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Dyes and Pigments 62 (2004) 83–92

DYES and PIGMENTS
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Novel disperse dyes from benzo[*b*]thiophene-3(2H)-one-1,1-dioxide and ethyl benzo[*b*]thien-3(2H)-ylidenecyanoacetate,*S*,*S*-dioxide: synthesis and properties

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Received 11 August 2003; received in revised form 14 November 2003; accepted 15 November 2003

Abstract

Benzo[*b*]thiophene-3(2H)-one-1,1-dioxide was subjected to a variety of synthetic transformations via the Knovenagel, Gewald and Vilsmeier–Haack reaction. A range of styryl disperse dyes, novel annelated 2-aminothiophene based azo dyes, hydazone disperse dyes and arylated aldehydes for polyester were prepared. The colouristic and dyeing properties of these dyes on polyester were studied.

Keywords: Benzo[*b*]thiophene-3(2H)-one-1,1-dioxide; Gewald reaction; Vilsmeier–Haack reaction; Aminothiophene; Dyeing properties

1. Introduction

Thiophene and its benzo analogues find wide ranging applications in pharmaceuticals [1–3], pesticides [4], polymers [5], liquid crystals [6] and dyes [7]. The commercialisation of the brilliant disperse polymethine dye Foron Blue SR (C.I. Disperse Blue 354) [8] by Sandoz based on the strongly methylene active dicyanovinyl derivative of **1** attracted our attention [9–11]. As a part of our ongoing research program focused on the synthetic utility of heterocycles as intermediates for dyes [12,13], the utility of benzo[*b*]thiophene-3(2H)-one-1,1-dioxide **1** and ethyl benzo[*b*]thien-3(2H)-ylidenecyanoacetate,*S*,*S*-dioxide **2** as intermediates for the synthesis of a range of disperse dyes was explored. In the present paper, the ramification of the introduction of the cyano carbethoxy substituent into the benzothiophene nucleus was studied vis-à-vis the colour and dyeing properties of styryls **4a**–**d** (Table 1), aminothiophene based azo dyes **7a**–**d** and hydrazone disperse dyes **9a**–**c**. Encouraged by our experience in exploiting the synthetic usefulness of Vilsmeier reagent [14–19], the active methylene function conjugated to the α-carbonyl group of **1** was subjected to the Vilsmeier–Haack reaction [20] with the aim of generating the chloroformyl derivative **11a**. The functional formyl group and the labile chlorine atom of these derivatives offer interesting synthetic options [21]. However, under the usual

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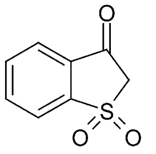
doi:10.1016/j.dyepig.2003.11.010

Table 1
Physical and visible absorption data of the styryl dyes **4a–d**

Dye	m.p. (°C)	Yield (%)	Mol. formula	Absorption max λ (nm)	log ϵ	Elemental analysis (%)		
						C	H	N
4a	226[a]	75	$C_{22}H_{21}N_2O_4S$	534	4.69	R 64.54	5.13	6.84
						F 64.51	5.10	6.82
4b	95[a]	70	$C_{29}H_{26}N_2O_4S$	547	4.62	R 69.87	5.22	5.62
						F 69.83	5.21	5.60
4c	192[a]	75	$C_{29}H_{25}N_3O_4S$	446	4.36	R 68.10	4.89	8.21
						F 68.09	4.85	8.20
4d	220[a]	73	$C_{26}H_{24}N_2O_4S$	590	4.57	R 67.82	5.21	6.08
						F 67.80	5.20	6.05

[a] Recrystallisation solvent: ethanol.

aqueous work up conditions the intermediate **11** failed to yield the desired β-chlorovinyl aldehyde. By modifying the synthetic approach subsequent to the formylation reaction, *N*,*N*-dialkylated anilines were reacted in situ with the Vilsmeier reaction mass to yield deep red coloured compounds. The deep colour of these products was attributable to the presence of extended conjugation. The spectral and dyeing properties of various arylated aldehydes **13a–c** and the corresponding dicyano **14a–c** and cyanocarbethoxy derivatives **15a–c** so synthesised were assessed.



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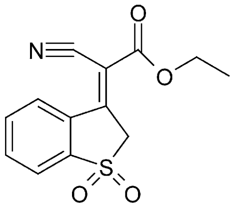

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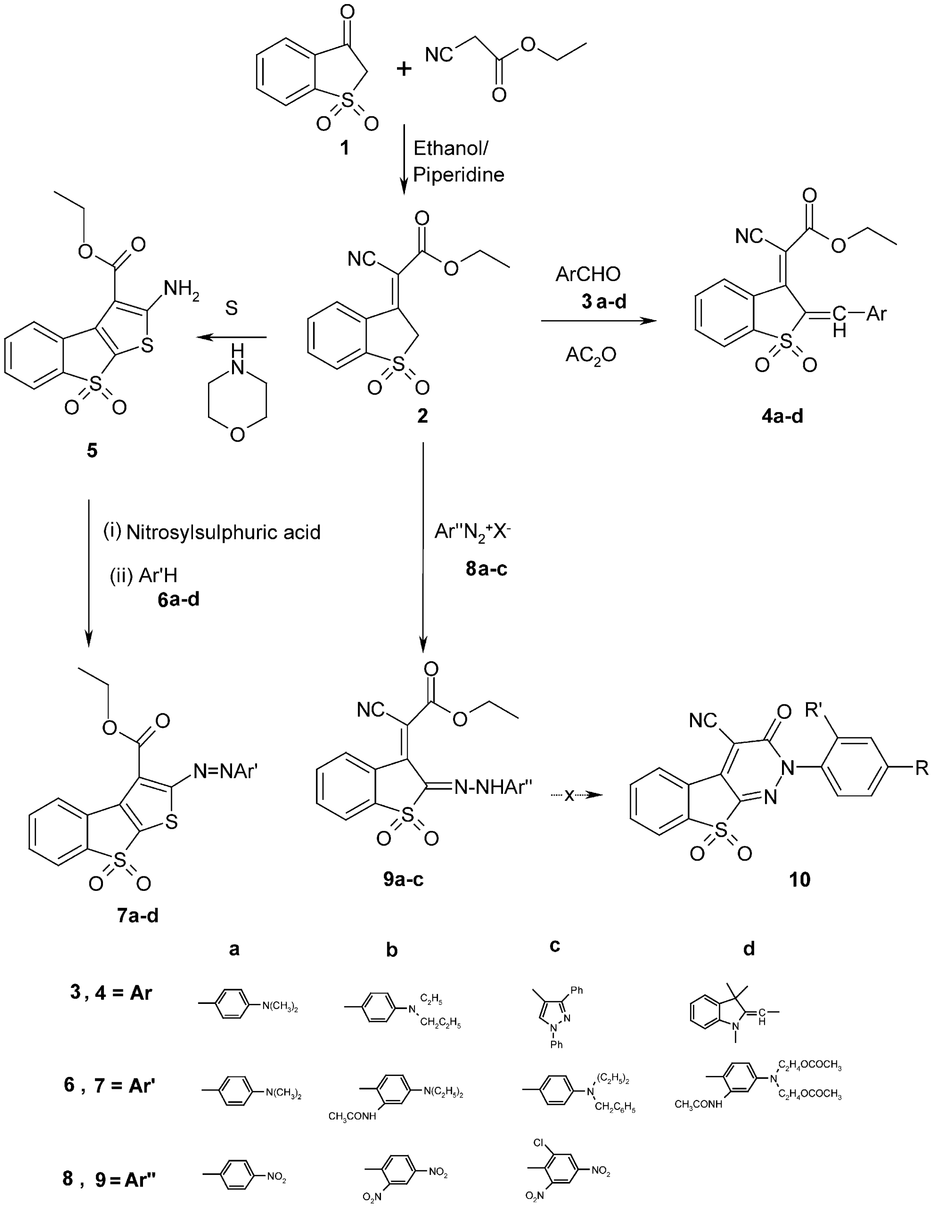
2. Results and discussion

2.1. Synthesis of styryls, aminothiophene based azo dyes and hydrazone disperse dyes based on ethyl benzo[b]thien-3(2H)-ylidenecyanoacetate,S,S-dioxide 2

Compound **1** was known to react with an equivalent amount of malononitrile in the presence of catalytic amount of piperidine/acetic acid [9] to yield the dicyanovinyl derivative. The reaction of **1** with ethylcyanoacetate was expected to proceed on similar lines. However, extrapolation of the above mentioned reaction conditions failed to give the desired product. Employment of catalytic amount of piperidine/acetic acid in ethanol, piperidine in cellosolve, piperidine in DMF and sodium ethoxide in ethanol also failed to yield **2**. The key intermediate **2** (Scheme 1) was subsequently synthesised in very good yields by the reaction of **1** with an excess of ethylcyanoacetate (1:2) in ethanol in the presence of catalytic amount of piperidine. These anomalous reaction conditions could be rationalised by the relatively weaker reactivity of the $-CH_2$ group of ethylcyanoacetate as compared to malononitrile. The compound **2** isolated was characterised by elemental analysis and its structure was further confirmed by IR and ^1H NMR spectra.

The reaction of **2** with various aldehydes to give the desired styryl dyes was expected to proceed smoothly under the classical Knovenagel reaction conditions. However, the desired product could not be obtained. Modification in the reaction conditions, using piperidine in ethanol, catalytic amount of piperidine/acetic acid in methanol, $NaOC_2H_5$ in DMF and P_2O_5 in xylene also failed to give the desired styryl dyes. The styryls **4a–d** (Table 1) were subsequently synthesised by reacting **2** with suitable aldehydes (as shown in Scheme 1) in presence of acetic anhydride at controlled temperatures. The relatively harsh reaction conditions employed to accomplish the synthesis of styryl dyes can be attributed to the lowered reactivity of the methylene function of **2** due to the introduction of the carbethoxy substituent into the benzo[*b*]thiophene-3(2H)-one-1,1-dioxide nucleus. These compounds were applied as disperse dyes to polyester under high-temperature and pressure dyeing conditions and yielded yellow to blue shades of poor to very good pick-up, poor light fastness but good sublimation fastness. The dyeing properties of the styryl dyes **4a–d** are summarised in Table 2.

It was considered of interest to study the Gewald reaction [22] with compound **2** containing a methylene group conjugated to a nitrile



Scheme 1.

Table 2
Dyeing properties of the styryl dyes **4a**–**d**

Dye	Colour on polyester	Pick- up	Light fastness	Sublimation fastness
4a	Dull violet	< 1	1	4
4b	Purple	1	1	4
4c	Yellow	2	1	4
4d	Blue	4	1	3

Table 4
Dyeing properties of the azo dyes **7a**–**d**

Dye	Colour on polyester	Pick-up	Light fastness	Sublimation fastness
7a	Reddish violet	4	1	4
7b	Violet	4	1	4
7c	Violet	4	1	4
7d	Blue	4	1	4

functionality. Therefore **2** was subjected to the classical Gewald synthesis, the usual work up gave a yellow coloured crystalline compound which was characterised by elemental analysis to be 3-carbethoxy-2-aminothiophene **5** and its structure was further confirmed by IR and ^{1}H NMR spectra. This novel annelated aminothiophene **5** containing an electron withdrawing substituent at the 3-position was then used as a diazo component. The conjugation of the $-NH_2$ function of **5** with the $-SO_2$ function of benzo[b]sulfone makes it weakly basic in character. Thus, **5** was diazotised with nitrosylsulfuric acid at 5–10 °C and coupled with various dialkylated couplers **6** in acidic medium at 5–15 °C to yield azo disperse dyes **7a–d** (Table 3). The structure of a representative azo dye was confirmed by IR and ^{1}H NMR spectra. Azo dyes **7a–d** dyed polyester in reddish violet to bluish shades of very good pick-up, poor light fastness and good sublimation fastness. The dyeing properties of the azo dyes **7a–d** are summarised in Table 4.

It was shown previously [11] that methylene groups activated by substituents with an –I effect couple smoothly with aryldiazonium salts to yield hydrazones. However, compound **2** failed to couple with aryldiazonium salts. This lowered reactivity of the methylene function of **2** attributable to the carbethoxy substituent prompted the use of nitro substituted aniline derivatives as diazo components. The synthesis of hydrazono dyes **9a–c** (Table 5) as depicted in Scheme 1, was achieved by coupling the methylene function of **2** with diazotised nitro substituted aniline derivatives at 5–15 °C at pH 7–8 for 5–6 h. The structure of a representative dye was confirmed by IR and ^{1}H NMR spectra. Inspite of literature [23] precedence attempts to cyclise the hydrazono dyes to the pyridazine derivatives **10** were unsuccessful. The hydrazono disperse dyes were characterised by

Table 3
Physical and visible absorption data of the azo dyes **7a**–**d**

Dye	M.p. (°C)	Yield (%)	Mol. formula	Absorption max λ (nm)	log ϵ	Elemental analysis (%) C	H	N
7a	245[a]	79	$C_{21}H_{19}N_3O_4S_2$	540	4.59	R 57.14	4.30	9.52
						F 57.12	4.29	9.50
7b	230[b]	76	$C_{25}H_{26}N_4O_5S_2$	557	3.97	R 57.03	4.94	10.64
						F 57.04	4.92	10.62
7c	155[b]	76	$C_{28}H_{25}N_3O_4S_2$	541	3.95	R 63.27	4.71	7.91
						F 63.26	4.68	7.89
7d	162[a]	66	$C_{29}H_{30}N_4O_9S_2$	570	4.59	R 54.21	4.67	8.72
						F 54.20	4.65	8.71

[a] Recrystallisation solvent: $CH_3OH/CHCl_3$.

[b] Recrystallisation solvent: DMF/EtOH.

Table 5
Physical and visible absorption data of the hydrazone dyes **9a–c**

Dye	M.p. (°C)	Yield (%)	Mol. formula	Absorption max λ (nm)	log ϵ	Elemental analysis (%)		
						C	H	N
9a	175	72	$C_{19}H_{14}N_4O_6S$	407	4.37	R 53.52	3.28	13.14
						F 53.50	3.25	13.12
9b	175	77	$C_{19}H_{13}N_5O_8S$	399	4.16	R 48.41	2.76	14.86
						F 48.40	2.75	14.82
9c	175	75	$C_{19}H_{12}ClN_5O_8S$	400	4.05	R 45.14	2.37	13.86
						F 45.09	2.35	13.84

dull yellow shades of very poor exhaustion, poor light fastness but good sublimation fastness.

2.1.1. Vilsmeier–Haack reaction of 1

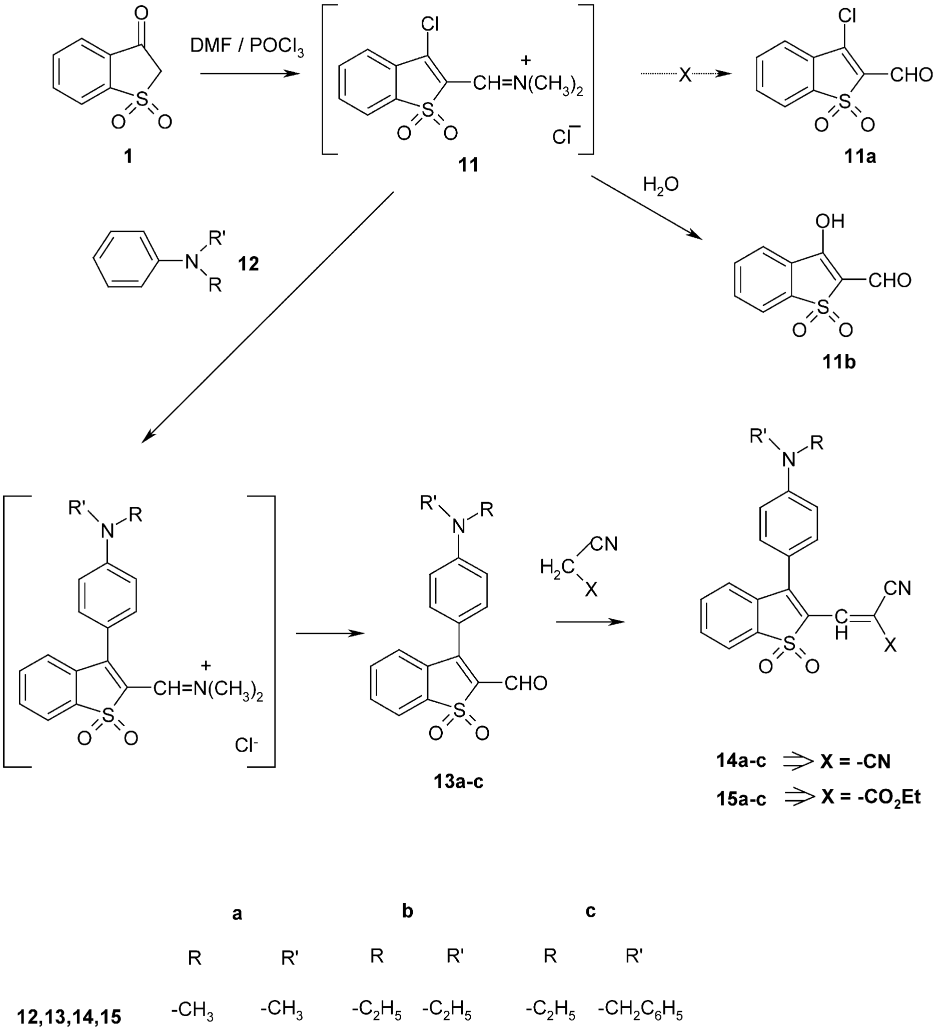
As depicted in Scheme 2, compound **1** was treated with the Vilsmeier reagent derived from DMF and $POCl_3$ at 80 °C. The β-chlorovinyl aldehyde **11a** was the expected product. However, elemental analysis of the isolated product after the usual aqueous work up indicated the absence of chlorine. The isolation of this product suggested that the chlorine atom of the intermediate **11** was highly labile and thereby susceptible to nucleophilic substitution during aqueous work up. The reactivity of the chlorine atom could be further attributed to its conjugation with the $–SO_2$ group. The IR spectra showed characteristic absorption bands at 1690 cm^{-1} and 3450 cm^{-1} (Broad) attributable to the –CHO function and the hydroxyl group respectively. An absorption band at 2720 cm^{-1} attributable to the C–H stretching band of aldehyde was also seen suggesting that the isolated product was a hydroxyaldehyde. (This structural deduction was only an approximation and the nomenclature “hydroxyaldehyde” was adopted for convenience of discussion.)

Hence, we pursued reaction conditions wherein the formylation of **1** was followed by an in situ reaction with *N*,*N*-dialkylated anilines to yield arylated aldehydes **13a–c** (Table 6). These compounds were characterised by ^1H NMR spectra. The arylated aldehydes dyed polyester in orange to reddish orange shades. Although these compounds were characterised by poor exhaustion and poor light fastness they exhibited high sublimation fastness. The dyeing properties of the arylated aldehydes **13a–c** are summarised in Table 7. The reaction of **13a–c** with suitable active methylene compounds in the presence of piperidine in ethanol, catalytic amounts of piperidine and acetic acid in methanol, $NaOC_2H_5$ in DMF, dehydrating agents (Ac_2O, P_2O_5 in xylene) failed to give the desired styryl derivatives. However, in presence of DMF containing catalytic amount of fused $ZnCl_2$ [24] deep coloured styryl dyes **14a–c** and **15a–c** were obtained which were characterised by ^1H NMR spectra (Table 8). These dyes were found to be unstable under the conditions of dyeing.

3. Experimental

3.1. General information

All melting points were recorded on a metler apparatus and are uncorrected. ^1H NMR spectra were recorded on Varian XL-300/Bruker AMX-500 spectrometer, chemical shifts are in p.p.m. from the internal standard TMS. IR spectra were recorded on “Bomen, Hartmann and Braun” FTIR. Elemental analysis was done on “Hareus Rapid Analyser”. UV-Visible spectra were recorded on “SPS-400 PYE UNICAM” spectrophotometer. The absorption spectra were recorded by dissolving 1.0 mg of the compound in 1 ml of DMF and 9 ml of methanol. A further 1 ml of this stock solution was diluted to 10 ml with methanol. The dyeing of polyester was done on HTHP dyeing equipment. Evaluation of 1.0% dye shades on polyester fabric was carried out according to standard fastness testing procedures [25]. The



Scheme 2.

Table 6
Physical and visible absorption data of the arylated aldehydes **13a**–**c**

Dye	M.p. (°C)	Yield (%)	Mol. formula	Absorption max λ (nm)	log ϵ	Elemental analysis (%) C	H	N
13a	203	45	$C_{17}H_{15}NO_3S$	501	3.61	R 65.17	4.79	4.47
						F 65.12	4.75	4.43
13b	175	45	$C_{19}H_{19}NO_3S$	487	3.77	R 66.86	5.57	4.11
						F 66.82	5.52	4.10
13c	150	35	$C_{24}H_{21}NO_3S$	477	4.01	R 71.82	5.23	3.49
						F 71.83	5.20	3.45

Table 7
Dyeing properties of the arylated aldehydes **13a**–**c**

Dye	Colour on polyester	Pick-up	Light fastness	Sublimation fastness
13a	Pale orange	<1	1	2
13b	Dull orange	<1	1	2–3
13c	Reddish orange	4	1	2–3

pick-up values (tinctorial power) are based on standard depth wherein 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.

The starting materials *p*-dimethylaminobenzaldehyde, 1,3-diphenylpyrazole-4-carboxaldehyde were prepared by known methods [26,27]. 4-(*N*-Benzyl-*N*-ethyl) aminobenzaldehyde **3b** was synthesised by the conventional Vilsmeier reaction on *N*-benzyl-*N*-ethylaniline. Fischer aldehyde **3d** and *N*,*N*-dialkylaniline couplers used were commercial samples. Substituted aniline derivatives **8a**–**c** were diazotised by known methods [28].

3.2. Benzo[b]thiophene-3(2H)-one-1,1-dioxide (1)

This was utilized in Schemes 1 and 2 was synthesised according to the procedure reported in literature [29].

3.2.1. Preparation of ethyl benzo[b]thien-3(2H)-ylidenecyanoacetate,S,S-dioxide (2)

A mixture of **1** (10 g, 0.05 mol), ethylcyanoacetate (12.4 g, 0.10 mol), ethanol (9 ml) and piperidine (0.15 ml) was heated under reflux for nearly 12 h. The solid that separated out on cooling was filtered, washed with ethanol (2×25 ml) and suction dried. This product was purified by crystallisation from ethanol/DMF to give **2**. 9.2 g (61%), m.p. 195 °C. IR (KBr) 2210 cm^{-1}(–CN), 1720 cm^{-1}(–$CO_2C_2H_5$). ^1H NMR (DMSO-d_6): δ;1.3 (3H, t, –CH_3, $J = 7.07$ Hz), 4.3 (2H, q, –CH_2, $J = 7.08$ Hz), 5.0 (2H, –CH_2, s), 8.0 (2H, m, ArH), 8.1 (1H, d, ArH, $J = 7.55$ Hz), 8.7 (1H, d, ArH, $J = 7.7$ Hz). Elemental analysis: found C, 56.30; H, 3.94; N, 5.01; S, 11.52% ($C_{13}H_{11}NO_4S$ requires C, 56.31; H, 3.97; N, 5.05; S, 11.55%).

3.2.2. Preparation of styryl dyes (4a–d)

A mixture of **2** (2.77 g, 0.01 mol), appropriate aldehydes **3a**–**d** (0.01 mol) and acetic anhydride (5 ml) was gradually heated to 110 °C on an oil bath and maintained at the same temperature for 3 h. The solid that separated out on cooling was filtered, washed with methanol (2×25 ml) and suction dried to give the styryl derivatives **4a**–**d**. The derivatives were characterised by their melting points, IR spectra, elemental analysis and in some cases PMR spectra. ^1H NMR ($CDCl_3$) of the representative styryl dye **4a**: δ 1.24 (3H, t, –CH_3, $J = 7.0$ Hz), 3.0 (6H, –$N(CH_3)_2$, s), 4.26 (2H, q, –CH_2, $J = 7.08$ Hz), 6.7 (2H, d, ArH, $J = 8.75$ Hz), 7.2 (1H, s), 7.7 (1H, s, ArH), 7.8 (2H, d, ArH, $J = 8.97$ Hz), 7.9 (2H, m, ArH), 8.8 (1H, d, ArH).

Relevant physical and visible absorption data of the styryl dyes is given in Table 1

3.2.3. Preparation of 2-amino-3-carbethoxy-thieno[2,3-b][1]benzothiophene-8,8-dioxide (5)

A mixture of **2** (2.77 g, 0.01 mol), sulphur (0.32 g, 0.01 mol), morpholine (0.87 g, 0.01 mol) and ethanol (15 ml) was gradually heated to 70 °C on an oil bath and maintained at the same temperature for 2 h. The solid that separated out on cooling was filtered, washed with ethanol (2×10 ml) and suction dried. This product was purified by crystallisation from ethanol to give **5**. 2.5 g (81%), m.p. 202 °C. IR (KBr) 1720 cm^{-1} (–$CO_2C_2H_5$), 3420 cm^{-1}, 3300 cm^{-1} (–NH_2). ^1H NMR (DMSO-d_6): δ 1.2 (3H, t, –CH_3, $J = 7.07$ Hz), 4.4 (2H, q, –CH_2, $J = 7.08$ Hz), 7.52 (1H, t, ArH, $J = 7.55$ Hz), 7.66 (1H, d, ArH, $J = 7.70$ Hz), 7.8 (1H, d, ArH, $J = 7.55$ Hz), 8.2 (2H, s, –NH_2, D_2O exchangeable), 8.5 (1H, d, ArH, $J = 7.85$ Hz). Elemental analysis: found C, 50.45; H, 3.53; N, 4.52; S, 20.70% ($C_{13}H_{11}NO_4S_2$ requires C, 50.49; H, 3.55; N, 4.53; S, 20.71%).

3.2.4. Preparation of azo dyes (7a–d)

To sulphuric acid (98%, 8.0 ml) was added at room temperature sodium nitrite (0.8 g, 0.012 mol) and the mixture was digested at 60 °C on a water bath for 30 min. The clear solution of nitrosylsulphuric acid was cooled to room temperature and then to 0–10 °C. The 2-aminothiophene derivative **5** (3.09 g, 0.01 mol) was dissolved with stirring in sulphuric acid (98%, 8.0 ml) and cooled to 0–10 °C. Ice cold nitrosylsulphuric acid was slowly added to the above mixture (15 min) and the solution was further stirred at 0–10 °C for 1 h. The diazotised solution was diluted with acetic acid (10 ml) and the excess nitrous acid destroyed with urea (2.0 g). To the coupler solution **6a–d** (0.01 mol) dissolved in acetic acid (10.0 ml) was added the above diazo liquor over 30 min. The pH was adjusted to 4–5 using sodium acetate, stirring was continued at this pH for nearly 2–3 h. The azo dyes were precipitated at pH 6 by addition of sodium carbonate. These were filtered, washed and suction dried. The azo dyes were characterised by their melting points, elemental analysis and in some cases the IR and PMR spectra. ^{1}H NMR ($CDCl_3$) of the representative azo dye **7a**: δ 1.5 (3H, t, –CH_3, $J=7.10$ Hz), 3.1 (6H, –$N(CH_3)_2$, s), 4.5 (2H, q, –CH_2, $J=7.11$ Hz), 6.7 (2H, d, ArH, $J=9.15$ Hz), 7.4 (1H, t, ArH, $J=7.55$ Hz), 7.6 (1H, t, ArH, $J=7.6$Hz), 7.7 (1H, d, ArH, $J=7.55$ Hz), 7.82 (2H, d, ArH, $J=9.05$ Hz), 8.1 (1H, d, ArH, $J=7.8$ Hz).

Relevant physical and visible absorption data of the azo dyes **7a–d** are given in Table 3.

3.2.5. Preparation of hydrazono dyes (*9a–c*)

A solution of **5** (2.77 g, 0.01 mol) in 5% NaOH (25 ml) was cooled to 0–5 °C. To this was added in a dropwise manner previously prepared diazotised aniline derivatives **8a–c**. Care was taken that the temperature never rose above 10 °C and the pH was maintained at 7–8. The coupling reaction was continued till the test portion showed complete consumption of the diazo component (confirmed by spotting the reaction mixture against R-salt solution). The hydrazono dyes **9a–c** were precipitated at pH 6 by addition of dilute HCl (10% w/v). These were filtered, washed and suction dried. These dyes were purified by column chromatography [silica gel column (100–200 mesh) eluent; benzene/ethylacetate = 4/1]. The hydrazono dyes were characterised by their melting points, elemental analysis and in some cases the IR and PMR spectra.

IR (KBr) of representative azo dye **9a**: 1720 cm^{-1} (–$CO_2C_2H_5$), 2200 cm^{-1} (–CN), 3320 cm^{-1} (–NH). ^{1}H NMR (DMSO-d_6) of the representative azo dye **9a**: δ 1.2 (3H, t,–CH_3, $J=7.07$ Hz), 4.3 (2H, q, –CH_2, $J=7.08$ Hz), 5.0 (1H, s,–NH), 7.9–8.13 (3H, m, ArH), 8.1–8.2 (3H, m, ArH), 8.5 (1H, d, ArH, $J=7.14$ Hz), 8.7 (1H, d, ArH, $J=7.23$ Hz).

Relevant physical and visible absorption data of **9a–c** are given in Table 5.

3.2.6. Preparation of arylated aldehydes (*13a–c*)

DMF (10 ml) was stirred and cooled to 0 °C in an ice salt mixture. $POCl_3$ (2.52 g, 0.04 mol) was added dropwise, after completion of addition, the mixture was stirred for 30 min. Subsequently **1** (3 g, 0.02 mol) was added in one lot, the temperature of the reaction mass was gradually raised to 80 °C on a water bath and maintained for 6 h. The reaction mixture was cooled to room temperature, *N*,*N*-dialkylated anilines **12a–c** (0.02 mol) were added under stirring. The temperature of the reaction mixture was raised to 60 °C and maintained for 2 h. The reaction mixture was cooled once again and run into a well stirred ice–water mixture (25 ml). Neutralisation to pH 4 with sodium acetate, yielded red coloured solids, which were filtered, washed with water and suction dried. The red solids were crystallised from a methanol/chloroform mixture. The arylated aldehydes were characterised by their melting points, elemental analysis and in some cases the IR and PMR spectra.

IR (KBr) of representative **13a**: 1690 cm^{-1} (–C = O). ^{1}H NMR ($CDCl_3$) of the representative **13a**: δ 3.1 (6H, s, –$N(CH_3)_2$,), 6.8 (2H, d, ArH, $J=8.65$ Hz), 7.5 (2H, d, ArH, $J=8.15$ Hz), 7.6–7.75 (3H, m, ArH), 7.88 (1H, d, ArH, $J=7.4$ Hz), 9.8 (1H, s, CHO).

Relevant physical and visible absorption data of the arylated aldehydes **13a–c** are given in Table 6.

3.2.7. Preparation of styryl dyes (*14a–c and 15a–c*)

A mixture of **13a–c** (0.01 mol), appropriate active methylene compound (0.01 mol) DMF (4 ml) and fused $ZnCl_2$ (0.5 gm) was gradually heated to 120 °C on an oil bath and maintained at the same temperature for 1 h. Methanol (8 ml) was

Table 8
Physical and visible absorption data of the styryl dyes **14a–c** and **15a–c**

Dye	M.p. (°C)	Yield (%)	Mol. formula	Absorption max λ (nm)	log ε	Elemental analysis (%)		
						C	H	N
14a	270	70	$C_{20}H_{15}N_3O_2S$	548	3.91	R 66.48	4.15	11.63
						F 66.43	4.10	11.62
14b	175	65	$C_{22}H_{19}N_3O_2S$	558	4.62	R 67.86	4.88	10.79
						F 67.85	4.85	10.75
14c	115	75	$C_{27}H_{21}N_3O_2S$	535	4.77	R 71.84	4.65	9.31
						F 71.82	4.62	9.30
15a	220	80	$C_{22}H_{20}N_2O_4S$	529	4.67	R 66.50	4.96	6.94
						F 66.45	4.95	6.92
15b	140	70	$C_{24}H_{24}N_2O_4S$	535	3.95	R 66.05	5.50	6.42
						F 66.02	5.45	6.40
15c	98	76	$C_{29}H_{26}N_2O_4S$	525	4.46	R 69.87	5.22	5.62
						F 69.85	5.20	5.60

added to the cold reaction mixture and the methanolic solution was run into ice cold water (15 ml), The solid that separated out was filtered, washed with methanol (2×10 ml) and suction dried to give the styryl derivatives **14a–c** and **15a–c**. These derivatives were crystallised from a methanol/chloroform mixture. The derivatives were characterised by their melting points, elemental analysis and in some cases the IR and PMR spectra.

IR (KBr) of representative **14a**: 2200 cm^{-1} (–CN). ^1H NMR ($CDCl_3$) of the representative styryl dye **14a**: δ 3.1 (6H, s, –$N(CH_3)_2$), 6.8 (2H, d, ArH, $J=8.97$ Hz), 7.2 (1H, s), 7.4 (2H, d, ArH, $J=9.1$ Hz), 7.6–7.8 (3H, m, ArH), 7.9 (1H, d, ArH, $J=8.2$ Hz).

Relevant physical and visible absorption data of the styryl dyes are given in Table 8.

4. Conclusion

Styryl disperse dyes, novel annelated aminothiophene based azo dyes and hydrazone disperse dyes for polyester based on ethyl benzo[*b*]thien-3(2H)-ylidenecyanoacetate,*S*,*S*-dioxide were prepared in good yields. Application properties of the dyes on polyester and their fastness properties were evaluated.The versatility of the intermediate dimethylaminoformylidene generated during the Vilsmeier reaction of benzo[*b*]thiophene-3(2H)-one-1,1-dioxide was successfully demonstrated. A range of novel arylated aldehydes and the corresponding styryl disperse dyes were prepared. The colouristic and dyeing properties of these dyes were assessed. Although the dyeing results on polyester were not encouraging the study highlighted the verstality and variety of application of the Vilsmeier–Haack reaction.

Acknowledgements

The authors thank the microanalytical section of UICT for elemental analysis and Indian Dyestuff Industries Ltd for evaluation of the dyed samples. One of the authors (H.S.B.) is thankful to Colour Chem Limited, Thane, India, for a research fellowship.

References

[1] Yamaguchi H, Ishikawa F. J Heterocyclic Chem 1981;18:67.
[2] Press JB. Chem Heterocycl Compd 1985;44:353.
[3] Sugawara T, Masuya H, Matsuo T, Miki T. Chem Pharm Bull 1980;28:2116.
[4] Ram VJ. Arch Pharm 1979;19:312.
[5] Zerbino JO, Plieth WJ, Kossmehl G. J Appl Electrochem 1991;21:935.
[6] Cai R, Samulski ET. Liq Cryst 1991;9:617.

[7] Keil D, Hartmann H, Mosehny T. Dyes and Pigments 1991;17:19.
[8] Werner B. (Sandoz Ltd) Brit UK patent 1980;2(026):528.
[9] Patel VP, PhD thesis, University of Bombay, 1990.
[10] Shenoy VU, Patel VP, Seshadri S. Dyes and Pigments 1989; 11:37.
[11] Bhuta SH, PhD thesis, University of Bombay, 1993.
[12] Seshadri S, Rajagopal R. Dyes and Pigments 1990;13:161.
[13] Seshadri S, Rajagopal R. Dyes and Pigments 1991;17:193.
[14] Seshadri S. Journal of Scientific and Industrial Research 1973;32:128.
[15] Seshadri S, Barnela SB, Pandit RS. Indian J Chem 1976; 14B:668.
[16] Tatke DR, Seshadri S, Das A, Rajarama Rao M. Indian J Chem 1979;17B:491.
[17] Barnela SB, Seshadri S. Indian J Chem 1984;23B:161.
[18] Chodankar NK, Seshadri S. Dyes and Pigments 1985;6:313.
[19] Jayant MR, Seshadri S. Dyes and Pigments 1987;8:399.
[20] Vilsmeier A, Haack A. Chem Ber 1927;60:119.
[21] Gokhale UV, Seshadri S. Dyes and Pigments 1987;8:157.
[22] Gewald K. Chem Ber 1966;99:94.
[23] Zacharius H, Junek H. Naturforsch(b) 1976;31:371.
[24] Rao PS, Venkataratnam RV. Tetrahedron Lett 1991; 32(41):5821.
[25] Standard methods for the determination of the colour fastness of textile and leather. 4th ed. Bradford: Society of Dyers and Colourists; 1985 [including the supplements upto 1985].
[26] Campaigne E, Archer WL. In: Rabjohn N, editor. Organic synthesis, coll. vol. IV. New York: John Wiley; 1963. p. 331.
[27] Kira MA, Abdel Rehman MO, Gadalla KJ. Tetrahedron Lett 1969;14:109.
[28] Saunders KH, Allen RLM. Aromatic diazo compounds. 3rd ed. London: Edward Arnold; 1985.
[29] Matskanova MA, Vanags GYa. Doklady Akad Navk SSSR 1960;132:615–8 [Chem Abstr 1960;54:24636].