; $\alpha = 90$, $\beta = 105.53(3)$, $\gamma = 90°$, $V = 1727(2)$ Å^3, $Z = 4$, $T = 293$ K, $\mu = 2.001$ mm^{-1}, 4427 reflections measured, 4255 unique ($R_{\text{int}} = 0.0501$); final $R_1 = 0.0574$, $R_w = 12.613$.

5b: $C_{10}H_{14}INO_6S$, $M = 403.18$, triclinic, space group $P1$, $a = 7.5196(15)$, $b = 8.1049(16)$, $c = 11.426(2)$ Å; $\alpha = 101.53(3)$, $\beta = 96.26(3)$, $\gamma = 100.54(3)°$, $V = 663.1(2)$ Å^3, $Z = 2$, $T = 293$ K, $\mu = 2.594$ mm^{-1}, 3256 reflections measured, 3026 unique ($R_{\text{int}} = 0.1594$); final $R_1 = 0.0658$, $R_w = 15.24$.

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