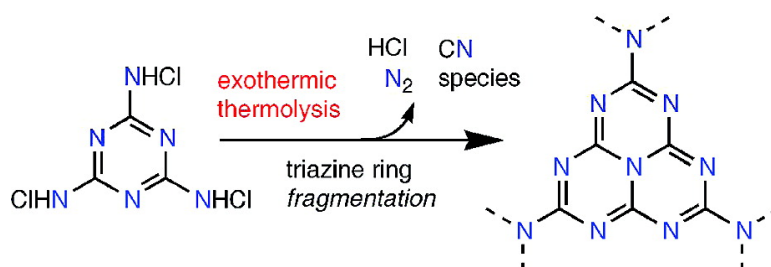


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From Triazines to Heptazines: Deciphering the Local Structure of Amorphous Nitrogen-Rich Carbon Nitride Materials

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Abstract: Nitrogen-rich carbon nitride (CN_x , $x \geq 1$) network materials have been produced as disordered structures by a variety of precursor-based methods, many that involve solid-state thermolysis at or above 500 °C. One popular precursor building block is the triazine unit (C_3N_3), and most postulated amorphous CN_x network structures are based on cross-linked triazine units. Since hydrogen is most often observed in the product, these materials are usually more appropriately described as CN_xH_y materials. Results from recent carbon nitride studies using larger conjugated heptazine (C_6N_7) precursors and from rigorous structural investigations of triazine to heptazine thermal conversion processes have prompted a reexamination of likely local structures present in amorphous carbon nitride networks formed by triazine thermolysis reactions. In the present study, the formation and local structure of a CN_xH_y material formed via the rapid and exothermic decomposition of a reactive triazine precursor, $\text{C}_3\text{N}_3(\text{NHCl})_3$, was examined by byproduct gas mass spectrometry, NMR and IR spectroscopy, base hydrolysis, and crystallographic analysis. The combined results clearly indicate that the moderate-temperature (~ 400 °C) self-sustaining decomposition of trichloromelamine results in ring fragmentation and reorganization into a CN_xH_y product that contains predominantly larger heptazine-like structural building blocks. These results may have applicability to many other disordered carbon nitride materials that are formed via triazine thermolysis. It also provides clearer and more accurate structural guidance in the use of these carbon nitrides as photoactive materials or coordination supports for metal and nonmetal species.

Introduction

Interest in covalently bonded carbon nitride (CN_x) materials was initially spurred by theoretical studies on an sp^3 -hybridized carbon analogue of silicon nitride, C_3N_4 ($\text{CN}_{1.33}$), that could have a hardness comparable to that of diamond.¹ To date, there have been no reproducible syntheses of this proposed ordered three-dimensional nitrogen-rich carbon nitride structure. High-energy physical deposition processes (e.g., laser ablation and RF magnetron sputtering) produce nitrogen-poor CN_x materials (where $x \ll 1$) with nitrogen-doped graphitic sp^2 carbon and amorphous sp^3 carbon regions.² In carbon nitride syntheses, as the CN_x nitrogen content increases to $x \approx 1$ or greater, the structures transform from disordered (black) graphite analogues to extended cross-linked (tan to brown) polymerlike materials. A chemical synthetic approach to nitrogen-rich CN_x materials utilized frequently over the past decade involves reactive precursors containing prebonded C–N core structures, such as triazine rings (C_3N_3 , Figure 1) and related heterocyclic arenes.³ Molecular triazines have been widely studied in other areas including pesticide synthesis, molecular organic chemistry,

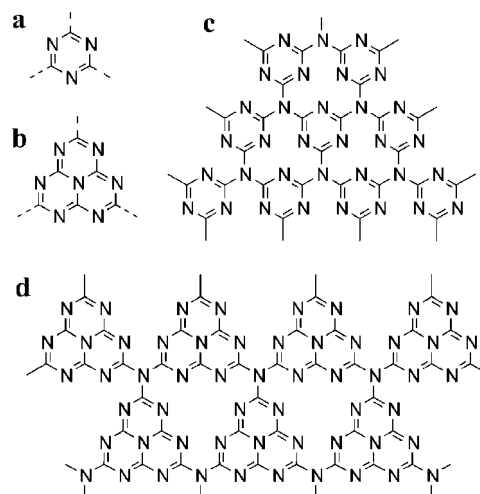


Figure 1. Structures for (a) triazine and (b) heptazine precursor cores and postulated planar C_3N_4 extended structures formed from (c) triazine and (d) heptazine building blocks.

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molecular magnetism, and hydrogen-bonded crystal formation.⁴ Concurrent with nitrogen increases in CN_x products, there is very frequently significant hydrogen incorporation in the final product (CN_xH_y), though this is often ignored in many CN_x structural proposals, as was detailed in a review of carbon nitride precursor approaches.⁵ Our research focus has been on thermally

unstable triazine and heptazine precursors that convert to nitrogen-rich carbon nitride powders and films.^{6–8}

The widespread use of the “carbon nitride” term to describe a diverse class of C–N-containing solids with nitrogen contents ranging from a few to over 60 mol % is somewhat of a misnomer. Inorganic metal and nonmetal nitrides are composed of nitrogen species that exhibit a range of bonding modes from ionic to covalent and form crystalline networks with well-defined chemical compositions. In contrast to such nitrides, nitrogen-rich carbon nitrides contain covalently bonded nitrogen in disordered structures with variable compositions and little or no long-range crystalline order. Regardless of the lack of details of local structure and composition, carbon nitrides and nitrogen-doped carbons have found use as metal-free organocatalysts and as components of fuel cell electrodes, and they show utility in light-emitting and chemical sensor applications.⁹

Over the past few years, there has been resurgent interest in studying larger conjugated C–N molecules, particularly those with planar heptazine (C₆N₇) core structures (Figure 1b). The heptazine structure has a colorful chemical and structural history, dating back to the days of Pauling¹⁰ and even further back to syntheses by Liebig.¹¹ Several heptazine molecular and anionic structures have been synthetically targeted for their structural coordination and optical emission interest.^{12,13} Heptazine-based precursors have been utilized in several recent carbon nitride network-forming reactions.¹⁴ Several thorough thermolysis

studies by Schnick and co-workers¹⁵ have convincingly shown that the solid-state thermolysis of small-molecule cyanamides and triazines can structurally rearrange to more stable heptazine structures at elevated temperatures (~400–600 °C). Generally, polymeric materials form in higher temperature thermolysis studies (~550–800 °C), though near these temperatures high-nitrogen-content CN_xH_y materials decompose into volatile gaseous species.

It has been frequently proposed that triazine-derived nitrogen-rich carbon nitride products retain the triazine structural fragment in the extended network structure (Figure 1), but recent studies indicate that this may not generally be the case, which calls for a structural reinvestigation of carbon nitride structures.^{15f} One recent triazine precursor thermolysis study concluded that their analytical data on the amorphous carbon nitride product could be fit to a triazine or heptazine extended network.¹⁶ Extended carbon nitride structures and molecular products that contain larger conjugated heptazine building blocks have been formed under forcing solid-state triazine thermolysis conditions¹⁵ and the first crystallographically characterized heptazine, tri-s-triazine (C₆N₇H₃), was produced via flash vacuum pyrolysis of a reactive triazine precursor at 400 °C.^{12a–c} Theoretical studies also indicate that the heptazine structure should be thermodynamically more stable than corresponding triazine arrangements.^{13a,17}

The intractable nature of most nitrogen-rich CN_xH_y network materials limits structural analyses to spectroscopic (e.g., X-ray photoelectron, IR, and solid-state NMR methods), mass spec-

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trometric (in special cases), and compositional analyses. Komatsu and co-workers employed boiling aqueous KOH as a useful chemical “deconstruction method” in the analysis of carbon nitrides derived from heptazine precursor thermolysis at 550 °C^{14a} and from triazine precursor condensation at 650 °C.^{3k} These studies showed that cyameluric acid [C₆N₇(OH)₃] was extracted from CN_xH_y products from heptazine precursors, while cyanuric acid [C₃N₃(OH)₃] was obtained from products formed by triazine precursors. This type of base hydrolysis has also been successfully utilized by Kroke and co-workers¹³ to isolate heptazine anions [C₆N₇O₃³⁻] from melon/heptazine polymers derived from the thermal decomposition of thiocyanates, and its utility was noted in early heptazine structural studies.^{10a} This deconstruction technique in conjunction with other analytical methods produces a more consistent and complete picture of the local structures present in disordered nitrogen-rich CN_xH_y network materials.

In light of recent heterocyclic C–N structural studies, we reexamined the local structure of nitrogen-rich CN_xH_y network materials synthesized in our laboratory via a rapid (in seconds) and exothermic decomposition of a commercially available triazine precursor, trichloromelamine (TCM), C₃N₃(NHCl)₃.⁶ In addition to residual gas mass spectrometry and solid-state NMR and IR analysis, we utilized base hydrolysis reactions to clearly determine that the local structure of TCM-derived carbon nitride materials contain larger, more stable heptazine fragments. Thus rapid self-propagating exothermic TCM decomposition represents a facile method to grow thermally stable heptazine-based network structures. A clear picture of true CN_xH_y local structures will greatly aid in their application as functional optical or coordination materials. These triazine to heptazine results are likely applicable to many prior CN_xH_y syntheses involving thermal conversion of triazine precursors to nitrogen-rich carbon nitride products at temperatures above ~400 °C.

Experimental Section

Thermal Decomposition of Trichloromelamine. The synthesis of CN_xH_y materials via exothermic and self-propagating TCM decomposition has been previously reported in detail.⁶ Typically, 3.0 g (13.1 mmol) of trichloromelamine (Aldrich, 98+%) was placed inside a 125 mL steel Parr reactor inside an argon atmosphere glovebox, which was refilled with 1 atm of N₂ and heated rapidly to 250 °C. After about 45 min, the internal temperature reached ~165 °C and a rapid jump in the internal temperature was observed, accompanied with an increase in pressure to approximately 300 psi. The yellow-tan solid product was isolated in air, rinsed with 15 mL of acetone, and then dried overnight in air. Bulk CHN analysis of the CN_xH_y used in this experiment had the following composition (wt %): C 34.17, H 2.23, N 58.55. This is close to prior analyses (C 34.21, H 1.56, N 60.01, Cl 0.60)⁶ but demonstrates that there is product composition variability from experiment to experiment for these amorphous CN_xH_y structures. **Safety note:** *The above exothermic reaction rapidly releases hot gases, including HCl and CN species, so care should be taken to perform this decomposition reaction in a ventilated hood and in a reactor with a pressure release valve.*

Base Hydrolysis of TCM-Derived Carbon Nitride (CN_xH_y) Powder. In a typical reaction, 400 mg of the CN_xH_y product was placed in a 50 mL round-bottom flask with 15 mL of a 3 M aqueous KOH solution (Fisher ACS-grade KOH diluted in 18 MΩ deionized water) and a Teflon-coated stir bar. All manipulations were carried out in the air. The flask was fitted with a reflux condenser containing an internal thermocouple and heated with a heating mantle to an internal temperature of 102 °C, at which point the solution with the suspended carbon nitride powder began to reflux. After 45 min

at refluxing conditions, the tan-orange CN_xH_y suspension had fully disappeared, leaving a clear, amber-colored solution. The solution was refluxed for 4 h and then it was cooled to room temperature. Long pale-yellow needles slowly formed upon cooling to ambient temperature over the course of several hours. The needles were isolated by vacuum filtration, rinsed with 2 × 15 mL of ethanol and 10 mL of diethyl ether, and air-dried overnight. Chemical analysis of the final product was (wt %): C 18.75, H 1.44, N 24.84, K (ICP-AE) 31.96 (calcd for K₃C₆N₇O₃·3H₂O: C 18.50, H 1.55, N 25.18, K 30.12). The yield, when production of K₃C₆N₇O₃·3H₂O from the CN_xH_y starting powder was assumed, was 82% (based on wt % carbon) after reduction of the filtrate volume to recover additional hydrolysis product.

Reaction and Product Analysis. Thermogravimetric-differential analysis (TG-DTA) was performed on a Seiko ExStar 6300 system under flowing argon. Fourier transform infrared (FT-IR) absorption spectra were taken with a Nicolet Nexus 670 spectrometer with KBr pellets. Elemental analyses were performed on a Perkin-Elmer 2400 CHN/O analyzer with ultralightweight tin capsules or were obtained from Desert Analytics (www.desertanalytics.com). Semi-quantitative energy-dispersive spectroscopy (20 kV, 20 μA) was run on a field emission Hitachi S4000 microscope with an IXRF X-ray microanalysis system to examine alkali metal content. Metal contents were determined quantitatively by inductively coupled plasma atomic emission (ICP-AE) spectroscopy on a Perkin-Elmer 400 emission spectrometer. Powder X-ray diffraction was performed on a Siemens D5000 X-ray diffractometer with Cu Kα radiation on samples mounted on glass slides. Solution ¹³C NMR was collected on a Bruker DRX-400 spectrometer, with D₂O containing a small amount of CH₃OH as the solvent. Solid-state ¹³C MAS NMR was obtained on a Bruker wide-bore MSL 300 with a CP-MAS sequence mode (20 000 scans, 10 s delay). The samples were loaded into 4 mm ZrO₂ rotors and spun at 8 kHz, and data were referenced to hexamethylbenzene.

Evolved gas analysis was performed with a Stanford Research Systems QMS 300 residual gas analyzer. TCM (3.0 g) was placed in the Parr reactor, which was tightly sealed under argon. The reactor was connected to a 500 mL three-neck gas collection flask via a gas inlet adapter and PVC tubing. The center neck was connected to the RGA-MS capillary with a sidearm connection to an argon gas Schlenk line, and the third neck was connected to an oil bubbler. The flask underwent three cycles of evacuation (~200 mTorr) and backfilling with argon. The valve to the reactor was then opened and three more cycles of evacuation and backfilling were performed. Three spectra of this atmosphere were recorded as background blanks. The reactor was then placed in a heating mantle and the temperature controller was set to 300 °C; the TCM rapidly decomposed near its decomposition temperature of 165 °C. After decomposition, the steel reactor was removed from the mantle and cooled to room temperature. The gas collection flask was continuously purged with argon through the oil bubbler while the decomposition took place in the attached Parr reactor. When the reactor reached ~35 °C, the argon purge was stopped and the reactor was *slowly* opened to allow the byproduct gases to escape into the glass collection flask and out the bubbler. After the flask was flushed with gases for a short period of time, three spectra were recorded in the 1–100 amu range. A fourth survey of 1–300 amu showed no evidence of volatile species beyond the 100 amu range.

Crystals of the CN_xH_y base hydrolysis product used for X-ray structure analysis were recrystallized from a 1:1 water/acetone mixture. A colorless needle of approximately 0.31 × 0.065 × 0.035 mm in size was mounted on a glass capillary and cooled under a N₂ gas stream (200 K). The data was collected on a Nonius KappaCCD diffractometer by use of Mo Kα radiation with a graphite monochromator, and 21 714 total reflections (5665 unique reflections) were obtained. Lorentz and polarization corrections were applied to the data, as well as an absorption correction by the multiscan technique. The structure was solved by direct methods

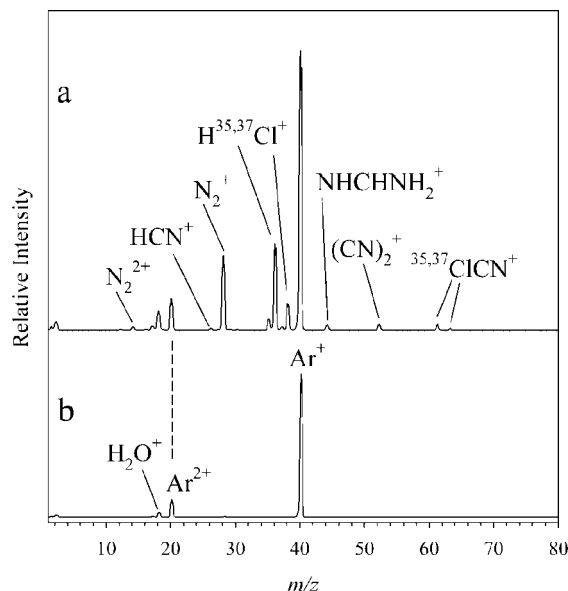


Figure 2. RGA-MS data for (a) TCM decomposition product gases and (b) an argon background blank.

with the ShelXTL v6.1 XS program. Least-squares refinement of the model versus the data was performed with the XL software. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were found by difference Fourier maps, geometrically constrained, and refined with isotropic thermal parameters.

Results and Discussion

Carbon Nitride Synthesis via the Self-Propagating Thermal Decomposition of TCM. Our initial studies on exothermic trichloromelamine decomposition indicated that TCM converted to CN_xH_y materials as noted in eq 1.⁶ The absence of chlorine by elemental analysis along with HCl detected by gas-phase IR and AgCl precipitation supported this initial proposed reaction (for $x \geq 1.33$).



Since bulk elemental analysis showed that hydrogen remained in the product, forming a CN_xH_y material, chlorine gas or chloramine elimination byproducts may also form during the exothermic TCM decomposition ($T_{dec} \geq 400$ °C in seconds).

The identity of evolved gases from the exothermic TCM decomposition was determined by use of a residual gas analysis mass spectrometer (RGA-MS). The background blank and spectrum of evolved gases from rapid TCM decomposition are shown in Figure 2. Two expected species were identified, namely, HCl and N_2 ; however several other cyanide-based signals were also detected, namely, HCN, $(CN)_2$, C1CN, and possibly formamidine ($HN=CH-NH_2$).

While some Cl_2 gas was observed in small-scale (~500 mg) TCM decomposition experiments, the large-scale decomposition RGA-MS data did not show evidence of Cl_2 . The detection of CN-containing gases is our first direct evidence that the rapid, self-propagating, and exothermic TCM decomposition process involves some degree of triazine ring fragmentation. Without quantifying the relative amounts of evolved gases, a revised (unbalanced) equation for TCM decomposition is shown in eq 2.

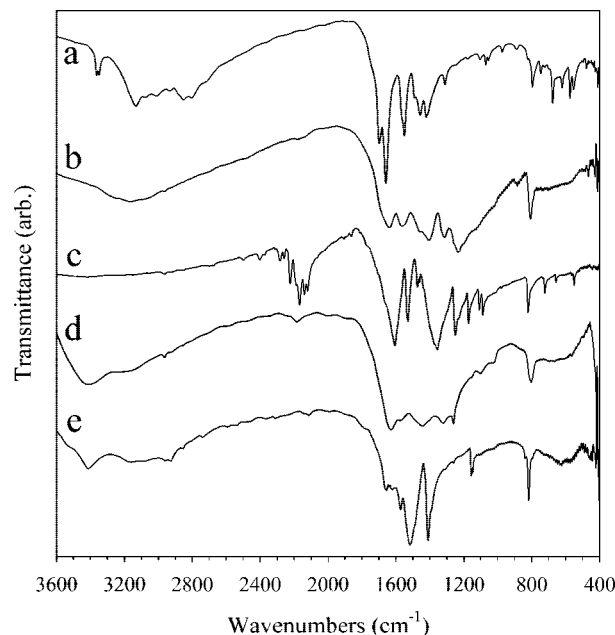
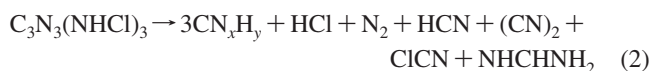


Figure 3. Solid-state FT-IR transmittance data for (a) trichloromelamine precursor, (b) TCM- CN_xH_y decomposition product, (c) triazidoheptazine (TAH), (d) TAH- CN_xH_y product, and (e) crystalline product from KOH base hydrolysis of TCM- CN_xH_y .

The new byproducts in eq 2 versus those in eq 1 will lead to carbon and nitrogen removal from the TCM, consistent with overall chemical yields that are ~62% for CN_xH_y from TCM (based on carbon).⁶ The carbon nitride solid from TCM decomposition will be referred to as TCM- CN_xH_y .

The TCM- CN_xH_y product is insoluble in common organic solvents, acids and bases, and is amorphous by powder X-ray diffraction analysis (broad peak near 3.3 Å),⁶ consistent with related disordered nitrogen-rich carbon nitride materials synthesized by others.^{3,9,14} As noted in the Introduction, bulk CHN compositions of CN_xH_y materials are variable and dependent on the precursor choice and synthetic conditions. The TCM- CN_xH_y material used in this study had an overall composition of $CN_{1.47}H_{0.78}$ (or $C_3N_{4.4}H_{2.3}$) and was thermally stable to ~600 °C under inert conditions before decomposing to gaseous byproducts (TGA; Figure S1, Supporting Information).

Solid-State IR and NMR Analysis of TCM- CN_x Powders. The disordered nature of the TCM- CN_xH_y products makes unambiguous IR assignments difficult. In comparing the TCM precursor with the carbon nitride product, it is seen that both solids have major absorption bands in the 1200–1700 cm^{-1} C=N region and show a characteristic triazine ring bending mode near 800 cm^{-1} (Figure 3a,b). The TCM- CN_xH_y product has broader peaks and increased absorption in the 1000–1300 cm^{-1} region that might be due to new C–N stretching vibrations associated with a cross-linked structure. A band near 3200 cm^{-1} is related to N–H and O–H residues arising from precursor or air exposure. These hydrogen-centered vibrations are seen in a majority of nitrogen-rich CN_xH_y materials, even ones that propose triazine extended structure models that do not include hydrogen.^{3,5}

Our recent results on the thermal decomposition of triazidoheptazine, $C_6N_7(N_3)_3$, revealed striking similarities between the IR spectra of its heptazine-based CN_xH_y product and the IR spectrum of TCM- CN_xH_y (Figure 3c,d).⁸ Both disordered carbon nitride structures show similarities in the ring breathing and

Table 1. Comparison of ^{13}C NMR for Various Heptazine Structures

	C (internal, junctional)	C (external)	ref
X for solution-state $\text{C}_6\text{N}_7(\text{X})_3$			
H	159.7	171.6	12a, c
Cl	158.2	175.0	13a
N_3	158.7	171.4	8a
$\text{O}^- \text{M}^+$; M = Li, Na, K, Rb, Cs	159.1–161.0	169.3–171.5	13b
$\text{OSi}(\text{CH}_3)_3$	158.9	169.5	13d
$\text{N}(\text{Et})_2$	155.0	162.4	12g
solid-state CP-MAS			
CN_xH_y from TCM	156.6	164.6	this work
$\text{C}_6\text{N}_7(\text{NH}_2)_3$	155.1, 156.0	164.3, 166.4	15b
CN_xH_y from $\text{C}_6\text{N}_7(\text{N}_3)_3$	156.0	163.7	8b
melon (heptazine polymer)	157.0	164.0	15g

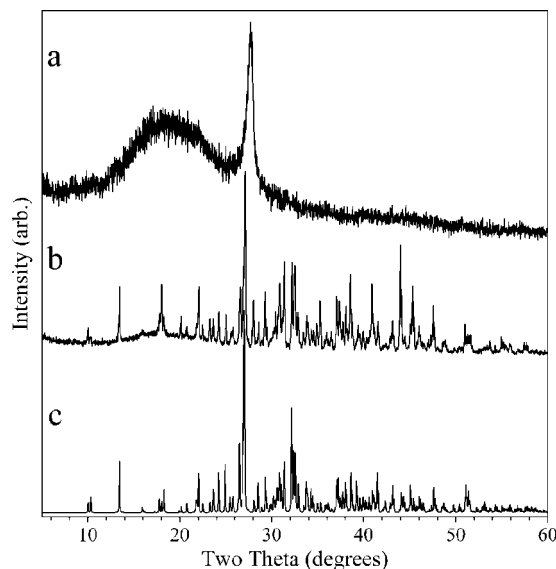
$\text{C}=\text{N}$ bonding regions. Previous XPS analysis showed that nitrogen in TCM- CN_xH_y may be present in an sp^2 -hybridized graphite-like environment.⁶ Solid-state magic-angle spinning (MAS) NMR data also showed a broad peak centered at 156 ppm with a small shoulder at 163 ppm. Clear structural interpretations of the local $\text{C}-\text{N}$ bonding environments in disordered TCM- CN_xH_y based on previous data were limited.

Cross-polarization MAS (CP-MAS) ^{13}C NMR of TCM- CN_xH_y clearly resolved two separate peaks at 157 and 165 ppm (Figure S2, Supporting Information). This NMR result more definitively shows that two different carbon chemical environments are present in the carbon nitride product. A comparison of these ^{13}C NMR data with those from other solid-state and solution studies on heptazine molecules and extended structures is shown in Table 1.

The ^{13}C peak positions for the TCM- CN_xH_y disordered network are similar to most of the heptazine structures. For comparison, N-substituted triazines have ^{13}C chemical shifts near ~ 163 – 168 ppm,^{4,7b} while internal heptazine carbons (junctional, bonded to central nitrogen and two nitrogens on the ring periphery) are found below 160 ppm. These NMR data are in reasonable agreement with recent theoretical NMR calculations.^{15h} The surprising similarity of IR and NMR of the TCM- CN_xH_y product with heptazines makes it clear that a reexamination of the proposed local structure of the TCM-derived carbon nitride networks was necessary.

Base Hydrolysis of TCM- CN_xH_y . In the absence of long-range crystallographic order, it is difficult to unambiguously determine if there is a local repeat structure in the amorphous and insoluble TCM- CN_xH_y product. Spectroscopic data indicates that the triazine precursor may convert to an extended structure based on predominantly heptazine-like fragments. We embarked on a structural “unzipping” strategy to directly probe the nature of local repeat structures in these materials. This approach was pioneered in studies on triazine and heptazine precursor approaches to extended $\text{C}-\text{N}$ solids where intractable solids were boiled in aqueous KOH and molecular decomposition products were isolated.^{3k,13,14a} This deconstruction method can essentially carve stable molecular fragments or building blocks out of the polymeric carbon nitride structure.

We examined the stability of the orange-tan TCM- CN_xH_y in 3 M aqueous KOH. While this solid is unreactive in KOH at room temperature, upon heating to reflux temperatures (~ 102 °C) for several hours, the powder completely dissolved/decomposed to form a dark orange solution. RGA-MS data collected from the gaseous headspace above the boiling KOH solution showed that ammonia ($m/z = 17$) is evolved during the hydrolysis. After

**Figure 4.** Powder XRD data for (a) TCM- CN_xH_y product, (b) product from KOH base hydrolysis of TCM- CN_xH_y , and (c) $\text{K}_3\text{C}_6\text{N}_7\text{O}_3 \cdot 3\text{H}_2\text{O}$ derived from ref 13b single-crystal data.

the solution was cooled to room temperature, long needlelike crystals formed. The IR spectrum of the hydrolyzed product shows the disappearance of $\text{C}-\text{N}$ stretches in the ~ 1100 – 1300 cm^{-1} region that may be related to broken extended network connections (Figure 3e). Chemical analysis and solution ^{13}C NMR of the needles (159 and 169.4 ppm) is consistent with a heptazine salt with the formula of $\text{K}_3\text{C}_6\text{N}_7\text{O}_3 \cdot 3\text{H}_2\text{O}$, which was previously synthesized, fully characterized, and crystallographically studied by Kroke and co-workers.^{13b,c} They produced a series of related anionic heptazine compounds by metal hydroxide hydrolysis of a heptazine-based polymer (melon) synthesized from NH_4SCN decomposition at ~ 300 °C. The crude solution mixture from our KOH hydrolysis experiment was evaporated to dryness under vacuum, and solution ^{13}C NMR of the isolated solid still showed only two peaks at 159 and 169 ppm, indicating that only heptazine-like species are present after hydrolysis. For reference, the ^{13}C NMR shift for the triazine analogue, $\text{C}_3\text{N}_3\text{O}_3^{3-}$, has a single resonance at 166.9 ppm.¹⁸

The needlelike solid from TCM- CN_xH_y base hydrolysis exhibits thermal properties consistent with larger conjugated rings versus triazines. These crystals irreversibly lost mass around 75 °C, corresponding to 3 mol of water (if a $\text{K}_3\text{C}_6\text{N}_7\text{O}_3$ formula is assumed), and decomposed at 550 °C (Figure S3, Supporting Information). For comparison, triazine analogues generally decompose at lower temperatures (~ 380 °C for $\text{K}_3\text{C}_3\text{N}_3\text{O}_3$).¹⁹ Further support that the base hydrolysis product is related to a previously structurally characterized heptazine compound, $\text{K}_3\text{C}_6\text{N}_7\text{O}_3 \cdot 3\text{H}_2\text{O}$, is found in strong similarities in the powder X-ray diffraction (XRD) pattern shown by both potassium salts (Figure 4). The amorphous XRD pattern for the starting TCM- CN_xH_y materials is also shown for reference. The powder XRD data for $\text{K}_3\text{C}_6\text{N}_7\text{O}_3 \cdot 3\text{H}_2\text{O}$ was generated from single-crystal structural data.^{13b}

The powder XRD structural similarities were verified by single-crystal X-ray structural analysis on the isolated needles from the TCM- CN_xH_y base hydrolysis. Their structure was

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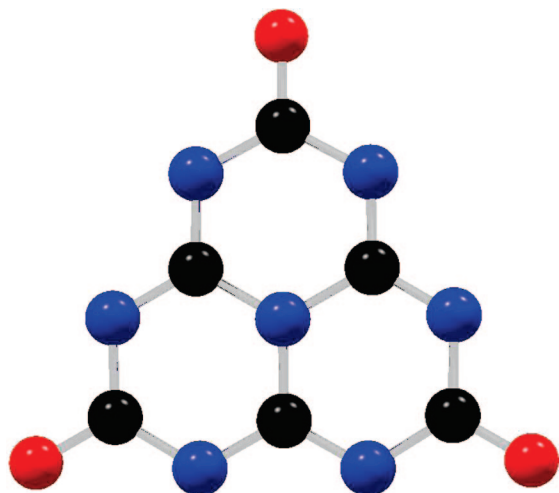


Figure 5. Heptazine oxyanion $C_6N_7O_3^{3-}$ structure from single-crystal structural analysis of $K_3C_6N_7O_3 \cdot 3H_2O$ produced by KOH hydrolysis of TCM- CN_xH_y . This structure agrees with the single-crystal analysis reported by Kroke and co-workers in ref 13b. Legend: C (black), N (blue), O (red).

identical to that described by Kroke and co-workers^{13b} for $K_3O_3C_6N_7 \cdot 3H_2O$ (Figure 5). This result confirms that heptazine structural building blocks were isolated from base-hydrolyzed amorphous nitrogen-rich TCM- CN_xH_y material.

The KOH base hydrolysis results show that heptazine building blocks were either extracted from the amorphous TCM- CN_xH_y starting material or possibly may form during the hydrolysis process. While prior studies have shown that triazine and heptazine anions have been extracted intact from their respective polymeric starting materials,^{3k,13b,14a} two control experiments were conducted to show that triazines do not convert to heptazines under our base hydrolysis conditions. A molecular triaminotriazine, $C_3N_3(NH_2)_3$, was dissolved by boiling KOH under the same conditions as those for TCM- CN_xH_y hydrolysis. The isolated white crystalline powders from this experiment were not needles and had one ^{13}C NMR peak at 161.5 ppm, which is consistent with symmetric substitution on carbon of a triazine ring, suggesting that uniform hydrolysis occurs under these forcing conditions, as has been observed by others.^{3k} A second KOH boiling experiment with cyanuric acid, $C_3N_3(OH)_3$, produced a solid with one ^{13}C NMR peak at 165.5 ppm. The powder XRD of the two triazine products from KOH hydrolysis have very similar powder XRD patterns (see Figure S4, Supporting Information), which are distinct from that for $K_3C_6N_7O_3 \cdot 3H_2O$ shown in Figure 4.

Luminescent Support for Heptazine Components in TCM- CN_xH_y . Solid and aqueous solutions of $K_3C_6N_7O_3 \cdot 3H_2O$ and related materials are intensely emissive in the UV-violet region (~ 250 – 370 nm) with emission tails reaching well into the blue-green region near 550 nm.^{8a,13b} Triazine precursors (solid or solution) examined in our group do not show appreciable visible luminescence under illumination with a hand-held UV lamp. In contrast, several TCM- CN_xH_y powders and sublimation products exhibit a clear greenish emission that is visible to the naked eye.^{6,7} Thus, the optical emission properties of CN_xH_y disordered solids give an indication whether or not larger conjugated ring structures are present in solids produced from triazine precursor decomposition.

Revised Local Structure of CN_xH_y Materials from Rapid, Exothermic TCM Decomposition. The IR and NMR of the

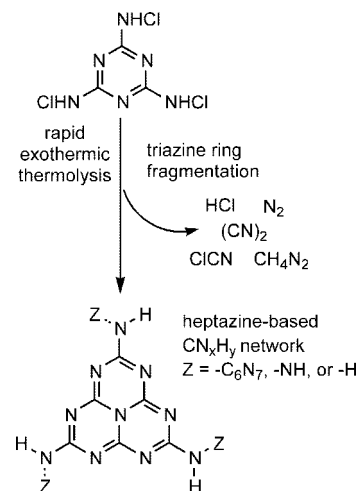


Figure 6. Reaction schematic for TCM decomposition reaction and TCM- CN_xH_y product.

amorphous TCM- CN_xH_y solid indicate that heptazine (C_6N_7) units are present and this is clearly supported by X-ray analysis of base hydrolysis products. Solid-state triazine thermolysis to heptazines has been previously demonstrated in certain cases, and these conversion processes occur in the 400–550 °C range,^{12,15} which is very near the temperatures recorded during the exothermic and self-propagating TCM decomposition processes (~ 420 °C).⁶ Note that these temperatures are also near the decomposition temperature of most nitrogen-rich carbon nitride materials. Theoretical thermochemical studies on triazines and heptazines show that the heptazine structure is thermodynamically stable relative to the triazine structure due to enhanced π conjugation,¹⁷ so reactive triazine intermediates may rearrange and convert to more thermodynamically stable heptazine-based structures. In the case of exothermic TCM decomposition, these rearrangements may be facilitated by nitrile elimination, nitrene or imide formation, or HCl vapor interactions that lead to heptazine-based nitrogen-rich CN_xH_y products in seconds. A summary reaction based on the experimental data discussed above is shown in Figure 6.

Since hydrogen is present in the bulk carbon nitride product, the structural connectivity of the external nitrogen attached to the heptazine core probably contains some combination of NH bonds and connections to other heptazine units. This material bears structural similarities to other melon-type polymeric systems. There is also recent structural evidence that, under some conditions, hydrogenation of nitrogen sites on the heptazine ring also occurs.^{13d} Given the disordered nature of these products, it is too speculative to definitively propose long-range structural connections for TCM- CN_xH_y .

Many triazine precursor decompositions and solvothermal carbon nitride syntheses are performed at temperatures in excess of 400 °C and yield materials with very similar IR data to our TCM- CN_xH_y products, but products are described by triazine-based structural models. For example, a high-pressure synthesis study produced a carbon nitride material from triazine precursors that was described as an extended triazine structure. The ^{13}C NMR of this material showed two peaks, one of which was near 157 ppm, consistent with the internal carbon of the heptazine unit, so alternate structures based on heptazine units may be applicable.²⁰ Another study utilized solid-state triazine thermolysis to produce a $\sim C_3N_4$ carbon nitride product with ^{13}C NMR peaks at 157 and 165 ppm, also consistent with

heptazine linkages versus a proposed linked triazine structure.²¹ It is likely that many previously postulated triazine-based CN_xH_y amorphous network structures actually contain heptazine-based local environments, which could be detected by solid-state NMR analysis and base hydrolysis studies similar to those described above. Recent proposals along these lines by other researchers are timely and correct.^{13,15}

Conclusions

Spurred on by recent triazine to heptazine conversion studies, a structural examination was performed on an amorphous nitrogen-rich carbon nitride material formed via the rapid and exothermic self-propagating decomposition of a triazine (C_3N_3) precursor, trichloromelamine. The thermally stable and insoluble CN_xH_y product was determined to be built up of heptazine (C_6N_7) repeat units that were formed via the thermally induced triazine degradation and conversion. The case for heptazine building blocks was supported by ^{13}C solid-state NMR and isolation of stable heptazine molecular anions after corrosive base hydrolysis (structural deconstruction) of the CN_xH_y network material. These results provide strong reinforcement to recent

calls for a reexamination of popular triazine-based carbon nitride structural models for disordered extended CN_xH_y materials produced from triazine thermolysis reactions. This study concludes that the rapid decomposition of a commercially available triazine precursor is a convenient method for the production of a heptazine-based nitrogen-rich CN_xH_y extended solid. The base hydrolysis of this TCM- CN_xH_y solid is also a facile method to produce heptazine oxyanions. A more chemically accurate view of disordered carbon nitride networks will aid in their use as optically emissive materials and as metal and nonmetal coordination structures.

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Supporting Information Available: TGA of TCM- CN_xH_y and $\text{K}_3\text{C}_6\text{N}_7\text{O}_3 \cdot 3\text{H}_2\text{O}$, CP-MAS NMR spectrum of TCM- CN_xH_y , and powder XRD of triazine KOH hydrolysis products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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