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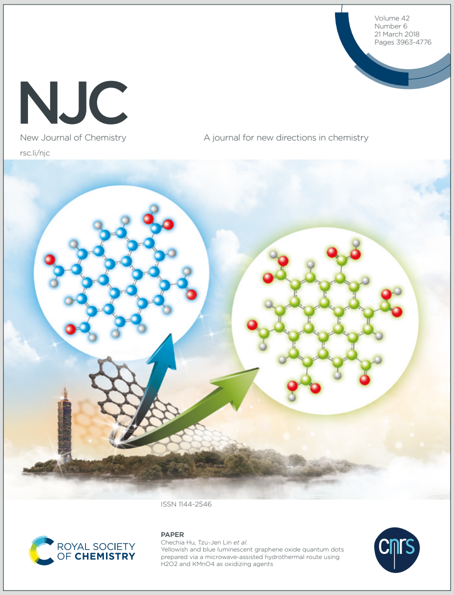

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Substituent-dependent reactivity of triarylantimony(III) toward I_2: isolation of $[Ar_3SbI]^+$ salt

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The outcome of reactions of triarylantimony (Ar_3Sb) with diiodine in benzene is strongly affected by the identity of substituents. For R = 4-MePh, 3-MePh and 4-FPh, there form Sb^V deivatives Ar_3SbI_2, while for $(2\text{-MeO-5-BrC}_6H_4)_3Sb$ the reaction results in $[(2\text{-MeO-5-BrC}_6H_4)_3SbI](I_3)$ where I is bound to the Sb center. The features of noncovalent interactions in the structure of the latter compound, as well as electronic structure of the $[(2\text{-MeO-5-BrPh})_3SbI]^+$ cation, were studied by theoretical methods.

The compounds belonging to the triarylantimony(III) family, Ar_3Sb, are known for more than a century and it is not unexpected that many aspects of their structural chemistry and reactivity were subjects of a substantial number of reviews and text-book considerations.[1–5] It is generally believed that the most common redox reactivity mode of Ar_3Sb is their oxidation by dihalogens to give corresponding triarylantimony(V) derivatives, Ar_3SbX_2. These reactions are well-studied for X = Cl and Br[6,7] and, to the best of our knowledge, products or intermediates other than from the most thermodynamically stable Ar_3SbX_2 were isolated or identified in situ only in few cases.[8] For diiodine, this exhaustive oxidation was realized for Ph_3Sb to furnish Ph_3SbI_2.[9,10] Taking into account that diiodine is significantly weaker oxidant under the same conditions than Br_2 and especially Cl_2, we assumed that its interplay with other Ar_3Sb could proceed differently to the conventional instances.

By planning this work, in addition, we were also inspired by the reported reactivity of other trialkyl- or arylpnictogens (P and As) toward I_2. As the closest neighbor to Sb, As demonstrates strikingly different behavior in the reactions between R_3As and I_2, forming complexes with either linearly-coordinated I_2 (R_3As–I–I, R = Ph,[11,12] 4-Me, 2-MePh,[13] Me[14] etc.) or I (the cationic R_3AsI^+; the I^- remaining aster I–I bond cleavage bonds I_2 to give triiodide counter-anion[15]). The R_3AsI^+ are especially interesting from the viewpoint of electronic structure and their ability to form noncovalent interactions: it can be expected that R_3AsI^+ has a energetically deep σ-hole on the I atom, so that it can become a suitable building block for construction of halogen bonding-based supramolecular architectures.

Based on abovementioned ideas, we decided to perform a series of experiments of general scheme "$Ar_3Sb + I_2$", involving Ar_3Sb precursors with various aryl substituents with either electron-donating or –withdrawing group or groups (see SI for details). For Ar = 4-MePh, 3-MePh, and 4-FPh and the equimolar amount of I_2, these reactions proceeded in the conventional way to achieve Ar_3SbI_2 (Scheme 1; Ar = 4-MePh (**1**), 3-MePh (**2**), 4-FPh (**3**)) isolated in up to 92% yields (see SI). In all cases, the coordination environment of Sb is trigonal bipyramidal (Fig. 1). In the structures of **1**–**3**, the Sb–I and Sb–C bond lengths are 2.723-–2.841, 2.873–2.876, 2.848–2.896 Å and 2.117, 2.119–2.126, 2.120–2.152 Å, respectively, being similar to those in Ph_3SbI_2.[9] Both ^1H and ^{13}C NMR spectra (see SI, Table S2) agree well with the molecular structures.

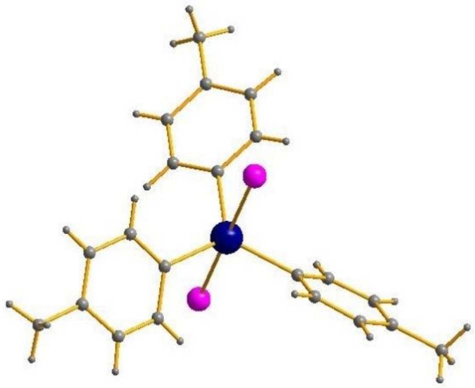

Fig. 1. Structure of $(4\text{-MePh})_3SbI_2$; C is grey, Sb dark blue, I purple

Interestingly, the crystal of **1** selected for XRD revealed the presence of minor quantity of Br ligands co-occupying the

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Electronic Supplementary Information (ESI) available: Synthetic procedures, XRD and NMR characterization details for **1**-**3** and **5**, computational details. See DOI: 10.1039/x0xx00000x

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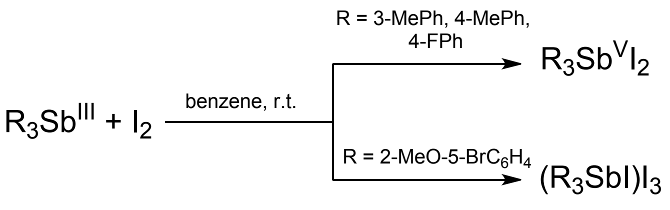
same position as iodides. Considering that the nature of bulk **1** was independently confirmed by element analysis, ^{1}H and ^{13}C NMR (see SI for full details), we suggest that this artefact appears due to contamination by bromide and preferential crystallization of Br-containing substance in the beginning.

The reaction with I_2 (molar ratio 1:1) proceeds dramatically different for (2-MeO-5-$BrC_6H_4)_3Sb$,[16] to give the product which resembles several of the abovementioned organoarsenic derivatives. In this case, there forms the triiodide salt of the [(2-MeO-5-$BrPh)_3SbI]^+$ cation (**4**) (Fig. 2). To our best knowledge, this is the first structurally characterized example of such Sb derivatives. Earlier, Prtichard et al. reported on the reaction between Ph_3SbI_2 and metallic Co that leads to the product with the "Co($SbPh_3)I_4$" brutto-formula. Since no X-ray characterization was performed, the structure was conditionally attributed to [Ph_3SbI][Co($SbPh_3)I_3$], following the analogy with related phosphines.[17] Chlorine-containing compounds with [$R_3SbCl]^+$ cations were described as well.[18,19] Also, similar observations were made by Tailor et al.:[8,20] in the course of studies of reactions between Ph_3Sb and I_2 in water-containing organic solvents, compounds containing $(Ph_3SbI)_2O$ units were isolated and characterized.



Scheme 1. Pathways of reactions between R_3Sb and I_2

In **4**, the Sb–C bond lengths fall in the 2.037–2.079 Å range, being noticeably shorter than those in parent compound (2.166–2.174 Å, respectively[16]); this shortening favours strong electron-withdrawing effect of I. The Sb–I distance is 2.639 Å, which is significantly less than those in **1**–**3**. The tetrahedral geometry of the Sb center in **4** is only slightly distorted (∠(X–Sb–X) are 106.6–114.0°).

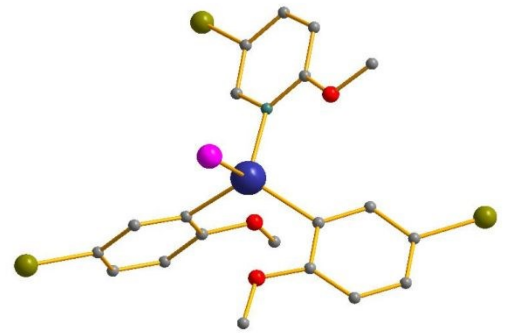


Fig. 2. Structure of the [(2-MeO-5-$BrC_6H_4)_3SbI]^+$ cation. C is grey, Sb dark blue, Br olive-green, O red, I purple; H atoms were omitted for the clarity.

Inspection of the halogen···halogen distances in the structure of **4** and their comparison with the sums of the corresponding Bondi van der Waals radii[21,22] indicate the presence of corresponding noncovalent interactions between I ligand and I_3^- (I···I 3.654 Å), which can be regarded as halogen bonding (XB)[23] (I–I–I 121.9°) based on the IUPAC distance and angle criteria.[24] Besides, we also identified Type I[23] packing-induced interactions involving the Br atom of the 2-MeO-5-Br substituent and the triiodide (Br···I 3.692 Å) so that there form supramolecular dimers (Fig. 3).

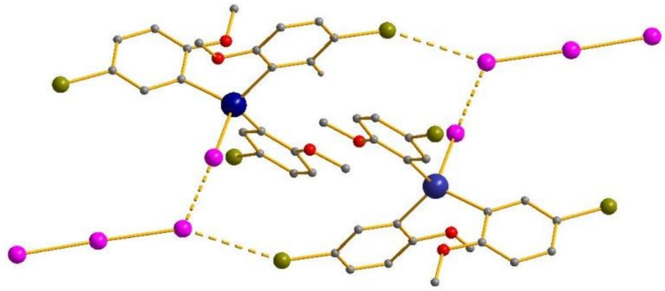


Fig. 3. Halogen···halogen contacts (dashed) in the structure of **4**.

To estimate the energies of the abovementioned halogen···halogen contacts, we performed DFT calculations at the M06/DZP-DKH level of theory and topological analysis of the electron density distribution (QTAIM method)[25] for the model tetrameric supramolecular associate {[(2-MeO-5-$BrPh)_3SbI]^+\}_2$···$\{I_3^-\}_2$ based on the experimental X-ray geometry of **4** (see SI for details; this approach was previously used by us for analysis of other relevant systems[26–30]). Depending on the applied method (see SI[31]), the strength of I···I and I···Br interactions vary in the 2.9–3.0 and 2.1–2.5 kcal/mol ranges; such values are relatively common for typical XBs.[28,32,33] According to the criteria proposed by Espinosa et al.[34] and Johnson et al.,[35] it can be stated that these interactions are purely noncovalent and attractive.

The distribution of frontier molecular orbitals in the optimized equilibrium structure of [$Ar_3SbI]^+$ is shown on Fig. 4. LUMO is mainly associated with antibonding σ*-orbitals located on the Sb–I fragment, whereas HOMO is localized exclusively on the Ar moieties.

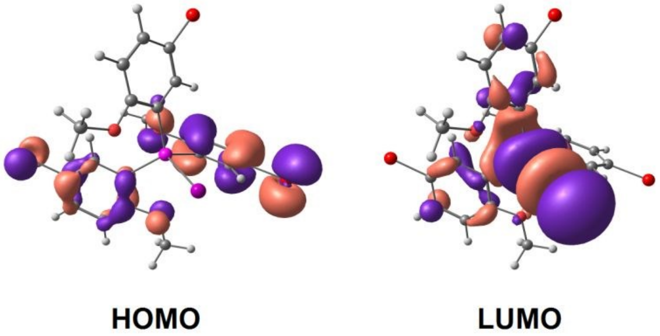


Fig. 4. Distribution of frontier molecular orbitals in the optimized equilibrium structure of [$Ar_3SbI]^+$

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Results of electrostatic surface potential (ESP) calculations reveal the presence of σ-hole regions on the Sb (86 kcal/mol, the global surface maxima), I (73 kcal/mol, the local surface maxima) and Br (60 kcal/mol, the local surface maxima) atoms in the optimized equilibrium structure of $[Ar_3SbI]^+$ (Fig. 5). Thus, potentially, this iodine-containing positively charged system is perspective for noncovalent catalyst involving simultaneous pnictogen/halogen bonding.

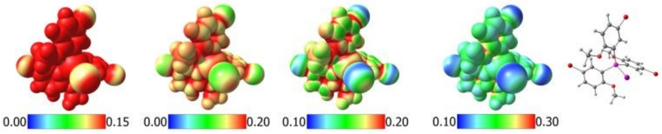

Fig. 5. Visualization of ESP distribution in the optimized equilibrium structure of $[Ar_3SbI]^+$.

In summary, we provided the experimental evidence that the reactions between Ar_3Sb and I_2 proceeds by two different routes depending on the identity of Ar: most commonly, those results in the oxidation to give $R_3Sb^VI_2$, and we reported here on the unconventional route to achieve the Ar_3SbI^+ cation. The latter reactivity mode of Ar_3Sb is similar to that of R_3As, and it can be theoretically expected that other scenarios (i.e. "linear coordination" of I_2) are possible. The facile generation of Ar_3SbI^+ deserves further investigation utilizing a broader range of substrates; corresponding experiments are underway in our group. Besides, analysis of the electronic structure of $[(2\text{-MeO-}5\text{-BrPh})_3SbI]^+$ demonstrates the simultaneous presence of σ-holes on I and Sb atom, so that such cations can be considered as very promising building blocks for XB-based supramolecular architectures and XB-involving noncovalent organic catalysis.[36–39]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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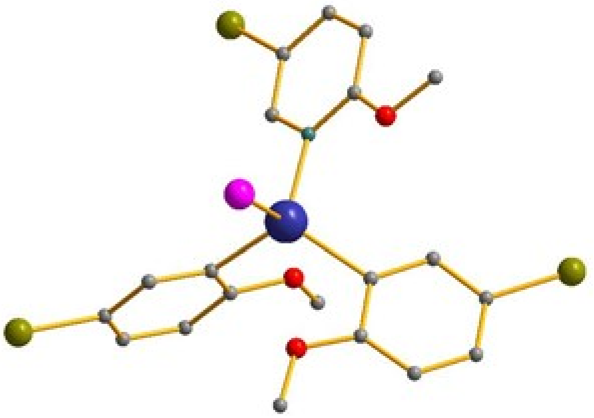

R_3SbI^+: dual σ-hole donor