

Communication

# Synthesis and Properties of *ortho-t*-BuSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-Substituted Iodonium Ylides

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**Abstract:** Iodonium ylides have recently attracted much attention on account of their synthetic applications. However, only a limited number of reports concerning the properties and reactivity of iodonium ylides exist, which is partly due to their instability. In this study, we synthesized several iodonium ylides that bear both an electron-withdrawing group and an aromatic ring with an *ortho-t*-BuSO<sub>2</sub> group. Based on the crystal structures of the synthesized iodonium ylides in combination with natural-bond-orbital (NBO) calculations, we estimated the strength of the intra- and intermolecular halogen-bonding interactions. In addition, we investigated the reactivity of the iodonium ylides under photoirradiation.

**Keywords:** halogen bonding; hypervalent iodine; NBO analysis; photochemistry; radical reactions



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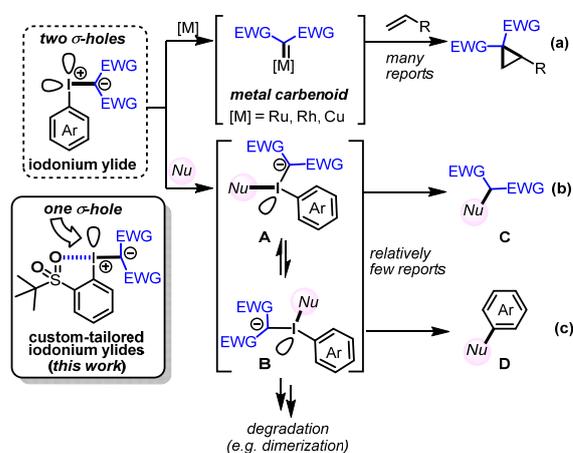
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## 1. Introduction

Iodonium ylides, a class of hypervalent iodine compounds [1], have attracted much attention due to their use as carbene precursors for C-H-insertion and cyclopropanation reactions (Scheme 1a) [2,3]. Moreover, iodonium ylides have been used for various synthetic applications, including condensations with thioamides to produce thiazole rings in aqueous media (Scheme 1b; Nu = thioamide) [4,5], and for the introduction of <sup>18</sup>F atoms into aromatic rings (Scheme 1c; Nu = F<sup>-</sup>) [6,7]. It has also been reported that depending on the iodonium ylide and nucleophile that is employed, the equilibrium between the T-shaped intermediates A and B can be influenced [6,7], and thus, the ratio of coupling products C and D can be controlled.



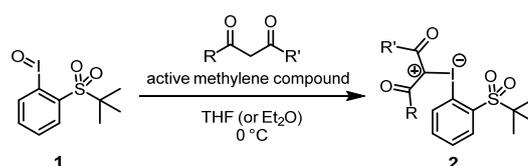
**Scheme 1.** General synthetic utility of iodonium ylides. (a) Cyclopropanation of alkenes (b) Introduction of nucleophile into active methylene compound (c) Introduction of nucleophile into aromatic rings.

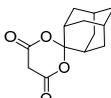
However, to date, only a limited number of reports concerning the properties and reactivity of iodonium ylides have been published, which is at least in part due to their instability (e.g., degradation via intermediates A and/or B) on account of the remaining  $\sigma$ -hole of intermediates A and B, which can react with nucleophiles such as water. We anticipate that the synthesis of a variety of iodonium ylides and the investigation of their properties would provide essential information for the advancement of synthetic applications such as chemoselective coupling reactions. Of particular interest to us are iodonium ylides that contain a coordinating *ortho* group on the aromatic ring [8], as such groups are known to stabilize iodonium ylides and other hypervalent iodine compounds [5–9], thus increasing their solubility via intramolecular halogen bonding (XB) [10]. In this study, we synthesized several iodonium ylides bearing both an electron-withdrawing group and an aromatic ring with an *ortho*-*t*-BuSO<sub>2</sub> group [8,11]. Based on the crystal structures of the synthesized iodonium ylides in combination with natural-bond-order (NBO) analysis, we also estimated the strength of the intra- and intermolecular XBs [12–23]. In addition, we investigated the reactivity of these iodonium ylides under photoirradiation [24–27].

## 2. Results

We began by synthesizing iodonium ylides **2** via the condensation of iodosobenzene **1** [11] with a variety of active methylene compounds (Table 1). The reaction of **1** and the active methylene compounds proceeded at 0 °C in etheric solvents such as THF or Et<sub>2</sub>O to furnish the corresponding iodonium ylides (**2**) as precipitates with H<sub>2</sub>O, as the sole byproduct. The desired products were collected by simple suction filtration and, following an *n*-hexane wash, produced the pure compounds in acceptable yield (for details, see the Supplementary Materials). The major advantage that this method [28] has over the conventional method that uses iodoarene diacetate and an active methylene compound under basic conditions is that it eliminates the need to remove the formed salt (e.g., KOAc or NaOAc) with an H<sub>2</sub>O wash [29]. We tested a wide range of active methylene compounds, which produced iodonium ylides **2a–h** in 27–89% yield without significant decomposition during the purification. This is presumably due to the enhanced electrophilicity of the iodosobenzene compound and the increased stability of the product due to the presence of the coordinating *ortho*-sulfonyl group.

**Table 1.** Synthesis of various iodonium ylides that bear an *ortho*-*t*-BuSO<sub>2</sub> group on the aromatic ring (**2**) from iodosobenzene **1**.

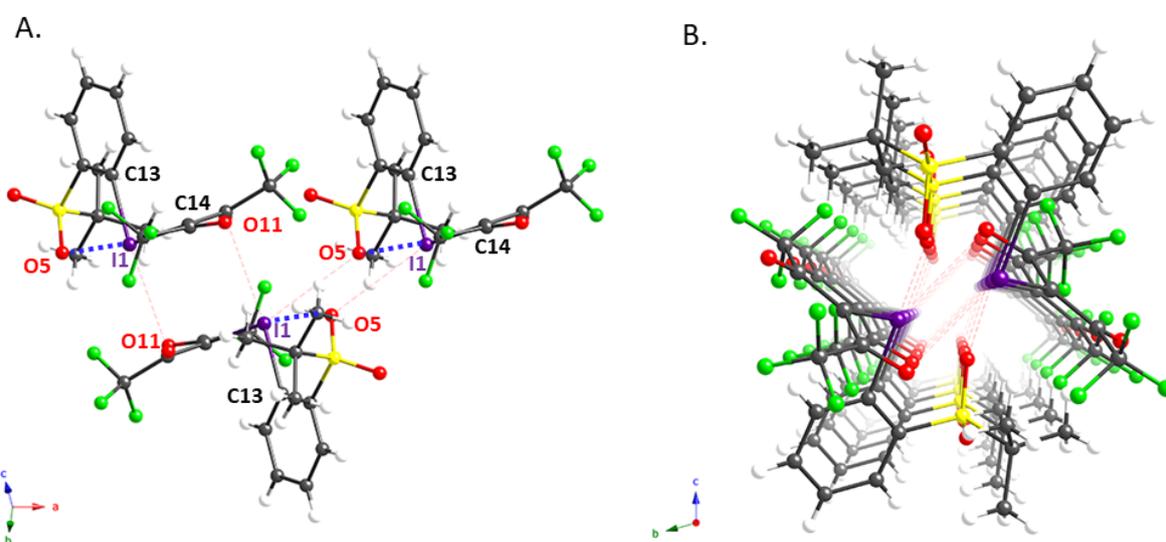


Entry	Active Methylene Compound	Solvent	Time	Product	Yield (%) <sup>a</sup>
1	R = R' = OMe	THF	22 h	<b>2a</b>	67
2	R = Me, R' = OEt	THF	4 h	<b>2b</b>	43
3	R = CF <sub>3</sub> , R' = OEt	Et <sub>2</sub> O	23 h	<b>2c</b>	78
4	R = R' = Me	THF	16 h	<b>2d</b>	57
5	R = R' = CF <sub>3</sub>	THF	1 min	<b>2e</b>	27
6	Dimedone	THF	1.5 h	<b>2f</b>	89
7	Meldrum's acid	THF	10 min	<b>2g</b>	56
8		THF	15 min	<b>2h</b>	74

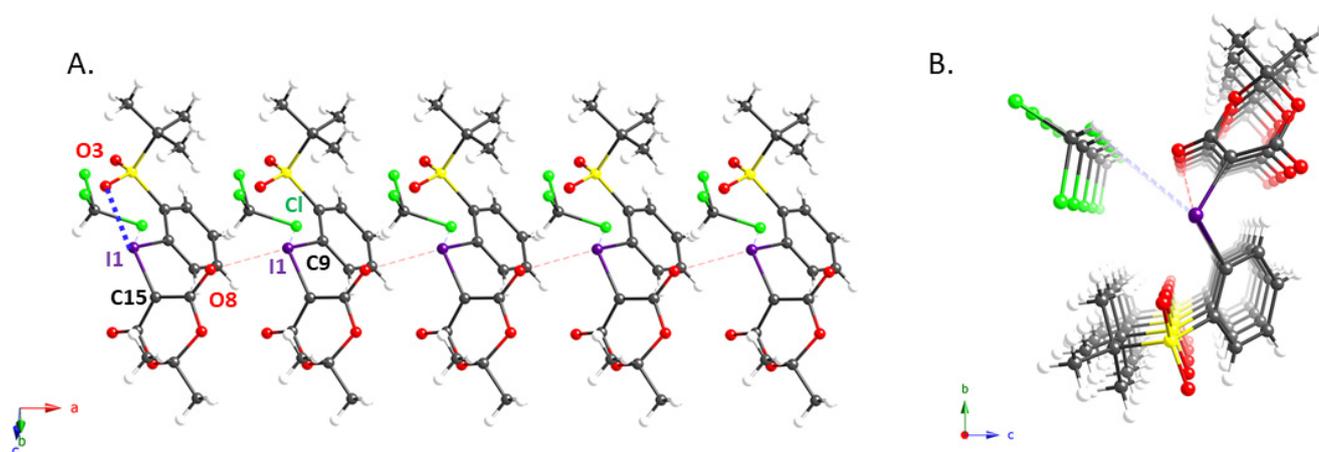
<sup>a</sup> Isolated yields.

We also succeeded in obtaining single crystals of **2e** and **2g** that were suitable for an X-ray diffraction analysis; the molecular structures of these compounds are shown in

Figures 1 and 2, while pertinent crystallographic parameters are summarized in Table 2. As expected, the distance between the iodine atom (I1) and the oxygen atom (O5) of the *ortho*-sulfonyl group in **2e** (2.737(3) Å) is within the sum of the van der Waals radii, implying the presence of an intramolecular XB interaction [10,19]. In addition, the analysis of the packing structure suggested the presence of an intermolecular XB in the solid state, in which the carbonyl oxygen (O11) and sulfonyl oxygen (O5) interact with the hypervalent iodine atom of **2e** (Figure 1A). It is probably due to these interactions that **2e** aligns to form the dimeric columnar structure shown in Figure 1B. The X-ray structure of **2g**, which contains a residual molecule of chloroform, shows an intermolecular XB in addition to the intramolecular XB with the *ortho*-*t*-BuSO<sub>2</sub> group seen in **2e** (Figure 2). This implies that this iodonium ylide may be able to recognize the substrates in coupling reactions via XB interactions.



**Figure 1.** Crystal structure of iodonium ylide **2e**: (A) sideview of **2e**; (B) dimeric columnar structure formed by two stacked columns of **2e**.

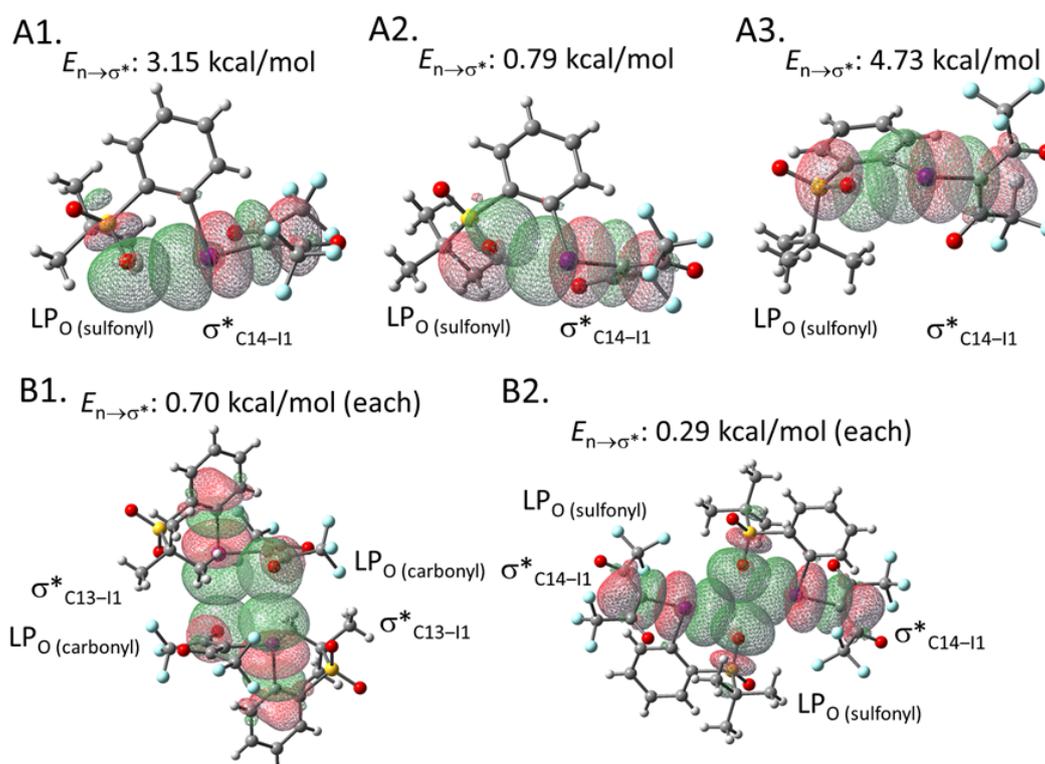


**Figure 2.** Crystal structure of iodonium ylide **2g**: (A) sideview of **2g**; (B) columnar structure formed by one stacked column of **2g** and residual chloroform molecules.

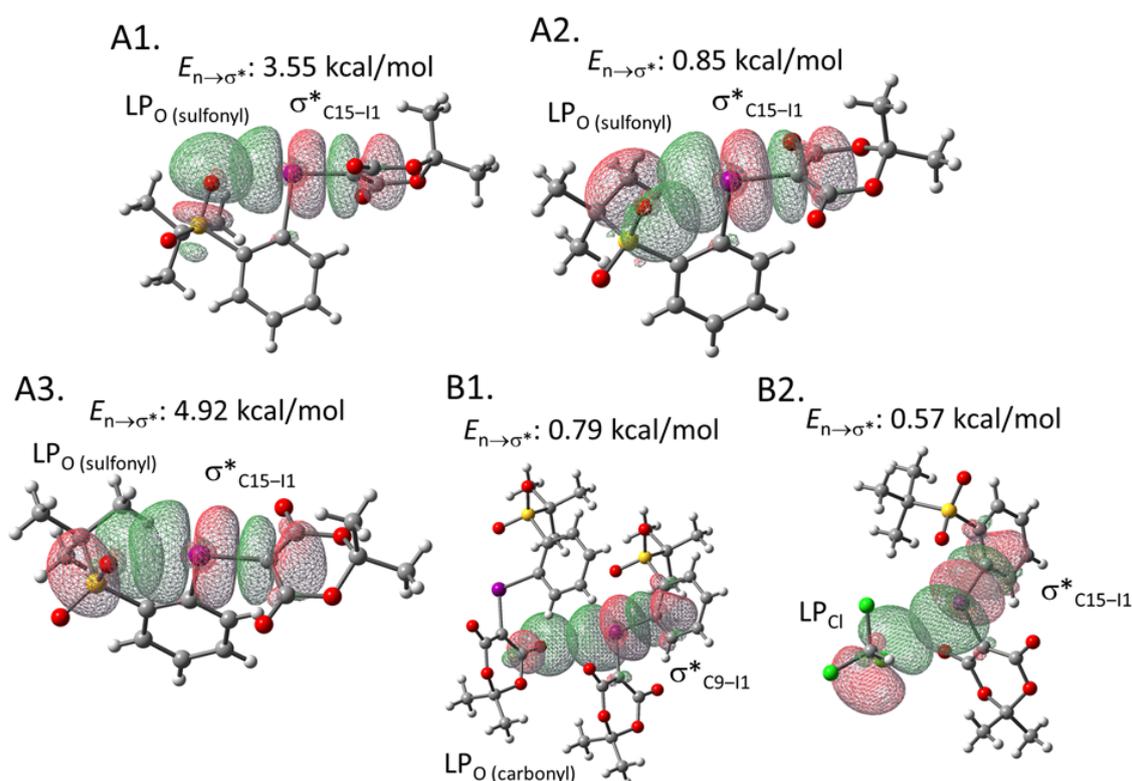
**Table 2.** Crystallographic parameters of the intra- and intermolecular XB interactions in the crystals of iodonium ylides **2e** and **2g**.

Compound	C-I⋯O (or C-I⋯Cl)	$d(I⋯O)/\text{\AA}$	$\angle(C-I⋯O)$ or $\angle(C-I⋯Cl)/\text{Deg}$
<b>2e</b>	C14-I1⋯O5 (intramolecular)	2.737 (3)	164.0
	C13-I1⋯O11 (intermolecular)	3.269 (4)	156.3
	C14-I1⋯O5 (intermolecular)	3.451 (3)	132.5
<b>2g</b>	C15-I1⋯O3 (intramolecular)	2.695 (3)	170.5
	C9-I1⋯O8 (intermolecular)	3.411 (4)	159.5
	C9-I1⋯Cl (intermolecular)	3.673	136.4

To estimate the interaction energies of the intra- and intermolecular XBs, we performed an NBO analysis based on the crystal structure of **2e**, using the gaussian software package (Figure 3) [30,31]. The analysis demonstrated that the C14-I1  $\sigma^*$  orbital of the hypervalent iodine moiety in **2e** overlaps with the three types of lone pairs (LPs) of the intramolecular sulfonyl oxygen (O5) (See the Supplementary Materials for the details of orbitals). The energies of these interactions were calculated to be 3.15, 0.79, and 4.73 kcal/mol, respectively (Figure 3A). Moreover, the intermolecular XB energies were estimated to be 0.70 and 0.29 kcal/mol, respectively (Figure 3B). These interaction energies may contribute to the relative stability of this type of iodonium ylide. The corresponding results of the NBO analysis performed for iodonium ylide **2g** are summarized in Figure 4. The interaction energies seem to be stronger when the interaction distance is shorter and the interaction angle is closer to  $180^\circ$ , which is an ideal situation for XB interactions (Table 2).

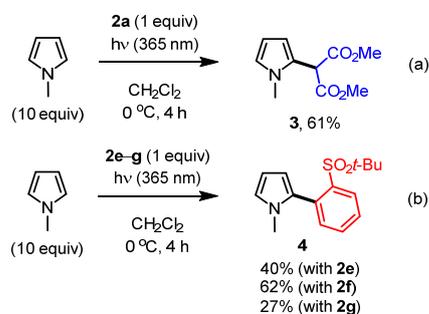


**Figure 3.** NBO analysis of iodonium ylide **2e**. (A1) Intramolecular XB between a lone pair of the sulfonyl group (Orbital#71) and the C14-I1  $\sigma^*$  orbital (Orbital#136) (type 1). (A2) Intramolecular XB between a lone pair of the sulfonyl group (Orbital#120) and the C14-I1  $\sigma^*$  orbital (Orbital#136) (type 2). (A3) Intramolecular XB between a lone pair of the sulfonyl group (Orbital#119) and the C14-I1  $\sigma^*$  orbital (type 3) (Orbital#136). (B1) Intermolecular XB between a lone pair of the carbonyl group and the C13-I1  $\sigma^*$  orbital. (B2) Intermolecular XB between a lone pair of sulfonyl group and the C13-I1  $\sigma^*$  orbital.



**Figure 4.** NBO analysis of iodonium ylide **2g**. (A1) Intramolecular XB between a lone pair of the sulfonyl group (Orbital#58) and the C15-I1  $\sigma^*$  orbital (Orbital#123) (type 1). (A2) Intramolecular XB between a lone pair of the sulfonyl group (Orbital#105) and the C15-I1  $\sigma^*$  orbital (Orbital#123) (type 2). (A3) Intramolecular XB between a lone pair of the sulfonyl group (Orbital#104) and the C15-I1  $\sigma^*$  orbital (Orbital#123) (type 3). (B1) Intermolecular XB between a lone pair of the carbonyl group and the C9-I1  $\sigma^*$  orbital. (B2) Intermolecular XB between a lone pair of the Cl group and the C9-I1  $\sigma^*$  orbital.

Finally, we investigated the reactivity of the synthesized iodonium ylides under photoirradiation conditions (Scheme 2) [9,24–27]. When ylide **2a** and ten equivalents of *N*-methylpyrrole were irradiated at 365 nm, the active methylene group was introduced at the C2 position of *N*-methylpyrrole in 61% yield (Scheme 2a). Unexpectedly, when ylide **2e–g** and ten equivalents of *N*-methylpyrrole were irradiated at 365 nm, the aryl group (2-*t*-BuSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) of the ylide was exclusively introduced at the C2 position of *N*-methylpyrrole (Scheme 2b).



**Scheme 2.** (a) Reactivity of iodonium ylide **2a** under photoirradiation conditions. (b) Reactivity of iodonium ylide **2e–g** under photoirradiation conditions.

Based on these observations and recent related reports by other groups [7], the reaction seems to proceed via a T-shaped tri-coordinated intermediate, which is different from a free carbene species [32]. The T-shaped tricoordinated intermediate could be formed via

a biradical species generated via photoirradiation [33]. The unexpected selectivity of the reductive elimination might be explained by the steric hindrance of the dione and Meldrum's acid moieties in **2f** and **2g**, although a detailed mechanism for this transformation, including the selectivity in the case of **2e**, is not clear at this stage. Iodonium ylides **2c** and **2h** gave the coupling product **4** in 43% and 31%, respectively, while **2b** and **2d** did not afford any coupling products, presumably due to degradation under photoirradiation.

### 3. Conclusions

We have synthesized a series of novel iodonium ylides that bear a coordinating *ortho-t*-BuSO<sub>2</sub> group on their aryl rings, and we have analyzed the crystal structures of two of these molecules. Intra- and intermolecular halogen bonding (XB) interactions were observed in the crystal structures of two ylides that were structurally characterized by X-ray diffraction analysis. The synthesized iodonium ylides were found to serve as active transfer reagents of methylene or aryl groups. Further synthetic applications and mechanistic studies are currently under investigation in our laboratory.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/cryst11091085/s1>: Detailed compound characterization data and copies of NMR charts.

**Author Contributions:** Conceptualization, Y.K. and Y.T.; methodology, T.K.; software, S.H., T.F. and Y.K.; validation, S.H., T.F. and Y.K.; formal analysis, T.K.; investigation, T.K.; resources, T.K.; data curation, T.K.; writing—original draft preparation, Y.K.; writing—review and editing, S.H., T.F. and Y.T.; visualization, Y.K.; supervision, Y.K. and Y.T.; project administration, Y.K. and Y.T.; funding acquisition, Y.K. All authors have read and agreed to the published version of the manuscript.

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