

Synthesis and Characterization of C₁₅N₁₂: A New Cyanoazacarbon

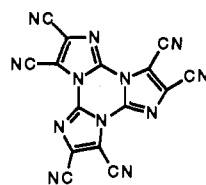
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Materials that contain only carbon and nitrogen have properties that are desirable for high-performance composites and matrices.¹ In general, they are chemically inert and have high thermal stability and low flammability.²⁻⁶

Our work in cyanoazacarbon chemistry⁷ has led us to explore the reactivity of 4,5-dicyanoimidazole derivatives in an effort to prepare C-N only material precursors. In this communication we report the unusual, thermal decomposition⁸ of 1-iodo-2-halo-4,5-dicyanoimidazoles to give a novel trimer of C₁₅N₁₂ composition. Our report describes the synthesis and characterization of hexacyanotris(imidazo)triazine (HTT) from 1-iodo-2-halo-4,5-dicyanoimidazole derivatives.



Tris(imidazo)[1,2-a:1,2-c:1,2-e]-1,3,5-triazine-2,3,5,6,8,9-hexacarbonitrile
Hexacyano Tris(imidazo)triazine

HTT

Iodination of 2-halo-4,5-dicyanoimidazoles **1a-c** with ICl in aqueous base easily gives the 1-iodo-2-halo derivatives **2a-c** (Scheme 1).⁹⁻¹¹ These novel, but simple, compounds contain no hydrogen and were viewed as precursors to a carbon nitrogen material. The lability¹² of the N-I and C-Cl bonds of **2a** is apparent upon examination of the TGA of **2a** (Figure 1, under

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- (5) (a) Wixom, M. R. *J. Am. Ceram. Soc.* **1990**, *73*, 1973. (b) Maya, L.; Harris, L. A. *J. Am. Ceram. Soc.* **1990**, *73*, 1912.
- (6) For an earlier example of the preparation of amorphous hydrogenated carbon nitride, see: (a) Han, H. X.; Feldman, B. J. *Solid State Commun.* **1988**, *65*, 921. There are even earlier reports of the attempted preparation of "carbonic nitride": (b) Franklin, E. C. *J. Am. Chem. Soc.* **1922**, *44*, 486.
- (7) Apen, P. G.; Rasmussen, P. G. *J. Am. Chem. Soc.* **1991**, *113*, 6178.
- (8) Previously other imidazotriazines have been prepared from thermal decomposition of 2-halo derivatives. From 2-fluoroimidazole: (a) Kirk, K. L.; Nagi, W.; Cohen, L. A. *J. Am. Chem. Soc.* **1973**, *95*, 8389. (b) Takeuchi, Y.; Kirk, K. L.; Cohen, L. A. *J. Org. Chem.* **1979**, *44*, 4243. From 2-chlorobenzimidazole: (c) Lavagnino, E. R.; Thompson, D. C. *J. Heterocycl. Chem.* **1972**, *9*, 149.
- (9) Compound **1a** synthesized from 1-methyl-2-bromo-4,5-dicyanoimidazole via transhalogenation and subsequent demethylation with LiCl/NMP. 1-Methyl-2-bromo-4,5-dicyanoimidazole was prepared as reported: Apen, P. G.; Rasmussen, P. G. *Heterocycles* **1989**, *29*, 1325. See supplementary material for details.
- (10) Compound **1b** synthesized as reported previously: Apen, P. G.; Rasmussen, P. G. *Heterocycles* **1989**, *29*, 1325. See supplementary material for details.

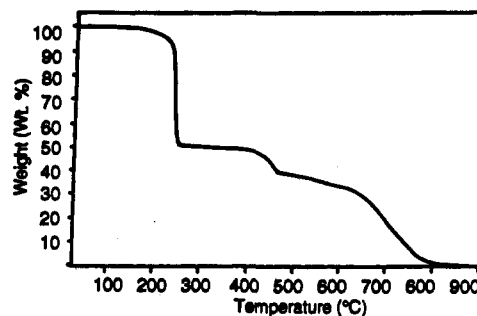
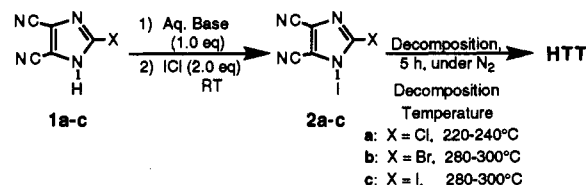


Figure 1. TGA of 1-iodo-2-chloro-4,5-dicyanoimidazole (**2a**).

Scheme 1



N₂(g), heating rate = 5 °C/min) which shows a weight loss corresponding to loss of ICl.

The thermal decomposition of **2a-c** (Scheme 1) gives the novel trimer HTT of C₁₅N₁₂ composition.¹³ Elemental analysis observed for HTT prepared from **2b** shows the following weight percentages: C, 51.48; N, 47.45; H, 0.39; I, 0.00; Br, 0.12; O, 0.56 (by difference).¹⁴

The mass spectrometry of HTT was possible by electron impact (EI) using a direct chemical ionization (DCI) probe, and also by chemical ionization (CI) using methane. High-resolution mass spectrometry of HTT yielded the following results: HRMS (EI with DCI probe) calculated for C₁₅N₁₂: 348.0369. Observed: 348.0356. No mass spectrum of HTT was observed by EI using a direct probe, by CI using ammonia, or by fast atom bombardment. Similar problems in observing fullerene mass spectra have been noted.¹⁵ The combination of low volatility and low base strength sometimes requires special conditions to observe the molecular ion. Under the most favorable conditions, no evidence of higher order mass fragments was found by mass spectral analysis.

The infrared spectrum of HTT shows a medium-strength nitrile stretching band at 2252 cm⁻¹. A very strong band at 1609 cm⁻¹

(11) Our investigations have shown that the iodination of 4,5-dicyanoimidazole in acidic or basic media using ICl gives 1-iodo-4,5-dicyanoimidazole in good yield. Thermal decomposition of 1-iodo-4,5-dicyanoimidazole gives **1c** via a 1,2-rearrangement reaction. See supplementary material for details. *N*-Haloimidazoles have been reported previously: (a) Grimmett, M. R. *Adv. Heterocycl. Chem.* **1970**, *12*, 703. (b) Grimmett, M. R. *Adv. Heterocycl. Chem.* **1980**, *27*, 241. (c) Katritzky, A. R.; Lagowski, J. M. *Comprehensive Heterocyclic Chemistry, Vol. 5*; Potts, K. T., Ed.; Pergamon Press: New York, 1984. (d) Grimmett, M. R. *Comprehensive Heterocyclic Chemistry, Vol. 5*; Potts, K. T., Ed.; Pergamon Press: New York, 1984. (e) Sheinker, V. N.; Tischenko, L. G.; Gaarnovskii, A. D.; Siminov, A. M. *J. Org. Chem. USSR (Engl. Transl.)* **1977**, *13*, 1872. (f) Maeda, K.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 2057.

(12) Addition of aqueous KI to **2a** gives a dark purple solution indicating I₂ formation. Decomposition of **2a** occurs in polar solvents, leading to I₂ formation and recovery of 2-chloro-4,5-dicyanoimidazole. The mass spectrum of **2a** shows fragments due to I₂⁺ (*m/z* 254, 96%), ICl₂⁺ (164, 162, 35.9%), I⁺ (127, 68.8%).

(13) **2b** was heated under N₂(g) as a neat solid in a typical sublimation apparatus equipped with a cold finger. Decomposition of **2b** occurs at 280-300 °C over 5 h. Purple crystals of IBr sublime onto the cold finger. HTT remains as an orange brown powder, which after washing with 10% aqueous Na₂S₂O₃ (3×) and H₂O followed by drying is recovered (70%).

(14) Anal. Calcd for (C₁₅N₁₂): C, 51.73; N, 48.27.

(15) (a) Hsu, C. S.; Cox, D. M.; Dechert, G. J. All Carbon Fullerenes Characterized By Mass Spectrometry. Proceedings of The 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, TN, May 19-24, 1991. (b) Callahan, J. H.; Mc Elvany, S. W.; Doyle, R. J.; Ross, M. M. Chemical Ionization Mass Spectrometry of Fullerenes, Proceedings of The 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, TN, May 19-24, 1991.

appears in HTT and corresponds to the C=N stretching band¹⁶ in the triazine ring. HTT has a λ_{max} of 302 nm in DMSO, which is nearly identical with reported values for azolo- and imidazotriazines¹⁷ and which is not observed for a single cyanoimidazole ring.⁷ The carbon-13 NMR data show five carbon resonances at 135.0, 123.2, 110.3, 106.5, and 106.2 ppm (relative to TMS in DMSO-*d*₆) corresponding to the five different carbons in the imidazotriazine repeat unit of HTT.

HTT is moderately soluble in polar aprotic solvents such as DMF and DMSO and in concentrated H₂SO₄.

HTT shows very high thermal stability. The thermal decomposition point of HTT is greater than 400 °C. The TGA of the HTT portion of the curve shows weight losses of 21% at 489 °C and 51% between 518 and 765 °C which could correspond to loss of (CN)₂ and N₂. Additional heating to 900 °C yields further weight loss. The unusually high nitrogen content material which forms in this temperature range is under further investigation. Qualitative flammability tests show that HTT and its thermal decomposition products possess remarkable kinetic resistance to combustion.

The mechanism proposed for the formation of HTT is believed to involve a benzyne-like intermediate based on the identification

(16) Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. *Spectral Data for Structure Determination of Organic Compounds*; Fresenius, W., Huber, J. F. K., Pungor, E., Rehnitz, G. A., Simon, W., West, Th. S., Eds.; Springer-Verlag: Berlin, 1989.

(17) (a) Anderson, K. E.; Pederson, E. B. *Liebigs Ann. Chem.* **1986**, 1012. (b) Sliskovic, D. R.; Siegel, M.; Lin, Y. *Synthesis* **1986**, 71. (c) Baig, G. U.; Stevens, M. F. G. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1, 1424.

of a 9,10-[1,2-(4,5-dicyanoimidazole)]-9,10-dihydroanthracene derivative from reactions using anthracene as a trapping agent.¹⁸ After thermally induced loss of halogen from **2a-c**, the diradical (or dipolar) intermediate in the absence of a diene undergoes a cyclization. No evidence of dimeric¹⁹ or other discrete oligomers was found in the reaction mixture.

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Supplementary Material Available: Experimental details for the synthesis of new 4,5-dicyanoimidazole derivatives (**1a-c**, **2a-c**) and the thermal decomposition reactions of **2a,b** and IR spectra, NMR spectra, and thermal analysis data of **2a** and HTT (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(18) Trapping studies with anthracene yielded the 9,10-[1,2-(4,5-dicyanoimidazole)]-9,10-dihydroanthracene product: ¹H NMR [200 MHz, (CD₃)₂CO, ppm] δ 8.98 (s, 1H), 8.58 (s, 1H), 8.29 (m, 2H), 7.69 (m, 4H), 7.55 (m, 2H); HRMS (EI with DCI probe) *m/z* calcd 294.0905, obsd 294.0886.

(19) Quenching studies of **2a** and **2b** with 4,5-dicyanoimidazole, 1-methyl-4,5-dicyanoimidazole, benzonitrile, and phthalonitrile failed to form dimeric materials or to indicate the reaction of nitrile functionality at the specified decomposition temperatures.