Non-Covalent Interatomic Interactions in Crystals of Halogen-Substituted Trinitromethanes

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Interatomic interactions in crystals of substituted trinitromethanes, $ClC(NO_2)_3$ and $IC(NO_2)_3$ containing intra- and intermolecular interactions O...Cl, O…I, have been carried out from Quantum Topological Theory of Atoms in Molecules and Crystals (QTAIMC)[1] and the Non-Covalent Interactions (NCI) method analyzing the Reduced Density Gradient function (RDG) [2]. Zero-flux condition for the gradient of electron density allows tracing boundaries of bounded atoms as closed surfaces around the nuclei.

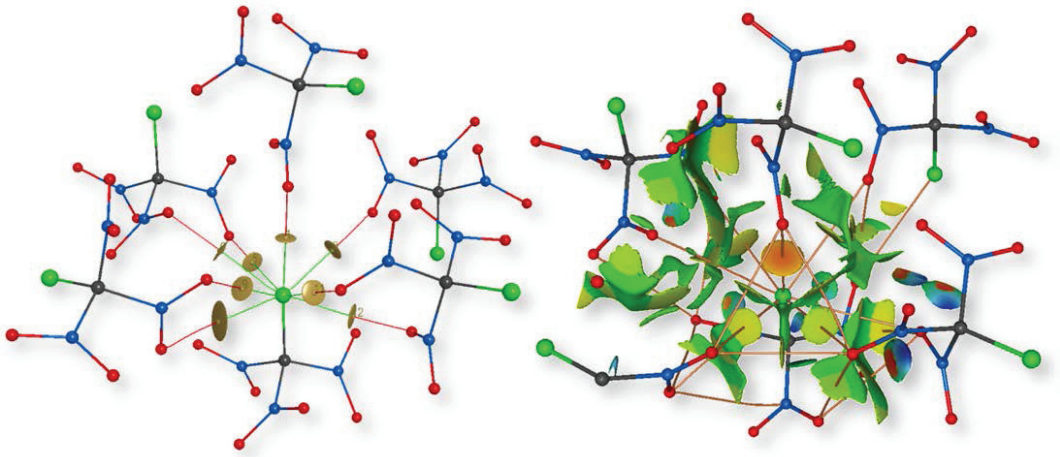

Fig.1. Intermolecular interactions O…Cl in solid chlorotrinitromethane: a) QTAIMC, b) NCI

Periodic 3D calculations B3LYP-D/TZVP were performed with optimization of atomic positions keeping fixed the space group and unit cell parameters (CRYSTAL09/14). The electron density was converted to the space-extended Hansen-Coppens multipole model and the features of the bond critical points and atoms were used to characterize the non-covalent interactions in the crystals under study with WinXPRO program.

In the crystals $ClC(NO_2)_3$ and $IC(NO_2)_3$ we can distinguish three types of low RDG regions: 1) intermolecular halogen bonds[3] Cl...O, I...O; 2) intermolecular van der Waals interactions Cl...O, I...O; 3) intramolecular interactions Cl...O, I...O. From the standpoint of NCI, both intra- and intermolecular interactions between halogen and oxygen atoms are of the same nature. However, the corresponding QTAIMC bond paths are not found; instead, such contacts, which we call “uncompleted links”, are accompanied by "quasi-bonding channels" corresponding to $\lambda_2(r)<0$ regions on the sign$[\lambda_2(r)]\rho(r)$ contour maps. Both QTAIMC and NCI-RDG use the perpendicular curvature of electron density, $\lambda_2(r)$, as a parameter for conclusions about the character of atomic interactions.

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