ESRF	**Experiment title:** Pressure effect on the arene-perfluoroarene interaction	**Experiment number:** CH-5078
Beamline: ID15B	**Date of experiment:** from: 26/04/2017 to: 29/04/2017	**Date of report:** 29/08/2017 *Received at ESRF:*
Shifts: 9	**Local contact(s):** Ines E. Collings	

Names and affiliations of applicants (* indicates experimentalists):

Alexandra Friedrich[1]*, Krzysztof Radacki[1]*, Javier Ruiz-Fuertes[2]*, Todd B. Marder[1]

[1] Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

[2] ICMUV-Departament de Física Aplicada i Electromagnetisme, MALTA-Consolider Team, Universitat de València, C/ Doctor Moliner 50, 46100 Burjassot, Spain

Report:

The arene–perfluoroarene interaction is a robust supramolecular synthon, which is used for the development of highly oriented, stacked π-systems [1-3]. It describes the attractive interaction between fluorinated and non-fluorinated aromatic molecules, which have opposite charge distributions due to the differences in electronegativity for hydrogen and fluorine atoms with respect to the carbon atoms, resulting in a face-to-face association (Fig. 1). High-pressure investigations on the arene–perfluoroarene interaction have been limited to a Raman-spectroscopic study on a 1:1 co-crystal of naphthalene and octafluoronaphthalene (NOFN) at up to 8 GPa, which revealed its stability [4].

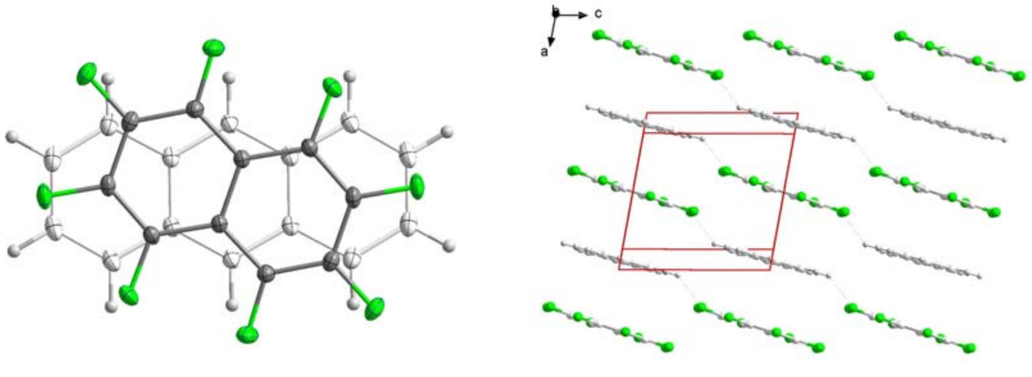

Fig. 1. Molecular π-stacking of octafluoronaphthalene with anthracene [3].

In order to investigate the evolution, stability, and strength of the arene–perfluoroarene interaction at high pressure, single-crystal synchrotron X-ray diffraction data were collected on NOFN and the 1:1 co-crystal of anthracene: octafluoronaphthalene (AOFN, Fig. 1) up to

20 and 30 GPa, respectively. In the case of NOFN intensity data were collected for two crystals of different orientations and combined in the crystal structure refinement, which improved the completeness of the data (73% up to 0.8 Å resolution, 48% to 0.6 Å compared to 41% and 54% up to 0.8 Å and 29% and 33% up to 0.6 Å for the two single sets, respectively) and hence the quality of the refined structural model. Data of higher resolution and completeness (89%, 81%, 59% up to 0.8, 0.6, 0.5 Å resolution, respectively) were collected at 8 GPa by additional rotation of the diamond anvil cell and lateral translation of the detector for multipole refinement of the charge density distribution. Unfortunately, the separate data reduction of the single data sets and hence different data scaling resulted in a high internal residual value on merging intensities. Data collection using a four-circle diffractometer at the synchrotron would probably provide better, more coherent data.

Main results

The π–π stacked structures of NOFN and AOFN, and hence the arene-perfluoroarene interaction in general, are remarkably stable at high pressure up to 20 GPa and 23 GPa, respectively, where they start to undergo phase transitions. While the crystals of NOFN were damaged at >20 GPa, the crystal of AOFN remained intact in the high-pressure phase although the low reflection intensities did not allow us to solve its structure (Fig. 2). The strongest compression occurs along the direction of molecular stacking, i.e. the *a* axis. The mean intercomponent distances are compressed from 3.46 and 3.43 Å at ambient conditions to 2.82 Å for NOFN at 19 GPa and 2.68 Å for AOFN at 22.5 GPa, respectively (Fig. 2). It was previously proposed for phenanthrene and other π-stacked compounds that the π–π intermolecular interaction breaks down at a pressure of about 20–25 GPa when the intermolecular separation is about 2.6 Å [5]. Similar behaviour is observed in NOFN and AOFN. Especially the strong compression of the stacking direction (*a* axis) in AOFN at the high-pressure phase transition points towards a breakdown of the π–π stacking interaction.

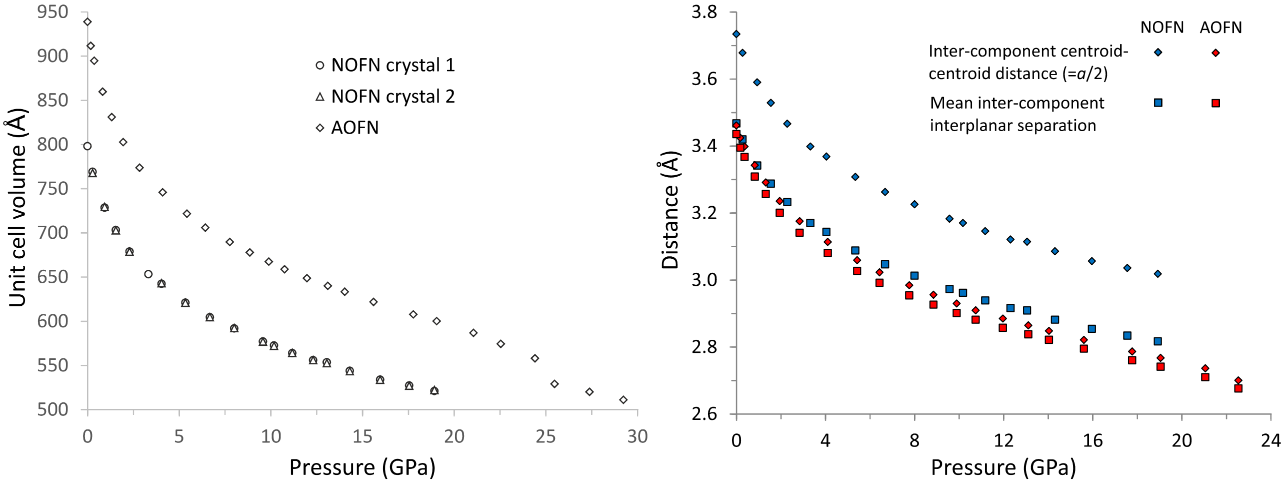

Fig. 2. Compression of the unit-cell volume (left) and intermolecular distances (right).

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