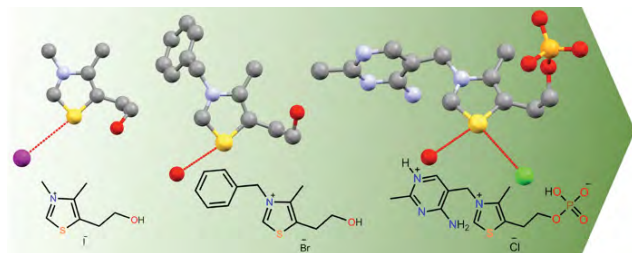


**Fig. 1** – Crystal structures of thiamine monophosphate (right) and two model compounds showing the presence of CBs between the sulphur atom of thiazole ring and neutral and/or anionic electron-donors.



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**Keywords:** Chalcogen bond, Crystal engineering,  $\sigma$ -Hole interactions

## MS30-O4

### Chalcogen and halogen bonding in case of multiple i...i and i...s interactions with ambiguous mutual orientations

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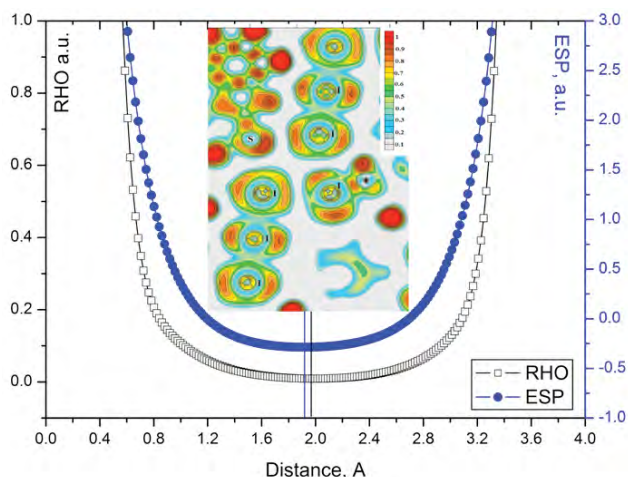
The question of identification and characterization of non-covalent interactions lies in the center of modern crystal engineering problems. Ambiguity of geometric criteria generates the necessity to use electronic descriptors in cases with competitive interactions or unobvious orientation of nucleophilic and electrophilic sites of interacting atoms in molecule and crystals.

In this study we demonstrate several examples of multiple I...I and I...S interactions and test reliability and visibility of the series of electronic criteria. Organic crystals with polyiodide anions and S,N-containing heterocyclic cations open possibility for the design of wide row of nonlinear optical and semiconductor materials as well as dye-sensitized solar cell devices. Variety of crystal structures, available for material engineering is due to the ability of sulfur and iodine atoms form different types of noncovalent interactions, organized in various types of 3D structure motives: nets, layers, chains, cages.

Our computational approach includes solid state quantum-chemical calculations with periodic boundary conditions and atomic basis sets, implemented in CRYSTAL14 package. Electronic criteria based on characteristics of calculated electron density such as ELF distribution and superposition of atomic basin boundaries in the electron density and electrostatic potential are used (TOPOND14).

Testing these computational tools on the series of boundary cases, different types of mutual orientations of interacting atoms can increase reliability of these criteria. The central point of the work is the demonstration of possibility of computational approaches to elucidate which of the interacting atoms acts as acceptor and which as a donor and thus to assign the type of interaction: halogen or chalcogen bond.

In the unusual orientation of I-CH<sub>2</sub> fragment so that equatorial part of iodine atom is directed towards  $\sigma$ -hole region of triiodide anion leads to the situation where iodine atom of organic cation acts as the donor and acceptor of the halogen bond simultaneously. ELF distribution in the plane, containing multiple covalent interactions allows indicating the type of bonding and visualizing features of electron shells distortion due to formed noncovalent interactions. Here we discuss features of  $\sigma$ -hole interactions and their impact on crystal packing and properties of the polyiodide structures.



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**Keywords:** halogen bonding, chalcogen bonding, organic polyiodides

**MS30-O5**

**Halogen, chalcogen and pnictogen bonding: other bricks in the wall**

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The understanding of the relative importance and effect of intermolecular interactions in the solid state is highly valuable in a range of applied research areas, not least in the pharmaceutical industry where control of polymorph stability is crucial. Within pharmaceutical crystal structures, hydrogen bonding tends to dominate – for these interactions there are already a range of established methodologies [1,2] to help understand the most probable outcomes and assess the stability or risk of polymorphism. How important in this context are other intermolecular interactions though? What is likely to be the effect of halogen bonds, chalcogen bonds or pnictogen bonds? This presentation will review the statistics on some typical halogen, chalcogen and pnictogen bonds in the CSD in the context of other intermolecular interactions in organic crystals. We focus on the impact of these interactions for an organic crystal designer or engineer. There are nearly a million structures in the CSD – what do they tell us about the significance of these interactions and do we have enough data?

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