Synthesis of Condensed Quinoxalines

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A novel efficient synthesis of fluorescent, fused quinoxalines was achieved. 6-Triazolylthiazolo[4,5-*b*]quinoxalines were synthesized by the diazotisation of 6-amino-2-methylthiazolo[4,5-*b*]quinoxaline and coupling with selected aromatic amines followed by air oxidation. Diazotised aryl amines were coupled with 6-amino-2-methylthiazolo[4,5-*d*]quinoxaline followed by subsequent air oxidation afforded 1,2,3-triazolo[5,4-*f*]quinoxalino[2,3-*d*]thiazoles. 6-Amino-2-methylthiazolo[4,5-*b*]quinoxaline was condensed with conjugated enol ethers followed by cyclization in dowtherm resulted in thiazolo[4,5-*b*]quinoxalino[6,5-*b*]pyridine.

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Many novel heterocyclic compounds have been synthesized and reported as dyes and fluorescent brighteners in the recent past. A fluorophoric heterocycle such as 1,2,3-triazole pendant to another heterocycle in a suitable position finds an exceedingly important place in some commercial fluorescent whiteners described in the patent literature [1-3]. Compounds with 1,2,3-triazole ring system attract special attention on account of their strong fluorescence [4]. Some fused and pendant 1,2,3-triazolyl compounds have been reported by us previously [5,6]. The condensation of a variety of aromatic and heterocyclic amino compounds with conjugated enol ethers followed by cyclisation of the α-aminoethylene-β-carboxylates resulted in useful fused pyridine derivatives [7-8]. Several patents describe the synthesis and technical importance of quinoxalines as useful cyanine dyes [9], reactive dyes [10], azo dyes [11], fluorescent dyes [12] and pigments [13]. However, in general there has been little exploitation of quinoxaline derivatives in the field of dyestuffs. We have recently reported the synthesis of novel heterocyclic dyes and fluorescent brighteners such as thiophenes [14], benzo[*b*]thiophenes [15], pyridines [16], thiazoles [17] and their application on synthetic fibres. The versatility of quinoxalines in the dyestuff field [18-22] was also demonstrated by us. The results of this study have encouraged us to explore the utility of compound **1** in the synthesis of fused and pendant heterocyclic fluorescent compounds. Quinoxaline moiety has been extensively studied in the field of medicine [23] and fungicides [24].

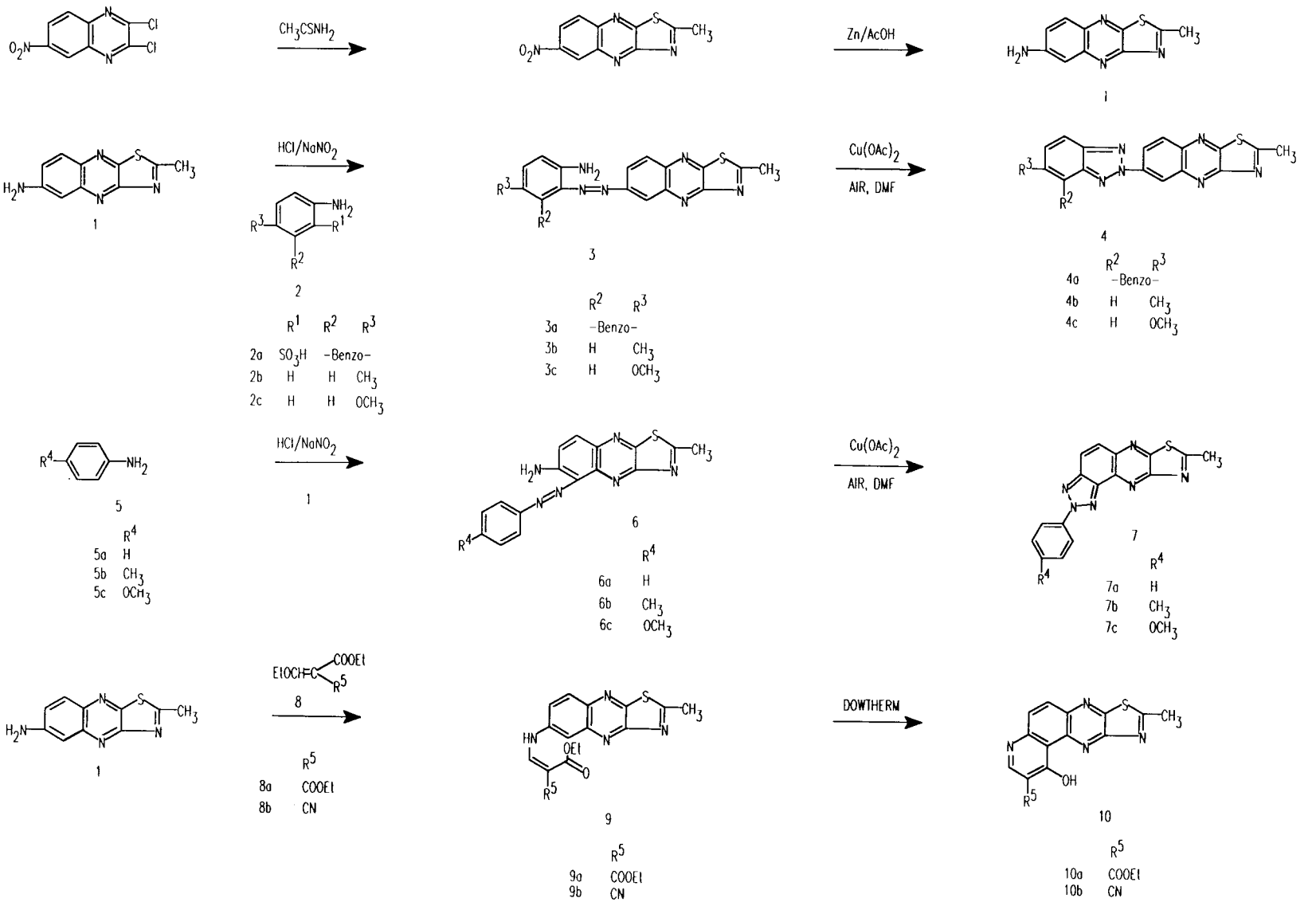
In this communication, we wish to report a facile synthesis of few hitherto unknown condensed quinoxalines by a novel method. 6-Amino-2-methylthiazolo[4,5-*b*]quinoxaline **1** is a versatile intermediate in the synthesis of heterocyclic systems. It is interesting to study various characteristics reactions of **1** in developing novel, fluorescent heterocycles. The key compound **1** has been synthesized by the cyclocondensation reaction of 2,3-dichloro-6-nitroquinoxaline with thioacetamide followed by reduction [18].

In connection with our interest to study fluorescent properties of **4**, we have devised the following route for the efficient synthesis of **3**, a precursor of **4**. The sequence involved in the present synthesis consists of the diazotisation of **1** using hydrochloric acid and sodium nitrite and coupling with selected aromatic amino coupling components **2**, such as tobias acid (2-aminonaphthalene-1-sulfonic acid) **2a**, *p*-toluidine **2b**, *p*-anisidine **2c** to give excellent yields of 78-89% *o*-aminoarylazo compounds **3a-3c**. The compounds **3a-3c** were converted to 6-triazolylthiazolo[4,5-*b*]quinoxalines using cupric acetate, in refluxing *N,N*-dimethylformamide, in a current of bubbling air [25].

As a part of our study to enhance the fluorescent characteristics of the heterocycles, it was planned to introduce two five membered heterocyclic rings condensed to quinoxalines at 2,3- and 5,6-positions. It was envisaged to develop most compact structure of the heterocycles. Because of the compactness of structures of heterocyclic systems and flow of electrons from one part to the other resulted in enhancing the fluorescent properties of the compounds. Diazotised aryl amines such as aniline **5a**, *p*-toluidine **5b**, *p*-anisidine **5c** were coupled with **1** to give *o*-aminoarylazo compounds **6a-6c**, which were oxidized with cupric acetate in DMF, in a current of bubbling air [25] afforded triazolo[5,4-*f*]quinoxalino[2,3-*d*]thiazoles **7a-7c**.

The object of this present study was the synthesis of fused heterocyclic compounds. It was therefore planned to develop a six membered fluorophore such as pyridine fused to quinoxaline at 5,6-position and study the fluorescent properties of fused quinoxalines. 6-Amino-2-methylthiazolo[4,5-*b*]quinoxaline **1** has been condensed with conjugated enol ethers such as diethyl ethoxymethylene malonate (EMME) **8a** and ethyl ethoxymethylenecyanoacetate (EMCA) **8b** afforded ethyl 6-aminoacrylates **9a-9b** which were cyclised in dowtherm to yield thiazolo[4,5-*b*]-quinoxalino[6,5-*b*]pyridines **10a-10b**.

The fluorescent properties of the compounds **4a-4c**, **7a-7c** and **10a-10b** have been studied and the wave-length


CH3CSNH2
Zn/AcOH
HCl/NaNO2
Cu(OAc)2
AIR, DMF
DOWTHERM
8
1
2
3
4
5
6
7
9
10
R1 R2 R3
2a SO3H -Benzo-
2b H H CH3
2c H H OCH3
3a -Benzo-
3b H CH3
3c H OCH3
4a -Benzo-
4b H CH3
4c H OCH3
R4
5a H
5b CH3
5c OCH3
6a H
6b CH3
6c OCH3
7a H
7b CH3
7c OCH3
R5
8a COOEt
8b CN
9a COOEt
9b CN
10a COOEt
10b CN

of absorption maxima, fluorescence emission maxima and the values of the logarithms of the extinction coefficients were recorded. The application to synthetic fibres (polyester) resulted in moderate whitening of the fibres. The compounds **4a-4c**, **7a-7c** and **10a-10b** possessed bluish green fluorescence in daylight in most of the organic solvents.

EXPERIMENTAL

All melting points are uncorrected and are in °C. The infrared spectra were recorded on Perkin-Elmer Model 397 spectrophotometer in Nujol mull. The ^{1}H nmr spectra were recorded on Varian-60 MHz instrument EM-360-L using TMS as internal standard and the chemical shifts are given in δ (ppm) scale. Mass spectra were recorded on a Varian Mat-311 instrument (70 eV). Absorption and fluorescence emission spectra in DMF solution were recorded on Beckman Model-25 spectrophotometer and Aminco Bowman Spectrophotofluorometer, respectively.

6-(2-Amino-1-naphthyl)azo-2-methylthiazolo[4,5-*b*]quinoxaline (**3a**).

To a solution of 20 ml of concentrated hydrochloric acid, was dissolved 1.08 g (0.005 mole) of 6-amino-2-methylthiazolo[4,5-*b*]-quinoxaline **1** by warming and the solution was then cooled to 0-5°. With vigorous stirring, 0.38 g (0.0055 mole) of sodium nitrite in 3 ml of water was gradually added to this solution in 1 hour at 0-5°. The reaction mixture was stirred for a further 1 hour, maintaining the temperature of 0-5°. The excess of nitrous acid was decomposed by the addition of urea. The clear diazonium salt solution was slowly added to 1.115 g (0.005 mole) of tobias acid **2a** in 5 ml of acetic acid at 0°. The *p*H of the reaction mixture was maintained at 4-5 throughout the coupling period by addition of sodium carbonate in portions for 2 hours at 0°. After the addition of diazonium salt was over, the reaction mixture was stirred for a further period of 4 hours and the partially separated dye was completely precipitated by neutralization. The dye was filtered, washed with water and dried. Recrystallisation from ethanol yielded 1.64 g (89%) of **3a**, mp 286-287°.

Anal. Calcd. for $C_{20}H_{14}N_6S$: C, 64.86; H, 3.78; N, 22.70; S, 8.64. Found: C, 64.92; H, 3.84; N, 22.63; S, 8.61.

6-(2-Amino-5-methylphenyl)azo-2-methylthiazolo[4,5-*b*]quinoxaline (**3b**).

The same procedure as described for **3a** was applied except *p*-toluidine **2b** was used in place of **2a**, yielding 6-(2-amino-5-methylphenyl)azo-2-methylthiazolo[4,5-*b*]quinoxaline **3b**, recrystallised from ethanol to yield 1.40 g (84%) of **3b**, mp 194°.

Anal. Calcd. for $C_{17}H_{14}N_6S$: C, 61.07; H, 4.19; N, 25.14; S, 9.58. Found: C, 61.11; H, 4.23; N, 25.11; S, 9.61.

6-(2-Amino-5-methoxyphenyl)azo-2-methylthiazolo[4,5-*b*]quinoxaline (**3c**).

The same procedure as described for **3a** was applied except *p*-anisidine **2c** was used in place of **2a**, yielding 6-(2-amino-5-methoxyphenyl)azo-2-methylthiazolo[4,5-*b*]quinoxaline **3c**, recrystallised from methanol to yield 1.36 g (78%) of **3c**, mp 148°.

Anal. Calcd. for $C_{17}H_{14}N_6OS$: C, 58.28; H, 4.00; N, 24.00; S, 9.14. Found: C, 58.22; H, 4.09; N, 24.04; S, 9.11.

2-Methyl-6-(naphtho[1,2-*d*]-1,2,3-triazol-2-yl)thiazolo[4,5-*b*]quinoxaline (**4a**).

To a solution of 1.85 g (0.005 mole) of **3a** in 15 ml of *N,N*-dimethylformamide was added 1 g (0.0052 mole) of cupric acetate. The reaction mixture was brought to reflux temperature. Air was continuously bubbled through the reaction mixture and the reflux was continued for 4 hours. The reaction mixture was cooled and then added to 100 ml of 5% ice cold hydrochloric acid with constant stirring. The precipitated solid was filtered, washed with water, dried and recrystallised from DMF to yield 1.34 g (73%) of **4a**, mp 329-331°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 2.9 (s, 3H, CH_3), δ 8.1-8.6 (m, 9H, aromatic); ms: m/z 368 (M^+); λ max absorption 384 nm, λ max emission 441 nm, log ϵ 4.31.

Anal. Calcd. for $C_{20}H_{12}N_6S$: C, 65.21; H, 3.26; N, 22.82; S, 8.69. Found: C, 65.18; H, 3.21; N, 22.86; S, 8.73.

2-Methyl-6-(5-methylbenzo[1,2-*d*]-1,2,3-triazol-2-yl)thiazolo[4,5-*b*]-quinoxaline (**4b**).

The same procedure as described for the oxidation of **3a** to **4a** was applied to the oxidation of **3b**, yielding 2-methyl-6-(5-methylbenzo[1,2-*d*]-1,2,3-triazol-2-yl)thiazolo[4,5-*b*]quinoxaline **4b**, recrystallized from DMF to yield 1.09 g (66%) of **4b**, mp 344°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 3.0 (s, 6H, $2CH_3$), δ 8.0-8.5 (m, 6H, aromatic); ms: m/z 332 (M^+); λ max absorption 375 nm, λ max emission 437 nm, log ϵ 4.19.

Anal. Calcd. for $C_{17}H_{12}N_6S$: C, 61.44; H, 3.61; N, 25.30; S, 9.63. Found: C, 61.48; H, 3.65; N, 25.34; S, 9.67.

2-Methyl-6-(5-methoxybenzo[1,2-*d*]-1,2,3-triazol-2-yl)thiazolo[4,5-*b*]quinoxaline (**4c**).

The same procedure as described for the oxidation of **3a** to **4a** was applied to the oxidation of **3c**, yielding 2-methyl-6-(5-methoxybenzo[1,2-*d*]-1,2,3-triazol-2-yl)thiazolo[4,5-*b*]quinoxaline **4c**, recrystallised from DMF to yield 1.20 g (69%) of **4c**, mp >360°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 2.8 (s, 3H, CH_3), δ 3.95 (s, 3H, OCH_3), δ 8.1-8.65 (m, 6H, aromatic); ms: m/z 348 (M^+); λ max absorption 379 nm, λ max emission 448 nm, log ϵ 4.23.

Anal. Calcd. for $C_{17}H_{12}N_6OS$: C, 58.62; H, 3.44; N, 24.13; S, 9.19. Found: C, 58.66; H, 3.49; N, 24.11; S, 9.13.

6-Amino-5-(phenyl)azo-2-methylthiazolo[4,5-*b*]quinoxaline (**6a**).

To a solution of 10 ml of concentrated hydrochloric acid, was dissolved 0.46 g (0.005 mole) of aniline **5a** and the solution was then cooled to 0-5°. With vigorous stirring 0.38 g (0.0055 mole) of sodium nitrite in 3 ml water was gradually added to this solution in 1 hour at 0-5°. The reaction mixture was stirred for a further 1 hour, maintaining the temperature at 0-5°. The excess of nitrous acid was decomposed by the addition of urea. The clear diazonium solution was slowly added to 1.08 g (0.005 mole) of 6-amino-2-methylthiazolo[4,5-*b*]quinoxaline **1** in 5 ml of acetic acid at 0°. The *p*H of the reaction mixture was maintained at 4-5 throughout the coupling period by addition of sodium carbonate in portions for 1 hour at 0°. After the addition of the diazonium salt was over, the reaction mixture was stirred for a further period of 3 hours and the partially separated dye was completely precipitated by neutralization. The dye was filtered, washed with water and dried. Recrystallisation from ethyl acetate yielded 1.37 g (86%) of **6a**, mp 210°.

Anal. Calcd. for $C_{16}H_{12}N_6S$: C, 60.00; H, 3.75; N, 26.25; S, 10.00. Found: C, 60.06; H, 3.81; N, 26.31; S, 10.03.

6-Amino-5-(4-methylphenyl)azo-2-methylthiazolo[4,5-*b*]quinoxaline (**6b**).

The same procedure as described for **6a** was applied except *p*-toluidine **5b** was used in place of **5a**, yielding 6-amino-5-(4-methylphenyl)azo-2-methylthiazolo[4,5-*b*]quinoxaline **6b**, recrystallised from benzene to yield 1.36 g (82%) of **6b**, mp 176°.

Anal. Calcd. for $C_{17}H_{14}N_6S$: C, 61.07; H, 4.19; N, 25.14; S, 9.58. Found: C, 61.02; H, 4.23; N, 25.11; S, 9.52.

6-Amino-5-(4-methoxyphenyl)azo-2-methylthiazolo[4,5-*b*]quinoxaline (**6c**).

The same procedure as described for **6a** was applied except *p*-anisidine **5c** was used in place of **5a**, yielding 6-amino-5-(4-methoxyphenyl)azo-2-methylthiazolo[4,5-*b*]quinoxaline **6c**, recrystallised from benzene to yield 1.38 g (79%) of **6c**, mp 193-194°.

Anal. Calcd. for $C_{17}H_{14}N_6OS$: C, 58.28; H, 4.00; N, 24.00; S, 9.14. Found: C, 58.31; H, 4.05; N, 24.09; S, 9.10.

2-Methyl-6-*N*-(phenyl)-1,2,3-triazolo[5,4-*f*]quinoxalino[2,3-*d*]thiazole (**7a**).

To a solution of 1.6 g (0.005 mole) of **6a** in 15 ml of *N*,*N*-dimethylformamide was added 1 g (0.0052 mole) of cupric acetate. The reaction mixture was brought to reflux temperature. Air was continuously bubbled through the reaction mixture and the reflux was continued for 4 hours. The reaction mixture was cooled and then added to 100 ml of 5% ice cold hydrochloric acid with constant stirring. The precipitated solid was filtered, washed with water, dried and recrystallised from DMF to yield 1.25 g (79%) of **7a**, mp 310°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 2.9 (s, 3H, CH_3), δ 7.9-8.4 (m, 7H, aromatic); ms: m/z 318 (M^+); λ max absorption 386 nm, λ max emission 446 nm, log ϵ 4.36.

Anal. Calcd. for $C_{16}H_{10}N_6S$: C, 60.37; H, 3.14; N, 26.41; S, 10.06. Found: C, 60.41; H, 3.19; N, 26.37; S, 10.11.

2-Methyl-6-*N*-(4-methylphenyl)-1,2,3-triazolo[4,5-*f*]quinoxalino-[2,3-*d*]thiazole (**7b**).

The same procedure as described for the oxidation of **6a** to **7a** was applied to the oxidation of **6b**, yielding 2-methyl-6-*N*-(4-methylphenyl)-1,2,3-triazolo[5,4-*f*]quinoxalino[2,3-*d*]thiazole **7b** recrystallised from DMF to yield 1.22 g (74%) of **7b**, mp 354°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 3.1 (s, 6H, $2CH_3$), δ 7.8-8.6 (m, 6H, aromatic); ms: m/z 332 (M^+); λ max absorption 389 nm, λ max emission 451 nm, log ϵ 4.22.

Anal. Calcd. for $C_{17}H_{12}N_6S$: C, 61.44; H, 3.61; N, 25.30; S, 9.63. Found: C, 61.40; H, 3.57; N, 25.36; S, 9.64.

2-Methyl-6-*N*-(4-methoxyphenyl)-1,2,3-triazolo[5,4-*f*]quinoxalino-[2,3-*d*]thiazole (**7c**).

The same procedure as described for the oxidation of **6a** to **7a** was applied to the oxidation of **6c**, yielding 2-methyl-6-*N*-(4-methoxyphenyl)-1,2,3-triazolo[5,4-*f*]quinoxalino[2,3-*d*]thiazole **7c**, recrystallised from DMF to yield 1.23 g (71%) of **7c**, mp >360°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 2.9 (s, 3H, CH_3), δ 4.1 (s, 3H, OCH_3), δ 7.9-8.5 (m, 6H, aromatic); ms: m/z 348 (M^+); λ max absorption 391 nm, λ max emission 453 nm, log ϵ 4.31.

Anal. Calcd. for $C_{17}H_{12}N_6OS$: C, 58.62; H, 3.44; N, 24.13; S, 9.19. Found: C, 58.57; H, 3.41; N, 24.19; S, 9.17.

Ethyl 2-Methylthiazolo[4,5-*b*]quinoxaline-6-(β-carbethoxyaminoacrylate) (**9a**).

A mixture of 1.08 g (0.005 mole) of 6-amino-2-methylthiazolo-[4,5-*b*]quinoxaline **1** and (0.005 mole) of ethyl ethoxymethylenemalonic ester (EMME) **8a** was heated in oil bath at 160° for 2 hours. The reaction mixture was cooled to room temperature and slowly added over ice-water mixture with constant stirring. The precipitated solid was filtered, washed with water, dried and recrystallised from methanol to yield 1.23 g (64%) of **9a**, mp 328°.

Anal. Calcd. for $C_{18}H_{18}N_4O_4S$: C, 55.95; H, 4.66; N, 14.50; S, 8.29. Found: C, 55.99; H, 4.71; N, 14.56; S, 8.22.

Ethyl 2-Methylthiazolo[4,5-*b*]quinoxaline-6-(β-cyanoaminoacrylate) (**9b**).

The same procedure as described for **9a** was applied except ethyl ethoxymethylenecyanoacetate (EMCA) **8b** was used in place of **8a**, yielding ethyl 2-methylthiazolo[4,5-*b*]quinoxaline-6-(β-cyanoaminoacrylate) **9b**, recrystallised from methanol to yield 1.16 g (69%) of **9b**, mp 284°.

Anal. Calcd. for $C_{16}H_{13}N_5O_2S$: C, 56.63; H, 3.83; N, 20.64; S, 9.43. Found: C, 56.69; H, 3.81; N, 20.60; S, 9.49.

3-Carbethoxy-4-hydroxy-7-methylthiazolo[4,5-*b*]quinoxalino[6,5-*b*]pyridine (**10a**).

A mixture of 1.93 g (0.005 mole) of **9a** and 10 ml of dowtherm was refluxed for 6 hours. The reaction mixture was then cooled and diluted with 50 ml of petroleum ether. The precipitated solid was filtered, washed with petroleum ether and dried. Recrystallisation from DMF yielded 1.19 g (70%) of **10a**, mp >360°; ir (nujol): 1700, 3500 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 2.9 (s, 3H, CH_3), δ 8.00-8.5 (m, 3H, aromatic), δ 4.2 (q, 2H, CH_2), δ 1.4 (t, 3H, CH_3), δ 11.4 (s, 1H, OH); ms: m/z 340 (M^+); λ max absorption 394 nm, λ max emission 461 nm, log ϵ 4.39.

Anal. Calcd. for $C_{16}H_{12}N_4O_3S$: C, 56.47; H, 3.52; N, 16.47; S, 9.41. Found: C, 56.44; H, 3.56; N, 16.43; S, 9.39.

3-Cyano-4-hydroxy-7-methylthiazolo[4,5-*b*]quinoxalino[6,5-*b*]pyridine (**10b**).

The same procedure as described for the cyclisation of **9a** to **10a** was applied for the cyclisation of **9b**, yielding 3-cyano-4-hydroxy-7-methylthiazolo[4,5-*b*]quinoxalino[6,5-*b*]pyridine **10b**, recrystallised from DMF to yield 1.11 g (76%) of **10b**, mp 352-353°; ir (nujol): 2210, 3400 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 2.8 (s, 3H, CH_3), δ 7.9-8.4 (m, 3H, aromatic), δ 11.5 (s, 1H, OH); ms: m/z 293 (M^+); λ max absorption 396 nm, λ max emission 466 nm, log ϵ 4.43.

Anal. Calcd. for $C_{14}H_7N_5OS$: C, 57.33; H, 2.38; N, 23.89; S, 10.92. Found: C, 57.31; H, 2.34; N, 23.94; S, 10.97.

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