

CHARACTERIZING NONCOVALENT INTERACTIONS IN N,S-HETEROCYCLE COMPLEXES WITH IODINE

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The ability of iodine molecule to form the complexes with S and N electron-donor centers in heterocyclic organic bases is well known, these complexes exist in both solutions and a crystalline state. Among the C, H, N, I-containing compounds listed in the crystallographic database CSD v.5.33, the most common are the iodine complexes with pyridine derivatives as well as C, H, S, I-complexes with the fulvalene derivatives. The halogen N \cdots I or S \cdots I bonding is the main type of noncovalent interactions in such complexes. However in some new heterocyclic compounds, there is a possibility of competition between atom N and atom S for the priority in the interactions with the iodine in the condensed state. The noncovalent interactions of iodine with heterocyclic compounds which have two donor centers linked to a common fragment N–C–C–S or N–C–S is even more difficult to identify. In principle, the large iodine atom may cooperatively interact with both nitrogen and sulfur atoms. The main aim of our work is to characterize the types and features of the interactions between iodine atom and N,S-donor centers in heterocyclic compounds. For this purpose, we have analyzed the electronic density features in a number of N,S-heterocyclic molecular complexes with iodine as existing in different crystals.

Based on the calculated electron density, the QTAIMC analysis of noncovalent interactions of iodine was carried out for a number of known crystal structures (programs Firefly 8.0.0., CRYSTAL09, AIMALL 12.06.03 and Multiwfn 2.6.1). In particular, the complexes of quinoxaline \cdot I₂ (NULBUR), quinoxalino[2',3':5,6][1,4]dithiino[2,3-b]quinoxaline \cdot I₂ (IHISEY) and new derivatives of thioquinoline as 2-allylthioquinoline C₁₂H₁₁INS \cdot I₂ and 8-allylthioquinoline C₁₂H₁₁INS \cdot I₂ have been studied. The existence of latter compounds in solutions gives evidence of iodine ability to form the complexes with thioquinoline systems.

The iodine halogen bond N \cdots I in complexes and crystals has also been analyzed from the standpoint of the total electrostatic potential features corresponding to the outer molecular contour of the electron density (0.001 a.u.). All of the observed noncovalent interactions in the complexes were also characterized using diagrams «Reduced Density Gradient – Electron density multiplied to the sign of the second eigenvalue of the Hessian»; i.e. the RDG – sign(λ_2) ρ diagrams. The orientation of Localization Electron Function (ELF) maxima in the donor fragments and disposition of RDG-function extremes were compared. The following features were observed: the electron density critical points with $\rho_b > 0.01$ a.u.; the one-to-one orientation of electron-donor lone pairs and halogen σ -hole on the electrostatic potential mapped into the electron density surface («LP \rightarrow σ -hole»); the wide spike in the left side of the RDG – sign(λ_2) ρ diagram, the electrons attraction of the donor atoms to the iodine nucleus, and the large total dipole moment, $\mu(I)$, of iodine atom in each of the complexes.

It was detected, that I \cdots S and I \cdots H interactions have likely the dispersion origin as opposed to the halogen bonds N \cdots I. The RDG – sign(λ_2) ρ diagrams allowed us to characterize the regions with multiple and weak noncovalent interactions I \cdots S, I \cdots H and to distinguish them from the more stronger halogen bonds. Indeed, the iodine atom's electrons are attracted to the sulfur atom nucleus, while the ELF maxima of the sulfur atom are not orientated towards the center of the halogen σ -hole. In this case, the iodine atom serves as a donor, not an electron acceptor. Such interactions cannot be attributed to halogen bonds despite the relatively small angle between the I–I–S atoms.

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