Dyes and Pigments 11 (1989) 37–46

Disperse Dyes Derived from 3-Oxo-2,3-dihydrobenzo-[*b*]thiophene-1,1-dioxide and 3-Dicyanomethylene-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide

V. U. Shenoy, V. P. Patel & S. Seshadri*

Dyes Research Laboratory, University Department of Chemical Technology,
Matunga, Bombay 400019, India

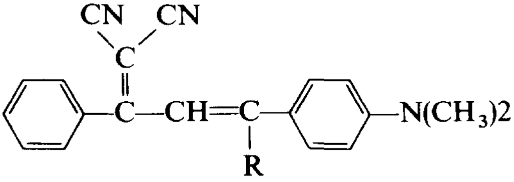
(Received 6 May 1988; accepted 24 June 1988)

ABSTRACT

The synthesis of a series of bright deeply colored styryl dyes derived from the title compounds and various aromatic and heteroaromatic aldehydes is described. Some of the dyes were subjected to oxidative cyanation to obtain the cyanated analogues. The absorption–emission spectra of the dyes were recorded and the dyeing properties on polyester of some of the dyes was studied.

1 INTRODUCTION

A series of bright disperse dyes based on the 1,1-dicyano-2,4-diarylbutadiene system (1) has been recently reported.[1] These compounds were

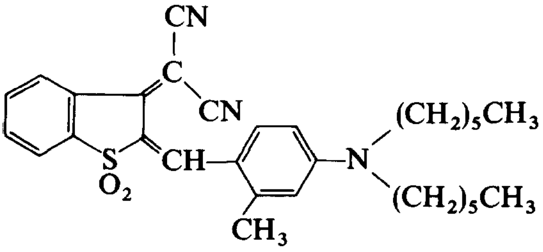


(1) R=H
R=CN

---

* To whom all correspondence should be addressed.

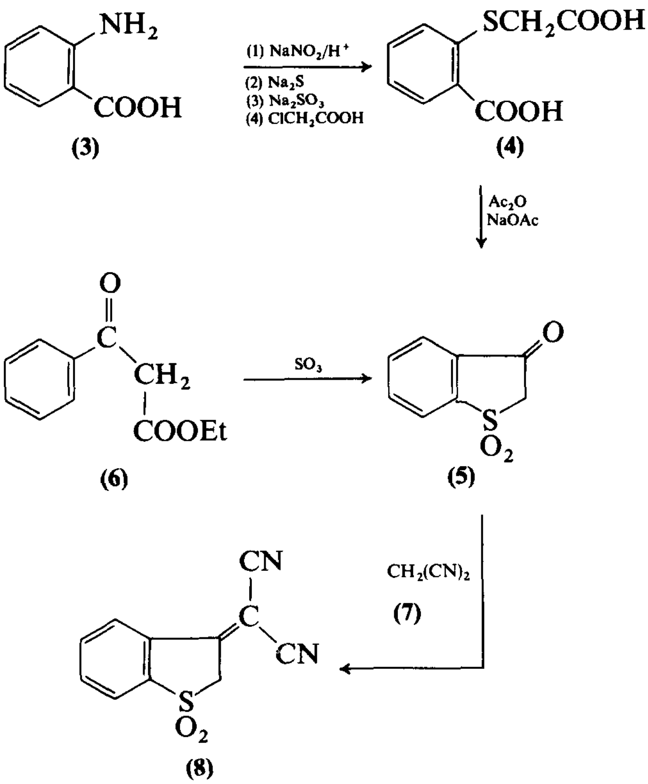
Dyes and Pigments 0143-7208/89/\$03·50



(2)

Foron Blue SR

the acyclic analogues of the deeply colored dyes described in patent specifications relating to the dicyanostyryl product[2,3] (**2**) derived from the benzothiophene dioxide heterocycle. Whereas the dyes thus patented are blue, the analogues of them synthesized by us were red. The bathochromicity observed in the former dyes can be attributed to the rigidity imparted to the



Scheme 1

double bonds of the bis-styryl system by the five-membered ring, in addition to the strong electron-withdrawing nature of the sulfone group.

The benzothiophene system and its potential to yield deep attractive colors attracted our attention. It was our aim to study whether it could be employed to generate a range of colored products which could be applied to polyester to yield good lightfast dyeings. The present paper describes the synthesis of disperse dyes derived from 3-oxo-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (**5**) and 3-dicyanomethylene-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (**8**) (Scheme 1).

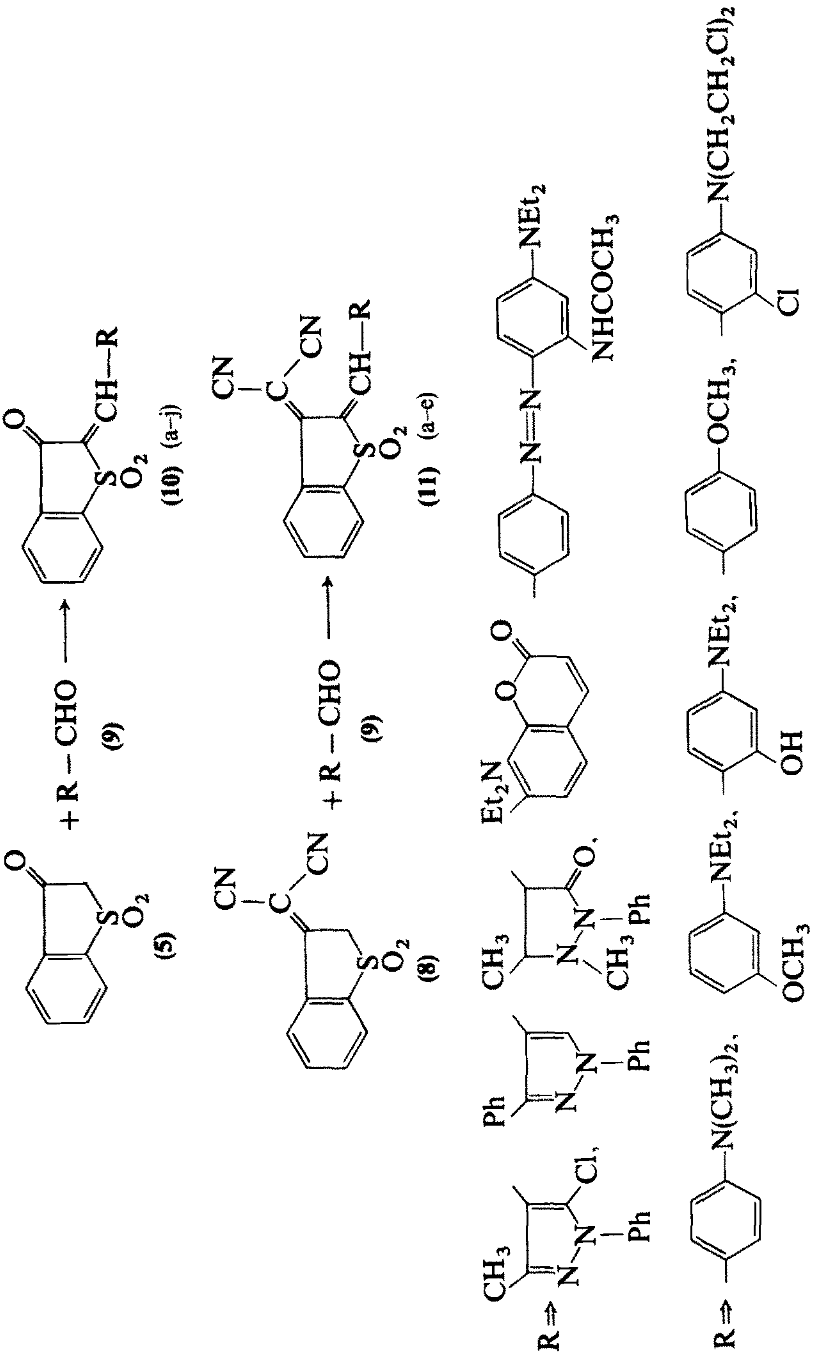
2 RESULTS/DISCUSSION

The synthesis of the key intermediate (**5**) starts from anthranilic acid[4] (**3**) or ethyl benzoylacetate[5] (**6**) as described in the literature. The synthesis of the dicyanomethylene derivative was achieved by the reaction of **5** with malononitrile (**7**) under controlled conditions.

The reaction of the active methylene group in **5** with various aromatic and heteroaromatic aldehydes (**9**) under the usual conditions of the Knoevenagel reaction gave the 3-oxobenzothiophene-2-styryl dyes **10a–10j** in good yields. Some compounds of this type have been previously reported.[6] Similarly the reaction of 3-dicyanomethylene-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (**8**) with aromatic and heteroaromatic aldehydes (**9**) resulted in the very deeply colored dyes **11a–11e** (Scheme 2). Some of these compounds were applied as disperse dyes to polyester under high-temperature and -pressure dyeing conditions and yielded yellow to greenish-blue shades.

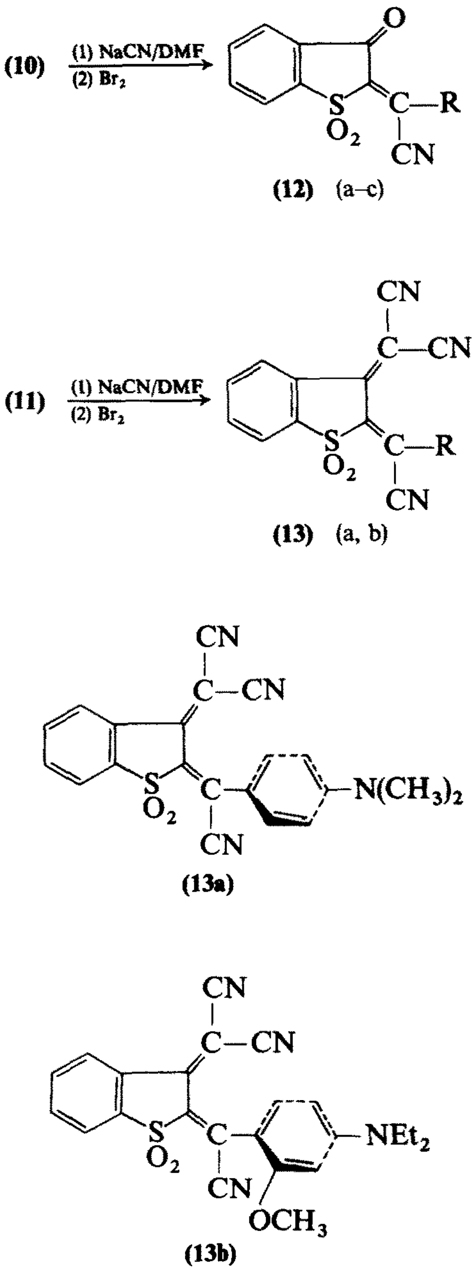
It was felt that the cyanation of the styryl dyes **10** and **11** would lead to more deeply colored products. Thus, in accordance with usual cyanation procedures, the dyes **10a–10c** and **11a–11b** were reacted in dimethylformamide with sodium cyanide, followed by oxidation with bromine. A bathochromic shift, in the order of 70–80 nm, was obtained in the case of dyes derived from **5**. However, a reverse effect was observed in the case of the dicyanostyryl dyes **11a–11b**, which showed pronounced hypsochromic shift in their absorption maxima after the introduction of the third nitrile function. This was attributed to the loss of planarity of the dye structure in **13a–13b** (see Scheme 3). The cyanated dyes **12a** and **12b** gave excellent violet to bluish-violet shades on polyester, whilst the tricyano dyes **13a** and **13b** were unstable under the conditions of dyeing.

The absorption–emission spectra of the dyes show that the dyes are fluorescent, thus rationalizing their bright hues on polyester, although with the exception of dye **10j** all showed poor light and sublimation fastness.


(5) (9) (10) (a–j)

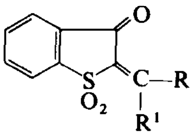
(8) (9) (11) (a–e)

Scheme 2


(10)
(1) NaCN/DMF
(2) Br_2
O
S
O_2
C—R
CN
(12) (a–c)
(11)
(1) NaCN/DMF
(2) Br_2
CN
C—CN
S
O_2
C—R
CN
(13) (a, b)
CN
C—CN
S
O_2
C
CN
$N(CH_3)_2$
(13a)
CN
C—CN
S
O_2
C
CN
NEt_2
OCH_3
(13b)

Scheme 3

TABLE 1



Compound no.	*R*[1]	*R*	*Mol. formula*	*M.p. (°C) crystn solvent*	*Yield (%)*	*Absorption max. λ(nm)*		*log ε (DMF)*	*Emission max. λ(nm)*	*PMR data: δ (ppm)*
						DMF	*CH_3COOEt*			
10a	H	*p*-Dimethylaminophenyl	$C_{17}H_{15}NO_3S$	254·5 PhCl	70	488	473	4·2	520	$CDCl_3$: 3·2[s, 6H, $N(CH_3)_2$], 7·1–8·2 (m, 9H, aromatic CH), 8·2 (s, 1H, —CH)
10b	H	2-Methoxy-4-diethylaminophenyl	$C_{20}H_{21}NO_4S$	201–203 PhCl	65	500	484	4·7	527	1·3 (t, 6H, N—CH_3), 3·7 (m, 7H, 3-proton singlet of OCH_3 superimposed on quartet of CH_2)
10c	H	2-Hydroxy-4-diethylaminophenyl	$C_{19}H_{19}NO_4S$	200 EtOH	75	502	481	4·3	532	7·0 (s, 2H, *o*-NEt_2 protons), 7·8 (s, broad, 5H, aromatic protons), 8·5 (s, 1H, —CH)
10d	H	2-Chloro-4-dichloroethylaminophenyl	$C_{19}H_{16}Cl_3NO_3S$	197 PhCl	78	480	462	4·2	512	—
10e	H	5-Chloro-3-methyl-1-phenyl-4-pyrazolyl	$C_{19}H_{13}ClN_2O_3S$	240 EtOH	75	460	448	4·0	498	—
10f	H	1,3-Diphenyl-4-pyrazolyl	$C_{14}H_{16}N_2O_3S$	216–217 PhCl	82	432	422	4·3	470	—

10g	H	2,3-Dimethyl-1-phenyl-4-pyrazolyl-5-one	$C_{20}H_{16}N_2O_3S$	198 PhCl	80	446	426	4·1	476	—
10h	H	2-Chloro-7-methoxy-3-quinolinyl	$C_{19}H_{12}NO_4S$	320(d) DMF	78	484	464	4·2	502	—
10i	H	7-Diethylamino-3-coumarinyl	$C_{22}H_{19}NO_5S$	232–235 DMF	70	562	548	4·6	590	1·1 (t, 6H, $N(CH_3)_2$, 3·3 (q, 4H, CH_2), 6·7 (m, 2H, 6,8-position of coumarin), 7·2–8·0 (m, 5H, aromatic H, coumarin 5-position H), 8·7 (m, 2H, coumarin 4-position and —CH proton)
10j	H	4-(2-Acetamido-4-diethylaminophenylazo)-phenyl	$C_{27}H_{26}N_4O_4S$	240 DMF	75	500	496	4·6	—	—
12a	CN	*p*-Dimethylamino-phenyl	$C_{18}H_{14}N_2O_3S$	275 EtOH	80	560	540	4·3	618	$CDCl_3$ + TFA: 3·2 (s, 6H, $N(CH_3)_2$, 7·0–8·0 (m, 8H, aromatic)
12b	CN	2-Methoxy-4-diethyl-aminophenyl	$C_{21}H_{20}N_2O_4S$	220 EtOH	85	580	552	4·4	610	$CDCl_3$ + TFA: 1·2 (t, 6H, CH_3—), 3·5 (m, 7H, 3H of OCH_3 superimposed on quartet of CH_2), 7·0 (d, 2H, ortho protons of —$N(Et)_2$, 7·6 (m, 5H, aromatic protons)
12c	CN	2-Hydroxy-4-diethyl aminophenyl	$C_{20}H_{18}N_2O_4S$	201 EtOH	72	582	570	4·3	580	—

All compounds gave satisfactory elemental analysis.

3 EXPERIMENTAL PROCEDURES

All melting points are uncorrected. Infrared spectra were recorded in Nujol mull on a Perkin–Elmer 397 spectrophotometer, and PMR spectra on a Varian EM-360L spectrophotometer using TMS as internal standard.

The starting materials *p*-dimethylaminobenzaldehyde,[7] 7-diethylaminocoumarin-3-carboxaldehyde,[8] 7-methoxy-3-chloroquinoline-3-carboxaldehyde,[9] 5-chloro-4-formyl-3-methyl-1-phenylpyrazole,[10] 1,3-diphenylpyrazole-4-carboxaldehyde[11] and 4-(2-acetamido-4-diethylamino)phenylazobenzaldehyde[12] were prepared by known methods.

3.1 Preparation of 3-oxo-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (5)

3-Oxo-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (**5**) was prepared by the literature procedure.[5] The intermediate ethyl 1-thianaphth-3-one-2-carboxylate was obtained in 75% yield, m.p. 140°C. [IR: 1670 cm^{-1} (ester function). PMR ($CDCl_3$): 1·3 (t, 3H, methyl protons of the ester function), 4·3 (q, 2H, methylene protons of the ester function), 7·6 (s, 4H, aromatic protons), 9·1 (s, 1H, hydroxylic proton).]

A suspension of ethyl 1-thianaphth-3-one-2-carboxylate (25·4g, 0·01 mol) in alcoholic sulfuric acid (100 ml, 10%) or aqueous sulfuric acid (150 ml, 10%) was refluxed for 3–5 h. The crystalline white solid which separated on cooling was filtered, washed well with cold water and dried. It was recrystallized from ethanol, giving **5** (14 g; 77%), m.p. 134–135°C (ethanol). [IR: 1730 cm^{-1} carbonyl function; PMR ($CDCl_3$): 4·0 (s, 2H, methylene protons), 7·8 (m, 4H, aromatic protons).

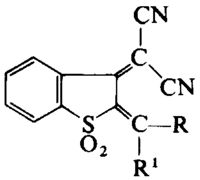
3.2 Preparation of 3-dicyanomethylene-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (8)

To a suspension of **5** (18·2 g, 0·01 mol), in anhydrous ethanol (50 ml), containing piperidine (1 ml) and glacial acetic acid (3 ml), was added malononitrile (7·3 g, 0·011 mol). The mixture was heated gradually to reflux, and after refluxing for 1 h, it was cooled to 10–15°C. The yellow crystalline solid was filtered with cold ethanol and dried, giving 17·5 g (76%) of **8**, m.p. 197–199°C (ethanol). [IR: 2220 cm^{-1} (CN function). PMR ($CDCl_3$): 4·5 (s, 2H, CH_2), 7·9 (m, 3H, 4-, 5- and 6-position protons).]

3.3 Preparation of styryl derivatives from 3-oxo-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (5) and 3-dicyanomethylene-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (8)

To a suspension of 3-oxo-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (**5**) or 3-dicyanomethylene-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (**8**)

TABLE 2



Compound no.	R^1	R	Mol. formula	M.p. (°C) Crystn solvent	Yield (%)	Absorption max. λ(nm)		log ε (DMF)	Emission max. λ(nm)	PMR data: δ (ppm)
						DMF	CH_3COOEt			
11a	H	*p*-Dimethylaminophenyl	$C_{20}H_{15}N_3O_2S$	240 DMF	78	592	570	4·3	600	3·0[s, 6H, N(CH_3)$_2$], 7·5 (m, 8H, aromatic H), 8·4 (broad s, 1H, —CH)
11b	H	2-Methoxy-4-diethylaminophenyl	$C_{23}H_{21}N_3O_3S$	230 DMF	75	608	596	4·7	611	1·0[t, 6H, N(CH_3], 3·4 (m, 7H, OCH_3 protons, and CH_2 protons), 6·7 [broad singlet 2H, protons *ortho* to N(CH_2CH_3)$_2$ group], 7·5 (m, 5H, aromatic 8·3 (broad singlet, 1H, —CH protons)
11c	H	4-methoxyphenyl	$C_{19}H_{12}N_2O_3S$	210 EtOH	70					
11d	H	5-Chloro-3-methyl-1-phenyl-4-pyrazolyl	$C_{22}H_{13}ClN_4O_2S$	182 EtOH	72					
11e	H	7-diethylamino-3-coumarinyl	$C_{25}H_{19}N_3O_4S$	215 DMF	65	628	608	4·4	641	
13a	CN	*p*-Dimethylaminophenyl	$C_{21}H_{14}N_4O_2S$	180(d) PhCl	80	502	482	4·2		
13b	CN	2-Methoxy-4-diethylaminophenyl	$C_{24}H_{20}N_4O_3S$	187(d) PhCl	82	462	440	3·9		

(0·01 mol) in 10 ml of ethanol was added the appropriate aromatic or heteroaromatic aldehyde (**9**) (0·01 mol). (In the case of 5-chloro-4-formyl-3-methyl-1-phenylpyrazole, piperidine acetate was used as catalyst.) The suspension was refluxed for 2–3 h, after which the solution was cooled and the crystalline styryl derivatives (**10a–10j** and **11a–11e**) filtered, washed with a little ethanol and dried. The derivatives were characterized by their melting points, IR spectra, elemental analyses and, in some cases, PMR spectra. Relevant data are shown in Tables 1 and 2.

3.4 Cyanation of the styryl dyes 10a–10c and 11a–11b

The appropriate styryl dye **10a–10c** or **11a–11b** (0·01 mol) was suspended in dimethylformamide (10 ml) and sodium cyanide (0·02 mol) added. The solution was stirred at room temperature for 1–2 h and then cooled to 0·5°C in an ice-bath. To the cooled solution was added bromine (0·01 mol) dropwise, and the solution stirred at room temperature for 1 h and then added to ice–water. The cyanated styryls **12a–12c** and **13a–13g**) were filtered, washed with water and dried. The yields, melting points and other characteristics are given in Tables 1 and 2.

ACKNOWLEDGEMENTS

The authors thank the Microanalytical Section of UDCT for the elemental analysis. One of us (V.P.P.) thanks the UGC for a research fellowship.

REFERENCES

1. Gokhale, U. V. & Seshadri, S., *Dyes and Pigments*, **7** (1986) 389.
2. Sandoz, British Patent 2 026 528 (1980); *Chem. Abstr.*, **93** (1980) 48539.
3. Sandoz, French Patent 2 438 045 (1980); *Chem. Abstr.*, **94** (1981) 4953.
4. Regitz, M., *Berichte*, **98** (1965) 36.
5. Matskanova, M. A. & Vanags, G. Ya., *Doklady Akad. Nauk SSSR*, **132** (1960) 615; *Chem. Abstr.*, **54** (1960) 24636.
6. Mackanova, M. & Vanags, G., *Latvijas PSR Zinatnu Akad. Vestis, Kim. Ser.*, **1963**(3) (1963) 385; *Chem. Abstr.*, **60** (1964) 1678.
7. Campaigne, E. & Archer, W. L., *Organic Synthesis*, Coll. Vol. IV, ed. N. Rabjohn. John Wiley, New York 1963, p. 331.
8. Shenoy, V. U., PhD. Thesis, University of Bombay (1988).
9. Meth Cohn, O. & Narine, B., *Tetrahedron Lett.*, **23** (1978) 2045.
10. Kvitko, I. Ya. & Porai-Koshits, B. A., *Zh. Organ. Khim*, **2** (1966) 169; *Chem. Abstr.*, **64** (1966) 15867.
11. Kira, M. A., Abdel Rehman, M. O. & Gadalla, K. J., *Tetrahedron Lett.*, **14** (1969) 109.
12. Datar, R. V., M.Sc. (Tech.) Thesis, University of Bombay (1987).