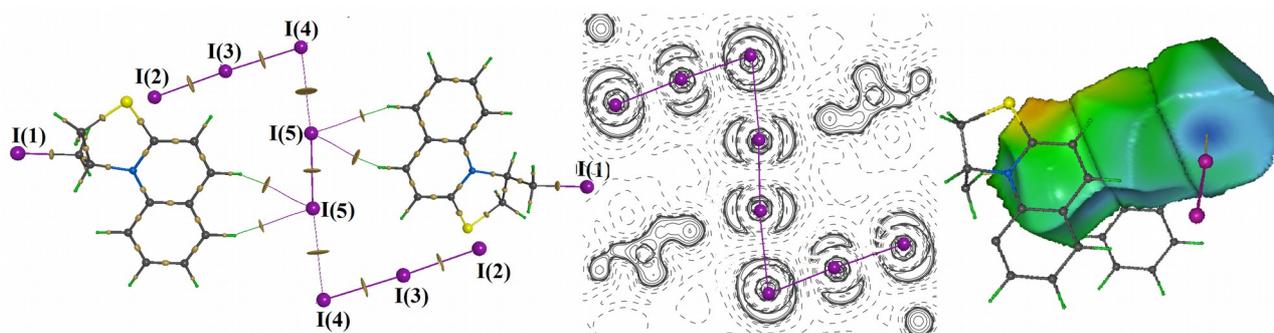


Charge Density Study of Iodide – Iodine Interactions in Chalcogenazolo(ino)quinolinium Oligoiodide Crystals

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The spatial organization of electron density in iodine-derived chalcogenazolo(ino)-quinolinium mono-, tri- and oligoiodide crystals of various structures [1] has been studied using 3D periodic Kohn-Sham calculations. CRYSTAL09/14 program package has been used. The coherent application of QTAIMC, one-electron potential and electrostatic potential has revealed the significant differences between halogen bonds [2] (Type II interactions) and van der Waals (Type I) interactions for iodine atoms in a crystalline environment. The traces of σ -holes in electrostatic potential on the zero-flux interatomic surfaces of iodine moieties are the distinctive feature of halogen bonding; they do not appear in the weak van der Waals I...I interactions at all.



The superposition of the gradient fields of the electron density and electrostatic potential has allowed detecting the strong electron delocalization along the oligoiodide chain $[I_3^- \dots I - I \dots I_3^-]$; the electron density is shifted from I_3^- moiety to the cation *via* iodine molecule I_2 as a mediator. Atomic basin boundaries and electron populations of atomic basins have been obtained by using WinXPRO program package, version 3.0.13 [3].

Analysis of iodine-derived chalcogenazolo(ino)quinolinium mono- and triiodides shows that the covalently bonded iodine atoms $C(sp^2)-I$ and $C(sp^3)-I$ differ significantly in iodide-iodine halogen bonding ability. The local and integrated characteristics of kinetic, potential and total electronic energy for C–I covalent bond have been examined. It has been found that both delocalization indices of iodine covalent bond and the total electronic energy density integrated over carbon – iodine interatomic surface can be used as quantitative criteria of iodine-derived cation ability to form the halogen bond with triiodide anion in crystals.

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