Identification of new pillared-layered carbon nitride materials at high pressure

Ashkan Salamat1,2, Malek Deifallah2, Raul Quesada Cabrera2, Furio Corà2 & Paul F. McMillan2

1Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138, USA, 2Department of Chemistry, University College London, London WC1H 0AJ, UK.

The compression of the layered carbon nitride C6N9H3·HCl was studied experimentally and with density functional theory (DFT) methods. This material has a polytriazine imide structure with Cl2− ions contained within C12N12 voids in the layers. The data indicate the onset of layer buckling accompanied by movement of the Cl− ions out of the planes beginning above 10–20 GPa followed by an abrupt change in the diffraction pattern and c axis spacing associated with formation of a new interlayer bonded phase. The transition pressure is calculated to be 47 GPa for the ideal structures. The new material has mixed sp2–sp3 hybridization among the C and N atoms and it provides the first example of a pillared-layered carbon nitride material that combines the functional properties of the graphitic-like form with improved mechanical strength. Similar behavior is predicted to occur for Cl-free structures at lower pressures.

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Correspondence and requests for materials should be addressed to A.S. (salamat@physics.harvard.edu); F.C. (f.cora@ucl.ac.uk) or P.F.M. (p.f.mcmillan@ucl.ac.uk)
ambient pressure lattice spacings obtained from experiment (a, b = 100 GPa in 10 GPa steps, starting each optimization from the optimized structure of g-C$_{6}$N$_{9}$H$_{3}$).

The prominent (002) interlayer reflection shifts rapidly to smaller d spacing (2$\theta$ ~ 10$^\circ$) with increasing pressure (Fig. 2). Above 10 GPa the diffraction peaks become significantly broadened but the general features of the graphitic material are still recognizable up to P ~ 36 GPa. However at P = 40 GPa the nature of the pattern has changed to become dominated by a main broad asymmetric peak near 13$^\circ$. This result signals a structural change into a new high-density form (Fig. 2). After the transformation has occurred the peak positions vary little with continued compression up to 70 GPa indicating that the high pressure structure is significantly less compressible than the graphitic layered phase. The substantial peak broadening that occurred as a function of pressure did not permit us to carry out detailed refinement of the diffraction data. Instead we investigated the nature of the structural changes at high pressure using density functional theory (DFT) calculations, that enabled us to gain understanding of the pressure induced transformation by comparing the predicted diffraction profiles with experiment (Fig. 3).

**DFT calculations.** In a first series of DFT studies we geometry-optimized the structure of g-C$_{6}$N$_{9}$H$_{3}$·HCl between P = 0–100 GPa in 10 GPa steps, starting each optimization from the ambient pressure lattice spacings obtained from experiment (a, b = 8.42 Å; c = 6.34 Å). We generated a proton ordered version of the 40-atom crystallographic unit cell within space group P1, removing all local symmetry constraints to allow the atoms to relax both within and away from the graphitic planes. This differs from our experimental data analysis that assumed a spatially averaged P6$_{3}$/m unit cell. The proton-ordered structure exhibits a small shear distortion between adjacent planes along (010) to maximize electrostatic interactions between the H$^+$ and Cl$^-$ ions within layer voids. This leads to a small separation between a and b cell parameters that increases slightly with compression but that remains insignificant until above 20 GPa (Fig. 4). At P = 0 GPa the optimized lattice parameters were found to be a, b = 8.37 Å; c = 6.23 Å, slightly smaller than those found experimentally (8.42, 6.34Å) as is typical for LDA results. During compression there is a rapid decrease in the c-axis parameter consistent with experiment: between 0–40 GPa there is a 17% reduction in c, compared with 3.7% and 5.8% in the a and b lattice parameters (Fig. 4). Between 60–70 GPa a sudden collapse of the c-axis occurred in these initial compression experiments, and then this parameter remained approximately constant up to 100 GPa (Fig. 4).

These initial results showed that a dramatic change had occurred in the structure as the c axis dimension was reduced by compression, implying a separation between the initially planar layers of approximately 2.0 Å, without considering the reduction in distances due to layer buckling. A small interlayer separation could lead to the onset of C-N interlayer bonding and we investigated this possibility by analyzing the fully relaxed structures as a function of densification. The results led us to identify the structure optimised at high pressure as a new phase of the material, characterized by the occurrence of bonding between a subset of sp$^3$ hybridized C and N atoms in adjacent layers (Fig. 5). This new phase is termed the ILB1 structure to distinguish it from the densified graphite-like phase with buckled but independent layers obtained at lower compression (ILB0). The C-N bonding occurs between atoms associated with triazine rings that in the ambient pressure phase overlapped each other in adjacent layers; the others located above and below the C$_{12}$N$_{12}$ voids remain sp$^2$-hybridised giving rise to a unique new pillared-layered structure that contains a mixture of sp$^2$- and sp$^3$-bonded C and N atoms (Fig. 5).

Once we had identified the occurrence and connectivity of the new high-pressure phase, we examined the relative enthalpies of the ILB0 and ILB1 polymorphs over a wide pressure range, starting the studies using the compressed but still graphite-like (ILB0) structure obtained at 60 GPa and then gradually increasing P, compared with results during gradual decompression of the ILB1 phase obtained at 70 GPa (Fig. 6). Each calculation was initiated from the geometry-optimized structure at the immediately adjacent pressure value. The C-N connectivity was maintained throughout in both series of calculations, indicating that the ILB0 and ILB1 phases correspond to separate functions in the potential energy surface of the system and that their interconversion is an activated process that does involve interlayer...
but not intralayer C-N bond breaking or formation. Comparing the calculated enthalpies we identified 47 GPa as the equilibrium transition pressure between the ILB0 and ILB1 polymorphs at T = 0 K (Fig. 6). Following the compression studies we relaxed the ILB1 structure to ambient pressure, and found that the pillared connectivity was retained. Similar calculations repeated for the hypothetical Cl-free compound showed a similar structural transformation occurring at high pressure, but with the isoenthalpic point between ILB0 and ILB1 phases reduced to ~5 GPa. That result indicates that vary-
ing the Cl content of these gCNM phases should cause the transition pressures and recoverability of the pillared-layered material to be adjusted experimentally.

In order to fully characterize the structural changes associated with compression of C₆N₉H₃·HCl from its ambient pressure graphitic phase to the denser ILB1 polymorph at high pressure, we measured a set of dihedral angles in the minimum energy structures relaxed at each pressure. These angles (Fig. 7a) are chosen to describe

Figure 2 | Angle dispersive synchrotron X-ray diffraction data for C₆N₉H₃·HCl obtained up to P = 70 GPa (Å = 0.4441 Å). Peaks of interest are labelled with hkl designations according to the P6₃/m space group. (a) Selected patterns showing the onset of peak broadening for the layered phase above 10 GPa followed by the rapid emergence of the new pattern above 40 GPa. (b) Variation of d spacings measured for the principal peak maxima assigned to the low pressure graphitic phase as a function of pressure.

Figure 3 | Comparison of experimental (black line) with the DFT predicted (ILB0 phase, red line) X-ray patterns for the graphitic phase at various pressures. At 40 GPa the blue pattern corresponds to dense forms with interlayer bonding (ILB1) as described in the text.

Figure 4 | Changes in the DFT calculated lattice parameters for a proton ordered version of the g-C₆N₉H₃·HCl structure as a function of pressure.
the distortion of the initially planar graphitic layers: 1) the internal dihedral angle of a protonated C₃N₃ ring (ABCD); 2) the dihedral angle formed by the skeletal proton (i.e. the bridging NH group) with respect to the neighbouring triazine ring (ABFG); and 3) the internal dihedral angle of a non-protonated C₃N₃ ring (HIJK). All these values are identically zero for fully planar layers and any deviations thus record buckling of the gCNM framework. Achieving a value of 60° in any of these parameters indicates a change of hybridization at the central C and N atoms from sp² to sp³. At each pressure reported in Fig. 7 we employ the thermodynamically stable phase from the DFT calculations, i.e. ILB0 below the transition pressure of 47 GPa, and ILB1 above.

At ambient pressure the ILB0 structure is nearly planar with all dihedral angles <2°, as expected for a graphitic phase with delocalized sp² bonds. However, this condition is lost as soon as the structure is compressed even slightly. By 10 GPa the dihedral angles HIJK and ABFG differ noticeably from zero but those within the C₃N₃ rings (ABCD) remain constant. This reveals a buckling of the layers around the bridging -NH- groups (ABFG) beginning at low pressure that is accompanied by a displacement of the Cl⁻ ions out of the graphitic planes (Fig. 7b). Between 40–50 GPa the ABCD dihedral angle jumps from 2° to 65°, indicating the sp² to sp³ hybridization

Figure 5 | Left: The ILB1 phase of C₆N₉H₃Cl obtained at high pressure from DFT calculations. In the real structure studied experimentally the Cl⁻ displacements above and below the layers can occur in a random or locally ordered fashion. Right: picture highlighting the formation of pillars with three-dimensional connectivity between the carbon nitride layers produced by interlayer bonding within a mixed sp²–sp³ bonded state; the pillars are connected within the planes by relatively undistorted triazine rings.

Figure 6 | Calculated enthalpy as a function of P for the layered-pillared ILB1 phase relative to the layered graphitic (ILB0) polymorph of C₆N₉H₃Cl and of the hypothetical Cl⁻ free C₆N₉H₃ system.

Figure 7 | (a) Dihedral angles with reference to the initially planar g-C₆N₉H₃Cl structure as a function of pressure. Here the dihedral angle changes are shown with reference to the fully relaxed and thermodynamically stable ILB0 or ILB1 states at each pressure. The structural phase transformation occurs at 47 GPa. (b) Displacement of the Cl⁻ ions along the c axis relative to the initial graphitic planes within the calculated ILB0 structure.
distortions and displacements of the Cl$_2$ to further characterize the evolution of the graphitic ILB0 phase at not only to identify the structural features of the new high-pressure phase. The computational results enabled us to analyze our data in this range using lower symmetry space group solutions P6$_3$/m. We fitted the V(P) data up to 21 GPa using a third order Birch-Murnaghan (BM-3) equation of state:

$$P(V) = 3K_0f(1 + 2f)^{3/2} \left(1 + \frac{3}{2}(K_0' - 4f)\right)$$

with $K_0$ the zero pressure bulk modulus and $K_0'$ its pressure derivative, and the volume strain variable expressed by

$$f = \frac{1}{2} \left(\frac{V_0}{V}\right)^{2/3} - 1$$

This fit yielded $K_0 = 32.8 \pm 7.3$ GPa and $K_0' = 4.8 \pm 0.5$, in good agreement with our DFT results for the ILB0 polymorph ($K_0 = 29.1$ GPa; $K_0' = 6.7$). The compressibility is comparable with crystalline graphite ($K_0 = 34$ GPa), although polycrystalline samples have been reported with $K_0$ values extending down to 10 GPa.

We fitted our experimental data (Fig. 8) to the BM-3 EoS yields a bulk modulus $K_0 = 130 \pm 5$ GPa and $K_0' = 3.57 \pm 0.2$, clearly showing that the ILB1 structure has much lower compressibility than the sp$^2$ bonded graphite-like ILB0 phase ($K_0 = 29.1 \pm 4.1$ GPa). The new high pressure ILB1 phase, despite partly retaining the void intralayer structure of the low pressure ILB0 polymorph, has therefore substantially higher structural strength, a feature of potential interest for practical applications.

**Discussion**

We conducted a high pressure study of graphitic C$_6$N$_9$H$_3$·HCl using complementary experimental and theoretical approaches. The structural analysis in the highest pressure ranges where substantial peak broadening was present (Fig. 2). The variations in refined $a,b,c$ cell parameters led to the V(P) plot shown in Figure 9.

Between 20–30 GPa we note a slight deviation of the V(P) relation upwards from the expected equation of state (EoS) curve obtained by analyzing the data using the spatially averaged space group P6$_3$/m. This can occur due to layer buckling along with displacements of the Cl$^-$ ions away from the graphitic planes, that become significant above 20 GPa as shown by the DFT results (Fig. 7b). We attempted to analyze our data in this range using lower symmetry space group solutions P6$_3$, P6 and P1 but these all gave similar $R_{wp}$ and $\chi^2$ values despite the increased structural degrees of freedom.

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graphic layered compound C\textsubscript{6}N\textsubscript{9}H\textsubscript{3}·HCl was subjected to pressures of up to 70 GPa in a diamond anvil cell, and its structural behaviour was examined using synchrotron X-ray diffraction. The structural model proposed by Zhang et al. with a layered hexagonal (P\textsubscript{6}\textsubscript{3}/m) structure was employed for the experimental data analysis, for which it provides a useful description up to a pressure of \(~40\) GPa. Closer examination of the V(P) relation indicates an anomaly near 20 GPa that can be explained by a deviation of the structure from P\textsubscript{6}\textsubscript{3}/m symmetry that can be interpreted from the computational results. On increasing pressure from ambient conditions, we observe three distinct structural rearrangements: at ambient pressure the carbon nitride layers are atomically flat and host the Cl\textsuperscript{−} ions within the layers; between 10–20 GPa the layers buckle and the Cl\textsuperscript{−} ions displace vertically but not horizontally with respect to the layers; above 20 GPa the Cl\textsuperscript{−} ions can displace significantly both horizontally and vertically, making the P\textsubscript{6\textsubscript{3}/m} model less and less appropriate for a detailed structural description.

The calculations identify the formation of a new pillared structure (referred to as ILB1), that is thermodynamically stable compared to the graphic phases above 47 GPa. Simulated XRD patterns using graphic and pillared phases from the computational work were compared with the experimental XRD data, and these indicate that the predicted pillared structure provides the most plausible match to the experimental XRD data, and these indicate that graphitic and pillared phases from the computational work were referred to as ILB1, that is thermodynamically stable compared to detailed structural description.

vertically, making the P\textsubscript{6\textsubscript{3}/m} model less and less appropriate for a compression of the layered compound g-C\textsubscript{6}N\textsubscript{9}H\textsubscript{3} calculations.

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Author contributions

A.S. carried out experiments and analysis assisted by R.Q.C. Calculations were carried out by F.C. and M.D. P.F.M. A.S. and F.C. conceived and wrote the paper.

Additional information

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