Electron Density Based Quantitative Tools for Revealing and Characterizing the Halogen Bonds in Crystals

Ekaterina Bartashevich[1], Vladimir Tsirelson[2]
[1]*South Ural State University, Chelyabinsk, Russia*
[2]*D.I.Mendeleev University of Chemical Technology, Moscow, Russia*

E-mail: bartashevichev@susu.ru

To establish what quantitative descriptors are suitable for identification and categorizing the halogen bonds in crystals, we study the anisotropy of electron density, ρ(r), within the Bader's atomic basins. We analyze and discuss the following quantitative descriptors and their spatial behavior in crystals: Laplacian of electron density, electrostatic potential, ESP, and potential acting on an electron in a molecule, PAEM. All these functions can be obtained from both high-resolution experimental ρ(r) and by Kohn-Sham calculations with periodic boundary conditions. The ESP distribution illustrates the predisposition of a molecule to electrostatically driven bonding, meanwhile the PAEM is suitable for quantitative description of actual halogen bond properties in complexes and crystals. By virtue of including an electron exchange contribution, PAEM is a promising tool for halogen bond characterization that surpasses ESP. Superposition of gradient fields of ρ(r) and ESP allows us to formulate a useful quantitative criterion [1] for noncovalent bonds categorizing in difficult cases of nucleophilic and electrophilic sites orientation. For example, different types of S…I interactions we observed an urgent need for such criterion. The categorizing dilemma, which atom, a halogen or a chalcogen, delivers the electrophilic site for bonding and dictates the name of bonding is solved using the electronic criterion that based on the order of minima of ρ(r) and ESP along the interatomic line.

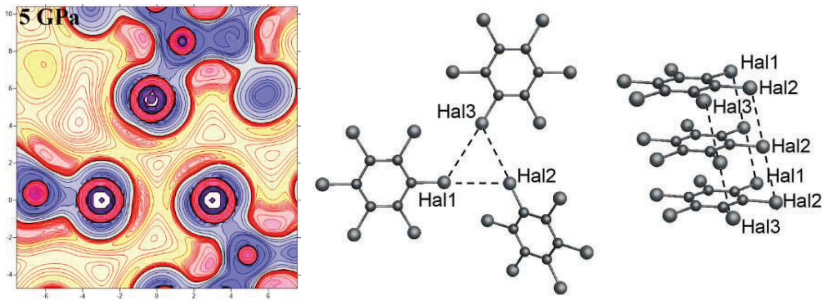

Figure 1: Quantum electronic pressure for Hal_3-synthon in C_6I_6 crystal

Also, we recommend a new tool, the quantum electronic pressure, QEP [2], which illustrates the features of ρ(r) anisotropy in the area of halogen bond in crystals. The spatial distribution of QEP formed by electrons and nuclei shows the potential regions of resistance to compression (QEP>0) and regions with high compressibility (QEP<0). It is the latter that is observed for halogen bonds. This effect was found by modeling crystals with Cl…Cl, Br…Br, I…I halogen bonds under the external hydrostatic compression.

The study is supported by the Ministry of Science and Higher Education, FENU-2020-0019.

References

1. E.Bartashevich, S.Mukhitdinova, I.Yushina, V.Tsirelson, *Acta Cryst.B,* **2019**, 117-126.
2. V.Tsirelson, A.Stash, I.Tocatly. *Acta Cryst.B,* **2019**, B75, 201-209.