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Synthesis, Characterization and Photographic Properties of Some New Styryl Cyanine Dyes

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ABSTRACT

Two series of 3-sulfopropyl styryl cyanine dyes were synthesized by condensation of (un)substituted benzothiazole betaine with a view to studying their spectral characterization and silver halide photosensitization properties. The structures of the dyes evaluated by elemental analysis, ^1H NMR, IR and MS. An attempt was made to correlate colorant structure with photophysical properties and applied performance in photographic silver halide emulsion. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

A very extensive variety of styryl dyes have been developed since they were first synthesized by Konig. Styryl cyanine dyes are widely used as sensitizers and other additives in the photographic industry [1–6] as optical recording medium in laser disks [7], flexible dyes [8], laser dyes [9], and as optical sensitizers in various other fields [10]. The aim of this paper is to study some styryl dyes containing a sulfopropyl on the heterocyclic nitrogenation, and to contrast the photophysical properties of dyes carrying different substituents in the 5-position of the benzothiazole ring, and also their photographic performance.

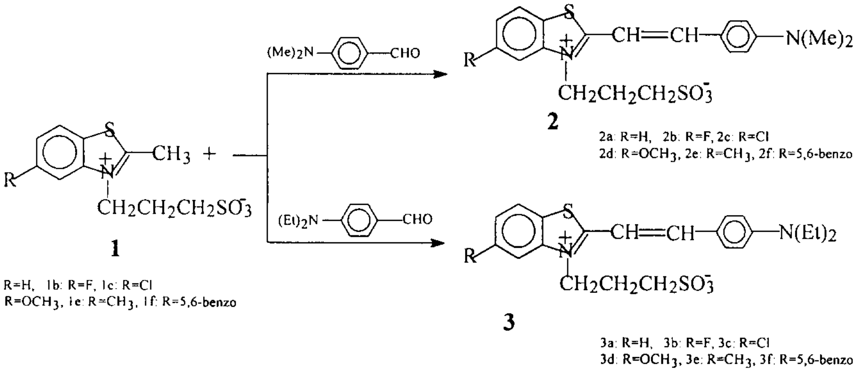
RESULTS AND DISCUSSION

Synthesis

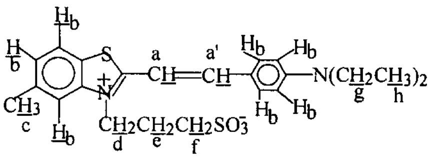
Dyes **2** and **3** were synthesized by reaction of (un)substituted benzothiazole betaine **1** with 4-diethylbenzaldehyde or 4-dimethylbenzaldehyde in equimolar amount in basic solution. Compounds **1** were obtained by heating the appropriate benzothiazole and sulfopropyl sultone at 120–140°C in a sealed tube. The route of synthesis is as shown in Scheme 1.

Characterization

The structures of the dyes were confirmed by ^{1}H NMR, IR and MS. Relevant data are listed in Table 3. Scheme 2 shows proton magnetic resonance spectrum parameters of dye **3e**. It is apparent from Scheme 2 that the ^{1}H NMR spectrum of compound **3e** shows chemical shift data in accordance with the structure of **3e**; moreover, the chemical shift of Ha has almost same value as that of Ha′, which shows that the charges on the molecular skeleton are not distributed alternately on the conjugation linkage. This result is different from that observed on a carbocyanine [9].



Scheme 1 Synthetic pathway for dyes **2** and **3**.



a: 6.77-6.84 (d, 2H)
b: 7.43-8.13 (m, 7H)
C: 2.55 (s, 3H)
d: 4.9 (t, 2H)
e: 2.25 (f, 2H)
f: 2.65 (t, 2H)
g: 3.45 (q, 4H)
h, 1.2 (t, 6H)

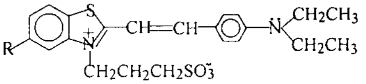
Scheme 2 Proton magnetic resonance spectrum of dye **3e**.

Electronic spectra

Table 2 shows electron spectra data for the compounds **2** and **3** in methanol. Dyes containing different substituents in the 5-position of the benzothiazole moiety exhibit different absorption and fluorescence maxima. The bathochromic order induced by the substituents on the 5-position of the heterocycle is as follows:

$$Cl > F > H = 5,6\text{-benzo} > OCH_3 > CH_3$$

From these results, it is apparent that dyes **2d**, **2e**, **2f**, **3d**, **3e**, and **3f**, having electron-donating groups OCH_3, CH_3, and 5,6-benzo group in the benzothiazole ring are hypsochromic with respect to dyes **2a** and **3a**, respectively, whereas dyes **2b**, **2c**, **3b** and **3c**, with fluoro and chloro electron-withdrawing groups in the benzothiazole moiety show a bathochromic shift of 6–8 nm. The results are in contrast to our previous conclusions [11,12]. The results can, however, be explained by the influence of the substituents on the charge distribution within the molecular skeleton. Styryl dyes have an acceptor-π–donator molecular model. The most stable state of such dyes can be regarded as:



when R is an electron-withdrawing group. Both the charge density on the amino group, and the degree of charge separation in the molecule will decrease and therefore the basicity of the dye molecule will decrease, and the molecular structure shown above will become stabler. In contrast, when the R substituent on the benzothiazole ring is an electron-donating group, it can be presumed that the basicity of the dye molecule will increase. Hence, electron-withdrawing groups give maximum absorption and emission wavelength bathochromic shift and electron-donating substituents a hypsochromic shift. Additionally, there are P–π conjugation in dyes containing chloro and methoxy groups, which results in a decrease in dye basicity. The absorption and emission wavelength of dyes **2c** and **3c**, containing a chloro substituent, is therefore longer than that of dyes **2b** and **3b** containing the fluoro substituent; the same conclusion also pertains to dyes containing the methoxy group.

Furthermore, the maximum bathochromic or hypsochromic shift value in these dyes is only ±6 nm with respect to dyes **2a** and **3a**, respectively, which implies that the nature of the substituent on the heterocycle has only a very limited effect on the electronic structure of the dye.

When comparing dyes **2** and **3**, carrying the same heterocycle and different 4-alkylamino groups (one 4-methylamino, other 4-ethylamimo) the maxima absorption and emission wavelength of dyes **3** are respectively 8–12 nm longer than for dye **2**. The effect the of 4-alkylamino substituent on the electron spectra or electron structure is therefore greater than that of the substituent (R) on the heterocycle.

Photographic performance

Sensitometric results are shown in Table 4. From this data, it is apparent that dyes **2d**, **3c** and **3f** cause the sensitivity of the silver halide emulsion strip to increase 2–3 Din and not to induce fog. Therefore, dyes **2d**, **3c** and **3f** are better sensitizers for the studied silver halide emulsion. Dye **3d**, containing a methoxyl on the benzothiazole ring is not a good sensitizer for the emulsion owing to stronger fogging under the experimental conditions, although the dye is able to increase the sensitivity of the emulsion. Furthermore, the emulsion strip dyed by dyes **3b** and **3e** had almost the same sensitivity as the undyed emulsion strip, and dye **3b** increases the fog of the studied film strip; therefore, neither dye is a useful sensitizing agent. From the experimental results listed in Table 4, it can be seen that all the dyes added to the silver halide emulsion do not give rise to residual color; it is possible that the sulfopropyl group on the heterocyclic nitrogen increases the solubility in water. It is easier for the dyes to remove the residual color from the film strip in the development process, fixation and washing; similar results have been previously discussed by us [13].

EXPERIMENTAL

General

Absorption spectra of the dyes in methanol were recorded with a Hitachi 557 spectrophotometer and a Hitachi UV-8451A spectrophotometer at room temperature (20°C); the results are shown in Table 1. Fluorescence spectra in methanol solution were recorded with a Rini-MPF-4 spectrophotofluorimeter. ^{1}H and ^{13}C NMR spectra were taken with a 300 MHz Varian XL200, using TMS as internal standard and DMSO-d6 as solvent. Elemental analysis was performed by the Institute of Chemistry, Analytical Laboratory. Melting points are uncorrected. IR spectra were run in KBr discs on a Perkin–Elmer 683.

Photographic tests

A thick cubic iodobromide iodobromide (I_2 0.42 mol%) grain emulsion was precipitated using the double-jet method with automated control of pAg, at

TABLE 1
Characterization Data of the Salts (**1–6**)

Salt	*Yield*	*Formula*	*Analysis Found (Calcd)* *C*	*H*	*N*	*^1H NMR data (ppm)*
1a	55	$C_{11}H_{13}NS_2O_3$	45.63	5.24	4.67	4.9, 2.15, 2.65, 3.15, 7.7–8.6
			(45.66)	(5.23)	(4.84)	
1b	57	$C_{11}H_{12}NS_2O_3F$	42.90	4.65	4.57	4.85, 2.15, 2.65, 3.2, 7.7–8.5
			(42.99)	(4.59)	(4.56)	
1c	60	$C_{11}H_{13}NS_2O_3Cl$	40.42	4.33	4.08	4.87, 2.15, 2.65, 3.2, 7.7–8.6
			(40.80)	(4.36)	(4.33)	
1d	53	$C_{11}H_{13}NS_2O_3OCH_3$	45.47	5.47	4.41	4.9, 2.15, 2.65, 3.15, 7.7–8.6, 3.95
			(45.13)	(5.37)	(4.39)	
1e	55	$C_{11}H_{13}NS_2O_3CH_3$	47.75	5.75	4.60	4.9, 2.15, 2.65, 3.15, 7.-6-8.3, 2.55
			(47.51)	(5.65)	(4.62)	
1f	53	$C_{15}H_{15}NS_2O_3$	53.05	5.05	4.13	5.25, 2.3, 2.8, 3.25, 7.9–9.0[a]
			(53.08)	(5.14)	(4.05)	

[a] Solvent CD_3OD.

TABLE 2
Characterization Data of Compounds **2** and **3**

Dye	*Yield (%)*	*M.F.*	*Analysis Found (Calcd)* *C*	*H*	*N*	*λ_{max} abs (nm)*	$\varepsilon \times 10^{-5}$ *(litre $cm^{-1} mol^{-1}$)*	*λ_{max} (nm)*
2a	37	$C_{20}H_{22}N_2O_3S_2$	59.70	5.47	6.97	536	1.52	600
		(402)	(59.35)	(5.67)	(6.85)			
2b	36.6	$C_{20}H_{21}N_2O_3S_2F$	56.14	5.00	6.67	538	1.53	605
		(420)	(56.64)	(5.24)	(6.70)			
2c	34.3	$C_{20}H_{21}N_2O_3S_2Cl$	53.92	4.81	6.41	540	1.53	603
		(437)	(54.32)	(4.87)	(6.67)			
2d	34.7	$C_{21}H_{24}N_2O_4S_2$	57.33	5.56	6.48	532	1.55	605
		(432)	(57.79)	(5.64)	(6.47)			
2e	31.0	$C_{21}H_{24}N_2O_3S_2$	60.18	5.75	6.73	528	1.52	603
		(416)	(60.08)	(5.87)	(6.78)			
2f	30.8	$C_{24}H_{24}N_2O_3S_2$	63.52	5.31	6.19	536	1.49	610
		(452)	(63.42)	(5.30)	(6.22)			
3a	36.5	$C_{22}H_{26}N_2O_3S_2$	61.40	6.05	6.51	544	2.94	610
		(430)	(61.15)	(6.35)	(6.60)			
3b	35.8	$C_{22}H_{25}N_2O_3S_2F$	58.32	5.58	6.25	548	2.85	610
		(448)	(58.63)	(5.64)	(6.27)			
3c	33.6	$C_{22}H_{25}N_2O_3S_2Cl$	56.77	5.38	6.02	550	2.88	607
		(465)	(56.37)	(5.42)	(6.12)			
3d	35.9	$C_{23}H_{28}N_2O_4S_2$	59.55	6.00	6.00	542	2.93	615
		(460)	(60.00)	(6.09)	(6.09)			
3e	32.9	$C_{23}H_{28}N_2O_3S_2$	62.16	6.31	6.31	540	2.95	617
		(444)	(62.05)	(6.37)	(6.32)			
3f	29.7	$C_{26}H_{28}N_2O_3S_2$	65.00	5.83	5.83	544	2.99	610
		(480)	(64.79)	(5.93)	(5.82)			

TABLE 3

^{1}H NMR, IR and MS Spectroscopy Data of Compounds **2** and **3**

Dye	*IR*	*^{1}H NMR*	*MS*
2	1623, 1589, 1528, 1437, 1370, 1193	4.9 (t, 2H), 2.2 (m, 2H), 2.8 (t, 2H), 6.8 (d, 2H), 7.8–8.7 (m, 7H), 3.1 (s, 6H).	298, 254, 134, 77
2b	1562, 1526, 1477, 1348, 1229, 966.	4.9 (t, 2H), 2.15 (m, 2H), 2.7 (t, 2H), 6.8 (d, 2H), 7.6–8.4 (m, 7H), 3.2 (s, 6H).	298, 254, 134, 77.
2c	1610, 1569, 1522, 1488, 1379, 966.	4.9 (t, 2H), 2.15 (m, 2H), 2.7 (t, 2H), 6.8 (d, 2H), 7.7–8.4 (m, 7H), 3.15 (s, 6H).	315, 270, 134, 77.
2d	1563, 1521, 1475, 1439, 1261, 966	4.8 (t, 2H), 2.2 (m, 2H), 2.8 (t, 2H), 6.8 (d, 2H), 7.5–8.2 (m, 7H), 3.15 (s, 6H), 3.95 (s, 3H)	309, 294, 266, 179, 134, 77.
2e	1607, 1568, 1516, 1468, 1152, 966	4.9 (t, 2H), 2.15 (m, 2H), 2.7 (t, 2H), 6.8 (d, 2H), 7.4–8.2 (m, 7H), 3.1 (s, 6H), 2.55 (s, 3H).	294, 250, 134, 77.
2f	1608, 1567, 1510, 1483, 1183, 966.	4.9 (t, 2H), 2.2 (m, 2H), 2.8 (t, 2H), 6.8 (d, 2H), 7.8–8.8 (m, 7H), 3.4 (s, 6H)	330, 286, 134, 77.
3a	1610, 1570, 1527, 1491, 1382, 977	4.6 (t, 2H), 2.35 (m, 2H), 3.05 (t,2H), 6.8 (d, 2H), 7.6–8.2 (m, 7H), 3.55 (q, 2H), 1.25 (t, 3H)[a]	308, 293, 162, 58, 77.
3b	1609, 1570, 1527, 1491, 1335, 977.	4.9 (t, 2H), 2.15 (m, 2H), 2.7 (t,2H), 6.8 (d, 2H), 7.6–8.2 (m, 7H), 3.55 (q, 2H), 1.25 (t, 3H)	326, 311, 162, 77, 58.
3c	1609, 1568, 1517, 1483, 1342, 966	4.9 (t, 2H), 2.1 (m, 2H), 2.7 (t,2H), 6.8 (d, 2H), 7.6–8.4 (m, 7H), 3.6 (q, 2H), 1.15 (t, 3H)	342, 327, 270, 162, 77.
3d	1609, 1567, 1517, 1484, 1334, 966	4.95 (t, 2H), 2.15 (m, 2H), 2.65 (t, 2H), 6.8 (d, 2H), 7.7–8.4 (m, 7H), 3.6 (q, 2H), 1.2 (t, 3H), 3.95 (s,3H)	338, 322, 266, 162, 77.
3e	1570, 1525, 1490, 1448, 1370, 966	4.9 (t, 2H), 2.2 (m, 2H), 2.65 (t, 2H), 6.8 (d, 2H), 7.4–8.2 (m, 7H), 3.5 (q, 2H), 1.2 (t, 3H), 2.55 (s, 3H) cv	322, 307, 250, 162, 77.
3f	1610, 1568, 1525, 1455, 1377, 966	5.35 (t, 2H), 2.15 (m, 2H), 2.65 (t,3H), 6.8 (d, 2H), 7.8–8.8 (m, 7H), 3.5 (q, 2H), 1.1 (t, 3H)	358, 343, 286, 172, 77.

[a] Solvent CD_3OD.

TABLE 4
The Photographic Performance of the Dyes

Dye	*V (ml)*	D_0	S	γ	D_{max}
2d	0	0.01	7.5	4.2	3.16
	1.8	0.01	9	4.0	4.46
	3	0.02	9	3.8	5.59
	4.2	0.01	9	4.0	3.85
3b	0	0.02	7.5	4.4	3.66
	1.8	0.05	7.0	4.0	3.14
	3	0.05	6.5	2.7	1.98
	4.2	0.01	7.0	4.4	3.41
3c	0	0.02	7.5	4.4	3.66
	1.8	0.02	10	4.8	4.61
	3	0.02	10	5.0	4.73
	4.2	0.02	10	4.8	4.63
3d	0	0.02	7.5	4.2	3.66
	1.8	0.06	12	4.4	4.64
	3	0.08	12	4.4	4.65
	4.2	0.08	11	4.2	4.20
3e	0	0.02	7.5	4.0	2.81
	1.8	0.02	7.5	3.5	3.05
	3	0.02	7.5	3.2	3.07
	4.2	0.02	7.5	3.0	1.90
3f	0	0.02	7.5	4.0	3.90
	1.8	0.01	9	4.4	3.76
	3	0.02	9	4.6	4.58
	4.2	0.02	9	4.6	4.87

V (ml): the number of millilitres of 0.1% methanol solution of dye added to 50 g emulsion. D_0, D_{max}: the minimum and maximum spectra density of film strip.
S: the sensitivity is defined by the following equation: $S = 10 \lg 1/(H_{D0+0.1})$ in which *H* represents the amount of exposure necessary to obtain a density of 0.1 above fog sensitivity.

initial gelatin concentration of 2%, temperature 60°C, and for a period of 40 min, then coagulated, washed, redispersed and chemically sensitized with S + Au sensitizers. Portions were spectrally sensitized with selected volumes of dye **2** and dye **3** in 0.1% methanol dye solution at 40°C for a given 50 g of emulsion, coated on film base, dried, exposed sensitometrically (1/20 s Xian Feng sensitometer, Shanghai, China), developed in D-19b developer at 20°C for 5 min, fixed in a F-11 fixing bath at 25°C for 30 min, and sensitometrically measured on a CMT Densito (China). The resultant data are shown in Table 2 (pAg of the emulsion was 7.8 and average grain size 1.0 μ).

Synthesis of the heterocyclic betaine (1)

A mixture of the benzothiazole and 1,3-propane sultone in equal molar ratios was heated for 6–8 h at 120–140°C to give a solid product. This was washed with ethyl ether and acetone, and then recrystallized. The purity of the betain **1** was confirmed by elemental analysis, and the structure confirmed by ^{1}H NMR, data for which is collated in Table 1.

Synthesis of dyes 2 and 3

Condensation of the heterocycle betaine with either 4-diethyl-benzaldehyde or 4-dimethylbenzaldehyde using methanol as solvent and triethylamine as catalyst, gave dyes **2** and **3**. On pouring the cold reaction mixture into ether, the resulting solid which separated was filtered and then recrystallized. Analytical data and physical properties of dyes **2** and **3** are shown in Tables 2 and 3.

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