



Synthesis of Styryl Cationic Dyes Derived from 2-Methyl-(1,3)-dithiolium[4,5-b]quinoxaline Perchlorate

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ABSTRACT

Styryl cationic dyes of colour range yellow to blue are synthesized by the condensation of 2-methyl-(1,3)-dithiolium[4,5-b]quinoxaline perchlorate with aromatic and heteroaromatic aldehydes or ketones. The dyes were applied to polyacrylic fibres and their spectral and dyeing properties are assessed.

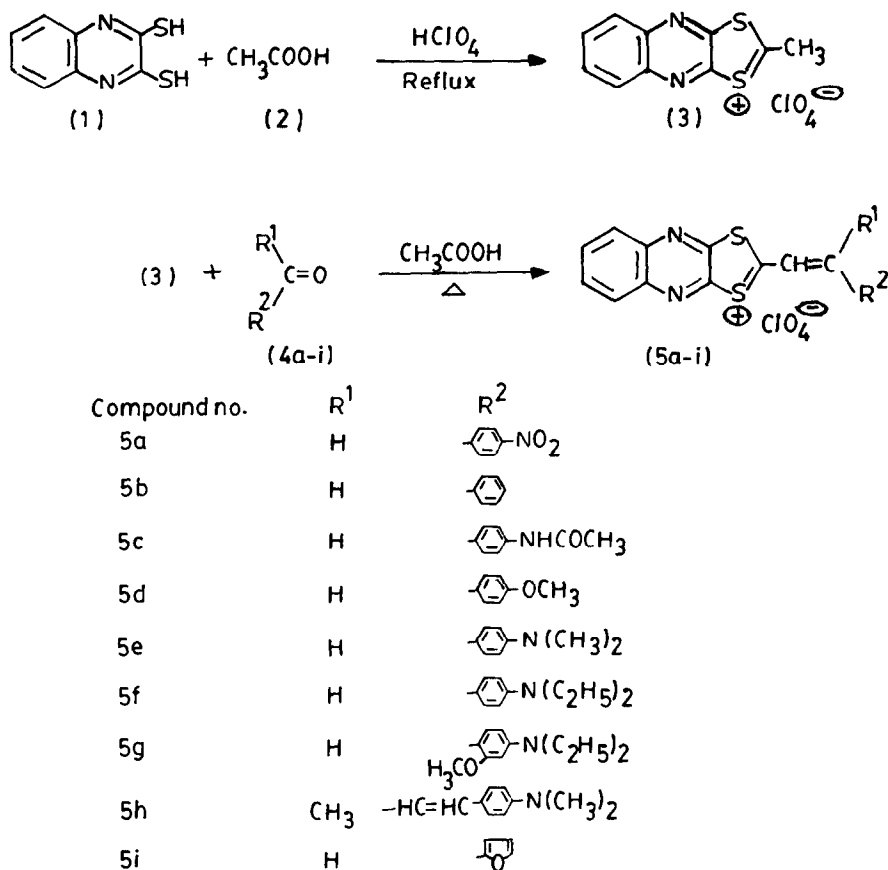
1 INTRODUCTION

1,3-Benzodithiole derivatives have been previously described as cyanine dyes and cationic dyes.^{1–3} The possibility of achieving a wider colour range of dyes for polyacrylic fibres has led the authors to synthesize some new cationic dyes based on heterofused 1,3-dithiole systems. Some 2-substituted-(1,3)-dithiolo[4,5-b]quinoxaline derivatives have been reported⁴ and cationic dyes containing substituted 1,3-benzodithiole⁵ moieties have also been described.

In the present study, the authors report the synthesis and application of some new styryl dyes derived from 2-methyl-(1,3)-dithiolium[4,5-b]quinoxaline perchlorate.

2 RESULTS AND DISCUSSION

2,3-Dimercaptoquinoxaline (1) was the starting material for the synthesis of the dyes, as shown in Scheme 1; it was condensed with acetic acid in the



Scheme 1.

presence of perchloric acid to give **3** in good yield. Compound **3** was condensed with arylaldehydes (**4a–h**) and a hetarylaldehyde (**4i**) in acetic acid yielding the corresponding styryl dyes (**5a–i**); characterization data for **5a–i** are given in Table 1.

Absorption maxima of the dyes in acetic acid varied from 421 to 576 nm. Dye **5a**, having an electron-withdrawing nitro group in the phenyl ring, is hypsochromic with respect to the phenyl derivative **5b**, whilst dye **5c** (λ_{\max} 452 nm), which has the electron-donating acetamido group substituent in the phenyl ring, shows a bathochromic shift of 14 nm. Dyes **5d–g**, with the electron-donating 4-methoxy (λ_{\max} 481 nm), 4-*N,N*-dimethylamino (λ_{\max} 538 nm), 4-*N,N*-diethylamino (λ_{\max} 545 nm) and 2-methoxy-4-*N,N*-diethylamino groups (λ_{\max} 553 nm) as substituents in the phenyl ring, show bathochromic shifts of 43, 100, 107 and 115 nm, respectively, compared to dye **5b**. The bathochromic shift in dye **5h** (λ_{\max} 576 nm) was the largest

TABLE 1
Physical and Spectral Data of 2-Styryl-(1,3)-dithiolium[4,5-b]quinoxaline Perchlorate (**5a-i**)

Compound number	Molecular formula ^a	M.p. ^b (°C)	Yield (%)	Visible spectral data (ACOH)		¹ H NMR spectral data	
				Absorption max, λ _{max} (nm)	Log ε	Solvent	δ (ppm)
5a	C ₁₇ H ₁₀ ClN ₃ S ₂ O ₆	> 350	68	421	3.86	—	—
5b	C ₂₇ H ₁₁ N ₂ S ₂ O ₄	228	76	438	3.95	—	—
5c	C ₁₉ H ₁₄ ClN ₃ S ₂ O ₅	325	83	452	3.98	DMSO-d ₆ : 2.3 (s, 3H, —OCH ₃); 6.8–7.7 (m, 10H, two olefinic and eight aromatic protons); 8.3 (s, 1H of NH, D ₂ O exchangeable)	—
5d	C ₁₈ H ₁₃ ClN ₃ S ₂ O ₅	185	71	481	4.27	—	—
5e	C ₁₉ H ₁₆ ClN ₃ S ₂ O ₄	179	78	538	4.04	DMSO-d ₆ : 2.7 (s, 6H, —N(CH ₃) ₂); 6.7–7.85 (m, 10H, two olefinic and eight aromatic protons)	—
5f	C ₂₁ H ₂₀ ClN ₃ S ₂ O ₄	265	72	545	4.28	CF ₃ COOH: 1.3 (t, 6H, —N(CH ₃) ₂); 3.95 (q, 4H, —N(CH ₂) ₂); 6.5–8.10 (m, 10H, two olefinic and eight aromatic protons)	—
5g	C ₂₂ H ₂₂ ClN ₃ S ₂ O ₅	168	69	553	4.21	—	—
5h	C ₂₂ H ₂₀ ClN ₃ S ₂ O ₄	330	69	576	4.35	—	—
5i	C ₁₅ H ₉ ClN ₂ S ₂	> 350	82	449	4.07	—	—

^a All compounds showed satisfactory elemental analysis $\pm 0.35\%$.

^b Solvent of crystallization is acetic acid.

TABLE 2
Dyeing Properties of 2-Styryl-(1,3)-dithiolium[4,5-b]quinoxaline Perchlorate

Compound number	Shade on polyacrylic fibre	Pick-up	Light-fastness	Wash-fastness at 90°C		
				STG-C	STG-W	
5a	Greenish yellow	1	3	1-2	3	2
5b	Yellow	1	3	1	3	2-3
5c	Lemon yellow	2	4	2	3-4	3
5d	Yellow	1	3	2	4	2
5e	Pink	3	5	1-2	4	2
5f	Magenta	3	4-5	2-3	4	3
5g	Red-violet	4	4-5	2-3	4	2-3
5h	Greenish blue	3	4-5	1	4	2
5i	Yellow	2	3	1-2	3	2

(138 nm), due to the extension of conjugation present. Replacement of the phenyl ring in **5b** by the furan ring (dye **5i**) gave a shift of only 11 nm.

On polyacrylic fibres, dyes **5a-i** gave brilliant hues with a colour range from yellow to greenish blue (Table 2). The pick-up of the dyes was generally good, particularly with dyes **5e-h**. Dyes **5e-h**, containing *N,N*-dialkylated groups conjugated with the dithiolium moiety, also showed good light-fastness (4-5).

3 EXPERIMENTAL PROCEDURES

All melting points are uncorrected. Absorption spectra were recorded in acetic acid on a Beckman Model 25 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 397 spectrometer. ¹H NMR spectra were recorded on a Varian 60 MHz EM-360-Z, using TMS as internal standard, and the chemical shifts are cited in δ (ppm). *p*-Nitrobenzaldehyde,⁶ *p*-acetamidobenzaldehyde,⁷ *N,N*-dimethylaminobenzaldehyde,⁸ *N,N*-diethylaminobenzaldehyde,⁸ 3-methoxy-*N,N*-diethylaminobenzaldehyde⁹ and *p*-dimethylaminobenzalacetone¹⁰ were prepared by reported methods; *p*-anisaldehyde and furaldehyde were commercial samples.

3.1 2-Methyl-(1,3)-dithiolium[4,5-b]quinoxaline perchlorate (3)

2,3-Dimercaptoquinoxaline (**1**)¹¹ (3.88 g, 0.02 mol) was dissolved in acetic acid (**2**) (20 ml) with cooling and stirring over 10-15 min. Perchloric acid (5 ml, 70%) was slowly added to the mixture and stirring was continued for a

further 15 min. During the addition of perchloric acid, liberation of hydrogen chloride gas was observed; after this had ceased, diethylether (100 ml) was added with stirring, when the red-brown 2-methyl-(1,3)-dithiolium[4,5-b]quinoxaline perchlorate salt precipitated from the mixture. This was filtered, washed with diethylether and recrystallized from acetic acid: yield, 84%; m.p. $>350^{\circ}\text{C}$; analysis, $\text{C}_{10}\text{H}_{17}\text{ClN}_2\text{S}_2\text{O}_4$. Calculated: C, 37.67; H, 2.19; Cl, 11.14; N, 8.79; S, 20.00%. Found: C, 37.18; H, 1.85; Cl, 11.05; N, 8.29; S, 19.85%. ^1H NMR ($\text{DMSO}-d_6$): 2.3 δ (s, 3H, methyl group); 6.8–7.7 δ (m, broad 4H, aromatic, phenyl ring). Mass spectrum: $m/z = 318.5$.

3.2 2-Styryl-(1,3)-dithiolium[4,5-b]quinoxaline perchlorates (5a–i); general procedure

A mixture of 2-methyl-(1,3)-dithiolium[4,5-b]quinoxaline perchlorate (3) (3.185 g, 0.01 M) and the appropriate aldehyde (4a–i) (0.01 mol) were refluxed in acetic acid (10–15 ml) with stirring for 20–30 min. The reaction mixture was cooled to room temperature and the separated solid was filtered, washed with diethylether and dried. Pertinent data for dyes 5a–i are given in Table 1.

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