Investigation of σ-hole based chalcogen and halogen bonding in cocrystals

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Keywords: Co-crystallization, Halogen bonding, Chalcogen bonding

Chalcogen/Halogen bonding is an attractive force between Lewis acid/electrophilic region of a chalcogen/halogen atom with a Lewis Base/nucleophile.[1,2] To investigate halogen bonding, synthesis of 5 stoichiometric co-crystals by combinations of triphenylphosphine sulphide (PS) with 1,3,5-triiodo-2,4,6-trifluorobenzene (I3F) and 1,4-diiodotetrafluorobenzene (IF) respectively, consisting of I···S halogen bonding interaction were synthesized.[3] These I-centred interactions have been investigated using the geometrical criteria and computational methods. The nature of short and directional I···S halogen bonds (shortest: 3.163Å; most directional C-I···S, 179°) in different stoichiometric cocrystals were investigated. The interaction energy is in the range of -16 to -32 kJ/mol, as established from DFT calculations. Topological analysis unequivocally establishes the presence of a (3, -1) bond critical point (Fig 1a.) and the NCI-RDG analysis establishes the attractive nature of the interaction. The elongation of the C-I bond length as a consequence of evident charge transfer from sulfur to iodine for I···S interaction is reflected via Natural Bonding Orbital. The atomic polarizability analysis establishes the mutual polarization of the iodine atom in the presence of the sulfur atom and vice-versa (Fig 1b).[4] On the other hand, the nature of chalcogen bonding (ChB) is investigated in Tellurium based promising as-catalysts cations and their synthesised cocrystals.[5] These tellurium based compounds are characterized using SCXRD, PXRD, 125Te- NMR followed by analysis of different noncovalent interactions, primarily ChB, by utilizing several computational tools. Thus, a detailed experimental and computational analysis establishing the electronic characteristics of the chalcogen and halogen bonded cocrystals will be discussed in detail.

Figure 1.a. Bond critical point shown between I···S halogen bond; b. Mutual atomic polarizability between I and S computed through PolaBer.