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Synthesis of Azo Benzo[*b*]thiophene Derivatives and their Application as Disperse Dyes

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ABSTRACT

*2-Amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile and ethyl-2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate were synthesised by reaction of cyclohexanone and sulphur with malononitrile and ethyl cyanoacetate respectively. These 2-aminothiophene derivatives were diazotised and coupled with a variety of coupling components to give azo dyes. The spectral properties of these dyes are reported. The dyes had generally good colouration and fastness properties on polyester.*

1 INTRODUCTION

We have previously reported the synthesis of novel heterocyclic systems such as 1,3,4-oxadiazole,[1] pyrido[1,2-*a*]benzimidazoles,[2–4] fused quinoxalines,[5–8] pyrazolo-1,2,3-triazoles,[9] pyrazolopyridines and pyrazolyl-1,2,3-triazoles,[10] naphthalimidotriazoles and 1,2,3-triazolyl naphthalimides,[11] naphthalimidopyridones,[12] pyrroloquinolines,[13] quinolines,[14] isoquinolines[15] and their application as fluorescent brightening agents and dyes.

In the present study, we report the synthesis of azo dyes derived from 2-aminobenzo[*b*]thiophene derivatives and their use as disperse dyes for polyester fibres.

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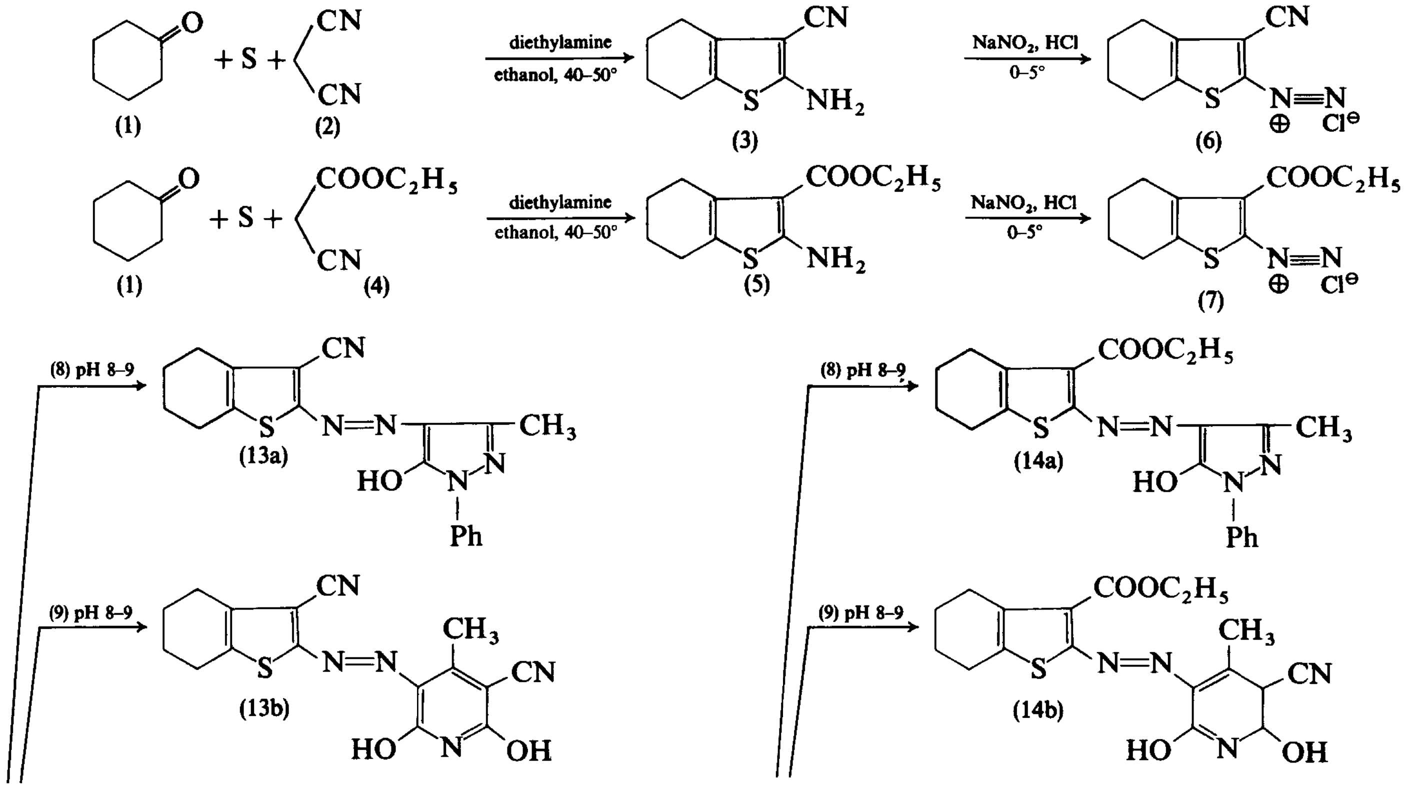
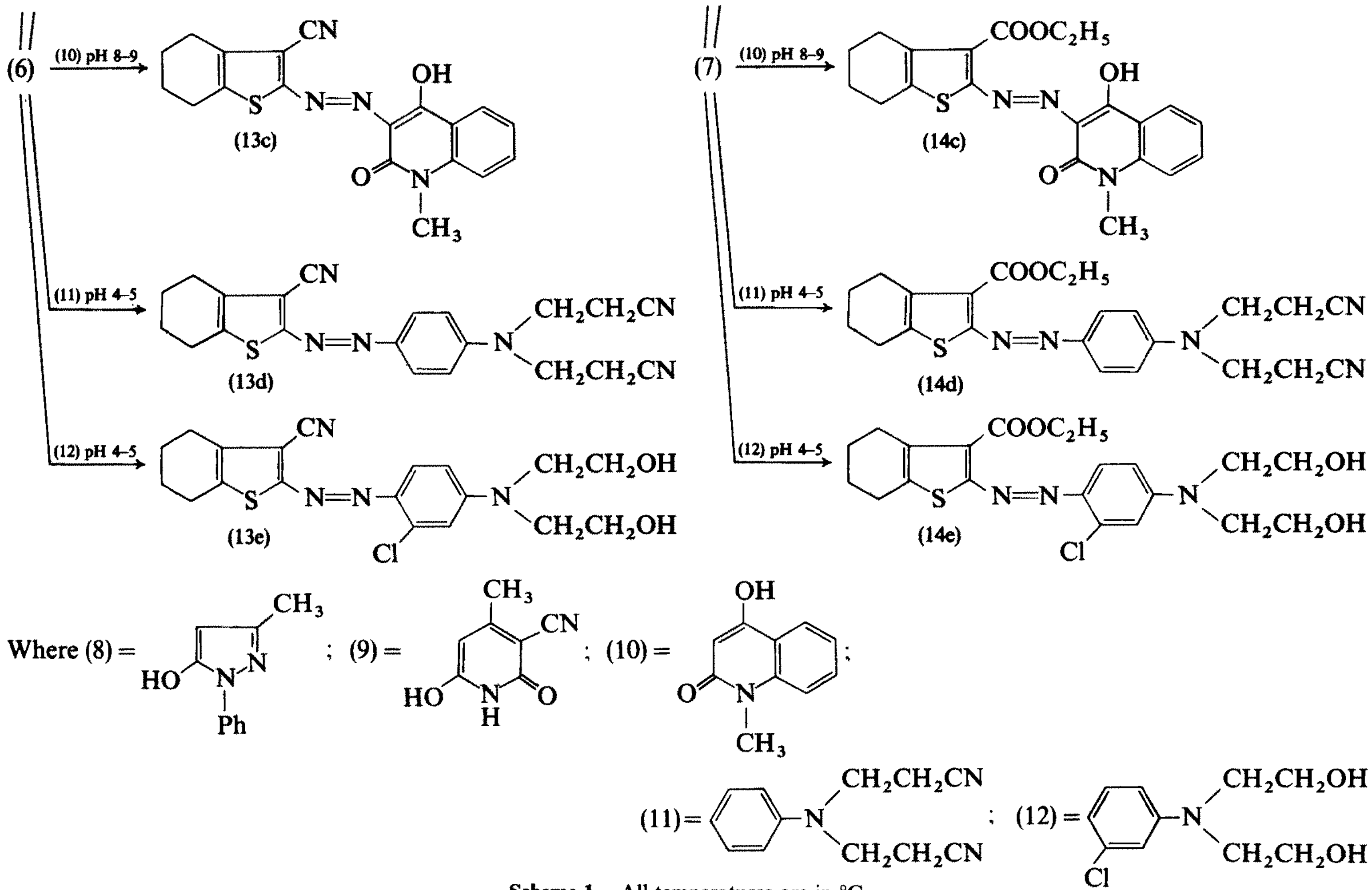

(1)
(2)
diethylamine
ethanol, 40–50°
(3)
NaNO2, HCl
0–5°
(6)
(1)
(4)
diethylamine
ethanol, 40–50°
(5)
NaNO2, HCl
0–5°
(7)
(8) pH 8–9
(13a)
(9) pH 8–9
(13b)
(8) pH 8–9
(14a)
(9) pH 8–9
(14b)



Scheme 1. All temperatures are in °C.

2 RESULTS AND DISCUSSION

The thiophene intermediates, 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (**3**) and ethyl-2-amino-4,5,6,7-tetrahydrobenzo[*b*]-thiophene-3-carboxylate (**5**) were synthesised by the condensation of cyclohexanone, sulphur and malononitrile and of cyclohexanone, sulphur and ethyl cyanoacetate, respectively, following the Gewald Reaction.[16]

These new thiophene intermediates were diazotised with cold hydrochloric acid and sodium nitrite and coupled with a variety of heterocyclic couplers such as 1-phenyl-3-methyl-5-hydroxypyrazole, 2,6-dihydroxy-3-cyano-4-methylpyridine, 4-hydroxy-1-methylquinolin-2-one and aromatic couplers such as *N*,*N*-biscyanoethylaniline and 3-chloro-*N*,*N*-bis(hydroxyethyl)aniline to give 2-(hetaryl or aryl)-azo-4,5,6,7-tetrahydrobenzo[*b*]-thiophene-3-carbonitrile and ethyl-2-(hetaryl or aryl)-azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (see Scheme 1).

The IR spectra of the compounds were recorded in Nujol mull, and showed the principal functional groups in the dyes, viz. compounds **13a–13e**, sharp peak at 2200–2220 cm^{-1}, cyano group; compounds **13a–13c** and **13e**, broad peaks at 3200–3400, 3280–3380, 3380–3400 and 3200–3400 cm^{-1} respectively, hydroxy group; compound **13c**, peak at 1680 cm^{-1}, keto group; compounds **14a–14e**, peak at 1650–1660 cm^{-1}, —COOEt group; compounds **14b** and **14d**, sharp peak at 2200–2220 cm^{-1}, cyano group; compounds **14a**, **14b**, **14c**, **14e**, broad peak at 3200–3400, 3280–3380, 3300–3400 and 3200–3400 cm^{-1}, respectively, hydroxy group; and compound **13c**, peak at 1680 cm^{-1}, keto group.

The absorption maxima of the dyes **13a–13e** and **14a–14e** were recorded in DMF solution and are shown in Table 1. The absorption maxima of dyes **13a–13e** varied from 465 to 540 nm and those of dyes **14a–14e** from 480 to 510 nm. It was observed in general that the dyes **13a–13e** derived from 3-cyanothiophene derivatives were bathochromic when compared with analogous dyes **14a–14e** derived from 3-carboethoxythiophene derivatives. This is relatable to the stronger electron-acceptor nature of the cyano group with respect to the carboethoxy group, thus enhancing electron delocalisation in the dye molecule.

The dyes **13a–13e** and **14a–14e** were dyed on polyester fibres at 1% shade and gave yellow to red–violet hues as shown in Table 1. The dyeings of dyes **13a**, **13e**, **14a**, **14b** and **14c** were very bright, whereas those from the other dyes were pale.

The fastness properties of the dyes are shown in Table 1. The pick-up values of the dyed polyester fibres varied from 2 to 3, with most of them having a 3 rating. The lightfastness of these dyes varied from 3 to 6. Thus, dyes **13b**, **14d** and **14e** had poor lightfastness (3), dyes **13a**, **13c**, **13d** and **14c**

TABLE 1
Absorption Spectra and Dyeing Properties of 2-Azothiophene Derivatives

Dye	*Colour on dyed polyester fibres*	*Absorption maximum λ_{max} nm (in DMF)*	*log e*	*Pick-up*	*Light fastness*	*Sublimation fastness*
13a	Very bright orange-yellow	505	4·10	3	4	4
13b	Pale red	515	3·64	2	3	4
13c	Red–brown	509	3·60	2	4	4
13d	Red–violet	525	3·30	3	4	3
13e	Very bright pink	540	3·95	3	5	5
14a	Very bright golden yellow	498	4·12	3	6	5
14b	Very bright pink	497	3·76	3	5	4
14c	Very bright red	492	3·89	3	4	5
14d	Pale red–violet	510	3·37	2	3	3
14e	Pale red–violet	480	3·60	3	3	4

had fair lightfastness (4), dyes **13e** and **14b** had good lightfastness (5) and the lightfastness of the dye **14a** was very good (6). The sublimation fastness of these dyes was in the range of 3 to 5. Thus the dyes **13d** and **14d** showed good sublimation fastness (3), dyes **13a**, **13b**, **13c**, **14b** and **14e** showed very good sublimation fastness (4) whereas the sublimation fastness of dyes **13e**, **14a** and **14c** showed excellent sublimation fastness (5). The dyes **13e**, **14a** and **14b** in particular showed good general fastness properties on polyester.

3 EXPERIMENTAL

All melting points are uncorrected and are in °C. Absorption spectra in DMF solutions were recorded on a Beckman Model 25 spectrophotometer. Infrared spectra were recorded on a Perkin–Elmer model 397 spectrometer.

3.1 Preparation of starting materials

2-Amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (**3**)[16] and ethyl-2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (**5**)[16] were prepared by known methods.

3.2 2-(1-Phenyl-3-methyl-5-hydroxypyrazol-4-yl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (13a)

Compound **3** (8·9 g, 0·05 mol) was dissolved in hydrochloric acid (50 ml conc. hydrochloric acid in 50 ml water) by warming and the solution was then cooled to 0–5°C. Sodium nitrite (3·45 g, 0·05 mol) in water (10 ml) was gradually added to this solution over 2 h at 0–5°C with stirring. The reaction mixture was stirred for a further 1 h, maintaining a temperature at 0–5°C. Excess nitrous acid was destroyed with urea.

1-Phenyl-3-methyl-5-hydroxypyrazole (**8**) (8·7 g, 0·05 mol) was dissolved in dilute sodium bicarbonate and the resulting solution was cooled to 0–5°C. The diazo solution above was gradually added over 2 h with stirring at 0–5°C, maintaining the pH at 8–9 by addition of solid sodium carbonate. The mixture stirred for a further 4 h at 0–5°C and the partially separated dye was completely precipitated by neutralising with dilute hydrochloric acid (5%). It was filtered, washed with water, dried and recrystallised from ethanol as bright orange–yellow crystals (85%), m.p. 218°C. Calculated for $C_{19}H_{17}N_5OS$: C, 62·8; H, 4·6; N, 19·2; S, 8·8. Found: C, 62·7; H, 4·5; N, 19·0; S, 8·6%.

The above procedure was also used to synthesise dyes **13b, 13c, 13d** and **13e**.

3.3 2-(2,6-Dihydroxy-3-cyano-4-methylpyridin-5-yl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (13b)

Crystallised from ethanol as pale red needles (92%), m.p. 154°C. Calculated for $C_{16}H_{13}N_5O_2S$: C, 56·6; H, 3·8; N, 20·6; S, 9·4. Found: C, 56·6; H, 3·75; N, 20·5; S, 9·1%.

3.4 2-(Hydroxy-1-methylquinolin-2-one-3-yl)azo-4,5,6,7-tetrahydroxybenzo[*b*]thiophene-3-carbonitrile (13c)

Crystallised from ethanol as red–brown flakes (78%), m.p. 181°C. Calculated for $C_{19}H_{16}N_4O_2S$: C, 62·6; H, 4·3; N, 15·3; S, 8·7. Found: C, 62·4; H, 4·28; N, 15·25; S, 8·5%.

3.5 2-[4-*N*,*N*-(*β*,*β*-Biscyanoethyl)phenyl]azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (13d)

The coupling was carried out at pH 4–5; the product was crystallised from ethanol/DMF (1:1) mixture as red–violet needles (81%), m.p. 116°C. Calculated for $C_{21}H_{20}N_6S$: C, 64·9; H, 5·1; N, 21·6; S,8·2. Found: C, 64·8; H, 5·0; N, 21·5; S, 8·0%.

3.6 2-[2-Chloro-4-*N*,*N*-(*β*,*β*-bishydroxyethyl)phenyl]azo-4,5,6,7-benzo[*b*]thiophene-3-carbonitrile (13e)

The coupling was carried out at pH 4–5; the product was crystallised from ethanol/DMF (1:1) mixture as bright pink crystals (65%), m.p. 236°C.

Calculated for $C_{19}H_{21}ClN_4O_2S$: C, 56·4; H, 5·1; Cl, 8·6; N, 13·8; S, 7·9. Found: C, 56·2; H, 5·1; Cl, 8·4; N, 13·6; S, 7·6%.

3.7 Ethyl-2-(1-phenyl-3-methyl-5-hydroxypyrazol-4-yl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (14a)

Compound **5** (11·25 g, 0·05 mol) was dissolved in hydrochloric acid (50 ml conc. hydrochloric acid in 50 ml water) by warming and then cooled to 0–5°C. Sodium nitrite (3·45 g, 0·05 mol) in water (10 ml) was gradually added to the above solution over 3 h at 0–5°C with continuous stirring. The reaction mixture was stirred for a further 2 h, maintaining a temperature of 0–5°C, and excess nitrous acid was then destroyed with urea.

1-Phenyl-3-methyl-5-hydroxypyrazole (**8**) (8·7 g, 0·05 mol) was dissolved in dilute sodium carbonate solution. The resulting solution was cooled to 0–5°C and the above diazo solution was gradually added over 2 h with stirring at 0–5°C, maintaining the pH at 8–9 by addition of solid sodium carbonate. The mixture was stirred for 5 h at 0–5°C and the partially separated dye then completely precipitated by neutralising with dilute hydrochloric acid (5%). It was filtered, washed with water, dried, and recrystallised from ethanol in bright golden yellow needles (86%), m.p. 148°C. Calculated for $C_{21}H_{22}N_4O_3S$: C, 61·4; H, 5·3; N, 13·6; S, 7·8. Found: C, 61·3; H, 5·1; N, 13·5; S, 7·6%.

The above procedure was used to synthesise dyes **14b**, **14c**, **14d** and **14e**.

3.8 Ethyl-2-(2,6-dihydroxy-3-cyano-4-methylpyridin-5-yl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (14b)

Crystallised from benzene as bright pink needles (79%), m.p. 203°C. Calculated for $C_{18}H_{18}N_4O_4S$: C, 55·9; H, 4·6; N, 14·5; S, 8·2. Found: C, 55·8; H, 4·7; N, 14·4; S, 8·15%.

3.9 Ethyl-2-(4-hydroxy-1-methylquinolin-2-one-3-yl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (14c)

Crystallised from ethanol as dark red crystals (84%, m.p. 110°C. Calculated for $C_{21}H_{21}N_3O_4S$: C, 61·3; H, 5·1; N, 10·2; S, 7·7. Found: C, 61·25; H, 5·0; N, 10·0; S, 7·5%.

3.10 Ethyl-2-[4-*N*,*N*-(β,β-biscyanoethyl)phenyl]azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (14d)

Crystallised from ethanol/DMF (1:1) mixture as red–violet needles (92%), m.p. 126°C. Calculated for $C_{23}H_{25}N_5O_2S$: C, 63·4; H, 5·7; N, 16·0; S, 7·3. Found: C, 63·3; H, 5·5; N, 15·85; S, 7·25%.

3.11 Ethyl-2-[2-chloro-4-*N*,*N*-(β,β-bishydroxyethyl)phenyl]azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (14e)

Crystallised from ethanol/DMF mixture as red–violet crystals (80%), m.p. 145°C. Calculated for $C_{21}H_{26}ClN_3O_4S$: C, 55·8; H, 5·7; Cl, 7·7; N, 9·3; S, 7·0. Found: C, 55·7; H, 5·6; Cl, 7·55; N, 9·1; S, 7·1%.

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