

Synthesis and Some Reactions of 3-Chloro-2-(cyanomethylene)-1,2-dihydroquinoxalines

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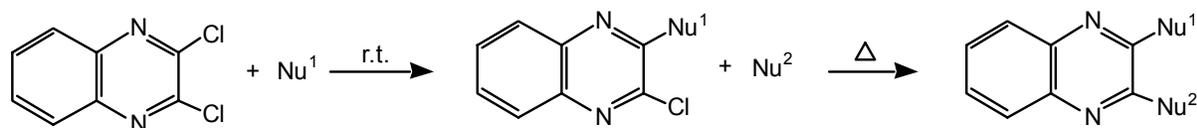
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Abstract: 2,3-Dichloroquinoxaline and some of its derivatives have been reacted with malononitrile and ethyl cyanoacetate to yield a variety of 3-chloro-2-(cyanomethylene)-1,2-dihydroquinoxaline derivatives. The reaction of 3-chloro-2-(dicyanomethylene)-1,2-dihydroquinoxaline (**2e**) with pyridine and its methyl derivatives led to the zwitterionic structures **6a-6c**. The structures of the newly synthesized compounds were assigned by spectroscopic data and elemental analyses.

Keywords: 2,3-Dichloroquinoxaline, ethoxycarbonylcyanomethylene- and dicyanomethylene-3-chloro-1,2-dihydroquinoxalines, betaine structures, spectroscopic data

Introduction

The two reactive chlorine atoms in 2,3-dichloroquinoxaline (**1a**) are prone to nucleophilic displacement reactions by a wide variety of nucleophiles which react in a stepwise manner [1,2]:



The reaction of 2,3-dichloroquinoxaline (**1a**) with carbanions generated from active methylene compounds has not been fully investigated. Pratt and Keresztesy [3] have reported the synthesis of indolizino – and dihydroindolizinoquinoxalines from either the reaction of **1a** with ethyl cyanoacetate and isoquinoline in a one-step process, or the isolation of the monosubstituted intermediates derived from the reaction with ethyl cyanoacetate or malononitrile, followed by the treatment of the reaction products with isoquinoline or pyridine. Novel colored compounds containing the dicyano-methylidene groups conjugated with other chromophores have also been reported [4–7]. In the present paper, detailed synthesis, analysis and spectroscopic properties of some colored quinoxaline compounds containing the ethoxycarbonylcyanomethylene and dicyanomethylene groups are reported.

Results and Discussion

2,3-Dichloroquinoxaline and its derivatives **1a–d** were prepared following the procedure of Komin and Carmack [8], by treatment of 1,2,3,4-tetrahydroquinoxaline-2,3-diones with thionyl chloride in the presence of dimethylformamide (DMF). The reaction of dichloroquinoxalines **1a–d** and the appropriate active methylene compounds (ethyl cyanoacetate or malononitrile) in dimethoxyethane, with sodium hydride as a base, gave good yields of colored crystals of a variety of 3-chloro-2-(cyanomethylene)-1,2-dihydroquinoxaline derivatives as isomeric mixtures of **2** and **3** (Scheme 1). The main reaction products **2** were isolated in pure form, whereas the isomers **3** have been detected only by their NMR-spectra. The structures of the newly synthesized compounds were assigned by their IR-spectra, ¹H- and ¹³C-NMR spectra (see Experimental section).

The products can occur as tautomers **2** and **2'**, however, according to their ¹H-NMR spectra the compounds exist mainly as the 2-(cyanomethylene)-1,2-dihydroquinoxaline derivatives **2** or **3** (in CDCl₃ or DMSO-d₆), with the NH protons (exchangeable with D₂O) showing broad singlets in the downfield region (in the range δ 10.99–14.49 ppm). In the ¹³C-NMR spectra, the central carbon in the =C(CN)R grouping resonates as a quaternary carbon in the δ 41.9–69.3 ppm region, according to Attached Proton Test (APT) experiments. This is in the region reported for the ¹³C- chemical shifts of the central carbon of the =C(CN)₂ in some compounds containing the dicyanomethylene group [9–12].

The 2-position of 6-substituted-2,3-dichloroquinoxalines is presumed to be preferentially attacked by nucleophiles, especially when the substituent at the 6-position is electron-withdrawing, based on greater stability of the intermediate σ-complex and molecular orbital calculations [13]. Inspection of

The infrared spectra of **2a** – **2d**, **4a** and **5** further show that in the solid state, these compounds exist in the methyldene tautomeric form, most probably with an intramolecular hydrogen bond, as shown by the presence, in each infrared spectrum, of carbonyl absorptions at around 1650–1630 cm^{-1} , instead of the normal absorption expected at $> 1700 \text{ cm}^{-1}$ for unconjugated esters. In addition, all the quinoxaline derivatives showed IR absorption bands at around 2200 cm^{-1} , characteristic of the cyano group. The predominant existence of **4a** and **4b** in the tetrazolo forms was supported by the absence of absorption bands at around 2140 cm^{-1} in their IR spectra, as expected for the azido (N_3) group.

As mentioned earlier, excess hydrazine converted **2a** into **5** at room temperature. The ester group (COOEt) does not react under these mild conditions, showing that it is deactivated, most probably due to conjugation of the carbonyl function of the COOEt with the NH group in the HN-C=C-C=O(OR) system [14], and the $\text{-NH}\cdots\text{O=C}$ -hydrogen bonding.

3-Chloro-2-(dicyanomethylene)-1,2-dihydroquinoxaline (**2e**) was reported to react with pyridine to give 12,12-dicyano-12,12a-dihydroindolizino[2,3-b]quinoxaline (**9**) [3]. We have found that the reaction of **2e** with pyridine and its methyl derivatives did not produce **9**, but rather gave red or orange crystals of dicyano(3-pyridinium-1-ylquinoxalin-2-yl)methanides **6a-c** (Scheme 1), whose structural assignments were based on their spectra and analytical data.

The yields, infrared, ^1H - and ^{13}C -NMR spectral and analytical data for the dicyanomethanides, **6**, are given in the Experimental section. In the ^{13}C -NMR spectra, the cyano groups resonate at around δ 120.7 ppm, compared to δ 116.5 ppm observed for the cyano groups in the starting material and related structures **2**.

The formation of the dicyanoquinoxalinemethanides **6**, instead of the reported dicyanoindolizinoquinoxalines **9**, may account for the observation of Pratt and Keresztesy [3] that hydrogen cyanide could not be eliminated from their products. Also in the same report, they suggested structure **10** (based on analysis only) for the product obtained upon heating 3-chloro-2-(ethoxycarbonylcyanomethylene)-1,2-dihydroquinoxaline (**2a**) with quinoxaline. However, in the present studies, the main product obtained upon reacting **2a** with quinoxaline is 2-chloro-3-cyanomethylquinoxaline (**8**), as proven by analysis, ^1H -NMR and mass spectral data.

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Experimental

General:

Melting points were recorded on a Gallenkamp (variable heater) melting point apparatus and are uncorrected. UV spectra were run in MeOH solution on a Lambda-15-Perkin Elmer spectrometer (λ_{max}

in nm ($\log \epsilon$), sh = shoulder). Infrared spectra were recorded on a Buck spectrometer as potassium bromide pellets. ^1H - and ^{13}C -NMR were recorded as CDCl_3 or DMSO-d_6 solutions on a Bruker- AC-250 or JEOL-JNM-GX 400-MHz spectrometers (δ in ppm relative to Me_4Si and H_3PO_4). Mass spectra (E1-MS) were recorded on a Finnigan MAT 312 machine [in m/z (rel. %)].

General Preparation of 3-Chloro-2-(cyanomethylene)-1,2-dihydroquinoxalines (**2a-g**).

The 3-chloro-2-(cyanomethylene)-1,2-dihydroquinoxalines were prepared by reacting 2,3-dichloroquinoxaline derivatives **1a-d** with the appropriate active methylene compound in the presence of sodium hydride. This is exemplified by the preparation of compound **2a** as follows: ethyl cyanoacetate (1.1 mL, 10 mmoles) was added dropwise with stirring to a suspension of sodium hydride (0.25 g, 10.4 mmoles) in dimethoxyethane (20 mL). After the addition, the stirring was continued for 30 min. and then 2,3-dichloroquinoxaline (1.0 g, 5 mmoles) was added. The reaction mixture was stirred at room temperature for 3 h and then heated under reflux for 1 h. The dimethoxyethane was removed on a rotatory evaporator *in vacuo* and the resulting residue was treated with cold aqueous hydrochloric acid to give a yellow product. This was filtered, washed with cold water, dried and then recrystallized from ethanol to give yellow crystals of 3-chloro-2-(ethoxycarbonylcyanomethylene)-1,2-dihydroquinoxaline (**2a**, yield: 85%); m.p. 175–177°C (lit. [3] 174–175°C); IR (cm^{-1}) (KBr): 2200 (ν_{CN}), 1630 (sh) ($\nu_{\text{C=O}}$); ^1H -NMR: 14.49 (br s, NH, D_2O exchangeable), 7.78 (d, 1H, ArH), 7.63 (t, 1H, ArH), 7.37–7.50 (m, 2H, ArH), 4.37 (q, 2H, CH_2), 1.41 (t, 3H, CH_3); ^{13}C -NMR: 170.7 (C=O), 146.0, 143.6, 134.2, 132.3, 128.6, 126.6, 116.5 (CN), 116.4, 69.3 ($=\text{C}(\text{CN})_2$), 62.1 (OCH_2), 14.2 (CH_3); MS: 275 (19.4, M^+), 240 (2.2, $[\text{M}-\text{Cl}]^+$), 231 (7.3, $[\text{M}-\text{CO}_2]^+$), 212 (10.5, $[\text{M}-\text{Cl}-\text{C}_2\text{H}_4]^+$), 203 (100, $[\text{M}-\text{CO}_2-\text{C}_2\text{H}_4]^+$), 167 (62.4, $[\text{M}-\text{CO}_2\text{C}_2\text{H}_5-\text{Cl}]^+$), 114 (14.2), 102 (53.5), 76 (23.9), 75 (21.0).

Compounds **2b-2g** were obtained similarly:

3,6-Dichloro-2-(ethoxycarbonylcyanomethylene)-1,2-dihydroquinoxaline (2b): golden yellow crystals (yield: 82%); m.p. 162–164°C (dec.); IR (cm^{-1}): 2200 (ν_{CN}), 1640 (ν_{CO}); ^1H -NMR: 13.84 (br s, NH, D_2O exchangeable), 8.01 (s, 1H, H-5), 7.72 (d, 1H, H-8), 7.46 (d, 1H, H-7), 4.28 (q, 2H, CH_2), 1.30 (t, 3H, CH_3); Analysis: Calc. For $\text{C}_{13}\text{H}_9\text{Cl}_2\text{N}_3\text{O}_2$: C, 50.34; H, 2.93; N, 13.55. Found: C, 50.15; H, 2.85; N, 13.39.

3,7-Dichloro-2-(ethoxycarbonylcyanomethylene)-1,2-dihydroquinoxaline (3b): ^1H -NMR: 13.85 (br s, NH, D_2O exchangeable), 8.10 (s, 1H, H-8), 7.80 (d, 1H, H-5), 7.66 (d, 1H, H-6), 4.28 (q, 2H, CH_2), 1.21 (t, 3H, CH_3).

3-Chloro-6-methyl-2-(ethoxycarbonylcyanomethylene)-1,2-dihydroquinoxaline (2c): golden yellow crystals (yield: 79%); m.p. 159–161°C (dec.); IR (cm^{-1}): 2190 (ν_{CN}), 1640 ($\nu_{\text{C=O}}$); ^1H -NMR: 14.46 (br s, NH, D_2O exchangeable), 7.51 (s, 1H, H-5), 7.45 (d, 1H, H-7), 7.31 (d, 1H, H-8), 4.35 (q, 2H, CH_2),

2.48 (s, 3H, CH₃), 1.40 (t, 3H, CH₃); ¹³C-NMR: 170.8 (C=O), 145.5, 143.2, 137.2, 134.2, 133.8, 127.9, 125.9, 116.5 (CN), 68.3 (=C-(CN)₂), 62.5 (OCH₂) 21.0 (CH₃), 14.0 (CH₃); Analysis: Calc. For C₁₄H₁₂ClN₃O₂: C, 58.04; H, 4.17; N, 14.5. Found: C, 58.00; H, 4.10; N, 14.26.

3-Chloro-7-methyl-2-(ethoxycarbonylcyanomethylene)-1,2-dihydroquinoxaline (3c): ¹H-NMR: 14.39 (br s, NH, D₂O exchangeable), 7.59 (d, 1H, H-5), 7.26 (d, 1H, H-6), 7.15 (s, 1H, H-8), 4.35 (q, 2H, CH₂), 2.51 (s, 3H, CH₃). 1.35 (t, 3H, CH₃); ¹³C-NMR: 170.7 (C=O), 145.8, 143.8, 133.8, 132.5, 128.3, 128.1, 128.0, 116.0 (CN), 68.6 (=C(CN)₂), 61.9 (OCH₂), 21.8 (CH₃), 14.1 (CH₃).

3-chloro-2-(ethoxycarbonylcyanomethylene)-6-nitro-1,2-dihydroquinoxaline (2d): golden yellow crystals (yield: 88%); m.p 191-1993°C (dec.); IR (cm⁻¹): 2210 (ν_{CN}), 1650 (ν_{CO}); ¹H-NMR: 11.42 (br s, NH, D₂O exchangeable), 8.48 (s, 1H, H-5), 8.27 (d, 1H, H-7), 7.48 (d, 1H, H-8), 4.37 (q, 2H, CH₂) 1.39 (t, 3H, CH₃); Analysis: Calc. for C₁₃H₉ClN₄O₄: C 48.69, H 2.83, N 17.47. Found C, 48.51; H. 2.80; N, 17.28.

3-Chloro-2-(dicyanomethylene)-1,2-dihydroquinoxaline (2e): golden brown crystals (yield: 78%); m.p. 240-243° C (dec.) (lit. [3] 217° C); IR (cm⁻¹): 2210 (ν_{CN}); ¹H-NMR: 10.99 (br s, NH, D₂O exchangeable), 7.85 (d, 1H, Ar-H), 7.63-7.75 (m, 2H, Ar-H), 7.46 (t, 1H, Ar-H). ¹³C-NMR: 147.3, 142.3, 134.1, 132.0, 130.8, 127.7, 126.1, 118.0, 116.7 (CN), 47.3 (=C(CN)₂); UV (MeOH): 206 (4.18), 222 (4.43), 290 (4.32), 315(sh) (3.95), 435 (4.03); MS: 228 (79.8, M⁺), 192 (20.7, [M-HCl]⁺), 163 (100, [M-CH(CN)₂]⁺), 114 (8.3), 102 (83.8), 76 (37.7), 75 (38.3).

3,6-Dichloro-2-(dicyanomethylene)-1,2-dihydroquinoxaline (2f): brown crystals (yield: 75%); m.p. 190-191° C (dec.); IR (cm⁻¹): 2200 (ν_{CN}); ¹H-NMR: 10.14 (br s, NH, D₂O exchangeable), 8.27 (s, 1H, H-5), 7.63 (d, 1H, H-8), 7.30 (d, 1H, H-7); ¹³C-NMR: 150.0, 142.3, 135.3, 133.6, 129.1, 125.5, 119.7, 118.5 (CN), 45.6 (=C(CN)₂). MS: 264 (54.8, [M+2]⁺), 262 (79.5, M⁺), 226 (23.4, [M-HCl]⁺), 197 (100, [M-CH(CN)₂]⁺), 162 (12.4, [M-CH(CN)₂-Cl]⁺), 136(52.5), 110 (9.1), 100 (42.4), 75 (28.9). Analysis : Calc. for C₁₁H₄Cl₂N₄: C, 50.22; H, 1.53; N, 21.30. Found: C, 50.41; H, 1.50; N, 21.18.

3-Chloro-2-(dicyanomethylene)-6-nitro-1,2-dihydroquinoxaline (2g): brown crystals (yield: 80%); m.p 255-257°C (dec.); IR (cm⁻¹): 2208 (ν_{CN}); ¹H-NMR: 8.33(s, 1H, H-5), 8.19 (d, 1H, H-7), 7.50 (d, 1H, H-8); ¹³C-NMR: 155.5, 145.6, 144.5, 143.4, 142.0, 134.3, 125.8, 123.9, 123.3 (CN?), 44.5 (-C(CN)₂); MS: 273 (41.9, M⁺), 243 (27.6, [M-NO]⁺), 237 (10.8, [M-HCl]⁺), 227 (25.2 [M-NO₂]⁺), 215 (24.21), 208 (12.7, [M-CH(CN)₂]⁺), 162 (16.0), 117 (13.0), 101 (30.0), 75 (48.5); Analysis: Calc. for C₁₁H₄ClN₅O₂: C, 48.28; H, 1.47; N, 25.59. Found: C, 48.20; H, 1.44; N, 25.40.

The Reaction of 2a and 2e with Sodium Azide.

A solution of **2a** (0.5 g, 1.8 mmol) in DMF (20 mL) was stirred with sodium azide (0.3 g, 4.6 mmol) at room temperature for 12 h. The reaction mixture was poured into water and the resulting solid filtered, washed with water and dried in the oven. It was then recrystallized from ethanol to give *tetrazolo[1,5-a]quinoxalin-4(5H)-ylidenecyanoacetic ester (4a)* (0.44 g, yield: 86%); m.p. 315–316°C (dec.); IR (cm⁻¹): 2200 (ν_{CN}), 1635 (ν_{CO}); MS: 282 (27.8, M⁺), 254 (2.0, [M–N₂]⁺), 226 (9.4, [M–N₂–C₂H₄]⁺), 210 (17.4, [M–CO₂–C₂H₄]⁺), 208 (17.6), 182 (67.7, [M–CO₂–C₂H₄–N₂]⁺), 181 (100, [M–CO₂–C₂H₅–N₂]⁺), 155 (46.5), 128 (26.7), 102 (40.8), 90 (48.7), 77 (22.2); Analysis: Calc. for C₁₃H₁₀N₆O₂: C, 55.32; H, 3.57; N, 29.78. Found: C, 55.02; H, 3.38; N, 29.49.

In a similar manner *tetrazolo[1,5-a]quinoxalin-4(5H)-ylidenemalononitrile (4b)* was synthesized: yellow crystals (yield: 85%); m.p. > 340°C; IR (cm⁻¹): 2200 (ν_{CN}); ¹H-NMR: 8.20 (d, 1H, Ar-H), 7.49–7.65 (m, 2H, Ar-H), 7.36 (t, 1H, Ar-H); ¹³C-NMR: 148.9, 140.5, 138.0, 129.3, 125.0, 123.6, 121.5, 120.7, 115.5 (CN), 41.8 (=C(CN)₂); MS: 235 (30.3, M⁺), 207 (36.4, [M–N₂]⁺), 181 (28.5, [M–N₂–CN]⁺), 180 (33.9, [M–N₂–HCN]⁺), 155 (100), 128 (26.1), 102 (52.1), 90 (71.5), 77 (24.8); Analysis: Calc. for C₁₁H₅N₇: C, 56.17; H, 2.14; N, 41.69. Found: C, 56.26; H, 2.00; N, 41.57.

Reaction of 2a with Hydrazine

A solution of **2a** (0.5 g, 1.8 mmol) and hydrazine hydrate (0.9 mL, 18.5 mmol) in DMF (20 mL) was stirred at room temperature for 15 h, after which the solvent was removed on a rotatory evaporator under reduced pressure. The resulting residue was recrystallized from ethanol to give light yellow crystals (0.26 g) of *3-hydrazino-2-(ethoxycarbonylcyanomethylene)-1,2-dihydroquinoxaline (5)* (yield: 53%); m.p. 222–225°C (dec.); IR (cm⁻¹): 2200 (ν_{CN}), 1590 (ν_{CO}); ¹H-NMR: 8.14 (br s, 1H, NH, D₂O exchangeable), 7.86–7.96 [m, 3H, 2Ar-H+NH (D₂O exchangeable)], 7.49–7.60 (m, 2H, Ar-H), 5.81 (br s, NH₂, D₂O exchangeable), 4.32 (q, 2H, CH₂), 1.34 (t, 3H, CH₃); MS: 271 (70.7, M⁺), 227 (19.4 [M–CO₂]⁺), 225 (76.5, [M–C₂H₅–NH₃]⁺), 199 (100, [M–C₂H₅–NH₃–CN]⁺), 169 (21.0), 102 (24.0), 90 (18.7); Analysis: Calc. for C₁₃H₁₃N₅O₂: C, 57.56; H, 4.83; N, 25.82. Found: C, 57.50; H, 4.81; N, 25.71.

Typical Procedure for the Synthesis of Dicyano(3-pyridinium-1-ylquinoxalin-2-yl)methanides 6a-c from 2e

To a solution of **2e** (0.5 g, 2.2 mmol) in absolute EtOH (40 mL) was added pyridine (3.5 mL, 43 mmol) and the resulting solution refluxed for 6 h. The reaction mixture was cooled and the colored solid was filtered off, washed with EtOH and then dried *in vacuo* to give 0.56 g of *dicyano(3-pyridinium-1-ylquinoxalin-2-yl)methanide (6a)* as orange crystals (yield: 95%); m.p. 342–345°C; IR (cm⁻¹): 2200, 2160 (ν_{CN}); ¹H-NMR: 9.53 (d, 2H, J_{2,3'} = 5.45, 2'-PyH), 8.89 (t, 1H, J_{4,3'} = 7.89, 4'-PyH),

8.42 (t, 2H, $J = 7.24$, 3'-PyH), 7.72 – 7.79 (m, 3H, quinoxaliny-H), 7.42-7.49 (m, 1H quinoxaliny-H); $^{13}\text{C-NMR}$: 120.7 (CN) 144.0 (C-2) 150.2 (C-3) 128.3 (C-5), 125.4 (C-6), 132.0 (C-7), 125.6 (C-8), 141.5 (C-9), 134.5 (C-10), 145.5 (C-2'), 128.5 (C-3'), 148.5 (C-4'), 128.5 (C-5'), 145.4 (C-6'), 37.1 ($=\text{C}(\text{CN})_2$); UV (MeOH): 220 (4.52), 277 (4.28), 311 (4.30), 415 (3.68), 460 (sh) (3.64); MS: 271 (100, M^+), 245 (11.2, $[\text{M-CN}]^+$), 192 (22.6, $[\text{M-C}_5\text{H}_5\text{N}]^+$), 167 (74.3), 102 (67.9), 79 (19.6); Analysis: Calc. for $\text{C}_{16}\text{H}_9\text{N}_5$: C, 70.84; H, 3.34, N, 25.82. Found: C, 70.65; H, 3.11; N, 25.80.

In a similar manner, **6b** and **6c** were synthesized:

Dicyano(3-(3'-methylpyridinium)-1-ylquinoxalin-2-yl)methanide (6b): red crystals (yield: 94%); m.p. 297-300°C; IR (cm^{-1}): 2210, 2160 (ν_{CN}); $^1\text{H-NMR}$: 9.43 (s, 1H, 2'-pyH), 9.35 (d, 1H, $J_{6,5'} = 6.01$. 6'-PyH), 8.73 (d, 1H, $J_{4,5'} = 8.11$, 4'-PyH), 8.29 (t, 1H, $J = 7.06$, 5'-PyH), 7.69-7.78 (m, 3H, quinoxaliny-H), 7.41-7.48 (m, 1H quinoxaliny-H), 2.59 (s, 3H, CH_3); $^{13}\text{C-NMR}$: 120.7 (CN), 144.0 (C-2), 150.2 (C-3), 127.8 (C-5), 125.4 (C-6), 132.0 (C-7), 125.6 (C-8), 141.3 (C-9), 134.5 (C-10), 142.7 (C-2'), 139.4 (C-3), 148.6 (C-4'), 128.3 (C-5'), 144.5 (C-6') 37.2 ($=\text{C}(\text{CN})_2$), 17.9 (CH_3). MS: 285 (100, M^+), 270 (5.0, $[\text{M-CH}_3]^+$), 259 (45.1, $[\text{M-CN}]^+$), 192 (11.1, $[\text{M-CH}_3\text{-C}_5\text{H}_4\text{N}]^+$), 167 (40.3), 129 (8.9), 102 (53.5), 93 (26.7); Analysis: Calc for $\text{C}_{17}\text{H}_{11}\text{N}_5$: C, 71.56; H, 3.89; N, 24.55. Found: C, 71.27; H, 3.68; N, 24.50.

Dicyano(3-(4'-methylpyridinium)-1-ylquinoxalin-2-yl)methanide (6c): as red crystals (yield: 96%); m.p. 283-285°C; IR (cm^{-1}): 2210, 2170 (ν_{CN}); $^1\text{H-NMR}$: 9.33 (d, 1H, $J = 6.77$, 2'-PyH), 8.23 (d, 2H, $J = 6.47$, 3'-PyH), 7.68-7.77 (m, 3H, quinoxaliny-H), 7.40-7.47 (m, 1H, quinoxaliny-H), 2.72 (s, 3H, CH_3); $^{13}\text{C-NMR}$: 120.8 (CN), 144.0 (C-2), 150.5 (C-3), 128.4 (C-5), 125.3 (C-6), 132.0 (C-7), 125.7 (C-8), 141.3 (C-9), 144.2 (C-2'), 128.7 (C-3'), 162.4 (C-4'), 128.7 (C-5'), 144.2 (C-6'), 37.2 ($=\text{C}(\text{CN})_2$), 22.0 (CH_3); MS: 285 (100, M^+), 270 (2.0, $[\text{M-CH}_3]^+$), 259 (14.3, $[\text{M-CN}]^+$), 192 (8.5, $[\text{M-CH}_3\text{-C}_5\text{H}_4\text{N}]^+$), 167 (47.0), 142 (9.4), 102 (40.2), 93 (15.6); Analysis: Cal. For $\text{C}_{17}\text{H}_{11}\text{N}_5$: C, 71.56; H, 3.89; N, 24.55. Found: C, 71.33; H, 3.71; N, 24.46.

Reaction of **2a** with Quinoxaline

A mixture of **2a** (1.0 g, 3.6 mmoles) and quinoxaline (1.1 g, 8.5 mmoles) in dimethoxyethane (50 mL) was heated under reflux for 20 h. TLC showed the presence of two main spots, corresponding to the starting material **2a** and the main reaction product, *2-chloro-3-cyanomethylquinoxaline (8)*. Separation was achieved by column chromatography (silica gel) to give **8** as orange crystals (0.2 g, yield: 27%); m.p 140-143°C (dec.); IR (cm^{-1}): 2240 (ν_{CN}); $^1\text{H-NMR}$: 8.13-8.19 (m, 1H, Ar-H), 8.02-8.09 (m, 1H, ArH), 7.81 – 7.89 (m, 2H, Ar-H), 4.29 (s, 2H, CH_2); $^{13}\text{C-NMR}$ (CDCl_3): 145.4, 144.3, 141.7, 140.6, 131.7, 131.0, 129.1, 128.2 (quinoxaliny group), 114.7 (CN), 25.8 (CH_2); MS: 205 (31.9, $[\text{M}+2]^+$), 203 (100, M^+), 168 (74.9, $[\text{M-Cl}]^+$), 163 (8.9, $[\text{M-CH}_2\text{CN}]^+$), 102 (38.4), 76

(12.9); Analysis: Calc. for C₁₀H₆ClN₅ : C, 58.98; H, 2.97; N, 20.64. Found: C, 58.90; H, 2.80; N, 20.54.

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