Synthesis and Structure of 2,5,8-Triazido-*s*-Heptazine: An Energetic and Luminescent Precursor to Nitrogen-Rich Carbon Nitrides

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Aromatic nitrogen heterocycles have a wide variety of uses in coordination chemistry and optical science. As one example, the 1,3,5-triazine ring motif (*s*-triazine, C_3N_3) has shown extensive utility in synthetic chemistry,[1] coordination chemistry,[2] and optical and magnetic studies.[3] Over the past few years, *s*-triazine has played a key role in molecular routes to carbon nitride (CN_x) materials investigated by various groups,[4] including ours.[5] Several of our triazine ring precursors contrast with those of others in that they are energetically unstable and rapidly decompose to CN_x materials.

In an effort to incorporate larger C–N fragments in a precursor structure, several groups have begun to examine the larger, related 1,3,4,6,7,9,9b-heptaazaphenalene ring system (tri-*s*-triazine or *s*-heptazine, C_6N_7, see Scheme 1). The *s*-heptazine structure was first postulated as a component of the polymer melon, $[-C_6N_7(NH_2)-NH-]_n$, by Pauling and Sturdivant over 75 years ago.[6a] The posthumous discovery of an azidoheptazine structure, $[C_6N_7(OH)_2N_3]$, on Pauling's chalkboard verifies his continued interest in *s*-heptazines.[6b] Contemporary synthetic work on *s*-heptazine-derived materials includes: (i) the isolation and structure of melem, $[C_6N_7(NH_2)_3]$, which decomposes and graphitizes above 560 °C,[7] (ii) the pyrolysis of tricarbodiimide-*s*-heptazine, $[C_6N_7(NCNH)_3]$, at 550 °C to form a C_3N_3H extended network material,[8] (iii) the pyrolysis of a mixture of $C_6N_7(NCNH)_3$ and $C_6N_7Cl_3$ (**1**) at 600 °C to form an oligomeric $C_{91}N_{124}H_{14}$ product,[9] and (iv) the crystal structure and optical properties of $C_6N_7Cl_3$ (**1**).[10] An extensive theoretical study on the structure, stability, and optical properties of 10 heptazine molecules, including the title compound, was recently reported.[11] These studies show that, like their *s*-triazine counterparts, *s*-heptazine-based precursors are promising, thermally robust candidates as precursors to nitrogen-rich, sp²-bonded carbon nitride materials.

This Communication describes the synthesis and crystal structure of 2,5,8-triazido-*s*-heptazine (**2**). This polycyclic, completely conjugated molecule is comprised of only carbon and nitrogen and is energetically unstable due to its high azide content. The molecule **2** exhibits visible light photoluminescence and rapidly decomposes at 185 °C to nitrogen-rich CN_x materials.

Scheme 1. Synthesis of 2,5,8-Triazido-*s*-heptazine (**2**)*a*

$NH_4SCN \xrightarrow{a} [-C_6N_7(NH_2)NH-]_n$
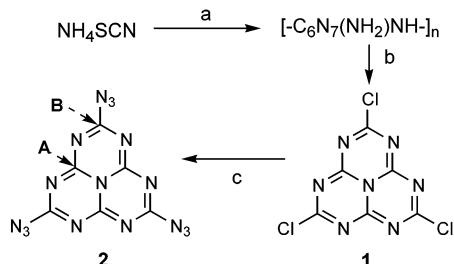
a Reaction and conditions: (a) (1) 300 °C, air, (2) 400 °C, N_2; (b) (1) 2.5 M $KOH_{(aq)}$, reflux, 4 h, (2) PCl_5, 130 °C, N_2, 10 h; (c) neat $(CH_3)_3SiN_3$, 100 °C, N_2, 12 h.
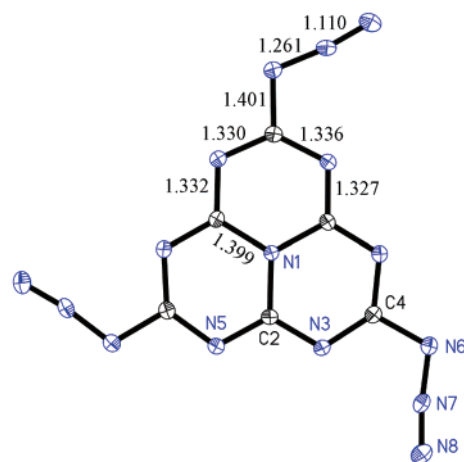

Figure 1. Crystal structure representation of **2**. Thermal ellipsoids drawn at 35% probability and bond lengths (Å) are noted.

The synthesis of **2** was accomplished via a melon intermediate produced by the pyrolysis of NH_4SCN.[8,12] Melon was converted to the potassium salt of 2,5,8-trihydroxy-*s*-heptazine, $[C_6N_7(OK)_3]$, which was then treated with PCl_5 to generate 2,5,8-trichloro-*s*-heptazine (**1**, Scheme 1).[10] After purification by Soxhlet extraction in benzene, **1** was heated at 100 °C in neat trimethylsilyl azide under N_2 for 12 h, yielding a quantitative conversion to 2,5,8-triazido-*s*-heptazine (**2**). Soxhlet extraction in dry acetone was used to obtain the purified orange-tan product.

An FT-IR comparison of **1** with **2** clearly shows the appearance of the azide vibrations centered at 2168 cm⁻¹ and several peak shifts and intensity changes in the 600–1000 cm⁻¹ region (see Supporting Information). Mass spectrometry data on **2** show the parent ion peak at 296 amu and minor peaks consistent with successive N_2 loss. The solution ¹³C NMR spectrum of **2** shows resonances at 158.7 ppm (Scheme 1, carbon **A**) and 171.4 ppm (Scheme 1, carbon **B**) that agree very well with those of other *s*-heptazines.[7,10,13]

Single-crystal X-ray diffraction analysis of crystals grown from dry acetone resulted in the structure of **2** represented in Figure 1. The molecule is planar with bent azide groups giving rise to C_{3h} symmetry. The bond distances around the heptazine periphery are very similar, indicating significant π bond delocalization. The central nitrogen (N1) lies in the plane of the heptazine ring and has sp²-like character, so its lone pair has some π overlap with neighboring carbons. There are angular distortions along the outer ring, such that the C2–N3–C4 angle is 116.6° while the N3–C4–N5 angle is 128.8°. These results closely agree with data on other *s*-heptazines[7,10,13] and with theoretical predictions on **2**.[11]

The azide groups show π bond localization with a short N7–N8 bond distance (bond order ≈ 2.5) and a longer N6–N7 bond distance (bond order ≈ 1.5). The C4–N6–N7 angle is 111.9°, and
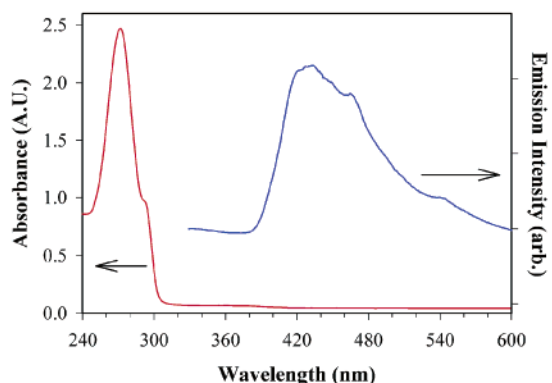
Figure 2. UV–visible (red curve, left) and photoluminescence (blue curve, right) spectra for **2**.

the N6–N7–N8 angle is slightly bent at 172.6°. The azides lie in the plane of a flat *s*-heptazine core. These results agree very well with structural data from other conjugated nitrogen heterocycles with azides[14] and with theoretical structure calculations on **2**.[11]

The molecules of **2** pack into an AB layer-like structure. The azides and heptazines are offset from one layer to another leading to a C_3 symmetric channel at the origin running down the *c* axis (see Supporting Information). The molecules in adjacent layers are separated by roughly twice the nitrogen van der Waals distance (3.08 Å), consistent with near molecule contacts.

The UV–visible absorption spectrum for **2** in ethanol is shown in Figure 2. The peaks at 275 and 295 nm are likely due to $\pi–\pi^*$ and $n–\pi^*$ transitions. Two very weak absorptions are also observed at 360 and 385 nm and may contribute to the orange-tan appearance of **2**. Theoretical studies predict a HOMO–LUMO gap of 4.14 eV (300 nm) for **2**,[11] consistent with the UV–visible data. Under 290 nm excitation, **2** shows a broad photoluminescence peak in ethanol at 430 nm. This emission is in the range of luminescence observed for other *s*-heptazines[10,13] and π-conjugated nitrogen-containing polycyclic systems.[15] Note that extended illumination of **2** below 270 nm results in slow degradation, likely via photolytic azide decomposition.

The thermal stability of **2** was examined by thermogravimetric-differential thermal analysis (TG-DTA). Under argon flow and a 2 °C/min ramp rate, TG-DTA revealed a rapid weight loss at ∼185 °C accompanied by a sharp exothermic event (see Supporting Information). The decomposition product was a tan-colored, visibly porous solid with thermal stability up to ∼500 °C. An isothermal 150 °C TG-DTA experiment shows that **2** is relatively stable for 3 h (<5 wt % loss), then over the next 5 h it steadily loses 23 wt %, achieving a constant weight equivalent to the loss of 3 N_2 per molecule. The material at this point no longer rapidly decomposes upon heating at higher temperatures. The large-scale rapid decomposition of **2** was initiated with a heated filament in a closed stainless steel reactor under argon as previously described.[5c] The product obtained by this method has a bulk elemental formula near C_3N_4 and an FT-IR spectrum typical for sp²-bonded CN_x materials.[4,5] Further characterization of this carbon nitride product is ongoing.

Molecular azides are often thermodynamically unstable, shock and impact sensitive, and should be handled with caution. For example, triazido-*s*-triazine has explosive properties,[16] violently detonates during vigorous grinding in a polished agate mortar, and produces pure carbon nanoflakes[5a] or carbon nanotubes[17] when it explodes. In contrast, the larger polycyclic triazide **2** can be safely ground in a polished agate mortar, but visibly and moderately decomposes when ground in an unpolished ceramic mortar, leaving

behind a tan-brown residue. It also has an impact sensitivity near 6 N·m, which is similar to that of lead azide, an established primary explosive.[16]

In summary, we report the synthesis and crystal structure of 2,5,8-triazido-*s*-heptazine (**2**), a rare example of a fully conjugated, polycyclic all carbon and nitrogen molecular compound. This planar heptazine is photoluminescent near 430 nm and shows potential as an energetic single-source precursor for the rapid synthesis of nitrogen-rich C_3N_4 network materials. The large number of nitrogen lone pairs present in **2** also makes it an attractive candidate as a component in supramolecular metal coordination frameworks.

Supporting Information Available: Experimental procedures for preparation and characterization of **2**. FT-IR spectrum, TG-DTA plot, crystallographic data, and packing structures for **2**. Table comparing data on **2** and related *s*-heptazines (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA048939Y