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|   | <b>Experiment title:</b><br>Structure and chemistry of TCT (2,4,6-tricyano-1,3,5,-triazine) as a building block for graphite-like carbon nitrides | <b>Experiment number:</b><br>CH 5084   |
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## Report:

### Background

TCT (2,4,6-tricyano-1,3,5,-triazine),  $C_6N_6$ , is a potential building block for the synthesis of graphitic carbon nitrides retaining the triazine ring units, and high-energy-density materials due to its high nitrogen content. The pressure/temperature-induced irreversible reaction was previously identified by infrared spectroscopy at different thermodynamic conditions in the phase diagram (empty dots in Fig 1). Aim of this experiment was to identify the structure of the product (amorphous or crystalline) and determine the crystal structure of the starting material (molecular TCT) near the reaction conditions, in order to investigate the solid-state reaction mechanism. In a preliminary experiment TCT was found to exist in a low pressure and a high-pressure phase (phases I and II, respectively), the transition at room temperature occurring around 3 GPa, but the structure of phase II was not characterised.

### Runs performed

- 1) **Single TCT crystal in helium, room T compression up to 10.5 GPa.** The I-II transition occurred at 2.35 GPa. No sign of reaction is observed and the transition is fully reversible. The crystal structure of phase II was solved and the EOS was determined for both phases (Fig 2).
- 2) **Powder with no pressure medium, room T compression up to 10 GPa.** The I-II transition is observed at 2.35 GPa, and at 10 GPa an irreversible loss of the diffraction rings in time is observed. The product is amorphous and mixed with the unreacted TCT phase I.
- 3) **Powder with no pressure medium, compression and heating** (Fig1, blue dotted line). Upon isobaric heating at 6 GPa, a decrease of the diffraction ring intensity with time is observed at 555 K. Also in this case the recovered product is amorphous and contains remnants of TCT phase I.
- 4) **Powder with no pressure medium, compression to 1.8 GPa and heating.** A second point on the I-II line is found at 1.8 GPa, 331 K. A sudden loss of the Bragg peaks is observed at 430K, reversible and thus probably due to melting. The pressure at this point was not measured (the ruby was lost).
- 5) **Several recovered samples from TCT reactions performed at our laboratory in different P, T conditions.** All of them show only amorphous XRD patterns except for two, discussed below.

## Results

The 3<sup>rd</sup> order Vinet equations of state at room temperature for both phases are reported in Fig 2.

The **structure of Phase II** was solved with direct methods (at P=3.1 GPa) and refined using JANA2006 software, from the single crystal data. The space group is P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> and atomic positions are refined for all collected experimental points.

The **I-II transition line** is identified by two points: 2.35 GPa, 298 K and 1.8 GPa, 331 K.

A **melting point** is located at 1 GPa, 430K with a large uncertainty on the pressure determination due to the loss of the ruby used as pressure gauge, during melting. A tentative melting line is reported in Fig 2 (melting point at room temperature is from Beilstein database).

Concerning the reactivity, the first observation is that the **chemical stability limits** depend on the compression conditions. In fact, the sample hydrostatically compressed did not show any sign of chemical transformation up to the highest pressure reached in the run (10.5 GPa) whereas a sample non-hydrostatically compressed reacted at 10 GPa. All the samples compressed non-hydrostatically underwent an irreversible amorphisation. The previous stability limits detected by IR spectra, indicated by the empty dots in Fig2 (all determined on polycrystalline TCT with no pressure medium) are lower than those found here, probably due to the higher sensitivity of IR in detecting low concentrations of amorphous material and the averaged information on the non-homogenous sample provided by IR.

The **reaction product is in most cases amorphous**, but **two recovered samples showed new diffraction peaks** (Fig. 3 and 4). Both are products of reactions performed at 9 GPa and room temperature and left for several days under these conditions before pressure release. In Fig 3 we report the pattern of one of these samples, which is completely transformed and shows three rings consistent with a g-CN structure. In Fig 4, an XRD pattern of the other sample, revealing only one new diffraction ring with a strong preferential orientation at d=4.5Å, is shown along with TCT phase I peaks.

In most of the probed conditions, the reaction is not complete and even after waiting several hours or days (at our lab) the estimated yield is ~30% or less. This behaviour, along with the higher stability under hydrostatic compression, could indicate that reactivity is induced preferentially at crystal defects. This observation is consistent with the structure of phase II, here resolved. In fact, an essential requirement for reactivity in aromatics is the possibility of  $\pi$  stacking, that is forbidden here except at defects.

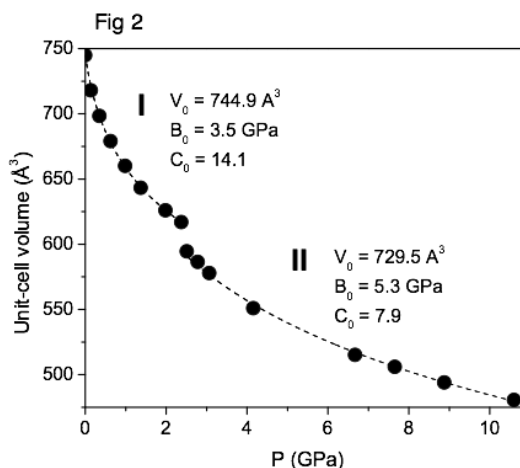
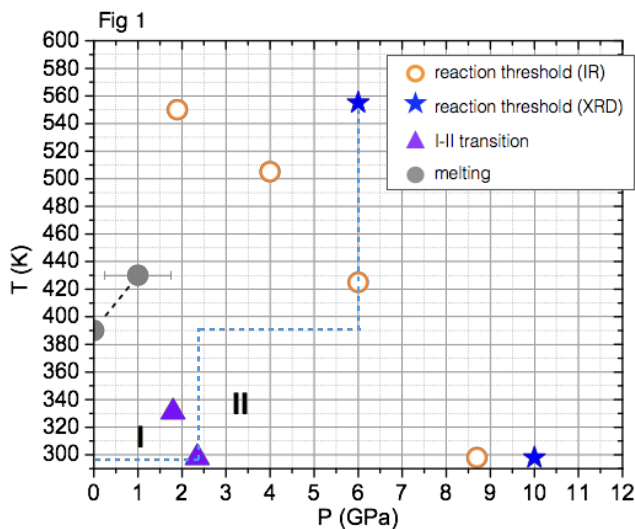


Fig.3

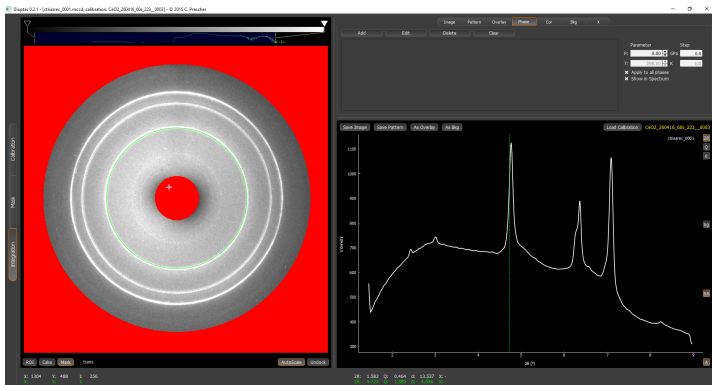


Fig.4

