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Synthesis and application of 2-styryl-6(7)-bromothiazolo[4,5-b]quinoxaline based fluorescent dye chromophores: Part 2 ☆

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Abstract

A novel efficient synthesis of 2-styryl-6(7)-bromothiazolo[4,5-b]quinoxaline based fluorescent dyes was achieved by the condensation of 2-alkyl-6(7)-bromothiazolo[4,5-b]quinoxaline with selected 4-*N,N*-dialkylamino-substituted arylaldehydes and heteroarylaldehydes in the presence of piperidine or acid anhydride. The colouristic, fluorophoric, and dyeing properties of these dyes were studied.

Keywords: Bromothiazolo[4,5-b]quinoxaline; Synthesis; Fluorescent dyes; Fluorescence lifetimes; Absorption and emission spectra; Dyeing properties

1. Introduction

Fluorescent heterocyclic compounds are of interest as functional materials for applications involving tunable dye lasers [1], molecular probes for biochemical research [2], and traditional textile and polymer fields [3]. Fluorophores are also useful tools in the search for new biologically active compounds, and in the development of new diagnostic methods [4,5]. While heterocyclic systems such as coumarins [5,6], triazoles [7], benzimidazoles [8], pyrazines [9], napthalimides [10] and oxadiazoles [11] are well established fluorescent dye chromophores, there has been little exploitation of fused quinoxaline systems as fluorescent styryl dyes. Styryl dyes are of interest because of their strong fluorescence [12,13].

Recently the synthesis of novel dyes and fluorescent brighteners containing thiazoles [14], thiophenes [15], pyridines [16], benzopyrans [17] and their application to synthetic fibers have been reported. In earlier work from our laboratories, the versatility of quinoxalines has been demonstrated [18–21]. In addition, the thiazolo[4,5-b]quinoxaline system [22], was employed to develop new fluorescent dyes. These results led us to explore the utility of 2-alkyl-6(7)-bromothiazolo[4,5-b]quinoxaline (**7**) in the synthesis of 2-styryl-6(7)-bromothiazolo-[4,5-b]quinoxaline daylight fluorescent dyes.

In the present paper, the chemistry of new fluorescent dyes is reported. A key goal of this work was to determine the effects of bromo-substitution on the colouristic and fluorophoric

☆ For part 1, see Ref. [22].

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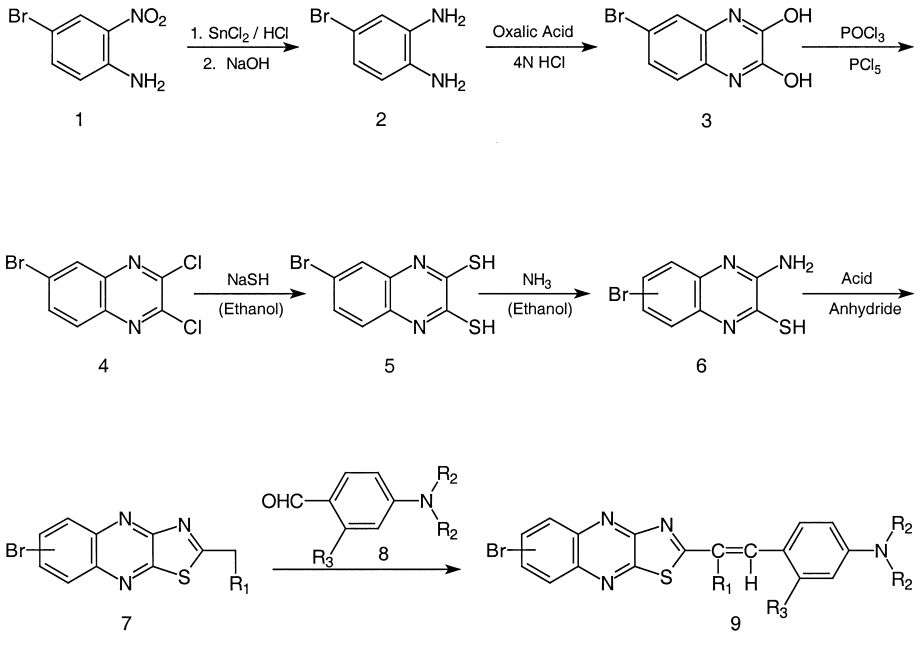
properties of styryl dyes **9a–f** and **11a–d**. The key intermediate (**7**) was synthesized by the interaction of 2,3-dichloro-6-bromo-quinoxaline (**4**) with NaSH followed by successive reactions involving NH_3/EtOH and hot acid anhydride. The synthesis involved the condensation of **7** with 4-*N,N*-dialkylaminosubstituted aryl and heteroarylaldehydes in the presence of piperidine or acid anhydride. The photophysical properties of these fluorescent compounds were evaluated in various organic solvents, and their dyeing properties were assessed on polyester fibers.

2. Results and discussion

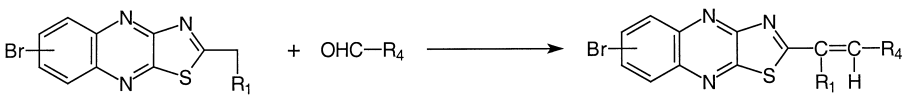
2.1. Synthesis of intermediates 7a, b

2,3-Dimercapto-6-bromoquinoxaline (**5**), was synthesized from 4-bromo-1,2-benzenediamine in three steps (Scheme 1) [23] starting from 4-bromo-1,2-benzenediamine. The advantages of this chemistry include good yields, short reaction times, and straightforward procedures. In most of the cases, the products precipitated from the reaction medium.



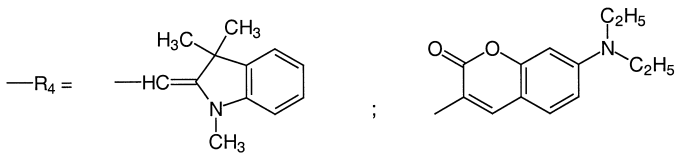
	R_1		R_2	R_3		R_1	R_2	R_3
a	H	**a**	CH_3	H	**a**	H	CH_3	H
a	H	**b**	C_2H_5	H	**b**	H	C_2H_5	H
a	H	**c**	C_2H_5	OCH_3	**c**	H	C_2H_5	OCH_3
b	CH_3	**a**	CH_3	H	**d**	CH_3	CH_3	H
b	CH_3	**b**	C_2H_5	H	**e**	CH_3	C_2H_5	H
b	CH_3	**c**	C_2H_5	OCH_3	**f**	CH_3	C_2H_5	OCH_3

Scheme 1. Synthesis of (a) type **9** dyes and (b) type **11** dyes.



7 10 11

	R_1		R_4		R_1	R_4
a	H	**a**	I	**a**	H	I
a	H	**b**	II	**b**	H	II
b	CH_3	**a**	I	**c**	CH_3	I
b	CH_3	**b**	II	**d**	CH_3	II



I II

Scheme 1 (*continued*).

Partial ammonolysis of compound **5**, using alcoholic ammonia, yielded crystalline **6**. Optimum conditions for this temperature-sensitive reaction, 100–120°C for 3 h, gave a 70% yield. Refluxing compound **6** in acetic anhydride or propionic anhydride yielded **7a** and **7b**, respectively. Following recrystallisation of compounds **7a** and **7b** from aqueous methanol, ^{1}H NMR spectra showed signals for the methyl and methylene protons at 2.9 and 2.82 ppm, respectively.

2.2. Reaction of 7a and 7b with aryl and heteroaryl aldehydes

The methyl group of **7a** was found to be more reactive than the methylene group of **7b**. Knoevenagal condensation reaction involving **7a** with aldehydes, using piperidine as catalyst, occurred smoothly, giving dyes **9a–c** and **11a–b**. Compound **7b** failed to react with aldehydes under standard Knoevenagal reaction conditions. However, it was possible to react **7b** with aldehydes in refluxing propionic anhydride to give **9d–f** and **11c–d**. The condensation of **7b** with coumarin aldehyde **10b** was very slow, requiring prolonged reaction times to complete the reaction. The positional isomers (6- and 7- bromo) generated in these reactions were separated by column chromatography, and the individual isomers were employed in spectral analyses. Dyeing properties, melting points, and reaction yields were based on the mixture of isomers.

2.3. Visible absorption spectra and solvatochromism

The visible absorption spectra of **9a–f** and **11a–c** were recorded in solvents of varying polarity, to assess the solvatochromic properties of these dyes (Table 1). Absorption maxima were observed at 467–546 nm in chloroform. Examination of absorption spectra of this dialkylaminophenyl-donor and thiazolo[4,5-b]quinoxaline-acceptor system showed the following:

1. Placing a methyl group on the olefinic moiety caused hypsochromic shifts compared to the corresponding analogues.
2. The dyes showed high molar extinction coefficients.
3. The molar extinction coefficients for **9d–f** and **11c** were significantly lower than **9a–c** and **11a**. This could be attributed to the presence of methyl group on olefinic double bond.
4. The dyes showed positive, albeit modest, solvatochromism

2.4. Fluorescence spectra

Fluorescence spectra were recorded in various solvents, and the emission maxima are listed in Table 2. The compounds exhibited orange to reddish pink fluorescence in most of the solvents. In general the fluorescence of styryl dyes **9a–f** and **11a–c** was strong in chloroform and ethyl acetate, and weak in other solvents, methanol and acetone. We found that the presence of a methyl group on the olefinic moiety decreased fluorescence intensity (Table 2). Fluorescence maxima varied with the polarity of the solvent employed (Fig. 1). The fluorescence maxima of all dyes shifted from orange, in chloroform and ethyl acetate, to reddish-orange in methanol and acetone. Stokes shifts were highest in acetone (Table 2), with compound **9a** showing the highest Stokes shift and **11a** the lowest. The compounds having a methyl group on the olefinic moiety had larger Stokes shifts (in cm^{-1}) than the corresponding analogues, except for **9d**.

Table 1
Visible spectral data for **9a–f** and **11a–c** (λ_{max} in nm)

Compound no.	Chloroform (log ε)	Ethyl acetate	Acetone	Methanol
9a	478 (4.70)	478	480	499
9b	515 (4.81)	495	514	513
9c	522 (5.05)	505	526	526
9d	467 (3.98)	453	464	472
9e	488 (4.05)	483	493	496
9f	502 (4.08)	489	515	512
11a	546 (4.93)	522	553	553
11b	505 (4.62)	504	513	515
11c	541 (4.85)	533	553	553

2.5. Fluorescence lifetimes

Fluorescence lifetimes, designated as τ_1 (short) and τ_2 (long), and the amplitude of the components (α_1 and α_2), given in Table 3. Compounds **9a–c** exhibited remarkably longer fluorescence lifetimes than analogues **9d–f**, and were single exponential (Fig. 2). This could be attributed to the presence of a methyl group on the olefinic group. In general, longer fluorescence lifetimes correlated with their high quantum yields. Hence, the efficiencies of **9d–f** were less than **9a–c** (Table 2).

Dyes **9d–f** and **11a,c** exhibited biexponential fluorescence lifetimes, which denotes either the

Table 2
Fluorescence spectral data for **9a–f** and **11a–c** (λ_{emis} in nm)

		Stoke's shifts [nm (cm^{-1})]		
Compound no.	Chloroform (quantum efficiencies ϕ[a])	Ethyl acetate	Acetone	Methanol
9a	582 (0.50)	601	642 [162 (5257.0)]	636
9b	593 (0.61)	600	649 [135 (4046.9)]	639
9c	596 (0.58)	599	644 [118 (3483.4)]	636
9d	525 (0.10)	527	546 [82 (3236.7)]	547
9e	593 (0.12)	601	623 [130 (4232.6)]	616
9f	597 (0.09)	604	633 [118 (3619.7)]	633
11a	596 (1.00)	602	633 [80 (2285.4)]	636
11b	586 (0.78)	604	656 [143 (4249.3)]	657
11c	605 (0.14)	609	646 [93 (2603.3)]	644

[a] Quantum efficiencies were calculated relative to the compound **11a**, whose quantum efficiency was 85–90% as compared to Rhodamine 6G ($CHCl_3$).

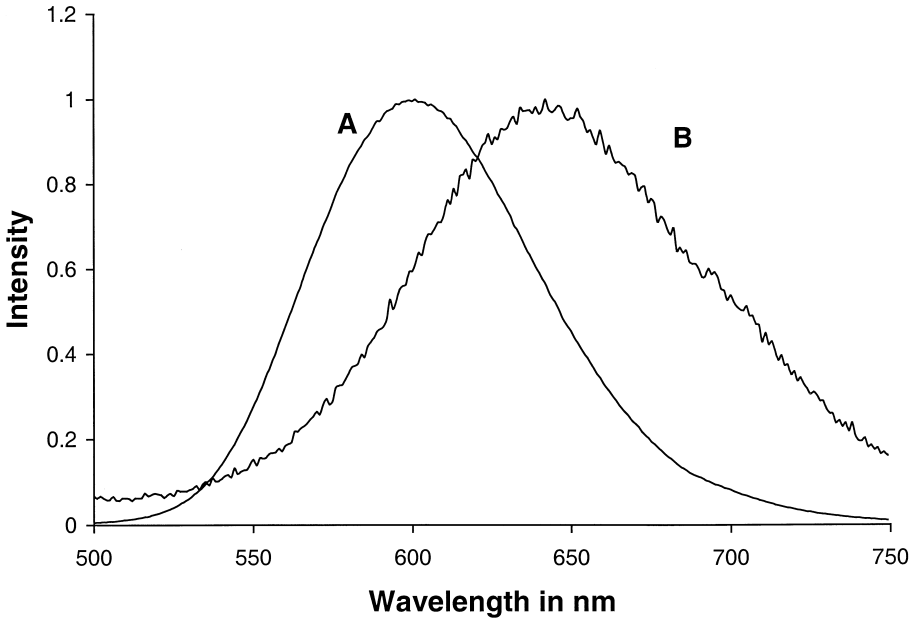


Fig. 1. Fluorescence spectra for **9a** in (**A**) ethyl acetate and (**B**) acetone.

Table 3
Fluorescence lifetimes for **9a–f** and **11a–c** (in ethyl acetate) ($\lambda_{exc} = 574$ nm, $\lambda_{emis} = 620$ nm)

Compound no.	τ_1 (ns) short	α_1	τ_2 (ns) long	α_2	χ^2
9a	1.770	1.0	–	–	1.16
9b	1.874	1.0	–	–	1.08
9c	1.394	1.0	–	–	1.29
9d	0.230	0.98	2.27	0.02	1.48
9e	0.190	0.99	1.02	0.01	1.40
9f	0.085	0.992	7.36	0.008	1.14
11a	0.470	0.64	1.56	0.36	1.20
11b	1.700	1.0	–	–	1.11
11c	0.217	0.60	0.718	0.40	1.16

existence of two components, quenched and unquenched, or complex fluorescence dynamics (Fig. 3). The amplitudes of **11a** and **11c** did not vary significantly, whereas it was nearly same for **9d–f**. The τ_1 difference between **11a** and **11c** was less than that between **9a** and **9d**. This could be the combined effect of an additional double bond and the indolyl group. Interestingly, the presence of a methoxy group on the donor-aryl moiety also affected fluorescence lifetimes. In this case, **9c** and **9f** had shorter lifetimes than analogues **9b** and **9e**.

2.6. Dyeing properties

Dyes **9a–f** and **11a–d** were applied on polyester fibres as fluorescent disperse dyes. The dyes produced the color range from bright orange to pink. The dyeing properties such as pick up, light fastness and sublimation fastness are evaluated on polyester fabric and are summarized in Table 4.

Dyes **9a–c** and **11a–b** afforded better brightness than analogues **9d–f** and **11c–d,** suggesting that the methyl group on olefinic moiety of dyes **9d–f** and **11c–d** decreased brightness. Except for **9e** and **11c**, these novel dyes possessed excellent sublimation fastness. Typical of fluorescent dyes the light fastness of all dyes was poor.

3. Experimental

All melting points are uncorrected and are expressed in °C. The ^{1}H NMR spectra were recorded on Varian-300 MHz and Hitachi-60 MHz instruments, using TMS as internal standard. Chemical shifts are given in δ (ppm). Absorption and fluorescence emission spectra were recorded on a Beckmann model-25 spectro-

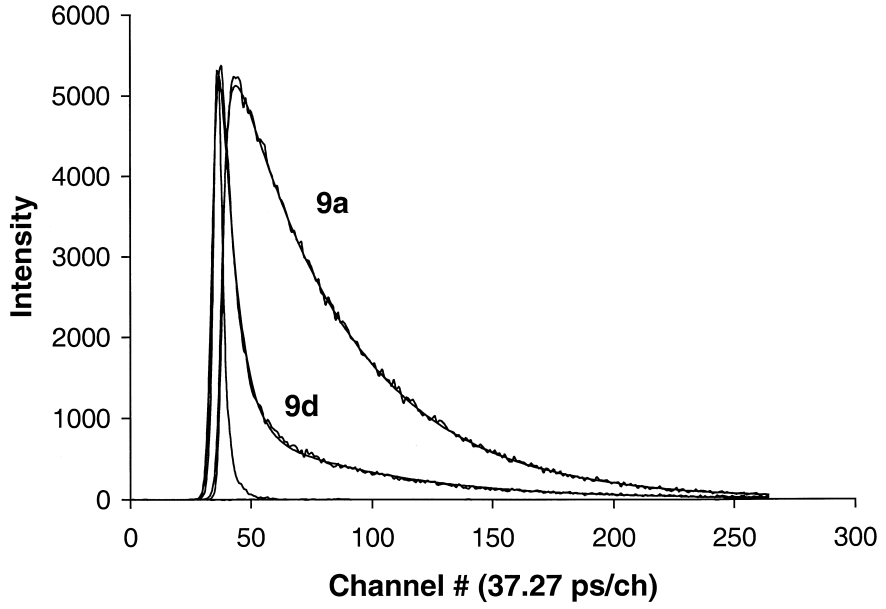


Fig. 2. Fluorescence decay profile for **9a** and **9d** in ethyl acetate [Channel#(37.27 ps/ch) = channel no., 37.27 ps per channel].

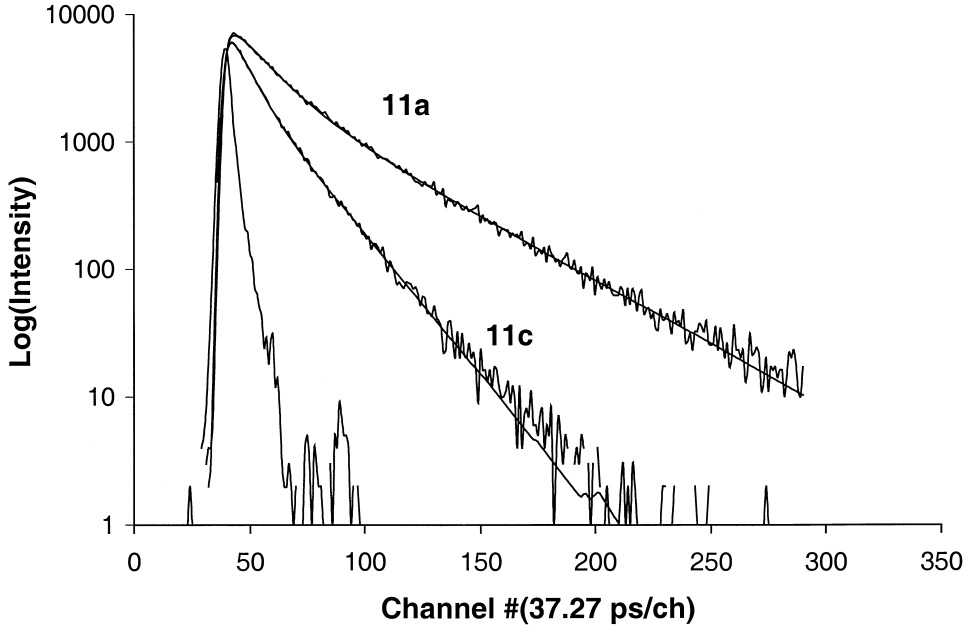


Fig. 3. Fluorescence decay profile for **11a** and **11c** in ethyl acetate [Channel#(37.27 ps/ch) = channel no., 37.27 ps per channel].

photometer and SPEX 1681 Fluorolog T-format fluorimeter, respectively. Fluorescence decays were measured using a picosecond laser coupled with a time correlated single photon counting spectrophotometer [24]. Fluorescence lifetimes were calculated from the decay curves by using the least-squares method. For all fluorescence measurements, the excitation wavelength was the

Table 4
Properties[a] of **9a–f** and **11a–d**

Compound no.	Color on polyester fiber	Pick-up[b]	Light fastness	Sublimation fastness
9a	Brilliant orange	5	1	5
9b	Luminescent reddish orange	5	1	5
9c	Bright red	4	1	4
9d	Orange	3	1	4
9e	Bright orange	3	1	3
9f	Deep red	4	1	4
11a	Fluorescent pink	5	1	5
11b	Fluorescent scarlet	4	1	4
11c	Dark reddish pink	4	1	3
11d	Bright reddish orange	3	1	4

[a] 1% o.w.f.
[b] Pink-up values (tinctorial power): 5 (excellent), 2×standard depth; 4 (very good), 1×standard depth; 3 (good), 0.5×standard depth; 2 (poor), 0.33×standard depth; 1 (very poor), 0.16×standard depth.

wavelength of maximum absorption. Evaluation of 1.0% dye shades on polyester fabric (1.0% o.w.f.) was carried out according to standard fastness testing procedures [25]. The B02: 1978 test was used to asses the light fastness, and sublimation fastness was evaluated using P01: 1978 test, with polyester as an adjacent fabric at 180°C ± 2°C [25]. Aldehydes **8a–b** were obtained from Aldrich Chemicals and **8c**, **10a** were procured from M/S Jalan Dyes & Chemicals, Boisar, Maharashtra, India. Coumarin aldehyde **10b** was synthesized from 7-*N,N*-diethylaminocoumarin via a Vilsmeier reaction.

3.1. 2-Methyl-6(7)-bromothiazolo[4,5-b]quinoxaline (**7a**)

A mixture of **5** (2 g) [23] and alcoholic ammonia (20 ml, saturated at 20°C) was heated in an autoclave at 100–120°C for 3 h. The reaction mixture was evaporated and the residue was dissolved in NaOH solution (50 ml, 5%) at 50–60°C. The mixture was filtered and the filtrate was neutralized with HOAc, to produce a bright yellow precipitate. The precipitate was filtered, washed with water, dried and recrystallised from ethanol to yield 1.36 g (72%) **6**, as yellow needles. Microanalysis: calculated for $C_8H_6BrN_3S$: C, 37.51; H, 2.34; N, 16.41; found: C, 37.40; H, 2.39; N, 16.62.

Compound **6** (2 g), was stirred at reflux with acetic anhydride (20 ml) for 4 h. The excess anhydride was removed by vacuum distillation, and the residue obtained was diluted with Na_2CO_3 solution (50 ml, 5%) and left overnight. The dark brown precipitate was collected by filtration, washed with water, dried and recrystallised from aq. methanol (water:methanol, 30:70 by volume), to yield 1.69 g (77%) pale yellow needles (**7a**). Mp: 167–168°C; ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.90 (s, 3H, CH_3), 7.84–8.23 (m, 3H, aromatic). Microanalysis: calculated for $C_{10}H_6BrN_3S$: C, 42.87; H, 2.14; N, 15.00; found: C, 42.80; H, 2.09; N, 15.18.

3.2. 2-Ethyl-6(7)-bromothiazolo[4,5-b]quinoxaline (**7b**)

The procedure as described above for **7a** was employed except that propionic anhydride was used in place of acetic anhydride. Crude **7b** was recrystallised from aqueous methanol (20 water: 80 methanol, v/v) to yield 1.73 g (75%) pale yellow crystals. Mp: 150–152°C; ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.11 (t, 3H, C_2H_5), 2.82 (q, 2H, C_2H_5), 7.78–8.20 (m, 3H, aromatic). Microanalysis: calculated for $C_{11}H_8BrN_3S$: C, 44.91; H, 2.72; N, 14.29; found: C, 44.98; H, 2.61; N, 14.35.

*3.3. 2-[2-(4-*N,N*-Dimethylaminophenyl)ethenyl]-6(7)-bromothiazolo[4,5-b] quinoxaline* (**9a**)

A mixture of **7a** (2.80 g, 0.01 mol) and **8a** (1.49 g, 0.01 mol) in absolute ethanol (10 ml) and

piperidine (2–3 drops) was stirred at reflux for 5 h. The precipitate was filtered, washed with ethanol, dried and recrystallised from benzene:ethyl acetate (10:5), to yield 3.25 g (79%) **9a**, as shiny red crystals. Mp: 172–174°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.23 [s, 6H, $N(CH_3)_2$], 6.69 (d, 2H, aromatic, $J=8.9$ Hz), 7.21 (d, 1H, olefinic CH, $J=15.6$ Hz), 7.52 (d, 2H, aromatic, $J=8.9$ Hz), 7.73–7.79 (m, 2H, olefinic CH and aromatic), 7.91 (d, 1H, aromatic, $J=8.7$ Hz), 8.32 (d, 1H, aromatic, $J=2.1$ Hz). Microanalysis: calculated for $C_{19}H_{15}BrN_4S$: C, 55.48; H, 3.65; N, 13.62; found: C, 55.31; H, 3.43; N, 13.69.

*3.4. 2-[2-(4-*N,N-*Diethylaminophenyl)ethenyl]-6(7)-bromothiazolo[4,5-b]quinoxaline* (**9b**)

The procedure described above for **9a** was employed, except that **8b** was used in place of **8a**. Crude **9b** was recrystallised from benzene:ethyl acetate (5:2) to yield 3.76 g (86%) **9b** as a reddish-black solid. Mp: 205–207°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (t, 6H, $N(C_2H_5)_2$, $J=7.1$ Hz), 3.44 (q, 4H, $N(C_2H_5)_2$, $J=7.1$ Hz), 6.67 (d, 2H, aromatic, $J=8.9$ Hz), 7.21 (d, 1H, olefinic CH, $J=15.7$ Hz), 7.52 (d, 2H, aromatic, $J=8.9$ Hz), 7.74–7.80 (m, 2H, olefinic CH and aromatic), 7.94 (d, 1H, aromatic, $J=8.7$ Hz), 8.33 (d, 1H, aromatic, $J=2.1$ Hz). Microanalysis: calculated for $C_{21}H_{19}BrN_4S$: C, 57.41; H, 4.32; N, 12.75; found: C, 57.52; H, 4.40; N, 12.61.

*3.5. 2-[2-(4-*N,N-*Diethylamino-2-methoxyphenyl)ethenyl]-6(7)-bromothiazolo[4,5-b] quinoxaline* (**9c**)

The procedure described above for **9a** was employed, except that **8c** was used in place of **8a**. Crude **9c** was recrystallised from benzene:ethyl acetate (5:2) to yield 3.43 g (73%) **9c**, as a reddish violet solid. Mp: 188–190°C; ^{1}H NMR (60 MHz, $CDCl_3$): δ1.19 (t, 6H, $N(C_2H_5)_2$, $J=7.0$ Hz), 3.43 (q, 4H, $N(C_2H_5)_2$, $J=7.0$ Hz), 3.90 (s, 3H, OCH_3), 6.01 (s, 1H, aromatic), 6.25 (d, 1H, aromatic, $J=9.0$ Hz), 7.36–7.50 (m, 2H, olefinic CH and aromatic), 7.80–7.92 (m, 2H, olefinic CH and aromatic), 8.18–8.29 (m, 2H, aromatic). Microanalysis: calculated for $C_{22}H_{21}BrN_4OS$: C, 56.30; H, 4.47; N, 11.94; found: C, 56.12; H, 4.52; N, 12.08.

*3.6. 2-[2-(4-*N,N-*Dimethylaminophenyl)-1-methyl-ethenyl]-6(7)-bromothiazolo[4,5-b] quinoxaline* (**9d**)

A mixture of **7b** (2.93 g, 0.01 mol) and **8a** (1.49 g, 0.01 mol) in propionic anhydride (20 ml) was stirred at reflux for 8 h. The excess solvent was removed under vacuum, and the residue was slowly added to ice water mixture, neutralized with dilute Na_2CO_3 solution. The brown precipitate was filtered, washed with water, dried and recrystallised from ethanol, to yield 1.88 g (44%) **9d**. Mp: 201–204°C ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.64 (s, 3H, olefinic CH_3), 3.08 [s, 6H, $N(CH_3)_2$], 6.75 (d, 2H, aromatic, $J=8.9$ Hz), 7.55 (d, 2H, aromatic, $J=8.8$ Hz), 7.68 (s, 1H, olefinic CH), 7.83 (dd, 1H, aromatic, $J=8.8$, 2.0 Hz), 8.04 (d, 1H, aromatic, $J=8.9$ Hz), 8.28 (d, 1H, aromatic, $J=2.0$ Hz). Microanalysis: calculated for $C_{20}H_{17}BrN_4S$: C, 56.48; H, 4.00; N, 13.17; found: C, 56.60; H, 4.12; N, 13.08.

*3.7. 2-[2-(4-*N,N-*Diethylaminophenyl)-1-methyl-ethenyl]-6(7)-bromothiazolo[4,5-b]quinoxaline* (**9e**)

The procedure described above for **9d** was employed, except that **8b** was used in place of **8a**. Crude **9e** was recrystallised from ethanol to yield 2.92 g (64%) **9e**, as black solid. Mp: 179–182°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (t, 6H, $N(C_2H_5)_2$, $J=7.0$ Hz), 2.64 (s, 3H, olefinic CH_3), 3.44 [q, 4H, $N(C_2H_5)_2$, $J=7.0$ Hz], 6.71 (d, 2H, aromatic, $J=8.9$ Hz), 7.53 (d, 2H, aromatic, $J=8.8$ Hz), 7.67 (s, 1H, olefinic CH), 7.81 (dd, 1H, aromatic, $J=8.9$, 2.1 Hz), 8.03 (d, 1H, aromatic, $J=8.9$ Hz), 8.27 (d, 1H, aromatic, $J=2.1$ Hz). Microanalysis: calculated for $C_{22}H_{21}BrN_4S$: C, 58.28; H, 4.63; N, 12.36; found: C, 58.41; H, 4.52; N, 12.30.

*3.8. 2-[2-(4-*N,N-*Diethylamino-2-methoxyphenyl)-1-methyl-ethenyl]-6(7)-bromothiazolo[4,5-b]quinoxaline* (**9f**)

The procedure described above for **9d** was employed, except that **8c** was used in place of **8a**.

Crude **9f** was recrystallised from ethanol to yield 2.96 g (61%) **9f**. Mp: 171–174°C; ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.17 (t, 6H, $N(C_2H_5)_2$, $J=7.0$ Hz), 2.40 [s, 3H, olefinic CH_3], 3.37 (q, 4H, $N(C_2H_5)_2$, $J=7.0$ Hz), 3.90 (s, 3H, OCH_3), 6.17 (s, 1H, aromatic), 6.29 (d, 1H, aromatic, $J=9.0$ Hz), 7.10–7.30 (m, 1H, aromatic), 7.52–7.93 (m, 3H, olefinic CH and aromatic), 8.12–8.35 (m, 1H, aromatic). Microanalysis: calculated for $C_{23}H_{23}BrN_4OS$: C, 57.15; H, 4.76; N, 11.59; found: C, 57.03; H, 4.72; N, 11.72.

3.9. 2-[2-(1,3,3-Trimethyl-2-methyleneindolyl)ethenyl]-6(7)-bromothiazolo[4,5-b]quinoxaline (**11a**)

A mixture of **7a** (2.80 g, 0.01 mol) and **10a** (2.01 g, 0.01 mol) in absolute ethanol (10 ml) piperidine (2–3 drops) was stirred at reflux for 8 h. The precipitated solid was filtered, washed with ethanol, dried and recrystallised from benzene:ethyl acetate (10:3) to yield 3.66 g (79%) **11a**, as a blackish violet crystalline solid. Mp: 145–148°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.70 (s, 6H, $2CH_3$), 3.31 (s, 3H, N-CH_3), 5.66 (d, 1H, olefinic, $J=12.8$ Hz), 6.52 (d, 1H, olefinic, $J=14.1$ Hz), 6.82 (d, 1H, $J=8.4$ Hz), 7.03 (m, 1H, aromatic), 7.24–7.30 (m, 2H, aromatic), 7.72 (dd, 1H, aromatic, $J=8.7$, 2.1 Hz), 7.89 (d, 1H, aromatic, $J=8.9$ Hz), 8.25–8.33 (m, 2H, aromatic). Microanalysis: calculated for $C_{23}H_{19}BrN_4S$: C, 59.62; H, 4.10; N, 12.09; found: C, 59.80; H, 4.05; N, 12.16.

*3.10. 2-[2-(7-*N,N-*Diethylamino-3-coumarinyl)ethenyl]-6(7)-bromothiazolo[4,5-b]quinoxaline* (**11b**)

The procedure described above for **11a** was employed, except that **10b** was used in place of **10a**. Crude **11b** was recrystallised from ethanol, to yield 3.19g (63%) **11b**. Mp: 259–261°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (t, 6H, $N(C_2H_5)_2$, $J=6.9$ Hz), 3.47 [q, 4H, $N(C_2H_5)_2$, $J=6.9$ Hz], 6.52 (d, 1H, aromatic, $J=2.2$Hz), 6.66 (dd, 1H, aromatic, $J=2.2$, 9.0 Hz), 7.37 (d, 1H, aromatic, $J=9.1$ Hz), 7.83–7.87 (m, 2H, olefinic CH and aromatic), 7.89–8.01 (m, 2H, olefinic CH and aromatic), 8.07 (d, 1H, aromatic, $J=9.1$Hz), 8.30 (d, 1H, aromatic, $J=2.2$Hz). Microanalysis: calculated for $C_{24}H_{19}BrN_4O_2S$: C, 56.81; H, 3.74; N, 11.04; found: C, 56.65; H, 3.80; N, 11.20.

3.11. 2-[2-(1,3,3-Trimethyl-2-methyleneindolyl)-1-methyl-ethenyl]-6(7)-bromothiazolo[4,5-b]quinoxaline (**11c**)

A mixture of **7b** (2.93 g, 0.01 mol) and **10a** (2.01 g, 0.01 mol) in propionic anhydride (20 ml) was stirred at reflux for 8 h. The excess solvent was removed under vacuum and the residue was slowly added to ice water mixture. The solution was neutralized with dilute Na_2CO_3 solution, and the blackish precipitate was filtered, washed with water, dried and recrystallised from benzene:ethyl acetate (10:3), to yield 3.08 g (64%) **11c**. Mp: 151–154°C; ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.66 (s, 6H, $2CH_3$), 2.30 (s, 3H, olefinic CH_3), 3.27 (s, 3H, N-CH_3), 5.60 (d, 1H, olefinic CH, $J=12.8$ Hz), 6.55–7.40 (m, 3H, olefinic CH and aromatic), 7.60–8.05 (m, 3H, aromatic), 8.15–8.50 (m, 2H, aromatic). Microanalysis: calculated for $C_{24}H_{21}BrN_4S$: C, 60.38; H, 4.40; N, 11.74; found: C, 60.51; H, 4.32; N, 11.62.

*3.12. 2-[2-(7-*N,N-*Diethylamino-3-coumarinyl)-1-methyl-ethenyl]-6(7)-bromothiazolo[4,5-b]quinoxaline* (**11d**)

The procedure described above for **11c** was employed, except that **10b** was used in place of **10a**. Crude **11d** was recrystallised from ethanol, to yield 0.83 g (16%) **11d**. Mp 161–163°; ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.16 [t, 6H, $N(C_2H_5)_2$, $J=7.1$ Hz], 2.36 (s, 3H, olefinic CH_3), 3.40 [q, 4H, $N(C_2H_5)_2$, $J=7.1$ Hz], 6.43–6.55 (m, 2H, aromatic), 7.20–7.53 (m, 1H, aromatic), 7.60–7.92 (m, 3H, olefinic CH and aromatic), 8.11–8.30 (m, 2H, aromatic). Microanalysis: calculated for $C_{25}H_{21}BrN_4O_2S$: C, 57.59; H, 4.03; N, 10.75; found: C, 57.68; H, 3.97; N, 10.88.

4. Conclusion

Daylight fluorescent dyes were synthesized from 2-alkyl-6(7)-bromothiazolo[4,5-b]quinoxaline and

their technical properties were studied. The experimental results showed that the presence of a methyl substituent on the olefinic double bond of styryl-6(7)-thiazolo[4,5-b]quinoxaline led to a decrease in extinction coefficients and to hypsochromic shifts. This substitution also decreased quantum yields, fluorescence lifetimes and brightness of the shade on polyester.

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