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Solid state aggregation of cyclic iodonium ylides

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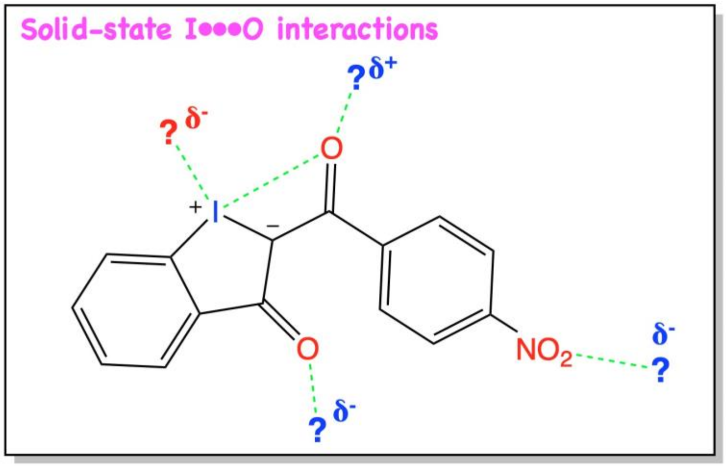
Abstract

Iodonium ylides (ArI=CR(R")) represent unusual hypervalent iodine(III) sources of carbene equivalents. While their reactivity is well-described, their detailed structural chemistry is somewhat limited due to their thermal instability. Cyclic iodonium ylides typically have greater thermal stability than acyclic ylides, but so far few such materials have been examined by single crystal X-ray diffraction methods. This report details the synthesis of two cyclic iodonium ylides and their association in the solid state by intermolecular I•••O interactions.



Keywords: Hypervalent iodine, crystal structure, iodonium ylide, secondary bonding

Introduction

Iodonium ylides of the form ArI=CR(R") are an important subclass of hypervalent iodine (HVI) compounds that have found widespread utility.[1-6] Applications of iodonium ylides continue to grow, in particular, as sources of carbene equivalents.[7-15] While a large number of acyclic iodonium ylides have been reported, fewer cyclic iodonium ylides have been described.[16-24] Enhanced thermal stability is noted for ylides where the iodine atom is part of a five membered ring. Many iodonium ylides of the form PhI=CR(R") also display poor solubility.[22-24] Notable exceptions include *ortho*-alkoxy-substituted derivatives *o*-RO-$C_6H_4I=C(CO_2Me)_2$ reported by Zhdankin and coworkers.[23] This novel compound features a pseudo-cyclic five membered ring with an intramolecular I•••O interaction that discourages intermolecular I•••O interactions as well as aggregation and thus improves solubility.[25]

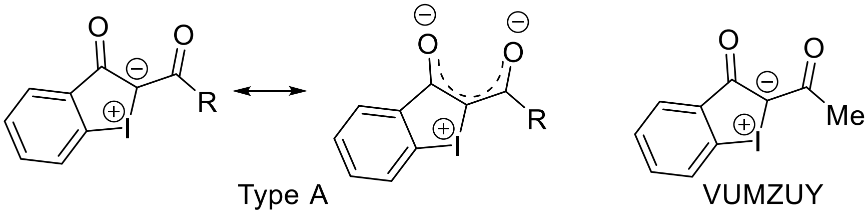


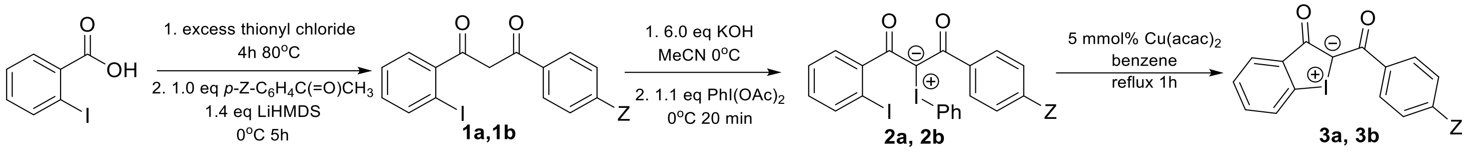
Figure 1. Thermal stable five-membered ring iodonium ylides (type A) and structure VUMZUY.

We have recently reported on crystal structural analyses of *para*-donor-substituted $ArI(OAc)_2$ and their associated intra- and inter-molecular I•••O interactions, with the goal of rationally designed supramolecular materials.[26] These studies revealed that intramolecular I•••O interactions from the vicinal carbonyl oxygen atoms of the carboxylate groups tended to block access to the iodine(III) centers from prospective electron rich donor groups of neighboring molecules. Cyclic iodonium ylides thus offered the opportunity to examine HVI compounds free of interference of the directly bound carboxylate groups. As an extension of our studies, we have thus explored the potential of cyclic iodonium ylides to give organized structures in the solid state that might capitalize upon both the electrophilic iodine center and the somewhat more distant electron rich carbonyl atoms in structures of the type A (Figure 1). Since cyclic iodonium ylides displace greater thermal stability, our initial studies have focused on two cyclic ylides. Prior to this study, only one other related single crystal structure analysis was reported for a cyclic iodonium ylide (Figure 1, VUMZUY).[22] This report adds important structural details from single crystal X-ray diffraction studies on two more cyclic iodonium ylides.

Results and Discussion

For this work, our attention was focused on a pair of cyclic iodonium ylides as shown in Scheme 1. Compound **3b** was targeted since our previous work on $ArI(O_2CR)_2$ showed that remote nitro groups promoted intermolecular I•••O interactions and extended structures. Compound **3a** was reported previously, and was prepared in order to ascertain its solid state structure in comparison to nitro-substituted **3b**.[22]

Synthesis of cyclic iodonium ylides



Scheme 1. Synthesis of cyclic iodonium ylide compounds**.** (a: Z=H, b: Z=NO_2).

The synthesis of **3b** followed the reported synthesis of **3a** as shown in Scheme 1. Commercially available 2-iodobenzoic acid was treated with excess thionyl chloride to generate an intermediary benzoyl chloride, which was not isolated but was directly reacted with the appropriate acetophenone to produce compounds **1a** and **1b**.[27] Compounds **1a** and **1b** upon reaction with (diacetoxyiodo)benzene afforded iodonium compounds **2a** and **2b**.[28] Cyclization of compounds **2a,2b** to **3a**,**3b** was achieved by the reaction of copper (II) acetylacetonate catalysis under reflux in benzene.[29] Compounds **3a** and **3b** were isolated as pale yellow, thermally stable (r.t.), crystalline compounds in yields of around 25%, sufficient for crystallographic analyses. In solution, however, these compounds slowly decompose. The NMR spectra in DMSO-d_6 for these materials are in general agreement with the expected structures, but the presence of missing, broad, and/or additional resonances probably reflects the Lewis acidic character of the hypervalent iodine centers. In particular, it is likely that strong donor DMSO oxygen atoms interact in a dynamic manner with the iodine center to complicate the NMR spectra.

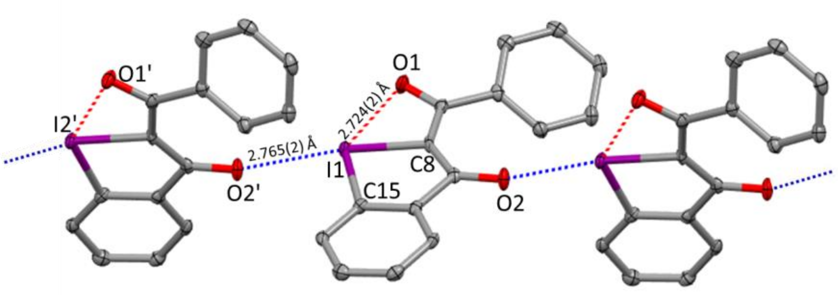


Figure 2. Structural representation of compound **3a** in the solid state. (ellipsoids drawn at 50% probability). Selected bond lengths (Å) I1—C8, 2.090(3); I1—C15, 2.099(3).

Structure Analysis of 3a & 3b

Crystals suitable for single-crystal X-ray diffraction analyses for **3a** were grown by vapor diffusion of hexanes into a solution of **3a** in DCM, and the results confirmed a cyclic iodonium ylide (Figure 2). The structural analysis reveals a ylidic C—I bond length of 2.090(3) Å, which is only slightly contracted compared to the phenyl C—I bond 2.099(3) Å. The C—I—C bond angle is 82.5(1)°. Located approximately *trans* (137.5°) to the phenyl C—I bond is one of the carbonyl oxygen atoms (O1) at 2.724(2) Å, which is shorter than the sum of iodine and oxygen van der Waal radii of 3.50 Å.[30] The iodine also has a short I1•••O2' contact with a neighboring molecule at a distance of 2.765(2) Å. This intermolecular O•••I—C angle is 166.3(2)°, which is indicative of secondary or halogen bonding between iodine and oxygen atoms.[31-32] These intermolecular contacts bridge molecules **3a** into a linear polymer as portrayed in (Figure 2) in the solid state.

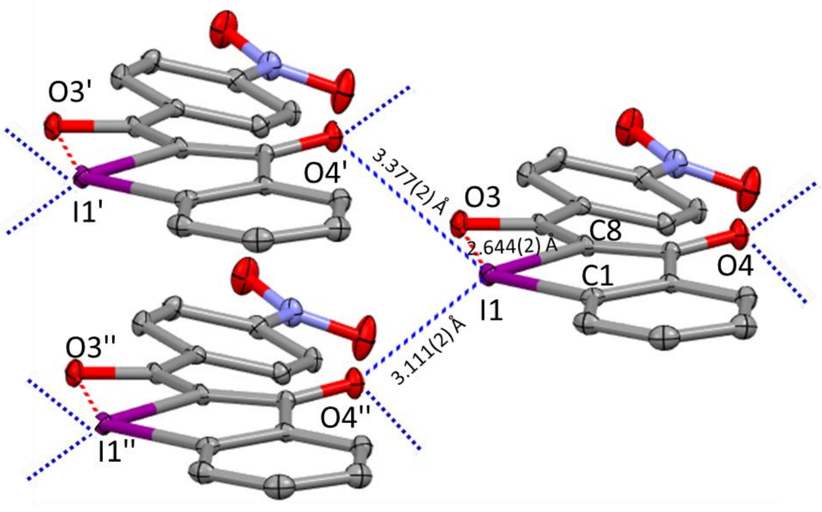


Figure 3. Structural representation of compound **3b** in the solid state. (ellipsoids drawn at 50% probability). Selected bond lengths (Å):I1—C1, 2.103(3); I1—C8, 2.101(3).

Crystals suitable for single-crystal X-ray diffraction analyses for nitro-derivative **3b** were grown by vapor diffusion of diethyl ether into a solution of **3b** in DMF, and the resulting analysis also confirmed it as an analogous cyclic iodonium ylide (Figure 3). In the structure, the ylidic C—I bond length is 2.102(3) Å, the phenyl C—I bond length is 2.101(3) Å and C—I—C bond angle is 82.5(1)°. As seen for **3a**, there is an intramolecular I•••O interaction (2.724(2) Å) located approximately *trans* (138.8°) across from the phenyl C—I bond in **3b**. Compound **3b**, however, has two weaker intermolecular I•••O interactions (3.111(2) Å and 3.377(2) Å) replacing the single I•••O intermolecular interaction in **3a**. This results in molecules of **3b** packing in stacks bridged by these associations (Figure 3). A direct comparison of the individual structures of **3a** and **3b** is highlighted in Figure 4 where a best overlay of the iodonium rings of both compounds are made. The key difference between the two molecules is a slight rotation of the peripheral phenyl ring of **3a** out of the plane of the iodonium ring, which is presumably induced by the packing in the solid state.

Table 1. Comparison of key structural parameters of **3a**, **3b** and VUMZUY. Note: R* indicated R group of type A in Figure 1

Structure	R*	Ylidic C—I bond length (Å)	Ph C—I bond length (Å)	C—I—C bond angle (°)	Intra I•••O interactions (Å)	Inter I•••O interactions (Å)
3a	Ph	2.090(3)	2.099(3)	82.5(1)	2.724(2)	2.765(2)
3b	*p*-nitro-Ph	2.101(3)	2.103(3)	82.5(1)	2.644(2)	3.111(2)/3.377(2)
VUMZUY	Me	2.084(5)	2.096(5)	82.1(2)	2.898(4)	3.312(5)

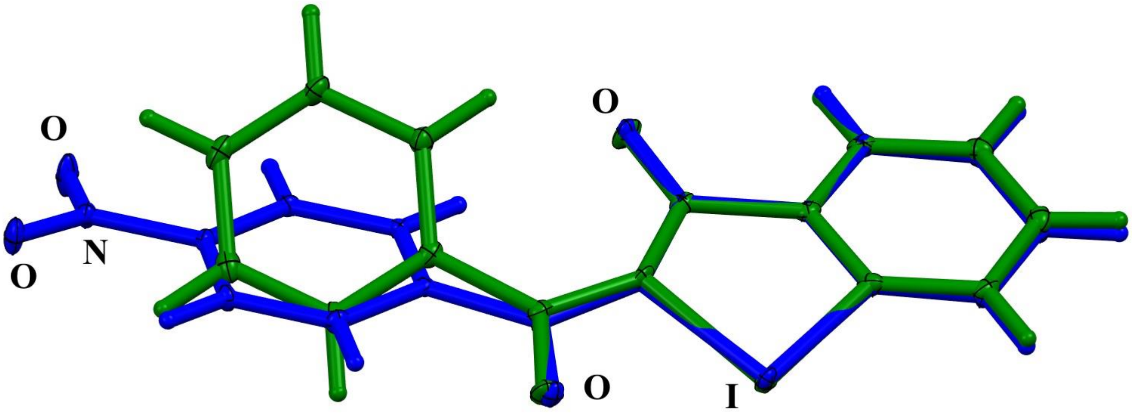


Figure 4. The overlay comparison of **3a** (green) and **3b** (blue).

The structures of **3a** and **3b** can be also compared to the related cyclic iodonium ylide structurally characterized (VUMZUY, Figure 1, Table 1).[22] The values of ylidic C—I bond length (2.084(5) Å), the phenyl C—I bond length (2.096(5) (Å)), and C—I—C bond angle (82.1(2)°), are similar to those found in **3a** and **3b**. A pair of weaker bifurcated intermolecular I•••O interactions bridges molecules of VUMZUY, as does a stronger I•••O interaction is found as 2.898(4) Å.

Conclusions

In summary, two cyclic iodonium ylide structures have been obtained and detailed comparisons were made. The introduction of nitro group did not introduce NO•••I interactions, but did trigger a change in the intermolecular I•••O interactions, shifting compound **3a** from a linear polymer type packing to a zig-zag stacked type structure found in **3b**. Intramolecular parameters in compounds **3a** and **3b** are remarkably similar despite marked differences in packing. This work should aid future efforts to design iodonium ylides having rationally designed intermolecular I•••O interactions.

Experimental Section

General. All starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. ^1H NMR and ^{13}C {^1H} NMR spectra were obtained on Bruker Avance III HD 500 MHz NMR Spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to residue solvent signals. Melting points were determined with Mel-Temp apparatus and are uncorrected. Compounds **1a**-**3a** and **1b**-**2b** were prepared as previously described and found to have matching NMR properties with those as reported.[22, 27-29, 33-34] The synthesis and handling of HVI compounds in general should be done carefully and on small scales, owing to reports of explosive decomposition under heating and/or extensive drying.[35-36]

Compound 3b. 2-(4-Nitrobenzoyl)-3-oxo-2,3-dihydrobenzo[b]iodolyl ylide**:** Compound **2b** (0.60 g, 1.0 mmol) and benzene (30 mL) was added into a 100 mL flask to make a solution. The solution was then added copper(II) acetylacetonate (13.1 mg, 5 mmol %) and refluxed for 1h. Filtered to get the solid and washed with diethyl ether and dried. Recrystallized via vapor diffusion (diethyl ether into a solution of **3b** in DMF). Yield: 0.24 g, 61.5%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.31 (s, 4H), 8.19 (d, J = 7.9 Hz, 1H), 7.82 – 7.71 (m, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 177.58, 172.12, 163.08, 148.71, 144.28, 142.71, 134.08, 131.30, 130.38, 130.10, 122.97, 112.01, 35.86, 30.83. Mp 205 °C dec.

Acknowledgements

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Supplementary Material

The Supporting Information is available free of charge at XXXX. It includes details info of synthetic and experimental procedures, NMR spectral (^{1}H and ^{13}C (^{1}H)) and X-ray crystallographic structures.

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