

Crystallographic evidence for Bi(I) as the heaviest halogen bond acceptor

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ABSTRACT: Complexation of a bismuthinidene (R₂Bi) with two equivalents of a highly fluorinated aryl iodide at low temperature allows the crystallographic identification of an unstable species that can be regarded as an intermediate of an oxidative addition reaction. Both C-I bonds are orientated towards the filled 6p orbital of bismuth (Bi-I distances 3.44-3.52 Å), leading to an elongation of the C-I bonds by 0.05 and 0.07 Å. DFT calculations confirm that the bismuth center is indeed acting as an electron donor, establishing two strong and directional halogen bonds. As such, this study presents the first structural proof of bismuth, (and more generally of heavy organopnictogen compounds in oxidation state +1), acting as halogen bond acceptors.

In the past years, heavier main group elements have become increasingly popular for the activation of small molecules.¹ In this context, bismuth is of great interest due to its low toxicity and rich redox chemistry, the latter showing parallels with transition metal chemistry.^{2,3} Due to the inert pair effect, the 6s² orbital is low in energy, resulting in the low basicities of Bi(III) compounds and highly oxidative behaviour of the +V oxidation state. Recently, interest in the reduced oxidation state +I of bismuth has significantly increased. Pioneering work by Dostal has given access to bismuthinidenes, compounds in which the bismuth atom in the formal oxidation state +I is stabilized by a NCN pincer framework.^{4,5} The second lone pair associated with Bi(I) is localized in a p-orbital which lies perpendicular to the plane of the pincer ligand.⁶ Besides fundamental studies regarding the electronic structure of Bi(I) compounds^{7,8} the increased nucleophilicity of Bi(I) compounds allows them to act as donor ligands to metals.⁹ Furthermore, they have also been shown to mediate important organic transformations, e.g. transfer hydrogenations or hydrodefluorination reactions.^{10,11} Additionally, bismuthinidenes have been reported to undergo oxidative addition of alkyl iodides and aryl halides.^{12,13}

Whereas halogen bonding between aryl iodides and nitrogen-based molecules has found widespread use in many areas of crystal engineering, compounds of the heavier pnictogens have rarely been used as halogen bond acceptors. Only very few examples have been reported in the past years, e.g. using tertiary phosphines.¹⁴⁻¹⁶ In a seminal work, Friščić and Cinčić reported the successful cocrystallization of the halogen bond donor 1,3,5-trifluoro-2,4,6-triiodobenzene with Ph₃P, Ph₃As and Ph₃Sb. However, no adduct could be isolated in case of Ph₃Bi.¹⁷ Recently, Bujak and Mitzel reported cocrystals of Me₃As/Me₃Sb with C₆F₅I.¹⁸ The fact that no solid-state structures with a bismuth compound acting

as a halogen bond acceptor have been reported, and such structural motifs are typically not even considered in theoretical investigations,¹⁹⁻²¹ prompted us to pursue this synthetic challenge.

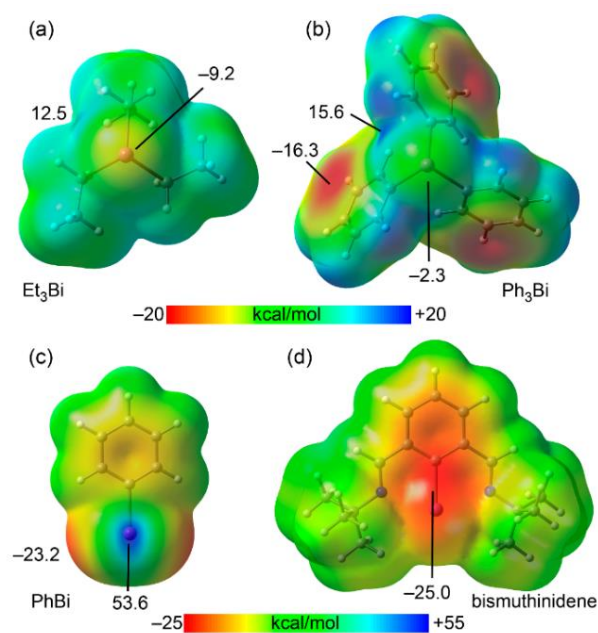
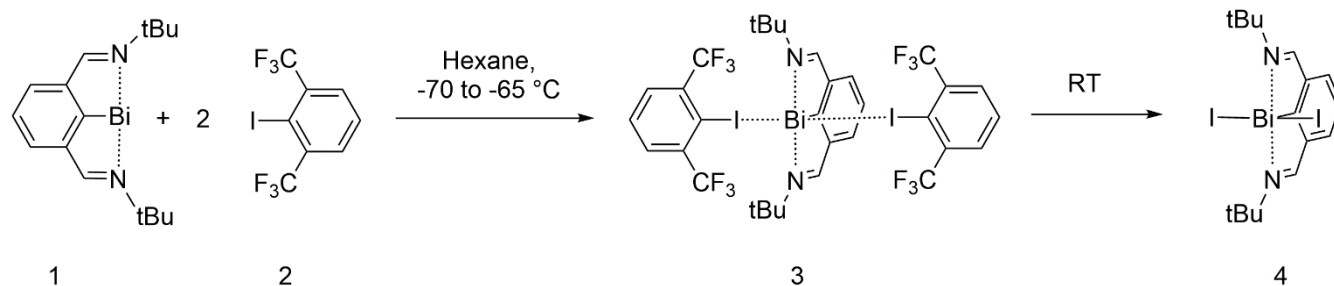


Figure 1. Molecular Electrostatic Potential (MEP) surfaces of Et₃Bi (a), Ph₃Bi (b), PhBi (c) and bismuthinidene **1** (d). Energies in kcal/mol



Scheme 1. Complexation of bismuthinidene **1** and 2,6-bis(trifluoromethyl)iodobenzene **2** and its subsequent reactivity.

Bismuth's primary challenge lies in the inert pair effect, which refers to the low energy of the 6s orbital, resulting in the diminished nucleophilicity of Bi(III) compounds. The Molecular Electrostatic Potential (MEP) surface plots of Et₃Bi and Ph₃Bi (Figure 1, top), reveal its unsuitability as a halogen bond acceptor. For Ph₃Bi, the minima/electron-rich regions are concentrated on the aryl rings, with a MEP value of -16.3 kcal/mol, being compared to that of the bismuth 6s lone pair (LP), -2.3 kcal/mol. Despite the presence of electron-donating alkyl substituents in Et₃Bi, its MEP value remains modest (< 10 kcal/mol). To counteract the inert pair effect, we shifted our focus to Bi(I) compounds instead of Bi(III). Nonetheless, the MEP of the basic PhBi model compound indicates an anisotropic MEP surface at Bi (Figure 1c). This surface displays two π -holes (positive areas) and two negative areas, attributed to the stereo-active lone pairs positioned coplanar with the aromatic ring. As expected, the MEP values at these LPs are significantly more negative (-23.2 kcal/mol) than those found in the Bi(III) compounds. Furthermore, the pronounced MEP maximum values (53.6 kcal/mol, representing π -holes) reveal Bi(I)'s dominant electrophilic nature over its nucleophilic one, rendering it unsuitable as a halogen bond acceptor. To circumvent this limitation, we considered using the NCN-stabilized bismuthinidene **1**. We reasoned that the LPs on the imine N-atoms could engage with the π -holes at Bi, positioning the stereo-active lone pairs above and below the plane of the aromatic ring (as shown in Figure 1c). Within this configuration, Bi(I) demonstrates pronounced nucleophilicity, as evidenced by a MEP value of -25.0 kcal/mol.

Green bismuthinidene **1** was reacted with 2,6-bis(trifluoromethyl)iodobenzene **2** at -70°C in dry and degassed n-hexane. Upon warming to -65°C the appearance of a red colour in the reaction mixture was apparent after several minutes. Cooling to -70°C led to the formation of red crystals, while warming to room temperature led to discoloration, oxidation to Bi(III) and crystallization of known RBiI₂ **4**.²² The highly unstable red species **3** crystallizes in the monoclinic space group P2₁/n, and the solid-state structure obtained by X-ray crystallography reveals a trinuclear complex formed by interaction of two intact aryl iodide molecules with the bismuth center. The alignment of the bismuth and two iodine atoms is almost linear (I-Bi-I angle of 160.659(12)°), implying the presence of interactions with the filled p-orbital of bismuth perpendicular to the NCN plane (Figure 2).

The distances between bismuth and iodine are 3.4382(5) Å (I1A) and 3.5226(5) Å (I1B), i.e. significantly below the sum of the respective van der Waals radii ($\sum vdW_{BiI} = 4.05$ Å),²³ and corresponding to RXB values of 0.849 and 0.870.²⁴ Interestingly, the pnictogen-iodine distances are similar or even shorter than in adducts of Ph₃As·C₆I₃F₃ (3.4211(3) Å), Ph₃Sb·C₆I₃F₃ (3.5747(3) Å)¹⁷ or Me₃Sb·C₆F₅I (3.4951(4) Å).¹⁸

With regards to the C-I bond lengths (C1A-I1A 2.171(3) Å and C1B-I1B 2.147(4) Å), a significant increase is observed when compared with free C₆H₃(CF₃)₂I (2.100(5) Å), consistent with population of the $\sigma^*(C-I)$ orbital.²⁵

In addition to the electron-withdrawing effect of the CF₃ groups, we hoped that their placement in the ortho-positions would additionally provide the possibility for weak H··F contacts with the tert-butyl groups of the bismuthinidene to augment the halogen bonded assembly. However, the crystal structure shows that these moieties are, in the main, too far away from each other: only one such contact (F2B-H14A: 2.607(3) Å) is observed. Instead, intermolecular H··F contacts between the CF₃ groups and the hydrogen atoms of the tert-butyl groups (F2A-H15B 2.587(2) Å) and the aryl ring of the bismuthinidene are observed (H3-F5B 2.564(3) Å, H5-F2A 2.465(3) Å) (see Figure S1). Furthermore, the four CF₃ groups in the assembly form strong intramolecular hydrogen bonds to the hydrogen substituents in ortho-position (2.277(2)-2.283(3) Å).

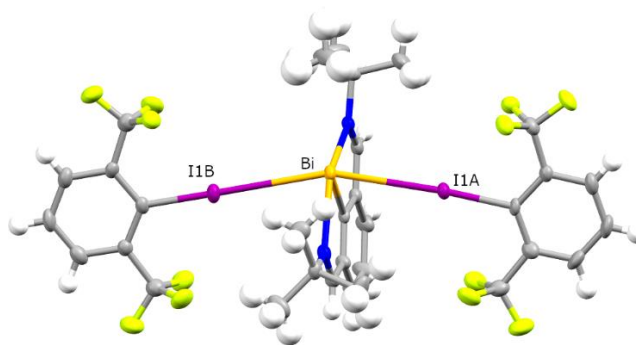


Figure 2. Molecular structure of **3**, ellipsoids shown at 50% probability, color code: hydrogen white, carbon gray, fluorine yellow-green, nitrogen blue, bismuth dark yellow, iodine purple.

We have examined the potential halogen bonds present in the bismuthinidene·2,6-bis(trifluoromethyl)iodobenzene adduct **3** using Density Functional Theory (DFT) calculations. Initially, we compared the geometry of the halogen-bonded (HaB) adduct in the solid state with its optimized counterparts (Figure S2, ESI). Specifically, two DFT geometry optimizations were undertaken: one for the isolated adduct in the gas phase and another employing Periodic Boundary Conditions (PBC) to account for packing effects. Notably, the gas phase geometry closely resembles both the experimental and PBC geometries, with the latter two being nearly identical regarding the relative orientation of the crystal conformers (Figure S2). Importantly, the I··Bi halogen bonds persist in the gas phase with analogous distances (3.456 and 3.459 Å). This observation underscores the structure-directing capability of the halogen bonds and

refutes any notion that they could be manifested merely due to packing effects. The primary variance between the gas phase and the experimental/PBC configurations is evident in the I–Bi–I angle. In the gas phase, this angle is calculated to be 147.9°, compared to 161.6° for PBC and 160.6° for the X-ray study. This reduced angle in the gas phase arises as the isolated adduct attempts to maximize intramolecular interactions.

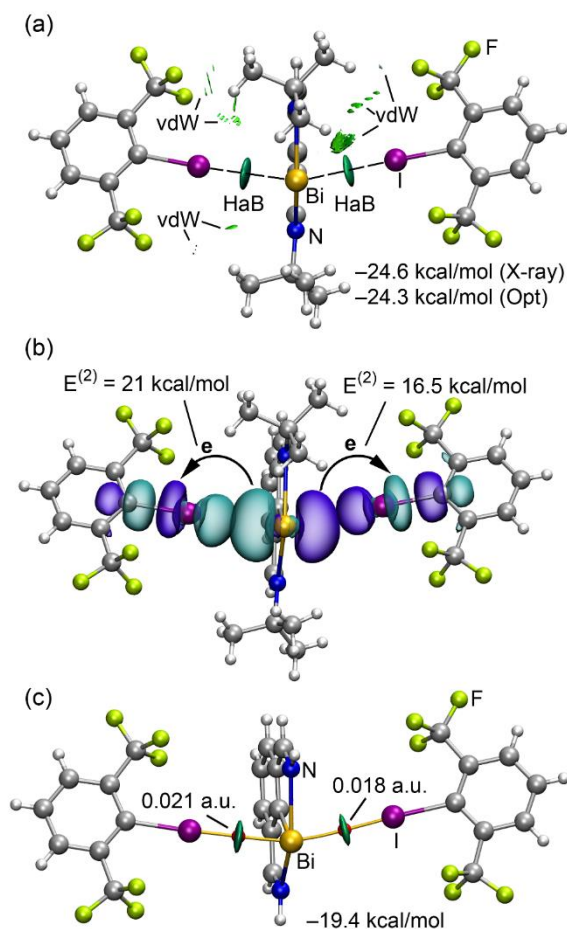


Figure 3. (a) NCIplot analysis of the trimeric assembly. Only intermolecular interactions are represented. (b) NBOs involved in the LP(Bi) \rightarrow σ^* (C–I) charge transfer. The second order perturbation energies $E^{(2)}$ are indicated. (c) Combined QAIM (BCP as red spheres) and NCIplot analysis of the mutated trimer (tBu \rightarrow H).

Figure 3a presents the non-covalent interaction plot (NCIplot) of the trinuclear assembly. The Reduced Density Gradient (RDG) isosurfaces provide a visual representation of interactions in real space. Dual disk-shaped RDG isosurfaces are observed between the Bi and I-atoms, corroborating the presence of halogen bonds. Additionally, the NCIplot highlights (in green) RDG iso-surfaces between the methyl-iodine atoms, signifying weak van der Waals (vdW) interactions (Figure 3). When examining the formation energy of the trinuclear assembly against isolated monomers, values of -24.6 kcal/mol (experimental geometry) and -24.3 kcal/mol (DFT-optimized, isolated adduct) have been calculated. This finding further affirms the assertion that packing effects are not the primary force behind adduct formation. The Natural Bond Orbital (NBO) analysis has been used to probe the

significance of orbital donor-acceptor interactions within the halogen bonds. This analysis reveals that the two bis-muth LPs reside in the 6s and 6p atomic orbitals. The LP within the 6p orbital participates in electron donation from bismuth to the antibonding σ^* (C–I) orbitals (Figure 3b). The LP(Bi) \rightarrow σ^* (C–I) charge transfer energies (21 and 16.5 kcal/mol), further underscore the idea of predominant system stabilization arising from the HaB formation. To evaluate the HaB energies independent of the influence of vdW interactions, we also modelled a mutated adduct, substituting tert-butyl groups with H-atoms. This effectively eliminates the $\text{CF}_3 \cdots \text{H}_3\text{C}$ and $\text{CH}_3 \cdots \text{I}$ interactions. Figure 3c depicts this model, integrating both the quantum theory of atoms-in-molecules (QTAIM) and NCIPlot analyses. These methods confirm the exclusive establishment of HaBs in the mutated adduct, each characterized by a Bond Critical Point (BCPs) and bond path linking the I and Bi-atoms. The electron density values at the BCPs are consistent with strong halogen bonds.²⁶ The interaction energy diminishes to -19.4 kcal/mol, relative to a value of -24.6 kcal/mol for the “full” system. Such findings underscore the assertion that the formation energy is predominantly attributed to the I \cdots Bi interactions, aligning with the pronounced and negative MEP value observed at the Bi-atom, as visualized in Figure 1d.

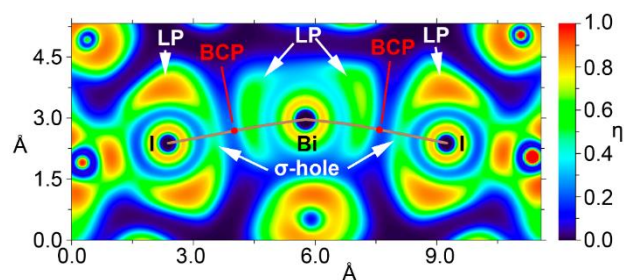


Figure 4. Electron localization function of the trimeric assembly represented in the I–Bi–I plane. The bond paths are represented as brown lines and the BCPs as red dots

The two-dimensional (2D) electron localization function (ELF) plot of the trimeric assembly is depicted in Figure 4, offering further insight into the role(s) of the σ -holes in the interactions. This figure provides a sectional view of the ELF 2D map, focusing on the plane demarcated by the Bi-atom and its two interacting iodine counterparts. Through this ELF visualization, it becomes evident that the σ -holes on the iodine atoms are oriented towards the LP of the bismuth atom. Indeed, the bond path connecting I to Bi passes through both the iodine σ -hole and bismuth LP. This specific electron localization in the I–Bi–I plane at the Bi-atom aligns well with the findings from the NBO analysis, particularly emphasizing the involvement of the LP located at the atomic 6p orbital.

In summary, we provide the first crystallographic and computational evidence for Bi(I) as the heaviest halogen bond acceptor. The crystal structure of this highly reactive adduct **3** displays Bi–I distances significantly below the sum of van der Waals radii as well as elongated C–I bonds of the fluorinated aryl iodide moieties. Upon warming, it decomposes to the Bi(III) species RBiI_2 **4**. Consequently, this crystal structure can be regarded as a snapshot of an intermediate

formed during an oxidative addition reaction of an aryl iodide with a low valent main group element.

This study not only sheds light on the unique potential of bismuth in halogen bonding but also paves the way for further explorations into the realm of heavy main group elements. The findings underscore the utility of comprehensive computational and experimental investigations to truly understand the potential of these unique elements in molecular chemistry. Furthermore, the results emphasize the importance of considering alternative oxidation states and molecular frameworks to unlock unexpected bonding and reactivity avenues, as evident from the successful employment of the Bi(I) state in halogen bonding. As the field continues to grow and diversify, we anticipate that the learnings from this study will serve as a foundational reference, inspiring chemists to explore the uncharted territories of main group element chemistry.

ASSOCIATED CONTENT

The supporting information contains synthetic, crystallographic and computational details.

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Notes

The authors declare no competing financial interest.

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