Advances and drawbacks of quantum topological approaches: QTAIMC *vs* NCI

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Noncovalent interactions in crystals of substituted trinitromethanes, Hlg-C$(NO_2)_3$ (Hlg = Cl, I) containing intra- and intermolecular interactions O...Hlg, O...N have been considered from the standpoint of two approaches based on different approaches - Quantum Topological Theory of Atoms in Molecules and Crystals (QTAIMC) [1] and the low-valued regions of Reduced Density Gradient (RDG) from Non-Covalent Interactions (NCI) method [2]. Both methods are based on consideration of the gradient of electron-density field and electron density curvatures in a system. In QTAIMC, it is postulated that each pair of the density gradient lines, which originate at the (3,-1) critical points in electron density and terminate at the neighboring atomic nuclei, can be associated with a signature of bonding of corresponding atoms. It corresponds to line of maximal density linking the atoms and is called the bond path. Zero-flux condition for the gradient of electron-density allows tracing boundaries of bounded atoms as closed surfaces surrounding the nucleus. The features of the bond critical points and atoms are used in QTAIMC to characterize the bonding picture in a system. NCI approach focuses on analysis of the spatial intermolecular distribution of dimensionless RDG – quantity that characterizes the deviation of electron density from the homogeneous distribution. Compact information of noncovalent atomic interactions provides diagrams RDG(**r**)–sign[λ_2(**r**)]ρ(**r**), where λ_2(**r**) is the second eigenvalue of the Hessian of electron density (ED). In addition, the NCI authors postulated that the low RDG(**r**) regions are correlated to relevant interactions, either attractive (if sign[λ_2(**r**)] < 0), or repulsive (if sign[λ_2(**r**)] >0). In this point, QTAIMC and NCI methods disagree (see Fig. 1).

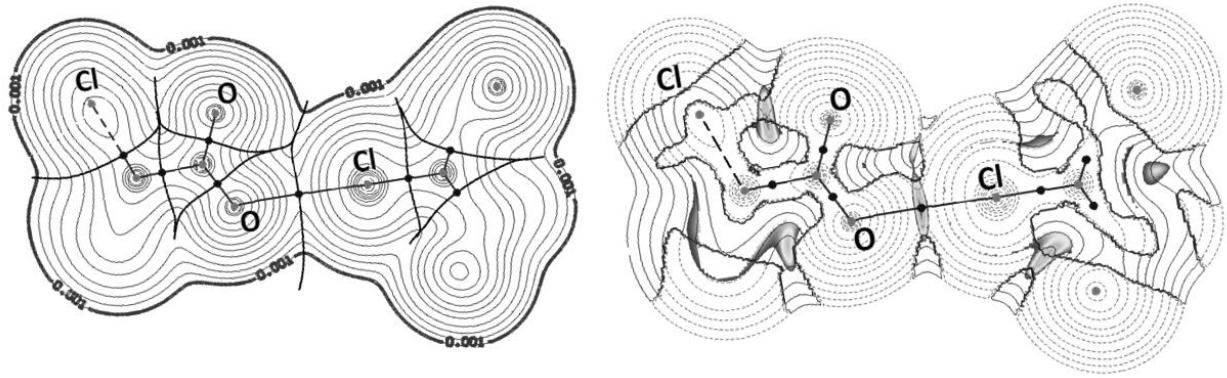

Fig 1. The halogen O…Cl bonding in halotrinitromethane dimer, plane N–O–Cl: a) electron density, ρ(**r**), the bond paths, traces of atomic basins and critical points; b) the RDG(**r**)–sign[λ_2(**r**)]ρ(**r**) function: areas with λ_2(**r**) < 0 are dotted and λ_2(**r**) > 0 are shown by black solid lines.

We performed the QTAIMC and NCI analysis of crystals Cl-C$(NO_2)_3$ and I-C$(NO_2)_3$ using calculated (B3LYP/TZVP/DZVP, CRYSTAL09) electron density expressed via the space-extended multipole model. The noncovalent interaction characteristics were computed using the computer program WinXPRO[5]. The substituted halotrinitromethanes illustrate few specific features of the manifestations of interatomic interactions. First, the three zero-flux surfaces of four atoms Hlg-C-N=O converges in the area of intramolecular interactions Hlg...O, however there is no the bond paths there. Second, among the intermolecular interactions Hlg...O, the halogen bonding (XB)[3], the noncovalent interaction, in which the halogen acts as

an acceptor of electron density, necessarily occurs. Furthermore, extremely short carbon-chlorine bond of 1.694(1) Å (at 100 K) has been detected in the crystal Cl-C$(NO_2)_3$ [4].

We found that QTAIMC for the crystals and the corresponding gas-phase molecular dimers leads to consistent conclusions about the presence of bond paths and critical points in the ED for the halogen bond O…Cl and O…N interactions.

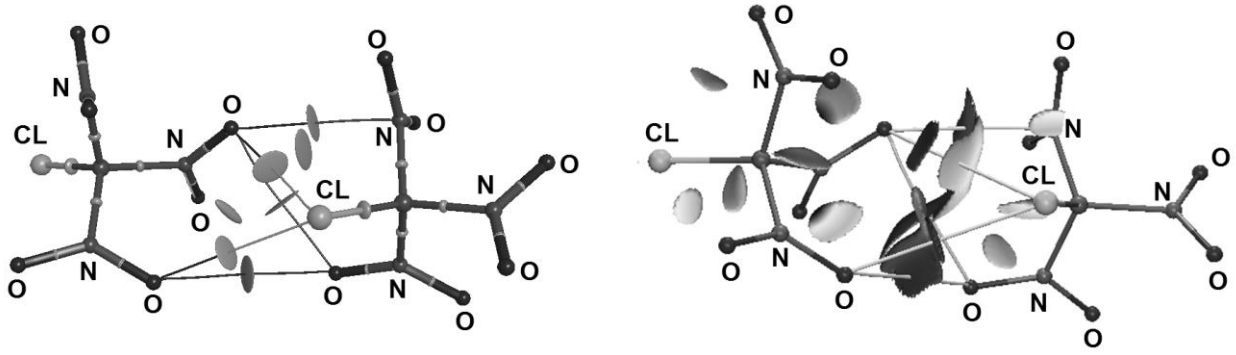

Fig. 2. The QTAIMC (a) NCI (b) bonding picture for cluster removed from Cl-C$(NO_2)_3$ crystal

Thus we found that QTAIMC and NCI, which are increasingly used in conjunction, characterize the different effects: QTAIMC identifies the presence of bond paths in molecules and crystals while NCI reveals the electron density features around the ED critical points and packing voids.

In the crystals Cl-C$(NO_2)_3$ and I-C$(NO_2)_3$, we can distinguish three types of low RDG(**r**) regions: 1) intermolecular halogen bond Hlg...O and O...N interaction between neighboring nitro groups; 2) intermolecular van der Waals interactions Hlg...O and O...O; 3) the intramolecular interactions Hlg...O and O...N between halogen and nitro groups belonging to the one molecule. From the standpoint of NCI both intra- and intermolecular interactions Hlg...O and O...N are of the same nature. However, QTAIMC does not detect the bond paths for intramolecular interactions in Hlg-C$(NO_2)_3$. Along to Hlg...O and O...N lines, the three interatomic boundaries of the four atoms are converged extremely close, and a saddle point in the ED is not formed.

Both approaches use the curvature of ED λ_2(**r**) as a parameter for conclusions about the character of atomic interactions. However, the low RDG(**r**) regions of van der Waals Hlg...O and O...O interactions can exhibit the change in sign of λ_2(**r**) function. In this case the conclusions about the binding nature of these interactions will be more complicated.

Finally, we note that the characteristics of the bond critical points in QTAIMC are used to quantitative estimate the heat of sublimation in molecular crystals. On the contrary, similar tools within NCI have not yet been developed.

This work was supported by Russian Foundation for Basic Research, grant 13-03-00767a, and by the Russian Ministry for Education and Science.

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