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Preparation and X-ray Structural Study of Dibenziodolium Derivatives

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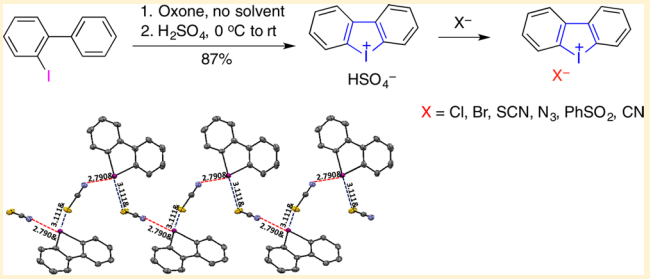
Supporting Information

ABSTRACT: New experimental procedures for the preparation of dibenziodolium salts by oxidative cyclization of 2-iodobiphenyl in the presence of appropriate strong acids are described. Particularly useful is a convenient one-pot synthesis of dibenziodolium hydrogen sulfate from 2-iodobiphenyl using Oxone as an inexpensive and environmentally safe oxidant. Dibenziodolium hydrogen sulfate, bis(triflyl)imidate, or triflate can be readily converted to various other dibenziodolium derivatives (chloride, bromide, thiocyanate, azide, cyanide, phenylsulfinate) by anion exchange. Structures of key products have been established by single-crystal X-ray diffraction analysis. Particularly interesting is the X-ray structure of dibenziodolium thiocyanate, which represents the first example of a structurally characterized hypervalent iodine compound with a relatively short iodine−sulfur secondary bond distance.

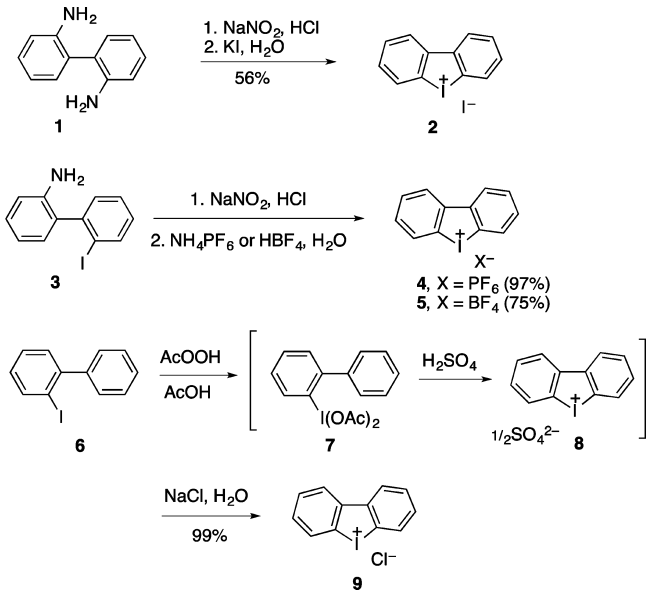


1. INTRODUCTION

Hypervalent iodine compounds have emerged as versatile and environmentally benign reagents for organic synthesis.[1−18] Iodonium salts belong to a particularly useful class of hypervalent iodine derivatives due to their useful reactivity and broad practical applications as radical initiators,[2] biologically active compounds,[2] and reagents for positron emission tomography.[19] Five-membered cyclic iodonium salts, derivatives of the iodolium heterocyclic system, are especially interesting because of the enhanced stability and applications in biological studies.[2] For example, dibenziodolium chloride (which is commonly known under the name of diphenyleneiodonium chloride or DPI) has found numerous applications in biological studies.[20−40] In particular, DPI is a potent hypoglycaemic agent at a dose as low as 4 mg/kg body weight.[20] DPI inhibits gluconeogenesis in isolated rat hepatocytes,[21] causes swelling of rat liver mitochondria,[22] induces cardiomyopathy,[23] induces mitochondrial myopathy,[24,25] and inhibits the superoxide production of neutrophils,[26] as well as nitric oxide synthase.[27] In modern biochemical and pharmacological research, DPI is commonly used as a NADPH oxidase inhibitor.[28−40]

Typical synthetic approaches to dibenziodolium salts are outlined in Scheme 1. Dibenziodolium iodide **2** was originally prepared by Mascarelli and Benati in 1909 by diazotization of 2,2′-diaminodiphenyl **1** with sodium nitrite in a hydrochloric acid solution followed by addition of potassium iodide.[41] A similar diazotization reaction starting from 2-amino-2′-iododiphenyl **3** affords dibenziodolium as hexafluorophosphate **4** or tetrafluoroborate **5**.[42] The third method involves peracetic oxidation of 2-iodobiphenyl **6** to an iodine(III) intermediate **7**, which cyclizes to dibenziodolium sulfate **8** in acidic solution and is finally isolated

Scheme 1. Synthetic Approaches to Dibenziodolium Salts



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as the chloride salt **9**.[43] A recent modification of the approach to dibenziodolium salts starting from 2-iodobiphenyl employs *m*-CPBA instead of peracetic acid and trifluoromethanesulfonic acid in place of sulfuric acid.[44,45]

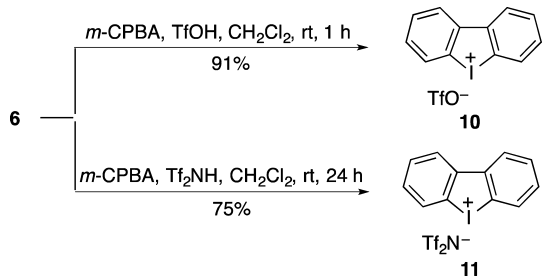
Dibenziodolium salts have a relatively high thermal stability. For example, tetrafluoroborate salt **5** melts at 239−240 °C without decomposition; however, the X-ray structural data do not support any aromatic character of the iodolium ring.[46] On the basis of the available literature data, it can be stated that iodine is not capable of forming conjugated cyclic systems with aromatic stabilization because of the large atom size and the semi-ionic nature of the hypervalent I−C, I−N, and I−O bonds.[2] Moreover, the high level computational studies using adaptive natural density partitioning bond modeling technique (AdNDP) reveal that the double bond between iodine atom and other elements does not exist.[47] Despite the lack of aromatic conjugation, five-membered heterocyclic iodine compounds have a considerably higher thermal stability as compared to their acyclic analogues. The greater stability of five-membered iodine−oxygen heterocycles enabled the preparation and isolation of otherwise unstable iodine(III) derivatives with I−OOR, I−N_3, I−CF_3, and other substituents.[2] A computational study on the reactivity of dibenziodolium ions with nucleophiles was recently published by de Magalhaës, Lüthi, and Togni.[48]

2. RESULTS AND DISCUSSION

In this Article, we describe experimental procedures for the preparation of dibenziodolium hydrogen sulfate, bis(triflyl)imidate, and triflate by oxidative cyclization of 2-iodobiphenyl in the presence of the corresponding strong acids. Dibenziodolium salts of strong acids can be further converted to numerous other dibenziodolium derivatives by anion exchange.

In the search for optimized preparation of dibenziodolium derivatives, we have initially investigated oxidative cyclization reactions of 2-iodobiphenyl using trifluoromethanesulfonic acid (TfOH) and bis(trifluoromethane)sulfonimide (Tf_2NH), both of which are strong acids. Both reactions readily proceed at room temperature affording the respective triflate **10** and bis(triflyl)imidate **11** in good yields (Scheme 2). The preparation of triflate **10** by a similar procedure was previously reported by Wen and coauthors.[44,45]

Scheme 2. Preparation of Dibenziodolium Triflate and Bis(triflyl)imidate by Oxidative Cyclization of 2-Iodobiphenyl Using *m*-CPBA as Oxidant



The structure of dibenziodolium bis(triflyl)imidate **11** was established by single-crystal X-ray crystallography (Figures 1 and 2). Two different pseudopolymorphs of the product **11** were studied by X-ray crystallography. The first pseudopolymorph (**11a**) was crystallized from chloroform and has a molecule of solvent per molecule of salt. It crystallizes in triclinic unit cell and

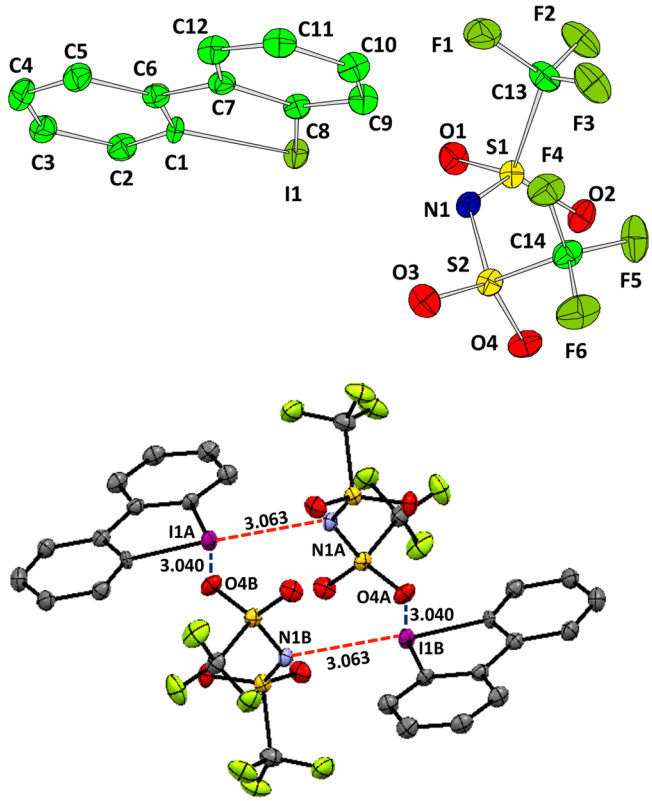


Figure 1. Perspective view of dibenziodolium bis(triflyl)imidate **11** (pseudopolymorph **11a**) with 50% ellipsoid probability. Solvent chloroform molecule is omitted for clarity. Selected distances [Å] and angles [deg] for **11a**: I(1)−C(1) = 2.096(6), I(1)−C(8) = 2.100(6), N(1)−S(1) = 1.595(6), N(1)−S(2) = 1.577(6), C(1)−I(1)−C(8) = 82.7(3), S(1)−N(1)−S(2) = 125.0(4).

forms dimers as a main structural motif (Figure 1). The first coordination sphere of hypervalent iodine centers in **11a** is close to square planar geometry and has CCNO configuration. Iodine atom has two typical (~2.1 Å) I−C bonds and two relatively short intermolecular contacts with bis(triflyl)imide anion. One of these short contacts is between the iodine and oxygen O(4) atom (~3.04 Å), while the second is between iodine and the nitrogen atom of anion (~3.06 Å). The torsion angle N(1)−O(4)−C(1)−C(8) is 11.74°, which is reasonable close to the square planar configuration around iodine center. The hydrogen atom of chloroform forms two hydrogen bonds with O(1) (~2.39 Å) and O(3) (~2.45 Å) oxygen atoms located at two different anions. Interconnected by the solvent molecules, dimers are arranged along the crystallographic *b*-axis. The second pseudopolymorph of **11** (pseudopolymorph **11b**) crystallizes in monoclinic unit cell and has no solvent molecules in the structure (Figure 2). This pseudopolymorph has polymeric nature with polymeric chains aligned along crystallographic *a*-axis. Each chain consists of repeated units of two independent dibenziodolium cations, which interact with two neighboring bis(triflyl)imide anions each. In both independent dibenziodolium cations, iodine centers were found in square-planar geometry with very small O(8)−O(4)−C(13)−C(20) (2.62°) and O(3)−O(7)−C(1)−C(8) (0.68°) torsion angles. Iodine centers in both crystallographically independent molecules have a CCOO first coordination sphere, which is different from CCNO coordination of triclinic pseudopolymorph **11a**. Again, all covalent I−C bonds were found in the typical range. The

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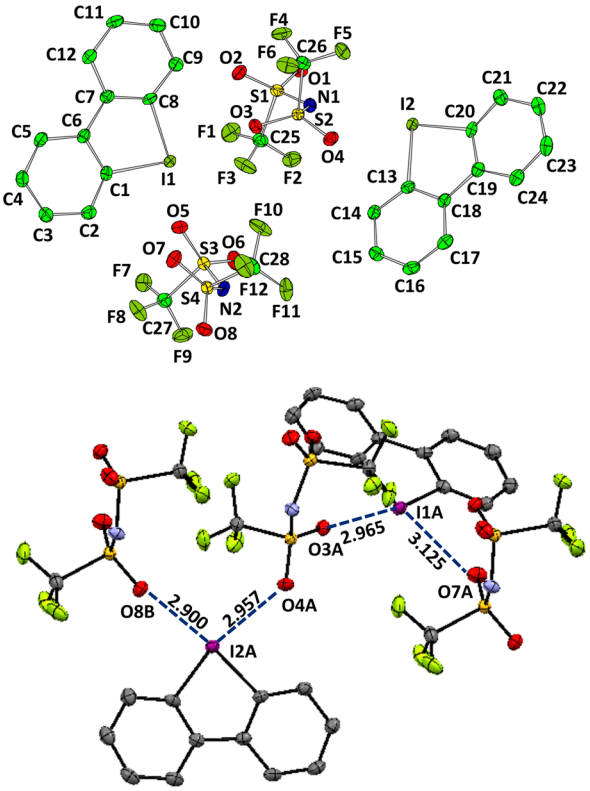
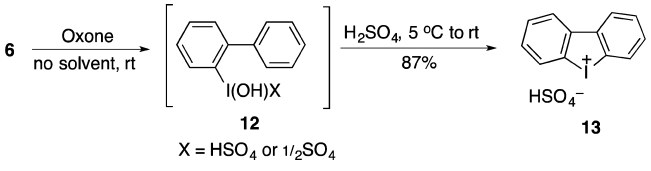


Figure 2. Perspective view of dibenziodolium bis(triflyl)imidate **11** (pseudopolymorph **11b**) with 50% ellipsoid probability. Selected distances [Å] and angles [deg] for **11b**: I(1)−C(1) = 2.094(3), I(1)−C(8) = 2.102(3), I(2)−C(13) = 2.090(3), I(2)−C(20) = 2.097(3), N(1)−S(1) = 1.585(3), N(1)−S(2) = 1.578(3), N(2)−S(3) = 1.588(3), S(4)−N(2) = 1.569(3), C(1)−I(1)−C(8) = 82.32(12), C(13)−I(2)−C(20) = 82.39(12), S(1)−N(1)−S(2) = 123.22(17), S(4)−N(2)−S(3) = 125.14(17).

intermolecular short contacts, however, are significantly different for the two crystallographically independent dibenziodolium molecules. Indeed, the first iodine center I(1) has one short (~2.96 Å) and one long (~3.12 Å) intermolecular contact to O(3) and O(7) oxygen atoms, respectively. Similar intermolecular contacts for the second iodine center, I(2), are much closer to each other (~2.90 and ~2.96 Å for I(2)−O(8) and I(2)−O(4) contacts, respectively).

At the next step, we have developed a convenient one-pot synthesis of dibenziodolium hydrogen sulfate from 2-iodobiphenyl using Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) as an inexpensive and environmentally safe oxidant (Scheme 3). On the basis of the ESI−MS study of the reactions of ArI with Oxone,[10] we assume that the initial oxidation of 2-iodobiphenyl **6** affords iodine(III) intermediate **12**, which cyclizes to dibenziodolium sulfate **13** upon subsequent treatment with concentrated sulfuric acid. The final product **13** is isolated in high yield as a pale yellow

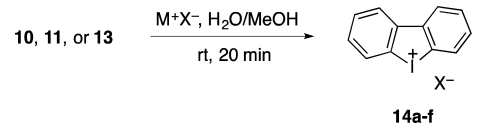
Scheme 3. One-Pot Synthesis of Dibenziodolium Hydrogen Sulfate from 2-Iodobiphenyl Using Oxone as Oxidant



crystalline solid by filtration of the reaction mixture after addition of ice-cold water.

Dibenziodolium salts of strong acids **10**, **11**, and **13** can be further converted to other dibenziodolium derivatives by anion exchange. We have found that the treatment of a methanolic solution of dibenziodolium sulfate, triflate, or bis(triflyl)imidate in methanol with an aqueous solution of an appropriate inorganic salt results in immediate precipitation of a new dibenziodolium derivative. Using this simple and general procedure, we were able to prepare various other dibenziodolium derivatives **14a−f** (Table 1).

Table 1. Preparation of Dibenziodolium Derivatives by Anion Exchange[a]



14a-f

entry	substrate	M^+X^-	product	yield (%)[b]
1	**13**	NaCl	**14a**	85
2	**13**	NaBr	**14b**	80
3	**13**	KSCN	**14c**	90
4	**13**	NaN_3	**14d**	75
5	**10**	$PhSO_2Na$	**14e**	75
6	**10**	NaCN	**14f**	85
7	**10**	NaCl	**14a**	75
8	**10**	NaBr	**14b**	93
9	**10**	KSCN	**14c**	87
10	**10**	NaN_3	**14d**	80
11	**11**	$PhSO_2Na$	**14e**	81
12	**11**	NaCN	**14f**	90
13	**11**	NaCl	**14a**	85
14	**11**	NaBr	**14b**	82
15	**11**	KSCN	**14c**	93
16	**11**	NaN_3	**14d**	78

[a]For detailed procedures, see the Experimental Section. [b]Yields of isolated, analytically pure products.

This procedure affords analytically pure products **14** in generally high yields in the form of thermally stable, white, microcrystalline, solids. All new products were analyzed by ^1H and ^{13}C NMR, elemental analysis, and structures of products **14c** and **14d** were established by single-crystal X-ray crystallography. X-ray structures of the dibenziodolium derivatives **14c** and **14d** are shown in Figures 3 and 4. The X-ray structure of **14c** is rather unique as, for the best of our knowledge, it represents the first proven short I−S contact. Indeed, it crystallizes in monoclinic unit cell with iodine centers in close to square-planar geometry (torsion N(1)−S(1)−C(8)−C(1) angle is 5.17°) and CCNS coordination. Such geometry formed by two typical (~2.1 Å) covalent I−C bonds and two short intermolecular contacts between iodine center and two thiocyanate anions. One of these contacts (~2.79 Å) is between iodine and nitrogen, while the second (~3.11 Å) is between iodine and sulfur atoms. Each thiocyanate anion coordinated to two dibenziodolium centers, thus forming a polymeric chain along the crystallographic *a*-axis. An azido derivative of dibenziodolium, **14d**, crystallizes in monoclinic unit cell and has dimeric structure (Figure 4). Again, iodine center was found in square-planar geometry (torsion N(3)−N(1)−C(8)−C(1) angle is 0.98°) and CCNN coordination. The first coordination sphere of iodine atom consists of two

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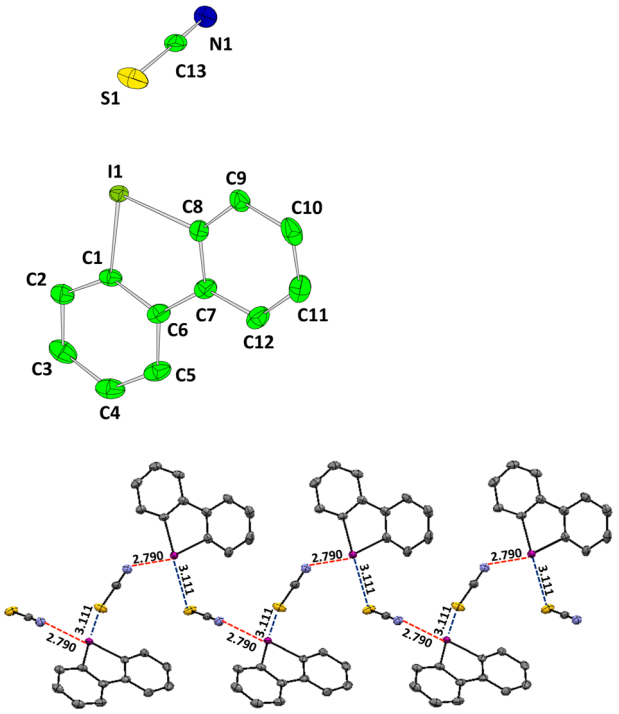

Figure 3. Perspective view of dibenziodolium thiocyanate **14c** with 50% ellipsoid probability. Selected distances [Å] and angles [deg] for **14c**: I(1)−C(1) = 2.111(3), I(1)−C(8) = 2.110(4), I(1)−S(1) = 3.111(11), S(1)−C(13) = 1.639(4), C(13)−N(1) = 1.172(5), S(1)−I(1)−C(1) = 172.84(9), S(1)−I(1)−C(8) = 94.50(10), C(1)−I(1)−C(8) = 81.49(14), S(1)−C(13)−N(1) = 178.8(4).

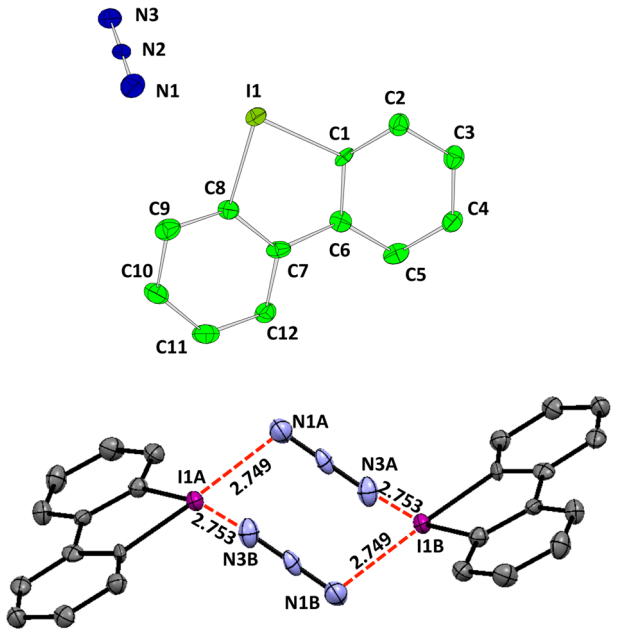

Figure 4. Perspective view of dibenziodolium azide **14d** with 50% ellipsoid probability. Selected distances [Å] and angles [deg] for **14d**: I(1)−C(1) = 2.108(6), I(1)−C(8) = 2.104(6), N(1)−N(2) = 1.179(9), N(2)−N(3) = 1.174(8), C(1)−I(1)−C(8) = 81.4(2), N(1)−N(2)−N(3) = 179.1(7).

typical I−C covalent bonds and two almost equivalent short I−N contacts with two azide anions (~2.74 and ~2.75 Å for I(1)−N(1) and I(1)−N(3) contacts, respectively).

We should emphasize that thiocyanate **14c** represents the first structurally characterized example of a hypervalent iodine compound molecule with a short iodine−sulfur secondary bonding. The only previously reported compounds of this type are represented by diaryliodonium thiophenolates[49] and diaryliodonium dithiocarboxylates.[50,51] The I···S distance in thiocyanate **14c** (~3.11 Å) is significantly shorter than the calculated sum of van der Waals radii (3.78 Å), but longer than the sum of the covalent radii for sulfur and iodine (2.37 Å). Several compounds of monovalent iodine with covalent I−S bond are known, and a single-crystal X-ray structure of triphenylmethyliodosulfane, Ph_3CSI, with the sulfur−iodine bond length of 2.406(4) Å has been reported in the literature.[52]

It should be also noted that azide **14d** is the first example of isolated and structurally characterized azide derivative of an iodonium salt. Recently, the in situ generation of azide **14d** and its use in the efficient synthesis of triazolophenanthridines have been reported.[45]

3. CONCLUSIONS

In summary, we have developed new, convenient experimental procedures for the preparation of dibenziodolium salts by oxidative cyclization of 2-iodobiphenyl in the presence of appropriate strong acids. Particularly useful is a one-pot synthesis of dibenziodolium hydrogen sulfate from 2-iodobiphenyl using Oxone as an inexpensive and environmentally safe oxidant. Dibenziodolium hydrogen sulfate, bis(triflyl)imidate, or triflate can be readily converted to various other dibenziodolium derivatives (chloride, bromide, thiocyanate, azide, cyanide, phenylsulfinate) by anion exchange. Structures of key products, including the first known examples of stable aryliodonium thiocyanate and aryliodonium azide, have been established by single-crystal X-ray diffraction analysis. Particularly interesting is the X-ray structure of thiocyanate **14c**, which represents the first structurally characterized hypervalent iodine compound with a relatively short iodine−sulfur secondary bond distance.

4. EXPERIMENTAL SECTION

General Experimental Remarks. All reactions were performed under air atmosphere. 2-Iodobiphenyl and other reagents and solvents were from commercial sources and used without further purification from freshly opened containers. NMR spectra were recorded at 500 MHz (^{1}H NMR), 470 MHz (^{19}F NMR), and 125 MHz (^{13}C NMR). Chemical shifts (δ) are reported in parts per million.

Synthesis of Dibenziodolium Salts by Oxidative Cyclization of 2-Iodobiphenyl. *Preparation of Dibenziodolium Trifluoromethanesulfonate (**10**).*[44,45] To a stirred solution of 2-iodobiphenyl (0.56 g, 0.35 mL, 2.0 mmol) in anhydrous CH_2Cl_2 (6 mL) were added *m*-CPBA (77%, 0.736 g, 3.2 mol) and trifluoromethanesulfonic acid (0.57 mL, 6.5 mmol). The solution was stirred for 1 h at room temperature, and then CH_2Cl_2 was removed using rotary evaporation. Et_2O (4 mL) was added to the remaining solid. The mixture was stirred for 20 min, and then filtered. The obtained solid was washed with Et_2O three times and dried in a vacuum to provide dibenziodolium trifluoromethanesulfonate **10** (0.781 g, 91% yield) as a white solid; mp 247−249 °C. ^{1}H NMR (500 MHz, CD_3OD): δ 8.32 (d, J = 8.0 Hz, 2H), 8.1 (d, J = 8.0 Hz, 2H), 7.84 (t, J = 8.0 Hz, 2H), 7.68 (t, J = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, CD_3OD): δ 142.2, 131.18, 130.9, 130.8, 130.2, 126.9, 119.9 (q, $^1J_{CF}$ = 496.6 Hz). ^{19}F (470 MHz, CD_3OD): δ −80.06 (s).

*Preparation of Dibenziodolium Bis(trifluoromethane)sulfonimide (**11**).* To a stirred solution of 2-iodobiphenyl (0.56 g, 0.35 mL, 2.0 mmol) in anhydrous CH_2Cl_2 (6.0 mL) were added *m*-CPBA (77%, 0.736 g, 3.2 mmol) and a solution of $HNTf_2$ (1.26 g, 4.5 mmol) in CH_2Cl_2 (5.0 mL). The solution was stirred for 24 h at rt, and then the solvent was removed on a rotary evaporator. Et_2O (10 mL) was added to

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the remaining solid. The mixture was stirred for 20 min, and then filtered. The obtained solid was washed with Et_2O three times, and dried in a vacuum to provide dibenziodolium bis(trifluoromethane)-sulfonimide **11** (0.84 g, 75% yield) as a pale yellow solid; mp 148−149 °C. ^{1}H NMR (500 MHz, CD_3OD): δ 8.37 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H), 7.86 (t, J = 7.0 Hz, 2H), 7.71 (t, J = 6.5 Hz, 2H). ^{13}C NMR (125 MHz, CD_3OD): δ 142.2, 131.1, 130.9, 130.8, 130.1, 126.9, 120.0 (q, $^1J_{CF}$ = 318.9 Hz). ^{19}F (470 MHz, CD_3OD): δ −80.66 (s). Anal. Calcd for $C_{14}H_8F_6INO_4S_2$: C, 30.07; H, 1.44; I, 22.69; N, 2.5; S, 11.47. Found: C, 30.09; H, 1.33; I, 22.49; N, 2.46; S, 11.45. Single crystals of product **11** suitable for X-ray crystallographic analysis were obtained by slow evaporation of chloroform solution. For details on the crystal structure of compound **11**, see the CIF file in the Supporting Information. Selected crystallographic data for **11a**: triclinic, $P\bar{1}$, a = 10.2961(3) Å, b = 10.9654(3) Å, c = 11.4803(8) Å, α = 107.119(8)°, β = 105.292(7)°, γ = 104.881(7)°, V = 1113.45(14) Å^3, Z = 4, R ($I > 2.0/\sigma(I)$) = 0.0716, R_w (all) = 0.1959, CCDC 1055744. Selected crystallographic data for **11b**: monoclinic, $P2_1/c$, a = 11.8176(2) Å, b = 20.2033(4) Å, c = 14.6196(10) Å, β = 93.472(7)°, V = 3484.1(3) Å^3, Z = 8, R ($I > 2.0/\sigma(I)$) = 0.0342, R_w (all) = 0.0913, CCDC 1055745.

*Optimized Preparation of Dibenziodolium Hydrogen Sulfate (**13**) from 2-Iodobiphenyl Using Oxone As Oxidant.* 2-Iodobiphenyl **6** (2 mmol, 0.56 g, 0.35 mL) was mixed with finely powdered Oxone (1.3 mmol, 0.8 g) in a 25 mL round-bottom flask and stirred without solvent until a homogeneous reaction mass was formed. The reaction mixture then was cooled with ice to 5 °C, and precooled to 5 °C concentrated H_2SO_4 (0.8 mL) was added by 0.2 mL portions to the center of the reaction mixture under magnetic stirring. After addition of each portion of H_2SO_4 the reaction mass was mechanically shaken to achieve better mixing; the color of the resulting mass can vary from pale yellow to gray depending on the intensity of mixing. After all H_2SO_4 was added, the stirring was continued for 1 h at 5 °C and then 1 h at room temperature. The mixture of water with crushed ice (15.0 mL) then was added to the reaction mixture. The pale yellow solid was formed immediately. Stirring was continued until melting of all ice. The solid was filtered off, washed by cold water (2 × 10.0 mL), and dried under vacuum. Dibenziodolium hydrogen sulfate **13** was isolated as pale yellow crystals (0.658 g, 87% yield); mp 260−261 °C (lit.[53] >260 °C). ^{1}H NMR (500 MHz, CD_3OD): δ 8.37 (d, J = 8.0 Hz, 2H), 8.17 (d, J = 8.5 Hz, 2H), 7.86 (t, J = 7.5 Hz, 2H), 7.70 (t, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, CD_3OD): δ 142.1, 130.9, 130.8, 130.3, 126.8, 120.1. Anal. Calcd for $C_{12}H_9IO_4S\cdot H_2O$: C, 36.57; H, 2.81; I, 32.19; S, 8.13. Found: C, 36.24; H, 2.64; I, 32.07; S, 8.12.

*General Procedure for Preparation of Dibenziodolium Salts from Dibenziodolium Hydrogen Sulfate (**13**).* An aqueous solution of a ligand source (3 mL of solution containing 3 mmol of the ligand source) was added to the solution of dibenziodolium hydrogen sulfate **13** (1 mmol, 0.375 g) in 15.0 mL of methanol under vigorous stirring. An immediate formation of a white precipitate was observed. Stirring was continued for 20 min. The solid was filtered off, washed by cold water (2 × 5.0 mL), and dried under vacuum.

*Dibenziodolium Chloride (**14a**).* The reaction of dibenziodolium hydrogen sulfate **13** with NaCl (0.176 g, 3 mmol) according to the general procedure afforded 0.27 g (85%) of dibenziodolium chloride **14a** as a white crystalline solid; mp 345−348 °C with decomposition (lit.: mp 293−294 °C,[54] >310 °C,[55] >300 °C[56]). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.55 (d, J = 8.5 Hz, 2H), 8.42 (dd, J = 1.5, 8.0 Hz, 2H), 7.79 (t, J = 8.0 Hz, 2H), 7.65 (t, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 141.7, 131, 130.8, 130.7, 126.7, 124.5. Anal. Calcd for $C_{12}H_8ClI$: C, 45.82; H, 2.56; I, 40.35; Found: C, 45.51; H, 2.65; I, 40.35.

*Dibenziodolium Bromide (**14b**).*[53] The reaction of dibenziodolium sulfate **1** with NaBr (0.357 g) according to the general procedure afforded 0.28 g (80%) of dibenziodolium bromide **14b** as a white crystalline solid; mp 335−336 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.53 (d, J = 8.0 Hz, 2H), 8.42 (dd, J = 1.5, 8.0 Hz, 2H), 7.81 (t, J = 7.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 141.6, 131.1, 130.99, 130.95, 126.8, 124.1. Anal. Calcd for $C_{12}H_8BrI$: C, 40.15; H, 2.25; I, 35.35. Found: C, 39.92; H, 2.27; I, 35.07.

*Dibenziodolium Thiocyanate (**14c**).* The reaction of dibenziodolium hydrogen sulfate **13** with KSCN (0.291 g) according to the general procedure afforded 0.3 g (90%) of dibenziodolium thiocyanate **14c** as a white crystalline solid; mp 239−241 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.47 (dd, J = 1.0, 7.5 Hz, 2H), 8.21 (d, J = 8.5 Hz, 2H), 7.84 (t, J = 8.0 Hz, 2H), 7.7 (t, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.1, 131.5, 131.2, 130.9, 130.1, 127.5, 123.2. Anal. Calcd for $C_{13}H_8INS$: C, 46.31; H, 2.39; I, 37.64; N, 4.15; S, 9.51. Found: C, 46.20; H, 2.42; I, 37.82; N, 4.12; S, 9.45. Single crystals of product **14c** suitable for X-ray crystallographic analysis were obtained by slow evaporation of MeOH solution. For details on the crystal structure of compound **14c**, see the CIF file in the Supporting Information. Selected crystallographic data for **14c**: monoclinic, $P2_1/c$, a = 7.8592(3) Å, b = 15.6109(5) Å, c = 9.4890(6) Å, β = 90.895(6)°, V = 1164.06(9), Z = 4, R ($I > 2.0/\sigma(I)$) = 0.0310, R_w (all) = 0.0844, CCDC 1055743.

*Dibenziodolium Azide (**14d**).* The reaction of dibenziodolium hydrogen sulfate **13** with NaN_3 (0.195 g) according to the general procedure afforded 0.24 g (75%) of dibenziodolium azide **14d** as a white crystalline solid; mp 236 °C (with explosive decomposition). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.43 (d, J = 7.5 Hz, 2H), 8.22 (d, J = 8.5 Hz, 2H), 7.81 (t, J = 7.5 Hz, 2H), 7.66 (t, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 141.8, 131.2, 131.1, 130.9, 127.0, 123.4. Anal. Calcd for $C_{12}H_8IN_3$: C, 44.88; H, 2.51; I, 39.52; N, 13.09. Found: C, 44.73; H, 2.40; I, 39.41; N, 12.93. Single crystals of product **14d** suitable for X-ray crystallographic analysis were obtained by slow evaporation of MeOH−water solution. For details on the crystal structure of compound **14d**, see the CIF file in the Supporting Information. Selected crystallographic data for **14d**: triclinic, $P\bar{1}$, a = 7.4374(6) Å, b = 8.7655(8) Å, c = 9.8437(9) Å, α = 113.251(8)°, β = 92.400(7)°, γ = 111.062(8)°, V = 537.44(10) Å^3, Z = 2, R ($I > 2.0/\sigma(I)$) = 0.0438, R_w (all) = 0.1225, CCDC 1055742.

*General Procedure for Preparation of Dibenziodonium Salts (**14**) from Dibenziodolium Trifluoromethanesulfonate (**10**).* An aqueous solution of a ligand source (3 mL of solution containing 3.0 mmol of the ligand source) was added to the solution of dibenziodolium trifluoromethanesulfonate **10** (1.0 mmol, 0.428 g) in 10.0 mL of methanol under vigorous stirring. An immediate formation of a white precipitate was observed. The stirring was continued for 20 min. The solid was filtered off, washed by cold water (2 × 5.0 mL), and dried under vacuum.

Dibenziodolium salts **14a−d** (X = Cl, Br, SCN, N_3) were synthesized from dibenziodolium trifluoromethanesulfonate according to this procedure; see Table 1 for the yields.

*Dibenziodolium Phenylsulfinate (**14e**).* The reaction of dibenziodolium trifluoromethanesulfonate **10** with sodium phenylsulfinate (0.492 g, 3.0 mmol) according to the general procedure afforded 0.31 g (75%) of dibenziodolium sulfinate **14e** as a white crystalline solid; mp 219−220 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.40 (t, J = 8.5 Hz, 4H), 7.85 (t, J = 7.5 Hz, 2H), 7.61 (t, J = 8.0 Hz, 4H), 7.37 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.0, 131.4, 130.9, 130.7, 128.8, 128.7, 128.4, 126.8, 124.5, 123.2. Anal. Calcd for $C_{18}H_{13}IO_2S$: C, 51.44; H, 3.12; I, 30.20; S, 7.63. Found: C, 51.06; H, 3.24; I, 30.53; S, 7.51.

*Dibenziodolium Cyanide (**14f**).* The reaction of dibenziodolium trifluoromethanesulfonate **10** with sodium cyanide (0.147 g, 3.0 mmol) according to the general procedure afforded 0.25 g (85%) of dibenziodolium cyanide **14f** as a white crystalline solid; mp 166−168 °C (with explosive decomposition). ^{1}H NMR (500 MHz, CD_3OD): δ 8.32 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 8.0 Hz, 2H), 7.81 (t, J = 7.5 Hz, 2H), 7.65 (t, J = 8.0 Hz, 2H). ^{13}C NMR (CD_3OD, 125 MHz): δ 141.8, 130.6, 130.2, 133.1, 126.3, 121.5, 121.1. Anal. Calcd for $C_{13}H_8IN\cdot 1/2H_2O$: C, 49.71; H, 2.89; I, 40.40; N, 4.46. Found: C, 50.04; H, 2.70; I, 40.86; N, 4.48. The presence of $1/2H_2O$ in cyclic iodonium derivatives is a common phenomenon confirmed by X-ray structural data.[57]

*General Procedure for Preparation of Dibenziodonium Salts (**14**) from Dibenziodolium Bis(trifluoromethane)sulfonimidate (**11**).* A solution of the ligand source (5.0 mL, containing 3.0 mmol of the ligand source) in 7.5 mL of methanol/water mixture (2:1 v/v) was added to the solution of dibenziodolium bis(trifluoromethane)sulfonimidate **11** (1 mmol, 0.428 g) in 7.5 mL of methanol/water mixture (2:1 v/v) under vigorous stirring. Immediate formation of a white precipitate was

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observed. The stirring was continued for 20 min. The solid was filtered off, washed by cold water (2 × 5.0 mL), and dried under vacuum.

Dibenziodolium salts **14a–f** (X = Cl, Br, SCN, N_3, CN, OSOPh) were synthesized from dibenziodolium bis(trifluoromethane)-sulfonimidate **11** according to this procedure; see Table 1 for the yields.

■ ASSOCIATED CONTENT

Supporting Information

X-ray data for compounds **11**, **14c**, and **14d** (CIF files) and copies of NMR spectra for all compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00741.

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Notes

The authors declare no competing financial interest.

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