Carbon Nitrides | Hot Paper

Simple Molecules under High-Pressure and High-Temperature Conditions: Synthesis and Characterization of α- and β-C(NH)₂ with Fully sp³-Hybridized Carbon

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Abstract: The elements hydrogen, carbon, and nitrogen are among the most abundant in the solar system. Still, little is known about the ternary compounds these elements can form under the high-pressure and high-temperature conditions found in the outer planets' interiors. These materials are also of significant research interest since they are predicted to feature many desirable properties such as high thermal conductivity and hardness due to strong covalent bonding networks. In this study, the high-pressure high-temperature reaction behavior of malononitrile $H_2C(CN)_2$, dicyandiamide $(H_2N)_2C=NCN$, and melamine $(C_3N_3)(NH_2)_3$ was investigated in laser-heated diamond anvil cells. Two previously unknown compounds, namely α-C(NH)₂ and β-C(NH)₂, have been synthesized and found to have fully sp³-hybridized carbon atoms. α-C(NH)₂ crystallizes in a distorted β-cristobalite structure, while β-C(NH)₂ is built from previously unknown imide-bridged 2,4,6,8,9,10-hexaazaadamantane units, which form two independent interpenetrating diamond-like networks. Their stability domains and compressibility were studied, for which supporting density functional theory calculations were performed.

*T*he chemistry between the elements carbon, hydrogen, nitrogen, and oxygen is quintessential to a vast array of research fields. These elements play a fundamental role as key ingredients of life, in our quest to produce ever more advanced technological materials and in our understanding of extraterrestrial bodies. Indeed, the ice giants Uranus and Neptune consist mainly of these four elements.[1] In their interiors high-pressure (HP) and high-temperature (HT)

conditions prevail. Under these conditions, CH_4, NH_3 and H_2O molecules are expected to break apart and recombine into fully extended covalent network structures with properties anticipated to explain many of the peculiarities of such extraterrestrial bodies.[1] Before this complex quaternary system can be investigated, it is crucial to improve our understanding of the simpler binary and ternary systems,

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Table 1: Experimental details of the conducted LHDAC-experiments.

DAC-no.	Starting material	p [GPa]; T [K]	Identified reaction products
DAC-1	malononitrile	37; 2400	α-C(NH)$_2$, dwur-C$_2$N$_2$(NH), powdered diamond
DAC-2	DCDA	45; 1800	α-C(NH)$_2$, dwur-C$_2$N$_2$(NH), NH$_3$-phase V
DAC-3	melamine	36; 1400	β-C(NH)$_2$, dwur-C$_2$N$_2$(NH)

essential to benchmark theoretical calculations and guide future experiments.

A series of crystalline and fully extended covalent C/O and C/N solids have already been prepared. The behavior of CO$_2$ under HPHT conditions has been thoroughly studied in laser-heated diamond anvil cells (LHDAC).[2] While being a molecular gas at ambient conditions, CO$_2$ can be transformed into solids consisting purely of CO$_4$ tetrahedra at pressures above 40 GPa. These phases have similar structures to known SiO$_2$ phases like tridymite and β-cristobalite.[3] Regarding the C/N system, recently Stavrou et al. were able to prepare a carbon subnitride CN isostructural to β-InS by nitridation of graphite at pressures between 55–70 GPa.[4] Building on this approach, Laniel et al. were able to synthesize the first true carbon(IV) nitrides C$_3$N$_4$ and carbon pernitride CN$_2$ by nitridation of tetracyanoethylene at pressures higher than 70 GPa.[5] tI14-C$_3$N$_4$ crystallizes in a defect sphalerite structure, while hP126-C$_3$N$_4$ has a structure similar but not identical to β-Si$_3$N$_4$. In contrast to HPHT CO$_2$ phases, all four C/N phases can be recovered to ambient conditions and the bulk moduli K_0 of hP126-C$_3$N$_4$ (417 GPa) and CN$_2$ (419 GPa) almost reach that of diamond (446 GPa).[5]

Opposite to the binary systems, little is known about the chemistry of the ternary systems. Of these, C/N/H is extremely attractive from a materials science perspective since HPHT phases of these three elements should contain imide-groups. The introduction of NH-moieties allows the formation of hydrogen bonds, enabling increased stability and potentially unique properties such as proton conductivity that are not possible in purely binary C/N and C/O compounds. The only HPHT C/N/H phase featuring NH-groups known so far is carbon nitride imide C$_2$N$_2$(NH) which crystallizes in a defect wurtzite (dwur) structure as the mineral sinoite (Si$_2$N$_2$O). Horvath-Bordon et al. prepared this phase by treatment of dicyandiamide (DCDA) at temperatures >1700 K and pressures >28 GPa in a LHDAC.[6] Its compressibility and formation conditions have been studied by Salamat et al. using in situ powder X-ray diffraction (XRD). They found that dwur-C$_2$N$_2$(NH) can be prepared from DCDA in a pressure range of 30–45 GPa. Its K_0 was determined to be 258 GPa, which is high but nonetheless lower than those found for binary HPHT C/N phases.[7] During their analysis they observed additional XRD reflections, which could not be identified. For the full conversion of the sample into dwur-C$_2$N$_2$(NH), prolonged heating ($\approx$15 min) or several consecutive laser heating runs were needed, after which solid NH$_3$ was also observed. Since DCDA has an empirical formula of CH$_2$N$_2$, it can be reasoned that these unidentified reflections most likely stem from a HPHT carbon diimide (i.e. C(NH)$_2$)

phase, which transforms into dwur-C$_2$N$_2$(NH) and NH$_3$ at elevated temperatures (i.e. 2 CH$_2$N$_2$→C$_2$HN$_3$+NH$_3$). Elucidating the structure of potential HPHT C(NH)$_2$ phases has been the focus of recent theoretical works.[1] These predict that such phases should be structurally similar to HPHT CO$_2$ phases as NH and O are isolobal. Next to dwur-C$_2$N$_2$(NH), the only other reported HPHT C/N/H phase is the isolobal C$_2$N$_2$(CH$_2$) by Sougawa et al. However, its synthesis is questionable as no single-crystal XRD (SCXRD) measurements were conducted and the lattice parameters from powder XRD rather fit dwur-C$_2$N$_2$(NH) than the claimed dwur-C$_2$N$_2$(CH$_2$) based on the authors' own theoretical calculations.[8]

The main goal of this research was to explore the exotic chemistry of the C/N/H system under HPHT conditions to discover novel materials and shed first light on potential solids found in the mantle of the ice giants. To elucidate the formation mechanism of C/N/H compounds and resolve incongruities in the literature, three BX90-type DACs loaded with three distinct chemical precursors were prepared (Table 1 and S1, Figure 1). DAC-1 was loaded with malononitrile, a molecular compound with the same empirical formula as the elusive dwur-C$_2$N$_2$(CH$_2$). DAC-2 was loaded with DCDA with the goal to synthesize and characterize the unidentified intermediate phase reported by Salamat et al.[7] DAC-3 was loaded with melamine to investigate if it would yield the same reaction products as DCDA under HPHT conditions, both having the same empirical formula. All DACs were compressed to their target pressure p, followed by laser heating. The laser's power was increased stepwise until an intense flash of light was observed, sustained for about five seconds. During this time lapse, the oversaturation of the detector prevented accurate temperature determination using the samples' thermoemission. Right before the flash of light, temperatures T of over 1000 K were measured.

All resulting products were analyzed by in situ XRD at the Extreme Conditions Beamline P02.2 of the Deutsches
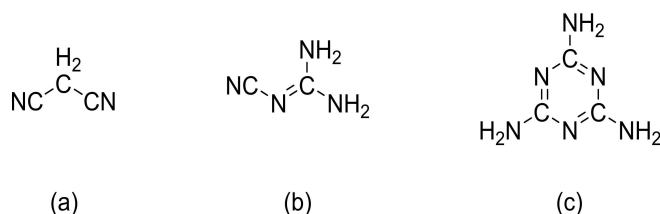

Figure 1. Molecular structures of the starting materials employed in the different LHDAC-experiments: malononitrile (a), DCDA (b), and melamine (c).

Elektronen Synchrotron (DESY) or the High Pressure Beamline ID27 of the European Synchrotron Research Facility (ESRF). In DAC-1, reflections coinciding with the expected dwur-structure were observed. Upon close inspection of the obtained SCXRD data, it was found that these crystals were dwur-$C_2N_2(NH)$, and not dwur-$C_2N_2(CH_2)$ (Table S7, Figure S1). In addition, a hitherto unknown phase was identified. SCXRD analysis revealed that this compound crystallizes in a distorted β-cristobalite structure isostructural to γ-Be(OH)$_2$:[9] α-C(NH)$_2$ (space group *Fdd*2 (no. 43) with $a = 5.3617(14)$, $b = 5.6277(16)$, $c = 6.130(4)$ Å at 37 GPa; Figure 2, Table S2 and S3).[10] Lastly, powdered diamond was observed, most likely produced during the transformation of malononitrile into α-C(NH)$_2$ (i.e. $C_3H_2N_2 \rightarrow CH_2N_2 + 2\,C$).

In α-C(NH)$_2$, all carbon atoms are tetrahedrally coordinated by nitrogen, itself bonded to one hydrogen and two carbon atoms (Figure 3). The C(NH)$_4$-tetrahedra form exclusively *sechser*[11] rings thereby building up a diamond-like network. However, compared to the idealized β-cristobalite structure, the tetrahedra are rotated by ≈36° along [001]. This rotation is smaller than in β-cristobalite type CO_2 (≈41°).[3] The N–C–N bond angles are between 103.65(8)° and 118.8(3)° and therefore deviate from the regular tetrahedral angle of 109.5°. This distortion of the tetrahedra is most likely caused by the hydrogen-bond network formed between the hydrogen and nitrogen atoms. The C–N bond lengths are 1.421(3) and 1.435(3) Å, which is similar to the C–N bond lengths found in dwur-$C_2N_2(NH)$ and both sp^3-C_3N_4 phases. The C–N–C bond angle is 120.06(11)°, indicating the sp^2-hybridization of nitrogen.
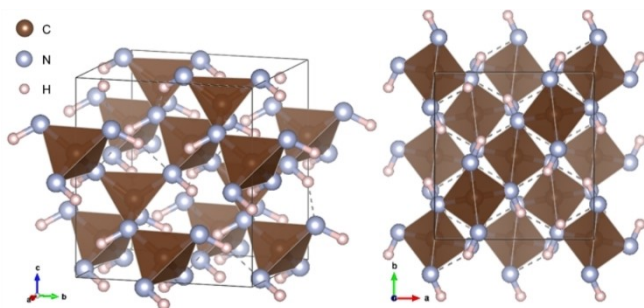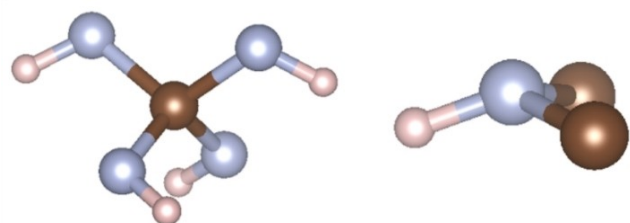
However, when taking the hydrogen into account, it becomes apparent that nitrogen is not perfectly planar coordinated. Indeed, the C–N–H angles are slightly lower than the ideal 120°, measuring 115(4)° and 111(4)°. The N–H bond length was refined to 0.92(5) Å. Both aforementioned C/N/H phases were also observable in DAC-2, suggesting that α-C(NH)$_2$ is the unidentified phase reported by Salamat et al. (Figure S3).[7] In addition, NH$_3$-phase V could be unequivocally confirmed as a reaction product due to the superior signal-to-noise ratio of the powder XRD data (Figure S4).

In DAC-3, however, α-C(NH)$_2$ was undetectable and only small amounts of dwur-$C_2N_2(NH)$ were found. Instead, another novel phase was predominantly observed: β-C(NH)$_2$ (space group *Fddd* (no. 70) with $a = 10.85(4)$, $b = 11.391(12)$, $c = 12.396(11)$ Å at 36 GPa; Figure 4 and S5, Table S2 and S4).[10] This phase is built up from nitrogen-bridged 2,4,6,8,9,10-hexaazaadamantane (HAA) units. The HAA units form two independent interpenetrating diamond-like networks. Analogous structural motifs have also been found in Li_2SiN_2 and Li_2SiP_2.[12] As in α-C(NH)$_2$, the carbon atoms are tetrahedrally coordinated by nitrogen, while each nitrogen is bound to two carbon atoms. N–C bond lengths are between 1.381(9) and 1.475(4) Å, implying that they are exclusively single bonds. From this it can be concluded that each nitrogen must also be bound to an additional hydrogen, resulting in the same stoichiometry as for α-C(NH)$_2$. Unlike in α-C(NH)$_2$, however, the position of the hydrogen atoms could not be refined. The C–N–C bond angles inside the HAA units are in the range of 106.4(5)° to 112.4(5)°, implying sp^3-hybridization. In contrast, the C–N–C bond angle at the nitrogen bridging the HAA units is 119.0(5)°, which is similar to that found in α-C(NH)$_2$ and suggests a hybridization closer to sp^2. Although other molecular azaadamantanes such as hexamine (1,3,5,7-tetraazaadamante) have long been known and studied, no successful synthesis of any HAA derivative has been reported so far.[13] However, it has been investigated by theorists as the core of
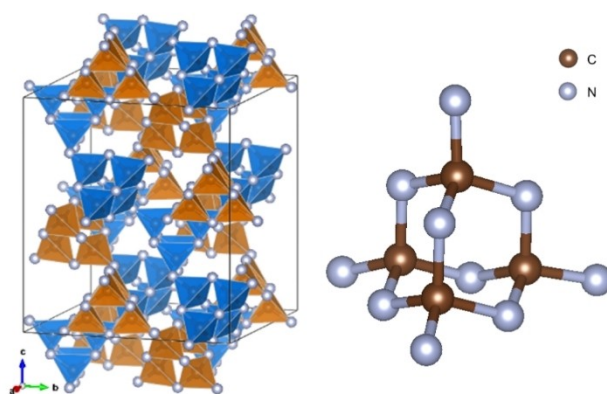
Figure 2. Crystal structure of α-C(NH)$_2$ at 37 GPa viewed from different angles.

Figure 3. First coordination spheres of carbon (left) and nitrogen (right) found in α-C(NH)$_2$ at 37 GPa.

Figure 4. Crystal structure of β-C(NH)$_2$ at 36 GPa with the C(NH)$_4$ tetrahedra of the two intercalating networks highlighted in orange and blue (left), and close up of a single 2,4,6,8,9,10-hexaazaadamantane unit (right).

high-energy-density materials due to its high nitrogen content cage structure.[14]

All three DACs were stepwise decompressed and SCXRD data was collected at each step to determine the K_0 and stability domain of both $C(NH)_2$ phases (Table S5 and S6). For α-$C(NH)_2$, a K_0 of 148(2) GPa was determined using a 3rd order Birch-Murnaghan equation of state (BMEOS) (Table S12).[15] In both DAC-1 and DAC-2, no sign of this phase was found at ambient pressure, suggesting its lack of recoverability. For β-$C(NH)_2$, a K_0 of 93(4) GPa was calculated with a 2nd order BMEOS. Using a 3rd order BMEOS gave no reasonable fit. Remarkably, β-$C(NH)_2$ was found to be fully recoverable to ambient conditions and stable in air.

To determine the exact hydrogen positions and to verify the obtained K_0, density functional theory (DFT) calculations were conducted. For α-$C(NH)_2$, the experimentally obtained structure could be perfectly reproduced (Table S8 and S9). Furthermore, the calculated unit cell volumes at different pressures are in excellent agreement with the experimental values. Consequently, the resulting calculated K_0 of 145.4(4) GPa is close to the experimental value (Figure 5).

For β-$C(NH)_2$, the hydrogen atoms could not be placed in sensible coordination environments without a symmetry
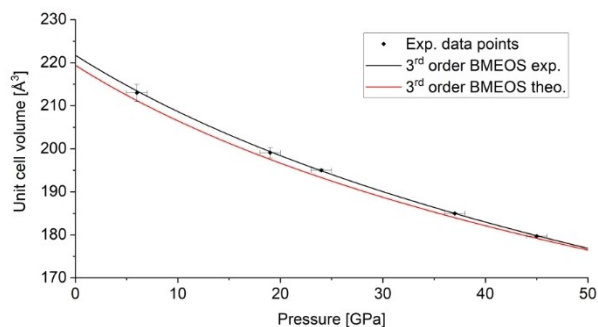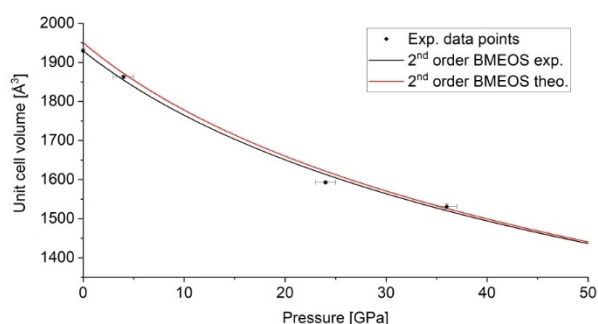
reduction to $P2_12_12_1$ (Table S10 and S11). This and the fact that only non-primitive unit cells are found in the experimental data could imply that the hydrogen atoms are disordered to some extent. The theoretical unit cell volumes match well with the experimental values. Furthermore, the theoretical K_0 obtained by a 2nd order BMEOS (89.8 (10) GPa) is similar to the experimental value (Figure 6). Both α- and β-$C(NH)_2$ are dynamically stable in the calculations, i.e. have no imaginary phonon frequencies (Figure S2).

To better understand the reason for the different reaction products that were obtained, calculations of their relative thermodynamic stabilities were conducted (Figure 7). These show that at all three reaction pressures, α-$C(NH)_2$ has the lowest enthalpy of formation compared to other forms of CH_2N_2. β-$C(NH)_2$ only becomes more stable than α-$C(NH)_2$ at pressures below $\approx$11.5 GPa. However, comparing their Gibbs free energies at 35 GPa shows that the decomposition into dwur-$C_2N_2(NH)$ + NH_3 becomes energetically more favorable at higher temperatures. β-$C(NH)_2$ also becomes comparatively more stable with increasing temperature but to a lesser extent.

These calculations agree well with the HPHT experiments on DAC-1, which contains DCDA. The short heating timespan of five seconds should have resulted in a pronounced temperature gradient inside the DAC. Then, dwur-$C_2N_2(NH)$ was formed at the hottest parts, while α-$C(NH)_2$ is produced at the colder parts of the sample. However, using longer heating times, as used by Salamat et al.,[7] results in higher temperatures across all of the sample, leading to the full conversion into dwur-$C_2N_2(NH)$ + NH_3. In contrast, the results obtained with DAC-3 cannot be explained by the thermodynamic calculations. At its synthesis pressure of 36 GPa, β-$C(NH)_2$ is never the most stable compound at any temperature and should thus not have been formed from a purely thermodynamical perspective. A possible explanation for this phenomenon may be derived from melamine's behavior during compression, which differs from that of both DCDA and malononitrile. In DAC-3, reflections assignable to melamine became evident at every position of the cell after decom-

Figure 5. Determined unit cell volumes for α-$C(NH)_2$ at different pressures with the resulting interpolation graph from a 3rd order BMEOS (black) alongside the theoretical one, determined from unit cell volumes calculated by DFT (red).
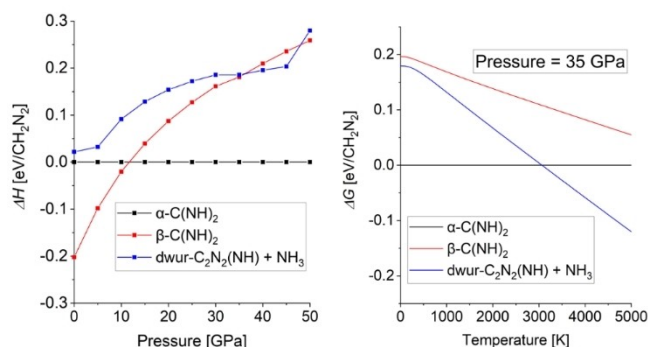

Figure 6. Determined unit cell volumes for β-$C(NH)_2$ at different pressures with the resulting interpolation graph from a 2nd order BMEOS (black) alongside the theoretical one, determined from unit cell volumes calculated by DFT (red).

Figure 7. Calculated relative enthalpies of formation ΔH at different pressures (left) and relative free energies ΔG at 35 GPa and different temperatures (right) for α-$C(NH)_2$ (black), β-$C(NH)_2$ (red), and dwur-$C_2N_2(NH)$ + NH_3 (blue).

pression to ambient pressure (Figure S6 and S7), while in DAC-1 and DAC-2 no signs of the respective starting materials were visible, not even at spots where the sample was not heated. This suggests that DCDA and malononitrile transform irreversibly under pressure. This transformation may be some form of polymerization, to which malononitrile is already prone to at ambient conditions in the presence of a catalyst.[16] In contrast, as melamine amorphizes reversibly under compression, its molecular units, i.e. the low-to-mid range order, are preserved. This implies a larger activation energy to cross into the global energetic minimum, being α-$C(NH)_2$ or dwur-$C_2N_2(NH)$ + NH_3 depending on the temperature, while the formation of β-$C(NH)_2$ appears to be more accessible to melamine as both contain *dreier*[11] rings. However, unequivocally confirming this hypothesis requires additional experiments and calculations.

In summary, we conducted LHDAC-experiments under HPHT conditions found in the interiors of extraterrestrial bodies such as Uranus and Neptune by employing the simple C/N/H molecules malononitrile, DCDA, and melamine as starting materials. All obtained samples were analyzed using in situ XRD. The experiments with malononitrile and DCDA allowed identification of the previously reported dwur-$C_2N_2(NH)$ and hitherto unknown α-$C(NH)_2$, which crystallizes in a distorted β-cristobalite structure. An additional novel $C(NH)_2$ phase, namely β-$C(NH)_2$, thought to be a metastable reaction product, built from imide-bridged 2,4,6,8,9,10-HAA units, which form two interpenetrating diamond-like networks, was predominantly detected in the experiment with melamine. The K_0 values for both previously unknown phases were determined through a stepwise decompression of the samples. DFT calculations were carried out to compare the relative thermodynamic stabilities of the three observed phases at different pressures and their relative free energies at different temperatures at 35 GPa. This allowed a better comprehension of the vastly different reaction behaviors under high pressure of DCDA and melamine, two compounds with the same empirical formula. Overall, this study significantly contributes to our understanding of the chemistry and therefore the inner workings of extraterrestrial bodies.

Supporting Information

The authors have cited additional references within the Supporting Information.[17–28]

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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