ESRF	**Experiment title:** Crystalline, non-molecular, saturated CH networks formed from benzene under high pressure and temperature	**Experiment number**: **CH-4118**
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Report:

The aim of this proposal was to transform benzene into potential all saturated, crystalline CH networks at high pressures similar to those predicted by Xiao-Dong Wen, et al. (JACS **133**, 9023, 2011), using the diamond anvil cell (DAC) and high temperatures as those provided by laser heating techniques. These novel materials, once obtained, could be recovered at ambient conditions, which would be of paramount importance for technological applications (ex. hard materials).

Two DACs of the ESRF where used, DAC_A and DAC_B, equipped with Ia diamonds with 300 μm and 250 μm culet, respectively, and 60-120 μm gasket (Re) holes. The two DACs were loaded with pure benzene without diamond coatings. KCl chips were also inserted in the sample chamber for measuring the pressure. These cells where prepared for laser heating with the CO_2 laser. Two DACs from LENS were also brought, but they did not fit the laser heating apparatus, due to their limited aperture. Therefore, two sample have been prepared:

1) DAC_A. This sample was compressed to 42 GPa, a pressure where benzene starts to transform into amorphous hydrogenated carbon, according to our previous works (see for instance L. Ciabini, et al. *Nature Materials* **6**, 39, 2007). The sample was then laser heated to 1900 K, and temperature was measured in situ by the thermal radiation emission. The laser power was slowly increased to the maximum value, in 30-40 minutes. The coupling between the CO_2 laser and benzene was good and very stable. On the temperature quenched sample we observed a very transparent region along with the KCl chips. We then decided to scan the sample by XRD (λ=0.3738 Å), and discovered that the largest part of the initial molecular benzene was indeed transformed into a highly disordered extended phase characterized by a highly textured Debye-Scherrer ring with a characteristic intensity fluctuations of sixfold axis symmetry (Figure), which corresponds to *d* spacing of ca. 4.55 Å. The other diffraction rings present at the recorded images were attributed either to the Re gasket or KCl at 30 GPa. Recently discovered close-packed bundles of carbon nanothreads capped with hydrogen (Fitzgibbons et al., *Nature Materials* **14**, 43, 2015) gives a diffraction pattern with a very strong, nanocrystalline-like 100 reflection at d = 5.6 Å. This material can serve as a model for our reaction product, however we do not know the EOS and cannot calculate the d_{100} spacing at 30 GPa. DAC_A with the sample still at about 30 GPa was finally brought to our home laboratory where we performed

FTIR and Raman measurements upon lowering pressure. Micro-Raman spectroscopy has been showing the presence of what are most likely intermediate molecular/non-molecular phases, inhomogeneously distributed over the sample area. Also, FTIR spectroscopy shows that the sample is dominated by an a-C:H form, which was also recovered at room P and looks to be very similar to the one already found by us by compressing (30-50 GPa) and heating (300-650 K) benzene (Ciabini et al, *Nat. Mater*. 2007).

2) DAC_B. This sample was compressed to 46 GPa. The sample was then laser heated to 1600-2000 K. The laser power was slowly increased to the maximum value, in 30 minutes. The coupling between the CO_2 laser and benzene was not very stable in this case, and a severe instability was observed, most likely due to the absence of insulating layers between the sample and the diamonds. Anyway, we preferred not to use this kind of layers, in order to have a clean chemical environment to deal with. In the temperature quenched sample there were three different regions: (i) a very transparent one, extending to about 50% of the area or more, (ii) a slightly grey one, most likely polycrystalline in nature, and (iii) the transparent KCl chips. We then decided to scan the sample by XRD (λ=0.3738 Å), and discovered that the largest part of benzene was indeed transformed. In this case, the only phase we could identify was the single crystal one with very weak peaks, similarly to what we have been finding in DAC_A. We suspect that an important part of the sample was indeed transformed into an amorphous form, which we may have lost just because its weak and broad FSDP was overwhelmed by the Compton background of diamonds. Anyway, the single crystal phase was analyzed through several single crystal scans, performed in several different points of the sample, which showed at least 60 different Bragg peaks. These measurements were performed upon reducing pressure, down to room pressure, with the specific aim to determine the EOS of such a new phase. This phase was not recovered below 14 GPa, whereas an amorphous FSDP at about 11 nm^{-1} was observed at room P, similar to the one of the material identified by Fitzgibbons et al.. Preliminary analysis led us to determine two of the three cell parameters of a tentative, roughly orthogonal single crystal lattice: a = 5.6 Å and b = 5.7 Å. Also in this case, FTIR spectroscopy performed at LENS, shows that the sample is dominated by an a-C:H form.

In conclusions, we found a single crystal phase, probably a new phase, whose structure needs to be better determined. We are now continuing the analysis of single crystal XRD data on samples DAC_A and _B. We may need to perform additional experiments in the future in order to better unveil this phase.

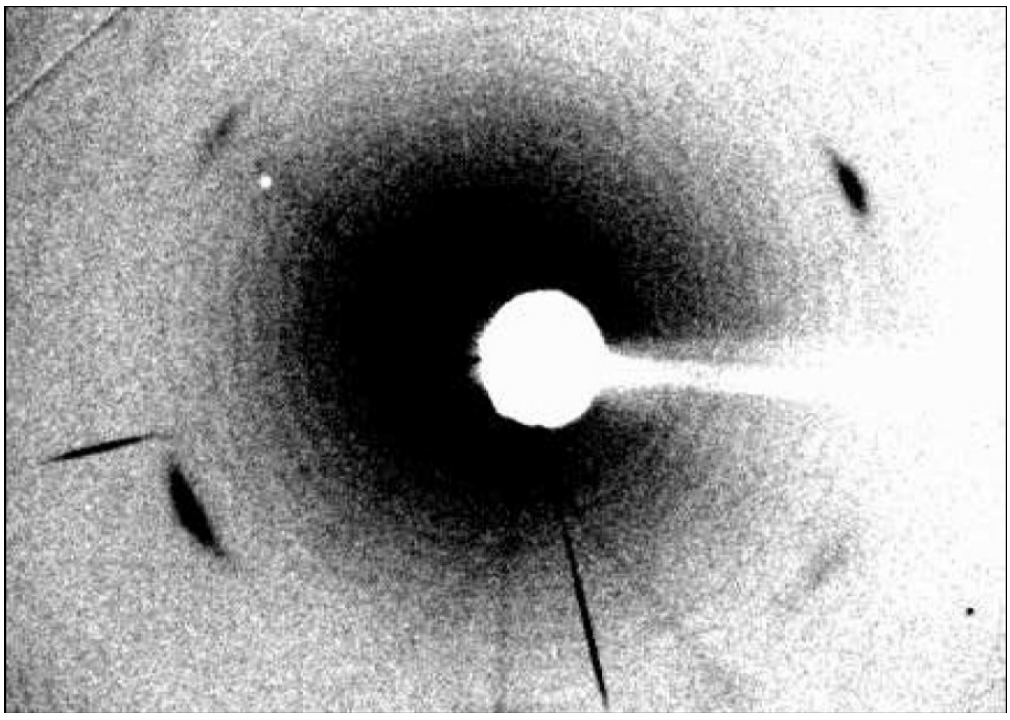

Figure. DAC_A. Fragment of the diffraction image of the benzene extended phase with the characteristic textured powder diffraction ring.