Synthesis of 2-Styrylthiazolo[4,5-*b*]quinoxaline Based Fluorescent Dyes

D. W. Rangnekar [a], N. D. Sonawane [a] and R. W. Sabnis* [b]

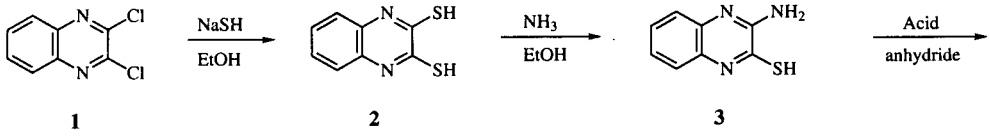
[a] Dyes Research Laboratory, Department of Chemical Technology, University of Mumbai, Matunga, Mumbai 400 019, India
[b] Brewer Science Inc., 2401 Brewer Drive, Rolla, MO 65401, USA

Received June 11, 1998

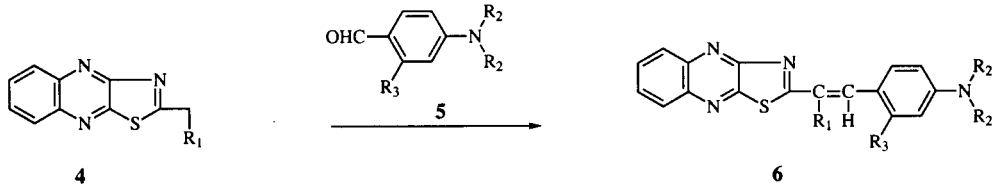
A novel efficient synthesis of 2-styrylthiazolo[4,5-*b*]quinoxaline based fluorescent dyes was achieved by the condensation of 2-alkylthiazolo[4,5-*b*]quinoxaline with selected 4-*N*,*N*-dialkylamino-substituted aryl-aldehydes or hetarylaldehydes in the presence of piperidine or acid anhydride. The coloristic, fluorophoric and dyeing properties of these dyes were studied.

J. Heterocyclic Chem., **35**, 1353 (1998).

Quinoxalines are commercially important as agrochemicals [1], herbicides [2], fungicides [3], antagonists [4], and antibiotics [5]. Several patents describe the synthesis and technical importance of quinoxalines as cyanine dyes [6],



1 2 3



4 5 6

	R_1
a	H
a	H
a	H
b	CH_3
b	CH_3
b	CH_3

	R_2	R_3
a	CH_3	H
b	C_2H_5	H
c	C_2H_5	OMe
a	CH_3	H
b	C_2H_5	H
c	C_2H_5	OMe

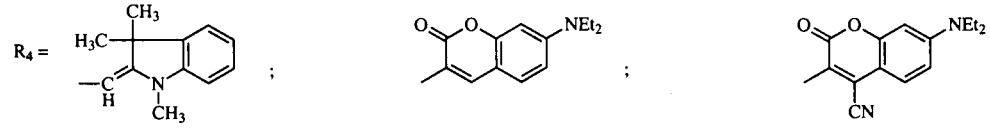
	R_1	R_2	R_3
a	H	CH_3	H
b	H	C_2H_5	H
c	H	C_2H_5	OMe
d	CH_3	CH_3	H
e	CH_3	C_2H_5	H
f	CH_3	C_2H_5	OMe

4 7 8

	R_1
a	H
a	H
a	H
b	CH_3
b	CH_3
b	CH_3

	R_4
a	I
b	II
c	III
a	I
b	II
c	III

	R_1	R_4
a	H	I
b	H	II
c	H	III
d	CH_3	I
e	CH_3	II
f	CH_3	III



I II III

azo dyes [7], reactive dyes [8], hair dyes [9], and pigments [10]. However, in general there has been little exploitation of fused quinoxaline derivatives in the field of styryl dyes. We have recently reported the synthesis of novel heterocyclic dyes and fluorescent brighteners such as thiazoles [11], thiophenes [12], pyridines [13], benzopyrans [14] and their applications on synthetic fibers. The versatility of quinoxalines in the dyestuff field [15-18] was also demonstrated by us. The results of this have encouraged us to explore the utility of 2-alkylthiazolo[4,5-*b*]quinoxaline **4** in the synthesis of 2-styrylthiazolo[4,5-*b*]quinoxaline fluorescent dyes. Styryl dyes attract special attention on account of their strong fluorescence [19,20].

In this communication, we wish to report a facile synthesis of few hitherto unknown fluorescent styryl dyes by a novel method. It is interesting to study various characteristic reactions of **4** in developing novel, fluorescent heterocycles. The key compound **4** has been synthesized by condensation reaction of 2,3-dichloroquinoxaline with sodium hydrogen sulfide, followed by subsequent reaction with ammonia and acid anhydride [21]. In connection with our interest to study fluorescent properties of **6** and **8**, we have devised the route for the efficient synthesis of dyes. The sequence involved in the present synthesis consists of condensation of 2-alkylthiazolo[4,5-*b*]quinoxalines **4a-b** with 4-*N,N*-dialkylamino-substituted aryl and hetarylaldehydes in the presence of piperidine.

As a part of our study to enhance the fluorescent characteristics of the heterocycle, it was planned to introduce 2-ethylthiazolo[4,5-*b*]quinoxaline **4b** in place of **4a** and study the fluorescent properties of dyes. Condensation of **4b** with 4-*N,N*-dialkylamino-substituted aryl and hetarylaldehydes in the presence of acid anhydride generated brighter dyes **6d-f** and **8d-f** having larger stoke's shifts values with respect to the corresponding methyl-substituted dyes **6a-c** and **8a-c**, respectively. In another effort towards enhancing the fluorescence properties, the coumarin-3-aldehydes **7b-c** have been condendensed with thiazolo[4,5-*b*]quinoxaline system which afforded bright deep colored dyes **8b-c**, **8e-f**.

The fluorescent properties of the compounds **6a-f** and **8a-f** have been studied and the wavelength of absorption maxima, fluorescence maxima, stoke's shifts and the values of the logarithms of the extinction coefficients were recorded. The absorption maxima and fluorescence maxima were in the range of 465-528 nm and 568-605 nm, respectively. These dyes show high molar extinction coefficients and their stoke's shifts were in the range of 60-103 nm. The electron donating groups in dyes **6a-f** and **8a-f** generate the bathochromic shifts. These compounds were applied on polyester fibers as fluorescent disperse dyes. The dyes produced the color range from orange to pink. The dyeing properties such as pickup, light fastness and sublimation fastness are evaluated on polyester fibers and are summarized in Table 1. The compounds **6a-f** and **8a-f** possessed strong orange to reddish pink fluorescence in daylight in most of the organic solvents.

Table 1

Dyeing Properties of **6a-f** and **8a-f**

Compound	Color on Polyester Fiber	Pickup	Light Fastness	Sublimation Fastness
6a	Brilliant orange	4	2	4
6b	Brilliant reddish orange	4	2	3
6c	Brilliant red	5	2	4
6d	Orange	4	1	3
6e	Deep orange	3	1	3
6f	Brilliant red	4	2	4
8a	Deep pink	5	1	4
8b	Fluorescent scarlet	4	2	5
8c	Brilliant dark red	4	3	4
8d	Pink	4	1	3
8e	Brilliant reddish orange	4	1	4
8f	Reddish pink	3	2	4

EXPERIMENTAL

All melting points are uncorrected and are in °C. The infrared spectra were recorded on Perkin-Elmer Model 397 spectrophotometer in potassium bromide pellets. The ^{1}H nmr spectra were recorded on Varian-300 MHz instrument using tetramethylsilane as the internal standard and the chemical shifts are given in the δ (ppm) scale. Mass spectra were recorded on a Varian Mat-311 instrument (70 eV). Absorption and fluorescence emission spectra were recorded on a Beckmann Model-25 spectrophotometer and Aminco spectrophtofluorometer, respectively. Evaluation of dyes was done as per international standards. The various aldehydes such as **5a-c**, **7a** are commercially available. Coumarin aldehyde **7b** was synthesized by the conventional Vilsmeier reaction on 7-*N,N*-diethylaminocoumarin. The oxidative cyanation of **7b** afforded a cyanated coumarin aldehyde **7c**. 2-Methyl- and 2-ethylthiazolo[4,5-*b*]quinoxalines **4a-b** were synthesized by a known method [21].

2-[2-(4-*N,N*-Dimethylaminophenyl)ethenyl]thiazolo-[4,5-*b*]quinoxaline (**6a**).

A mixture of 2.01 g (0.01 mole) 2-methylthiazolo[4,5-*b*]quinoxaline **4a** and 1.49 g (0.01 mole) of 4-*N,N*-dimethylaminobenzaldehyde **5a** in absolute ethanol (10 ml) and catalytic amount of piperidine (2-3 drops) was stirred and refluxed for 5 hours. The precipitated solid was filtered, washed with ethanol, dried and recrystallised from benzene:ethyl acetate (10:4) to yield 2.89 g (87%) of **6a** as a red crystalline solid, mp 272°; ^{1}H nmr (deuteriochoroform): δ 3.07 (s, 6H, $N(CH_3)_2$), 6.71 (d, 2H, aromatic), 7.28 (d, 1H, olefinic CH), 7.55 (d, 2H, aromatic), 7.72-7.83 (m, 3H, olefinic CH and aromatic), 8.09-8.12 (m, 1H, aromatic), 8.18-8.21 (m, 1H, aromatic); ms: m/z 332 (M^+); λ max absorption 486 nm, log ε 4.81, λ max emission 577 nm, stoke's shift 91 nm.

Anal. Calcd. for $C_{19}H_{16}N_4S$: C, 68.67; H, 4.81; N, 16.86. Found: C, 68.50; H, 4.71; N, 16.79.

2-[2-(4-*N,N*-Diethylaminophenyl)ethenyl]thiazolo[4,5-*b*]quinoxaline (**6b**).

The same procedure as described for **6a** was applied except 4-*N,N*-diethylaminobenzaldehyde **5b** was used in place of **5a** yielding 2-[2-(4-*N,N*-diethylaminophenyl)ethenyl]thiazolo-[4,5-*b*]quinoxaline **6b**, recrystallised from benzene:ethyl acetate (10:3) to yield 3.06 g (85%) of **6b** as a reddish black crystalline solid, mp 230-231°; ^{1}H nmr (deuteriochloroform): δ 1.22 (t, 6H, $N(C_2H_5)_2$), 3.45 (q, 4H, $N(C_2H_5)_2$), 6.70 (d, 2H, aromatic), 7.24 (d, 1H, olefinic CH), 7.53 (d, 2H, aromatic), 7.70-7.79 (m, 3H, olefinic CH and aromatic), 8.08-8.11 (m, 1H, aromatic), 8.18-8.21 (m, 1H, aromatic); ms: m/z 360 (M^+); λ max absorption 492 nm, log ε 4.94, λ max emission 581 nm, stoke's shift 89 nm.

Anal. Calcd. for $C_{21}H_{20}N_4S$: C, 70.00; H, 5.55; N, 15.55. Found: C, 69.78; H, 5.50; N, 15.48.

2-[2-(4-*N,N*-Diethylamino-2-methoxyphenyl)ethenyl]thiazolo[4,5-*b*]quinoxaline (**6c**).

The same procedure as described for **6a** was applied except 2-methoxy-4-*N,N*-diethylaminobenzaldehyde **5c** was used in place of **5a** yielding 2-[2-(4-*N,N*-diethylamino-2-methoxyphenyl)ethenyl]thiazolo[4,5-*b*]quinoxaline **6c**, recrystallised from benzene:ethyl acetate (10:3) to yield 2.80 g (72%) of **6c** as a violet crystalline solid, mp 156°; ^{1}H nmr (deuteriochloroform): δ 1.21 (t, 6H, $N(C_2H_5)_2$), 2.74 (s, 3H, OCH_3), 3.44 (q, 4H, $N(C_2H_5)_2$), 6.70-6.72 (m, 2H, aromatic), 7.21 (d, 1H, olefinic CH), 7.31 (d, 1H, aromatic), 7.73-7.79 (m, 3H, olefinic CH and aromatic), 8.08-8.12 (m, 1H, aromatic), 8.18-8.22 (m, 1H, aromatic); ms: m/z 390 (M^+); λ max absorption 498 nm, log ε 4.80, λ max emission 579 nm, stoke's shift 81 nm.

Anal. Calcd. for $C_{22}H_{22}N_4OS$: C, 67.69; H, 5.64; N, 14.35. Found: C, 67.60; H, 5.55; N, 14.20.

2-[2-(4-*N,N*-Dimethylaminophenyl)-1-methylethenyl]thiazolo[4,5-*b*]quinoxaline (**6d**).

A mixture of 2.15 g (0.01 mole) 2-ethylthiazolo[4,5-*b*]quinoxaline **4b** and 1.49 g (0.01 mole) of 4-*N,N*-dimethylaminobenzaldehyde **5a** in acetic anhydride (10 ml) was stirred and refluxed for 8 hours. The solvent was removed under vacuum and residue was slowly added to ice-water mixture and neutralized with dilute sodium carbonate solution when the product precipitated. The product was filtered, washed with water, dried and recrystallised from benzene:ethyl acetate (10:3) to yield 2.35 g (68%) of **6d**, mp 209°; ^{1}H nmr (detueriochloroform): δ 2.65 (s, 3H, CH_3), 3.07 (s, 6H, $N(CH_3)_2$), 6.73 (d, 2H, aromatic), 7.55 (d, 2H, aromatic), 7.64 (s, 1H, olefinic CH), 7.78-7.82 (m, 2H, aromatic), 8.10-8.13 (m, 1H, aromatic), 8.18-8.21 (m, 1H, aromatic); ms: m/z 346 (M^+); λ max absorption 465 nm, log ε 4.34, λ max emission 568 nm, stoke's shift 103 nm.

Anal. Calcd. for $C_{20}H_{18}N_4S$: C, 69.36; H, 5.20; N, 16.18. Found: C, 69.21; H, 5.25; N, 16.12.

2-[2-(4-*N,N*-Diethylaminophenyl)-1-methylethenyl]thiazolo-[4,5-*b*]quinoxaline (**6e**).

The same procedure as described for **6d** was applied except 4-*N,N*-diethylaminobenzaldehyde **5b** was used in place of **5a** yielding 2-[2-(4-*N,N*-diethylaminophenyl)-1-methylethenyl]thiazolo[4,5-*b*]quinoxaline **6e**, recrystallised from benzene:ethyl acetate (10:2) to yield 2.43 g (65%) of **6e**, mp 172-173°; ^{1}H nmr (deuteriochloroform): δ 1.22 (t, 6H, $N(C_2H_5)_2$), 2.64 (s, 3H, CH_3), 3.43 (q, 4H, $N(C_2H_5)_2$), 6.72 (d, 2H, aromatic), 7.53 (d, 2H, aromatic), 7.66 (s, 1H, olefinic CH), 7.73-7.78 (m, 2H, aromatic), 8.09-8.12 (m, 1H, aromatic), 8.17-8.21 (m, 1H, aromatic); ms: m/z 374 (M^+); λ max absorption 480 nm, log ε 4.64, λ max emission 579 nm, stoke's shift 99 nm.

Anal. Calcd. for $C_{22}H_{22}N_4S$: C, 70.58; H, 5.88; N, 14.97. Found: C, 70.42; H, 5.84; N, 14.90.

2-[2-(4-*N,N*-Diethylamino-2-methoxyphenyl)-1-methylethenyl]thiazolo[4,5-*b*]quinoxaline (**6f**).

The same procedure as described for **6d** was applied except 2-methoxy-4-*N,N*-diethylaminobenzaldehyde **5c** was used in place of **5a** yielding 2-[2-(4-*N,N*-diethylamino-2-methoxyphenyl)-1-methylethenyl]thiazolo[4,5-*b*]quinoxaline **6f**, recrystallised from benzene:ethyl acetate (10:2) to yield 2.70 g (67%) of **6f**, mp 182°; ^{1}H nmr (deuteriochloroform): δ 1.22 (t, 6H, $N(C_2H_5)_2$), 2.65 (s, 3H, CH_3), 2.71 (s, 3H, OCH_3), 3.44 (q, 4H, $N(C_2H_5)_2$), 6.68-6.71 (m, 2H, aromatic), 7.50 (d, 1H, aromatic), 7.66 (s, 1H, olefinic CH), 7.74-7.78 (m, 2H, aromatic), 8.08-8.11 (m, 1H, aromatic), 8.16-8.19 (m, 1H, aromatic); ms: m/z 404 (M^+); λ max absorption 490 nm, log ε 4.61, λ max emission 589 nm, stoke's shift 99 nm.

Anal. Calcd. for $C_{23}H_{24}N_4OS$: C, 68.31; H, 5.94; N, 13.86. Found: C, 68.21; H, 5.98; N, 13.71.

2-[2-(1,3,3-Trimethyl-2-methyleneindolyl)ethenyl]thiazolo-[4,5-*b*]quinoxaline (**8a**).

A mixture of 2.01 g (0.01 mole) 2-methylthiazolo[4,5-*b*]-quinoxaline **4a** and 2.01 g (0.01 mole) of 1,3,3-trimethyl-2-methyleneindolylcarboxaldehyde **7a** in absolute ethanol (10 ml) and catalytic amount of piperidine (2-3 drops) was stirred and refluxed for 10 hours. The precipitated solid was filtered, washed with ethanol, dried and recrystallised from ethanol to yield 2.30 g (60%) of **8a** as a blackish violet crystalline solid, mp 205°; ^{1}H nmr (deuteriochloroform): δ 1.13 (s, 6H, $2CH_3$), 3.09 (s, 3H, NCH_3), 6.70-6.76 (m, 2H, aromatic), 6.89-6.94 (m, 2H, aromatic), 7.21-7.25 (m, 2H, olefinic CH), 7.72-7.77 (m, 3H, olefinic CH and aromatic), 8.07-8.10 (m, 1H, aromatic), 8.15-8.18 (m, 1H, aromatic); ms: m/z 384 (M^+); λ max absorption 528 nm, log ε 4.87, λ max emission 588 nm, stoke's shift 60 nm.

Anal. Calcd. for $C_{23}H_{20}N_4S$: C, 71.87; H, 5.20; N, 14.58. Found: C, 71.92; H, 5.12; N, 14.22.

2-[2-(7-*N,N*-Diethylamino-3-coumarinyl)ethenyl]thiazolo-[4,5-*b*]quinoxaline (**8b**).

The same procedure as described for **8a** was applied except 7-*N,N*-diethylaminocoumarin-3-carboxaldehyde **7b** was used in place of **7a** yielding 2-[2-(7-*N,N*-diethylamino-3-coumarinyl)-ethenyl]thiazolo[4,5-*b*]quinoxaline **8b**, recrystallised from ethanol to yield 3.63 g (85%) of **8b**, mp 258°; ir (potassium bromide): 2965, 1709, 1670, 1330 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.22 (t, 6H, $N(C_2H_5)_2$), 3.44 (q, 4H, $N(C_2H_5)_2$), 6.62 (s, 1H, aromatic), 6.71 (d, 1H, aromatic), 7.27 (d, 1H, olefinic CH), 7.37 (d, 1H, aromatic), 7.75-7.79 (m, 4H, olefinic CH and aromatic), 8.09-8.12 (m, 1H, aromatic), 8.18-8.21 (m, 1H, aromatic); ms: m/z 428 (M^+); λ max absorption 510 nm, log ε 4.97, λ max emission 578 nm, stoke's shift 68 nm.

Anal. Calcd. for $C_{24}H_{20}N_4O_2S$: C, 67.28; H, 4.67; N, 13.08. Found: C, 67.10; H, 4.65; N, 13.00.

2-[2-(7-*N,N*-Diethylamino-4-cyano-3-coumarinyl)ethenyl]thiazolo[4,5-*b*]quinoxaline (**8c**).

The same procedure as described for **8a** was applied except 7-*N,N*-diethylaminocoumarin-4-cyano-3-carboxaldehyde **7c** was

used in place of **7a** yielding 2-[2-(7-*N,N*-diethylamino-4-cyano-3-coumarinyl)ethenyl]thiazolo[4,5-*b*]quinoxaline **8c**, recrystallised from ethanol to yield 3.85 g (85%) of **8c**, mp 242°; ir (potassium bromide): 2960, 2223, 1711, 1663, 1342 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.21 (t, 6H, $N(C_2H_5)_2$), 3.45 (q, 4H, $N(C_2H_5)_2$), 6.65 (s, 1H, aromatic), 6.72 (d, 1H, aromatic), 7.28 (d, 1H, olefinic CH), 7.42 (d, 1H, aromatic), 7.78-7.82 (m, 3H, olefinic CH and aromatic), 8.08-8.12 (m, 1H, aromatic), 8.16-8.19 (m, 1H, aromatic); ms: m/z 453 (M^+); λ max absorption 515 nm, log ε 4.58, λ max emission 605 nm, stoke's shift 90 nm.

Anal. Calcd. for $C_{25}H_{19}N_5O_2S$: C, 66.22; H, 4.19; N, 15.45. Found: C, 66.12; H, 4.11; N, 15.53.

2-[2-(1,3,3-Trimethyl-2-methyleneindolyl)-1-methylethenyl]thiazolo[4,5-*b*]quinoxaline (**8d**).

A mixture of 2.15 g (0.01 mole) of 2-ethylthiazolo-[4,5-*b*]quinoxaline **4b** and 2.01 g (0.01 mole) of 1,3,3-trimethyl-2-methyleneindolylcarboxaldehyde **7a** in acetic anhydride (10 ml) was stirred and refluxed for 10 hours. The solvent was removed under vacuum and residue was slowly added to ice-water mixture and neutralized with dilute sodium carbonate solution when the product precipitated. The product was filtered, washed with water, dried and recrystallised from ethanol to yield 2.22 g (56%) of **8d**, mp 236-237°; ^1H nmr (deuteriochloroform): δ 1.31 (s, 6H, $2CH_3$), 2.64 (s, 3H, CH_3), 3.74 (s, 3H, NCH_3), 6.79-6.83 (m, 2H, aromatic), 6.88-6.92 (m, 2H, aromatic), 7.20 (d, 1H, olefinic), 7.68 (d, 1H, olefinic CH), 7.72-7.78 (m, 2H, aromatic), 8.11-8.14 (m, 1H, aromatic), 8.18-8.20 (m, 1H, aromatic); ms: m/z 398 (M^+); λ max absorption 526 nm, log ε 4.82, λ max emission 601 nm, stoke's shift 75 nm.

Anal. Calcd. for $C_{24}H_{22}N_4S$: C, 72.36; H, 5.52; N, 14.07. Found: C, 72.15; H, 5.39; N, 14.09.

2-[2-(7-*N,N*-Diethylamino-3-coumarinyl)-1-methylethenyl]thiazolo[4,5-*b*]quinoxaline (**8e**).

The same procedure as described for **8d** was applied except 7-*N,N*-diethylaminocoumarin-3-carboxaldehyde **7b** was used in place of **7a** yielding 2-[2-(7-*N,N*-diethylamino-3-coumarinyl)-1-methylethenyl]thiazolo[4,5-*b*]quinoxaline **8e**, recrystallised from ethanol to yield 3.14 g (71%) of **8e**, mp 249-250°; ir (potassium bromide): 2971, 1706, 1673, 1320 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.22 (t, 6H, $N(C_2H_5)_2$), 2.62 (s, 3H, CH_3), 3.45 (q, 4H, $N(C_2H_5)_2$), 6.78-6.83 (m, 2H, aromatic), 7.35 (d, 1H, aromatic), 7.62 (s, 1H, olefinic CH), 7.80-7.86 (m, 3H, aromatic), 8.10-8.12 (m, 1H, aromatic), 8.18-8.21 (m, 1H, aromatic); ms: m/z 442 (M^+); λ max absorption 502 nm, log ε 4.64, λ max emission 582 nm, stoke's shift 80 nm.

Anal. Calcd. for $C_{25}H_{22}N_4O_2S$: C, 67.87; H, 4.97; N, 12.66. Found: C, 67.49; H, 4.92; N, 12.58.

2-[2-(7-*N,N*-Diethylamino-4-cyano-3-coumarinyl)-1-methylethenyl]thiazolo[4,5-*b*]quinoxaline (**8f**).

The same procedure as described for **8d** was applied except 7-*N,N*-diethylaminocoumarin-4-cyano-3-carboxaldehyde **7c** was used in place of **7a** yielding 2-[2-(7-*N,N*-diethylamino-4-cyano-3-coumarinyl)-1-methylethenyl]thiazolo[4,5-*b*]quinoxaline **8f**, recrystallised from ethanol to yield 2.94 g (63%) of **8f**, mp 234°; ir (potassium bromide): 2953, 2239, 1715, 1669, 1324 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.22 (t, 6H, $N(C_2H_5)_2$), 2.65 (s, 3H, CH_3), 3.44 (q, 4H, $N(C_2H_5)_2$), 6.79-6.83 (m, 2H, aromatic), 7.36 (d, 1H, aromatic), 7.69 (s, 1H, olefinic CH), 7.80-7.85 (m, 2H, aromatic), 8.09-8.12 (m, 1H, aromatic), 8.17-8.20 (m, 1H, aromatic); ms: m/z 467 (M^+); λ max absorption 505 nm, log ε 4.68, λ max emission 598 nm, stoke's shift 93 nm.

Anal. Calcd. for $C_{26}H_{21}N_5O_2S$: C, 66.80; H, 4.49; N, 14.98. Found: C, 66.75; H, 4.41; N, 14.80.

REFERENCES AND NOTES

[1] C. Kaneko and S. Katagiri, Asahi Glass Co. Ltd., Japan Kokai Tokkyo Koho Japan Patent 62,207,264 (1988); *Chem. Abstr.*, **109**, 231061 (1988).

[2] T. Hiramatsu, S. Azuma, K. Nakagawa and Y. Ichikawa, Teijin Ltd., Japan Kokai Tokkyo Koho, Japan Patent 62,263,163 (1988); *Chem. Abstr.*, **109**, 73473 (1988).

[3] W. Lunkenheimer and K. H. Buechel, Bayer AG, German Offen DE 2,342,724 (1975); *Chem. Abstr.*, **82**, 156379 (1975).

[4] R. Sarges, H. R. Howard, R. C. Browne, L. A. Lebel and P. A. Seymour, *J. Med. Chem.*, **33**, 2240 (1990).

[5] H. Kinashi, S. L. Otten, J. S. Dunkan and C. R. Hutchinson, *J. Antibiot.*, **41**, 624 (1988).

[6] C. H. Eldredge and J. D. Mee, Eastman Kodak Co., U. S. Patent 3,674,782 (1972); *Chem. Abstr.*, **77**, 128093 (1972).

[7] W. Sauer, A. Seifert and J. H. Binte, East German Patent 101,910 (1975); *Chem. Abstr.*, **83**, 61643 (1975).

[8] S. Ishii, M. Nakamoto and S. Kawasaki, Dainippon Printing Co. Ltd., Japan Kokai Tokkyo Koho, Japan Patent 62,44,077 (1988); *Chem. Abstr.*, **108**, 57836 (1988).

[9] D. Rose, E. Lieske and H. Hoeffkes, Henkel K-GaA, German Offen DE 3,825,212 (1990); *Chem. Abstr.*, **113**, 237554 (1991).

[10] G. Sarodnick, G. Kempter and M. Klepel, VEB Fahlberg-List, East German Patent DD 276,480 (1990); *Chem. Abstr.*, **113**, 231411 (1991).

[11] D. W. Rangnekar and P. Y. Kamat, *Synth. Commun.*, **20**, 2447 (1990).

[12] D. W. Rangnekar and R. W. Sabnis, *J. Chem. Tech. Biotechnol.*, **47**, 39 (1990).

[13] D. W. Rangnekar and R. C. Phadke, *Synthesis*, 484 (1987).

[14] D. W. Rangnekar and S. V. Dhamnaskar, *J. Heterocyclic Chem.*, **25**, 1767 (1988).

[15] D. W. Rangnekar and R. C. Phadke, *Bull. Chem. Soc. Japan*, **59**, 1245 (1986).

[16] D. W. Rangnekar and R. W. Sabnis, *J. Heterocyclic Chem.*, **29**, 65 (1992).

[17] D. W. Rangnekar and R. W. Sabnis, *J. Heterocyclic Chem.*, **28**, 1105 (1991).

[18] D. W. Rangnekar and S. V. Mavlankar, *Dyes Pigm.*, **19**, 259 (1992).

[19] E. Belgodere, R. Bossio, S. Chimichi, V. Parrini and R. Pepino, *Dyes Pigm.*, **4**, 59 (1983).

[20] J. Jaung, M. Matsuoka and K. Fukunishi, *Dyes Pigm.*, **31**, 141 (1996).

[21] H. Saikachi and S. Tagami, *Chem. Pharm. Bull.*, **9**, 941 (1961).