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FLUORESCENCE PROPERTIES OF POLYCYANOANILINES SYNTHESIZED FROM ELECTROPHILIC ETHYLENES AND MALONONITRILE DERIVATIVES

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Abstract – Various arylidene- or alkylidenemalononitriles are condensed with electrophilic ethylenes to obtain polycyanoaniline derivatives. All the anilines showed strong fluorescence and the fluorescence intensities was evaluated to the effect of substituents.

INTRODUCTION

Malononitrile, cyanoacetic acid esters, and their alkylidene derivatives are versatile nucleophilic reagents and have been used to produce raw materials for heteroaromatic compounds and polymers. Nucleophilic reactivity of these materials is so remarkable that they undergo various condensation reactions similar to enolate anion even in a weakly basic conditions. They had been utilized in various reactions described above.[1] In a process of investigation on nucleophilic reactivity of alkylidenemalononitriles, we obtained polysubstituted aniline derivatives which showed blue fluorescence even under weak room-light. In the cycloaromatization, we need electrophilic ethylenes substituted with proper electron withdrawing substituents which may leave at certain stage to form aromatic rings. Considering these points, we utilized polycyanoethylenes. In this report were described the reactions of alkylidenemalononitriles **1** with diethyl dicyanofumarate **2** (reaction A) and with (ethoxymethylene)malononitrile **4** (reaction B) to give polycyanoaniline. These two reactions were illustrated in Figure 1. Although some similar cycloaromatization reactions had been reported previously, the reaction introducing an extra cyano group at certain stage as in reaction B had not been described.[2] Since all these derivatives showed intense fluorescence, effect of substituents on the fluorescence were investigated.

MATERIALS AND METHODS

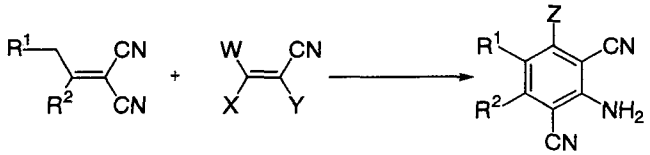
All the melting points are uncorrected. Infrared spectra were recorded on Hitachi 295 spectrometer. All the1H NMR and 13C NMR spectra were obtained on a JEOL GSX-400 spectrometer at 400 MHz and 100 MHz, respectively. Mass spectra were recorded on a JEOL JMS-DX300 spectrometer operating at 300 mA. Elemental analyses were performed with YANACO MT-5 CHN Corder at the Ibaraki University Instrumental Analysis Center. Absorption and fluorescence spectra were recorded on a Hitachi 200-10 spectrophotometer and Hitachi 650-60 fluorescence spectrophotometer. In the case of fluorescence spectra, excitation wavelength was 360 nm or 380 nm. Fluorescence quantum yields(Φ_f) of anilines were determined referring to fluorescence intensity of quinine sulfate (quantum yield; 0.55 in cyclohexane) as a standard using following equation.

$$\Phi_f = \frac{F_x \cdot A_q \cdot E_q \cdot n_x^2}{F_x \cdot A_x \cdot E_x \cdot n_q^2} \times \Phi_{f,q}$$

x=sample, q=quinine sulfate
F=integrated intensity

E = intensity of exciting line(Eq=Ex)
n = refractive index of solvent
A=absorbance at 360 or 380 nm
$\Phi_{f,q}$=fluorescence quantum yield of quinine sulfate(0.55)

Most of the starting alkylidene-, cycloalkylidene or arylalkylidenemalononitriles were prepared from the corresponding ketones under Knoevenagel conditions.[3] Acenaphthyli-



1 **2** W=Y=CO_2Et, X=CN **3** Z=CO_2Et
4 W=OEt, X=H, Y=CN **5** Z=CN

Figure 1. Polycyanoanilines were prepared from malononitrile derivatives and electrophilic ethylenes.

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denemalononitrile was prepared from the condensation reaction of acenaphthenone(2 mmol) with malononitrile (2 mmol) catalyzed with triethylamine(1 drop) in ethanol. Arylalkylidenemalononitriles were prepared from the reaction of corresponding ketone(22 mmol) with malononitrile(20 mmol) catalyzed with pyrrolidine(2 mmol) and acetic acid(10 mmol) in boiling benzene removing water with Soxhlet extracter packed with molecular sieves(4A). Diethyl dicyanofumarate **2**,[4] (ethoxymethylene)malononitrile **4**,[5] and (ethoxypropylidene)malononitrile[5] were prepared by known procedures, respectively.

Ethyl 3-Amino-2,4-dicyanobenzoates 3(Reaction A); General Procedure: A solution of 1 (5 mmol), 2 (5 mmol), and Et_3N (0.51 g, 5 mmol) in ethanol (20 mL) was stirred and refluxed for 1-7 h. The ethanol was evaporated. The crude products were crystallized from ethanol (3a-3i) or chromatographed on a silica gel column (3j).

Ethyl 6-Amino-5,7-dicyano-2,3-dihydro-1H-indene-4-carboxylate (**3a**); Yield 74%, mp 157-158 °C. ^{1}H NMR ($CDCl_3$): δ = 1.46 (t,3H, OCH_2CH_3), 2.15 (2H, m), 3.11 (4H, m), 4.49 (q, 2H, OCH_2CH_3), 5.27 (br s, 2H, NH_2). ^{13}C NMR ($CDCl_3$): δ = 14.0 (OCH_2CH_3), 24.4, 33.2, 33.6, 62.5 (OCH_2CH_3), 94.3, 97.0, 114.6(CN), 115.5 (CN), 133.0, 135.5, 151.4, 156.1, 164.3 (C=O). IR (KBr): δ = 3460, 3340, 3220 (NH_2), 2210 (CN), 2190 (CN), 1715 (C=O), and 1625 cm-1 (NH_2). MS: m/z (rel intens) 255 (M^+, 20), 226 (100). Anal. Calcd. for $C_{14}H_{13}N_3O_2$; C,65.87; H, 5.13; N, 16.46. Found; C, 65.79; H, 5.21; N, 16.41.

Ethyl 3-Amino-2,4-dicyano-5,6,7,8-tetrahydro-1-naphthalenecarboxylate (**3b**); Yield: 89%, mp 152-153 °C. 1H NMR (CDCl3) δ = 1.43 (3H, t, OCH_2CH_3) 1.80 (4H, m), 2.65 (2H, m), 2.92 (2H, m), 4.46 (2H, q, OCH_2CH_3), 5.14 (2H, br s, NH_2). 13C NMR ($CDCl_3$) δ = 14.0 (OCH_2CH_3), 21.5, 22.0, 26.0, 29.6, 62.7 (OCH_2CH_3), 92.3, 99.2 , 114.6 (CN), 115.1 (CN), 130.9, 139.6, 149.9, 154.7, 166.2 (C=O). IR (KBr): δ = 3450, 3350, 3240 (NH_2), 2220 (CN), 1720 (C=O), 1630 cm^{-1} (NH_2). MS: m/z (rel intens) 269 (M^+, 26), 240 (100). Anal. Calcd. for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.61. Found: C, 66.80; H, 5.61; N, 15.52.

Ethyl 3-Amino-2,4-dicyano-6,7,8,9-tetrahydro-5H-benzocycloheptene-1-carboxylate (**3c**); Yield 85%, mp 125-126 °C. ^{1}H NMR (CDCl3) δ =1.42 (t, 3H, OCH_2CH_3) 1.62 (2H, m), 1.70 (2H, m), 1.82 (2H, m), 2.68 (2H, m), 3.06 (4H, m), 4.46 (q, 2H, OCH_2CH_3), 5.15 (br s, 2H, NH_2). ^{13}C NMR ($CDCl_3$) δ =14.0 (OCH_2CH_3), 27.0, 27.2, 27.3, 31.4, 34.7, 62.7 (OCH_2CH_3), 92.3, 99.2 , 114.6(CN), 115.1 (CN), 130.8, 139.6, 149.9, 154.7, 166.2 (C=O). IR (KBr): δ = 3420, 3350, 3250 (NH_2), 2220 (CN), 1730 (C=O), 1655 cm^{-1} (NH_2).

MS: m/z(rel inten) 283 (M^+, 70), 254 (100). Anal. Calcd. for $C_{16}H_{17}N_3O_2$: C, 67.82; H, 6.05; N, 14.83. Found: C, 67.74; H, 5.93; N, 14.79.

Ethyl 3-Amino-2,4-dicyano-9,10-dihydro-1-phenanthrenecarboxylate (**3d**); Yield 72%, mp 114-116 °C. ^{1}H NMR ($CDCl_3$) δ =1.45 (t, 3H, OCH_2CH_3), 2.74 (4H, m), 4.50 (q, 2H, OCH2CH3), 5.41 (br s, 2H, NH_2), 7.31 (1H), 7.40 (2H, m), 8.21 (1H). ^{13}C NMR ($CDCl_3$) δ =14.0 (OCH_2CH_3), 25.8, 28.6, 62.8 (OCH_2CH_3), 93.4, 94.9, 114.8 (CN), 116.6 (CN), 126.9-151.9 (aromatic C), 165.5 (C=O). IR (KBr): δ = 3460, 3370, 3240 (NH_2), 2210 (CN), 1730 (C=O), 1640 cm^{-1} (NH_2). MS: m/z (rel inten) 317 (M^+, 100), 288 (27), 271 (40). Anal. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.92; H, 4.76; N, 13.24. Found: C, 71.97; H, 4.97; N, 13.26.

Ethyl 3-Amino-2,4-dicyano-5-methyl-5,6,7,8-tetrahydro-1-naphthalenecarboxylate (**3e**); Yield 78%, mp 129-130 °C. ^{1}H NMR ($CDCl_3$) δ =1.35 (d, 3H, J =7.2 Hz), 1.43 (t, 3H, OCH_2CH_3), 1.79 (4H, m), 2.56-2.71 (2H, m), 3.27 (1H, m), 4.46 (q, 2H, OCH_2CH_3), 5.14 (br s, 2H, NH_2). ^{13}C NMR ($CDCl_3$) δ =14.0 (OCH_2CH_3), 16.8 (CH_3), 21.9, 25.7, 28.4, 32.5, 62.7 (OCH_2CH_3), 93.6, 98.8, 114.5, 115.0 (CN), 124.3, 140.5, 149.9, 153.4, 165.7 (C=O). IR (KBr): δ = 3450, 3360, 3230 (NH_2), 2230 (CN), 1730 (C=O), 1630 cm^{-1} (NH_2). MS: m/z(rel inten) 283 (M^+, 35), 254 (100). Anal. Calcd. for $C_{16}H_{17}N_3O_2$: C, 67.82; H, 6.05; N, 14.83. Found: C, 67.82; H, 6.04; N, 14.75.

Ethyl 3-Amino-2,4-dicyano-6-methyl-5,6,7,8-tetrahydro-1-naphthalenecarboxylate (**3f**); Yield 78%, mp 152-153 °C. ^{1}H NMR ($CDCl_3$) δ =1.10 (d, 3H, J =6.4Hz), 1.31 (1H, m), 1.43(t, 3H, OCH2CH3), 1.85-1.92 (2H, m), 2.44 (dd, 1H, J gem=18 Hz), 2.67-2.75 (2H, m), 3.07 (dd, 1H, J gem=18Hz), 4.46 (2H, q, OCH_2CH_3), 5.10 (br s, 2H, NH_2). ^{13}C NMR ($CDCl_3$) δ =14.0 (OCH_2CH_3), 21.4 (CH_3), 25.9, 27.9, 30.2, 37.8, 62.7 (OCH_2CH_3), 93.5, 98.9, 114.5, 114.7 (CN), 125.1, 139.9, 148.0, 149.6, 165.6 (C=O). IR (KBr): δ = 3430, 3360, 3250 (NH2), 2225 (CN), 1730 (C=O), 1650 cm^{-1} (NH_2). MS: m/z(rel inten) 283 (M^+, 28), 254 (100). Anal. Calcd. for $C_{16}H_{17}N_3O_2$: C, 67.82; H, 6.05; N, 14.83. Found: C, 67.79; H, 5.98; N, 14.93.

Ethyl 3-Amino-2,4-dicyano-5-isobutylbenzoate (**3g**); Yield 38%, mp 149-150 °C. ^{1}H NMR ($CDCl_3$) δ =0.98 (3H, d, CH_3), 1.45 (t, 3H, OCH_2CH_3), 2.03 (m, 1H, CH), 2.71 (d, 2H, CH_2), 4.46 (q, 2H, OCH_2CH_3), 5.44 (br s, 2H, NH_2), 7.26 (s, 1H). 13C NMR ($CDCl_3$) δ =14.0 (OCH_2CH_3), 22.3 (CH_3), 30.1(CH), 44.3 (CH2), 62.8 (OCH_2CH_3), 94.1, 101.3, 114.9(CN), 115.0 (CN), 120.5, 136.0, 151.7, 152.8, 163.6 (C=O). IR (KBr): δ = 3490, 3360, 3240 (NH_2), 2230 (CN), 1730 (C=O), 1640 cm^{-1} (NH_2). MS: m/z(rel inten) 271 (M^+, 81), 229 (79), 263 (29). Anal. Calcd. for $C_{15}H_{17}N_3O_2$; C, 66.40; H, 6.32; N, 15.49. Found; C, 66.25; H, 6.33; N, 15.40.

Ethyl 9-Amino-8,10-dicyano-7-fluoranthenecarboxylate (**3h**); Yield 71%, mp 253-255 °C (Decomp.). ^{1}H NMR (DMSO-d6) δ =1.46 (t, 3H, OCH_2CH_3), 4.62 (q, 2H, OCH_2CH_3), 7.21 (br s, 2H, NH_2), 7.68-8.38 (6H). ^{13}C NMR (DMSO-d_6) δ =13.7 (OCH_2CH_3), 62.8 (OCH_2CH_3), 91.2, 91.5, 114.7(CN), 114.8 (CN), 121.1, 123.5, 123.9, 127.0, 128.3, 128.6, 129.3, 130.6, 131.1, 131.2, 132.1, 134.4, 145.7, 152.3 (Carom), 165.0 (C=O). IR (KBr): δ = 3460, 3360, 3370, 3240 (NH_2), 2220 (CN), 1735 (C=O), 1635 cm^{-1} (NH_2). MS: m/z(rel inten) 339 (M^+, 100), 311 (72). Anal. Calcd. for $C_{21}H_{13}N_3O_2$; C, 74.32; H, 3.86; N, 12.38. Found; C, 74.37; H, 4.12; N, 12.36.

Ethyl 5-Amino-4,6-dicyano-[1,1'-biphenyl]-3-carboxylate (**3i**);

Yield 55%, mp 191-193 ℃. ^{1}H NMR ($CDCl_3$) δ =1.44 (t, 3H, OCH_2CH_3), 4.48 (q, 2H, OCH_2CH_3), 5.57 (br s, 2H, NH_2), 7.48 (s, 1H, H_{arom}), 7.58-7.51 (m, 5H). ^{13}C NMR ($CDCl_3$) δ =14.0 (OCH_2CH_3), 62.9 (OCH_2CH_3), 95.1, 99.3, 114.9, 115.3 (CN), 120.3, 128.5, 129.2, 130.0, 136.4, 136.7, 150.1, 153.3, 163.3 (C=O). IR (KBr): δ = 3460, 3320, 3230 (NH2), 2220 (CN), 1740 (C=O), 1640 cm-1 (NH_2). MS: m/z(rel inten) 291 (M^+, 100), 263 (29). Anal. Calcd. for $C_{17}H_{13}N_3O_2$; C, 70.09; H, 4.50; N, 14.43. Found; C, 70.17; H, 4.60; N, 14.39.

Ethyl 3-Amino-2,4-dicyano-6-metylbenzoate (**3j**); Yield 8%, mp 120-121 ℃. ^{1}H NMR ($CDCl_3$) δ =1.44 (3H, t, OCH_2CH_3), 2.30 (s, 3H, CH_3), 4.48 (q, 2H, OCH_2CH_3), 5.27 (br s, 2H, NH_2), 7.47 (s, 1H). 13C NMR (CDCl3) δ =13.9 (OCH_2CH_3), 18.8 (CH_3), 62.9 (OCH_2CH_3), 96.3, 98.9 , 114.4(CN), 115.3 (CN), 126.1, 138.9, 139.7, 150.0, 165.1 (C=O). IR (KBr): δ = 3410, 3360, 3240 (NH_2), 2230 (CN), 1730 (C=O), 1660 cm^{-1} (NH_2). MS: m/z(rel inten) 229 (M^+, 62), 200 (100). Anal. Calcd. for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.89; H, 4.97; N, 18.19.

General Method for Synthesizing 2,3,6-Tricyanoanilines (**5**) (Reaction B): A mixture of substrate (2 mmol), 4 (2mmol), Et_3N (2mmol), and NaCN (2 mmol) in acetonitrile (20 ml) was stirred for 1-12 h at room temperature or refluxed. Only in the case of **5j**, ethoxypropylidenemalononitrile was used as substrate. Acetonitrile solvent was evaporated. The residue was dissolved in benzene. The benzene solution was washed with distilled water, dried (Na_2SO_4), and benzene was evaporated. The residues were chromatographed(silica gel) and the crude products were recrystallized from ethanol.

1,3,4-Tricyano-5,6,7,8-tetrahydro-2-naphthalenamine (**5b**); Yield 6%, mp 215-217 ℃ (Decomp.). ^{1}H NMR ($CDCl_3$) δ =1.86 (m, 4H), 2.86 (m, 2H,), 2.95 (m, 2H), 5.24 (br s, 2H, NH_2). ^{13}C NMR ($CDCl_3$) δ =21.4, 21.6, 27.4, 29.3, 97.1, 101.8, 113.5, 113.8, 114.0, 119.3, 131.9, 148.8, 149.6. IR (KBr): δ = 3430, 3360, 3240 (NH_2), 2220 (CN), 1645 cm^{-1} (NH_2). MS: m/z(rel inten) 222 (M^+, 91), 196 (100). Anal. Calcd. for $C_{13}H_{10}N_4$: C, 70.25; H, 4.54; N, 25.21. Found: C, 70.37; H, 4.41; N, 25.24.

1,3,4-Tricyano-6,7,8,9-tetrahydro-5H-benzocyclohepten-2-amine (**5c**); Yield 17%, mp 230-232 ℃ (Decomp.). ^{1}H NMR ($CDCl_3$) δ =1.70 (m, 4H), 1.88 (m, 2H), 3.03 (m, 2H), 3.09 (m, 2H), 5.27 (br s, 2H, NH_2). ^{13}C NMR ($CDCl_3$) δ =26.8, 27.2, 31.5, 33.0, 35.0, 96.1, 102.1, 113.7, 114.3, 114.7 (CN), 118.1, 137.8, 150.0, 154.8. IR (KBr): δ = 3450, 3370, 3240 (NH_2), 2220 (CN), 1645 cm^{-1} (NH_2). MS: m/z(rel inten) 236 (M^+, 100), 194 (76). Anal. Calcd. for $C_{14}H_{12}N_4$; C, 71.16; H, 5.12; N, 23.72. Found; C, 71.27; H, 5.14; N, 23.75.

1,2,4-Tricyano-9,10-dihydro-3-phenanthrenamine (**5d**); Yield 35%, mp 278-280 ℃ (Decomp.). ^{1}H NMR (DMSO-d_6) δ =2.82 (m, 4H), 7.13 (br s, 2H, NH_2), 7.43-7.51 (m, 3H, Harom), 8.15 (m, 1H). ^{13}C NMR (DMSO-d_6) δ =26.5, 27.6, 95.2, 96.9, 117.6, 114.5, 114.9, 116.1 (CN), 126.9, 127.2, 128.3, 129.5, 131.2, 131.2, 140.1, 143.6, 152.8. IR (KBr): δ = 3450, 3350, 3250 (NH_2), 2220 (CN), 1650 cm^{-1} (NH_2). MS: m/z (rel inten) 270 (M^+, 100). Anal. Calcd. for $C_{17}H_{10}N_4$: C, 75,54; H, 3.73; N, 20.73. Found; C, 75.51; H, 3.99; N, 20.59.

1,3,4-Tricyano-8-methyl-5,6,7,8-tetrahydro-2-naphthalenamine (**5e**); Yield 38%, mp 199-201 ℃. ^{1}H NMR ($CDCl_3$) δ =1.36 (3H, d, CH_3, J =7.2Hz), 1.78-1.93 (4H, m), 2.71 (1H, m), 3.00 (m, 1H), 3.30 (m, 1H), 5.29 (br s, 2H, NH_2). ^{13}C NMR ($CDCl_3$) δ =21.7 (CH_3), 16.4, 27.2, 28.2, 32.4, 97.4, 101.6, 119.5 , 113.5, 114.1, 114.1 (CN), 131.0, 149.9, 153.9. IR (KBr): δ = 3420, 3350, 3240 (NH_2), 2230 (CN), 1660 cm^{-1} (NH_2). MS: m/z (rel inten) 236 (M^+, 68), 221 (100), 207 (33). Anal. Calcd. for C14H12N4: C, 71.16; H, 5.12; N, 23.72. Found: C, 71.25; H, 5.23; N, 23.74.

1,3,4-Tricyano-7-methyl-5,6,7,8-tetrahydro-2-naphthalenamine (**5f**); Yield 6%, mp 227-229 ℃ (Decomp.). ^{1}H NMR (DMSO-d6) δ =1.05 (d, 3H, CH_3, J =6.4Hz), 1.28-1.38 (m, 1H), 1.80 (m, 1H), 1.86 (m, 1H), 2.39 (d, 1H, J gem=18Hz), 2.65-2.74 (m, 1H), 2.81(m,1H), 2.85 (m, 1H), 2.94 (d, 1H, J gem=18Hz), 7.02 (br s, 2H, NH2). ^{13}C NMR (DMSO-d_6) δ =21.2 (CH_3), 26.9, 27.4, 29.3, 37.0, 95.7, 101.1, 118.9, 114.3, 114.5, 114.9 (CN), 129.4, 149.0, 150.8. IR (KBr): δ = 3430, 3340, 3240 (NH2), 2230 (CN), 1640 cm^{-1} (NH_2). MS: m/z (rel inten) 236 (M^+, 85), 194 (100). Anal. Calcd. for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72. Found: C, 71.32; H, 5.26; N, 23.73.

2,4,5-Tricyano-[1,1′-biphenyl]-3-amine (**5g**); Yield 10%, mp 214-216 ℃ (Decomp.). ^{1}H NMR ($CDCl_3$) δ =5.56 (br s, 2H, NH_2), 7.16 (s, 1H), 7.54 (m, 5H). ^{13}C NMR ($CDCl_3$) δ =97.4, 100.3, 119.4 , 113.1, 114.4, 114.7 (CN), 122.7, 128.3, 129.1, 130.8, 135.5, 151.4, 152.4 . IR (KBr): δ = 3470, 3350, 3240 (NH2), 2240 (CN), 1650 cm^{-1} (NH_2). MS: m/z (rel inten) 244 (M^+, 100). Anal. Calcd. for $C_{15}H_{18}N_4$: C, 73.76; H, 3.30; N, 22.94. Found: C, 73.83; H, 3.38; N, 22.93.

2,4,5-Tricyano-6-methyl-[1,1′-biphenyl]-3-amine (**5h**); Yield 30%, mp 203-205 ℃ (Decomp.). ^{1}H NMR ($CDCl_3$) δ =2.24 (s, 3H, CH_3), 5.36 (br s, 2H, NH2), 7.23 (m, 2H), 7.54 (m, 3H). ^{13}C NMR ($CDCl_3$) δ =18.4 (CH3), 98.2, 102.9, 119.9, 113.4, 114.0, 114.5 (CN), 128.1, 128.7, 129.2, 129.9, 130.7, 135.5, 149.8, 151.8. IR (KBr): δ = 3440, 3370, 3250 (NH_2), 2230 (CN), 1655 cm^{-1} (NH_2). MS: m/z (rel inten) 258 (M^+, 100). Anal. Calcd. for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90; N, 21.70. Found: C, 74.41; H, 3.94; N, 21.57.

2,4,5-Tricyano-6-propyl-[1,1 -biphenyl]-3-amine (**5i**); Yield 13%, mp 164-165 ℃. ^{1}H NMR ($CDCl_3$) δ = 0.78 (t, 3H, CH_3), 1.40 (m, 2H), 2.56 (m, 2H), 5.37 (br s, 2H, NH_2), 7.23 (m, 2H), 7.53 (m, 3H). ^{13}C NMR ($CDCl_3$) δ =13.9, 24.1, 33.5, 98.6, 103.2, 119.7, 113.5, 114.0, 114.5 (CN), 128.1, 129.0, 129.8, 135.3, 135.7, 149.7, 151.7. IR (KBr): n = 3460, 3350, 3230 (NH_2), 2220 (CN), 1640 cm^{-1} (NH_2). MS: m/z (rel inten) 286 (M^+, 27), 257 (100). Anal. Calcd. for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.51; H, 4.99; N, 19.56.

2,4,5-Tricyano-5-ethoxy-4-methylaniline (**5j**); Yield 7%, mp 208 -210 ℃. ^{1}H NMR (DMSO-d_6) δ = 1.38 (t, 3H, OCH_2CH_3), 2.24(s, 3H, CH_3), 4.23(q, 2H, OCH_2CH_3), 7.14 (br s, 2H, NH_2), ^{13}C NMR(DMSO-d_6) δ =13.9(OCH_2CH_3), 15.5(CH_3), 71.3

(OCH_2CH_3), 92.2, 95.6, 113.3, 114.4, 114.8, 120.5, 152.6, 164.6. IR (KBr): δ = 3420, 3350, 3250 (NH2), 2230 (CN), 1660 cm^{-1} (NH_2). MS: m/z (rel inten) 226 (M+, 32), 198 (100). Anal. Calcd. for $C_{12}H_{10}N_4O$: C, 63.70; H, 4.46; N, 24.77. Found: C, 63.73; H, 4.35; N, 24.99.

RESULTS AND DISCUSSION

Although most of reaction A proceeded in satisfactory yields, chromatography had to be utilized in the case of reaction B. In order to identify these compounds, the crystal structures of **3g** and N-butyl derivative of **5e** were determined.[6] On the basis of crystal structure analyses, isomeric structure 3′ or 5′ of which formation were possible from half way of each respective long mechanistic steps were denied for these two series.

Reaction A.

Reactions of cycloalkylidenemalononitriles gave 2,6-dicyano-3-ethoxycarbonyl-4,5-polymethyleneaniline derivatives in good yields in most of the cases (entries 1-6). The nucleophiles derived from methyl ketones and aldehydes gave polycyanoanilines in low yields(entries 7, 9 and 10). In the case of unsymmetrical alkylidenemalononitriles, cycloaromatization proceeded regiospecifically on the less hindered side (entries 5-7). Structures of **3e** and **3f** were identified with 1H NMR including DEPT and C-H cosy techniques.

A plausible mechanism of reaction A is shown in Figure 2. In reaction A, carbanion generated from alkylidenemalononitrile with triethylamine adds in Michael addition manner to diethyl dicyanofumarate **2**, and resulted anion attacks the remote cyano carbon to cyclize. Subsequently, the cyclic species release hydrogen cyanide and diethyl carbonate to aromatize.[7]

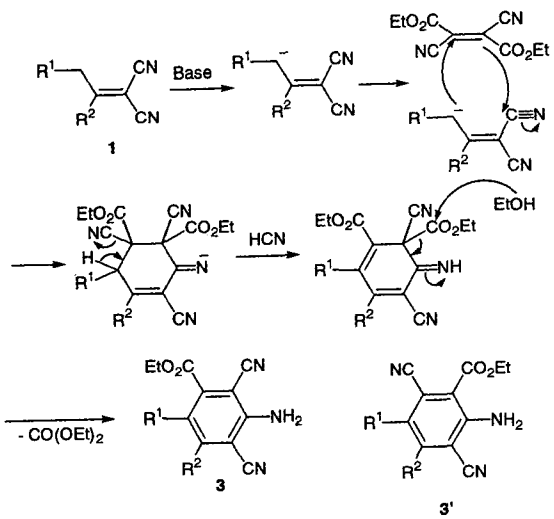


Figure 2. A possible mechanism for reaction A.

Reaction B.

Although the reactions showed some trends similar to those of reaction A, almost all the reactions resulted in only poor yields. When reactive sites are relatively limited in starting materials, relatively better results were obtained (entry 3 and 4). In the case of unsymmetrical cycloalkylidenemalononitriles, cycloaromatization occurred regiospecifically on the less hindered side (entries 4, 5, and 6) as in reaction A. Structures of **5e** and **5f** were identified in the same manner with those of series **3** with NMR.

A speculative mechanism of reaction B is shown in Figure 3. Cyclization and aromatization similar to the reaction A proceeded to form products. In reaction B, addition of

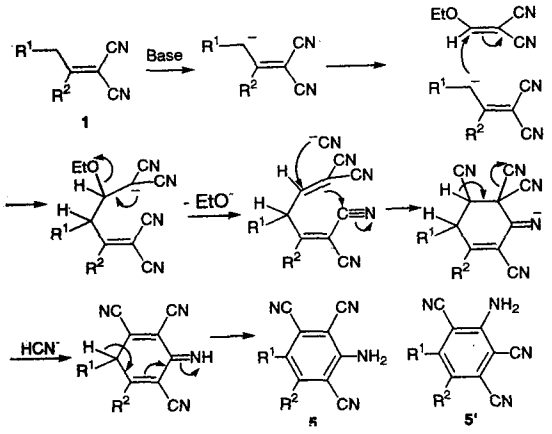


Figure 3. A possible mechanism for reaction B.

equimolar amount of sodium cyanide gave better results than those reactions without it, and all the reactions were carried out in the presence of equimolar amount of sodium cyanide. Extra cyano group was introduced at certain stage.

Fluorescence spectra

Data of fluorescence quantum yields, absorption maxima and wavelength of fluorescence maxima of two series are listed in Table 1 and 2, respectively. In Figure 4 is illustrated qualitatively the relation between the absorption and emission of 3c as an example. Fluorescence maxima of **3** and **5** series were observed at longer wavelength region than absorption maxima (Stoke's Law; 27 -100 nm in **3** and 36-46 nm in **5** series). In the case of 3 series, fluorescence spectra were measured in cyclohexane, acetonitrile had to be used in the case of **5** series due to low solubility of **5** series materials in cyclohexane. Since the quantum yield of fluorescence tends to increase in polar solvents, **3b** and **3c** were measured in cyclohexane and acetonitrile in order to evaluate qualitatively the polarity effect of solvents. Quantum yields of **3b** and **3c** were 0.33 and 0.39 in cyclohexane while 0.61 and 0.60 in acetonitrile, respectively. Indeed significantly large effects were observed. According to Yoshida's empirical rule shown in reference 8, electron-withdrawing groups at meta positions to amino group and electron releasing groups at para position will increase fluorescence intensities. Comparing

the quantum yield data of 3 and 5 series, cyano group has more enhancing effect than ethoxycarbonyl group. Results of fluorescence intensities were consistent with Yoshida's empirical rule. Similar enhancing effects of methyl group at para position to amino group were observed (**5g**-**5i**). This is

Table 1. Fluorescence of dicyanoanilines with ethoxycarbonyl group in cyclohexane.

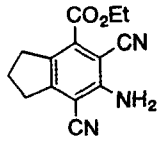
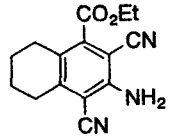
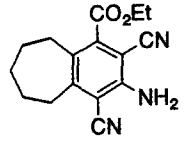
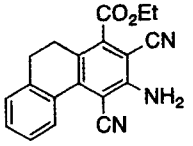
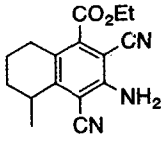
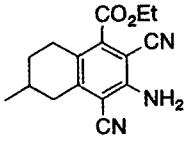
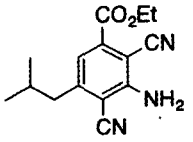
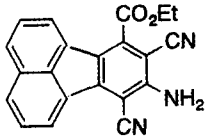
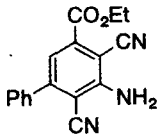
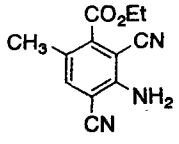
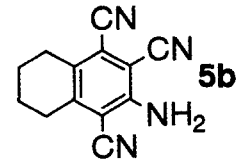
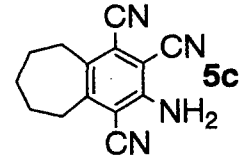
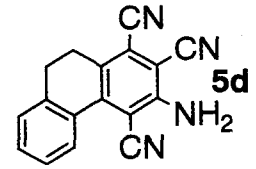
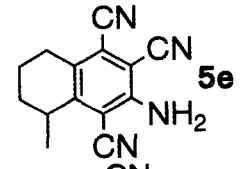
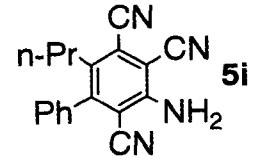
entry		Φ_F	λ_{max}/nm	λ^{fl}_{max}/nm
1	 **3a**	0.58	373	408
2	 **3b**	0.33	357	414
3	 **3c**	0.39	353	417
4	 **3d**	0.27	348	428
5	 **3e**	0.30	359	415
6	 **3f**	0.31	357	416
7	 **3g**	0.33	363	390
8	 **3h**	0.12	335	464,488
9	 **3i**	0.37	375	404
10	 **3j**	0.51	363	408

Table 2. Fluorescence spectra of tricyanoanilines in acetonitrile.

entry	polycyanoanilines	Φ_F	λ_{max}/nm	λ^{fl}_{max}/nm
1	 **5b**	0.93	390	436
2	 **5c**	0.85	392	428
3	 **5d**	0.47	413	456
4	 **5e**	0.86	392	437
5	 **5f**	0.87	393	433
6	 **5g**	0.46	393	432
7	 **5h**	0.80	398	438
8	 **5i**	0.86	335	464,488
9	 **5j**	0.51	388	428

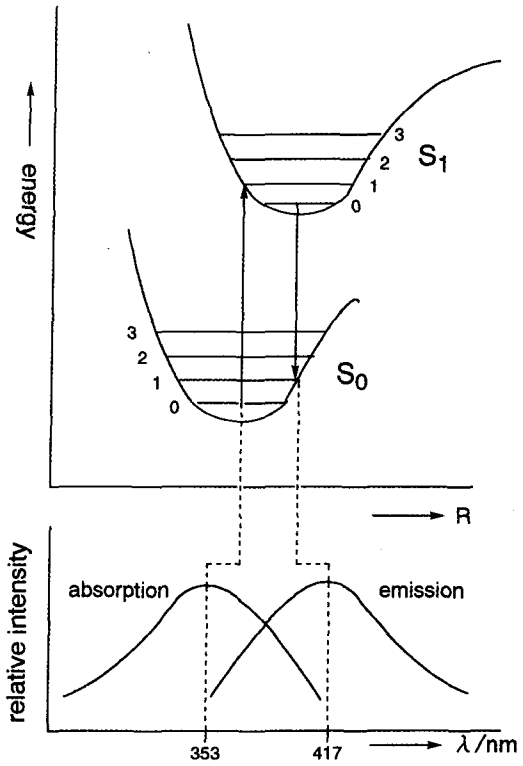


Figure 4. Relation between the absorption and emission maxima of **3C** is illustrated as an example.

probably due to electron-releasing effect of methyl group at para position to the amino group.

In addition to above facts, electronic effects of conjugated systems were observed. Due to large conjugated systems, the energy of excited molecules tends to disperse as a thermal energy. The small quantum yields of **3d** and **3h** were ascribed to the such effects of the conjugation systems. Although almost all the materials showed one fluorescence maximum, only **3h** showed two maxima. **3h** has two chromophores of naphthalene and 3-amino-2,6-dicyanobenzoate system. We assumed that the two emission maxima ascribed to the two exited states of these system.

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