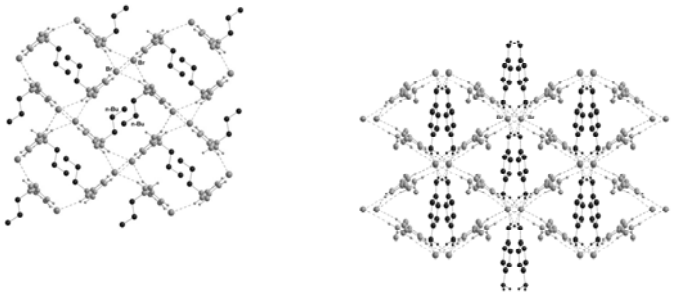
W0294

X-Ray Diffraction Analysis of "Ionic Liquids": What Can we Learn More About Ionic Liquid Solution?
Konstantin Lyssenko, Denis Golovanov, Mikhail Antipin, Alexander Shaplov, Yakov Vygodskii, A.N. Nesmeyanov, Inst. of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia.

Ionic liquids (IL) are organic salts that are liquid at room temperature or below 100ºC. This type of compounds is now established to be a perspective new class of solvents for a wide range of organic, organoelement and inorganic compounds for various applications. One of the most investigated and widely used IL are based on the various imidazolium cations (**im**). Despite of in salts "popularity" in green chemistry, X-ray diffraction analysis and thus the peculiarities of their supramolecular organization are still practically unexplored.

Taking into account that melting point of IL is affected both by the nature of anion and size of alkyl chains we have performed the X-ray diffraction analysis of a series of **im** salts with bromine and SiF_6 anions. The investigation of their supramolecular structure makes possible to explain a dependence of **im** salts m.p. from the water contents; estimate the role and energy (within the PBE/TZP calculation) of the Si-F...H-C contacts on m.p. of $[\mathbf{im}]_2SiF_6$. Utilising the high flexibility of alkyl chains we have managed to obtain and analyze the first example of cocrystal formed by 1,4-phenylenediamine (**PD**) with the ionic liquid 1-n-butyl-3-methyl imidazolium bromide (**Br[Bmim]**). It was found surprisingly that general features of supramolecular organization of the “solvent part” remain the same as in the crystal of pure ionic liquid.

Figure Orthorhombic channels formed by imidazolium cations (green) and bromine anions, filled in by n-butyl groups (blue) in the crystal of **Br[Bmim]** (**A**) and filled in by **P D** molecules (blue) in the cocrystal of **Br[Bmim]•PD**



The unusual type of solvation in IL solution can be also utilized for design of new polymorphic modifications of various compounds, that have been fulfilled, for example, by us in the case of triphenyl phosphite.