

Łódź, 03.07.2018

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## DOCTORAL DISSERTATION ABSTRACT

### *„Supramolecular systems organization in crystals of phosphorylated azaheterocycles”*

Organophosphorus compounds are important for medicine, chemical industry, and agriculture. Contrary to the phosphates with their P-O-C moiety prone to biochemical cleavage, phosphonates with the sturdy P-C bond are chemically and biochemically stable. The phosphoryl bond has a strong dipolar character with a substantial positive charge located on the phosphorus atom. Therefore, the phosphoryl group is longer and more polar structural equivalent of the carbonyl bond. It makes oxygen atom of phosphoryl group a good acceptor of hydrogen bonds. Therefore, phosphonates are interesting alternative for crystal engineering and important enhancement to carboxylic acids and carboxylates widely used in supramolecular strategies based on synthon concept. The latter approach put emphasis on spatial arrangement of intermolecular interactions and the similarity of resulting patterns formed by investigated series of structures. Supramolecular systems may be also defined by molecular building blocks, namely tectons. The tecton concept addresses the importance of shape and rigidity of molecular moieties. Contrary to the synthon strategy, tecton approach is dedicated to porous systems and its application to more densely packed organic crystals is quite limited indeed.

The essential goal of my work is identification and characterization of packing motifs existing in supramolecular systems formed by organic phosphonates. I have crystallized and determined by single crystal X-ray diffraction method (SC-XRD) ten crystal structures of azaheterocyclic phosphonates in which polycyclic moiety with fluorene skeleton is linked to the phosphonic moiety.

Supramolecular assemblies of all investigated systems were characterized using well established tools used in crystal engineering. Intermolecular energies were evaluated using computational methods based on density functional theory (DFT) as implemented in *Gaussian09*, *CLP-PIXEL* and *CrystalExplorer17* packages. Additionally, fingerprint plots derived from the Hirshfeld surfaces, were generated for each structure to characterize the crystal packing arrangements. Molecular electrostatic potential mapped over relevant Hirshfeld surfaces identified parts of molecules prone to electrostatic interactions.

Supramolecular architectures formed by investigated systems are defined accordingly to either tecton or synthon concept.

Six of investigated structures adopt ladder topology which were characterized by novel geometrical descriptors quantifying differences in their geometry. Structural and computational analysis of supramolecular motifs shows lack of common synthon responsible for the ladder packing arrangement. However, the geometry similarity of all molecules indicates that ladder packing is based on the shape oriented recognition and mostly driven by van der Waals forces. The intermolecular electrostatic effects are crucial for stabilizing and fixing geometry of the already formed clusters.

Another three compounds crystallize as hydrates and form pseudo-centrosymmetric  $P=O \cdots H-O-H \cdots O=P$  synthons, reported by me for the first time. In all systems, water molecules are disordered around inversion center over four positions and are encapsulated by ethoxy and phosphoryl groups. The resulting pockets are connected by narrow linkers and form tunnels with periodically changing diameters. The most likely, water molecules enter the crystal during crystallization. Their further transport is limited by the tight channel aperture. The TG/DTG and DSC analyses indicate that thermal stability of investigated crystals is closely related to their packing behavior which is not disturbed by associated water molecules. Topology of intermolecular interactions is identical over all systems.

One structure realize supramolecular arrangement dominated by two infinite stacks composed of unique symmetry independent molecules linked by distinctively different hydrogen bond systems. In both chains the phosphoryl group is involved in hydrogen bond formation with the amino group.

Additionally, local and global aromaticities of heterocyclic moieties in all azaheterocyclic phosphonates were evaluated with two popular geometry based methods, i. e. HOMA (Harmonic Oscillator Model of Aromaticity) and HOMHED (Harmonic Oscillator Model for Heterocycles with  $\pi$  electrons and for n-electron Delocalization).

Comprehensive structural characterization of a series of azaheterocyclic phosphonates showed that they may be interesting building blocks for crystal engineering strategies. Moreover, it has been proved that packing of molecular crystal may be conveniently interpreted by the simplified supramolecular tecton concept in which weak interactions support organization of molecular entities. This approach may be especially useful when applied to systems where formation of strong directional donor-acceptor interactions is unlikely.

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