Heterocyclic Hypervalent Iodine(III) Compounds with Fused Benziodazole and Tetrazole Rings (I-Substituted Tetrazolo[1,5-b][1,2]Benziodazoles)

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ABSTRACT

A series of heterocyclic hypervalent (HV) iodine(III) compounds containing fused tetrazole and benziodazole rings, i.e., derivatives of benziodazolotetrazole (BIAT) with various ligands attached to the iodine atom were prepared and studied. 5-Chloro-5H-5λ^3-tetrazolo[1,5-b][1,2]benziodazole (BIAT-Cl) was synthesized via chlorination of 5-(2-iodophenyl)-1H-tetrazole and subsequent spontaneous cyclo-dehydrochlorination of the initially formed dichloroiodo compound. The oxidation of the aforementioned parent monovalent iodine substrate with $NaIO_4$ yielded 5-hydroxy-5H-5λ^3-tetrazolo[1,5-b][1,2]benziodazole (BIAT-OH), which was in turn reacted with acetic anhydride to afford the *I*-acetoxy derivative (BIAT-OAc). 5-Methoxy-5H-5λ^3-tetrazolo[1,5 b][1,2]benziodazole (BIAT-OMe) was obtained by refluxing the latter compound or by dissolving (2-(1H-tetrazol-5-yl)phenyl)(hydroxy)iodonium tosylate in methanol. All heterocyclic HV iodine(III) compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, ESI-HRMS, and single crystal X-ray crystallography. The reaction of alkenes with BIAT-Cl in the presence of $Cu(OTf)_2$ at room temperature afforded chloro-tetrazolylated products in 70-88% isolated yields. The oxidation of thioanisole with BIAT-Cl under various reaction conditions is also reported. The thermal stabilities of all BIAT derivatives were examined as well. The enthalpies of exothermic degradation

were measured by thermal gravimetric analysis coupled with differential scanning calorimetry and were determined to be in the range between −35.3 and −305.3 kJ mol^{-1}, i.e., significantly larger than the enthalpy of decomposition (−29.4 kJ mol^{-1}) of the parent monovalent iodine-containing tetrazole – 5-(2-iodophenyl)-1H-tetrazole.

INTRODUCTION

The organic compounds of polyvalent iodine were discovered in 1886 by Willgerodt who showed that the chlorination of iodobenzene afforded a yellow crystalline solid, (dichloroiodo)benzene $C_6H_5ICl_2$.[1] Within several years, numerous additional organic compounds of both iodine(III) and (V) were reported, and the first monograph on the subject, by Willgerodt, published in 1914, contained hundreds of examples. The molecular structures of these compounds and especially the nature of the bonds involving the polyvalent iodine atom have been of significant interest to physical organic and theoretical chemists since at least the 1930s when the crystal structures of salts with iodine-containing polyhalide anions (e.g., triodide[2] and dichloroiodide[3]) were analyzed. These early structural studies became the inspiration for the first proposed bonding models, in which the p-orbitals (but not the d-orbitals) of the central polyvalent halogen were involved.[4,5] The most noticeable feature of HV iodine molecules is the presence of the almost linear fragment(s) L-I-L', where L and L' are electronegative ligands bonded to the tri- or pentavalent iodine atom *via* 3-center-4-electron (3c-4e) bonds, dubbed hypervalent (HV) bonds.[6] These bonds are weaker than the "classical" covalent (2c-2e) bonds and are responsible for the unique reactivity of HV iodine(III) and (V) compounds as electrophiles, radical sources (after homolysis of the HV bonds), and oxidants. Typical examples of L and L' include halide (fluoride and chloride), *O*-ligands (such as carboxylate, phsphonate, and sulfonate), *N*-ligands (e.g., azide or other pseudohalides, amide, and terazolylate), as well as perfluoralkyl groups. The major aspects of the structural and applied chemistry of HV iodine(III) and (V) compounds, including their utility in organic and polymer synthesis, have been summarized in several monographs[7-11] and review papers.[12-23]

There are numerous examples where one of the ligands and the iodine atom are a part of a ring, typically five-membered, which, in most known examples, is fused with an aromatic, e.g., benzene, ring. In fact, the existence of heterocyclic HV iodine(III) compounds was first suggested in 1892 when Meyer and Wachter studied the oxidation of 2-iodobenzoic acid **1**,[24] which yields *I*-hydroxybenziodoxolone **3b** (Scheme 1). The chlorination of the same acid affords the corresponding yellow dichloroiodo compound **2**, which, upon drying, undergoes rapid and spontaneous cyclo-dehydrochlorination to the heterocyclic compound **3a**.[25-27] The formation of a HV iodine-containing heterocycle fused with an aromatic ring leads to marked stabilization due to the bridging of the equatorial and apical positions at the HV center,[28] as well as the improved overlap of the nonbonding electrons at the HV iodine(III) atom with the π-orbitals of the conjugated aromatic system.[13] The stability of five-membered I-O heterocycles is the chief reason why benziodoxoles with I-F,[29-32] I-Br,[33] I-OR,[34-36] I-OOR,[37-40] I-N_3,[41-43] I-CN,[43-45] and I-CF_3[31,46] bonds could be easily prepared and isolated, despite the fact that many of the corresponding acyclic analogues with the same ligands decompose readily. The reactivity and single-crystal X-ray crystal structures of benziodoxoles have been studied in great detail and summarized in several reviews.[11,20,47] In general, benziodoxoles have a planar structure with distorted T-shaped geometry around the HV iodine atom. More recent examples of I-O heterocyclic compounds include benziodoxaboroles,[48] benziodoxathioles,[49,50] and cyclic phosphonates.[51] In 1965, Wolf and Steinberg reported another class of heterocyclic HV iodine(III) compounds, the benziodazoles, in which the I(III) atom is bonded to a nitrogen atom in a five-membered ring fused to a benzene ring.[52] The first example of a crystal structure was that of *I*-acetoxybenziodazole,[53] but a large variety of HV I-N-heterocycles have since been discovered and studied.[54] including benziodoxaboroles,[48] benziodoxathioles,[49,50] and cyclic phosphonates.[51]

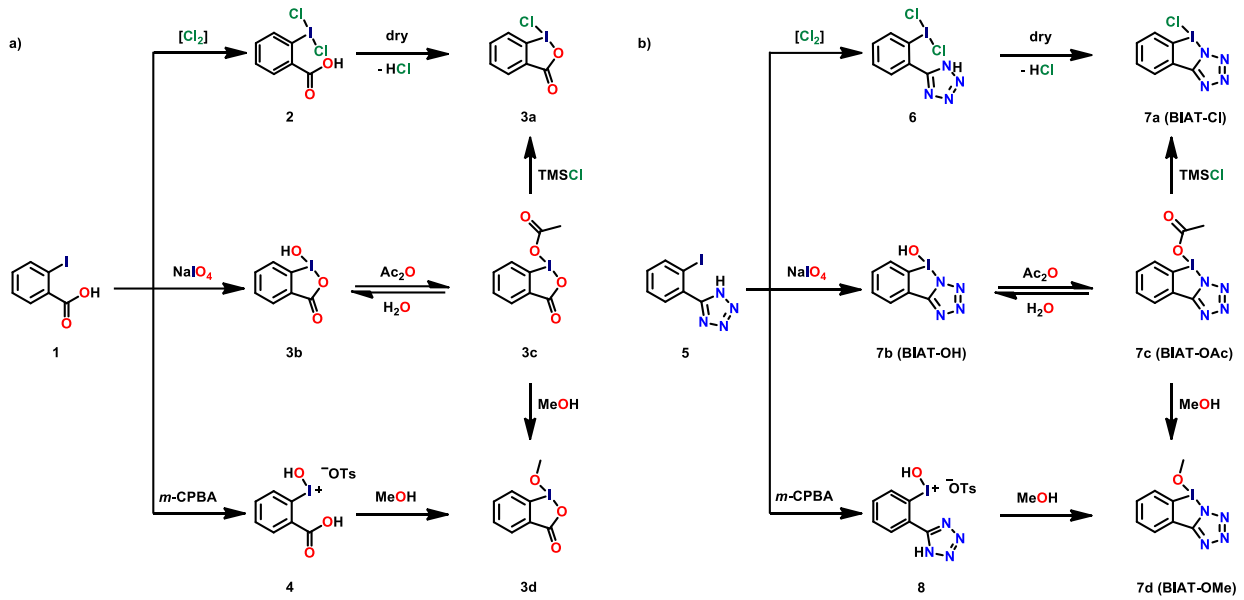
We recently demonstrated[55] that tetrazolates RCN_4^-, similarly to carboxylates RCO_2^-, bind efficiently to HV iodine(III) centers. The synthesis, structural characterization, thermal degradation, electrochemical behavior, and reactivity were reported for a number of tetrazole-containing HV iodine(III) compounds with the general formula RCN_4-[I(Ar)-O)]$_n$-I(Ar)-N_4CR (R = CH_3, C_6H_5, or 4-$CH_3C_6H_4$, and n

= 0, 1, ≥2; the compounds with n = 0 are the tetrazole analogues $ArI(N_4CR)_2$ of (diacyloxyiodo)arenes $ArI(O_2CR)_2$). Furthermore, we described the synthesis and characterization of an *N*-tetrazole-stabilized pseudocyclic HV iodine(III) compound, (2-(1H-tetrazol-5-yl)phenyl)(hydroxy)iodonium tosylate.[56]

Herein, we report that 5-(2-iodophenyl)-1H-tetrazole **5** can be successfully employed for the synthesis of compounds **7a-d** with the benzoiodazolotetrazole (BIAT) cyclic structure (consisting of fused tetrazole and benziodazole rings) with various ligands bonded to the HV iodine(III) center. The crystal structures, reactivities, and exothermic decomposition of these new compounds were studied and are presented as well.

RESULTS AND DISCUSSION

2-Iodobenzoic acid **1** can be readily converted to benziodoxolones **3a-d** with I-Cl,[57,58] I-OH,[57] I-O_2CR,[34] and I-OMe[34] bonds, as shown in Scheme 1a. There are multiple similarities between carboxylic acids (RCO_2H) and tetrazoles (RCN_4H), including their acidities, the coordination ability of the corresponding anions RCO_2^- and RCN_4^-, and stereochemical resemblance (e.g., including bond lengths, valence angles, and the planar structure, as well as the distances between the substituents R and R' in esters RCO_2R' and the analogous 1,5-disubstituted tetrazoles RCN_4R'). Inspired by these facts, along with our recent finding that the affinity of tetrazolates and carboxylates for HV iodine(III) atoms are similar,[55] we investigated the possibility to use 5-(2-iodophenyl)-1H-tetrazole **5** as a precursor of compounds with fused benziodazole and tetrazole rings, BIAT-L, **7a-d** (L is the exocyclic ligand attached to the HV iodine(III) atom), as shown in Scheme 1b.



Scheme 1. Synthetic routes to (a) benziodoxoles **3a-d** and (b) analogous *I*-substituted HV iodine(III) compounds with fused tetrazole and benziodazole rings, BIAT-L compounds **7a-d**.

The precursor **5** was synthesized from 2-iodobenzonitrile and sodium azide, using a modified published procedure[56] (see the Supporting Information). HV iodine(III) compounds with I-Cl bonds are of interest since they have found numerous applications in organic synthesis as efficient chlorinating and oxidizing agents,[59] as well as chain transfer reagents in radical (e.g., polymerization) reactions.[60] Initially, the possibility was investigated to prepare **6** by chlorination of **5**, followed by cyclo-dehydrochlorination of the produced dichloroiodo compound **7a**, which, in analogy with the transformations that 2-iodobenzoic acid undergoes under similar conditions, was expected to be slow in solution in acetic acid but spontaneous and fast in the solid-state. Indeed, when the monovalent iodine precursor **5** was chlorinated with SO_2Cl_2 (an easy to use alternative to chlorine[61]) in acetic acid,[62] the formation of 2-(dichloroiodo)benzyltetrazole **6** was deduced visually (appearance of yellow color, typical of compounds containing the -ICl_2 group) and ascertained by NMR spectroscopy (Figures 1a and S1). The yields of **7a** were low even when the reaction was carried out with an excess of SO_2Cl_2. For instance, when 4 eq. of the chlorinating agent vs. the iodocompound **5** were employed, only a small amount of **7a** was formed (*ca.* 25 %, Figure 1b). The yield did not increase at longer reaction times, most likely due to the establishment of an equilibrium between **5**

and **6** characterized with a comparatively low equilibrium constant (similar to equilibria between other iodo- and dichloroiodo compounds[63]). More in-depth kinetic studies of the conversion of **5** to **6** (Figure 1b) confirmed that the degrees of chlorination were limited, even when a large excess of the chlorinating agent (e.g., 50 eq.) vs. the aryl iodide precursor was employed. In all cases, the formation of dichloroiodocompound **6** took less than 1 h, even at low concentrations of the starting reactant **5** (e.g., 10 mM used in the spectral studies) and the compound was stable in solution in acetic acid, i.e., no formation of **7a** was observed. (The NMR spectral characteristics of the acyclic and the cyclic HV iodine(III) compounds are distinct (Figure 1a) and allow for the occurrence of cyclization to be examined.)

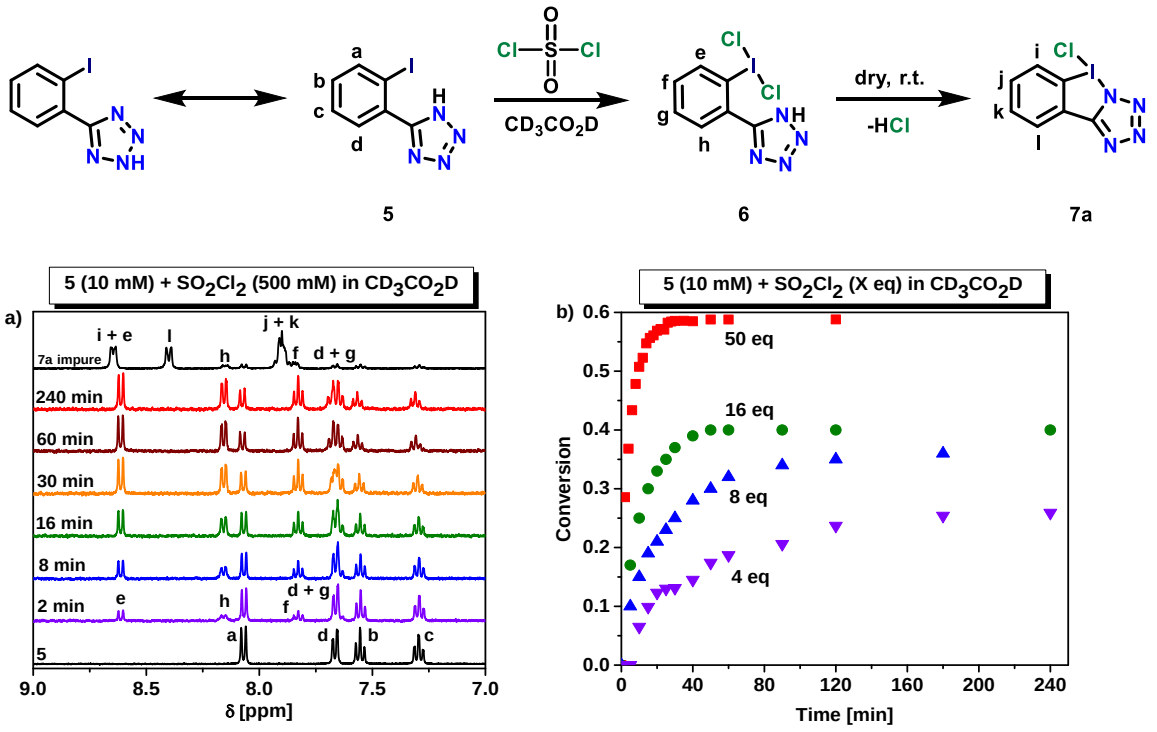


Figure 1. Evolution of ^{1}H NMR spectra during the chlorination of **5** to **6** with SO_2Cl_2 (50 eq) in CD_3CO_2D (a) and kinetics of conversion of **5** to **6** in the presence of variable amounts (with the number of equivalents indicated) of SO_2Cl_2 (b).

HV iodine(III) compounds with I-Cl bonds can also be prepared by alternative chlorination procedures. For instance, Cl_2 can be conveniently generated *in situ* in the reaction between sodium chlorite

($NaClO_2$) and concentrated HCl.[64,65] This methodology gave the desired product **7a** in 70 % yield in 16 h (Table 1, entry 2) as a light yellow powder. At first, the dichloroiodo derivative **6** was obtained as intensely yellow-colored material, which rapidly lost HCl upon drying and acquired paler yellow color. Another pathway to synthesize **7a** was the reaction of the monovalent iodine compound **5** with trichloroisocyanuric acid (TCICA) – a procedure that has been successfully utilized by Togni[31] and Xiao[66] in the preparation of various chloroiodanes. The side product of this reaction, isocyanuric acid, is insoluble in the reaction medium and can be removed by simple filtration. A suspension of **5** and TCICA in acetonitrile was refluxed for 10 min and filtered while hot. The solution was concentrated, and the resulting solid was collected by filtration. After washing with cold acetonitrile, the targeted compound **7a** was isolated (Table 1, entry 3) and found to be reasonably stable at room temperature. It could be stored for several weeks in a refrigerator (–20 ºC) in the absence of light without noticeable degradation. However, the compound is thermally unstable and decomposes explosively when heated to *ca.* 137 ºC (see video in the Supporting Information (SI)). In addition, it is extremely reactive towards reducing agents – even mild ones. For instance, the reaction of **7a** with both tribuylphosphine (moderately strong reducing agent) and DMSO (weakly reducing) is violent (see video in the SI). **7a** degrades readily in polar solvents, such as DMF and CH_3CN, as well as – as mentioned – in DMSO (Figure S2) and was found to be insoluble in many common solvents, which hampered further structural studies.

Table 1. Summary of chlorination reactions of **5** at 25 ºC under different conditions.

#	Reagent (eq vs 2)	Solvent	Time [h]	Yield [%]
1	SO_2Cl_2 (50)	CH_3CO_2H	1	60 [a]
2	$NaClO_2$ (3) + HCl (2)	H_2O	16	70 [b]
3	TCICA (0.6)	CH_3CN	0.17	65 [b]

[a] Yield of **7a** as calculated by ^{1}H NMR spectroscopy. [b] Isolated yield of **7a**.

The monovalent iodine compound **5** could also be successfully oxidized with $NaIO_4$ in aqueous acetic acid (50 % (v/v)) at 100 °C for 50 min to afford, after cooling, pale yellow crystals of the *I*-hydroxy

derivative, **7b** (Scheme 1b), the structure of which was confirmed by single-crystal X-ray crystallography (Figure 2). In order to isolate it in pure form, needed for synthesis of other BIAT compounds, a large amount of THF (*ca.* 10-fold excess by volume compared to the reaction mixture) was added to the reaction flask. This resulted in the precipitation of a byproduct, which was removed by filtration. Diethyl ether was added to this filtrate, which led to precipitation of **7b**, while the starting material **5** remained in solution. Isolated **7b** was characterized by ^{1}H and ^{13}C NMR spectroscopy, as well as ESI-HRMS. It must be noted that there remained a tiny amount of insoluble material in the NMR tube when isolated **7b** was air dried and dissolved in DMSO-d6. We speculate that it could be μ-oxo bridge-containing HV(III) iodine compound, which will be the subject of a future investigation.

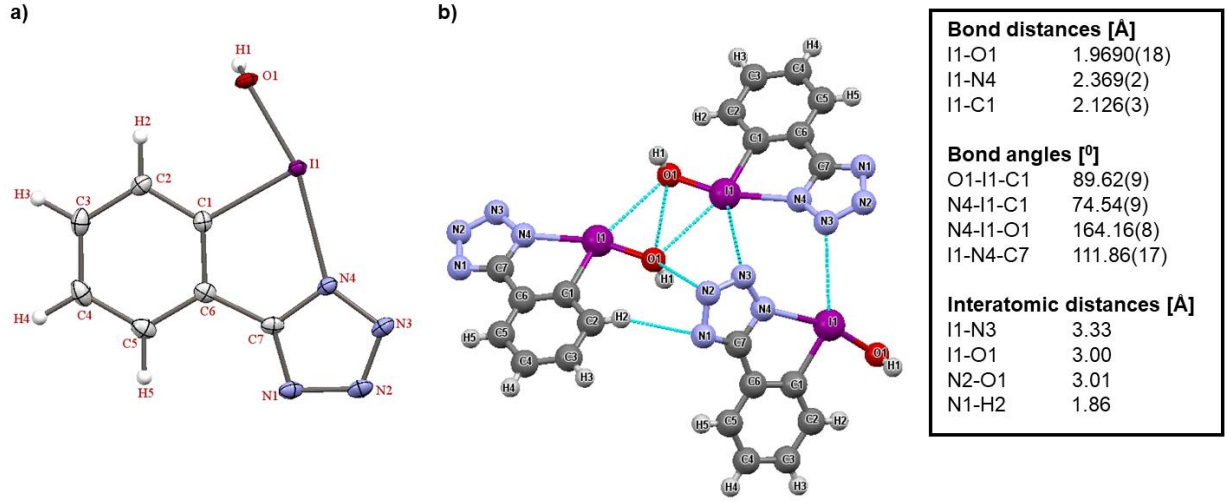


Figure 2. (a) Displacement ellipsoid plot (50% probability level) of BIAT-OH **7b** at 110(2) K. (b) Intermolecular secondary bonding in the crystals of **7b**. Selected bond lengths, angles, and interatomic distances are provided in the side panel.

The structure of **7b** has a characteristic distorted T-shaped geometry around the iodine center with N-I-O valence angle of 164.16(8)º. The HV I-O bond in **7b** (1.9690(18) Å) was determined to be markedly (by 7-10 %) shorter than the HV I-O bonds in compounds containing acetoxy ligands, e.g., both in the acyclic compounds $I(O_2CCH_3)_3$ (where the lenghts of the HV I-O bonds are in the range 2.16-2.17 Å)[67] and

$C_6H_5I(O_2CCH_3)_2$ (2.14-2.19 Å),[68] and in *I*-acetoxybenziodoxolone (where the length of exocyclic HV I-O bond is 2.11 Å).[69] However, it is comparable and only marginally shorter than the exocyclic HV I-O bond in the a related heterocylic compound with a hydroxy ligand, *I*-hydroxybenziodoxolone (2.00 Å),[70] and in the even more closely related benziodazole with methoxy ligands (2.23 Å).[54] More noteworthy is the length of the endocyclic I-N bond (2.369(2)), which was markedly longer than the I-N bonds in a bicyclic benziodazole with two HV I-N bonds (2.18 Å each),[71] *I*-chlorobenziodoazole (2.11 Å),[72] *I*-chlorosulfoximine (2.10 Å), *I*-trifluoromethylsulfoximine (2.28 Å),[73] and *I*-acetoxybenziodoazole (2.10 Å).[53] At the same time, the I-N bond in **7b** is shorter than I-N bonds with pronounced ionic character, e.g., in *I*-phenylbenziodazole (2.45),[74] and other compounds with pyridine coordinated to the HV iodine(III) atom (2.41-2.44 Å).[75] Several weak intermolecular contacts such as N2-O1, O1-I1, and I1-N3 were observed, which contributed to the formation of the dimeric assembly.

Polyvalent iodine compounds with one or more acyloxy (typically – acetoxy) ligands are among the most studied and widely used in practice.[20] They are commonly prepared by reacting iodosyl compounds or HV iodine(III) compounds with I-OH bonds with acid anhydrides. Thus, when **7b** was refluxed in acetic anhydride for 15 min, the original heterogeneous mixture turned into a clear solution, which, upon cooling to -20 ºC, afforded an off-white microcrystalline compound, 5-acetoxy-5H-5λ^3-tetrazolo[1,5-b][1,2]benziodazoles or BIAT-OAc **7c**, which was identified spectroscopically (^{1}H and ^{13}C NMR as well as ESI-HRMS), and by single-crystal X-ray crystallography (Figure 3).

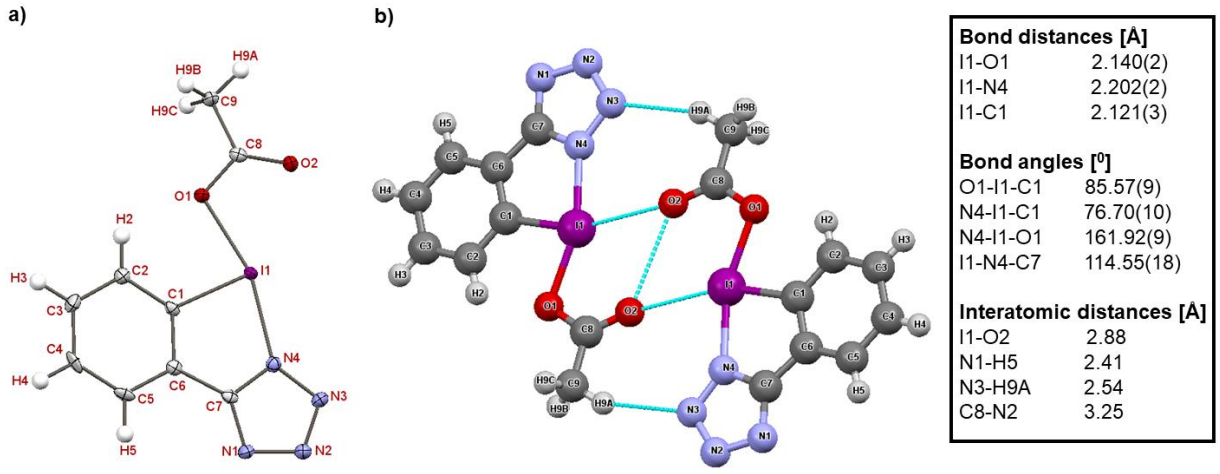


Figure 3. (a) Displacement ellipsoid plot (50% probability level) of BIAT-OAc **7c** at 110(2) K. (b) Intermolecular secondary bonding in the crystals of **7c**. Selected bond lengths, angles, and interatomic distances are provided in the side panel.

The structural data revealed the expected distorted T-shaped geometry with an N-I-O bond angle of 161.92(9)° – even more acute than in the *I*-hydroxy precursor. The lengths of the HV bonds I-N and I-O were respectively 2.202(2) and 2.140(2) Å, while the length of the I-C bond was 2.121(3), all within the typically observed ranges in similar heterocyclic compounds with an I(III) atom in the ring, e.g., the previously reported *I*-acetoxybenziodazole.[53] When compared to the I-N (2.369(2) Å) and I-O (1.9690(18) Å) bond distances in **7b** it was noted that in **7c**, the I-N bond was shorter by *ca.* 7% while the I-O bond was longer by almost 9%. Additional intermolecular I...O interactions (I1-O2) were also observed in the dimeric motifs of **7c**.

When the *I*-acetoxy derivative **7c** was refluxed for 10 min (until dissolved) in methanol, a new HV iodine(III) product was formed, namely 5-methoxy-5H-5λ^3-tetrazolo[1,5-b][1,2]benziodazole, BIAT-OMe **7d** (Scheme 1). It was found to be stable at –20 ºC for several weeks and was characterized by ^{1}H and ^{13}C NMR spectroscopy, ESI-HRMS, and single-crystal X-ray crystallography (Figure 4). Similar to the other BIAT derivatives, the structure of **7d** featured a distorted T-shaped geometry around the HV iodine(III) atom, with an N-I-O bond angle of 165.00(17)°. The lengths of the HV bonds I-N and I-O bonds were 2.276(5) and 2.014(4) Å, respectively, and that of the regular covalent I-C bond was 2.121(5) Å, similar to

reported structures of *I*-isopropoxybenziodazoles.[53] Additional intermolecular interactions between N1 and N2 of the tetrazole ring and the iodine atom from an adjacent molecule were observed in the dimeric motifs of **7d** (Figure 4b), resulting in pseudo-pentacoordinated HV iodine(III) centers. Interestingly, no intermolecular I-O interactions could be discerned.

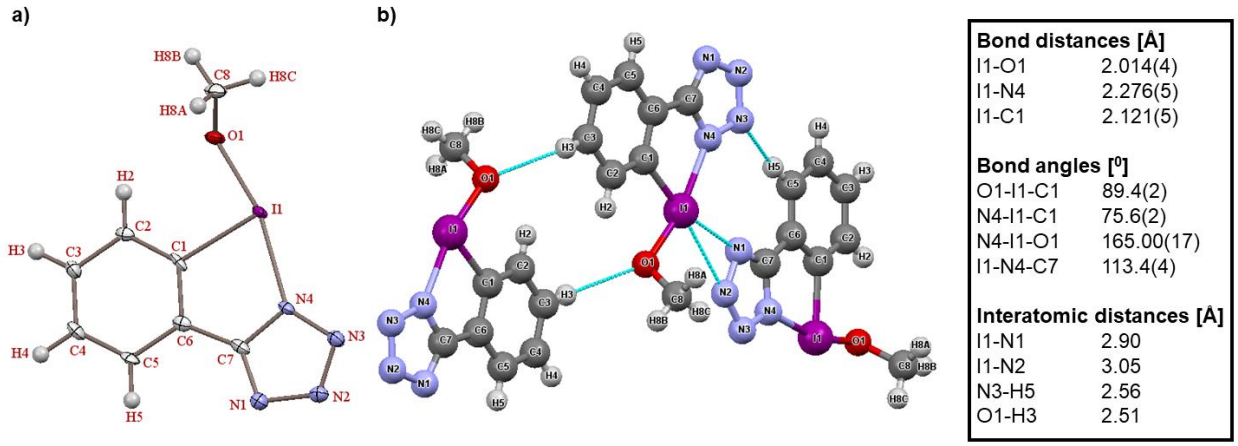
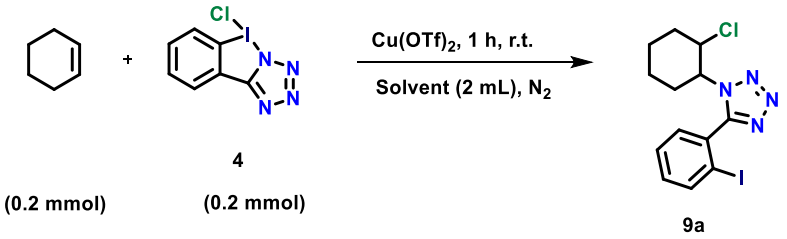


Figure 4. (a) Displacement ellipsoid plot (50% probability level) of BIAT-OMe **7d** at 110(2) K. Selected bond distances and angles are also provided. (b) Intermolecular secondary bonding in the crystals of **7d**. Selected bond lengths, angles, and interatomic distances are provided in the side panel.

Tetrazoles have found significant applications in coordination chemistry,[59,76,77] photography, specialty explosives, and in drug synthesis.[78-81] The last application is due to the fact that tetrazoles are metabolically (hydrolytically) stable analogues of carboxylate esters.[82,83] Hence, the synthesis of substituted tetrazoles and the ability to incorporate tetrazole moieties directly into a substrate are of great significance and interest. Previously, we have demonstrated the successful transfer of tetrazole groups to various olefins using HV iodine(III) compounds with tetrazole ligands.[55,84] Inspired by recent work by Loh and co-authors on the copper-catalyzed oxyazidation of styrenes by *I*-azidobenziodoxole,[85] we explored the possibility to conduct chloroterazolylation of alkenes using **7a** (Scheme 1). The simultaneous introduction of tetrazole and alkyl chloride functionalities may be advantageous and may enable further functionalizations by well-established nucleophilic substitution reactions.

To optimize the reaction conditions for the chlorotetrazolylation of alkenes with **7a**, cyclohexene was chosen as a model substrate (Table 2). The reactions were conducted in DCE at 25 °C. In the absence of $Cu(OTf)_2$, the desired product was obtained in trace amounts only (entry 1). When $Cu(OTf)_2$ (2 mol % vs. alkene) was used as the catalyst, it was gratifying to find out that after 1 h, the chlorotetrazolylation product **9a** was obtained in 33 % yield (entry 2). The yield of **9a** was further improved to 52% by extending the reaction time to 5 h (entry 3). The maximum yield of **9a** (78%) was obtained when the amount of catalyst was increeased to 10 mol %. The reactants (entry 4). Substituting DCE for other solvents, such as CH_3CN, DMF, or THF did not imporve the reaction outcome (entries 5-7). The particularly low yield (15%) observed when the reaction was carried out in THF (entry 7), was likely owing to the the low solubility of both **7a** and $Cu(OTf)_2$ in that solvent.

Table 2. Optimization of reaction conditions for addition of **7a** to cyclohexene.



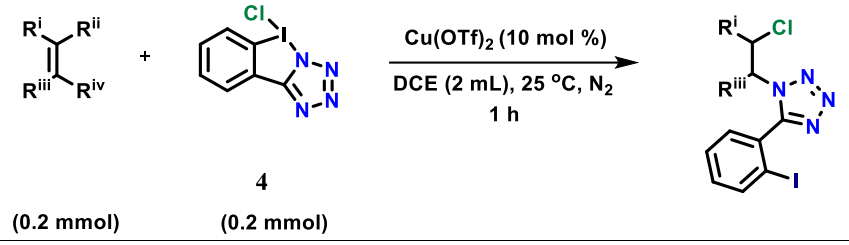
#	$Cu(OTf)_2$ [mol %]	Solvent	Isolated yield [%]
1	0	DCE	Trace
2	2	"	33
3	"	"	52 [a]
4	10	"	78
5	"	CH_3CN	37
6	"	DMF	53
7	"	THF	15

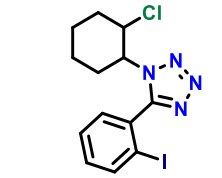
[a] The reaction time was 5 h.

With the conclusion of the optimization studies, the scope of the reaction with respect to the substrates was investigated next (Scheme 2). A variety of alkenes reacted smoothly to afford, in excellent

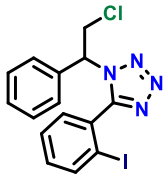
yields, the desired products of chlorotetrazolylation (**9a-f**), all of which were characterized by ^{1}H and ^{13}C NMR spectroscopy, as well as ESI-HRMS (SI).

Scheme 2. Scope of the copper-catalyzed chlorotetrazolylation of various alkenes with isolated yields.

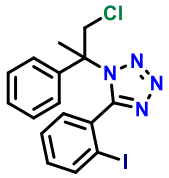




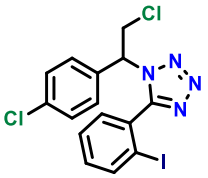
9a (78 %)



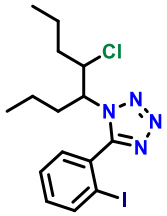
9b (70 %)



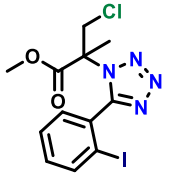
9c (75 %)



9d (72 %)



9e (88 %)

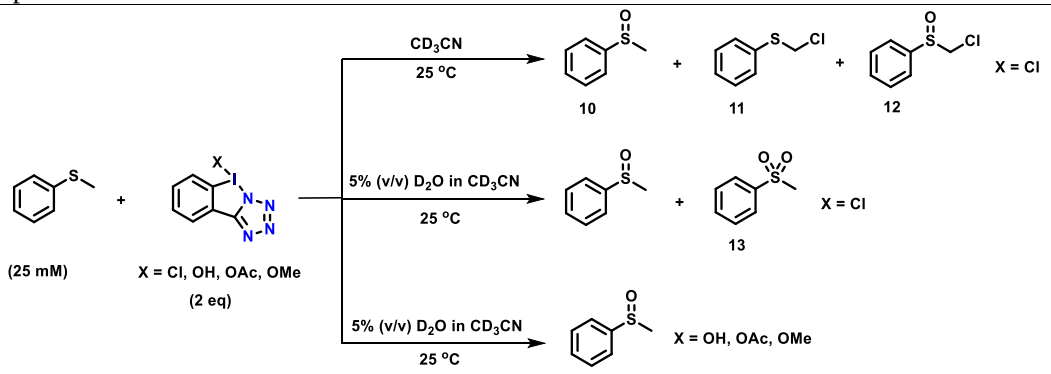


9f (71 %)

It was recently shown that HV iodine(III) compounds with tetrazole ligands (both the acyclic compounds $C_6H_5I(N_4CR)_2$[55] and the pseudocyclic derivative, (2-(1H-tetrazol-5-yl)phenyl)(hydroxy)iodonium tosylate[56] are strong oxidants and these studies were logically extended to BIAT derivatives. Thioanisole was chosen as the substrate and the reactions were conducted at room temperature in CD_3CN using, in all cases, 2 eq of the HV iodine(III)-based oxidant (**7a-d**). The oxidation with **7a** was fast (virtually complete within *ca.* 2 min) and it afforded the sulfoxide **10** as the main product. Under these conditions, the chlorination products of thioanisole and the sulfoxide **10**, i.e., compounds **11** and **12**, respectively, were also observed (Scheme 3, entry 1). Most likely, the O-containing products were formed due to the presence of small unknown amount of water in the reaction solvent. In order to achieve

better reproducibility, all further reactions were conducted in CD_3CN containing deliberately added water (5 % (v/v)). In this solvent, the reaction of thioanisole with **7a** afforded – once again, within ca. 2 min – the sulfoxide **10** as well as the product of its further oxidation, i.e., the sulfone **13** (entry 2). The oxidations with all other studied BIAT-based oxidants (**7b-d**) were markedly slower (entries 3-5) and yielded the sulfoxide **10** as the main product. The outcomes of all studied reactions are summarized in Scheme 3.

Scheme 3. Oxidation of thioanisole to **10** (or other products, which are specified) using BIAT-X **7a-d** at room temperature in the dark.



#	Solvent	Time [min]	NMR yields of 10 [%] with X =			
			Cl	**OH**	**OAc**	**OMe**
1	CD_3CN	2	64 + 8 (**11** + **12**) [a]	—	—	—
2	CD_3CN + D_2O (5% (v/v)	2	61 + 39 (**13**) [a]	—	—	—
3	“	60	complete	34	4	trace
4	“	120	“	73	10	1
5	“	240	“	99	25	2

[a] The numbers in parenthesis refer to the observed products shown in the reaction scheme.

The identities of all products shown in Scheme 3 were confirmed by GC-MS after the reactions were complete. It is noteworthy that the reaction mixtures were heterogeneous, and it is plausible to assume that the yields of the products could be highly dependent on the degree of dispersion of the oxidants and the efficiency of stirring.

Certain HV iodine(III) compounds are known for their explosive nature and their exothermic degradation upon heating or even friction,[86] but to the best of our knowledge, systematic studies and correlations between structure and stability have not yet been published. As mentioned, both **7a** and **7c** are highly oxidizing. Moreover, we have demonstrated[55,56] that when tetrazoles (which are intrinsically unstable and energetic compounds[78,80,81]) are coordinated to HV iodine(III) centers, the formed compounds are particularly prone to decompose upon heating. These initial findings stimulated the studying of the thermal properties of BIAT derivatives, which was accomplished by simultaneous differential scanning calorimetry and thermogravimetric analysis (SDT). Samples were heated from 30 ºC to 600 ºC at a rate of 5 ºC min^{-1} under a continuous flow of inert gas (N_2; 50 mL min^{-1}). The enthalpies of decomposition (ΔH_{dec}) were calculated by integrating the exothermic peaks in the DSC thermograms. The thermal stability and decomposition of all BIAT derivatives are summarized in Table 3 and the data are presented in Figure S3. In addition to the enthalpies of decomposition, the values of T_{d10} and T_{d50} are listed, i.e., the temperatures, at which respectively 10% and 50% of the original mass was lost. First, the thermal stability of **7a** was investigated, for it was found to be particularly reactive, especially when mixed with reducing agents (*vide supra*). The TGA curve of **7a** revealed a steep weight loss at 128 ºC with a "spike", suggesting that the decomposition was explosive. In the DSC thermogram a single exothermic peak was observed, and the value of ΔH_{dec} was determined to be –35.3 kJ mol^{-1}. The hydroxy derivative **7b** degraded on heating in two distinct steps, each of which was highly exothermic ($\Delta H_{dec,\,1}$ = –251.1 kJ mol^{-1} and $\Delta H_{dec,\,2}$ = –237.8 kJ mol^{-1} (entry 3), the first of the peak may correspond to decomposition of the compound itself while the second peak may correspond to the decomposition of the formed mu-oxo derivative (by elimination of water upon heating), which will be a subject of future investigation. Among all BIAT derivatives, the acetoxy compound **7c** (entry 4) turned out to be most energetic one (–305.3 kJ mol^{-1}).

Table 3. Decomposition temperatures and enthalpies of degradation of BIAT compounds and the parent monovalent iodine-containing tetrazole. The values shown in parenthesis for **5** corresponds to second exothermic peak.

Tetrazole	T_{d10} [°C]	T_{d50} [°C]	ΔH_{dec} [J g^{-1}]	ΔH_{dec} [kJ mol^{-1}]
2	217	275	–108	–29.4
7a	128	128	–115	–35.3
7b	215	400	–869 (-823)	–251.1 (-237.8)
7c	194	216	–925	–305.3
7d	149	236	–644	–194.5

All synthesized BIAT derivatives should be handled with extreme care and should be stored as small batches because triggers such as elevated temperature and friction (e.g., with metal spatulas) can lead to violent explosion, which occurred in our labs. Handling and storage recommendations are included in the SI. The discovery of BIAT derivatives will likely expand the utility of HV iodine(III) compounds as propellants and in ammunition.

CONCLUSIONS

We report the synthesis of novel HV iodine(III) compounds comprising fused tetrazoles, and benziodazole (BIAT) rings, with various ligands coordinated to the I(III)center. BIATs **7a-d** were characterized using ^{1}H and ^{13}C NMR spectroscopy, ESI-HRMS, and single crystal X-ray crystallography. BIAT-Cl **7a** was found to be functional for tetrazolylation reaction using $Cu(OTf)_2$ as catalyst. To assess and compare BIATs **7a-d** oxidizing ability, a model oxidation reaction of thioanisole was explored and it was observed that **7a** not only oxidized thioanisole instantaneously, but also produced chlorinated side-products. Furthermore, thermal analysis of these HV iodine(III) compounds was performed and the

enthalpies of decomposition (ΔH_{dec}) were measured using SDT. BIAT-OAc **7c** was noticed to be extremely energetic with heat of degradation of –305.3 kJ mol^{-1} (–925 J g^{-1}).

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