Targeting the iodine halogen bond: the role of C-I covalent interactions

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The analysis of local and integrated characteristics of kinetic, potential and total electronic energies of $C(sp^2)$-I and $C(sp^3)$-I bonds in chalcogenazoloquinolinium and chalcogenazinoquinolinium cations (Kohn-Sham/B3LYP/6-311G**) allowed us elucidating what properties the covalently bonded iodine must possess to act as a donor of halogen bond in triiodide crystals. It has been demonstrated that only relatively strong covalently bonded iodine atoms $C(sp^2)$-I reveal such ability.

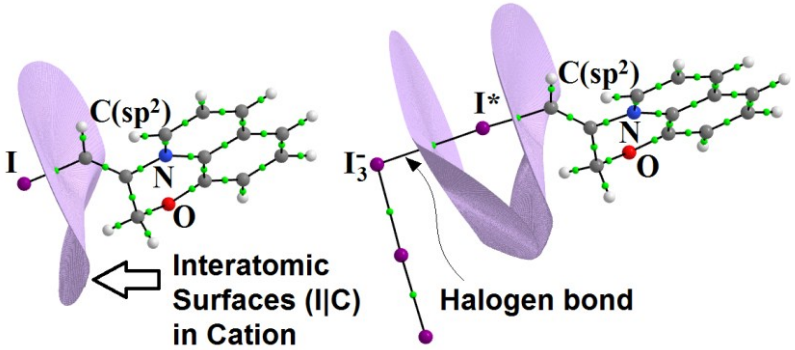

Figure 1: Interatomic surfaces (C|I) and (I*|I) in iodine-containing oxazinoquinolinium complexes

Integral electronic energy characteristics $h_S(C|I)$ calculated for the interatomic surfaces (C|I) [1, 2] are more informative quantitative criteria of cation predisposition to form a halogen bond, than the maxima of the electrostatic potential on the ED isosurface of iodine atoms at the epicenters of their σ-holes.
The ability to form a halogen bond with triiodide has been shown for iodine-containing cations for which $h_S(C|I) < -0.112$ a. u. Correlations between local and integral characteristics of the of kinetic or potential energy densities in a series of C(sp)-I, $C(sp^2)$-I and $C(sp^3)$-I bonds have not been found. Also, we have revealed that, at the formation of structural fragments C-I…I_x^-, x =1, 3, the electronic energy density integrated over the interatomic surface (C|I*) substantially decreases in comparison with that in isolated chalcogenazoloquinolinium and chalcogenazinoquinolinium cations. We can summarize that the quantities $h_S(C|I)$ and $\Delta h_S(C|I^*)$ are promising descriptors, which are suitable for *a priori* assumptions about potential ability of iodine-containing heterocyclic cations to form iodide-iodine halogen bonding in crystals.
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References

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