

# Oral Contributions

**[MS25 - 04] Appearance is deceptive. Pair-wise energy analysis of packing motifs in molecular complexes** Dmitry S.Yufit<sup>a</sup>, Oleg V.Shishkin<sup>b</sup>, Roman I. Zubatyuk<sup>b</sup>, Judith A.K. Howard<sup>a</sup>

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Low-melting molecular complexes of methyl halides (chloroform, dichloromethane, bromoform) with various common non-aromatic organic solvents (ethers, ketones, THF, etc.) display in their crystal structures a variety of types and motifs of intermolecular interactions in spite of seeming simplicity of the components [1]. Due to the small size of the components, such co-crystals can be effectively used as model systems for probing the factors affecting intermolecular interactions [2]. Traditional analysis of crystal packing of these complexes, based on the directionality and geometry of short intermolecular contacts, indicates that the components are typically held by various C-H...X (X=O, Hal) and dipole-dipole interactions while halogen bonds Br...O/Br are observed only in some complexes of bromoform. A new energy-based approach [3] for analysis of packing motifs, based on the calculations of pair-wise energies of intermolecular contacts and representation of the results using energy-vectors diagrams, provides an entirely new insight into the nature of packing, observed in studied co-crystals. Thus, it turned out that halogen bonds are usually far from being the strongest intermolecular contacts although they still participate in building of the crystal structure. The results obtained demonstrate that the traditional geometrical method of analysis in some cases might give rise to misleading conclusions. For example, the main building blocks in the structure of molecular complex of bromoform with cyclohexanone are not "obvious double ladders" but layers of heterotetramers. Using the energy-based approach the co-crystals

might be classified as "real", "composite" and "discrete" ones, which differ by number, character and directionality of strongest intermolecular interactions.

[1] D.S.Yufit, R.Zubatyuk, O.V.Shishkin & J.A.K.Howard, *CrystEngComm* (2012), **14**, 8222-8227.

[2] M.T.Kirchner, D.Blaser & R.Boese, *Chem. Eur.J.* (2010), **16** 2131-2146.

[3] O.V.Shishkin, V.V.Dyakonenko & A.V.Maleev, *CrystEngComm* (2012), **14**, 1795-1804.

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