The charge-density study of specificity of the atomic interactions in iodine – allylthio(oxy)quinoline complexes

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The electron-density features in the complexes of 2- and 8-allylthioquinoline and 2- and 8-allyloxyquinoline with iodine are studied. In these complexes, the donor (D) centers of substituted quinolones (D = N, O or S, C^{Allyl}) can be linked with an iodine molecule through the halogen bonds $N...I_2$, $O...I_2$, $S...I_2$, $C...I_2$. The complexes formed by an allyl group model the pre-reactionary state at the formation of the cyclic product – thio(oxy)quinolinium cation [1]. S ... I_2 interaction may precede the redox reaction of the iodide anion formation.

The geometry optimization and wave-function computations of the systems mentioned above were done by the Kohn-Sham method (B3LYP/6-311G**, the software package Firefly, version 7.1 [2]). Then, the Bader's [3] atomic charges were calculated and the electron localization function (ELF) has been analyzed [4, 5] using the Multiwfn package [6].
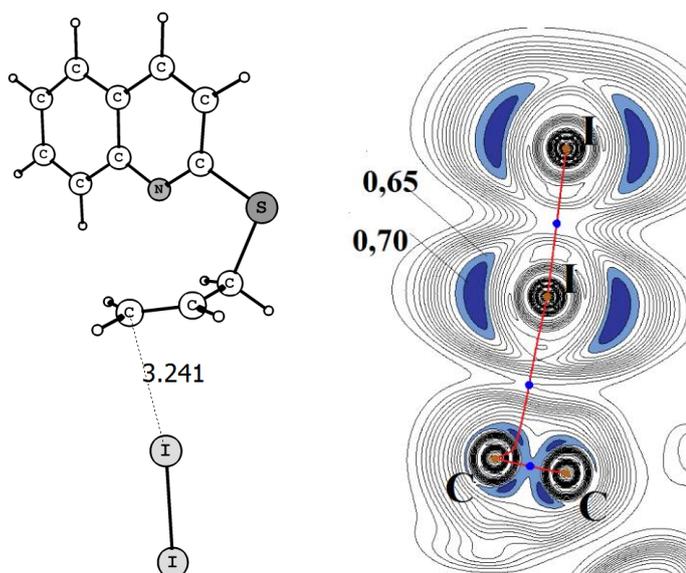

Fig. 1. Halogen bonding in complex of 2-allylthioquinoline with iodine

The charges of the S atoms in allylthioquinolines are positive; they are larger in complexes with iodine as compared with an isolated molecule. The charges of the basins of the N, O, C

atoms are negative; when these atoms are involved in halogen bonding, these charges are lower. The complex formation is accompanied by a contraction of the electron density in basins of atoms involved in the halogen bonding D ... I; the charge concentrates in the donor-atom basin and decreases in the acceptor atom basin. This leads to strengthening the electrostatic component in halogen bonds. At that, the electrostatic interaction D ... I is realized mainly due to deformation of the electron density within the donor (D = N, O) and acceptor (iodine) atomic basins. Also, the electron lone-pair of N atom in the isolated 2-allylthioquinoline molecule shows more smeared localization domain than in complexes with iodine.

The total charge transfer to the acceptor molecule manifests itself at the terminal iodine atom. The change of charge on the I_2 molecule enhances with increasing the interaction energy. For example, max $\Delta Q = -0{,}163$ e and $E_{int} = -6{,}8$ kcal/mol; min $\Delta Q = -0{,}011$ e and $E_{int} = -2{,}3$ kcal/mol, where $E_{int} = E_{D\ldots I\text{-}I} - (E_D + E_{I\text{-}I})$. The best quantitative correlation of the interaction energy E_{int} was observed with the charge of the terminal iodine atom, which is not involved in the halogen bonding (R = 0.96).

The complex formation is also accompanied with the charge density overflow to the donor atoms from the neighboring covalent bonds of the allyl fragment. This effect manifests itself in the change in the Cioslowski-Mixon [7] bond-order indices.

The set of the energy, charge and geometric characteristics of the complexes under investigation leads to conclusion that the low probability of complexing on the nitrogen atom caused by the steric hindrances created by substituents in position 2 and 8. The formation of the bond between iodine and allyl group C=C…I stabilizes the conformation, in which the reactivity centers (the N and C atoms) are more close to each other. This explains the mechanism of experimentally observed iodocyclization reaction.

All the calculations were performed in the supercomputer «SKIF Ural» Cluster of South Ural State University.

References

[1] D.Kim, Chem. Heterocycl. Comp. 44 (2008) 1355.

[2] A. Granovsky, Firefly 7.1.G. www.http://classic.chem.msu.su/gran/firefly/index.html.

[3] R.F.W. Bader, Atoms in Molecules. A Quantum Theory. Clarendon Press, Oxford, 1990.

[4] D. Becke, K.E. Edgecombe, J. Chem. Phys., 92 (1990) 5397.

[5] V. Tsirelson, A. Stash, Chem. Phys. Lett., 351 (2002) 142.

[6] T. Lu, F. Chen, J. Comp. Chem., 33 (2012) 580.

[7] J. Cioslowski, S.T. Mixon. J. Am. Chem. Soc., 113 (1991) 4142.