Synthesis, Characterization, and Thermolysis of C$_{15}$N$_{12}$

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Synthesis of 1-methyl-2-fluoro-4,5-dicyanoimidazole was done by halogen exchange between 1-methyl-2-bromo-4,5-dicyanoimidazole and potassium fluoride. Halogen exchange between 1-methyl-2-bromo-4,5-dicyanoimidazole and lithium chloride in *N*-methylpyrrolidinone at 150 °C yielded 1-methyl-2-chloro-4,5-dicyanoimidazole, and additional heating to 210 °C resulted in the demethylation to yield 2-chloro-4,5-dicyanoimidazole. Thermolyses of the 2-halo-4,5-dicyanoimidazole derivatives (F, Cl) and 1-iodo-2-halo-4,5-dicyanoimidazole derivatives (Cl, Br, I) between 100 and 290 °C were found to yield Tris(imidazo)[1,2-*a*:1,2-*c*:1,2-*e*]-1,3,5-triazine-2,3,5,6,8,9-hexacarbonitrile, or HTT, with (C$_5$N$_4$)$_3$ composition. HTT has been characterized and purified and the crystal structure obtained. Thermolysis of HTT at 490−500 °C gives a material with C/N = 1.020. The thermal properties of HTT and its decomposition products show thermal stability to 350 °C.

Introduction

Strategies that have been used to prepare thermally stable materials with low flammability are as follows: (1) incorporation of halogen or phosphorus, (2) increasing the carbon to hydrogen ratio, (3) increasing the nitrogen content, (4) incorporation of conjugation through aromatic or heteroaromatic ring systems, (5) incorporation of rigid structures into the material (semiladder or ladder polymers), (6) incorporation of strong interactions between polymer chains, and (7) incorporation of a high degree of crystallinity or cross-linking.[1] The following discussion will consider systems that employ strategies 2−7.

Heterocyclic rings and semiladder type structures are common in polymers that exhibit enhanced thermal stability.[2] The flammability is depressed by increasing the carbon to hydrogen ratio, and thermal stability is enhanced by the fused heteroaromatic ring systems.

Comparison of the oxygen index (OI)[3] values to the weight percent of nitrogen in nitrogen-containing materials shows that the flammability also goes down (OI value goes up) as the weight percent of nitrogen increases.[4] Nitrogen-containing polymers such as Nomex, Kapton, and polybenzimidazole have high OI values. The comparison of the OI value of a polymer to its carbon/hydrogen ratio indicates that as the carbon to hydrogen ratio goes up (hydrogen content decreases) the flammability goes down (OI values go up).[5] By making use of these trends in oxygen index data, we have prepared materials with high nitrogen and no hydrogen content to obtain thermally stable materials with low flammability. Here, we describe the synthesis and characterization of a new composition of carbon and nitrogen only that is prepared by thermolysis of 2-halo-4,5-dicyanoimidazole derivatives functionalized with −H and −I as leaving groups at the 1-position. The thermal stability of the new composition and studies on its thermolysis products are reported.

Results and Discussion

Previously, we have used 1-methyl-2-bromo-4,5-dicyanoimidazole to accomplish nucleophilic aromatic substitution reactions with a variety of amines and other moderately strong nucleophiles.[6] However, the 2-bromo derivative failed to react with weak nucleophiles. To attain enhanced reactivity at the 2-position of 4,5-dicyanoimidazoles the 2-fluoro and 2-chloro derivatives were synthesized.

Examples of imidazole chlorination via the Sandmeyer reaction are known.[7] Much of the diazo chemistry done previously on 4,5-dicyanoimidazoles has been on 2-amino-4,5-dicyanoimidazole for which a zwitterionic internal salt precipitates after diazotization.[8] In order to avoid the isolation of this zwitterion, we performed the Sandmeyer reaction on 1-methyl-2-amino-4,5-dicyanoimidazole, and the resulting diazo derivative is soluble. The diazotization is accomplished by treating the amine hydrochloride with sodium nitrite, and subsequent treatment of the diazo intermediate with cuprous chloride yields 1-methyl-2-chloro-4,5-dicyanoimidazole as well as hydrolyzed 1-methyl-2-chloro-4,5-dicyanoimidazole.

Application of the Schiemann reaction[9] to the diazonium salt of 1-methyl-2-amino-4,5-dicyanoimidazole led to 1-methyl-2-fluoro-4,5-dicyanoimidazole as well as nitrile hydrolysis products. Fluorination by this route was not pursued further due to the hydrolysis.

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(3) The oxygen index value provides a relative measure of the flammability of a substance, where the OI value is equal to 100 times the ratio of oxygen to the total amount of gas in the atmosphere required to sustain combustion.

(4) For comparison of the oxygen index values to the weight percent of nitrogen in nitrogen-containing materials see: Cullis, C. F; Hirschler, M. M. *The Combustion of Organic Polymers*; , Oxford University Press: New York, 1981; pp 49, 53−54, 254−255.
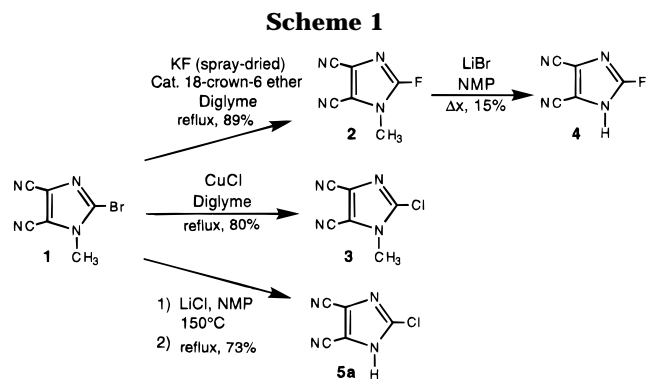
(5) For comparison of oxygen index values to the carbon to hydrogen ratios of polymeric materials see: Brydson, J. A. In *Developments in Plastics Technology-4*; Whelan, A., Goff, J. P., Eds.; Elsevier Science Publishers Ltd.: New York, 1989; pp 178−179.

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(9) Roe, A. In *Organic Reactions*; Bachmann, W. E., Blatt, A. H., Eds.; John Wiley & Sons, Inc.: New York, 1949; Vol. V, pp 193−226.

Scheme 1

Figure 1. TGA of 1-iodo-2-chloro-4,5-dicyanoimidazole (**6a**) under N_2.

Scheme 2

Scheme 3

Compound		Dec. Temp.
4:	X=H, Y=F,	120–140°C
5a:	X=H, Y=Cl,	200–220°C
6a:	X=I, Y=Cl,	220–240°C
6b:	X=I, Y=Br,	280–300°C
6c:	X=I, Y=I,	280–300°C

Fluorination of aryl bromides has been accomplished by transhalogenation.[10] The 1-methyl-2-bromo-4,5-dicyanoimidazole (**1**) was fluorinated using potassium fluoride and a catalytic amount of 18-crown-6 ether in diglyme (Scheme 1).

Transhalogenation reactions have been used successfully to chlorinate aryl bromides.[11] The chlorination of 1-methyl-2-bromo-4,5-dicyanoimidazole (**1**) was accomplished by transhalogenation with cuprous chloride in diglyme (Scheme 1).

We have dealkylated imidazole substrates with lithium chloride in NMP.[12] However, attempts at dealkylation of 1-methyl-2-fluoro-4,5-dicyanoimidazole (**2**) with lithium chloride resulted in transhalogenation. The dealkylation was carried out using lithium bromide in NMP at reflux (Scheme 1); however, difficulties in isolation kept the yields low.

In the dealkylation of 1-methyl-2-bromo-4,5-dicyanoimidazole (**1**) with lithium chloride in NMP, the starting material first undergoes transhalogenation when heated at 150 °C for a few hours to form 1-methyl-2-chloro-4,5-dicyanoimidazole (Scheme 1). Additional heating at reflux leads to dealkylation and the formation of 2-chloro-4,5-dicyanoimidazole (**5a**).

Iodination of 2-halo-4,5-dicyanoimidazoles **5a**−**c** with ICl in aqueous base gives the 1-iodo-2-halo derivatives **6a**−**c** (Scheme 2).[13] These novel, but simple compounds contain no hydrogen and were viewed as precursors to a carbon nitrogen material. The lability of the N−I and C−Cl bond of **6a** is apparent from the TGA of **6a** (Figure 1, under N_2 (g), heating rate = 5 °C/min), which shows a weight loss corresponding to loss of ICl.

Preparation of the 1-bromo- 2-bromo-4,5-dicyanoimidazole was also attempted using 1 equiv of base followed
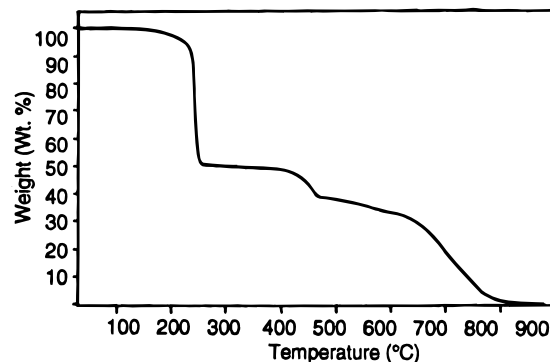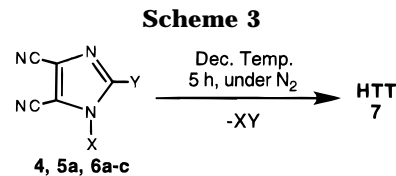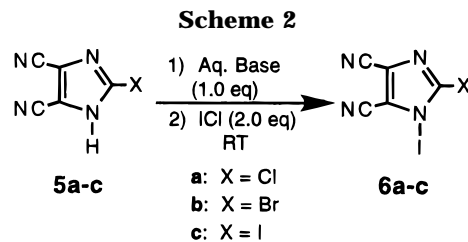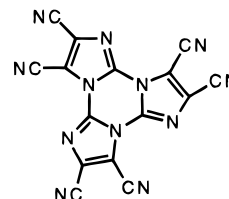
by the addition of bromine. The procedure was very sensitive to the quantity of base present, and yields varied significantly from run to run. The lack of reproducibility was also in agreement with the expected high reactivity of this bond.

The derivatives of 4,5-dicyanoimidazole, functionalized with good leaving groups at the 1- and 2-positions, were examined by thermal gravimetric analysis (TGA) to determine their thermolysis temperatures (Scheme 3). In each case the priamry product was Tris(imidazo)[1, 2-*a*:1, 2-*c*:1,2-*e*]-1,3,5-triazine-2,3,5,6,8,9-hexacarbonitrile or Hexacarbonitrile Tris (imidazo)...Triazine (HTT) of composition $C_{15}N_{12}$(**7**). While all of the derivatives in Scheme 3 thermolyzed to form HTT (**7**), the starting materials with lowest thermolysis temperatures minimized the side reactions which occur at higher temperatures.

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(13) 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 **5c** via a 1,2-rearrangement reaction. See supplementary material for details. *N*-Haloimidazoles have been reported previously: (a) Grimmett, M. R. *Adv. Heterocyclic Chem.* **1970**, *12*, 703. (b) Grimmett, M. R. *Adv. Heterocycl. Chem.* **1980**, *27*, 241. (c) Katritzky, A. R.; Lagowski, J. M. In *Comprehensive Heterocycl. Chemistry*; Potts, K. T., Ed.; Permagon Press: New York, 1984; Vol. 5. (d) Grimmett, M. R. *Comprehensive Heterocyclic Chemistry*; Potts, K. T., Ed.; Permagon Press: New York, 1984; Vol. 5. (e) Sheinker, V. N.; Tischenko, L. G.; Gaarnovskii, A. D.; Siminov, A. M. *J. Org. Chem. USSR (Engl. Trans.)* **1977**, *13*, 1872. (f) Maeda, K.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 2057.

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

Hexacarbonitrile Tris(imidazo)...Triazine

HTT

Although compounds **6b** and **6c** were the most easily synthesized, they have the higher thermolysis temperatures (280–300 °C). Compounds **4** and **5a** have lower thermolysis temperatures (120–140 and 200–220 °C), but they sublime readily, making it difficult to get complete reaction. Thus, compound **6a** was chosen as the best compromise due to its thermolysis temperature (220–240 °C) and low tendency to sublime.

As noted above, compounds **4**, **5a**, and **6a**–**c** undergo thermolysis to form HTT (**7**). Several products could result from the simultaneous loss of leaving groups from compounds **4**, **5a**, and **6a**–**c**. In addition to HTT, chains could form or the nitriles of the 1,2-bifunctionalized monomer could participate in forming crosslinks. Cyclic structures similar to HTT have been prepared by thermolysis of 2-fluoroimidazole,[14] 2-chlorobenzimidazole,[15] and 2-(methylthio)-4,5-diphenylimidazole.[16] Preparation of the cross-linked structure also might be favorable under conditions that lead to phthalocyanine from phthalonitrile. These reactions normally occur at temperatures greater than 300 °C. The cross-linked-type structure has been prepared by decomposition of 2-diazo-4,5-dicyanoimidazole in benzonitrile.[17]

The TGA data of compound **6a** (Figure 1) indicates a weight loss of 51% corresponding to the loss of ICl by 243 °C leading to the formation of HTT (**7**). The weight losses of 11% between 243 and 456 °C and 6% between 456 and 606 °C correspond to the loss of $(CN)_2$ and N_2 and to the formation of carbon–nitrogen (C–N) materials. Heating to 900 °C yields complete weight loss. The compound **6a** was thermolyzed at 220–240 °C for 5 h under nitrogen yielding 70% HTT (**7**) (Scheme 3). The trimer material, $C_{15}N_{12}$, prepared from **6b** gives the following analysis: C, 51.48; N, 47.45; H, 0.39; I, 0.00; Br, 0.12; O, 0.56 (by difference).[18]

The mass spectrum of HTT (**7**) was observed 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 (**7**) yielded HRMS (EI with DCI probe) calcd for $C_{15}N_{12}$ 348.0369, obsd 348.0356. No mass spectrum of HTT (**7**) was observed by direct probe, by CI using ammonia, or by fast atom bombardment. Similar problems in observing fullerene mass spectra have been noted.[19] The low volatility and low base strength requires special conditions to observe the molecular ion. Under the most favorable conditions no evidence of higher mass fragments were found.

The carbon-13 NMR shows 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 (**7**). The assignments shown in Figure 2 are based on com-
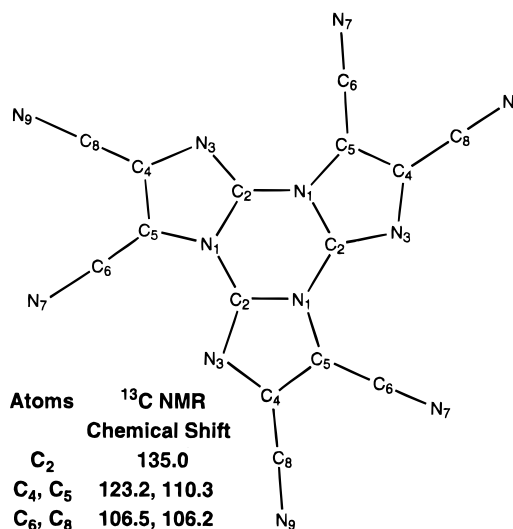
(14) (a) Kirk, K. L.; Nagi, W.; Cohen, L. A. *J. Am. Chem. Soc.* **1973**, *95*, 8389. (b) Takeuchi, Y.; Kirk, K. L.; Cohen, L. A. *J. Org. Chem.* **1979**, *44*, 4243.

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(18) Anal. Calcd for ($C_{15}N_{12}$): C, 51.73; N, 48.27.

(19) (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.

Atoms	^{13}C NMR Chemical Shift
C_2	135.0
C_4, C_5	123.2, 110.3
C_6, C_8	106.5, 106.2

Figure 2. Assignment of ^{13}C NMR chemical shifts of HTT (**7**).
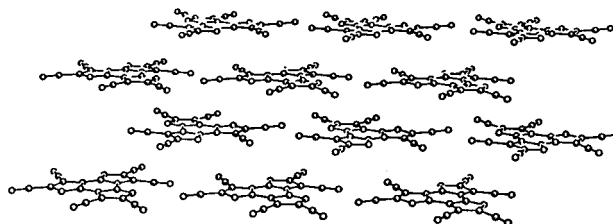

Figure 3. Side view perspective of stacks A and B from the packing diagram of HTT (**7**) while omitting perpendicular stacks.
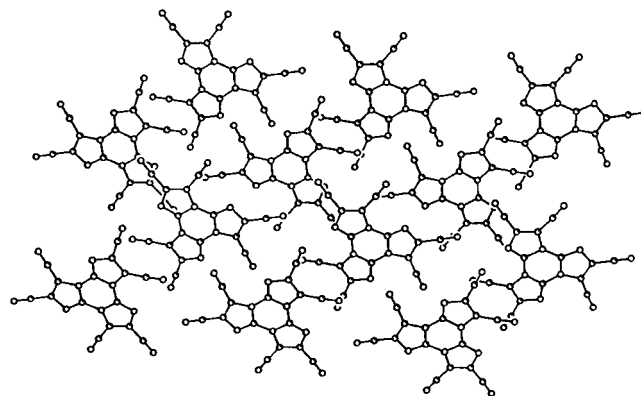

Figure 4. Top view perspective of stacks A and B from the packing diagram of HTT (**7**) while omitting perpendicular stacks.

parison to examples of other 4,5-dicyanoimidazole containing compounds.

The nitrogen-15 NMR spectrum shows four nitrogen resonances at 289.2, 276.9, 233.7, and 161.3 ppm (in DMSO-d_6 relative to nitromethane as an external standard) corresponding to the four different nitrogens in the imidazotriazine repeat unit of HTT (**7**).

The X-ray crystal structure of HTT (**7**) was solved in the monoclinic system of the $P2_1/n$(#14) space group. Details are on file with the Cambridge Crystallographic Data Centre.[26] Figures 3 and 4 show the side and top view perspectives of stacks A and B from the packing diagram of HTT (**7**) while omitting perpendicular stacks. Figures 3 and 4 show the strongly slipped stacks and that the HTT (**7**) units do not align directly over one another.

Figure 5. Cyclic voltammogram of HTT (**7**).

Figure 6. TGA of HTT (**7**) under nitrogen and air.

21% at 489 °C and 51% between 518−765 °C, which corresponds to loss of $(CN)_2$, N_2, and the formation of carbon nitrogen materials. Heating to 900 °C yields complete weight loss. Comparison of Figures 1 and 6 show that the thermal transitions of HTT (**7**) are also represented in Figure 1. In addition, examination of the flammability properties of HTT (**7**) and its decomposition products demonstrates a high resistance to combustion. The differential scanning calorigram of HTT (**7**) has a transition at 472 °C, which corresponds to the decomposition at 490−500 °C seen in the TGA of HTT (**7**) under nitrogen (Figure 6).

Thermolysis of HTT (**7**) in a quartz tube under N_2 at 490−500 °C for 1−2 h produced a carbon-nitrogen material (Scheme 5). Analysis of the gases evolved from the

Scheme 4

Scheme 5
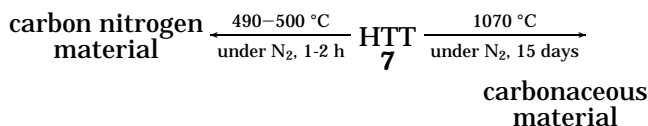
reaction confirmed the loss of $(CN)_2$. The IR spectra show a change in the nitrile stretch from 2252 to 2221 cm^{-1} as well as significant broadening. Elemental analysis yielded the following weight percentages (two determinations): C, 46.40, 46.40; H, 1.04, 0.99; N, 45.54, 45.47; O, 7.02, 7.14 (by difference) with average C/N = 1.020. Details of the thermal behavior of the C/N material and carbonaceous material are given in the supporting information.

Conclusions

The thermolyses of 2-halo-4,5-dicyanoimidazoles functionalized with −H and −I as leaving groups at the 1-position were investigated. Thermolysis of these compounds yields the novel cyclic trimer HTT (**7**) with $(C_5N_4)_3$ composition. Thermolysis of HTT (**7**) at 490−500 °C results in a material with C/N = 1.020, whereas the thermolysis at 1070 °C results in a carbonaceous material.

The chemistry we have described starts from diaminomaleonitrile, a simple tetramer of HCN, and in just a few steps provides HTT of formula $C_{15}N_{12}$. This rapid increase in molecular complexity provides a convenient entry to C/N materials by thermolysis and can provide novel precursors for other synthetic purposes. In addition, HTT can be incorporated into more complex structures. These possibilities are under investigation.

To identify potential reactive intermediates the thermolysis of **6a** was carried out in the presence of anthracene. Thermolysis in the presence of anthracene gave 9,10-[1,2-(4,5-dicyanoimidazo)]-9,10-dihydroanthracene (**8**) (Scheme 4). The synthesis of **8** suggests a benzyne-like intermediate.[20] Anthracene is one of the few trapping agents that remains in the reaction mixture at the temperatures 220−235 °C required to decompose **6a**.

Alkylation of HTT (**7**) was attempted with methyl iodide, dimethyl sulfate, and methyl *p*-toluenesulfonate using either acetone-d_6, acetonitrile-d_3, DMSO-d_6, or DMF-d_7 as the solvent at reaction temperatures of 27 or 100 °C for 24 h. The progress of the reaction was monitored by ^{1}H NMR and ^{13}C NMR. The reaction mixtures were compared to blanks of the indicated solvent and alkylating agent under the same reaction conditions. In most cases it was found that the alkylating agent had reacted with solvent.

The cyclic voltammetry of HTT (**7**) (Figure 5) shows three quasireversible reduction potentials at −1.45, −2.16, and −2.51 V relative to Ag/Ag$^+$. Reversing the scans at intermermediate stages of reduction did not alter the irreversibility. These results are in accord with calculations[21] that suggest that the LUMO is doubly degenerate and up to three-electron reduction may be possible.

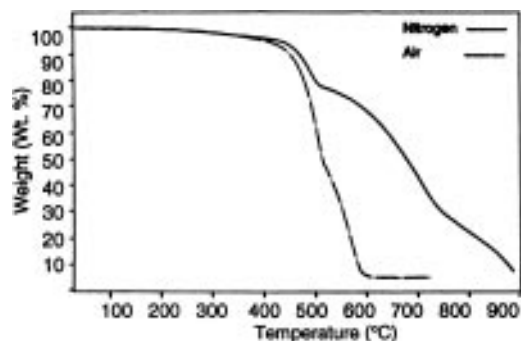The TGA of HTT (**7**) (Figure 6) shows weight losses of

(20) (a) Fields, E. K. In *Organic Reactive Intermediates*; McManus, S. P., Ed.; Academic Press: New York, 1973; pp 449−504. (b) Reinecke, M. G. in *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982; pp 367−510.

(21) We are grateful to M.-H. Whangbo and Weigen Liang, Department of Chemistry, North Carolina State University, for carrying out MNDO calculations for us.

Experimental Section

General Procedures. Melting points are uncorrected. Thin layer chromatography was done on Eastman Kodak silica gel sheets containing fluorescent indicator. Column chromatography was done using 220–400 mesh silica gel from Aldrich.

The 4,5-dicyanoimidazole was obtained from Nippon Soda Co., Ltd., recrystallized from H_2O, and dried prior to use. The 2-bromo-4,5-dicyanoimidazole (**5b**) and 1-methyl-2-bromo-4,5-dicyanoimidazole (**1**) were prepared as previously reported.[22] Solvents were purified and distilled under nitrogen prior to use. THF was distilled from sodium benzophenone ketyl. Acetonitrile was distilled from CaH_2. DMSO and triethylamine were distilled from BaO. DMAC and NMP were distilled from BaO or from phthalic anhydride.

For cyclic voltammetry, acetonitrile (HPLC grade) was distilled immediately prior to use. Et_4NBF_4 (99%, Aldrich) was recrystallized twice from freshly distilled acetonitrile and dried under vacuum prior to use. The electrolyte solution was 0.1 M Et_4NBF_4 in acetonitrile. Samples were 0.003–0.005 M in electrolyte solution. The reference solution was 0.010 M $AgNO_3$ in electrolyte solution. All solvents were degassed prior to use. Working/reference electrodes were platinum wires; the counter electrode was platinum foil.

1-Methyl-2-chloro-4,5-dicyanoimidazole (3). In a drybox, 10.00 g (47.0 mmol) of 1-methyl-2-bromo-4,5-dicyanoimidazole (**1**), 11.67 g (118.0 mmol) of CuCl, and 100 mL of freshly distilled diglyme were placed in a 250 mL round-bottomed flask equipped with magnetic stirrer, N_2 inlet, and reflux condenser. The mixture was heated at reflux for 24 h. The brown mixture was cooled to room temperature, the solution filtered off, and the brown residue (CuBr, CuCl) was washed with CH_2Cl_2 (3 × 100 mL). The CH_2Cl_2 was removed under vacuum, and the diglyme solution was added. The diglyme was removed under vacuum, producing yellow-brown crystals. The yellow-brown crystals were dissolved in absolute ethanol, treated with carbon, and recrystallized twice in absolute ethanol yielding 2.97 g (38%) of product **3**. The white solid: TLC EtOAc R_f 0.66; mp 114–116 °C; IR (KBr) 2243, 1473, 1423, 1318, 1214, 1133, 1121 cm^{-1}; UV–vis (CH_3CN) $\lambda_{max}(\epsilon)$ 256 (9241); ^{1}H NMR (200.1 MHz, $CDCl_3$, ppm) δ 3.81 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 138.6, 121.5, 114.2, 110.7, 107.3, 33.9; MS (E/I) m/z (relative intensity) 168 (M + 2, 41.4), 166 (M$^+$, 100.0), 151 (1.4), 131 (15.4), 125 (34.0); HRMS (EI with DCI probe) m/z calcd for $C_5H_3N_4^{35}Cl$ 166.0046, obsd 166.0044. Anal. Calcd for $C_6H_3N_4Cl$: C, 43.26; H, 1.82; N, 33.64. Found: C, 42.94; H, 1.51; N, 33.40.

1-Methyl-2-fluoro-4,5-dicyanoimidazole (2). In a drybox, the indicated quantity of 1-methyl-2-bromo-4,5-dicyanoimidazole (**1**), 1.25 equiv of spray-dried potassium fluoride, a catalytic amount of 18-crown-6 ether, and approximately 25 mL of freshly distilled diglyme per 20 g of 1-methyl-2-bromo-4,5-dicyanoimidazole (**1**) were placed in a round-bottomed flask equipped with magnetic stirrer, N_2 inlet, and reflux condenser. The mixture was heated at reflux 24 h, after which time the mixture was yellow-brown with a white salt precipitate (KBr/KF). The yellow-brown liquid was decanted from the salt, and the salt was washed with acetone (3 × 150 mL). The decanted liquid and acetone washes were combined. The acetone was removed under vacuum, and the diglyme was distilled off at 50–60 °C under reduced pressure. Purification details follow.

The reaction was carried out using 80.0 g (377.0 mmol) of 1-methyl-2-bromo-4,5-dicyanoimidazole (**1**). The resulting brown oil produced after workup was vacuum distilled twice, bp 95–110 °C at 0.02–0.03 mm yielding 50.0 g (89%) of product **2**. The white solid: TLC EtOAc R_f 0.64; mp 46–48 °C; IR (KBr) 2243, 1595, 1512, 1411, 1174 cm^{-1}; UV–vis (CH_3CN) $\lambda_{max}(\epsilon)$ 250 (12 120); ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm) δ 3.73 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 150.0 (d, J = 252.1 Hz), 117.3 (d, J = 12.7 Hz), 110.7, 110.4 (d, J = 3.9 Hz), 107.0, 31.4; MS (E/I) m/z (relative intensity) 151 (M + 1, 8), 150 (M$^+$, 100), 149 (20), 135 (2), 122 (5), 109 (5); HRMS (EI with DCI probe) m/z calcd for $C_6H_3N_4F$ 150.0342, obsd

(22) Apen, P. G.; Rasmussen, P. G. *Heterocycles* **1989**, *29*, 1325.

150.0338. Anal. Calcd for $C_6H_3N_4F$: C, 48.02; H, 2.00; N, 37.32. Found: C, 47.96; H, 1.85; N, 37.15.

2-Chloro-4,5-dicyanoimidazole (5a). In a drybox, 20.0 g (.094 mol) of 1-methyl-2-bromo-4,5-dicyanoimidazole (**1**), 40.0 g (.943 mol) of LiCl, and 200 mL of previously distilled NMP were placed in a 500 mL round-bottomed flask equipped with magnetic stir, N_2 inlet, and reflux condenser. The mixture was heated at 160–165 °C for 24 h and then at reflux for 2 h. The NMP was distilled from the reaction mixture under vacuum. The resulting lithium salt was dried in a vacuum oven overnight at 100 °C. The dried salt was boiled in 600 mL of $CHCl_3$, filtered, and dried. The salt was dissolved in 100 mL of 10% HCl and extracted with ethyl acetate (3 × 100 mL). The organic layers were combined and dried with Na_2SO_4 and the ethyl acetate removed under vacuum. The resulting off-white solid **5a** was recrystallized twice with H_2O, producing 10.4 g (72%) of product. The white solid **5a**: TLC 5/1 EtOAc/ MeOH R_f 0.82; mp 144–146 °C; IR (KBr) 2247, 1573, 1493, 1419, 1409, 1360, 1293, 1249, 1006 cm^{-1}; UV–vis (CH_3CN) λ_{max} (ϵ) 253 (9697); ^{1}H NMR (200 MHz, $(CD_3)_2CO$, ppm) δ 9.61 (br s, 1H); ^{13}C NMR (50 MHz, $(CD_3)_2SO$, ppm) δ 137.5, 116.5, 110.7; MS (EI with DCI probe) m/z (relative intensity) 154 (M + 2, 33.7), 152 (M$^+$, 100.0), 127 (18.0), 125 (50.5); HRMS (EI with DCI probe) m/z calcd for $C_5HN_4^{35}Cl$ 151.9890, obsd 151.9893. Anal. Calcd for C_5HN_4Cl: C, 39.38; H, 0.66; N, 36.72. Found: C, 39.10; H, 0.56; N, 36.46.

2-Fluoro-4,5-dicyanoimidazole (4). In a drybox, 4.0 g (27.0 mmol) of 1-methyl-2-fluoro-4,5-dicyanoimidazole (**2**), 2.9 g (33.0 mmol) of LiBr, and 200 mL of previously distilled NMP were placed in a 250 mL round-bottomed flask equipped with magnetic stirrer, N_2 inlet, and reflux condenser. The mixture was heated at reflux 18 h and then cooled. The NMP was distilled from the reaction mixture under vacuum. The resulting lithium salt was boiled with 600 mL of $CHCl_3$ and filtered. The salt was dissolved in 20 mL 10% HCl and extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and dried with Na_2SO_4, and the ethyl acetate was removed under vacuum. The resulting off-white solid was recrystallized twice with H_2O yielding 0.53 g (15%) of product **4**. The off-white solid: TLC 5/1 EtOAc/MeOH R_f 0.92; mp 141–143 °C; IR (KBr) 2250, 1611, 1590, 1551, 1488, 1472, 1312, 1290, 1072 cm^{-1}; UV–vis (CH_3CN) λ_{max} (ϵ) 247 (11 196); ^{1}H NMR (200.1 MHz, $(CD_3)_2CO$, ppm) δ 10.27 (br s, 1H); ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$, ppm) δ 151.5 (d, J = 248.9 Hz), 113.6 (d, J = 4.5 Hz), 110.4; MS (EI with DCI probe) m/z (relative intensity) 253 (19.4), 252 (100.0), 201 (8.6), 200 (49.9), 155 (10.5), 137 (M + 1, 5.8), 136 (M$^+$, 39.7), 121 (4.5), 109 (15.8); HRMS (EI with DCI probe) m/z (M$^+$) calcd for $C_5H_1N_4F$ 136.0185, obsd 136.0185.

1-Iodo-4,5-dicyanoimidazole derivatives. General Procedure. The appropriate 1H-4,5-dicyanoimidazole (1 equiv, 1–2 g, 10–12 mmol) was dissolved in 1.0 equiv NaOH (aq) or KOH (aq) (75 mL). ICl (1–1.2 equiv) was added and the slurry stirred at room temperature. A solid precipitated from the mixture after 30 min and was collected and rinsed with H_2O (100 mL) and then Et_2O (500 mL). The product was dried, giving an off-white powder . Note: Control of stoichiometry is essential! Excess OH$^-$ can react with ICl to give OI$^-$ + Cl$^-$ + H_2O. As a result, the iodinating agent is effectively destroyed and none of the desired product can be isolated. Excess OH$^-$ can also react with the product, giving HOI and the salt of the starting material.

1-Iodo-2-chloro-4,5-dicyanoimidazole (6a). Off-white powder **6a** (2.0 g, 73%): mp ~235 °C off-white solid emitted yellow-brown gas, ~250 °C sample decomposed more strongly turning brown, brown solid which formed had mp > 400 °C; IR (KBr) 2243, 1393, 1377, 1370, 1358, 1340, 1147 cm^{-1}; ^{13}C NMR (50.3 MHz, $(CD_3)_2SO$; ppm) δ 142.4, 119.5, 111.5; MS (EI with DCI probe) m/z (relative intensity) 280 (M + 2, 1.8), 278 (M$^+$, 5.4), 254 (I$_2^+$, 96.0), 164 (ICl$^+$, 15.5), 162 (ICl$^+$, 35.9), 154 (36.2), 152 (100), 127 (I$^+$, 68.8); HRMS (EI with DCI probe) m/z calcd for $C_5N_4I^{35}Cl$ 277.8856, obsd 277.8855.

1-Iodo-2-bromo-4,5-dicyanoimidazole (6b). Off-white powder **6b** (3.420 g, 83%): mp > 240 °C (turns yellow-brown), 290–300 °C (dec w/dark purple gas evolution); UV–vis (CH_3-CN) λ_{max} 272 nm; IR (KBr) 2245, 1386, 1365, 1356, 1327, 1288

cm^{-1}; MS (EI) *m/z* (relative intensity) 324 (M + 2, 13), 322 (M$^+$, 13), 254 (I$_2^+$, 89), 208 (IBr$^+$, 13), 206 (IBr$^+$, 14), 198 (75), 196 (81), 171 (25), 169 (26), 127 (I$^+$, 100), 117 (30), 108 (7), 106 (7), 93 (33), 91 (40). Anal. Calcd for C$_5$N$_4$IBr: C, 18.60; H, 0.00; N, 17.36. Found: C, 18.60; H, 0.00; N, 17.60.

1-Bromo-2-bromo-4,5-dicyanoimidazole. In a 50 mL beaker were placed 1.0 g (4.0 mmol) of the potassium salt of 2-bromo-4,5-dicyanoimidazole (**5b**) and 25 mL of H$_2$O. The contents were dissolved with stirring, and 0.44 mL (9.0 mmol) of Br$_2$ was added. The mixture thickened into an orange solution with a white precipitate. An additional 25 mL of H$_2$O was added, and the mixture was stirred overnight. The solid was filtered off and washed well with H$_2$O. The off-white solid was dried, producing 0.61 g (52%) of 1-bromo-2-bromo-4,5-dicyanoimidazole. The off-white powder: TLC decomposes; mp 175−180 °C orange gas was given off and solid turned yellow-brown, 180−200 °C; IR (KBr) 2242, 1386, 1368, 1341, 1305, 1278, 1147, 1135, 661, 549 cm^{-1}; MS (EI with DCI probe) *m/z* (relative intensity) 278 (31.2), 276 (50.4), 274 (31.4), 226 (12.6), 224 (24.0), 222 (13.8), 198 (98.4), 197 (100.0), 196 (97.7), 195 (96.1), 171 (36.4), 169 (40.3), 162 (44.9), 160 (76.0), 158 (46.8), 145 (23.1), 143 (23.7); HRMS (EI with DCI probe) *m/z* calcd for C$_5$N$_4$^{79}Br$_2$ 275.8469, obsd 275.8468.

Synthesis of Tris(imidazo)[1,2-*a*:1,2-*c*:1,2-*e*]-1,3,5-triazine-2,3,5,6,8,9-hexacarbonitrile (HTT) (7). Thermal dehydrohalogenation of 2-Fluoro-4,5-dicyanoimidazole (4). Attempted sublimation of crude 2-fluoro-4,5-dicyanoimidazole (**4**) under vacuum while gradually raising the temperature from rt to 250 °C over 6 h produced a black solid. The black solid was impure HTT (**7**): mp > 400 °C; IR (KBr) 2243, 1764, 1610, 1567, 1539, 1483, 1445, 1398, 1383, 1358, 1296, 1207, 702, 498 cm^{-1}; ^{1}H NMR (300.1 MHz, (CD$_3$)$_2$SO, ppm) δ 5.57 (br s); ^{13}C NMR (75.5 MHz, (CD$_3$)$_2$SO, ppm) δ 134.9, 123.2, 113.9, 110.1, 106.5, 106.0; MS (EI/w DCI probe) *m/z* 350 (4.7), 349 (28.0), 348 (M$^+$, 100.0), 264 (24.2), 244 (6.9), 198 (8.1), 196 (7.7), 154 (12.7), 136 (14.5).

Thermal Dehydrohalogenation of 2-Chloro-4,5-dicyanoimidazole (5a). In a small sublimation apparatus at rt was placed 0.59 g (4.0 mmol) of 2-chloro-4,5-dicyanoimidazole (**5a**). The apparatus was evacuated and back-filled with N$_2$ (3×). The sample was heated under N$_2$ from rt to 300 °C over 1 h. At 240 °C, a white gas (HCl) evolved. Upon evolution of HCl, the material in the apparatus darkened and a yellow-white solid formed on the cold finger. Heating at 300 °C was continued for 3 h. The 0.087 g of yellow-white sublimate appears to be a mixture of 2-chloro-4,5-dicyanoimidazole (**5a**) and 2-chloro-4,5-dicyanoimidazole with hydrolyzed nitriles: mp 238−254 °C; IR (KBr) 3435, 3400−2500 (H-bonding), 2247, 1685, 1622, 1601, 1571, 1514, 1491, 1418 cm^{-1}; MS (EI/w DCI probe) *m/z* 234 (4.5), 232 (4.8), 216 (12.1), 214 (11.8), 198 (8.2), 196 (3.8), 190 (12.1), 188 (30.5), 172 (35.6), 170 (100.0), 155 (24.4), 154 (61.1), 153 (56.5), 152 (25.9), 127 (35.1). The 0.271 g of a shiny black solid was impure HTT (**7**).

Thermal Dehalogenation Reactions of 1-Iodo-2-halo-4,5-dicyanoimidazoles. General Procedure. The 1-iodo-2-halo-4,5-dicyanoimidazole was placed in a sublimation apparatus preadjusted to produce the decomposition temperature (220−240 °C for 1-iodo-2-chloro-4,5-dicyanoimidazole (**6a**), 280−300 °C for 1-iodo-2-bromo-4,5-dicyanoimidazole (**6b**)). The apparatus was evacuated and back-filled with N$_2$ (3×) prior to starting the reaction. During heating, 5 h, the halogen decomposition components (I$_2$ and ICl or I$_2$ and IBr) condensed on the cold finger. On cooling to rt, the apparatus was evacuated and filled with N$_2$. Negligible sublimate was noted. In scale-up reactions, the sublimate was found to be the appropriate 2-halo-4,5-dicyanoimidazole. The brown solid isolated was impure HTT (**7**). The impure product was ground to a fine powder. The powder was suspended in a 10% solution of Na$_2$S$_2$O$_3$ (40mL) and stirred at room temperature for 30 min. The brown solid was spun down on a centrifuge and the aqueous solution decanted. The Na$_2$S$_2$O$_3$ treatment was repeated twice more. The solid was washed with water (3 × 40 mL) using the centrifuge treatment above. After removal of the aqueous solution, the solid was dried under vacuum.

Thermal Dehalogenation of 1-Iodo-2-chloro-4,5-dicyanoimidazole (6a). The reaction was carried out using 10.0 g (36.0 mmol) of 1-iodo-2-chloro-4,5-dicyanoimidazole (**6a**). The tan solid **was** 2.92 g (70%) of HTT (**7**).

Thermal Dehalogenation of 1-Iodo-2-bromo-4,5-dicyanoimidazole (6b). The reaction was carried out using 10.0 g (31.0 mmol) of 1-iodo-2-bromo-4,5-dicyanoimidazole (**6b**). The brown solid was HTT (**7**): mp > 400 °C; IR (KBr) 2251, 1610, 1570, 1538, 1472, 1443, 1401, 1357, 1295, 1206, 702 cm^{-1}; ^{13}C NMR (75.5 MHz, (CD$_3$)$_2$SO, ppm) δ 135.1, 123.4, 110.4, 106.8, 106.4; MS (EI with DCI probe) *m/z* (relative intensity) 350 (M + 2, 4.3), 349 (M + 1, 24.4), 348 (M$^+$, 100.0) 284 (4.0), 254 (50.0), 198 (5.3), 196 (5.6), 174 (5.4), 154 (10.3), 128 (17.0), 98 (20.5); An pure sample was prepared by dissolving HTT (**7**) in 500 mL of a 4/1 mixture of acetone/ethanol, and the solution was filtered and concentrated to a volume of 50 mL. The cream colored material that formed was filtered and dried (1.15 g, 32% yield). The infrared spectrum of HTT (**7**) shows a medium strength nitrile stretching band at 2252 cm^{-1}. A very strong band at 1609 cm^{-1} corresponds to the C=N stretching band[23] in the triazine ring. In the UV−vis spectrum, HTT (**7**) has a λ$_{max}$ of 302 nm in DMSO, which is nearly identical with reported values for azolo- and imidazotriazines[24] and which is not observed for a single cyanoimidazole ring.[25]

Anal. Calcd for C$_{15}$N$_{12}$: C, 51.73; H, 0.00; N, 48.27. Found: C, 51.48; H, 0.39; N, 47.45; Br, 0.12; I, 0.00; O, 0.56 (by difference).

Thermolysis of 1-Iodo-2-chloro-4,5-dicyanoimidazole in the Presence of Anthracene. Synthesis of 9,10-[1,2-(4,5-Dicyanoimidazo)]-9,10-dihydroanthracene (8). In a sublimation apparatus, 1.0 g (3.6 mmol, 1 equiv) of the 1-iodo-2-chloro-4,5-dicyanoimidazole (**6a**) and 1.6 g (9.0 mmol, 2.5 equiv) of anthracene were placed and mixed together. The system was evacuated and backfilled with N$_2$ (3×). The mixture was heated to 220−235 °C for 1 h under nitrogen. Upon heating, a purple gas was given off and the solid melted and turned to a dark black liquid. Some anthracene sublimed on the cold finger. After heating, the system was evacuated to remove ICl from the reaction. The black solid was removed and ground to a fine powder. The product was extracted from the powdered black solid using acetone and a Soxhlet extractor. After 24 h of extraction, 0.167 g (16%) of black solid **8** was isolated: IR (KBr) 3058 (br), 2235, 1623, 1518, 1476, 1448, 1406, 1384, 1230, 1145, 738 cm^{-1}; ^{1}H NMR (200 MHz, (CD$_3$)$_2$-CO, ppm) δ 8.98 (s, 1H), 8.58 (s, 1H), 8.29 (m, 2H), 7.69 (m, 4H), 7.55 (m, 2H); MS (EI with DCI probe) *m/z* (relative intensity) 295 (5.6), 294 (M$^+$, 23.6), 293 (6.4), 193 (8.8), 179 (19.6), 178 (100.0), 177 (9.6), 176 (16.7), 152 (7.3), 151 (6.1), 118 (15.7); HRMS (EI with DCI probe) *m/z* calcd 294.0905, obsd 294.0886.

Thermolysis of HTT (7) at 490−500 °C to a Carbon−Nitrogen Material. In a quartz tube equipped with septum and N$_2$ bubbler was placed 0.5 g (1.4 mmol) of HTT (**7**). The system was evacuated and backfilled with N$_2$ (3×). The quartz tube was then placed in a tube furnace at 490−500 °C. Analysis of head space gases indicated (CN)$_2$, HCN, N$_2$ by GC−MS (EI) *m/z* 52, 29, 28. The quartz tube was removed after 1 h. The product was a black foam that upon crushing turned to a black glassy substance. The 0.39 g black solid: mp > 400 °C; IR (KBr) 3600−2400 (vbr) with major stretch at 3431, 2221 (w), 1650−800 (vbr) with major stretches at 1736, 1616, 1511, 1455, 1272, 1152 cm^{-1}. Anal. Calcd for [(C$_{12}$N$_{10}$)· 1.4H$_2$O]$_x$: C, 46.59; H, .91; N, 45.26; O, 7.24 with C/N = 1.029.

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(26) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Found (two determinations): C, 46.40, 46.40; H, 1.04, 0.99; N, 45.54, 45.47; O, 7.02, 7.14 (by difference) with average C/N = 1.020.

Thermolysis of HTT (7) at 1070 °C to a Carbonaceous Material. In a quartz tube equipped with septum and N_2 bubbler was placed 1.0 g (2.9 mmol) of HTT (**7**). The system was evacuated and backfilled with N_2 (3×). The quartz tube was then placed in a tube furnace at 1070 °C. Analysis of head space gases indicated $(CN)_2$, HCN, N_2 by GC−MS (EI) *m/z* 52, 29, 28. The quartz tube was removed after 15 days. The product was a black foam that upon crushing turned to a black glassy substance. The 0.39 g black solid: mp > 400 °C; IR (KBr) 3438 (s), 2917, 2847, 1729, 1650−800 (br) with major stretches at 1631, 1448, 1384, 1195, 1152, 1110 cm^{-1}. Anal. Found (two determinations): C, 91.57, 91.66; H, 0.81, 0.71; N, 0.91, 0.91; O, 6.71, 6.72 (by difference).

Supporting Information Available: Details of the C/N materials thermolysis (3 pages). This material is contained in 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.

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