Synthesis of azobenzo[b]thiophene derivatives and their dyeing performance on polyester fibre

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Ethyl 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate was synthesised by the reaction of cyclohexanone and sulphur with ethylcyanoacetate. The 2-aminothiophene derivative was diazotised and coupled with various N-arylmaleimides to give monoazo disperse dyes. The dyeing performance of these dyes was assessed on polyester fabric. These dyes were found to give light pink to reddish pink shades with very good depth and levelness on polyester fabric. The dyed fabric showed fair light fastness and excellent washing, rubbing, perspiration and sublimation fastness. The dyebath exhaustion on polyester fabric was found to be good and acceptable.

Introduction

Heterocycles have been put to much use in disperse dyes chemistry which, it has been claimed, was the first area to foster the industrial exploitation of heterocyclic amines.[1] Numerous heterocyclic dyes are now marketed to produce a full range of dispersed dyestuffs without handling colorants based on heteroaromatic diazo components. Most heterocyclic dyes of technical interest for application to textiles are derived from diazo components consisting of five membered rings containing one sulphur heteroatom and to which a diazotisable amino group is directly attached. Systems of this kind are capable of providing red to blue disperse dyes that meet the rigorous technical and economic requirements demanded of them by both manufacturer and user.

The colours of hydrophobic monoazo dyes containing thiophene rings were investigated as long ago as 1949 by Dann.[2] A major advance was made by the research group of Dickey[3] of Eastman Kodak in the 1950s in heterocyclic azo dyes and they published a classic paper on thiophene-based disperse dyes in 1958. The development by Gewald[4] in the 1960s of a simple and versatile synthetic route for 2-aminothiophenes was also a major advance in the field. A recent important development is the resurgence of interest in dyes derived from 2-aminothiophene derivatives. The technical potential of such dyes for cellulose acetate and polyester was noted some time ago,[3] but their manufacture was not commercialised because of the lack of suitable economic synthetic procedures. Improvements in synthetic approaches to derivatives of 2-aminothiophene, stimulated by the work of Gewald,[5]sparked renewed commercial interest. The promise of Gewald's discovery signalled a steady steam of applications concerning thiophene-based azo disperse

dyes over the next 20 years.[6−8] Despite, or perhaps because of, commercial interest, few papers have been published recently[9−11] concerning the synthesis and properties of such dyes.

Recently, the revival of interest in the synthesis of disperse dyes based upon thiophene derivatives has played a significant role in the technology of disperse dyes.[12−13] A wide variety of information about the usefulness and technical importance of 2-aminothiophene derivatives as diazo components in the synthesis and application of greenish blue to blue disperse dyes have appeared in the literature.[14−17] The ethyl ester of 2-amino-4,5,6,7-tetrahydrobenzo[b] thiophene-3-carboxylic acid is a well-known heterocyclic diazo component. The versatility of this key compound and related analogues in the synthesis of various dyes and fluorescent brighteners has been well demonstrated.[18−21]

Earlier, we studied disperse[22−25]dyes based on 2-aminothiophene derivatives. The encouraging results prompted us to extend the study on thiophene moiety. Hence, a series of monoazo dyes of a general formula shown in Figure 1 were synthesised and tested as disperse dyes for polyester fabric. In addition to the characterisation of the dyes, an evaluation of their technical properties and a colour assessment were performed.
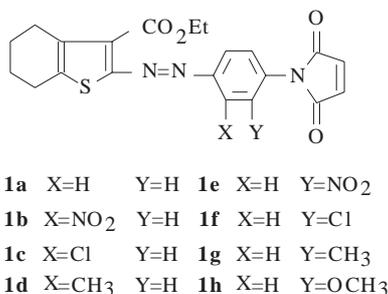

1a	X=H	Y=H	1e	X=H	Y=NO$_2$
1b	X=NO$_2$	Y=H	1f	X=H	Y=Cl
1c	X=Cl	Y=H	1g	X=H	Y=CH$_3$
1d	X=CH$_3$	Y=H	1h	X=H	Y=OCH$_3$

Figure 1. General structure formula.

Experimental

General information

All of the chemicals used in the synthesis of dyes **1** were of commercial grade and were further purified by crystallisation and distillation. All solvents used were of spectroscopic grade. Melting points were determined by the open capillary method. The visible absorption spectra were measured using a CARL ZEISS UV/VIS SPECORD Spectrometer. Elemental analyses were carried out on a Carlo Erba Elemental Analyser 1108. Infrared spectra were recorded in KBr pellets, on a Perkin-Elmer model 983 spectrophotometer.

Preparation of ethyl 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene 2

The title compound was synthesised by the method reported in the literature.[4]

Preparation of various N-arylmaleimides coupling components 4a-h

These compounds were synthesised by the general method reported in the literature.[26]

Preparation details of tetrahydrobenzo[b]thiophene dyes 1a-h

Diazotisation of ethyl 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate **2** (Figure 2) was effected with nitrosylsulphuric acid as follows.
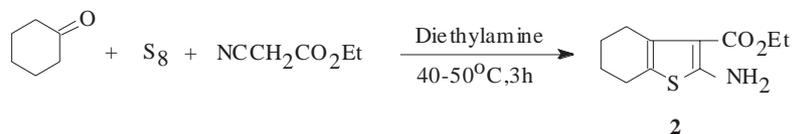

Figure 2. Preparation of ethyl 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene **2**.

Diazotisation

A total of 1.38 g (0.02 mol) dry sodium nitrite was slowly added, with stirring, to 1.1 ml concentrated sulphuric acid with stirring while allowing the temperature to rise to 65°C. The solution was then cooled to 5°C and a mixture (20 ml) of acetic acid and propionic acid (17:3) was added dropwise with stirring, allowing the temperature to rise to 15°C but no higher. The reaction mixture was then cooled to 0-5°C, and 4.5 g (0.02 mol) ethyl 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate was added portionwise and stirring was continued at this temperature for 2 h. The excess nitrous acid (tested for using starch-iodide paper) was decomposed with the required amount of urea. The clear diazonium salt solution **3** thus obtained was used immediately in the coupling reaction (Figure 3).
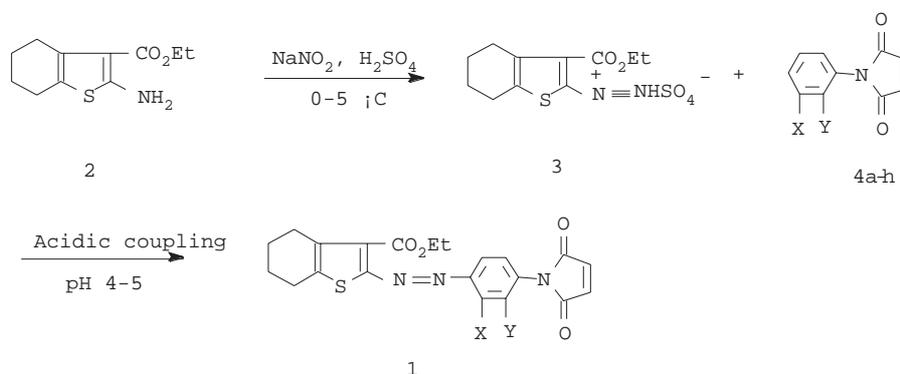

Figure 3. Synthetic route of dyes **1**.

General coupling procedure

The N-arylmaleimide (0.02 mol) was dissolved in 10 ml of acetic acid and 5 ml of water together with 5 g of sodium acetate. This solution was cooled in an ice-bath and the diazonium solution of **3** previously prepared was added dropwise over 30 min with vigorous stirring. The pH was maintained between 4 and 5 by addition of 10% sodium acetate solution. Stirring was continued for 2 h, allowing the temperature to rise to ambient. The dye was then filtered off, washed with warm water and then with cold water until acid-free, dried at 50°C in an oven to give azo dye **1**. Recrystallisation from DMF provided the pure dye. All other dyes, **1b** to **1h,** were prepared in a similar manner. The characterisation data are given in Tables 1 and 2.

Table 1. Absorption maxima, intensities and dyebath exhaustion of dyes **1** on polyester.

Dye	Substituents		Absorption in DMF		Exhaustion (%)
no.	X	Y	λ_{max}	$\log \varepsilon$	
1a	H	H	500	3.39	72
1b	NO$_2$	H	440	3.52	75
1c	Cl	H	400	3.69	73
1d	CH$_3$	H	540	4.20	70
1e	H	NO$_2$	400	3.84	68
1f	H	Cl	325	3.89	72
1g	H	CH$_3$	520	3.92	78
1h	H	OCH$_3$	510	3.74	75

Table 2. Characterisation data of dyes **1**.

Dye	Substituents		Melting point	Yield	R$_f$
no.	X	Y	(°C)	(%)	
1a	H	H	152-154	72	0.91
1b	NO$_2$	H	168-170	81	0.86
1c	Cl	H	180-181	74	0.93
1d	CH$_3$	H	185-187	71	0.89
1e	H	NO$_2$	164-165	85	0.85
1f	H	Cl	178-179	75	0.92
1g	H	CH$_3$	165-166	78	0.88
1h	H	OCH$_3$	178-180	75	0.87

Dyeing procedure

Dyeing at 130-135°C and high pressure (24-30psi) is a convenient method for dyeing polyester fabric in the laboratory. A laboratory model glycerin-bath high-temperature beaker dyeing machine was used. A paste of finely powdered dye (40 mg) was prepared with dispersing agent Dodamol (80 mg), wetting agent Tween-80 (5 mg) and water (1 ml) in a ball mill. To this paste, water (99 ml) was added with stirring and the pH was adjusted to 4.5-5 using acetic acid. The previously mentioned dye suspension (100 ml) was added to a beaker provided with a lid and a screw cap. Before closing the lid and tightening the metal cap over the beaker, a wetted pattern of polyester fabric was rolled into the beaker. The beaker was then placed vertically on the rotatory carrier inside the tank and the clamp plate was firmly tightened. The rotatory carrier was then allowed to rotate in the glycerin-bath and the temperature of which was raised to 130°C at the rate of 2°C/min. The dyeing was continued for 1 h, under pressure. After cooling for 1 h, the beaker was removed from the bath and washed with water. The dyed pattern was thoroughly washed with hot water at 50°C and then with cold water and dried at room temperature.

Reduction clear

Dyed fabric was reduction cleared by stirring in an aqueous solution containing 2 g/litre of sodium dithionite, 2 g/litre of sodium hydroxide and 1 g/litre of sodium hydrosulphite for 20 min at 60-65°C. The treated polyester was then rinsed hot and cold, and acidified in an 1 ml/litre acetic acid solution, and then rinsed with water.

Fastness properties

The fastness to light, sublimation and perspiration was assessed in accordance with BS:1006-1978. The rubbing fastness test was carried out using a crockmeter (Atlas) in accordance with AATCC-1961 and the wash fastness test in accordance with IS:765-1979. The details of various fastness tests are mentioned below.

Light fastness test

The light fastness study was carried out using a Microscal light fastness tester having a straight mercury vapour lamp (MB/V 400W). The dyed fabric is exposed to light along with the standard dye patterns of specific ratings. Such standard samples are a blue wool standard manufactured by Microscal Ltd and identified by the numerical designation 1 to 8. The higher the rating, the better is the light fastness. The results are given in Table 4.

Table 3. Elemental analysis of dyes **1**.

Dye	Substituents		Molecular	Molecular	C%		H%		N%	
no.	X	Y	formula	weight	Calcd.	Found	Calcd.	Found	Calcd.	Found
1a	H	H	$C_{21}H_{19}N_3O_4S$	409	61.61	61.00	4.64	4.20	10.26	10.00
1b	NO_2	H	$C_{21}H_{18}N_4O_6S$	454	55.50	55.10	3.96	3.50	12.33	12.00
1c	Cl	H	$C_{21}H_{18}N_3O_4SCl$	443.5	56.82	56.29	4.05	3.86	9.47	9.30
1d	CH_3	H	$C_{22}H_{21}N_3O_4S$	423	62.41	62.28	4.96	4.80	9.92	9.70
1e	H	NO_2	$C_{21}H_{18}N_4O_6S$	454	55.50	55.20	3.96	3.85	12.33	12.21
1f	H	Cl	$C_{21}H_{18}N_3O_4SCl$	443.5	56.82	56.62	4.05	3.81	9.47	9.25
1g	H	CH_3	$C_{22}H_{21}N_3O_4S$	423	62.41	62.25	4.96	4.75	9.92	9.68
1h	H	OCH_3	$C_{22}H_{21}N_3O_5S$	439	60.13	60.00	4.78	4.62	9.56	9.41

Table 4. Results of dyeing and various fastness properties of dyes **1** on polyester.

Dye	Shade	Fastness to						
no.	on polyester	Light	Wash	Rubbing		Perspiration		Sublimation
				Dry	Wet	Acid	Alkaline	
1a	Light pink	2-3	5	5	5	5	5	5
1b	Light pink	2-3	5	5	5	5	5	5
1c	Cream	2-3	5	5	5	5	5	5
1d	Reddish pink	2-3	5	5	5	5	5	5
1e	Light pink	2-3	5	5	5	5	5	5
1f	Light pink	2-3	5	5	5	5	5	5
1g	Pink	2-3	5	5	5	5	5	5
1h	Red	2-3	5	5	5	5	5	5

Wash fastness test

Fastness to washing was assessed by using an automatic Lander-O-meter under the following conditions.

The washing solution contained neutral soap at 5 g/litre and soda ash 2 g/litre, a washing temperature of 95°C, the duration of washing was 30 min; and the material-to-liquor ratio was 1:50. After washing, the specimen was removed and rinsed with hot water (35°C) until the rinsed showed no alkalinity with phenolphthalein. It was then squeezed and air dried. The effect on the colour was expressed and defined by reference to the international geometric grey scale. The results are given in Table 4.

Rubbing fastness test

The specimen is fastened in the crockmeter, which causes a piece of standard white cloth to rub against the coloured specimen under controlled conditions of pressure and speed. The rubbing fingers are covered with white cloth, both for the dry test and wet test, and slide back and forth for twenty rubbing strokes. The colour transferred to the white cloth is compared with a grey scale. The grey scale for the alteration of colour consisted of grades 1-5. The results are given in Table 4.

Perspiration fastness test

Specimens of the textile in contact with specified adjacent fibres are treated in two different solutions containing histidine, drained, and placed between two plates of 11.5 cm × 6 cm size and of 0.15 cm thickness under the pressure of a weight-piece of mass 5 kg in a testing device consisting of a stainless steel frame. It was kept in an oven for 4 h at $37\pm2^{\circ}$C. The specimen and the adjacent fibres are dried separately. The change in colour of each specimen and the staining of the adjacent fibres are assessed with the grey scales.

Acid perspiration test

An acid solution containing 5 g/litre sodium chloride (NaCl), 2.2 g/litre sodium dihydrogen orthophosphate (NaH$_2$PO$_4$·2H$_2$O) and 0.5 g/litre l-histidine mono-hydrochloride mono-hydrate (C$_6$H$_9$O$_2$N$_3$HCl·H$_2$O) was freshly prepared. The solution was brought to pH 5.5 with a 0.1 N acetic acid solution. The results are given in Table 4.

Alkaline perspiration test

An alkaline solution containing 5 g/litre sodium chloride (NaCl), 0.5 g/litre l-histidine mono-hydrochloride mono-hydrate (C$_6$H$_9$O$_2$N$_3$HCl·H$_2$O) and 2.5 g/litre disodium hydrogen orthophosphate (Na$_2$HPO$_4$·2H$_2$O) was freshly prepared. The solution was brought to pH 8 with a 0.1 N sodium hydroxide solution. The results are given in Table 4.

Sublimation fastness test

The composite specimens were placed in a heating device (Sublimation Tester, Model STE) equipped with two heating plates with an electrical heating system and kept there for 30 s at $150 \pm 2^{\circ}$C. Then dried fabric was then removed and kept in air for 4 h. The change in colour of the specimen was assessed with the grey scales. The results are given in Table 4.

Determination of the percentage exhaustion

The dyebath percentage exhaustion of the dyed fabric was determined according to the known method.[27]

Results and Discussion

Preparation of diazo component

The thiophene intermediate, ethyl 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate was synthesised by the condensation of cyclohexanone, sulphur and ethylcyanoacetate following Gewald's method[4] (Figure 2). This diazo component is a versatile key intermediate in the synthesis of various disperse dyes.

The principle advantage of the key compound used here is that the yield is high, reaction time is short, the procedure involves only one facile step, the work-up is convenient and thus the starting material can be easily prepared. The presence of an electron withdrawing group such as carbethoxy adjacent to the diazotisable amino group has a bathochromic influence on the hues of these dyes on polyester fabric and the hydrophobic nature of the tetrahydrobenzo structure is useful for better dispersability and dyeability. However, one disadvantage of the ester functionality is that its conjugation to the amino group reduces the basicity of the nitrogen atom and thus efficient diazotisation can only be achieved using nitrosylsulphuric acid obtained from sodium nitrite and concentrated sulphuric acid.

Thus, the thiophene intermediate **2** was diazotised satisfactorily at 0-5°C by nitrosylsulphuric acid in acetic acid. In order to determine the end point of diazotisation, it was found useful to check for the presence of unreacted diazo component on TLC by sampling the diazotisation mixture and extracting with ethyl acetate. Thus, when unreacted diazo components no longer persisted on TLC, the diazotisation was ended. The diazonium salt solution was used immediately since it decomposed on standing, even when cold. Subsequent coupling reactions took place readily on adding the diazonium salt continuously to the solution of coupling component in acetic acid. Coupling was usually accompanied by some evidence of decomposition; however, by careful addition of the diazonium salt solution at 0-5°C to a solution of the coupling component in an aqueous acetic acid, high yields (71-85%) of the dye were usually obtained. To complete coupling particularly for reactions using nitrosylsulphuric acid for the diazotisation, the pH of the reaction mixture was eventually adjusted to approximately 4-5 by addition of an appropriate amount of 10% sodium acetate solution below 5°C.

Physical properties of the dyes

The purity of the dyes was evaluated by TLC using ethyl acetate-benzene (1:4) as the solvent system. When adsorbed onto silica chromatography plates, the dyes produced yellow-red colours. The expected tendency of the more polar members of the dye series toward lower R_f values was observed. All the recrystallised dyes exhibited well-defined melting points characteristic of pure compounds. While it would be unwise to attempt to explain in detail their relative values, because of the complex dependence of the melting points on a number of factors (e.g. polarity, size, geometry, interaction), the characterization data are given in Table 2.

Spectral properties of the dyes

The visible absorption spectroscopic properties of dyes **1** were recorded in DMF solution and are shown in Table 1. As far as absorption maxima are concerned, λ_{max} values are directly proportional to the electronic power of the substituents in the aryl ring. The value of the logarithm of molar extinction coefficient (log ε) of the dyes **1** were in the range of 3.39-4.20, consistent with their high intensity of absorption. The introduction of electron-donating or electron-attracting groups at suitable positions in the coupler ring affects the absorption characteristics of the dyes. In dyes **1b** and **1d** possessing one substituent ortho to the azo linkage, the values of the λ_{max} are consistently higher than in their meta substituted analogues **1e** to **1h**. The extent of this shift is probably accounted for by the steric effects of the coupler substituents. When an electron-donating substituent is present on the coupling moiety of the dyes **1d** and **1h**, higher λ_{max} values are observed compared with those of the dyes that have electron-attracting substituents on the

coupler moiety appear.

Infrared spectra of dyes

The infrared spectra of dyes **1e**, **1f** and **1g** are shown in Figure 4. The characteristic band at 3,120-3,130 cm^{-1}indicates the C-H stretching of the N-arylmaleimide ring. The bands at 1,540-1,600 cm^{-1}, 825-835 cm^{-1} and 945-955 cm^{-1} are due to the stretching vibration of C=C conjugated with a C=O group. The strong bands observed at 1,700-1,710 cm^{-1} are indicative of the stretching vibration of the C=O unit of the cyclic maleimide ring. The band at 630-660 cm^{-1} and 570-580 cm^{-1} can be attributed to an in-plane and an out-of-plane deformation vibration of the C=O. The bands appear at 820-830 cm^{-1} corresponding to a para disubstituted ring, and those at 1,370 cm^{-1} and 1,350 cm^{-1} are due to -C-N-C stretching being asymmetrical and symmetrical respectively. The azo and carbethoxy groups are confirmed at 1,580-1,595 cm^{-1} and 1,650-1,660 cm^{-1} respectively. The characteristic bands at 2,850 cm^{-1}, 640-700 cm^{-1} and 1,390-1,450 cm^{-1} are due to a C-H bending vibration of -OCH$_3$, C-Cl and C-CH$_3$ stretching vibration respectively. The band at 1,320-1,360 cm^{-1} is due to the symmetric stretching of the -NO$_2$ group.
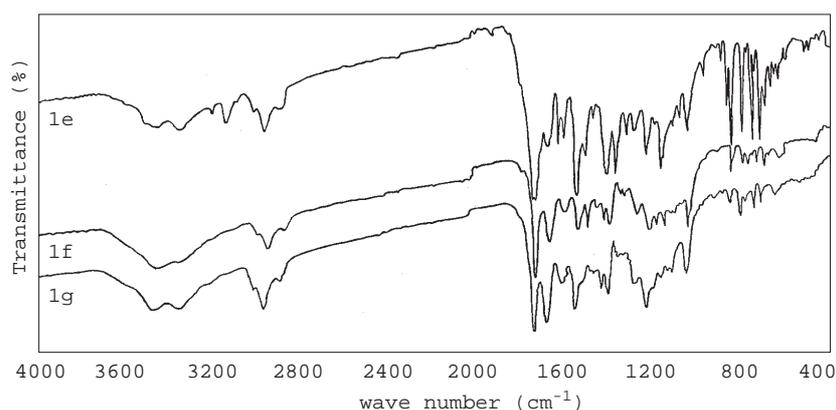

Figure 4. IR Spectra of **1e**, **1f** and **1g** dyes.

Dyeing properties of dyes

The disperse dyes **1** were applied at 2% depth on polyester fabric as disperse dyes. The dyeing properties are given in Table 4. These dyes are gave a narrow range of colour varying from light pink to reddish pink shades with good levelness, brightness and depth on the fabric. The variation in the shades of the dyed fabric result from both the nature and position of the various substituent present on the aryl ring.

The light fastness of dyes derived from tetrahydrobenzo[b]thiophene dyes on polyester was found to be similar (2-3). This observation implies that the poor fastness of dyes is linked to the tetramethylene group which form a less planar structure. Thiophene azo dyes possessing this substitution pattern have been found to exhibit poor light fastness.[28] The dyeing from tetrahydrobenzo[b]thiophene dyes on polyester substrate had excellent fastness. Fastness ratings were the same (5) for all the dyes except light fastness. This finding can be attributed in the polyester substrate to the hydrophobic, crystalline nature of the material inhibiting diffusion at the test temperature. The dyes had excellent fastness, because of high substantivity for polyester and smaller molecular size. This suggested that these two factors hold more import than that concerning

the slight difference in molecular structure. A remarkable degree of levelness after washing indicated good penetration and affinity of these dyes to the fabric.

Acknowledgement

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