Influence of the halogen bonds in context of crystal structure prediction problem

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Previously we proposed strategy to design non-linear optical materials by modifying molecular structures and predicting their crystal packing from the first principles [1]. Our strategy includes generation of the AMOEBA force field parameters to describe intermolecular interactions for given organic molecules in their crystal structures. It also includes the crystal structure prediction using this force field and USPEX evolutionary minimization of lattice energy [2]. Here we apply this strategy to predict non-centrosymmetric crystal structure of 2-iodo-3-hydroxypyridine and its virtual polymorphs.

Upon detailed analysis of the results, we found a match for experimental structure among several predicted ones. This structure had the lowest lattice energy after reoptimization using Density Functional Theory with Tkatchenko-Scheffler dispersion correction (DFT-TS). Thus, our prediction was successful. We also found disagreement in distribution in $|\theta_1 - \theta_2|$ between experimental set containing various molecular crystals and predicted polymorph set. Overall, I…I contacts of Type I are much more frequent among the predicted structures (Figure 1), than in experimental set. Consequently, we can conclude that DFT-TS (FHIaims-set) optimization increases the number of Type I interactions at the expense of Quasi-Type I interactions. The number of Type II interactions after DFT-TS optimization decreases. This indicates that isotropic repulsion potential may not be sufficient for the accurate crystal structure predictions, even when combined with anisotropic electrostatic model (atomic dipoles and quadrupoles, as implemented in AMOEBA).

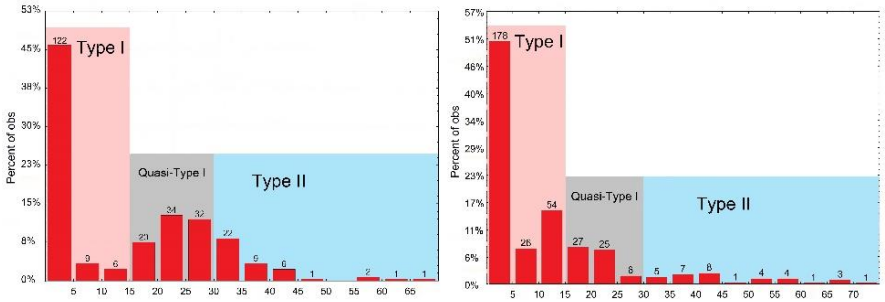

Figure 1: Parameters of noncovalent interaction according to the distribution of I…I contacts over parameter $|\theta_1 - \theta_2|$ in *a*) Tinker-set and ***b***) FHIaims-set. Type I is marked in pink, QuasiType I is in grey, Type II is in blue.

References

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2. Glass, C. W.; Oganov, A. R.; Hansen, N., *Comp. Phys. Comm.* **2006,** *175* (11-12), 713-720.