

*Visualization of non-covalent interactions in conformational polymorphs*Anton V. Savchenkov¹, Viktor N. Serezhkin¹¹Department of Inorganic Chemistry, Samara National Research University, Samara, Russian Federation

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Conformational polymorphism is highly attractive for theoretical investigations and various applications. Discovery of highly polymorphic systems raises a question of how polymorphic modifications are different from one another. Scientists from around the world apply quantum chemical calculations to determine most stable conformations and to search for subtle differences among modifications. One of the favored approach to analyze conformations is to draw a potential energy graph versus the most important torsion angle, responsible of the conformation of the molecule. However, such a theoretical approach has several drawbacks. For example, the potential energy is usually calculated for one molecule in a gas phase in respect to one torsion angle, and it is almost impossible to draw such a potential energy graph, which will consider rotation around several torsion angles.

As Bernstein in 2002 raised a question "Can the differences in energetic environment be understood on the basis of particular intermolecular interactions?" [1], we decided to look at how conformational adjustment affects non-covalent interactions in crystal structures of polymorphs. As opposed to quantum chemical calculations, analysis of non-covalent interactions in real crystal structures reveals every last feature of such structures. Thus, we decided to develop a method of visualization of adjustment of non-covalent interactions in crystal structures of conformational polymorphs.

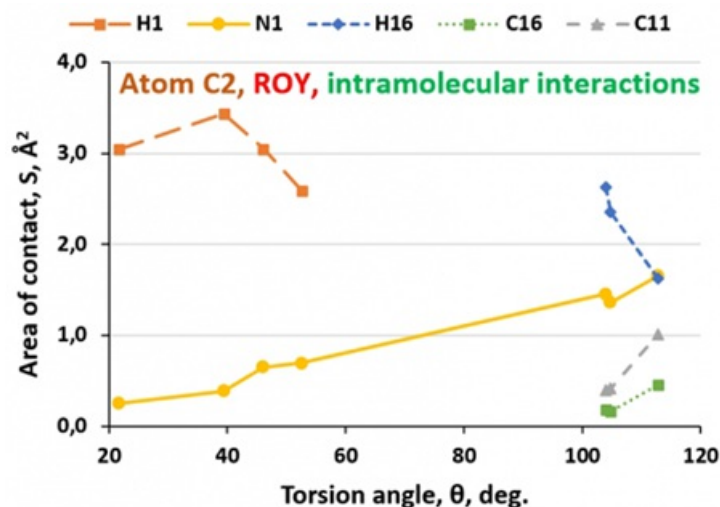
The first step is to establish characteristics of all intra- and intermolecular non-covalent interactions in the structures of conformational polymorphs. These characteristics are readily available within the stereoatomic model of crystal structures and Voronoi-Dirichlet tessellation [2]. The second step is to plot variation of non-covalent interactions versus torsion angles or other geometric parameters under discussion. Dependent on the objectives, one may visualize adjustment of non-covalent interactions of a given atom, or adjustment of total non-covalent interactions of a given type (intra- or intermolecular) or given nature (e.g. hydrogen bonds).

ROY and FFA are the most polymorphic systems with 7 and 8 structurally studied modifications respectively. Analysis of ROY and FFA using the proposed method shows, that conformational adjustment of molecules during crystallization results in variation of intra- and intermolecular non-covalent interactions in crystal structures of polymorphic modifications. As an example, the graph on the picture visualizes the adjustment of non-covalent intramolecular interactions of the nitrile carbon atom in crystal structures of ROY polymorphs. One can notice how interactions between atoms of different cycles (nitrophenyl and thiophene) of the ROY molecule change significantly, appear or disappear with the change of the torsion angle.

Overall, this abstract presents a powerful method, which allows to visualize adjustment of non-covalent interactions in crystal structures of conformational polymorphs and to understand the importance of different types of interactions in different conformations. The use of this method enables correlation between the variation of potential energy of polymorphic modifications and the variation of non-covalent interactions in their structures, what is a giant step forward towards the better understanding of structure–property relationship in crystals.

[1] Bernstein, J. (2002). *Polymorphism in Molecular Crystals*. New York: Oxford University Press.

[2] Serezhkin, V. N. (2007). Some features of stereochemistry of U(VI). In *Structural Chemistry of Inorganic Actinide Compounds*, edited by S. V. Krivovichev, P. C. Burns, I. G. Tananaev, pp 31–65. Elsevier Science.



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