



Preparation and X-ray structures of 2-[(aryl)iodonio]benzenesulfonates: novel diaryliodonium betaines

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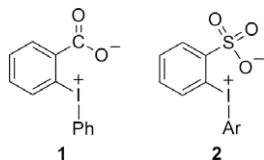
ABSTRACT

Herein we present a concise preparation and characterization of 2-[(aryl)iodonio]benzenesulfonates. Determination of the X-ray crystal structure reveals a distorted trigonal bipyramidal molecular geometry about iodine and a pseudo-square geometry within the unit cell. Initial experiments point to the promising application of these compounds for unique 2-sulfonyloxyarenes.

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1. Introduction

From the first preparation of phenyl(4-iodophenyl)iodonium bisulfate¹ through the pioneering work of Beringer and coworkers,² the application and study of arylidonium and heteroarylidonium salts experienced a relatively latent induction period.³ Since then, the remarkable nucleofugacity of the iodoarene moiety has led to the application of these compounds in a wide range of synthetic and practical applications. Substantial investigations into arylation of various nucleophiles, the preparation of ¹⁸F-labeled radiotracers as well as the generation of benzyne intermediates, photo-initiation of polymerization, and application as microbicides have been published and summarily reviewed.⁴ Having been observed to be more reactive than conventional haloarenes, the use of these compounds has shared the recent renaissance in metal-catalyzed cross-coupling reactions such as the Suzuki–Miyaura, Sonogashira as well as recently reported oxidative functionalization of C–H bonds.⁵



Although a myriad of structural types coupled with various anions are known, diaryliodonium salts with intramolecular anions are comparatively rare and for the most part are subtypes of one well researched example: diphenyliodonium-2-carboxylates, **1**.⁶ Several reports of (aryloxy)aryliodonium inner salts have also ap-

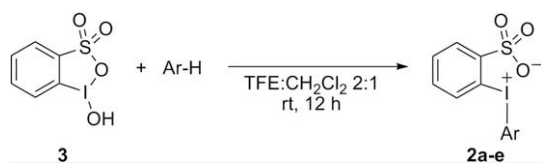
peared.⁷ Indeed, to our knowledge these are the only examples that have been structurally characterized.^{8,9} It must be noted that several examples of arylidonium salts have appeared in the literature with significant secondary bonding interactions with a group *ortho*- to the iodonium center,^{10,11} as well as those classified as heterocyclic iodanes,¹¹ diaryliodonium zwitterions,¹² or λ_5 -iodanes.¹³ Given the broad application of these compounds, the preparation of new examples to increase their structural diversity would be advantageous. Herein we present the synthesis, characterization, and X-ray structures of 2-[(aryl)iodonio]benzenesulfonates, **2** novel diaryliodonium betaines.

2. Results and discussion

Many methods are available for the preparation of arylidonium salts.⁴ Given the unique structure of the target molecule, it was reasoned that the dehydrative condensation starting from 1*H*-1-hydroxy-1,2,3-benziodoxathiole 3,3-dioxide (HBI, **3**) was the most efficacious approach.¹⁴ HBI was readily prepared using the modified procedure reported previously for the 5-methyl derivative.^{14b} Subsequent preparation of a series of **2a–e** was best effected by using the recently published direct dehydrative method for the preparation of diaryliodonium salts in fluoroalcohol solvents.¹⁵ To a 0.2 M solution of HBI in 2,2,2-trifluoroethanol:CH₂Cl₂ (2:1) was added the corresponding arene and the solution stirred for 12 h at room temperature. Concentration in vacuo of the reaction mixture to an oily semi-solid followed by trituration with ether and MeOH afforded the corresponding **2a–d** in high yields (Table 1). In the case of the comparatively unactivated phenyl derivative **2e**, this method afforded a low yield (12%). However, dehydrative condensation of **3** with benzene in the presence of trifluoromethanesulfonic acid gave **2e** in higher yield (entry 5).¹⁶ These compounds are highly stable—a sample stored open under ambient conditions having virtually identical spectral and physical properties after thirty days.

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Table 1
Preparation of 2-[(aryl)iodonio]benzenesulfonates **2a–e**



Entry	Ar=	Yield (%)	
1	2a	2,4,6-Trimethyl	91
2	2b	4-OCH ₃	92
3	2c	4-Cl	74
4	2d	4-CH ₃	88
5	2e	Ph	60

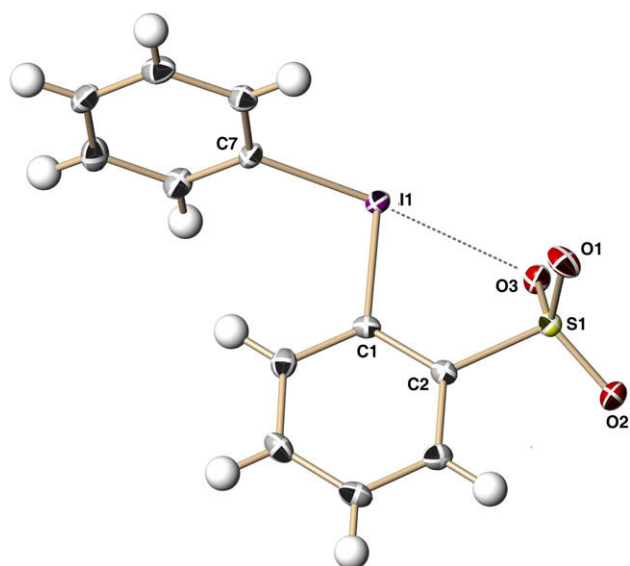


Figure 1. X-ray crystal structure of 2-[(phenyl)iodonio]benzenesulfonate **2e**. Selected distances [Å] and angles [°]: I1–O3 2.676, I1–C1 2.129(2), I1–C7 2.097(2), S1–O3 1.461(2), S1–O2 1.438(1), S1–O1 1.448(2), C7–I1–O3 170.16(6), C7–I1–C1 96.17(8), O3–I1–C1 74.79(6).

Crystals suitable for X-ray analysis were readily grown in aqueous acetonitrile for **2a–c** and **e**. Many iodonium salts with free anions have been structurally characterized, but for purposes of discussion, comparison with the more closely analogous **1** with an intramolecular counter-ion is presented here.⁸ Typical aryl-iodonium salts (with consideration of the anion) are formally 10-I-3 systems possessing distorted trigonal bipyramidal geometry. The apical positions are occupied by two more electronegative moieties. In the specific case of **1** and **2a–e** salts, this is not possible (Fig. 1). The C1–I1–C7 bond angle (96.17°) is similar to that observed for **1** (95.2(1)°) with roughly equivalent C1–I1 (2.129 Å) and C7–I1 (2.097 Å) bond lengths observed compared to **1** (2.119 Å and 2.106 Å, respectively). The C7–I1–O3 bond angle (170.16°) is markedly less linear than ‘classic’ diaryliodonium salts, but similar to **1** (169.0°). The I1–O3 bond (2.676 Å) is markedly longer than the analogous bond in **1** (2.478 Å), suggesting reduced covalent character and a greater contribution of the betaine form rather than covalent benzenesulfonate. For comparison, in the observed solid-state structure of **3**, this bond is markedly shorter (2.381 Å).^{14a}

Two major observations are apparent from the comparison of the crystal structures of **1** and **2e**. First, the 2-aryliodoniumbenzenesulfonates are non-hydrates. Second, there is a significant intermo-

lecular close contact observed between the I1 center in the unit cell and the O1 atom in an adjacent molecule (2.786 Å) which is not present in **1** (Fig. 2). This contact is close enough to classify the iodine center as a pseudo-square-planar in geometry. While at first inspection **2** seems unique in this regard many other iodonium salts display this phenomenon including the diphenyliodonium halides (Cl, Br, and I)¹⁷ as well as **3**^{14a}.

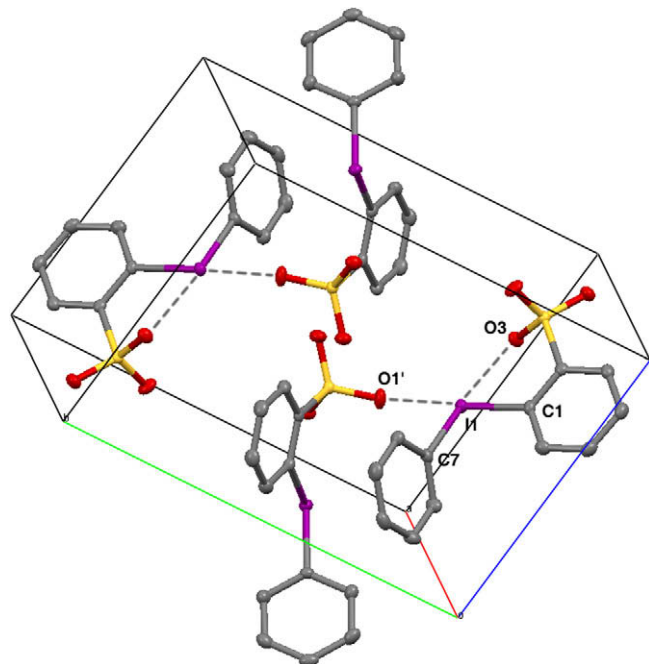


Figure 2. Unit cell of 2-[(phenyl)iodonio]benzenesulfonate **2e** showing the pseudo-square planar geometry about the iodine atom (hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]: I1–O1' 2.786, O1'–I1–C7 92.06(6), O1'–I1–O3 97.22(5).

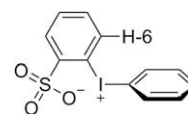
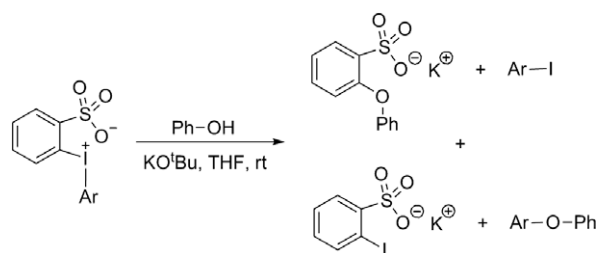
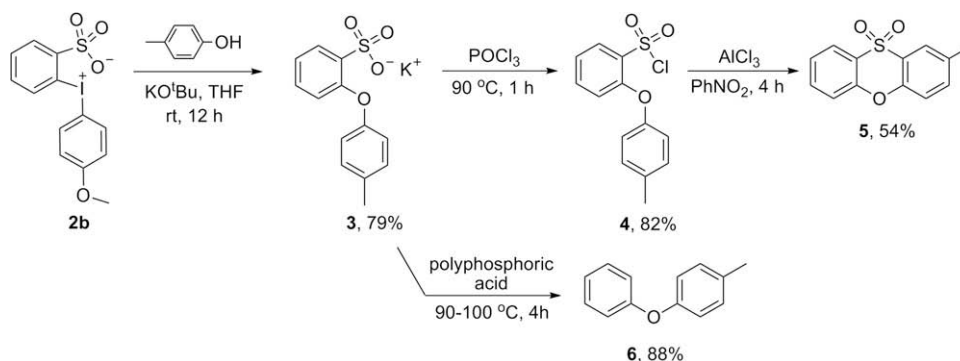


Figure 3. Suggested solution phase geometry of **2a–e** based on the magnetic anisotropy of ¹H-6.

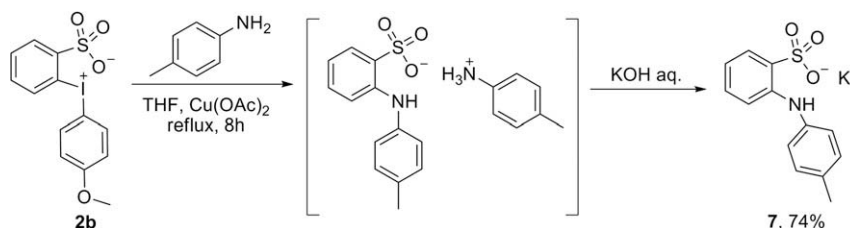
Table 2
Competition study: ratio of attack on benzenesulfonate versus aryl ring with phenoxide nucleophile



Entry	Ar=	Ratio Ar-I:Ar-O-Ph	
1	2a	2,4,6-Trimethyl	78:22
2	2b	4-OCH ₃	>99:1
3	2c	4-Cl	81:19
4	2d	4-CH ₃	95:5
5	2e	Ph	85:15



Scheme 1. Preparation of potassium 2-aryloxybenzenesulfonates and subsequent reactions.



Scheme 2. Arylation of *p*-toluidine with **2b**.

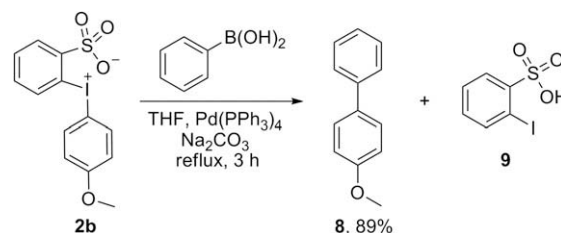
^1H NMR spectra reveal an upfield shift of the aromatic signal (δ 6.75–7.02) assigned to H-6 (Fig. 3) similar to that observed for **1**.¹⁸ The authors purport that this is an indication that the solution phase structure most closely resembles the solid-state structure where H-6 exhibits a strong magnetic anisotropy, given its proximity over the opposing aromatic ring.

A brief survey of typical arylodonium salt chemistry was performed on **2a–e**. While symmetric diarylodonium salts are most often applied in synthesis for the sake of simplicity, current trends are toward asymmetric salts where the reaction mode can quantitatively be directed to one of the two aryl moieties through electronic or steric effects. Initial experiments were directed to determine the ratio of nucleophilic attack between the two aryl rings using potassium phenoxide in THF (Table 2).¹⁹ The ratios were determined by comparison of the Ar-I and Ar-OPh resonances in the ^1H NMR spectra of the crude reaction mixtures. Nucleophilic attack proceeds predominately on the more electron-poor sulfonate-bearing aryl ring. However, only in the case of **2b** is nucleophilic attack directed quantitatively (to the limits of detection) to the sulfonate-bearing ring.

With this in mind, the arylation of phenoxide was carried out using **2b** as the precursor and potassium 2-(4-methylphenoxy)benzenesulfonate **3** was obtained (Scheme 1). Application of these compounds²⁰ is illustrated in the ring closure to effect the preparation of phenoxathiin 10,10-dioxides such as **5** with AlCl_3 in PhNO_2 . Attempts at ring closure under dehydrating conditions (polyphosphoric acid at 90–100 °C) yielded solely the 4-phenoxytoluene **6**.

Arylation of *p*-toluidine occurred only in a high yield with the addition of $\text{Cu}(\text{OAc})_2$ and heating under reflux with an additional equivalent of substrate (Scheme 2).²¹ Initially, the ammonium salt was isolated and subsequently converted to the diarylamine **7** by alkaline hydrolysis.

Given the recent focus on metal-catalyzed coupling reactions,⁵ the suitability of these compounds for aryl donors in Suzuki–Miyaura reactions was also explored. Previous observations show that the most electron-rich aryl ring is transferred.⁵ Indeed when **2b** was combined with phenylboronic acid in the presence of a palla-



Scheme 3. Demonstration of Suzuki–Miyaura coupling reactions with **2b**.

dium catalyst and a base under reflux, 4-phenylanisole **8** was isolated as the major product. The advantage of **2** for these transformations is the simplification of the reaction mixture. The reduced 2-iodobenzenesulfonate **9** is removed in the initial aqueous extraction and can be isolated and reused with high efficiency^{14b} (see Scheme 3).

3. Conclusion

In conclusion we have presented a concise preparation and characterization of 2-(aryliodonio)benzenesulfonates. While possessing the general molecular geometry of a distorted trigonal bipyramidal, iodine exhibits a pseudo-square geometry in the unit cell. Initial experiments point to the promising application of these compounds for unique 2-sulfonyloxyarenes and a potential recyclable aryl-carrier for metal-catalyzed cross-coupling reactions.

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Supplementary data

Crystallographic data for the structural analyses of **2a–c** and **e** have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 742878, 742879, 742880, and 742881). Copies of this information can be obtained free of charge via www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2009.08.067](https://doi.org/10.1016/j.tetlet.2009.08.067).

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