in Figure 2. What matters is the behavior of states obtained by the two spin coupling modes in Scheme 2. b) Density functional calculations of corresponding ferric–water complexes give $S=\frac{1}{2}$ ground state and a higher energy $S=\frac{5}{2}$ state. See: M. Filatov, N. Harris, S. Shaik, *J. Chem. Soc. Perkin Trans. 2* **1999**, 399; M. T. Green, *J. Am. Chem. Soc.* **1998**, *120*, 10772. This is supported by experimental assignment. See: H. Thomann, M. Bernardo, D. Goldfrab, P. M. H. Kroneck, V. Ulrich, *J. Am. Chem. Soc.* **1995**, *117*, 8243. However, a recent experimental investigation of a model compound with a spatially fixed thiophenoxy ligand shows an $S=\frac{5}{2}$ ground state and indicates the role of the protein in stabilizing the $S=\frac{1}{2}$ ground state, as predicted initially by Harris and Loew. See: H. Aissaoui, R. Bachmann, A. Schweiger, W.-D. Woggon, *Angew. Chem.* **1998**, *110*, 3191; *Angew. Chem. Int. Ed.* **1998**, *37*, 2998; D. Harris, G. H. Loew, *J. Am. Chem. Soc.* **1993**, *115*, 8775.

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[14] A direct OH transfer mechanism would entail spin-state crossing to the $S=\frac{5}{2}$ state of the five-coordinate ferric complex (for example, see: ref. [1]).

[15] All HS data are obtained with B3LYP using JAGUAR 3.5 (ref. [9]). The LS profile is calculated with the unrestricted B3LYP method in GAUSSIAN 98 (ref. [10]). For convenience, the zero of the energy scale in Figure 2 is common to the LS and HS curves.

[16] a) M. Filatov, W. Thiel, *Chem. Phys. Lett.* **1998**, *295*, 467; b) H. Basch, S. Hoz, *J. Phys. Chem. A* **1997**, *101*, 4416; c) S. Skokov, R. A. Wheeler, *Chem. Phys. Lett.* **1997**, *271*, 251; d) The average underestimation error of B3LYP (in ref. [16a–c]) for related reactions involving radicals is ≤ 6 kcal mol^{-1}, while for related reactions involving OH and CH_3 groups, the error is 0.5 kcal mol^{-1}.[16c] For reactions involving Fe, O, and H atoms, the underestimation error of the B3LYP barrier is approximately 1 kcal mol^{-1} relative to experimental data and 5.4 kcal mol^{-1} relative to the CASPT2 result which seems to overestimate the barrier.[17]

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Redirecting Secondary Bonds To Control Molecular and Crystal Properties of an Iodosyl- and an Iodylbenzene**

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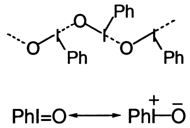
Noncovalent, attractive interactions are extremely important forces that can influence molecular, solution, and solid-state properties. For example, hydrogen bonding is unarguably the most important directing intermolecular force and structure generating motif in many chemical and biological systems. Much less appreciated (and utilized) are the related forces that exist between heavier atoms. A class of such attractive interactions have often been termed secondary bonds.[1] Like hydrogen bonds, these bonds have strong electrostatic components and show directional preferences.[2] From the similarity to hydrogen bonds, it has also been suggested that secondary bonds might have potential for the rational design of supramolecular structures.[3]

Secondary bonds, particularly I$\cdots$O bonds, are a pervasive feature of structural organoiodine(III) chemistry.[4] Recently, such secondary bond interactions have been exploited to introduce chiral environments about iodine(III) centers for enantioselective oxidation reactions.[5] In other cases, secondary bonds can be counterproductive. In iodosylbenzene $(PhIO)_n$, I$\cdots$O bonds dominate the structure to such an extent that this extremely potent and important reagent is essentially insoluble in all nonreactive media.[6] Nonetheless, this veritable “oxygen atom warehouse” has found widespread use in catalytic oxygenation reactions after the discoveries of its efficacy as a source of oxygen atoms for oxidations catalyzed by cytochrome P-450[7] and by discrete transition metal complexes.[8]

Though known for over 100 years,[9] structural details for iodosylbenzene—or any members of this class of materials—are still limited. Various spectroscopic studies have suggested that iodosylbenzene adopts the form of a zigzag polymer (Scheme 1),[10] whereby monomeric units of PhIO are linked by intermolecular I$\cdots$O secondary bonds. Within PhIO monomers, I–O single bonds (2.04 Å) and a C-I-O bond angle near 90° have been deduced from extended X-ray absorption fine-structure (EXAFS) analysis.[10g] The tight, solid-state aggregation of the PhIO monomers is undoubtedly caused by the strong electrostatic attractions between the oppositely charged iodine and oxygen atoms (right resonance structure, Scheme 1). Polymeric iodosylbenzene is also likely to be terminated by addition of water and thus iodosylbenzene can be further formulated as $HO(PhIO)_nH$.[11] We have recently discovered that soluble derivatives of (tosyliminoiodo)benzene and iodosylbenzene are realized if strong internal dipoles capable of introducing *intramolecular* I$\cdots$O secondary bonds, for the purpose of replacing *intermolecular* I$\cdots$N and I$\cdots$O secondary bonds, are incorporated into these materials.[12] Indeed, a single-crystal X-ray structure analysis of the (tosyliminoiodo)benzene derivative showed the presence of significant intramolecular I$\cdots$O secondary bonding and thus confirmed our expectations. We now have succeeded in obtaining single crystals suitable for X-ray diffraction studies of the corresponding soluble iodosylbenzene and herein report the first crystal structure of an iodosylbenzene derivative ArIO (**1**; Ar = 2-*t*$BuSO_2C_6H_4$). Furthermore, the crystal structure of the corresponding iodylbenzene $ArIO_2$ (**2**) has also been obtained. Comparisons between these two structures reveal interesting aspects of the nature of iodosyl and iodoxy bonds.



Scheme 1. Zigzag structure of iodosylbenzene.

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Single crystals of $\mathbf{1}\cdot CDCl_3$ for X-ray structural analysis were grown from a [D$_1$]chloroform/toluene mixture; Figure 1 presents the local crystalline environment of **1**.[13] Immediately apparent is a close contact (2.707(5) Å) of one of the sulfone oxygen atoms to the hypervalent iodine center.[14] The presence of this intramolecular I···O bond within the monomers of **1** enforces a planar array for the I, C1, C2, S, and O2 atoms (root-mean-square deviation from planarity is 0.08 Å) and results in a structure that resembles benziodoxoles.[15] Some structurally characterized representatives are depicted in Scheme 2.[16] Such species display an inverse relationship between the exocyclic I–O1 and the I–O2 bond lengths. The longer I–O2 bonds within the heterocycles **A**–**E** can be rationalized by the different basicities of the two iodine-bound oxygen atoms and their corresponding competition for engaging in the three-center four-electron bond.[6g] Compound **E** (as the $[Na(OH_2)_5]^+$ salt) displays the most extreme I–O bond lengths of of the group **A**–**E**, probably as a result of the increased charge and basicity of the exocyclic oxygen atom. Compared to **E**, **1** displays an I–O bond length that is only 0.04 Å shorter. This marginal decrease is most likely a result of the increased positive charge located on the iodine atom and corresponding increased electrostatic attractions between the iodine and oxygen atoms (ylide-type resonance structure), rather than the occurrence of any significant I–O multiple bonding.

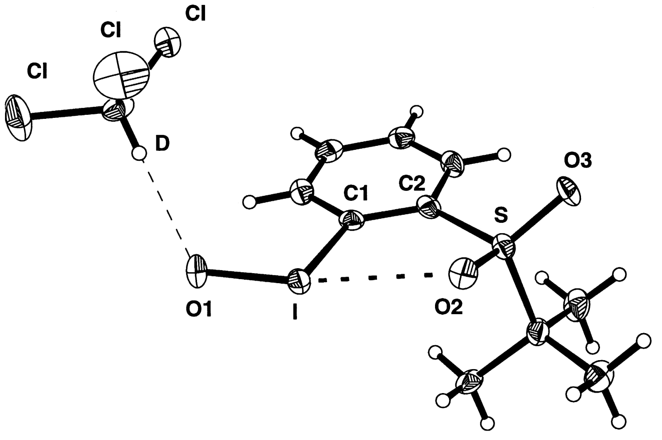
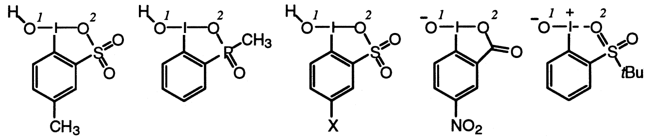


Figure 1. Structure of $\mathbf{1}\cdot CDCl_3$. Selected distances [Å] and angles [°]: I-O1 1.848(6), I···O2 2.707(5), I-C 2.128(7), S-O2 1.441(5), S-O3 1.425(5), C-D 0.81(7), D···O1 2.24(7); C1-I-O1 94.8(3), O2···I-O1 167.3(2), I-O2···S 113.3(3), D···O1-I 117(2), C-D···O1 174(6).



	A	B	C	D	E	1
			X = H	CH_3		
$d_{I\text{-}O1}$ (Å)	1.933(5)	1.951(7), 1.953(7)	2.005	1.939(6)	1.890(8)	1.848(6)
$d_{I\text{-}O2}$ (Å)	2.372(5)	2.289(8), 2.284(8)	2.298	2.347(5)	2.447(8)	2.707(5)

Scheme 2. Iodine–oxygen interatomic distances in **1** and in selected iodine–oxygen heterocyclic species.

The above trends also suggest that a further lengthening of the secondary contact between the I and O2 atoms would only result in a marginal decrease of the I–O1 bond length. The high basicity of O2 manifests itself by the establishment of weak hydrogen bonding to chloroform in the crystal structure of **1**. A $Cl_3CD\cdots O$ distance of 2.24(7) Å in **1** is slightly shorter than the mean value 2.31(1) Å found for hydrogen bonds between oxygen acceptors and chloroform.[17] A highly basic oxygen atom in PhIO is also indicated by the fact that Lewis acids, such as BF_3, can be used to form soluble adducts.[6c]

Figure 2 portrays the fashion in which molecules of **1** aggregate in the solid state. Each molecule of **1** achieves a pseudo square-planar geometry by the formation of an I···O secondary bond ($d_{I\cdots O} = 2.665(6)$ Å) to a neighboring iodosyl oxygen atom. The strength of this intermolecular interaction may be inferred to be weaker than analogous secondary bonds in iodosylbenzene ($d_{I\cdots O} = 2.37(1)$ Å). Remarkably, if one ignores the *ortho*-sulfonyl group in **1**, the structure depicted in Scheme 1 resembles that in Figure 2, except that the primary intermolecular I···O bond is turned through 90°, the O–I···O ensemble is now bent rather than linear.

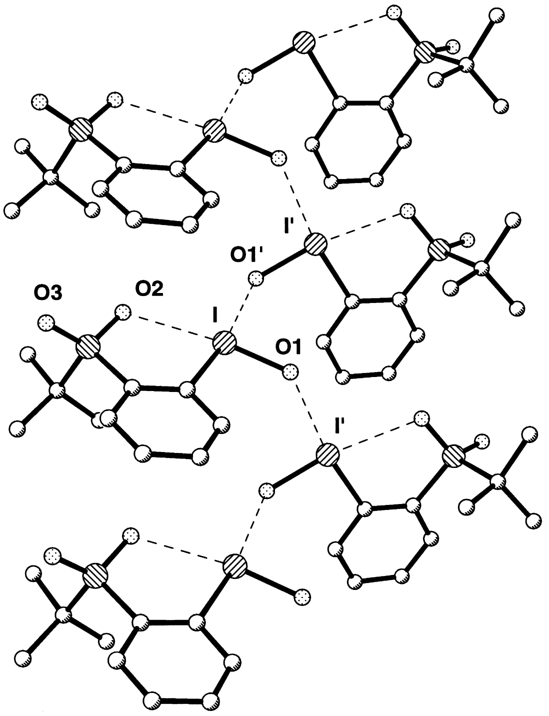


Figure 2. Structure of **1** showing the polymeric connectivity (chloroform and hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]: I···O1' 2.665(6); O1-I···O1' 93.7(1), I-O1···I' 128.4(3), O2···I···O1' 98.6(2).

Solutions of compound **1** slowly produce a colorless precipitate of the iodylbenzene **2**, which results from the disproportionation of **1** into **2** and ArI. The decreased solubility of **2** relative to **1** suggests that in **2** there is a greater number of intermolecular I···O secondary bonds in the solid-state structure and/or the intermolecular I···O secondary bonds are stronger. Indeed, an X-ray structural determination of crystalline $\mathbf{2}\cdot CH_2Cl_2$ confirmed that both of these factors play a role.[13] Each iodine atom of **2** uses both intramolecular (2.693(3) Å) and intermolecular I$\cdots$O bonds (2.777(3) and 2.566(2) Å) to adopt a pseudo octahedral geometry and a chainlike structure (Figure 3). Within the monomers of **2**, I–O bond distances of 1.796(2) and 1.822(2) Å are found (Figure 4). These distances are notably shorter than the corresponding values reported for either iodylbenzene (**F**; Scheme 3)[16, 18] or **1**. Again, the pseudo cyclic structure of **2** and I–O bond lengths are actually more comparable to cyclic iodyl analogues **G**–**I** (Scheme 3). A bond 0.026 Å longer for I–O2 compared to I–O1 is found in **2**; this reflects the fact that a shorter secondary interaction contact (intermolecular, 2.566(2) Å) is located *trans* to O2 rather than to O1 (intramolecular, 2.693(3) Å), which correlates well with the stronger interactions of the lone pairs from the oxygen atom with the corresponding σ* orbitals of the I–O bond. Compound **2** shows evidence for weak hydrogen bonding to dichloromethane: The 2.55 Å CH$\cdots$O bond length is slightly longer than the mean $Cl_2HC{-}H\cdots O$ hydrogen bond lengths (2.492(8) Å).[17] The presence of the iodosyl and iodyl units in the plane of the aromatic rings of **1** and **2** also results in short $C_{Ar}{-}H\cdots O$ contacts of 2.38 and 2.39 Å, respectively.

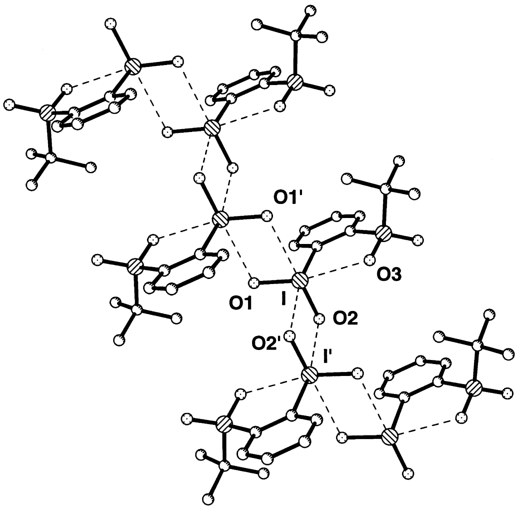


Figure 3. Structure of **2** showing the polymeric connectivity (dichloromethane and hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]: I$\cdots$O1′ 2.777(3), I$\cdots$O2′ 2.566(2); O1-I$\cdots$O1′ 74.7(1), O1-I$\cdots$O2′ 90.7(1), O2-I$\cdots$O2′ 74.5(1), I-O2$\cdots$I′ 105.5(1), I-O1$\cdots$I′ 105.3(1).

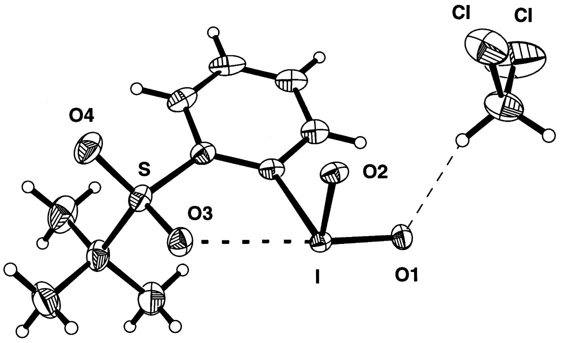
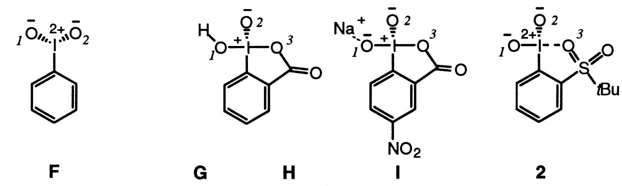


Figure 4. Structure of $2\cdot CH_2Cl_2$. Selected distances [Å] and angles [°]: I–O1 1.796(2), I–O2 1.822(2), I$\cdots$O3 2.693(2), S–O3 1.455(3), S–O4 1.439(3), I–C1 2.140(4); C1-I-O1 95.1(1), O3$\cdots$I-O1 166.1(1), I$\cdots$O3-S 114.4(1), I-O1$\cdots$H(CHCl$_2$) 99.0.



	F	G racemic	H chiral	I	2
$d_{I\text{-}O1}$ (Å)	2.021(9)	1.893(3), 1.895(3)	1.784(2)	1.798(2)	1.796(2)
$d_{I\text{-}O2}$ (Å)	1.924(9)	1.769 (3), 1.784(3)	1.925(2)	1.810(3)	1.822(2)
$d_{I\text{-}O3}$ (Å)		2.310(4), 2.324(3)	2.263(2)	2.481(3)	2.693(3)

Scheme 3. Iodine–oxygen interatomic distances in **2**, iodylbenzene, and in selected iodine–oxygen heterocyclic species.

While the impact of the intramolecular I$\cdots$O secondary bonding on the structural properties of **1** is significant, it is also interesting to note that introduction of similar *ortho*-subsituted groups bearing a partial negative charge into iodonium ylides of the form $ArICR_2$ can give rise to antimicrobial activity.[19] Furthermore, other derivatives of iodosylbenzene, such as 2-iodosylbenzoic acid (**C**; Scheme 1) have been examined as catalysts for the hydrolysis of toxic phosphonates.[20]

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[13] Crystals of **1** were grown from [D$_1$]chloroform/toluene at $-35\,^\circ$C. $C_{10}H_{13}IO_3S\cdot CDCl_3$, $M_r = 460.54$, monoclinic, space group $P2_1/c$, $a = 11.379(5)$, $b = 5.674(2)$, $c = 25.220(11)$ Å, $b = 94.089(8)^\circ$, $V = 1624.0(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.884\ g\,cm^{-3}$, $T = 150(2)$ K, yellow block $0.22\times0.34\times0.40$ mm^3, $2\theta_{max} = 59.82^\circ$, 10382 measured reflections, 4297 unique, R values ($I > 2\sigma(I)$): $R1 = 0.0655$, $wR2 = 0.1314$. Crystals of **2** were grown from dichloromethane at ambient temperature. $C_{10}H_{13}IO_4S\cdot CH_2Cl_2$, $M_r = 441.09$, monoclinic, space group $C2/c$, $a = 19.784(2)$, $b = 6.5461(6)$, $c = 24.647(2)$ Å, $b = 96.697(2)^\circ$, $V = 3170.2(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.848\ g\,cm^{-3}$, $T = 150(2)$ K, $2\theta_{max} = 60.02^\circ$, 17723 measured reflections, 4322 unique, R values ($I > 2\sigma(I)$): $R1 = 0.0345$, $wR2 = 0.0703$. Bruker SMART Platform with CCD detector, Mo radiation ($\lambda = 0.71073$ Å) with graphite monochromator, omega scans with 0.3° increments for the frames. Absorption corrections made with SADABS (G. M. Sheldrick, University of Göttingen, **1998**); structure solution and refinement with SHELXTL 5.10 (Bruker AXS, Inc., Madison, WI, **1997**) against F^2 (177 parameters for **1**, 173 parameters for **2**). All nonhydrogen atoms were refined with anisotropic temperature parameters, all hydrogen atoms (except $CDCl_3$ deuterium atom in **1**) were placed in calculated positions and refined isotropically. The $CDCl_3$ deuterium atom was located from the Fourier map and refined isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137694 and CCDC-137693. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)..CCDC

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A General Entry into Glycopeptide "Dendrons"[**]

Kashinath Sadalapure and Thisbe K. Lindhorst[*]

Dedicated to Professor Günter Wulff
on the occasion of his 65th birthday

In order to study and manipulate carbohydrate–protein interactions, carbohydrate and dendrimer chemistries have been combined in order to design multivalent glycoconjugate mimetics.[1] Such carbohydrate dendrimers potentially influence carbohydrate–protein interactions strongly due to the multivalency or cluster effects.[2, 3] Moreover, they may combine the properties of drug binding and transport with other, still unknown, qualities of synthetic biomaterials. Two main entries into the synthesis of carbohydrate dendrimers have been utilized so far: by the glyco-coating of noncarbohydrate dendrimers to form glycodendrimers[4] or by the convergent combination of molecular wedges derived from carbohydrate clusters[5] to yield carbohydrate dendrimers of different architectures.[6] Both synthetic approaches do not allow enlargement of the carbohydrate-containing molecules by the formation of successive generations,[7] although some reported carbohydrate dendrimers possess a relatively high sugar density.

We now report on the synthesis of glycopeptide dendrons in which the peptide coupling of orthogonally protected AB$_2$-type carbohydrate units form the basis for an iterative

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