

Poster Presentation

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Halogen- versus Hydrogen-Bonds Aggregation and Competition at High Pressure

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Halogen and hydrogen bonds [1] are most often associated with the structure of molecular crystals. Even weak specific interactions, such as halogen...halogen and CH...halogen contacts, can compete between themselves and with Kitaigorodski's close packing rule. The competition between halogen...halogen and CH...halogen interactions has been studied at high pressure for the series of six dihalomethanes CH₂XY (X,Y = Cl, Br, I). They crystallize in several structural types of space groups Pbcn, C2/c, Pnma, Pna2₁ or Fmm2. In all these compounds and in their polymorphs the halogen...halogen and CH...halogen interactions persist despite considerable structural differences. The group of monohalomethanes (CH₃X, X = Cl, Br, I) are the simplest organic polar compounds and ideal models for studying halogen...halogen and CH...halogen interactions. For these simplest haloalkanes, the halogen...halogen competition with CH...halogen bonds, scaled in the function of electrostatic potential in the Cl, Br, I series, is affected by pressure. Phase α-CH₃Br, isostructural with CH₃I (orthorhombic space group Pnma) and dominated by halogen...halogen bonds, is destabilized by pressure. At 1.5 GPa the ambient-pressure α-CH₃Br phase transforms into phase β-CH₃Br governed by CH...halogen interactions. Phase β of CH₃Br is isostructural with CH₃Cl, orthorhombic space group Cmc2₁ [2,3]. The CH₃Br molecules are more evenly accommodated in space group Cmc2₁ and CH...halogen interactions are favoured by the close-packing effect.

[1] P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, *Angew. Chem. Int. Ed.*, 2008, 47, 6114-6127, [2] M. Podsiadło, A. Katrusiak, *CrystEngComm.*, 2009, 11, 1951-1957, [3] M. Podsiadło, A. Olejniczak, A. Katrusiak, submitted to *CrystEngComm.*, 2014

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