ABSTRACT: Dicyanoacetylene (C₄N₂) is an unusual energetic molecule with alternating triple and single bonds (think miniature, nitrogen-capped carbyne), 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-dimentional, 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.10–17 Nevertheless, adventitious hydrogen incorporation within these materials limits the development of structure–property relationships for precise stoichiometries and diverse CN building blocks.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.33 Studies of the polymerization reactions of cyanogen,34 cyanoacetylene,35 tetracyanoethylene,36 phosphorus tricyanide,37 and acetonitrile38 under pressure have helped to clarify the influences of starting materials and reaction conditions for the synthesis of new CN materials.

Dicyanoacetylene (C2N2) is a linear molecule with alternating triple and single bonds (N≡C–C≡C–C≡N). The standard enthalpy of formation of C2N2 is 500 kJ/mol,40 leading to a flame temperature of over 5000 K.41 Thus, C2N2 represents an interesting, high-energy starting point to access novel extended CN networks. From the low-pressure side, people have examined C2N2 and found reactions with benzene to produce aromatic hydrocarbons via the Diels–Alder reaction,42 in addition to explosive decomposition via dinitrogen and graphite. Chien and Carlini synthesized poly(dicyanoacetylene) via anionic polymerization of C2N2 with n-butyllithium in THF, producing a linear polymer that cyclizes into a ladder polymer upon heating at 400 °C.43 Interestingly, the physiochemical behavior of C2N2 is also of astrophysical importance due to its presence in Titan’s north polar stratosphere,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≡N and C≡C stretching frequencies.48–51 Inconsistencies between spectroscopic assignments for C2N2 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, C2N2 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.34–38 In addition, C2N2 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 C2N4. Moreover, high-pressure behavior can help to understand 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 (C2N2) 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.

METHODS

**Synthesis.** C2N2 was prepared according to literature procedures.55 All reactions were performed under an inert atmosphere of either nitrogen or argon. Diethyl ether was dried and deoxygenated over sodium–benzenophenone ketyl prior to use. Sulfolane was purified by reaction with KMnO4 to remove alkene impurities, dried over KOH, and vacuum distilled prior to use.

Acetylene Dicarboxamide (1). A 100 mL aliquot of NH3 (4.8 mol) was condensed into a Schlenk flask and chilled to −78 °C. Separately, 13.41 g (94.36 mmol) of dimethyl acetylenedicarboxylate (Sigma-Aldrich, 99%) was dissolved in 100 mL of anhydrous diethyl ether (Et2O) and transferred dropwise to the chilled flask containing NH3; the reaction mixture quickly developed a red coloration. The reaction mixture was warmed to −45 °C and stirred for 16 h at this temperature. Residual NH3 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 °C, yielding 8.27 g (78% yield) of white, crystalline solid after filtering and drying the powder under vacuum.

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 P2O5 until homogeneous. Solids were added to the addition funnel, the apparatus was evacuated, the trap was cooled to −196 °C, and the sulfolane was heated to 110 °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 (∼3 h), the trap containing the crude product was removed and transferred to an argon-filled glovebox, and liquid was pipetted into a small H-tube after melting. The liquid was frozen with LN2; 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 °C under argon to prevent decomposition.

Poly-C2N2. Liquid dicyanoacetylene (2; ∼1 μL) was loaded into a ∼150–210 μm diameter hole in a Re gasket using a clean microsyringe. Before sample loading, Re gaskets were preindented to a thickness of 60–80 μm and mounted on 300–500 μm anvil culets of symmetric diamond anvil cells (DAC). Pressure was determined by measurement of fluorescence from a ruby standard placed inside the gasket hole.58 To avoid any possible contamination of the highly reactive C2N2, 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.

**Raman Spectroscopy.** A system based around a Princeton Instruments spectograph SP2750 (Trenton, NJ, USA) with a 750 mm focal length was used for the Raman spectra collection. 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 mm confocal pinhole, and two narrow-band notch filters (Onada) 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 re-collected 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 recollected through the sample using re-MAR345 image plate, whereby its position was calibrated using a LaB₆ standard. Detector calibration, image integration, and intensity correction for oblique X-ray-to-detector angle were performed using standard. The resulting data were optimized using a Kaplow-type potential ⁷¹ was adopted with the PAW potentials taken from the VASP library where 2s²2p² and 2s²2p³ were treated in the Perdew–Burke–Ernzerhof parameterization ⁷² of the generalized gradient approximation. We also conducted X-ray Photoelectron Spectroscopy. XPS experiments were performed using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al Kα X-ray source (hv = 1.4867 eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low-energy electrons (<5 eV) and argon ions. The binding energy axis was calibrated using sputter-cleaned Cu foil (Cu 2p3/2 = 927.2 eV; Cu 3p3/2 = 75.3 eV). We assigned the pyridinic-N band in the N 1s spectra to the energy of 398.5 eV. Measurements were placed at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3–6 nm. Quantification was done using locally derived sensitivity factors from a pure poly(vinylpyrrolidone) (PVP) reference sample. A soft surface cleaning was performed using 0.5 kV Ar⁺.

**TOF-SIMS.** Time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis was performed using a Physical Electronics nanoTOF II instrument. A Bi₃⁺ primary ion beam with an ion dose of 5.0 × 10¹¹ ions/cm² was applied to an area of 100 × 100 mm², and negative secondary ions were collected. Charge compensation was performed using 10 eV Ar⁺ and 12 eV electrons. The surface sputter cleaning was performed using 20 keV Ar⁺ ions. The sputtered area was 800 × 800 μm² with an ion dose of 5.0 × 10¹¹ ions/cm². The Melanie and highly oriented pyrolytic graphite (HOPG) analytical standards were purchased from Sigma-Aldrich and used without further purification.

**First-Principles Calculations.** Ab initio molecular dynamics (AIMD) simulations for C₄N₂ were performed within the NPT (N is the number of particles, P the pressure, and T the temperature) ensemble⁷⁹ implemented in Vienna ab Initio Simulation Package (VASP) code ⁸⁰ with Langevin dynamics. The electron projector-augmented wave (PAW) potential ⁷¹ was adopted with the PAW potentials taken from the VASP library where 2s²2p² and 2s²2p³ are treated as valence electrons for C and N atoms, respectively. We generated a 2 × 3 × 3 supercell of a conventional unit cell, containing 36 formula units (f.u.) in the simulation cell, which is big enough not to have a force field overlap with the nearest cells. The plane wave was expanded to an energy cutoff of 400 eV, and Brillouin zone sampling with a 1 × 1 × 1 k-mesh was employed. Exchange and correlation effects were treated in the Perdew–Burke–Ernzerhof parameterization ⁷² of the generalized gradient approximation. We also conducted Raman intensity calculations using the Quantum Espresso software package ⁸¹ based on density functional perturbation theory. ⁷⁴ Calculations for vibrational modes need highly accurate charge density, and thus we carefully relaxed the atomic positions and the cell volume at a given external pressure. For the structural relaxation, we used a 6 × 8 × 16 k-mesh with 700 eV energy cutoff, and for Raman intensity calculation we used a 4 × 6 × 12 k-mesh with 700 eV energy cutoff.

**RESULTS AND DISCUSSION**

**Molecular C₄N₂.** C₄N₂ is a centrosymmetric linear molecule.⁷⁹ Consequently, it has 3N − 5 = 13 fundamental vibrational modes, of which the Raman- and IR-active modes can be classified as \( \Gamma_{\text{Raman}} = 2 \Sigma_g^+(\nu_1\nu_2\nu_3) + 2 \Pi_1(\nu_4\nu_5\nu_7) \) and \( \Gamma_{\text{IR}} = 2 \Sigma_g^-(\nu_2\nu_3) + 2 \Pi_1(\nu_4\nu_5) \), given the molecule’s D₂h 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, to obtain vibrational mode frequencies and intensities. Experimentally, we observed all fundamental modes. The assignments of 618 ($v_9$), 505 ($v_6$), 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. The infrared spectrum of C$_4$N$_2$ exhibits a strong peak at 2241 cm$^{-1}$ ($v_9$), corresponding to asymmetric C$\equiv$N and C$\equiv$C stretching modes. The observed mode at 1161 cm$^{-1}$ ($v_6$) is appropriately assigned to C$\equiv$C asymmetric stretching. The strong mode at 2338 cm$^{-1}$ in the Raman spectrum is almost twice the frequency of this mode, which can be assigned to 2$v_9$.

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 $a = 3.878(1) \, \text{Å}$, $b = 6.058(1) \, \text{Å}$, $c = 9.0262(2) \, \text{Å}$, 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).

Polymerization 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 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 is lost and only a diffuse halo remains visible in X-ray diffraction patterns (Figure 2). These features are indicative of the sp carbon and nitrogen reacting to form a disordered network with largely sp$^2$ character.

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 3a and Figure S5). The recovered sample exhibits a smooth, uniform texture with homogeneous chemical composition near 30 at.% nitrogen.

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

<table>
<thead>
<tr>
<th></th>
<th>experiment (cm$^{-1}$)</th>
<th>theory (cm$^{-1}$)</th>
<th>assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman</td>
<td>$v_1$, F.r.</td>
<td>2270</td>
<td>2290$^a$ symmetric C$\equiv$N + C$\equiv$C stretching</td>
</tr>
<tr>
<td>Raman</td>
<td>$v_2$</td>
<td>2122</td>
<td>2117$^a$ symmetric C$\equiv$C stretching</td>
</tr>
<tr>
<td>Raman</td>
<td>$v_3$</td>
<td>618</td>
<td>621$^a$ Symmetric C=C stretching</td>
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<tr>
<td>IR</td>
<td>$v_4$</td>
<td>2241</td>
<td>2234$^a$ asymmetric C$\equiv$N + C$\equiv$C stretching</td>
</tr>
<tr>
<td>IR</td>
<td>$v_5$</td>
<td>1161</td>
<td>1195$^a$ asymmetric C=C stretching</td>
</tr>
<tr>
<td>Raman</td>
<td>$v_6$</td>
<td>505</td>
<td>565$^a$ C=C=N bending</td>
</tr>
<tr>
<td>Raman</td>
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<td>262</td>
<td>285−296$^c$ C=C=C bending</td>
</tr>
<tr>
<td>IR</td>
<td>$v_8$</td>
<td>477$^b$</td>
<td>509$^a$ bending</td>
</tr>
<tr>
<td>IR</td>
<td>$v_9$</td>
<td>129$^b$</td>
<td>120$^a$ bending</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$v_5$. $^c$Inferred from combinations.
**Figure 2.** Representative (a) X-ray diffraction patterns, (b) IR spectra, and (c, d) photographs showing the onset of polymerization above ~6 GPa.

\[ \text{(a) } \text{C}_4\text{N}_{1.8\pm0.1}. \] 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 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 T\(_{2g}\) 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.

**Figure 3.** (a) Backscattered electron SEM image showing smooth morphology with overlaid EDS elemental mapping for recovered C\(_4\)N\(_2\). The average composition was found to be C\(_4\)N\(_{1.8\pm0.1}\). (b) Multiwavelength Raman spectra of recovered samples.

**Structure of the Recovered Material.** In order to gain deeper insights into the local structure of the recovered C\(_4\)N\(_2\), we performed high-energy X-ray scattering experiments to obtain \(S(Q)\) to a momentum transfer of \(Q_{\text{max}} = 17\ \text{Å}^{-1}\), 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 C\(_4\)N\(_2\) 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 sp\(^3\) amorphous carbon (1.43–1.49 Å) and graphite (1.42 Å).\(^{87,88}\) 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 sp\(^2\) C\(_4\)C and C\(_4\)N bonds. Compared with known C\(_4\)C (1.42 Å in graphite and 1.399 Å in benzene) and C\(_4\)N distances (1.30 Å in furazan, 1.33 Å in pyrazole, 1.34 Å in pyridine, and 1.37 Å in pyrrole),\(^{87}\) the average first-neighbor distance observed here also confirms that the dominant bonding contributions are from C\(_4\)C and C\(_4\)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 sp\(^2\) rings that are sporadically connected by a fraction of sp\(^3\) 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.\(^{68}\) is 2.12 ± 0.1 g/cm\(^3\), compared with 2.17 g/cm\(^3\) from the MD simulation. These values are greater than 2.0 g/cm\(^3\) reported for CN(30%N),\(^{90}\) but smaller than 2.26 g/cm\(^3\) 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).

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 C₄N₁.₄±0.₁ 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 C₄N₁.₄±0.₁ 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. 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 CₓNₓ 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.⁹⁰⁻¹⁰⁹ 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.⁹⁰⁻¹¹² 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.⁴⁰⁻¹⁰⁹ 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 sp³ dominated carbon materials, The XPS literature generally assigns the low BE peak near 284.7 eV to C=O bonds and the higher 286.2 eV peak to C≡N bonds.⁹³,¹⁰⁰ 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 CCN, 52% are CCN, and 9% are CCC. Experimentally, the peaks at 287.7 and 286.2 eV comprise 52(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
network consisting predominantly of carbon–nitrogen and carbon–carbon bonds and are similar to previously reported results for carbon nitride thin films. 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 C$_4$N$_2$ shows similar low-mass ion fragmentation (e.g., C$^-$, CH$^-$, C$_2^-$, C$_2$H$^-$, CN$^-$, C$_3$N$^-$, and C$_2$N$_{3+}$); however, higher mass protonated fragments such as C$_{2}$H$^+$, C$_{2}$N$_{3H}^+$, and C$_{2}$N$_{3H}^-$ 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 phases including graphitic C$_4$N$_4$ and its modified allotropes. Here we work in the realm of metastability and examine potential reaction pathways of crystalline, molecular C$_4$N$_2$ using a combination of molecular dynamics and metadynamics simulations, as well as evolutionary metadynamics, as implemented in the USPEX code. 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 P$_{21}/c$ 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 C$_4$N$_2$ molecules that lie in a single plane when viewed approximately normal to the (210) direction (Figure 8). Within these sheets, side-aligned columns of C$_4$N$_2$ molecules propagate down the b-axis. Two types of columns exhibit ABAB stacking within the ~(210) plane where the A column is canted by ~65° 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 C$_4$N$_2$ 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 C$_4$N$_2$ 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

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**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 Ar$^{2+}$ 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 C-H peaks with low hydrogen content.

The negative ion spectrum of HOPG (as shown in Figure S6) exhibits features associated with C$^-$, CH$^-$, C$_2^-$, C$_2$H$^-$, C$_3^-$, C$_3$H$_2^-$, and C$_4^-$. These prominent features indicate a low hydrogen content and a fragmentation pattern consistent with an extended carbon network. The negative fragment ions are listed.

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**Figure 7.** TOF-SIMS negative ion spectrum of the sample after Ar$_{1500}^+$ ion sputtering. C$_{4}$N$_{2}$ fragments with low content of hydrogen were observed. Although the hydrocarbon contamination on the surface is largely removed by ion sputtering, the contamination is still detected. However, the C$_{4}$N$_{2}$ fragments’ peaks are prominent and therefore provide direct evidence of an extended carbon–nitrogen network presented. The negative fragment ions are listed.
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 sp³ carbon with “pyrrolic-like” and “pyridinic-like” nitrogen. A small fraction of sp³ 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)

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