MS17-03 | Crystal Structure Compression and Pressure-Induced Polymerization of Arene-Perfluoroarene Co-Crystals Leading to Columnar Hydrofluorocarbons

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The arene-perfluoroarene interaction is a robust supramolecular synthon, which is used for the development of highly oriented, stacked π-systems [1]. We investigated the structural compression of 1:1 arene-perfluoroarene co-crystals, naphthalene:octafluoronaphthalene (NOFN) and anthracene:octafluoronaphthalene (AOFN), using single-crystal synchrotron X-ray diffraction. Our study shows the remarkable pressure stability of the crystal structures and hence of the parallel arene-perfluoroarene stacking arrangement up to 20 and 25 GPa for NOFN and AOFN, respectively, at which they show pressure-induced phase transitions, irreversible on decompression. Increasing pressure leads, predominantly, to reduction of the interplanar π-stacking separations, which are strongly compressed at the phase transitions. This indicates the pressure-induced breakdown of π-π stacking via polymerization and formation of σ-bonded high-pressure phases. Complementary high-pressure infra-red spectroscopy measurements and quantum mechanical computations based on density-functional theory using CASTEP [2] confirm the pressure-induced polymerization and the formation of columns of σ-bonded hydrofluorocarbons along the arene-perfluoroarene π-stacking direction as well as the one-dimensionality of the chemical reactions. Structural models for the fully polymerized phases of NOFN and AOFN are presented, which are in agreement with experimentally determined unit cell parameters.

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[2] S.J. Clark et al. *Z. Kristallogr*. **2005**, *220*, 567