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, C₃N₃) has shown extensive utility in synthetic chemistry, coordination chemistry, and optical and magnetic studies. Over the past few years, s-triazine has played a key role in molecular routes to carbon nitride (CNₓ) materials investigated by various groups, including ours.¹ Several of our triazine ring precursors contrast with those of others in that they are energetically unstable and rapidly decompose to CNₓ 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, C₆N₇, see Scheme 1). The s-heptazine structure was first postulated as a component of the polymer melon, [-C₆N₇(NH₂)NH-]ₙ, by Pauling and Sturdivant over 75 years ago. These s-heptazine-based precursors are promising, thermally robust candidates as precursors to nitrogen-rich, sp²-bonded carbon nitride materials. Synthesis of ² was achieved from melon, an oligomeric s-heptazine synthesized by the pyrolysis of NH₄SCN. Melon was converted to molecular 2,5,8-trichloro-s-heptazine, which was then transformed to the triazide upon reaction with (CH₃)₃SiN₃. The crystal structure of ² verifies that the s-heptazine is planar and the azides adopt a pinwheel-like C₁₈h arrangement around the periphery. The s-heptazine core shows π delocalization in the C-N bonds around the periphery (ave. 1.33 Å), while the internal planar C-N bonds are longer (1.40 Å). The heptazine units pack into parallel, but offset layered sheets in the crystal. The triazide ² exhibits photoluminescence at 430 nm and rapidly and exothermically decomposes upon heating at 185 °C to produce a tan thermally stable carbon nitride powder with a formula near C₃Nₓ₄.


Scheme 1

Synthesis of 2,5,8-triazido-s-heptazine (²):
(a) 1) 300 °C, air 2) 400 °C, N₂; (b) 1) 2.5M KOH [aq], reflux, 4 h 2) PCl₅, 130 °C, N₂, 10 h; (c) neat (CH₃)₃SiN₃, 100 °C, N₂, 12 h.