From Linear Molecular Chains to Extended Polycyclic Networks: Polymerization of Dicyanoacetylene

Huiyang Gou,* Li Zhu,*†‡ Li-Tyng Huang,*§ Arani Biswas,§ Derek W. Keefer,§ Brian L. Chalouix,‖ Clemens Prescher,‖ Liuxiang Yang,†§ Duck Young Kim,†§ Matthew D. Ward,† Jordan Lerach,‡ Shengnan Wang,§ Artem R. Oganov,‖ Albert Epshteyn,‖ John V. Badding,§‖ and Timothy A. Strobel*†

†Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, United States
‡Center for High Pressure Science and Technology Advanced Research, Beijing 100094, China
§Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States
¶Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, United States
□Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802, United States
‖Naval Research Laboratory, 4555 Overlook Avenue, SW, Washington, DC 20375, United States
¶Department of Geosciences, Center for Materials by Design, and Institute for Advanced Computational Science, State University of New York, Stony Brook, New York 11794-2100, United States
∇Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, 3 Nobel Street, Moscow 143026, Russia

**Supporting Information**

ABSTRACT: Dicyanoacetylene (C4N2) is an unusual energetic molecule with alternating triple and single bonds (think miniature, nitrogen-capped carbine), which represents an interesting starting point for the transformation into extended carbon—nitrogen solids. While pressure-induced polymerization has been documented for a wide variety of related molecular solids, precise mechanistic details of reaction pathways are often poorly understood and the characterization of recovered products is typically incomplete. Here, we study the high-pressure behavior of C4N2 and demonstrate polymerization into a disordered carbon—nitrogen network that is recoverable to ambient conditions. The reaction proceeds via activation of linear molecules into buckled molecular chains, which spontaneously assemble into a polycyclic network that lacks long-range order. The recovered product was characterized using a variety of optical spectroscopies, X-ray methods, and theoretical simulations and is described as a predominately sp2 network comprising “pyrrolic” and “pyridinic” rings with an overall tendency toward a two-dimensional structure. This understanding offers valuable mechanistic insights into design guidelines for next-generation carbon nitride materials with unique structures and compositions.

INTRODUCTION

Carbon nitride materials have attracted continuous attention in research over past decades as indicated by extensive efforts from both theory and experiments. Sustained interest in nitrogen-bearing, carbon-rich materials stems from their multiple functionalities and diverse applications. For example, cubic carbon nitride (c-C3N4) is predicted to have hardness comparable to diamond, whereas graphitic carbon nitride (g-C3N4) has been demonstrated to act as a photocatalyst for various redox reactions. Furthermore, nitrogen-doped carbon materials often exhibit excellent properties compared with their pure carbon counterparts, e.g., conductivity, basicity, oxidation stability, and catalytic activity, although these properties are highly dependent on the amount of nitrogen incorporated within the structure. When long-range order within carbon nitride materials is lacking, disordered structures containing sp2 and sp3 bonding may still exhibit outstanding mechanical properties, which is...
fundamentally important for the realization of three-dimen-
sional, crystalline carbon nitride solids.

Previous attempts to produce novel CN solids have largely
revolved around varying deposition methods to manipulate
particle size and texture, together with control of nitrogen
content.\textsuperscript{10–17} Nevertheless, adventitious hydrogen incorpora-
tion within these materials limits the development of
structure–property relationships for precise stoichiometries
and diverse CN building blocks.\textsuperscript{27–32} High-energy molecules
can provide an alternative path toward the formation of unique
structures, and high-pressure chemistry may be a viable
approach to obtain novel extended CN networks with
predetermined architectures.\textsuperscript{33} Studies of the polymerization
reactions of cyanogen,\textsuperscript{34} cyanoacetylene,\textsuperscript{35} tetracyanoethylene,\textsuperscript{36}
phosphorus tricyanide,\textsuperscript{37} and acetonitrile\textsuperscript{38} under
pressure have helped to clarify the influences of starting
materials and reaction conditions for the synthesis of new CN
materials.

Dicyanoacetylene ($C_4N_2$) is a linear molecule with
alternating triple and single bonds ($N\equiv C=\equiv C\equiv C\equiv N$).\textsuperscript{39}
The standard enthalpy of formation of $C_4N_2$ is $500 \text{ kJ/mol}$.\textsuperscript{40}
leading to a flame temperature of over $5000 \text{ K}$.\textsuperscript{41} Thus, $C_4N_2$
represents an interesting, high-energy starting point to access
novel extended CN networks. From the low-pressure side,
people have examined $C_4N_2$ and found reactions with benzene
produce aromatic hydrocarbons via the Diels–Alder reaction,\textsuperscript{42}
in addition to explosive decomposition into
dinitrogen and graphite. Chien and Carlini synthesized
poly(dicyanoacetylene) via anionic polymerization of $C_4N_2$
with $n$-butyllithium in THF, producing a linear polymer that
cyclizes into a ladder polymer upon heating at $400 \text{ °C}$.\textsuperscript{43}
Interestingly, the physiochemical behavior of $C_4N_2$ is also of
astronomical importance due to its presence in Titan’s north
polar stratosphere,\textsuperscript{44–47} as detected by infrared spectroscopy.
However, the interpretation of Raman and IR spectra is
challenging, especially with regard to conflicting assignments
for $C\equiv N$ and $C\equiv C$ stretching frequencies.\textsuperscript{48–50} Inconsisten-
cies between spectroscopic assignments for $C_4N_2$ may arise
from difficulties associated with sample preparation and
handling due to its inherent instability and high reactivity;
although it is of great importance for the understanding of
intrinsic properties and conclusions regarding its detection.

To our knowledge, $C_4N_2$ has not yet been examined under
high-pressure conditions, which is of great interest from the
perspective of novel carbon nitride materials and fundamental
chemical transformations. The large fraction of unsaturated
bonds suggests potential for pressure-induced ring-forming
reactions, as has been documented for a large number of other
nitrile- and alkyne-based systems.\textsuperscript{34–38} In addition, $C_4N_2$
represents an interesting C:N stoichiometry to access extended
networks with nitrogen content intermediate between typical
deposition-based syntheses (nitrogen doping within a carbon
framework) and precursor-based systems such as graphitic
$C_3N_4$. Moreover, high-pressure behavior can help to under-
stand the nature of chemical bonding, reaction mechanisms,
atomic structure, and local environments of reaction products,
which will advance the general understanding of carbon nitride
materials.

Here, we study the high-pressure behavior of linear
dicyanoacetylene ($C_4N_2$) up to 10 GPa in diamond anvil
cells. We first resolve the standing controversy regarding
assignments of Raman and IR spectra, aided by first-principles
phonon spectrum calculations. We next uncover a pressure-
induced reaction process whereby discrete linear molecules
polymerize into a disordered extended network without
significant change to the bulk composition. This novel,
amorphous material is fully recoverable to ambient conditions,
and its local structure, composition, and chemical bonding
were established using a variety of optical and X-ray scattering
methods. The reaction mechanism was rationalized using
molecular dynamics simulations. The present results provide a
framework to further the understanding of the local mechanism
of polymerization and offer valuable mechanistic insights into
design guidelines for the next-generation carbon nitride
materials.

\section*{METHODS}

\textbf{Synthesis.} $C_4N_2$ was prepared according to literature procedures.\textsuperscript{55}
All reactions were performed under an inert atmosphere of either
nitrogen or argon. Diethyl ether was dried and deoxygenated over
sodium benzophenone ketyl prior to use. Sulfolane was purified by
reaction with KMnO$_4$ to remove alkene impurities, dried over KOH,
and vacuum distilled prior to use.

\textbf{Acetylene Dicarboxamide (1).} A 100 mL aliquot of NH$_4$ (4.8 mol)
was condensed into a Schlenk flask and chilled to $-78 \text{ °C}$. Separately,
13.41 g (94.36 mmol) of dimethyl acetylenedicarboxylate (Sigma-
Aldrich, 99\%) was dissolved in 100 mL of anhydrous diethyl ether
($Et_2O$) and transferred dropwise to the chilled flask containing NH$_4$;
the reaction mixture quickly developed a red coloration. The reaction
mixture was warmed to $-45 \text{ °C}$ and stirred for $16 \text{ h}$ at this
temperature. Residual NH$_4$ was boiled off at ambient temperature,
and the remainder was evaporated to dryness under vacuum, yielding
a crude, orange product that was subsequently washed with cold
ethanol. The resulting beige powder was recrystallized from 150 mL of
boiling ethanol at $-20 \text{ °C}$, yielding 8.27 g (78\% yield) of white,
crystalline solid after filtering and drying the powder under vacuum.

\textbf{Dicyanoacetylene (2).} A 125 mL aliquot of anhydrous sulfolane
was added to a Schlenk flask equipped with a solids addition funnel
and a secondary (detachable) vacuum trap. Using a mortar and pestle,
1.960 g (17.49 mmol) of acetylene dicarboxamide (1) was ground with
15.456 g (54.06 mmol) of P$_2$O$_5$ until homogeneous. Solids were added
to the addition funnel, the apparatus was evacuated, the trap was
chilled to $-196 \text{ °C}$, and the sulfolane was heated to $110 \text{ °C}$
with vigorous stirring. Solids were added slowly to the reaction mixture,
which changed from colorless to yellow to red over time. After
bubbling had ceased ($\approx 3 \text{ h}$), the trap containing the crude product
was removed and transferred to an argon-filled glovebox; liquid was
piped into a small H-tube after melting. The liquid was frozen with
LN$_2$; a static vacuum of 50 mTorr was applied on the assembly.
The dewar was transferred to the empty arm of the H-tube, and the
product was sublimed by warming the arm. The volatile, pale beige
(almost colorless) liquid product was weighed within the glovebox
at 0.794 g (60\% yield). The product was stored at $-35 \text{ °C}$ under argon
precondition in decomposition.

\textbf{Poly-C$_4$N$_2$.} Liquid dicyanoacetylene (2; $\approx 1 \mu L$) was loaded into a
$\sim 150–210 \mu m$ diameter hole in a Re gasket using a clean
microsyringe. Before sample loading, Re gaskets were preindented
with thickness of 60–80 $\mu m$ and mounted on 300–500 $\mu m$ and
pipes of symmetric diamond anvil cells (DAC). Pressure was determined
by measurement of fluorescence from a ruby standard placed inside the
gasket hole.\textsuperscript{56} To avoid any possible contamination of the highly
reactive C$_4$N$_2$, a pressure medium was not used in the runs, but the
molecular crystals are very soft and the influence of deviatoric stresses
is expected to be small. All sample loadings were conducted in an inert
Ar gas atmosphere glovebox with oxygen and moisture concentrations
of less than 1 ppm. All samples were sealed to a starting pressure of
0–1 GPa within the inert Ar atmosphere before removing from the
glovebox.

\textbf{Raman Spectroscopy.} A system based around a Princeton
Instruments spectrophotograph SP2750 (Trenton, NJ, USA) with a 750 mm
focal length was used for the Raman spectra collections. A 532 nm
diode laser was used as an excitation source and was focused through a 20× long working distance objective lens. The laser power was optimized to be ∼1 mW, and a short exposure time of ≤60 s was used to avoid local heating of the sample. Raman light was collected in the backscatter geometry through a 50 μm confocal pinhole, and two narrow-band notch filters (Ondax) were used to allow collection to within ∼10 cm⁻¹ from the laser line. Raman light was collected though a 50 μm slit and dispersed off of an 1800 or 300 gr/mm grating onto a liquid nitrogen cooled charge coupled device (CCD) detector providing a spectral resolution of about 2 cm⁻¹. The spectrometer was calibrated using the emission lines of Ne with accuracy < 1 cm⁻¹.

**Infrared Spectroscopy.** Infrared transmission spectra were collected using a Varian 670-IR spectrometer system (Santa Clara, CA, USA) utilizing a Globar source and KBr mid-/near-IR beam splitter ca. 500–4000 cm⁻¹. Infrared light was focused on and recollected through the sample using reflecting objective lenses. Transmitted light was collimated through a 50 μm pinhole for increased spatial resolution and passed to an HgCdTe detector. IR spectra were recorded at varying pressure. The same diamonds were used to obtain reference spectra after the cell was decompressed and cleaned.

**X-ray Diffraction.** Powder X-ray diffraction (XRD) measurements up to 13.0 GPa were collected in ∼0.2 GPa pressure increments at the Advanced Photon Source, sector 16-BMD. Monochromatic X-ray beams (up to 13.0 GPa were collected in a standard for pure 100% sp² carbon. Nascent REGAL 250 carbon black was purchased from Cabot Corp. and graphitized at 3573 K for 5 h to form highly crystalline CNOs.

**Results and Discussion**

**Molecular C₅N₂.** C₅N₂ is a centrosymmetric linear molecule. Consequently, it has 3N − 5 = 13 fundamental vibrational modes, of which the Raman- and IR-active modes can be classified as \( \Gamma_{\text{Raman}} = 32A_{1} + 21A_{2} \) and \( \Gamma_{\text{IR}} = 2S_{2} + 2I_{5} \), given the molecule’s D₅h symmetry.
Raman and IR spectra of solid C$_4$N$_2$ recorded at 0.2 GPa (the solidification pressure at room temperature (RT)) are shown in Figure 1. In order to provide accurate assignments of vibrational modes, we performed density functional perturbation theory calculations, based on the previously reported low-vibrational modes, and obtained vibrational mode frequencies and intensities. Experimentally, we observed all fundamental IR/ Raman modes except the low-frequency IR-active bending modes ($v_b$), although we are able to infer their experimental frequencies based on observed combination bands. All experimental peak positions exhibit agreement with calculations within a frequency difference of 10%, allowing for accurate assignments.

Significant differences occur between previous mode assignments in the literature, notably in the high-frequency region and the distinction between C=N and C=C stretching. Our observations indicate that the strongest Raman mode at 2270 cm$^{-1}$ ($v_1$) can be assigned to C=N symmetric stretching, although it is not a pure vibration and shows mixing with C=C stretching character. The weaker intensity mode at 2122 cm$^{-1}$ ($v_2$) is assigned to C=C stretching. Previously, inconsistent assignments of the C=N and C=C stretching modes were made by Miller et al. at 2290 and 2119 cm$^{-1}$, Khanna et al. at 2270 and 2331 cm$^{-1}$, Smith et al. at 2204 and 2224 cm$^{-1}$, and Winther et al. at 2268 and 2121 cm$^{-1}$, together with Bartel et al. at 2206 and 2287 cm$^{-1}$. Two extremely weak peaks at 2310 and 2138 cm$^{-1}$, also previously observed at 2309 and 2137 cm$^{-1}$ by Miller et al. and 2307 and 2137 cm$^{-1}$ by Winther et al., correspond to the naturally abundant $^{13}$C isotopologue. The assignments of 618 ($v_3$), 505 ($v_4$), and 262 ($v_5$) cm$^{-1}$ are consistent with previous reports as shown in Table I. Interestingly, two new lattice modes (83 and 51 cm$^{-1}$) are observed for the first time in our Raman spectrum.

Over 5 GPa, changes in the Raman/IR spectra, as well as distinctive color changes of the sample, indicate the onset of a chemical transformation. The fundamental vibrational modes of C$_4$N$_2$ decrease in intensity, while new, broad Raman/IR features (Figure 2b and Figures S3 and S4) are observed near 1200–1600 cm$^{-1}$. Above 6 GPa the sample transforms from a transparent molecular crystal into a black and visibly opaque solid. Simultaneously, all crystalline diffraction data show that this structure is maintained to 5.5 GPa with a corresponding volume decrease of ～28% (Figure S2).

### Table I. Observed and Calculated Raman and IR Modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman</td>
<td>$v_1$</td>
<td>2270</td>
</tr>
<tr>
<td>Raman</td>
<td>$v_2$</td>
<td>2122</td>
</tr>
<tr>
<td>Raman</td>
<td>$v_3$</td>
<td>618</td>
</tr>
<tr>
<td>IR</td>
<td>$v_4$</td>
<td>2241</td>
</tr>
<tr>
<td>IR</td>
<td>$v_5$</td>
<td>1161</td>
</tr>
<tr>
<td>Raman</td>
<td>$v_6$</td>
<td>505</td>
</tr>
<tr>
<td>Raman</td>
<td>$v_7$</td>
<td>262</td>
</tr>
<tr>
<td>IR</td>
<td>$v_8$</td>
<td>477$^b$</td>
</tr>
<tr>
<td>IR</td>
<td>$v_9$</td>
<td>129$^b$</td>
</tr>
</tbody>
</table>

$^a$Most prominent frequency (theory predicts a number of modes of this character due to crystal field splitting). $^b$Inferred from combinations. F.r. = Fermi resonance with 2$e_C$. 

The in situ behavior of C$_4$N$_2$ was also studied under pressure to 13.0 GPa using single-crystal/powder X-ray diffraction. Single-crystal and powder XRD confirm that C$_4$N$_2$ crystallizes in the same $P_{2_1}/c$ structure reported previously at low temperature. The lattice parameters obtained at 0.2 GPa of $a = 3.878(1)$ Å, $b = 6.058(1)$ Å, $c = 9.0262(2)$ Å, and $\beta = 98.94(3)^\circ$ are in good agreement with the low-pressure report (see the SI, Tables S1 and S2 and Figure S1). With increasing pressure, the spectroscopic and diffraction data show that this structure is maintained to 5.5 GPa with a corresponding volume decrease of ～28% (Figure S2).

### Polymorphism into an Extended Network. Above 5 GPa, changes in the Raman/IR spectra, as well as distinctive color changes of the sample, indicate the onset of a chemical transformation. The fundamental vibrational modes of C$_4$N$_2$ decrease in intensity, while new, broad Raman/IR features (Figure 2b and Figures S3 and S4) are observed near 1200–1600 cm$^{-1}$. Above 6 GPa the sample transforms from a transparent molecular crystal into a black and visibly opaque solid. Simultaneously, all crystalline diffraction data show that this structure is maintained to 5.5 GPa with a corresponding volume decrease of ～28% (Figure S2).

Upon releasing the pressure to ambient conditions, a solid phase with a black luster was recovered, in stark contrast to the transparent starting liquid phase, indicating the irreversibility of the chemical transformation. The morphology and composition of the recovered phase was examined using SEM with compositional EDS mapping (Figure S3a and Figure S5). The recovered sample exhibits a smooth, uniform texture with homogeneous chemical composition near 30 at.% nitrogen.

DOI: 10.1021/acs.chemmater.7b01446

thin features are associated with C also observed in previously amorphous carbon than under visible excitation due to resonance enhancement, as sp vibration detected by UV Raman (257 nm) is much stronger bonding is preserved after the pressure-induced reaction. This indicates that a fraction of unconverted sp C carbons carbon nitrides and carbon materials. The peak at 696 cm wavenumber, similar to the G and D bands in amorphous excitation wavelengh, these broad peaks shift to lower domains in the recovered material.

Figure 2. Representative (a) X-ray diffraction patterns, (b) IR spectra, and (c, d) photographs showing the onset of polymerization above ~6 GPa.

Figure 3. (a) Backscattered electron SEM image showing smooth morphology with overlaid EDS elemental mapping for recovered C4N2. The average composition was found to be C4N1.8±0.1. (b) Multiwavelength Raman spectra of recovered samples. (c) C4N2. The average composition was found to be C4N1.8±0.1. This composition indicates that the majority of nitrogen remains chemically bound within the sample with only a small degree of nitrogen loss, although EDS tends to overestimate carbon content due to various sources of carbon contamination.

Raman spectra from the recovered sample obtained at various laser excitation wavelengths are shown in Figure 3b. The spectra show three notable features, in contrast to the original spectra collected from the molecular crystal. A weak peak observed at 2222 (2227) cm−1 with 633 (514) nm indicates that a fraction of unconverted sp C≡N and/or C≡C bonding is preserved after the pressure-induced reaction. This sp vibration detected by UV Raman (257 nm) is much stronger than under visible excitation due to resonance enhancement, as also observed in previously amorphous carbon and nitride thin film. Broad Raman peaks are observed between 900 and 1800 cm−1, as previously observed for amorphous carbons or carbon nitrides. These “D-” and “G-like” features are associated with C≡N and/or C≡C sp2 bonds and indicate the presence of disorder or a range of graphitic domains in the recovered material. With increasing excitation wavenumber, these broad peaks shift to lower wavenumber, similar to the G and D bands in amorphous carbon nitrides and carbon materials. The peak at 696 cm−1 with 633 nm excitation (700 cm−1 with 514 nm) is attributed to ring bending modes; this peak is barely visible in the UV Raman results. We note that, due to overlap with the diamond T2g phonon, combined with very weak Raman intensity above 6 GPa, we were not able to study the D and G features using Raman under in situ, high-pressure conditions.

Structure of the Recovered Material. In order to gain deeper insights into the local structure of the recovered C4N2, we performed high-energy X-ray scattering experiments to obtain S(Q) to a momentum transfer of Qmax = 17 Å−1, and transformed this information into the radial distribution function, g(r). In order to help interpret g(r), we performed AIMD simulations at 12 GPa and 300 K and relaxed the reaction product at ambient conditions. We note that a simulation pressure of 12 GPa was required to observe the rare-event chemical reaction on time scales suitable for AIMD simulations. The obtained g(r) for the final disordered C4N2 from both experiment and theory are shown in Figure 4a. The g(r) derived from experiment yields an average first-neighbor distance of 1.36 Å, smaller than that of sp2 amorphous carbon (1.43−1.49 Å) and graphite (1.42 Å). The calculated first-neighbor distance is 1.35 Å, which is very close to the experimental result. As suggested from Raman analysis, the recovered sample is dominated by sp2 C=C and C≡N bonds. Compared with known C=C (1.42 Å in graphite and 1.399 Å in benzene) and C≡N distances (1.30 Å in furazan, 1.33 Å in pyrazole, 1.34 Å in pyridine, and 1.37 Å in pyrrole), the average first-neighbor distance observed here also confirms that the dominant bonding contributions are from C=C and C≡N bonds.

All general features of the experimental g(r) are reproduced by the calculations, suggesting that the calculated structure is a strong candidate to understand the polymeric structure of the disordered product. The structure consists of quasi-two-dimensional layers of sp2 rings that are sporadically connected by a fraction of sp3 carbon atoms (<5%) (Figure 4b). This extended polycyclic structure is comprised of mostly five- and six-membered rings, although a small fraction of rings with four and ≥7 members were also observed. The density estimate from the S(Q) and g(r) of the recovered material using the method of Eggert et al. is 2.12 ± 0.1 g/cm3, compared with 2.17 g/cm3 from the MD simulation. These values are greater than 2.0 g/cm3 reported for CN(30%N), but smaller than 2.26 g/cm3 for crystalline graphite. The calculated average C−C and C−N coordination numbers are 2.4 and 2.9, respectively.
While 5% of the carbon atoms are 4-fold-coordinated, a small fraction of unconverted sp and linear sp² carbon keeps the average coordination number below three.

The second-nearest-neighbor peak in \( g(r) \) relates to the second coordination shell and thus provides information on bond angles. Experimentally, this peak is located at 2.43 Å, which is slightly longer than 2.37 Å from calculations. These distances provide average bond angles of 124.8° and 122.3° for experiment and calculation, respectively, and indicate a disordered graphitic ring structure. The absence of any distinct features between 2.8 and 3.0 Å indicates that there is no significant fraction of ordered 6-fold rings (the ideal cross-ring, 6-fold peak in graphite occurs at 2.84 Å).^{89}

**X-ray Photoelectron Spectroscopy.** To provide additional information regarding the local structure and bonding features, we performed XPS measurements. The core-level XPS spectrum from the recovered sample is shown in Figure 5. The pristine recovered sample displays both carbon (C 1s) and nitrogen (N 1s) core-level peaks, in addition to a small oxygen contribution, resulting in the approximate chemical composition C₄N₁.₄O₀.₂₄. We confirmed that the bulk interior of the sample did not contain any oxygen by performing a soft Ar⁺ surface milling to remove ~0.5 Å of material (~20 s at 0.5 kV), after which there was no detectable signal from the O 1s peak above the level of noise (Figure 5a). Thus, the oxygen signal originates from surface oxidation and does not exist within the bulk. After the surface cleaning, the chemical composition of the material indicated partial nitrogen loss (C₄N₁.₃), and we therefore conclude that the chemical composition of the recovered sample falls within the range of C₄N₁₋₂O₁ based on XPS analysis, which is in general agreement with the SEM-EDS composition. We note that both XPS (~26% N) and EDS (~31% N) analyses indicate partial nitrogen loss as compared with the starting molecular C₄N₂, but both techniques typically bias carbon due to environmental (adventitious) surface sources, and thus we consider C₄N₁₋₂O₁ as a lower bound on the actual nitrogen concentration. Due to the observed nitrogen loss after Ar⁺ milling, which suggests possible alteration of the local chemical structure, we chose to analyze the raw XPS data, before cleaning. We note, however, that there were no major differences between the spectra obtained before and after milling, aside from minor changes in relative peak intensities (and the obvious absence of oxygen).

The carbon nitride literature contains numerous and varying reports concerning the interpretation of XPS spectra.^{90−109} XPS spectra provide information regarding the binding energies of core-level electrons, which are a function of the local environment including coordination number and nearest-neighbor constituents. To a first approximation, partial charge, e.g., how much electron density is withdrawn by neighbors, can be used to generalize trends in binding energies. All other factors being equal, an sp² carbon bound to another carbon...
atom will possess a lower binding energy than an sp² carbon bound to an oxygen atom. In well-ordered molecular or crystalline systems, it is often straightforward to assign observed binding energies to specific sites, given sufficient spectral resolution. Yet, in disordered materials, such as the recovered C₃N₂ presented here, numerous local environments exist, and spectra should be considered in a statistical manner. Because we do not have sufficient spectral resolution to observe all possible local chemical environments, we employed the following approach to understand the measured XPS spectra. All XPS spectra were processed by first subtracting a linear background function. A series of trial peak functions were tested for each energy region, and it was determined that simple Gaussian peak profiles could sufficiently describe the spectra as well as more complex functions using the fewest number of adjustable parameters. We used the minimum number of Gaussian peaks needed to adequately fit each spectrum, and each peak within the same binding energy region was constrained to have the same full width at half-maximum (fwhm). Using this approach we can qualitatively understand the prominent local environments present within the recovered samples.

The N 1s core-level region (Figure 5b) was deconvoluted into two different Gaussian components located at 398.5 and 400.3 eV, which are consistent with the general N 1s features reported for amorphous carbon nitride and N-doped graphene. The most intense feature at 398.5 eV is attributed to “pyridinic-type” local environments, whereas the less-intense feature at 400.3 eV is attributed to “pyrrolic-type” environments. We note that while this nomenclature is common in the XPS literature, these terms do not explicitly mean pyridine or pyrrole but refer to whether the nitrogen lone pair participates in the π system. We were unable to resolve the small contribution from unreacted nitrile groups or any fraction of sp³ nitrogen atoms. Analysis of structures produced by MD simulations indicates that approximately 46% of the N atoms can be classified as pyridinic (2-fold-coordinated), 29% as pyrrolic (3-fold-coordinated with short C≡N bonds), 19% as sp³ (3-fold-coordinated with long C≡N bonds), and 6% as sp. The remaining nitrile nitrogen likely contributes toward the “pyridinic” XPS contribution observed at low binding energy, whereas, the 3-fold-coordinate N atoms with long bonds likely contribute more toward the “pyrrolic” contribution at higher binding energy. Adding these together from calculation, the pyridinic + sp and pyrrolic + sp³ contributions are roughly 50% each, compared with 69(5)% and 31(5)% averaged over four independent experimental observations. These features are in general agreement, but we note again that it was not possible to precisely describe all expected N 1s chemical environments in the peak fitting.

The C 1s core-level spectrum (Figure 5c) is characterized by a broad peak, tailing toward higher binding energy, which is evidence for high sp² carbon content in the material. The spectrum could be described by three Gaussian components at 284.7, 286.2, and 287.9 eV. The highest BE peak is attributed to C≡O bonds on the surface and is expected on the basis of a weak O 1s peak in the survey scan. For sp² dominated carbon materials, the XPS literature generally assigns the low BE peak near 284.7 eV to C≡C bonds and the higher 286.2 eV peak to C≡N bonds. But this assignment is incomplete, and the real situation is more complex. Nearly every carbon atom in the recovered material is 3-fold-coordinated; thus the identity of these three neighbors is needed for a base-level interpretation, e.g., CCC, CCN, CNN, and NNN. Our MD simulations reveal no NNN environments, while approximately 39% of three-coordinated carbon atoms are CNN, 52% are CCN, and 9% are CCC. Experimentally, the peaks at 287.7 and 286.2 eV comprise 32(7)% and 48(7)% of the C 1s signal, respectively, when averaged over four independent observations (discounting the contribution of oxygen). Thus, the 284.7 eV peak could represent predominantly CCC and CCN environments, while the 286.2 eV peak could represent CNN environments. While the interpretations across experiment and theory are fully consistent (MD, CCC + CCN = 61% and CNN = 39%; experiment, CCC + CCN = 52(7)% and CNN = 48(7)%), we must emphasize that we cannot fully resolve all C 1s chemical environments. A small fraction of sp³ carbon and unreacted nitrile carbon will also contribute to the overall shape of the XPS spectrum, although the sp³ features will dominate.

**Transmission Electron Microscopy.** High-resolution TEM, together with selected-area electron diffraction (Figure 6. (a) Obtained TEM with diffraction pattern (inset), (b) HRTEM with fast Fourier transformation (inset), elemental analysis of (c) C and (d) N, and EELS of (e) carbon and (f) nitrogen K-edges for recovered sample of C₃N₂.)
6), confirms that the material lacks long-range order, in agreement with the X-ray diffraction results. The TEM and EELS measurements were carried out using low beam energy with short acquisition times in order to minimize potential sample damage. HRTEM (Figure 6b) indicates that the material has a smooth texture at the atomic scale and no local domains of order are present. In addition, STEM-EDS mapping (Figure 6c,d) of the recovered sample confirms that carbon and nitrogen are distributed homogeneously with no signs of chemical disproportionation. The full-range EELS spectrum exhibits the characteristic 1s to σ* and 1s to π* transitions in both the carbon and nitrogen K-edge regions, similar to previous measurements of CNx films. Zooming in on these regions (Figure 6e,f), the sample shows an abundance of sp² bonding in the carbon and nitrogen atoms, as indicated by the presence of 1s peaks at both C and N K-edge. The sp² content was calculated to be ∼90 ± 5% using graphitized carbon nano-onions as a standard utilizing the method proposed by Brydson et al.110

Mass Spectrometry. In order to further study the structure of the disordered carbon nitride, we carried out time-of-flight secondary ion mass spectrometry measurements. The sample surface was cleaned using 20 keV Ar²⁺ ion sputtering to remove signals from surface contaminants and to reveal the true characteristics of the bulk material. The mass spectra of graphitic materials, such as highly oriented pyrolytic graphite (HOPG), do not contain monomeric molecular ions owing to their extended structure. However, graphitic surfaces do exhibit characteristic fragmentation patterns in the negative ion spectrum that consist of a series of prominent CnHm peaks with low hydrogen content.112 The negative ion spectrum of HOPG (as shown in Figure S6) exhibits features associated with C⁺, CH⁻, C₂H⁻, C₃⁻, C₄⁺, C₅⁻, and C₆⁻. These prominent features indicate a low hydrogen content and a fragmentation pattern consistent with an extended carbon structure (2D graphite in this case). The negative ion spectrum for recovered C₄N₂ is presented in Figure 7, together with the table of major fragments. In this case, the most prominent fragments are C–N ions (such as CN⁺, C₂N⁻), C–C ions (such as C⁺, C₂⁻), and hydrogenated ions with low H content (such as CH⁻ and C₂H⁻). Furthermore, larger CₙNₓ fragments with high nitrogen content are also observed. These results confirm the formation of an extended carbon–nitrogen network consisting predominantly of carbon–nitrogen and carbon–carbon bonds and are similar to previously reported results for carbon nitride thin films.112 In addition, the negative spectrum shows a fragmentation pattern similar to that of the TOF-SIMS spectrum of melamine, but with lower hydrogen content (Figure S7). Compared with the spectrum of melamine, recovered C₄N₂ shows similar low-mass ion fragmentation (e.g., C⁺, CH⁻, C₂⁺, C₃⁻, CN*, CN⁺, CN⁻, and C₂N⁺); however, higher mass protonated fragments such as CNH⁺, C₂NH⁺, and C₃N⁺H²⁺ are far less prominent.

Polymerization Mechanism. Previously reported static ab initio calculations suggest that, below 14 GPa, there are no thermodynamically stable crystalline carbon nitride phases113 including graphitic C₄N₄114 and its modified allotropes.115 Here we work in the realm of metastability and examine potential reaction pathways of crystalline, molecular C₄N₂ using a combination of molecular dynamics and metadynamics simulations, as well as evolutionary metadynamics116 as implemented in the USPEX code.117,118 The former is intended to provide direct insights into the reaction mechanism, while the two versions of metadynamics are used to examine a larger portion of the potential energy landscape by overcoming rare-event barriers and to draw conclusions as the system evolves toward the ground state.

Molecular dynamics (NPT) trajectories were established from a supercell (36 molecules) of the starting P2₁/c structure at 300 K and 12 GPa. Initial polymerization was generally observed to occur within the first 2 ps of the run (the same polymerized structures were equilibrated at 0 GPa to obtain the g(r) data in Figure 4). The molecular structure can be viewed as two-dimensional sheets of C₄N₂ molecules that lie in a single plane when viewed approximately normal to the ⟨210⟩ direction (Figure 8). Within these sheets, side-aligned columns of C₄N₂ molecules propagate down the b-axis. Two types of columns exhibit ABAB stacking within the ~⟨210⟩ plane where the A column is canted by ~67° with respect to the B column. The shortest interatomic distance in the starting structure is between the nitrile nitrogen of a molecule in column A and the nitrile carbon atom of an adjacent molecule in column B (~3.3 Å at 1 atm). When compressed to 12 GPa, the linear C₄N₂ molecules began to kink. Some of the C–C≡C and N≡C–C angles drop to as low as 140° within the first 2 ps, indicating enhanced interactions between neighboring molecules. As expected from the starting crystal structure, the initial polymerization initiates between the shortest N···C distance within a single 2D “sheet”. The polymerization proceeds within individual sheets through cycloaddition reactions that produce predominantly five- and six-membered rings, giving the overall structure a tendency to propagate in two dimensions. Over time, unreacted bonds begin to form connections between the 2D layers, producing a more interconnected structure that still remains largely two-dimensional. Ultimately, the final disordered C₄N₂ structure is unchanged after ~20 ps. This process is summarized in Figure 9.

At 300 K, MD trajectories become essentially trapped within a single configuration after polymerization occurs—there is not enough energy relative to kT for the probable observation of rare-event, covalent-bond breaking at our simulation time scales. In order to gain insights into the tendency of the system to evolve over longer time scales, we performed metadynamics simulations from the starting molecular structure (Figure S8). The metadynamics algorithm uses scaled components of the
edge vectors of the simulation cell as collective variables. The driving force that guides the evolution of the simulation cell is the derivative of the Gibbs free energy with respect to the six collective variables, which were updated in every metastep toward a low-energy pathway to neighboring minima. In our metadynamics simulation, C4N2 ultimately transformed to a two-dimensional layered structure. The final layered structure has a very low symmetry with the space group of P1, which can be understood as an approximate amorphous structure. The structural evolutions and calculated $g(r)$ for the $P1$ structure and the experimental data are shown in the Supporting Information (Figure S9). The metadynamics reaction sequence and calculated $g(r)$ are very similar when compared with the MD simulations, confirming the mechanism of the reaction process, and the general tendency during the polymerization of C4N2 is toward a two-dimensional structure comprised of heterocyclic rings. Interestingly, the evolutionary metadynamics simulations also revealed low-energy 2D and 3D crystalline structures, as reported in the Supporting Information. These structures are reported in Figures S11 and S12 and represent interesting future targets for metastable synthesis.

**CONCLUSIONS**

In summary, by starting with a hydrogen-free C4N2 molecular precursor, an amorphous extended carbon nitride with similar composition can be synthesized via high-pressure, solid-state chemistry. The fundamental vibrational modes of the molecular precursor were also definitively assigned with the help of DFT calculations. The recovered product is a largely two-dimensional polycyclic network comprised of predominantly 3-fold-coordinated $sp^2$ carbon with “pyrrolic-“ and “pyridinic-like” nitrogen. A small fraction of $sp^3$ carbon connects disordered 2D layers in three dimensions. The reaction proceeds by the activation of linear C4N2 molecules into buckled chains that spontaneously assemble through cycloaddition reactions. This understanding of the high-pressure behavior and polymerization mechanism of C4N2 will provide fundamental contributions to carbon nitride chemistry.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b01446.

Single-crystal X-ray diffraction analysis, Raman and infrared spectra with pressure, SEM-EDS data, TOF-SIMS data, and metadynamics structures (PDF)

**AUTHOR INFORMATION**

Corresponding Authors
* (H.G.) E-mail: huiyang.gou@hpstar.ac.cn.
* (T.A.S.) E-mail: tstrobel@ciw.edu.

ORCID
Albert Epshteyn: 0000-0002-4489-2296
Timothy A. Strobel: 0000-0003-0338-4380

Author Contributions
H.G. and L.Z. contributed equally to this work.

Notes
The authors declare no competing financial interest.

NRC Postdoctoral Associate.
ACKNOWLEDGMENTS

This work was supported by DARPA under ARO Contract No. W31P4Q-13-1-0005. Portions of this work were performed at HPCAT (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT operations are supported by DOE-NNSA under Award No. DE-NA0001974 and DOE-BES under Award No. DE-FG02-99ER45775, with partial instrumentation funding by NSF. Portions of this work were also carried out at GeoSoilEnviroCARS (The University of Chicago, Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation—Earth Sciences (Grant EAR-1128799) and Department of Energy—Geosciences (Grant DE-FG02-94ER14466). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. H.G. acknowledges financial support from the National Natural Science Foundation of China (NSFC) under Grant Nos. 512011148 and U1530402, as well as the Thousand Youth Talents Plan. D.Y.K. acknowledges the Texas Advanced Computing Center (TACC) at the University of Texas at Austin and Argonne Leadership Computing Facility (ALCF), which is a DOE Office of Science User Facility supported under Contract No. DE-AC02-06CH11357, for providing high-performance computing resources.

REFERENCES


Lyakhov, A. O.; Oganov, A. R.; Stokes, H. T.; Zhu, Q. New developments in evolutionary structure prediction algorithm USPEX. 