



	Experiment title: Structural study of the pressure-induced reactivity of model nitrogen-bearing aromatics.	Experiment number: CH-4279
Beamline: ID27	Date of experiment: from: 21/10/2014 to: 23/10/2014	Date of report: 27/02/2015
Shifts: 7	Local contact(s): M. Mezouar	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Margherita Citroni*, LENS Florence

Samuele Fanetti*, LENS Florence

Roberto Bini*, LENS Florence

Kamil Dziubek*, LENS Florence

Carla Bazzicalupi*, Department of Chemistry, University of Florence

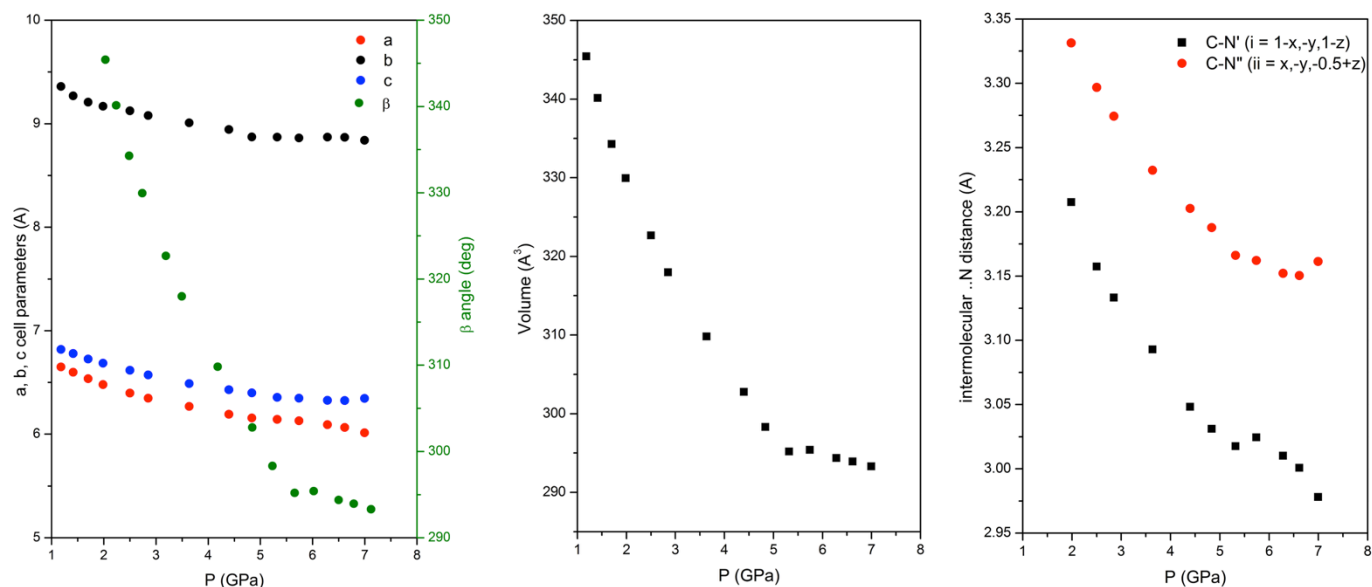
Report:

s-triazine is a model heteroaromatic, solid at room conditions with a $R-3c$ space group (phase I), undergoing a phase transition at 198 K at room P and at 0.6 GPa at room T. The low temperature structure is $C2/c$ (phase II) whereas the high-pressure structure has not been reported before. The high-pressure reactivity of triazine is under investigation because: a) pressure-induced reactivity in aromatics is a test-bench to understand solid state reactivity, and triazine is highly symmetric and simple b) triazine is formed by equal contents of N, C, and H atoms and may thus produce valuable energetic or hard CN materials. In previous IR experiments we evidenced the transformation into amorphous N-bearing materials, which reproducibly differ in IR spectrum, color, and mechanical resistance as a function of the P, T conditions at which the reaction is performed (an increasingly dark-red and stiff product is obtained at a lower reaction pressure by increasing the reaction T). With the present experiment we aim at obtaining the high-pressure crystal structure and its pressure evolution up to the reaction pressure at room T in order to detect the influence of the crystal structure on the preferred reactivity, which changes with P. We also want to investigate the structure of the reaction products, and to follow the time-evolution of a reacting sample at high P and T to obtain kinetic information on a timescale of minutes.

Investigation of the structure of s-triazine up to the reaction pressure

Triazine was investigated in a diamond anvil cell as a powder with no pressure medium. In fact, several efforts were made to prepare a sample in a hydrostatic medium but they were unsuccessful because triazine fast decomposes with polar solvents or with atmospheric moisture, is poorly soluble in apolar solvents, and sublimates very fast. The sample was thus just loaded as a polycrystal and treated as powder. Diffraction was measured as a function of pressure up to 7 GPa, that is near the threshold for room temperature reactivity, and in decompression run. The Rietveld refinement was performed for the lowest pressure point, 1.18 GPa, employing the low temperature structure of phase II (Smith and Rae, J. Phys. C:

Sold State Phys., 1978, 11, 1761) as structural model. The refinement confirmed that above 0.5 GPa phase II is formed and allowed for determining the positions for the C and N atoms. For all the higher-pressure points the cell parameters a , b , c , β were obtained and their variation is reported in the figure. The intermolecular C..N distances that may be responsible for the pressure-induced reactivity have been estimated assuming that triazine molecules remain rigid up to 7 GPa, and that the tilt angle (defined as ϕ in Smith & Rae, op. cit.) of the molecular plane is constant with pressure and equal to 12° . This angle is found in the experimental refinement at 1.18 GPa and a similar value has been obtained by DFT calculations. Analysis for the higher pressure points is in progress.



Recovered samples from reactions on triazine at high pressure

We examined five samples obtained from s-triazine at different reaction conditions:

- 1.1 GPa, 450 K (phase I)
- 3.0 GPa, 550 K (phase II)
- 4.5 GPa, 530 K (phase II)
- 6.0 GPa, 450 K (phase II)
- 4.4 GPa, 400 K and cw irradiation at $\lambda=457$ nm

and contained in free-standing gaskets. The amorphous diffraction patterns were measured, along with the background for the Compton scattering of air with a resolution up to $Q \approx 90 \text{ nm}^{-1}$. All the products are amorphous, just showing weak spots of crystal diffraction due to the ruby chips. The $S(Q)$ is under investigation to extract information on the local structure and evidence possible differences among the samples, due to the different reaction conditions. The preliminary analysis of the data indicates the presence of interatomic distances of about 2.5 Å.

Reaction monitored at 560 K, 6.5 GPa

The goal of this run is to follow the intensity of triazine powder rings as a function of time at reactive P, T conditions, to obtain kinetic information and monitor the possible growth of an amorphous or crystalline sample, and possible changes in triazine cell parameters. A resistively heated DAC was prepared and triazine was loaded with no pressure medium with a rhenium gasket 250 micron diameter and 85 microns thickness. 16 diffraction patterns were measured at constant $P = 6.5$ GPa and $T = 560$ K as a function of time for five hours. The reaction progress is evidenced by the considerable decrease of the Debye-Scherrer rings intensity, while the positions of the reflections are constant. The Mylar window peak was used as an internal standard.