COLOR REPRODUCTION OF INTERMEDIATE COMPLEXES OF NITROAROMATIC EXPLOSIVES WITH NUCLEOPHILES: A QUANTUM-CHEMICAL APPROACH

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Formation of colored Meisenheimer and charge-transfer intermediate complexes in reaction with nucleophiles is a well-known feature of nitroarimatic explosives, like 2,4,6-trinitrotoluene (TNT), picric acid, etc. This reaction is applied for visual colorimetric determination of such compounds [1]. Thus, we have used time-dependent density functional theory (TD-DFT) calculations to reproduce the corresponding absorption spectra in terms of the main transition energies and relative intensities. As a reference spectrum, we have applied a pale brown complex (color #C59966) of TNT with 2-(dimethylamino)ethyl methacrylate (DMAEMA) [2].

We have examined various DFT functionals (HSE06, B3LYP, TPSS, ωB97XD, M06-2X, B3PW91 and PBE0) in order to find the most appropriate approach. Thus, the hybrid functional HSE06 was found to be the most appropriate. The calculated absorption spectrum along with the corresponding experimental one are presented in Fig. 1

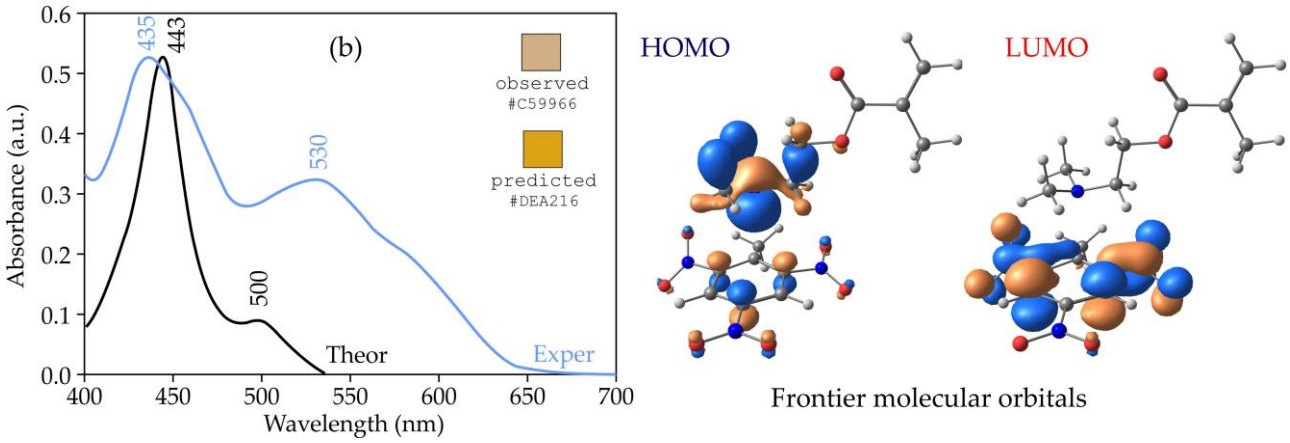

Fig. 1 Experimental and predicted absorption spectra and the corresponding sample colors

The first absorption band corresponds to the HOMO→LUMO transition. As one can see from the corresponding frontier orbitals, this is a typical charge-transfer complex with electron transition from DMAEMA to TNT (Fig. 1). Validity of such model of the complex was proven by molecular dynamics simulations in the supercell approximation with 50 molecules of DMAEMA and 50 molecules of TNT. The results suggest that an equilibrium interatomic distance between C1 atom of TNT and the N atom of DMAEMA is about 3Å. Thus, we can conclude that the model of contact ions calculated in polar continuum (polarizable continuum model, PCM) is appropriate for description of such intermolecular interactions.

Using this approach, we have also calculating intermolecular interactions of TNT and ionic nucleophiles (OH^-). In this case, a more strongly bound complex is formed (the Meisenheimer complex). Therefore, in order to determine the bonding nature in all these cases, we have performed quantum theory of atoms in molecules (QTAIM) analysis, which approved the coordination bond type in the case of DMAEMA and the covalent bond nature in the case of hydroxyl anion.

1. Almog J., Zitrin S. Colorimetric detection of explosives // Aspects of explosives detection. – 2009. – P. 41-58.
2. Pablos J.L., Trigo-López M., Serna F., García F.C., García J.M. Water-soluble polymers, solid polymer membranes, and coated fibres as smart sensory materials for the naked eye detection and quantification of TNT in aqueous media. Chem. Commun. – 2014. – N 50. – P. 2484-2487.