Poster

How do non-covalent interactions affect the sensitivity of high-energy materials? Analysis of crystal structures of nitroaromatic molecules

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Non-covalent interactions play an important role in the design of new materials, from catalysts to high-energy materials (HEM) [1]. Analysis of non-covalent bonding patterns in crystal structures is especially important in the case of high-energy compounds like explosives since the vast majority of these compounds are used in the solid state. Moreover, crystalline factors like free space per molecule in the crystal lattice are among the most important properties that define the sensitivity of solid-state HEMs towards impact [2]. Other factors like positive values of the Molecular Electrostatic Potential (MEP) in the central regions of the molecular surface and the presence of hydrogen bonds are also known to affect the sensitivity of these molecules. While studies clearly show that strongly positive values of MEP in the central regions of molecules are related to the high sensitivity of HEMs towards impact, the role of hydrogen bonding is not clear since it might both increase and decrease the sensitivity of HEM compounds [2].

In this work, we have performed an analysis of non-covalent bonding patterns in crystal structures of trinitroaromatic explosives. All crystal structures were extracted from the Cambridge Structural Database (CSD). A special focus of our analysis was on the role of hydrogen, halogen, and pnictogen interactions on the structures and values of the electrostatic potential in the central areas of the molecular surface of studied compounds [3, 4]. For selected crystal structures, MEPs were calculated in the case of free HEM molecules and molecules involved in non-covalent interactions, and values of electrostatic potentials were compared. Furthermore, the influence of non-covalent interactions on the geometry of the nitro group with respect to the aromatic plane was studied by analyzing the angle between the aromatic plane and the nitro group. It is known that tilting of nitro-groups in nitroaromatic HEM molecules leads to the higher sensitivity of these molecules due to broken delocalization. The results of the crystal data analysis were compared with the results of high-level ab initio calculations.

Results showed that hydrogen bonding decreases electrostatic potential values in the case when HEM molecules act as hydrogen atom donors by 20 to 25% and increases in the case when HEM molecules act as hydrogen atom acceptors (by approximately 10%). Significant changes in electrostatic potentials were calculated in the case of halogen and pnictogen bonding, too. The analysis of geometrical parameters in crystal structures of HEM molecules also showed that pnictogen bonding between nitrogen atoms from one nitro group, and oxygen atoms from the other nitro group may lead to the tilting of the nitro group with respect to the aromatic plane. High-level quantum chemical calculations confirmed the existence of strong pnictogen bonds in these structures. Analysis of geometrical data also showed that the presence of voluminous halogen substituents may lead to the tilting of the nitro-group with respect to the aromatic plane.

The results presented in this study show that non-covalent bonding can significantly affect some of the most important factors that determine the sensitivity of HEMs towards detonation. One of the ways by which non-covalent interactions affect sensitivity is a change in the electrostatic potential values in the central regions of HEMs, which is known to be one of the most important indicators of sensitivity toward detonation. The other way is by tilting the nitro group with respect to the aromatic plane, which leads to the weakening of the C-NO_2 bond, whose dissociation is the first step in the detonation process of nitroaromatic explosives. These results could be of great significance for the understanding of detonation characteristics of solid HEMs and could help in the design of new HEMs with improved sensitivity towards detonation.

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