MS32-P3 On the relation between topology of halogen-bonded molecular crystals and type of halogen-halogen contacts

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We have studied 3722 monomolecular crystal structures of organic compounds comprising halogen bonds (XB). The structural information was taken from the Cambridge Structural Database (release 5.36). We have described the structures by infinite periodic graphs (underlying nets), whose vertices and edges correspond to molecular centers of mass and intermolecular halogen bonds, respectively. To describe the topology of supramolecular complexes formed by molecules connected by halogen bonds we have used the concept of molecular connection type that was formalized with molecular connection type symbol (MCTS) [1]. Topological classification of molecular connection types and underlying nets has been performed with the ToposPro package [2]; for determination of the type of halogen-halogen contacts [3] we have developed a special procedure and implemented it into ToposPro. As a result, the distributions of topological types and MCTSs were built for all halogen-bond patterns. The most frequent connection types of molecules are K^4, B^4, T^4 for the 2D halogen-bonded motifs and K^4, G^{82}, P^6, G^6 for the 3D ones. Separately, for the structures containing symmetrical halogen bonds we have found correlations between the XB type and the local topology of the supramolecular complexes. For example, type II contacts are typical in structures with MCTS B^2, while type I contacts are inherent for the M^1 connection types.

The work was supported by the Russian government (grant No. 14.B25.31.0005).

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Keywords: halogen bond, topological properties, molecular crystals, supramolecular complexes

MS32-P4 Crystal engineering of metalloporphyrin assemblies by concerted halogen and hydrogen bonding interactions

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Metalloporphyrins have unique structural, photochemical, catalytic and electronic properties, and they provide magnificent building blocks for the construction of attractive supramolecular architectures.[1] The functional diversity that can be imparted to these tectons on the peripheral and axial sites of the porphyrin framework allows us to formulate supramolecular arrays of different topological features. The toolbox for obtaining materials of the desired structure contains in addition to the well characterized coordination and hydrogen bonds, newly exploited halogen bonding motifs. Concerted utilization of the non-covalent (and often competing) interactions in the porphyrin assembly process provides a new challenge in crystal engineering. In this presentation, we will highlight primarily the self-assembly of suitably functionalized metalloporphyrin scaffolds into halogen-bonds-driven networks. Successful designs of such architectures involved the use of di- and tetra-iodophenyl porphyrins metallated with either oxo-Mo^V(L=axial ligand) or $Sn^{IV}(L)_2$ centers, with halogen bond donors and acceptors positioned in a complementary manner on 'L' and the *meso*-aryl groups. Then, we will shed light on new systems where hydrogen and halogen bonds act in concert in stabilizing the assembled architectures.[2]

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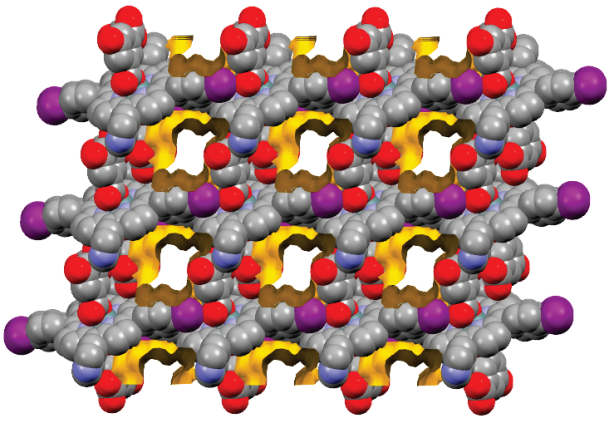

Figure 1. Supramolecular assembly of porphyrin moieties by directional non-covalent interactions

Keywords: Halogen Bonding, Hydrogen Bonding, Porphyrins