Invited Lecture

Understanding the electronic structure of halogen bonding with heavy pnictogen acceptor atoms: Insights from charge density and DFT analysis

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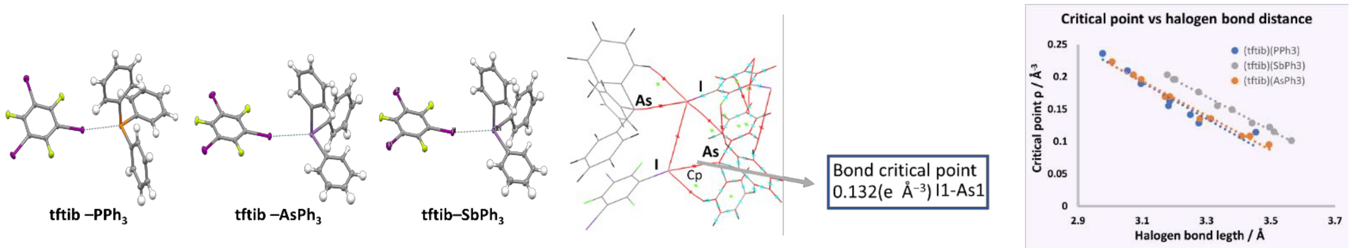
A halogen bond (XB) is a supramolecular interaction that involves a region of positive electrostatic potential (σ hole) [1] on the halogen donor atom and a nucleophilic acceptor atom or functional group. The use of XB therefore provides an opportunity to utilize heavy elements, such as bromine and iodine, which are not readily amenable to forming hydrogen bonds, in the construction of multicomponent solids, particularly cocrystals. The use of XB in crystal engineering enables materials with unprecedented supramolecular architectures. [2-3] These unusual supramolecular architectures find their way in diverse functional applications, including liquid crystals,[4] organic catalysis,[5] and room temperature phosphorescent materials.

Halogen bonding interactions sometimes could result in interaction with more diffuse atoms of Group V. In order to understand the nature of XB interactions formed between different combinations of donor-acceptor atoms, we need to look at their electronic structure. Experimentally this is enabled by high resolution single crystal X-ray diffraction (XRD) measurements, followed by multipole refinement of charge density and a topological analysis using quantum theory of atoms in molecules (QTAIM) [6]. In this presentation results of high resolution XRD measurements on high quality single crystals involving heavy pnictogen acceptors atoms of phosphorus, arsenic and antimony (P, As and Sb) with 1,3,5-Trifluoro-2,4,6-triiodobenzene (tftib) will be demonstrated. A bond critical point analysis will be employed to quantify the charge density within the halogen bonds with various acceptor atoms.

Moreover, correlations between the magnitude of charge density at the bond critical points (BCPs) and the calculated interaction energies will be discussed, highlighting the utility of charge density analysis in understanding the stability of halogen-bonded materials. Additionally, an experimental and theoretical correlation of properties at the bond critical points will be presented. Periodic density functional theory (DFT) calculations using different functionals and corrections will be compared with experimental findings. Given

that the choice of computational methods significantly impacts the results, especially for heavier atoms, this study aims to elucidate reliable methods for DFT calculations and address the associated uncertainties.



a) b) c)

Fig 1: a) cocrystals under discussion involving tftib and P, As, Sb b) Critical point density from the experimental electron density refinements for a cocrystal containing As and I c) Relativity of halogen bond length vs critical point density of the discussing compounds from the theoretical calculations

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