3RD INTERNATIONAL SYMPOSIUM ON HALOGEN BONDING

The quantitative criteria for the electrophilic properties of halogens and chalcogens at their co-presence in crystals

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We propose to apply the electron density characteristics as the quantitative criteria that confirm the electrophilic properties of halogens, pnictogens, and chalcogens involved in non-covalent interactions in molecular crystals. For the halogen bonding characterization, the following functions are justified: the Electron Localization Function (ELF), the One-Electron Potential (OEP), the superposition of atomic basins boundaries in the electron density (ED) and in the electrostatic potential (ESP) and the Potential Acting on an Electron in a Molecule (PAEM), which only recently has drawn our attention [1].

These quantitative criteria are useful for complicated cases of the multiple interactions, when the halogen bond coexists or competes with the chalcogen bond. For example, despite the provocative (Type II) geometrical orientation of the triiodide anion inherent in a halogen bond in the (Z)-4-chloro-5-((2-((4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)amino)-phenyl)amino)-1,2,3-dithiazol-1-ium oligoiodide crystal (1), the electronic criteria did not confirm the halogen bond S…I between the I_3^- anion and S in the cation [2]. Using these criteria, we are able to confirm that the interaction S…I is the chalcogen bond. The Raman spectra and thermal decomposition curves helped us to clarify the manifestation of the structural features in this crystal.

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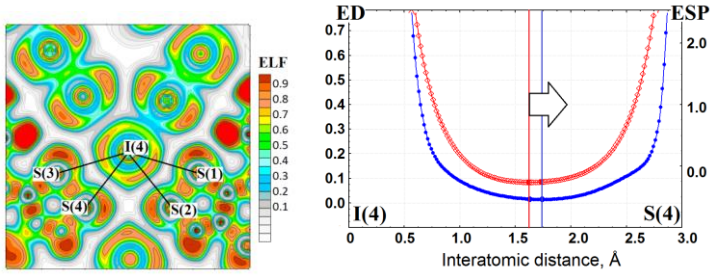

Figure 1: a) ELF for I…S interactions in 1; b) superposition of the ED (blue round filled points) and ESP (red square hollow points) profiles for I(4)…S(4) interaction.

References

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2. O.I. Bol'shakov, I.D. Yushina, E.V. Bartashevich, Y.V. Nelyubina, R.R. Aysin, O.A. Rakitin. Struct. Chem., 2017, 28, 1927-1934.