

# Synthesis and Properties of Bis- and Tris(4,5-dicyano-1-methyl-2-imidazolyl)amines: A New Acidic Secondary Amine and a Nonbasic Tertiary Amine

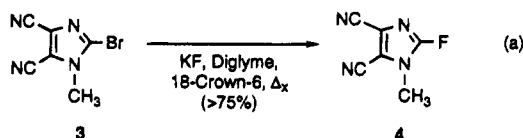
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## Introduction

Recently, we reported the syntheses of new organic/polymeric materials based on 4,5-dicyanoimidazole.<sup>1</sup> In many of these preparations, nucleophilic aromatic substitution (NAS) reactions were found to be a useful method. Synthesis of 2-bromo-4,5-dicyano-1-methylimidazole (3) and NAS reactions on it to synthesize new derivatives and polymeric materials have been reported.<sup>2</sup> Aromatic amines generally do not participate in NAS reactions on 3 due to their low nucleophilicity. However, the reactivity of the 2-carbon in 3 may be increased by transfluorination using potassium fluoride in diglyme to give 4,5-dicyano-2-fluoro-1-methylimidazole(4)<sup>3,4</sup> (eq a).

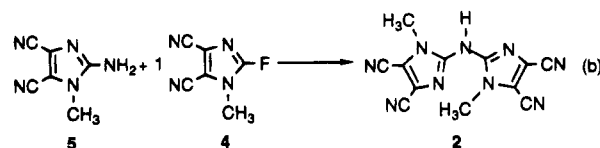


A fluoro substituent, in general, enhances the rate of nucleophilic substitution considerably compared to chloro, bromo, and iodo substituents.<sup>5</sup> Fluorine increases the electrophilicity of the 2-carbon in 4 and also stabilizes the transition state involved in the NAS reactions. Therefore, even weak nucleophiles undergo NAS reactions with 4. Aromatic primary amines such as aniline

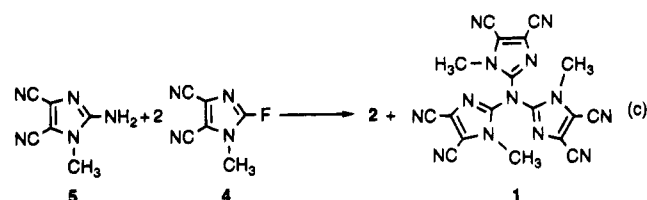
and its substituted derivatives react with 4 to give new secondary and tertiary amines.<sup>6</sup>

## Syntheses of Bis- and Tris(4,5-dicyano-1-methyl-2-imidazolyl)amines (2 and 1)

When a weakly basic amine such as 2-amino-4,5-dicyano-1-methylimidazole (5)<sup>1c</sup> was allowed to react with 4 under the reaction conditions shown in Table 1, a secondary amine, bis(4,5-dicyano-1-methyl-2-imidazolyl)amine (2), was obtained (eq b). Surprisingly, this reac-



tion goes even further. When 2 equiv of 4 was allowed to react with 1 equiv of 5 (see Table 1), tris(4,5-dicyano-1-methyl-2-imidazolyl)amine (1), was obtained in addition to the secondary amine, 2 (eq c). As shown in Table



1, the reaction leading to the secondary amine can be performed even at room temperature after deprotonation of the primary amine using sodium hydride. However, elevated temperatures are required for the formation of 1 in both DMAc and CH<sub>3</sub>CN. When K<sub>2</sub>CO<sub>3</sub> and DMAc are used, reaction temperatures below 70 °C are needed to avoid side reactions involving 5 and the solvent or moisture, resulting in the formation of imidazolones.<sup>6</sup> In all of these reactions, the tertiary amine 1 has been isolated along with the secondary amine 2.

## Physical Properties

**(i) Acid–Base Properties.** The secondary amine (2) is an unusual amine.<sup>7</sup> Unlike most amines, 2 is acidic due to the electron-withdrawing nature of the cyanoimidazole groups.<sup>8</sup> The pK<sub>a</sub> of 2 was determined by titration to be 4.2, comparable to that of many organic acids. The amine 2 can be recrystallized from water/acetonitrile. Acidic amine anions can be generally used as ligands in organometallic chemistry.<sup>9</sup> We are currently investigating similar reactions of 2.

The tertiary amine 1 is one of the few amines substituted by heterocycles only.<sup>7</sup> Amine 1 is a weak base, and

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<sup>†</sup> To whom correspondence should be addressed regarding crystal structure data.

(1) (a) Allan, D. S.; Thurber, E. L.; Rasmussen, P. G. *J. Polym. Sci.: Part A: Polym. Chem.* **1990**, *28*, 2475. (b) Allan, D. S.; Rasmussen, P. G. *J. Polym. Sci.: Part A: Polym. Chem.* **1992**, *30*, 1413. (c) Thurber, E. L.; Rasmussen, P. G. *J. Polym. Sci.: Part A: Polym. Chem.* **1993**, *31*, 351. (d) Thurber, E. L.; Subrayan, R. P.; Rasmussen, P. G. In *Contemporary Topics in Polymer Science*; Salamone, J. C., Riffle, J. S., Eds.; Plenum Press: New York, 1992; Vol. 7, pp 95–102. (e) Kim, Y.-K.; Rasmussen, P. G. *Macromolecules* **1991**, *24*, 6357. (f) Bouck, K. J.; Rasmussen, P. G. *Macromolecules* **1993**, *26*, 2077.

(2) (a) Apen, P. G.; Rasmussen, P. G. *Heterocycles* **1989**, *29*, 1325. (b) Apen, P. G.; Rasmussen, P. G. *J. Polym. Sci.: Part A: Polym. Chem. Educ.* **1992**, *30*, 203.

(3) Coad, E. C.; Rasmussen, P. G. The University of Michigan, Ann Arbor, unpublished results.

(4) For similar transfluorination reactions see: (a) Ichihara, J.; Matsuo, T.; Hanafusa, T.; Ando, T. *J. Chem. Soc., Chem. Commun.* **1986**, 793. (b) Finger, G. C.; Starr, L. D.; Dickerson, D. R.; Gutowsky, H. S.; Hamer, J. *J. Org. Chem.* **1963**, *28*, 1666. (c) Tullock, C. W.; Coffman, D. D. *J. Org. Chem.* **1960**, *25*, 2016. (d) Clark, J. H.; Macquarrie, D. J. *Tetrahedron Lett.* **1987**, *28*, 111. (e) Dolby-Glover, L. *Chem. Ind.* **1986**, 518. For general fluorination reactions see: Zemskov, G. S. *New Fluorinating Agents in Organic Synthesis*; Springer-Verlag: Berlin, 1989.

(5) The general trend in the reactivity toward nucleophiles for nitroaryl halides is F > Cl ≈ Br > I. See: Terrier, F. *Nucleophilic Aromatic Displacement: The Influence of the Nitro Group*; VCH Publishers: New York, 1991; pp 1–79.

(6) Subrayan, R. P. Ph.D. Thesis, The University of Michigan, Ann Arbor, 1993.

(7) The only other nitrogen-containing heterocyclic secondary and tertiary amines reported, that we have come across so far, are bis- and tris(4,6-dichloro-1,3,5-triazinyl)amines and their derivatives. See: (a) Nohara, N.; Sekiguchi, S.; Matsui, K. *J. Heterocycl. Chem.* **1970**, *7*, 519. (b) Fukushima, Y.; Nohara, N.; Hashida, Y.; Sekiguchi, S.; Matsui, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 794.

(8) There are a few amines reported in the literature that have acidic hydrogens. An example is dicyanamide, HN(CN)<sub>2</sub>, which has been characterized *in situ* but has not been isolated. See: (a) Madelung, W.; Kern, E. *Ann. Chem.* **1922**, *427*, 1. (b) Franklin, E. C. *J. Am. Chem. Soc.* **1922**, *44*, 486. (c) Burdick, W. L. *J. Am. Chem. Soc.* **1925**, *47*, 1485.

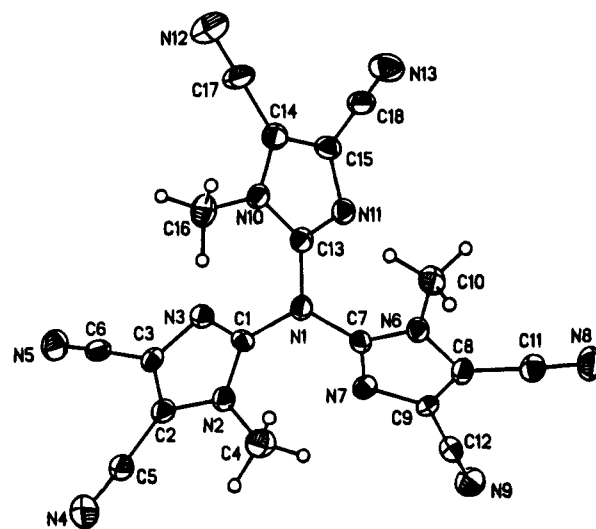
**Table 1. Reaction Conditions and Percent Yield Data**

no.	ratio of 5:4	reactn condns	% yield of 2	% yield of 1
1	1:1	1. K <sub>2</sub> CO <sub>3</sub> , DMAc, 50–60 °C, 24 h 2. HCl	57	0
2	1:2.2	1. K <sub>2</sub> CO <sub>3</sub> , DMAc, 60–70 °C, 24 h 2. HCl	57	54
3	1:2	1. K <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> CN, Δ <sub>x</sub> , 24 h 2. HCl	91	0
4	1:1	1. 2NaH, DMAc, rt, 24 h 2. HCl	64	0
5	1:1	1. K <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> CN, 70 °C, 48 h 2. HCl	56	0
6	1:2	1. 2NaH, CH <sub>3</sub> CN, rt-Δ <sub>x</sub> , 24 h 2. HCl	66	45

attempts to protonate it using moderately strong acids were not successful. The low basicity again reflects the electron-withdrawing nature of the dicyanoimidazolyl group. Amine 1 has poor solubility in polar aprotic solvents such as DMF, DMAc, and DMSO at rt but is soluble at elevated temperatures. However, 1 could be crystallized from acetonitrile/water or DMF/water but loses its crystallinity upon removal of the solvent.

(ii) **Crystal Structure Analysis of 1.** Amines typically have a pyramidal geometry. However, if the amine nitrogen is bonded to an aromatic group or atoms having d-orbitals or electron-withdrawing groups, then the lone pair of electrons on the nitrogen could be delocalized and the geometry around the amine nitrogen becomes planar. Several aromatic tertiary amines with near-planar geometry have been reported.<sup>10</sup> Planar, nonbasic amines substituted with heteroatoms are also reported.<sup>11</sup> Some of the aliphatic amines such as tris(isopropyl)amine<sup>12</sup> and 3-(dimethylamino)-2,2,4,4-tetramethylpentane<sup>13</sup> also have planar geometry due to steric hindrance.

Transparent, colorless, rectangular, needle shaped crystals of 1 were grown from acetonitrile/water by slow cooling. Crystal data collection and refinement parameters are listed in Table 2.<sup>14</sup> The compound crystallizes in a chiral space group. Mislow et al. were able to perform the separation of chiral amines for the first time

**Figure 1.** ORTEP diagram of tris(4,5-dicyano-1-methyl-2-imidazolyl)amine (1): top view.**Table 2. Crystal Data Collection and Refinement Parameters for 1**

space group	orthorhombic, $P2_12_12_1$ (#19)
unit cell param	
$a$ , Å	10.070 (2)
$b$ , Å	13.108(3)
$c$ , Å	17.551(3)
$\alpha$	90.000°
$\beta$	90.000°
$\gamma$	90.000°
$V$ , Å <sup>3</sup>	2316.8(7)
$Z$	4
$Q_{\text{calcd}}$ , g·cm <sup>-3</sup>	1.29
$F(000)$ , electrons	4920
unit cell dimens from 35 reflns	$7.5^\circ \leq 2\theta \leq 27.6^\circ$
no. of unique reflns	4557, $R_{\text{int}} = 0.0173$
no. of refined reflns with ( $F_o \geq 3s(F)$ )	3431
$R$	0.0683
$R_w$	0.0584
GOF	1.31
$m(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	0.83
crystal dimens, mm	$0.12 \times 0.08 \times 0.38$

(9) For examples involving dicyanamide anion as ligand see: (a) Golub, A. M.; Köhler, H.; Skopenko, V. V. *Chemistry of Pseudohalides*; Elsevier: Berlin, 1986; pp 434–454. (b) Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Williams, J. M.; Kwok, W. K.; Vandervoort, K. G.; Thompson, J. E.; Stupka, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 2555. (c) Eldridge, J. E.; Kornelsen, K.; Wang, H. H.; Williams, J. M.; Crouch, A. V. S.; Watkins, D. M. *Solid State Commun.* **1991**, *79*, 583. (d) Tokumoto, M.; Kinoshita, N.; Tanaka, Y.; Anzai, H. *J. Phys. Soc. Jpn.* **1991**, *60*, 1426. (e) Yamochi, H.; Komatsu, T.; Matsukawa, N.; Saito, G.; Mori, T.; Kusunoki, M.; Sakaguchi, K. *J. Am. Chem. Soc.* **1993**, *115*, 11319.

(10) Examples include (a) triphenylamine (Sobolev, A. N.; Belsky, V. K.; Romm, I. P.; Chernikova, N. Yu.; Guryanova, E. N. *Acta Crystallogr. Sect. C* **1985**, *41*, 967), (b) tri-*p*-tolylamine (Reynolds, S. L.; Scaringe, R. P. *Cryst. Struct. Commun.* **1982**, *11*, 1129), and (c) perchlorotriphenylamine (Hayes, K. S.; Nagumo, M.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2773).

(11) Examples include (a) perfluorotrimethylamine (Bürger, H.; Niepel, H.; Pawelke, G.; Oberhammer, H. *J. Mol. Struct.* **1979**, *54*, 159), (b) perfluorotriethylamine (Gaensslen, M.; Gross, U.; Oberhammer, H.; Rüdiger, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1467), (c) perfluorotripropylamine (Mack, H.-G.; Oberhammer, H. *J. Mol. Struct.* **1989**, *197*, 329), (d) tris(phenylthio)amine (Carruthers, J. R.; Prout, K.; Watkin, D. *J. Cryst. Struct. Commun.* **1981**, *10*, 1217), (e) tris-[(trifluoromethyl)thio]amine (Marsden, C. J.; Bartell, L. S. *J. Chem. Soc. Dalton Trans.* **1977**, 1582), (f) tris(trimethylsilyl)amine (Anderson, D. G.; Rankin, D. W. H.; Robertson, H. E.; Gundersen, G.; Seip, R. *J. Chem. Soc., Dalton Trans.* **1990**, 161), and (g) trigermylamine (Gledwell, C.; Rankin, D. W. H.; Robiette, A. G. *J. Chem. Soc. A* **1970**, 2935).

(12) Bock, H.; Goebel, I.; Havlas, Z.; Liedle, S.; Oberhammer, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 187.

(13) (a) Casarini, D.; Lunazzi, L.; Anderson, J. E. *J. Org. Chem.* **1993**, *58*, 714. (b) Berger, P. A.; Hobbs, C. F. *Tetrahedron Lett.* **1978**, 1905.

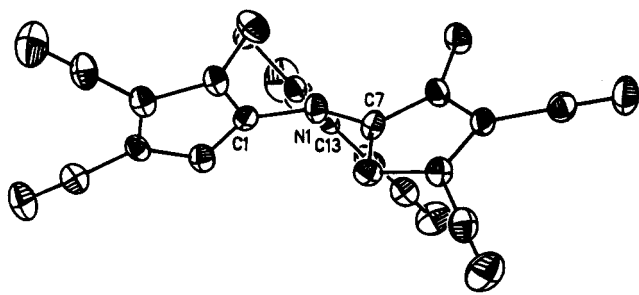
by chromatography for perchlorotriphenylamine<sup>10c,15</sup> and on methyl *N*-(biphenyl-2-yl)-*N*-(1-naphthyl) anthranilate by manual separation of the crystals.<sup>16</sup> However, it is difficult to separate the enantiomeric forms of 1 due to its poor solubility. Figures 1 and 2 show the ORTEP drawings of the molecule in top and side views, respectively.

Comparison of the carbon–nitrogen bond lengths suggest that there are four different types present. The C=N bond lengths are in the range of 1.138(5)–1.152(5) Å. The C=N bonds in the imidazole rings are in the range of 1.317(5)–1.322(5) Å (C1–N3, C13–N11, and C7–N9). The C–N bonds within the imidazole rings (C3–N3, C1–N2, C2–N2, C7–N6, C9–N7, C8–N6, C13–N10, C14–N10, and C15–N11) are longer than these double bonds (1.354(5)–1.382(5) Å). The central C–N bonds, C1–N1 (1.410(5) Å), C7–N1 (1.417(5) Å), and C13–N1

(14) The authors have deposited the atomic coordinates and other data for 1 with the Cambridge Crystallographic Data Centre. These data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(15) Okamoto, Y.; Yashima, E.; Hatada, K.; Mislow, K. *J. Org. Chem.* **1984**, *49*, 557.

(16) Glaser, R.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2777.



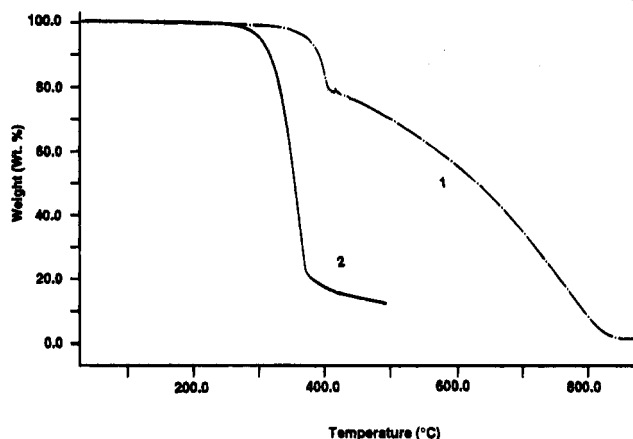
**Figure 2.** ORTEP diagram of tris(4,5-dicyano-1-methyl-2-imidazolyl)amine (1): side view.

(1.395(5) Å), are longer than all of these bonds. The corresponding C–N bond length between the 2-carbon and the 2-nitrogen in 2-amino-4,5-dicyanoimidazole is in the range of 1.334(4)–1.341(4) Å,<sup>17</sup> which is shorter than the C1–N1, C7–N1, and C13–N1 bond lengths in 1. This difference in the C–N bond lengths may be explained on the basis of the delocalization of the lone pair of electrons into the dicyanoimidazole ring due to resonance.

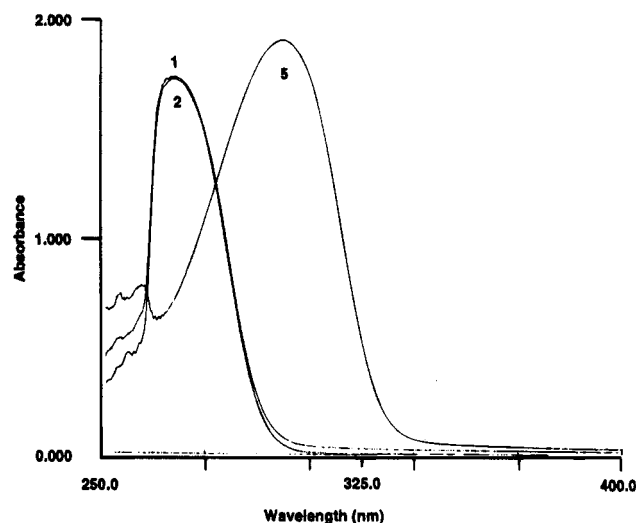
The C–N–C bond angles at the amine nitrogen are 116.8(3)° (C1–N1–C7), 117.2(3)° (C1–N1–C13) and 116.7(3)° (C7–N1–C13), making the sum of the C–N–C bond angles ( $\Sigma$ C–N–C) in 1 equal to 350.7(9)°. Comparison of the ( $\Sigma$ C–N–C) values for various aromatic tertiary amines in Mislow's paper<sup>16</sup> suggests that 1 has a lower degree of planarity compared to other aromatic tertiary amines. This deviation from the planarity may be explained on the basis of steric hindrance due to the methyl groups. In 1, the tertiary amine nitrogen N1 lies above the C1–C7–C13 reference plane. The perpendicular distance between N1 and the reference plane, which is known as the pyramidality, is 0.2505 Å, and this value is comparable to some of the sterically hindered tertiary amines described by Mislow et al. The pyramidality in sterically hindered tertiary amines is attributed to the imbalance in nonbonding interactions above and below the reference plane.

The dihedral angles between the imidazole rings and the plane containing the carbons C1, C7, and C13 are in the range 41.17°, 41.74°, and 43.86° (mean value 42.25°). The side view of the crystal structure shown in Figure 2 shows the deviation from the reference plane. The angles between the reference plane containing C1–C7–C13 and the planes that contain the atoms C1–N1–C7, C1–N1–C13 and C7–N1–C13 are  $19.76 \pm 0.50^\circ$ ,  $20.04 \pm 0.50^\circ$ , and  $19.86 \pm 0.50^\circ$ , respectively. In short, the amine 1 has a propeller geometry in its crystal lattice.

**(iii) Thermal Properties: Thermogravimetric Analysis.** High nitrogen content and electron-withdrawing groups confer oxidative stability on related compounds.<sup>18</sup> Thermogravimetric analyses of 1 and 2 are shown in Figure 3. The onset of decomposition, under nitrogen, for the secondary amine 2 is about 300 °C while that for the tertiary amine 1 is nearly 390 °C. The secondary amine loses 80% of its weight by 400 °C, while the tertiary amine showed an initial weight loss of about



**Figure 3.** Thermogravimetric analysis of bis-(2) and tris(4,5-dicyano-1-methyl-2-imidazolyl)amine (1): heating rate, 5 °C/min under N<sub>2</sub>.



**Figure 4.** UV-vis spectra of mono-(5), bis-(2), and tris(4,5-dicyano-1-methyl-2-imidazolyl)amines (1).

**Table 3.** UV-vis Spectral Data for (Cyanoimidazolyl)amine Derivatives<sup>a</sup>

compd	$\lambda_{\max}$	$\epsilon$	compd	$\lambda_{\max}$	$\epsilon$
5	301	13 000	aniline	294	2750
2	271	7000	diphenylamine	287	45 200
1	271	14 300	triphenylamine	300	29 800

<sup>a</sup>  $c = 0.01$ – $1.00$  mM in DMF.

20% by 400 °C and continued to lose weight upon further heating. A 10% residual weight was observed for 2 at about 500 °C, while for 1, this residual weight was recorded only by 800 °C.

**(iv) Optical Properties: UV-vis Spectroscopic Analysis.** UV-vis spectroscopic studies of the primary, secondary, and tertiary amines (5, 2, and 1) are shown in Figure 4. The corresponding  $\lambda_{\max}$  and  $\epsilon$  data are listed in Table 3 along with the data for aniline, diphenylamine, and triphenylamine for comparison.

Generally, substitution of an aromatic group in an amine increases the delocalization of the  $\pi$ -electrons, due to p– $\pi$  interaction, with the central nitrogen. The delocalization of electrons lowers the energy of excitation, and therefore the absorption is observed at longer wavelength,  $\lambda_{\max}$ . However, both primary amines, 5 and aniline, have longer wavelengths of absorption,  $\lambda_{\max}$ , than the secondary amines 2 and diphenylamine due to the

(17) Hardgrove, Jr., G. L.; Jons, S. D. *Acta Crystallogr.: Sect. C* 1991, 47, 337.

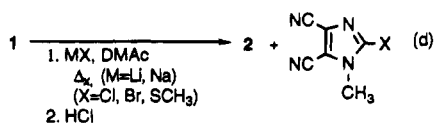
(18) (a) Coad, E. C.; Apen, P. G.; Rasmussen, P. G. *J. Am. Chem. Soc.* 1994, 116, 391 and references cited therein. For the thermal stability of high nitrogen-containing materials see: (b) Cullis, C. F.; Hirschler, M. M. *The Combustion of Organic Polymers*; Oxford University Press: New York, 1981; pp 229–318. (c) Shulman, G. P. In *Thermal Stability of Polymers*; Conley, R. T., Ed.; Marcel Dekker: New York, 1970; pp 549–576.

$n-\pi^*$  type transition. In the secondary aromatic amines the  $\pi-\pi^*$  transition may be predominant, perhaps due to the overlap of the  $\pi$  orbitals, and will be observed at shorter wavelength. This trend in the  $\lambda_{\max}$  does not conform with that of the tertiary amines **1** and triphenylamine. Triphenylamine shows a  $\lambda_{\max}$  at a longer wavelength than that of aniline and diphenylamine. There is greater overall delocalization of the  $\pi$ -electrons in triphenylamine than in diphenylamine resulting in lower energy of excitation. However, there was no change in the  $\lambda_{\max}$  for **1** from that of the secondary amine **2**, suggesting that the overall overlap of the  $\pi$  orbitals of the imidazole rings remains the same, probably, due to the steric hindrance from the methyl groups.

(v) **Electrochemical Properties: Cyclic Voltammetry.** Cyanoimidazoles are moderate electron acceptors.<sup>19</sup> Some of their derivatives exhibit quasireversible cyclic voltammograms at around  $-2$  V.<sup>6,20</sup> Some of the aromatic tertiary amines reported show reversible cyclic voltammograms,<sup>21</sup> and they have been suggested as candidates for electronic applications.<sup>22</sup> Cyclic voltammograms of **1**, **2**, and **5** are shown in Figure 5, and the reduction potentials are listed in Table 4.

The amine **1** exhibited irreversibility in its reduction wave. There are two subsequent reduction waves, suggesting that a stepwise reduction might be taking place. A possible explanation for this observation is the reductive elimination of a dicyanoimidazolyl group from **1**. The secondary amine **2** also showed no reversible reduction waves in the cyclic voltammogram, but there was a quasireversible oxidation wave at  $E \approx +0.3$  V. This might be attributed to the oxidation of the amine.

(vi) **Attempted Demethylation of 1.** We expected that if the tertiary amine **1** is demethylated, then the amine might be completely planar and there may be intramolecular hydrogen bonding involved between the nitrogens of the imidazole rings. Demethylation of 4,5-dicyano-1-methylimidazole and also 1,1'-dimethyl-4,4',5,5'-tetracyanobiimidazole have been accomplished by refluxing in polar aprotic solvents using lithium halides<sup>3,20b</sup> similar to the demethylation of methyl ethers.<sup>23</sup> When **1** was heated with LiBr in DMAc, no demethylation took place. Instead, the molecule fragmented to bis(4,5-dicyano-1-methyl-2-imidazolyl)amine (**2**) as confirmed by infrared and mass spectroscopy along with the formation of 2-bromo-4,5-dicyano-1-methylimidazole (**4**) which was identified by GC/MS (eq d). Formation of bis(4,5-dicyano-



1-methyl-2-imidazolyl)amine (**2**) was also observed when lithium chloride and sodium thiomethoxide were used as demethylating agents. This observation is in accord with the reductive fragmentation of **1** in its cyclic voltammogram.

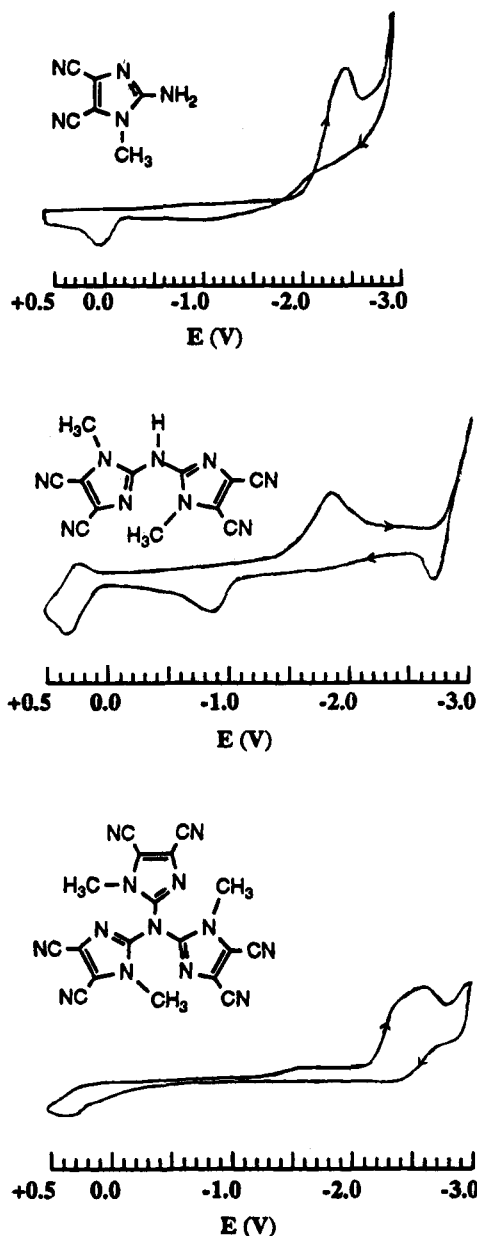
(19) Allan, D. S.; Bergstrom, D. F.; Rasmussen, P. G. *Synth. Metals* **1988**, *25*, 139.

(20) (a) Jang, T.; Rasmussen, P. G. Unpublished results. (b) Apen, P. G.; Rasmussen, P. G. *J. Am. Chem. Soc.* **1991**, *113*, 6178.

(21) Shirota, Y.; Kobata, T.; Noma, N. *Chem. Lett.* **1989**, 1145.

(22) Miyagi, H.; Murofushi, Y.; Ishikawa, M. *Jpn. Kokai Tokkyo Koho JP 61,168,625 1986; Chem. Abstr.* **1987**, *106*, 111408r.

(23) (a) Bernard, A. M.; Ghiani, M. R.; Piras, P. P.; Rivoldini, A. *Synthesis* **1989**, 287. (b) Buchanan, D. H.; Takemura, N.; Sy, J. N. O. *J. Org. Chem.* **1986**, *51*, 4291. (c) Tiecco, M. *Synthesis* **1988**, 749.



**Figure 5.** Cyclic voltammograms of (4,5-dicyano-1-methyl-2-imidazolyl)amines vs  $\text{Ag}/\text{Ag}^+$  in  $\text{CH}_3\text{CN}$ : starting potential = 0.00 V.

**Table 4. Electrochemical Data for Cyanoimidazolylamine Derivatives**

compd	$E$ (V)
<b>5</b> <sup>a</sup>	-2.26*
<b>2</b> <sup>b</sup>	+0.28 <sup>†</sup> , -0.98,* <sup>c</sup> -1.65*
<b>1</b> <sup>b</sup>	-2.18,* -2.31*

<sup>a</sup> Measured in  $\text{CH}_3\text{CN}$  vs  $\text{Ag}/\text{Ag}^+$ ; \*irreversible. <sup>b</sup> Measured in DMF vs  $\text{Ag}/\text{Ag}^+$ ; <sup>†</sup>quasireversible. <sup>c</sup> Seen in reverse oxidation wave.

It is likely that any nucleophile might attack the 2-carbon of one of the imidazole rings in **1** due to the resonance stabilization of the anion of **2** which makes the anion of **2** a good leaving group. The yield of **1** in eq c was only around 50% (see Table 1). The other product was the secondary amine **2**. Perhaps the fluoride ion generated as a result of the NAS reaction is facilitating the cleavage of **1** to give **2**. If the concentration of the reaction mixture is kept high, then the tertiary amine, **1**, precipitates out of the reaction mixture thereby inhibiting the fragmentation reaction.

The fragmentation of **1** upon reaction with halides is similar to the reaction of tetracyanomethane(C(CN)<sub>4</sub>) with halides resulting in cyanogen halides and salts of tricyanomethanide anion(C(CN)<sub>3</sub>)<sub>2</sub>.<sup>24</sup>

Since **1** reacts readily with nucleophiles, a protecting group other than methyl was needed. Syntheses of 2-fluoro-4,5-dicyanoimidazoles were attempted by trans-fluorination of 2-bromo-4,5-dicyanoimidazole with suitable protecting groups at the 1-position. These protecting groups include methoxymethyl (MOM), NCCH<sub>2</sub>, and NCCH<sub>2</sub>CH<sub>2</sub> groups. In all these reactions, the KF appeared to remove the protecting group and therefore no transhalogenation was observed. Bulkier protecting groups such as benzyl<sup>25</sup> and 4-methoxybenzyl<sup>26</sup> groups were able to withstand the transfluorination conditions, but the fluorinated derivatives gave only secondary amines due to steric hindrance.

### Conclusions

We have synthesized new secondary and tertiary amines substituted with 4,5-dicyano-1-methyl-2-imidazolyl groups. These compounds are thermally stable up to temperatures in excess of 300 °C. The tertiary amine **1** has a propeller structure in its crystal lattice due to the steric hindrance from the methyl groups. The electron-withdrawing nature of the dicyanoimidazolyl group makes the secondary amine acidic and the tertiary amine a nonbasic amine. Thus, the 4,5-dicyano-1-methyl-2-imidazolyl group may be considered as a somewhat sterically demanding functionality in the place of cyano groups. Therefore, compounds **1** and **2** may be considered to be analogous to tricyanamide, N(CN)<sub>3</sub>, and dicyanamide, HN(CN)<sub>2</sub>. Tricyanamide has not been synthesized, while dicyanamide, which is one of the strongest organic acids known, is proposed to be present in solution but has not been isolated. Efforts are underway to further explore this analogy by the syntheses of mixed amines substituted with cyano and dicyanoimidazolyl groups.

### Experimental Section

Melting points were recorded on a Mel-Temp apparatus and are uncorrected. TLC was done on Eastman Kodak silica gel sheets containing fluorescent indicator. Infrared spectra were recorded using a Nicolet 5-DX FTIR spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded using Bruker AM-300 or AM-360 or AC-200 spectrometers. Chemical shift values are reported relative to appropriate solvents. All <sup>13</sup>C NMR spectra were done using broad band proton decoupling. Nominal mass spectra were recorded on a Finnigan Model 4021 mass

(24) Mayer, E. *Monatsh. Chem.* **1969**, *100*, 462.

(25) The benzyl group may be deprotected by selective hydrogenation (Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; John Wiley & Sons: New York, 1991) or by oxidation using ruthenium tetroxide (a) Yoshifuji, S.; Arakawa, Y. *Chem. Pharm. Bull.* **1989**, *37*, 3380. (b) Tanaka, K.; Yoshifuji, S.; Nitta, Y. *Chem. Pharm. Bull.* **1988**, *36*, 3125).

(26) The 4-methoxybenzyl group may be deprotected by oxidation. For examples, see: (a) Horita, K.; Yoshioka, T.; Tanaka, T.; Oikawa, Y.; Yonemitsu, O. *Tetrahedron* **1986**, *42*, 3021. (b) Nakajima, N.; Abe, R.; Yonemitsu, O. *Chem. Pharm. Bull.* **1988**, *36*, 4244. (c) Dawson, I. M.; Gregory, J. A.; Herbert, R. B.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2585. (d) Fisher, T. H.; Dershem, S. M.; Schultz, T. P. *J. Org. Chem.* **1988**, *53*, 1504. The 4-methoxybenzyl group may also be removed by refluxing in trifluoroacetic acid. See: Iddon, B.; Khan, N. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1453.

spectrometer. High-resolution mass spectra were recorded on a VG analytical model 70-250S mass spectrometer. Elemental analyses were performed at the University of Michigan on a Perkin-Elmer 2400 CHN analyzer or by Oneida Research Services, Inc., Whitesboro, NY. UV-vis spectra were recorded on a Shimadzu UV-2101PC UV-vis spectrophotometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer 7/DX thermal analysis system. Solvents were purified and distilled under nitrogen prior to use.

**Bis(4,5-dicyano-1-methyl-2-imidazolyl)amine (2): Typical Procedure.** Into a solution of 2-amino-4,5-dicyano-1-methylimidazole (**5**, 0.122 g, 0.830 mmol) and 4,5-dicyano-2-fluoro-1-methylimidazole (**4**, 0.187 g, 1.247 mmol) in DMAc (1.5 mL) was added powdered and predried K<sub>2</sub>CO<sub>3</sub> (0.062 g, 0.449 mmol) under nitrogen, and the reaction mixture was heated to 50–60 °C for 24 h. The reaction mixture was cooled to rt and was poured into water. The aqueous solution was filtered, and the filtrate was acidified using 0.1 M HCl to pH ≈ 5–7 when off-white needle shaped crystals precipitated slowly. The crude solid was filtered and was crystallized from acetonitrile/water (1:4 v/v) (0.132 g, 57%): mp >300 °C dec; IR (KBr) 3130, 2238, 2225, 1634, 1594, 1518, 1479, 1392, 1386, 1361, 1328, 1167, 1050, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 3.57 (s); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 147.13, 116.31, 112.02, 110.97, 108.99, 32.37; MS (EI/70 eV) *m/z* 277 (M<sup>+</sup>, 100), 262 (8), 250 (5), 238 (4), 183 (7), 172 (20), 145 (30), 73 (17), 67 (19), 43 (28); HRMS calcd for C<sub>12</sub>H<sub>7</sub>N<sub>9</sub> 277.0824, found 277.0801. Anal. Calcd for C<sub>12</sub>H<sub>7</sub>N<sub>9</sub>: C, 51.99, H, 2.53, N, 45.49. Found: C, 51.72, N, 2.46, N, 45.07.

**Tris(4,5-dicyano-1-methyl-2-imidazolyl)amine (1): Typical Procedure.** Into a solution of 2-amino-4,5-dicyano-1-methylimidazole (**5**, 1.025 g, 6.973 mmol) and 4,5-dicyano-2-fluoro-1-methylimidazole (**4**, 2.106 g, 0.014 mol) in DMAc (3.0 mL) was added powdered and predried K<sub>2</sub>CO<sub>3</sub> (0.969 g, 7.011 mmol), and the reaction mixture was heated to 60–70 °C under nitrogen for 24 h. The reaction mixture turned red and viscous eventually. The reaction mixture was cooled to rt and was poured into aqueous NH<sub>4</sub>OH (3.0 M, 10 mL) upon which an off-white solid precipitated. The precipitate obtained was filtered, and the solid obtained was crystallized from water/acetonitrile (4:1 v/v) (0.954 g, 54%): mp >390 °C dec; IR (KBr) 2246, 2240, 1521, 1483, 1457, 1404, 1368, 1326, 1251, 1178, 760, 721, 716, 669, 485, 475 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 3.49 (s); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 142.41, 118.43, 114.86, 111.65, 108.12, 33.76; MS (EI/70 eV) *m/z* 407 (59, M<sup>+</sup>), 288 (6), 276 (5, C<sub>12</sub>H<sub>6</sub>N<sub>9</sub><sup>+</sup>), 262 (13), 172 (8), 158 (6), 145 (100%, C<sub>6</sub>H<sub>3</sub>N<sub>5</sub><sup>+</sup>), 104 (12), 67 (26); HRMS calcd for C<sub>18</sub>H<sub>9</sub>N<sub>14</sub> 407.1104, found 407.1119. Anal. Calcd for C<sub>18</sub>H<sub>9</sub>N<sub>14</sub>: C, 53.07, H, 2.23, N, 44.70. Found: C, 52.75, H, 2.04, N, 44.24. The aqueous extract gave the secondary amine (**2**) upon acidification using HCl which was worked up as in the previous experiment (0.73 g, 57%).

**Supplementary Material Available:** Infrared and <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **1** and **2** (6 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. X-ray data for **1** is also available.<sup>14</sup>