Structure and reactivity of 2,4,6-tricyano-1,3,5-triazine under high-pressure conditions

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Abstract

2,4,6-tricyano-1,3,5-triazine is an attractive precursor for the synthesis of extended layered and nanoporous carbon nitrides. Using high pressure can achieve this via one-step condensation reactions. As a first step towards this goal we have characterized the structural properties and stability P-T range of the monomer (phase I) using synchrotron X-ray diffraction combined with FTIR spectroscopy under combined high pressure and high temperature conditions in a resistively heated diamond anvil cell. A new high pressure structure (phase II) appeared following compression to above 2.4 GPa at ambient temperature. The structure was identified as orthorhombic belonging to space group $P2_12_12_1$. The pressure-temperature conditions of the I-II phase boundary, as well as the melting line have been established. The chemical transformation of the phase II crystal was studied between 4 and 10 GPa at temperatures ranging from 550 to 300 K. X-ray and spectroscopic examination of the reaction products revealed a crystalline phase that could be assigned to a layered carbon nitride containing linked *s*-triazine rings along with amorphous material. Analysis of the kinetics indicates that the structural transformation is driven by defect formation.

1 Introduction

Layered nanoporous materials represent an important class of emerging structures that are intermediate between three-dimensional (3D) porous frameworks represented by zeolites, MOFs, COFs etc and conventional 2D layered materials such as graphite. They can combine the intercalation properties of 2D structures with selective interlayer diffusion and encapsulation-release behaviour that is important for materials design. The targeted synthesis of porous organic polymers has developed rapidly in recent years¹. Following the seminal paper of Kuhn et al.², crystalline covalent triazine-based frameworks (CTFs) are attracting much attention for their potential applications in heterogeneous catalysis, sequestration and gas adsorption, and for the chemical stability and the range of possibilities to suitably tailor the CTF structure^{3,4}. Synthetic routes to these systems usually follow self-condensation of three nitrile groups to form structures based on *s*-triazine ring units. The reactions are typically carried out in the presence of Lewis acid catalysts, such as ZnCl₂, at high temperature (~ 400 °C). Depending on the nature of the starting nitriles, e.g. 1,4-dicyanobenzene (DCB)² or 1,3,5-tricyanobenzene (TCB)^{5,6}, various products with tunable pore sizes can be rationally designed and prepared. However, achieving single-step, one-pot "green" synthesis of highly crystalline materials, while avoiding the use of environmentally harmful catalysts, remains a challenge.

The use of high pressure (P) combined with high temperature (T) conditions can be applied to achieve crystalline carbon-based polymers^{7,8} including low-dimensional nanomaterials^{9,10}. The use of *s*-triazine derivatives as a convenient building block for the formation of CTFs and layered carbon nitrides

via polycondensation processes was discussed by^{11,12}. A summary of different molecular precursors used in high pressure syntheses of carbon nitride materials appears in ref.¹³. He et al. reported micron-sized crystals produced from $C_3N_4H_4$ (3-amino-1,2,4-triazine) at 7 GPa and 1400 °C in a belt-type high-pressure apparatus in the presence of a Ni-based alloy or Co catalyst¹⁴. Crystalline 2D graphitic carbon nitride oxide was reported to be produced by heating urea crystals to 420 K at pressures below 3 GPa¹⁵. Layered polytriazine imide (PTI) crystals were first obtained through the condensation of melamine (2,4,6-triamino-1,3,5-triazine) and cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) at pressures between 1-4 GPa and temperatures up to 600 °C^{16–18}. Crystalline polytriazine imide (PTI) phases containing intercalated Li^+ and Br^- or Cl^- ions have been produced by condensation reactions from dicyandiamide (DCDA) in a molten salt ($LiCl/KCl$ or $LiBr/KBr$) flux^{19,20} and triazine-based graphitic carbon nitride (TGCN) and related C-rich layered crystals have been found to form following deposition from the vapour or at the melt-vapour interface^{21–23}. A pillared-layer phase was obtained by further compression of one of these structures, $C_6N_9H_3 \cdot HCl$, resulting in interlayer C-N bonds formed above approximately 40 GPa²⁴. The pressure induced reactivity of *s*-triazine, the prototype molecule of this family, to form a graphitic carbon nitride was investigated using resistively-heated diamond anvil cell (DAC) techniques²⁵. The results were interpreted on the basis of a topochemical reaction involving molecules lying on adjacent crystal planes. Crystals of a novel sp^3 -bonded carbon nitride phase $C_2N_2(NH)$ were obtained by laser heating DCDA in a DAC above 24-27 GPa at temperatures near 1700 °C²⁶. An open framework crystalline compound

containing *s*-triazine rings linked via sp^3 -bonded carbon atoms was produced by laser heating TGCN in a DAC at $P \sim 47$ GPa and recovered to ambient conditions²⁷. Following the successful syntheses of CTFs using DCB and TCB as precursors, 2,4,6-tricyano-1,3,5-triazine (TCT) was investigated as the building block to produce H-free 2D nanoporous polymers with C:N ratio equal to 1 via polytrimerization in $ZnCl_2$ salt melts at 400 °C²⁸. This molecule provides a useful precursor leading to layered CTF materials using one-step compression to drive polymerization-condensation reactions by tuning the intermolecular distances²⁹. Here we present an initial characterization of the structural and spectroscopic properties of the TCT monomer under combined high pressure-high temperature conditions, using synchrotron X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR) techniques. Our results allowed us to identify a crystalline phase transformation occurring for the monomer and to establish the melting relations of both phases I and II. We also studied the self-condensation polymerization reaction of the monomer to produce a polymeric solid containing crystalline structural units that are consistent with layered carbon nitride materials.

2 Experimental

TCT was prepared under inert atmosphere by the procedure described by Del Sesto et al.⁶. The solid was filtered and then washed with hexane to dissolve unreacted cyanuric chloride. The product was then purified by horizontal sublimation and the resulting crystalline TCT was sealed into pyrex tubes under vacuum to prevent reaction with atmospheric moisture. These

tubes were opened just before transferring the TCT crystals into a membrane diamond anvil cell (MDAC) equipped with IIa type diamonds. A Re gasket with a 150 μm hole was used to contain the sample and a ruby chip was placed in the sample chamber for pressure measurement by ruby fluorescence. Helium was loaded into the cell as the pressure transmitting medium. High temperatures were achieved by resistive heating with a K-type thermocouple placed close to the diamonds to measure temperature to within ~ 0.1 K. FT-IR absorption spectra were measured using a Bruker-IFS 120 HR spectrometer modified for high-pressure experiments^{30,31}, whereas Raman data were obtained using the 752 nm line of a Kr^+ laser as an excitation source³². Angle-dispersive-single crystal X-ray diffraction (ADXRD) experiments were performed at the ESRF high-pressure beamline ID15B using monochromatic X-ray radiation of wavelength $\lambda=0.41112$ Å and a Mar555 flat panel detector at a distance 300 mm from the sample and calibrated using a Si powder standard. The focal spot (fwhm) of the beam was ~ 25 μm , the single crystal dimensions were ca. ~ 15 μm each. Data collection was carried out using steps of 0.5° oscillations over a total ω scan range of 64° around the vertical axis. The 2D diffraction patterns were imported into the CrysAlisPro software³³ and processed to determine lattice parameters and integrate the reflection intensities. The crystal structure of phase II was solved using direct methods. All the structures were refined using the SHELXL package³⁴. The XRD pattern of the crystalline recovered product prepared using a pure sample without pressure transmitting medium was measured at the ESRF ID27 beamline using monochromatic X-rays of wavelength $\lambda=0.3738$ Å focused to ~ 3 μm and a MARCCD 165 detector. The raw image data were

integrated using Dioptas software³⁵.

3 Results

3.1 X-ray diffraction experiments

Compression experiments were performed for both large (15-20 μm) single crystals of TCT selected under the microscope in a nitrogen atmosphere and loaded into the DAC in helium, and TCT powder with no pressure transmitting medium as in the case of the reactivity characterization by FTIR (see section 3.2). The single crystal study allowed us to refine the structures of the low pressure phase I and the new high pressure phase (II) (see Tables 1 and 2) and determine the equation of state parameters for both phases up to 10.5 GPa (Fig. 2). The I-II phase transition occurs at 2.4 GPa. It is accompanied by a sudden change in the diffraction pattern (see CIF files in SI) and a 3.7% reduction in the unit cell volume. It could also be detected visually as a loss in optical quality of the samples. The diffraction peaks of phase I could be indexed according to space group $P2_1$ ($Z=4$) in agreement with a previous study³⁶. The structure of phase II (see Figure 1) was identified as orthorhombic belonging to the $P2_12_12_1$ space group with $Z=4$. $V(P)$ data for both phases are reported in Figure 2 along with third order Birch-Murnaghan fit parameters.

There was no indication of further structural or chemical transformation of the sample during compression up to 10.5 GPa, as confirmed by the full recovery of the diffraction pattern measured after the loading and by the homogeneous sample appearance. Polycrystalline samples were then investigated

Figure 1: Packing diagram of the crystal structure of TCT phase I and II at 2.38 and 2.51 GPa, respectively. Displacement ellipsoids are at the 30% probability level. Carbon atoms are reported in grey and nitrogen atoms in blue.

Figure 2: Equations of state of TCT crystal phases up to 10.5 GPa. The volume data were obtained by synchrotron ADXRD on single crystal samples and fit using a third-order Birch-Murnaghan equation. The fit parameters (bulk modulus B_0 , its first derivative C_0 and zero pressure value V_0) are reported in the figure for both phases I and II.

Figure 3: X-ray diffraction patterns and corresponding 2D images collected during isobaric (1.8 GPa) heating and showing the melting of phase II.

under combined high pressure-high temperature conditions to establish the phase transition boundaries and the onset of any chemical transformations. No compression medium was employed in these studies. In one experiment phase I was heated isobarically at 1.8 GPa allowing us to detect the I-II phase transition at 331 K and melting that occurred at about 415 K (see Figure 3). Phase I was recovered after lowering the temperature to 298 K with no evidence for a reaction having occurred. Two further experiments

involving isobaric heating at 6.0 GPa up to 560 K and room temperature compression up to 10 GPa were carried to compare with the reactions onsets determined by FTIR spectroscopy. In both XRD experiments the reaction was observed at P-T conditions more drastic than FTIR. In particular, the temperature threshold at 6.0 GPa was 555 K, therefore more than 100 K higher than in the FTIR experiment. However, it should be remarked that XRD is much less sensitive to the identification of the reaction onset than FTIR, the latter being a quantitative technique for detecting forming and/or disappearing species.

3.2 Characterization of the reactivity

The pressure induced reactivity in TCT was investigated both at room temperature and in isobaric heating experiments performed at 1.9, 4.0 and 6.0 GPa. In room temperature compression studies we investigated samples of different thickness: a pure TCT sample (thickness on the order of 50 μm) and another using a TCT layer (~ 10 μm) prepared on a KBr substrate. In all of the high temperature experiments only pure TCT samples were used. The pressure was always first increased at ambient temperature in steps of 0.5-1.0 GPa and at each step the sample was probed by FTIR spectroscopy. In the isobaric heating studies, once the desired pressure was attained the temperature was increased in 10 K steps and an IR spectrum was measured at each temperature. In Figure 4 (left panel) representative spectra collected during the room temperature compression of a thin TCT sample are shown. The I-II phase transition revealed by the ADXRD single crystal hydrostatic compression study at 2.4 GPa is clearly revealed by changes in the IR spec-

Pressure (GPa)	2.38(5)	2.51(5)
Formula	C ₆ N ₆	C ₆ N ₆
Crystal dimensions (μm)	15x15x15	15x15x15
Crystal System	Monoclinic	Orthorhombic
Space Group	$P2_1$	$P2_12_12_1$
Z	4	4
Z'	2	1
a ($\text{\AA}$)	7.75291(15)	6.6822(5)
b ($\text{\AA}$)	8.41359(13)	8.4144(4)
c ($\text{\AA}$)	9.4554(19)	10.572(6)
β ($^\circ$)	89.589(5)	90
V ($\text{\AA}^3$)	616.76(12)	594.4(3)
Data collection		
wavelength ($\text{\AA}$)	0.41112	0.41112
reflections measured	1242	1072
unique	947	507
unique with $I > 2\sigma$	751	310
R_{int}	0.022	0.038
Refinement		
Number of parameters	217	109
R_1 [$I > 2\sigma(I)$]	0.067	0.067
wR_2 (all data)	0.197	0.226
$\Delta\rho_{max}/\Delta\rho_{min}$ ($\text{\AA}^{-3}$)	0.21/-0.26	0.14/-0.14

Table 1: Crystallographic details of TCT-I and TCT-II structural refinements at T=293 K. It should be emphasized that the β angle decreases from 90.82(9) (90.75(3) in ref.³⁶) at ambient pressure to the reported value just before the transition.

atom	x	y	z	$U_{eq} (\text{\AA}^2)$
C1	1.1085(18)	0.3804(10)	1.007(2)	0.060(16)
C2	1.0250(18)	0.4941(11)	0.828(2)	0.056(18)
C3	1.3058(13)	0.5615(11)	0.917(2)	0.039(12)
C4	1.4925(16)	0.6477(11)	0.927(3)	0.09(2)
C5	1.0635(16)	0.2683(14)	1.111(4)	0.060(18)
C6	0.887(2)	0.5125(13)	0.720(3)	0.058(10)
N1	1.2701(15)	0.4666(10)	1.020(3)	0.083(17)
N2	0.9787(13)	0.3830(10)	0.912(3)	0.074(17)
N3	1.1853(12)	0.5882(8)	0.824(3)	0.072(14)
N4	1.6454(18)	0.7018(9)	0.922(3)	0.070(18)
N6	0.778(2)	0.5292(13)	0.640(4)	0.107(19)
N5	1.0180(14)	0.1755(11)	1.185(3)	0.071(19)

Table 2: Refined fractional atomic coordinates and equivalent displacement parameters for TCT-II at 2.51(5) GPa.

tra such as the splitting of the band at 945 cm^{-1} , the appearance of the sharp peak at 1410 cm^{-1} and of the combination bands around 3100 cm^{-1} , observed by comparing the spectra recorded at 1.6 and 2.6 GPa. After the I-II phase transition all the bands, with the exception of those at 820 and 1410 cm^{-1} , exhibit a blue shift with increasing pressure. A large drop in the intensity of almost all the TCT peaks was observed in the spectrum recorded at 10.0 GPa, indicating that a major structural or chemical transformation had begun to take place. We therefore repeated the experiment with a further sample ($\sim 50\text{ }\mu\text{m}$ thick) in order to detect the reaction onset more precisely. The evolution of the spectral region where the most relevant changes occur during the first two hours of the reaction is reported in the right panel of Figure 4. As discussed below in our analysis of the reaction kinetics, the transformation from the monomer to a polymeric phase did not reach completion ($\sim 45\%$) over the time course of the experiment, between 20-30 h.

The chemical transformation was also probed by heating the sample isobarically at 1.9, 4.0 and 6.0 GPa. At 1.9 GPa the reaction occurred at 550 K with the sample turning suddenly black and the simultaneous loss of the monomer spectrum. The kinetics in this case were too fast to be measured by conventional FTIR spectroscopy. According to our X-ray data the sample is in its molten state at these P-T conditions. The other two experiments, as well as that conducted at ambient temperature, were all carried out relative to TCT crystal phase II. In Figure 5 the spectral changes at the onset of the reaction are reported for the experiment performed at 6.0 GPa. The reaction proceeds similarly to that at ambient temperature and a broad absorption

Figure 4: Left: room temperature pressure evolution of the IR absorption spectrum of a thin ($\sim 10\mu\text{m}$) sample of crystalline TCT. Right: in the upper panels an enlarged view of the spectral changes taking place at the I-II transition is reported; in the lower panel the time evolution of the IR absorption spectrum of a massive sample ($\sim 50\mu\text{m}$) of TCT at the onset of the chemical transformation is shown.

Figure 5: Left: time evolution of the IR absorption spectrum of crystalline TCT during the reaction at 6.0 GPa and 443 K. Right: difference between the spectra collected at the end (24 h) and at the beginning of the kinetic study; the sharp negative peaks indicate the intensity decrease of the TCT bands whereas the broad absorption extending between 1000 and 1750 cm^{-1} is due to the product formation.

band ascribable to the reaction product grows between 1000 and 1750 cm^{-1} . The amount of reacted TCT is reported as a function of the reaction time under different pressure and temperature conditions in Figure 6. The percentage of reacted TCT was determined from the intensity decrease of the monomer band at $\sim 1350 \text{ cm}^{-1}$ fitted with a Voigt profile. It can be seen that the reaction does not go to completion and it proceeds more slowly as the pressure is lowered, despite the increased temperature.

Figure 6: Time evolution of the percent amount of reacted TCT in the kinetic studies performed at 4.0, 6.0 and 10.0 GPa. The curves employed for the fit are described by eq.1, the fit parameters are reported in Table 3.

P(GPa)	T(K)	k (h ⁻¹)	n	% reacted
4.0	511	0.08	1.20	30
6.0	443	0.115	0.88	37
10.0	300	0.215	0.75	45

Table 3: Pressure and temperature conditions where the chemical transformation has been studied and fitting parameters, according to the Avrami model (eq.1), relative to the kinetics shown in Figure 5.

The kinetic data were fit using a model first developed for describing crystal growth from a liquid phase³⁷ and then extended to the study of diffusion controlled solid-state reactions³⁸ leading to the fitting function:

$$F(t) = A \{1 - e^{-[k(t-t_0)]^n}\} \quad (1)$$

where A is the percentage of reacted monomer at the end of the reaction, t_0 is the reaction starting time, k is the rate constant, and n is a parameter related to the dimensionality of the growth process. The excellent fit to the experimental data reported in Figure 5 was obtained using the parameters listed in Table 3.

The results of the kinetic analysis indicate that the reaction proceeds rapidly but less than 50% of the monomer reacts under the range of conditions investigated here. Both the rate and the amount of transformed monomer increase with pressure. These characteristics are suggestive of a reaction not driven by the crystal dynamics, that would be governed by temperature, but

instead one related to the possibility of creating short intermolecular contacts that nucleate product seeds that are not able to propagate throughout the entire crystal. The values determined for the n dimensional parameter decrease with increasing pressure, between 1.2 to 0.75. In general 1D growth processes are associated with $n \leq 1$ whereas values larger than 1 are suggestive of 2D growth. It is likely that the layered nature of the structural units in the starting phase combined with the need to reduce intermolecular contacts to achieve oligomerization causes this variability of the reaction kinetics. It is also possible that as the reaction proceeds more slowly at lower pressure there is a greater opportunity to extend the 2D network laterally.

3.3 Characterisation of the reaction product

All the materials recovered from the reaction present similar characteristics with a dark red colouration and the same IR absorption spectrum as shown in Figure 7. The colour appears lighter than that of the polymer obtained by catalytic reaction at ambient pressure²⁸ likely due to the presence of unreacted monomer. The IR spectrum does not change during decompression as has been reported for reactions initiated at crystalline defects^{39,40}. The broad band extending between 1000 and 1700 cm^{-1} appears to be the only signature of the product. The band is asymmetric with a tail towards lower wavenumber that may contain a weak maximum near 1150 cm^{-1} . This generally resembles the broad FTIR features obtained for nanocrystalline g- C_3N_4 ⁴¹ and macroscopic graphitic phases produced by polymerization of DCDA with C:N ratios reported between 1.2 to 0.75^{21,22}. The spectrum differs significantly from other heptazine- and triazine-based polymeric structures that

typically contain strong features due to N-H stretching vibrations⁴². It also differs from the IR data obtained for the ambient pressure catalytic reaction product which exhibits broad and strong bands ascribable to C-H and N-H stretching²⁸.

Although the sample exhibited strong fluorescence, we succeeded in recording a Raman spectrum of the product using the 752 nm Kr⁺ laser line. Its Raman signature contains two broad features between 1000-2000 cm⁻¹ that resemble the D and G bands of layered carbon and carbon nitride materials^{22,42,43}. The intensity of the "D" band is nearly twice that of the "G" feature, that has been associated with clustering at higher N content in graphitic carbon nitride samples⁴⁴. The D/G intensity ratio and fluorescence background are in close agreement with data for samples obtained by ambient pressure polymerization.²⁸

The product recovered from the reaction performed at 10 GPa and ambient temperature experiment was also characterized by synchrotron X-ray diffraction. The pattern of the quenched product reflects the polycrystalline nature of the sample, being characterized by rather homogeneous Debye-Scherrer rings (Fig. 9). Three intense reflections are accompanied by weaker features. This pattern is reminiscent of those calculated for triazine based graphitic carbon nitrides with buckled layer geometries^{22,42}, and observed in the polytriazine imide form of carbon nitride⁴⁵. The hypothetical hexagonal structure with lattice parameters $a = 7.13 \text{ \AA}$ and $c = 6.74 \text{ \AA}$ represents quite well the observed pattern with the three main peaks lying close to the predicted positions (Figure 9). Preferential orientation of the product obtained by the direct compression of TCT in the absence of a pressure transmitting

Figure 7: Comparison of the IR absorption spectra of TCT: (a) close to ambient pressure before starting to compress the sample; (b) after the reaction completion, at the pressure and temperature conditions indicated, and quenching to ambient conditions; (c) after the cell opening. The spectra obtained in the DAC have been cut to remove regions of strong absorption by the diamond windows ($\nu \geq 1850 \text{ cm}^{-1}$).

Figure 8: Raman spectrum of the material recovered from the reaction performed at ambient temperature and 10 GPa. The measured spectrum is shown at right, whereas in the left panel is reported the spectrum after subtraction of the fluorescence background along with deconvolution to highlight the D and G band contributions.

medium could explain the absence of the expected 100 reflection. The c lattice parameter (i.e., twice the interplanar distance) calculated from the d-spacing for the peak assigned to the 002 reflection is 6.738 Å, close to the value for graphitic- C_3N_4 predicted by Teter (6.7204 Å)⁴⁶ but slightly larger than those observed for other graphitic carbon (6.58 Å) and carbon nitride materials (6.48 Å)^{22,42}. This peak presents a pronounced shoulder on the lower 2θ angle side indicating a distribution of the interlayer distances. This kind of disorder can also originate the broad band underlying the 002 peak that could be due to amorphous "turbostratic" CN layers with random stacking⁴⁷. The peak indicated with an asterisk at d-spacing ~ 7.13 Å can be assigned to a reflection characteristic of intraplanar periodicity corresponding to the dimension of the macrocycle consisting of six TCT units (see Figure 9)^{22,42}.

4 Conclusions

In this study we have established the TCT phase diagram as a function of pressure and temperature conditions. We identified a new phase (II) occurring above 2.4 GPa at room temperature, and have determined the melting relation and phase I-II boundary as a function of P and T . We used angle-dispersive X-ray diffraction to determine the structure of the new high pressure phase II as belonging to the $P2_12_12_1$ space group ($Z=4$). We also probed the oligomerization reaction of TCT between 1.9 and 10 GPa both by increasing pressure at ambient temperature and by increasing temperature along different isobaric paths. These results are summarized in Figure 10.

Figure 9: XRD pattern of the quenched product from the reaction performed at ambient temperature and 10 GPa (left). The four blue bars represent the predicted reflection positions of the layered structure reported on the right side: bottom ab plane, top 3D perspective. The inset shows the 2D XRD raw data. The peak marked by a star corresponds to the intraplanar distance reported in the bottom right image.

We observe a reaction boundary with negative P-T slope that often characterizes systems where the reactivity is assisted by lattice phonons^{25,29,49}. However, in this case the transformation of the monomer is only partial and the amount of reacted monomer depends upon pressure and further reduces under hydrostatic compression. These observations along with analysis of the reaction kinetics indicate a reactivity initiated by defects. Spectroscopic and XRD analysis of the recovered material suggest the presence of layered carbon nitride domains or structurally disordered nanocrystalline phases within the sample.

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Figure 10: Phase and stability diagram resulting from this study. Full dots indicate the transition between phases I and II phase identified by XRD; full squares refer to melting from ref.^{6,48} and this study (XRD); full and empty stars are the onset of the chemical transformation as identified by IR absorption spectroscopy and XRD experiments, respectively. Dotted lines represent the suggested melting and I-II boundaries. Full line indicates the onset of the chemical stability not using hydrostatic pressure transmitting medium.

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