ESRF	**Experiment title:** High-pressure X-ray diffraction study of cage-like molecular structures adamantane and hexamethylenetetramine, and their capability of clathrate formation with helium	**Experiment number**: CH 4707
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Report:

We have studied two cagelike molecular compounds, adamantane (ADAM) and hexamethylenetetramine (HMTA) with closely packed structures devoid of obvious pores. Single crystals of ADAM and HMTA were loaded inside the diamond anvil cells with helium as the pressure transmitting medium to investigate the phenomenon of helium clathrate formation and "porosity without pores" recently revealed in this class of crystalline bodies (*cf.* CH 4272 experiment on arsenolite).

It has to be pointed out that due to the very fast sublimation of ADAM, the crystals decomposed immediately during the gas loading. Low diffraction quality of the patterns hampered effective structural analysis. After several unfruitful attempts we finally decided to terminate experiments on ADAM. Nevertheless, we managed to register XRD patterns up to 3.48 GPa and did not notice any "ghost" reflections in the diffraction pattern, which could evidence the gradual helium penetration inside the crystal structure of ADAM.

On the contrary, single crystals of HMTA gave high quality diffraction patterns and we managed to perform 19 experiments on compression up to 18.6 GPa and collect also 5 points on decompression. For all the measurements we were able to refine crystal structure with the satisfying *R*1-index (4-8%, except for the highest pressure point *i.e.* the one at 18.6 GPa where the refinement quality was noticeably worse). No "ghost" reflections were observed and all the efforts to refine helium atoms in the interstitial positions were unsuccessful.

We have noticed, however, that between 11.7 and 13.1 GPa volume increases by *ca.* 0.5%. While all the experimental points up to 11.7 GPa fit very well to the Birch-Murnaghan

isothermal equation of state (see inset at Fig. 1a corresponding to the red solid line), above this pressure the volume-pressure data follow different trend, which was roughly estimated with a green dashed curve at Fig 1a. This peculiarity also corresponds to the local maximum in the evolution of the C-N bond length (Fig. 1b; in both plots points above 11.7 GPa are in green for clarity). Besides, there is also a particular behavior of the C-N bond length at lower pressure: while it elongates initially on compression, it reaches a maximum at 2 GPa and then starts to decrease (*cf.* Fig. 1b). It should be stressed that after releasing pressure to ambient the crystal returned to its initial state.

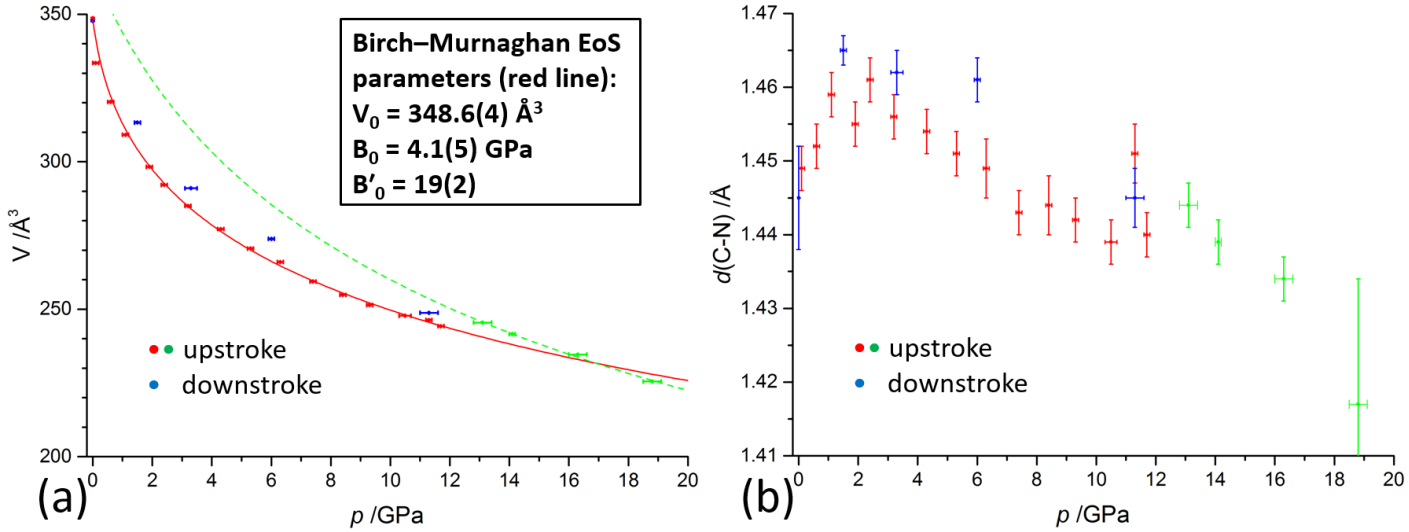

Figure 1. Evolution of unit-cell volume (a) and C-N bond length (b) with pressure.

The pressure values corresponding to these two peculiarities are in an agreement with the suggested phase transitions reported previously in literature basing on the Raman scattering experiments (Rao *et al.*, *Chem. Phys. Lett.*, 1999, *313*, 749-754). Noteworthy, these Raman studies were performed without use of pressure transmitting medium. On the other hand, our preliminary DFT calculations predicted that the C-N bond length should decrease monotonously with pressure up to 20 GPa.

In this respect, the results of the experiments are not wholly conclusive at that point. Further investigations are needed including more detailed measurements in the pressure ranges around 2 and 12 GPa, as well as the benchmark study with a non-penetrating pressure transmitting medium (neon).