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# Dyes Derived from Aminothiophenes. Part 7: Synthesis and Properties of Some Benzo[*b*]thiophene-based Azo Disperse Dyes

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## *ABSTRACT*

*A series of monoazo dyes has been synthesised from 2- and 3-aminobenzo[*b*]thiophene diazo components. The spectroscopic properties of the dyes were compared with literature data and theoretical expectations. Dispersions of the dyes were applied to hydrophobic fibres; the colorimetric and fastness properties of the resultant dyeings were evaluated. © 1997 Elsevier Science Ltd*

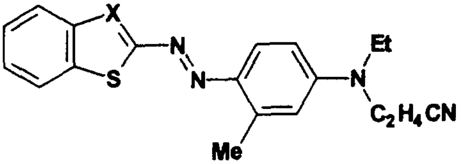
*Keywords*: aminobenzo[*b*]thiophenes, heterocyclic azo disperse dyes, spectroscopic properties, fastness properties.

## 1. INTRODUCTION

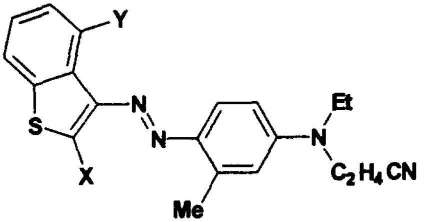
It has been claimed that the use of benzothiazolylazo disperse dyes was the first example of the commercial exploitation of heterocyclic amines [1] and a milestone event in disperse dye technology [2]. Since the issuing of patents concerning such colorants as early as 1935 [3], dyes of this type have become important commercially [4] owing to their economy, brightness and performance [5]. These properties have continued to motivate research efforts, both in industry, as indicated by patent applications [6, 7], and in academia, with papers appearing recently on methyl [8], methoxy [9], bromo [10, 11], dichloro [12–15], (di)nitro [16–18] and dichloronitro [19] derivatives.

Despite the success of benzothiazole-derived disperse dyes, nothing has been published outside the patent literature [20, 21] concerning the analogous fully aromatic benzo[*b*]thienyl-2-azo class. Similarly, little is known about benzo[*b*]thienyl-3-azo disperse dyes; the disclosure of novel routes to the requisite diazo components in the early 1970s [22–24] was followed by patent activity [25] and the appearance of two brief papers which described the application of such dyes to polyamide and acetate [26, 27]. While data relating to the performance of thieno[2,3-*b*]pyridyl-3-azo derivatives on polyester have been published recently [28, 29], no information appears to exist in the literature pertaining to benzo[*b*]thienyl-3-azo colorants on this substrate.

This paper details the synthesis of 2-amino- and 3-amino-benzo[*b*]thiophene-based monoazo dyes, **1** (X = C—$CO_2R$) and **2**, respectively, and their application to hydrophobic fibres. The spectroscopic properties of the dyes as well as the colorimetric and fastness properties of the dyeings were examined.



**1** X = N, C-$CO_2Me$, C-$CO_2Et$

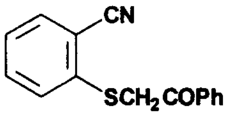


**2** X = $CO_2Me$, $CO_2Et$, Ac, COPh, CN, $NO_2$; Y = H
X = $CO_2Me$; Y = Cl, $NO_2$

## 2. RESULTS AND DISCUSSION

### 2.1 Synthesis of the intermediates and dyes

The 2-aminobenzo[*b*]thiophenes were prepared by a literature method [30] involving the successive *N*-acetylation, dehydrogenation and hydrolysis of the corresponding 4,5-tetramethylene compounds (see Section 3.1.1), whereas the 3-aminobenzo[*b*]thiophene derivatives were obtained by using an existing chemistry based on the synthesis of *o*-cyanothiophenol ether intermediates, which readily cyclise to thiophenes (see Sections 3.1.2–3.1.5). The 2-alkoxycarbonyl-substituted thiophenamines were synthesised by the reaction of *o*-cyanonitrobenzenes with alkyl mercaptoacetates in the presence of alkali [23] and the corresponding acyl-, cyano- and nitro-substituted diazo components were made by treatment of *o*-cyanothiophenol in aqueous alkali with an alkylating agent containing an active halogen atom [22]. The 2-benzoyl compound was obtained only after modification of the literature method [22] which gave the uncyclised thioether intermediate **3** (see Section 3.1.6); use of additional solvent and a higher temperature prevented precipitation of the intermediate, facilitating cyclisation to the benzo[*b*]thiophene derivative (see Section 3.1.5).



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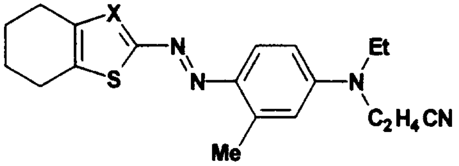


**4**

The stabilities of the 2-aminobenzo[*b*]thiophenes were observed to be greater than those of the 4,5-tetramethylene-substituted intermediates used in the preparation of **4** ($X=CO_2R$) since the diazotisation of the former compounds was performed successfully by means of an aqueous sodium nitrite/35% sulphuric acid system (in a similar fashion to 2-aminobenzothiazole, except that slightly more aqueous acid solvent was required), whereas the application of the procedure to the latter aminothiophenes gave products of negligible dye content [31].

The dyes **2** ($X=CO_2R$; $Y=H$) were prepared by using the diazotisation conditions described above or by means of nitrosylsulphuric acid, which was also utilised in the synthesis of the remaining benzo[*b*]thienyl-3-azo dyes.

## 2.2 Spectroscopic properties of the dyes

The spectral data of the dyes in DMF ($\lambda_{max}$, $\epsilon_{max}$, $\Delta\lambda_{1/2}$), ethanol ($\lambda_{max}$) and toluene ($\lambda_{max}$), as well as figures predicted by PPP-MO calculations, are listed in Table 1.

In line with resonance theory and PPP-MO predictions, alteration of the character of the tetramethylene ring of the derivatives **4** ($X=N$, $C{-}CO_2Me$ and $C{-}CO_2Et$) from saturated to aromatic, yielding the dyes **1**, results in bathochromic and hyperchromic shifts attributable to an increase in the size of the conjugated system; for example, **4** ($X=C{-}CO_2Me$ and $C{-}CO_2Et$), with $\lambda_{max}$ ($\epsilon_{max}$) values in DMF of 504 nm (34 400) and 503 nm (34 000), respectively [32], are more hypsochromic and less intense than their fully aromatic analogues **1**. The data also indicate, as observed with 5-nitrothienylazo and 5-nitrothiazolylazo dyes [33–35], that the $C{-}CO_2R$ function is a better electron acceptor than a ring nitrogen atom: the dyes **1** ($X=C{-}CO_2R$) and **4** ($X=C{-}CO_2R$) are slightly more bathochromic than **1** ($X=N$) and **4** ($X=N$), respectively, although the benzothiazole-based colorants are brighter and more intense, possessing slightly higher $\epsilon_{max}$ values partly

### TABLE 1

Observed and Predicted Spectral Data ($\lambda_{max}$ and $\Delta\lambda_{1/2}$ in nm and $\epsilon_{max}$ in dm$^3$ mol$^{-1}$ cm$^{-1}$) of the Dyes

| *Dye* | $\lambda_{max}(DMF)$ | $\epsilon_{max}(DMF)$ | $\Delta\lambda_{1/2}(DMF)$ | $\lambda_{max}(EtOH)$ | $\lambda_{max}(C_7H_8)$ | $\lambda_{max}(calc.)^a$ | $f^a$ |
|---|---|---|---|---|---|---|---|
| **1** (X = N) | 514.6 ± 0.2 | 45 600 ± 500 | 100 | 507 | 484 | | |
| **1** (X = C—CO$_2$Me) | 522.3 ± 0.6 | 43 100 ± 200 | 109 | 503 | 490 | 483 | 1.67 |
| **1** (X = C—CO$_2$Et) | 521.6 ± 0.3 | 43 400 ± 100 | 108 | 502 | 487 | 483 | 1.67 |
| **2** (X = CO$_2$Me; Y = H) | 465.5 ± 1.5 | 27 400 ± 500 | 109 | 451 | 446 | 445 | 1.37 |
| **2** (X = CO$_2$Me; Y = Cl) | 419.2 ± 0.8 | 22 500 ± 300 | 110 | 408 | 400 | 447 | 1.36 |
| **2** (X = CO$_2$Me; Y = NO$_2$) | 454.7 ± 1.7 | 23 900 ± 100 | 122 | 435 | 434 | 440 | 0.92 |
| **2** (X = CO$_2$Et; Y = H) | 465.0 ± 1.5 | 27 500 ± 200 | 111 | 451 | 445 | 445 | 1.37 |
| **2** (X = Ac; Y = H) | 493.6 ± 1.6 | 29 600 ± 400 | 118 | 474 | 464 | 452 | 1.35 |
| **2** (X = COPh; Y = H) | 484.3 ± 0.5 | 27 100 ± 500 | 112 | 470 | 456 | 453 | 1.31 |
| **2** (X = CN; Y = H) | 510.0 ± 0.6 | 33 300 ± 500 | 110 | 488 | 471 | 467 | 1.33 |
| **2** (X = NO$_2$; Y = H) | 546.8 ± 0.8 | 22 300 ± 300 | 156 | 516 | 508 | 513 | 1.11 |
| **4** (X = N) | 500.4 ± 0.9 | 36 300 ± 400 | 104 | 494 | 477 | | |

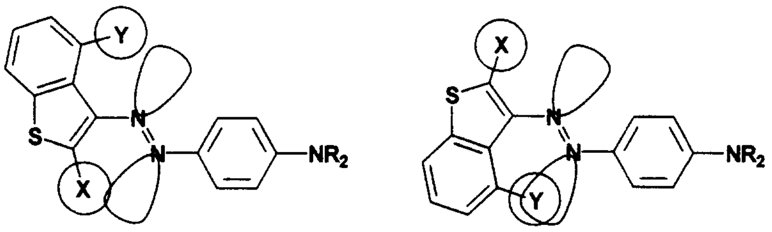
[a] Calculated by the PPO-MO method.

through a combination of lower molecular mass and reduced half-band width.

The PPP-MO calculations correctly forecast blue shifts and losses in intensity of the long-wavelength absorption band on swapping the positions of the ester and azo groups on the thiophene ring of **1** ($X = C—CO_2R$) to create **2** ($X = CO_2R$; $Y = H$). The latter dyes are hypsochromic (63–64 nm) relative to their thienyl-2-azo analogues and have lower $\epsilon_{max}$ values (by 15 700–15 900). In each series, as with 4,5-(di)alkyl(ene)thienyl-2-azo [32, 36] and 3-alkoxycarbonyl-5-nitrothienyl-2-azo dyes [35], there is little difference in the spectra of the methyl and ethyl esters.

Increasing the electron-accepting strength of the 2-substituent in the series **2** brings about bathochromic shifts in agreement with resonance theory; PPP-MO calculations predict these changes accurately, with the exceptions of the 4-substituted dyes **2** ($X = CO_2Me$; $Y = Cl$ or $NO_2$). Introduction of a chloro or nitro group into the 4-position of **2** ($X = CO_2Me$; $Y = H$) is expected to result in a bathochromic shift based on electronic effects alone, while the computed $\lambda_{max}$ values do not differ significantly from that of the parent dye; however, **2** ($X = CO_2Me$; $Y = Cl$ or $NO_2$) are hypsochromic and less intense than **2** ($X = CO_2Me$; $Y = H$) suggesting that steric interference is present in the 4-substituted dyes in which the chloro and nitro functions act in a similar fashion to a group *ortho* to an azo link in an aminoazobenzene system [37] or thienyl-3-azo [35] dye (see Fig. 1). The effect is greatest for the chloro group since the nitro substituent can twist out of plane to relieve steric hindrance; this behaviour was reproduced by computer modelling (Hyperchem, MM+/Polak–Ribiere optimisation).

With one exception, the $\lambda_{max}$ values of series **2** correspond well with figures reported by Nishida *et al.* [26] for the dyes **6** (see Table 2). The latter are generally slightly hypsochromic owing to the additional substituent on the terminal amino alkyl groups. The reason for the large difference between the

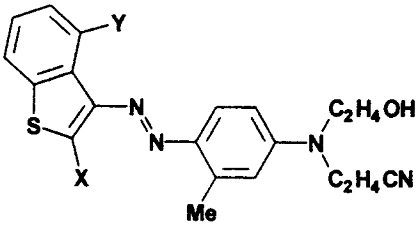


**5a** **5b**

**Fig. 1.** Steric hindrance in 2,4-disubstituted benzo[*b*]thienyl-3-azo dyes.

**TABLE 2**

Comparison of the Properties of Two Series of Benzo[*b*]thienyl-3-azo Dyes



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| *Substituents* | | λ_{ {*FUNC* {max}} $\lambda_{max}$ (*EtOH*)/*nm*/ }˜( {*FUNC* {*nm*}} ) | | *Light fastness of* **2** | | *Light fastness of* **6** [26] | |
|---|---|---|---|---|---|---|---|
| *X* | *Y* | **2** | **6** [26] | *Nylon*[a] | *Diacetate*[a] | *Nylon*[b] | *Diacetate*[b] |
| $CO_2Et$ | H | 451 | 517 | 4 | 4 | 5 | >5 |
| $CO_2Et$ | Cl | 408[c] | 400 | 4[c] | 4[c] | 4–5 | >5 |
| Ac | H | 474 | 470 | 4 | 3–4 | 1 | 4 |
| CN | H | 488 | 480 | 4 | 3–4 | >5 | 5 |
| CN | Cl | — | 490 | — | — | 4–5 | 4 |

[a] At 0.5% o.m.f.

[b] At 6.5% o.m.f., assessed with Fade-Ometer.

[c] For methyl ester.

$\lambda_{max}$ values of **6** ($X = CO_2Et$; Y = H) and **2** ($X = CO_2Et$; Y = H) is unclear although, like the transition between **2** ($X = CO_2Me$; Y = H) and **2** ($X = CO_2Me$; Y = Cl) mentioned above, the introduction of a chloro group into the 4-position of **6** ($X = CO_2Et$; Y = H) furnishes a more hypsochromic dye whose $\lambda_{max}$ is close to that of the analogue prepared in this study (see Table 2).

However, the application of the same transformation to **6** (X = CN; Y = H) causes a 10 nm bathochromic shift; presumably the dye produced can adopt conformation **5a** (X = CN; Y = Cl) which, because of the nature of the cyano group, is hindrance-free, and so avoid having to become non-planar with an attendant hypsochromic shift. The electronic effect of the chloro group is not swamped and is the agent of a small bathochromic shift. (PPP-MO calculations predict a shift of 2 nm to 469 nm for the analogous change in the corresponding *N*,*N*-diethylaniline-derived dyes.)

Nishida *et al.* claimed that the attempted preparation of **6** (X = COPh; Y = Cl) failed because diazotised 3-amino-2-benzoyl-4-chlorobenzo[*b*]thiophene would not couple, which they ascribed to the steric effect of the chloro group [26]. However, the presence of the benzoyl group is just as essential since crowding substituents in both the 2- and 4-positions are requisite for large steric interactions. With just one substituent, a relatively unhindered configuration is available, either **5a** ($X=H$; $Y=Cl$) or **5b** ($X=COPh$; $Y=H$), so that coupling can readily occur; in the latter instance, i.e. 2-benzoyl substitution, it was found that the dye **2** ($X=COPh$; $Y=H$) could be synthesised without difficulty (see Section 3.2).

As mentioned above, the derivatives **1** ($X=C—CO_2R$) have slightly broader bands than their benzothiazolyl analogue (see Table 1), the half-band widths being similar to those of the corresponding dyes **2** ($X=CO_2R$; $Y=H$), $\Delta\lambda_{1/2}$ 109–111 nm, and **4** ($X=C—CO_2R$), $\Delta\lambda_{1/2}$ 105–107 nm [32]. The values of the remainder of series **2** are little different, apart from the nitro-substituted derivatives (see Table 1), whose larger band widths are not unexpected given the tendency of nitro groups to cause dullness [38]. The relatively low $\epsilon_{max}$ of **2** ($X=NO_2$; $Y=H$) can be ascribed to the long-wavelength absorption band of the dye being unusually broad ($\Delta\lambda_{1/2}$ 156 nm), even in comparison with other nitrothienylazo dyes [35].

## 2.3 Application of the dyes

The dyes were roll-milled and the dispersions applied to polyester, nylon and diacetate by exhaustion dyeing techniques; the colour properties of the dyeings were measured and the wet, light and sublimation fastness of the samples assessed.

### *2.3.1 Colour properties of the dyeings*

The strengths of the dyeings, quantified as *fk*, a visually weighted function of *K*/*S*, are shown in Table 3 together with the hues of the polyester samples.

The colours of the dyeings correlated well with the observed $\lambda_{max}$ values of the dyes in solution; for example, the dyes **1** ($X=C—CO_2R$) conferred bluer shades than their benzothiazole-based analogue, and the series **2** yielded hues of increasing bathochromism on raising the electron-withdrawing strength of the 2-substituent.

Build-up on polyester was generally good apart from in the cases of dyes possessing bulky groups, **2** ($X=COPh$; $Y=H$), or non-planar structures caused by steric crowding, **2** ($X=CO_2Me$; $Y=Cl$ and $NO_2$). Fully aromatic benzo[*b*]thienyl-2-azo dyes furnished samples of greater depth than that of their more saturated analogues; for example, **1** ($X=C—CO_2Me$) yielded heavier depths compared to **4** ($X=C—CO_2Me$), with *fk* values of 292 and 233 [39], respectively, at 1.0% o.m.f., presumably because the fully aromatic colorant has a higher absorption intensity as well as a more planar structure, which aids diffusion of the dye into the fibre. The former reason may also explain the greater depths of the dyeings from **1** ($X=C—CO_2R$) relative to those from **2** ($X=CO_2R$; $Y=H$).

## TABLE 3
Colorimetric and Fastness Properties of the Dyes

| | | *fk* | | | *WF*[c] | | *PF*[d] | | *SF(180°C)*[e] | | *SF(210°C)*[e] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Dye* | *Shade on polyester*[a] | *P*[b] | *N*[a] | *D*[a] | *D* | *N* | *D* | *N* | *C* | *P* | *C* | *P* |
| **1** (X = N) | red | 27.9/184/240 | 191 | 159 | 3–4 | 3–4 | 4–5 | 4–5 | 4–5 | 4 | 3–4 | 1–2 |
| **1** (X = C—$CO_2Me$) | scarlet | 30.0/217/292 | 205 | 120 | 2–3 | 2–3 | — | — | 4–5 | 4 | 4 | 3 |
| **1** (X = C—$CO_2Et$) | scarlet | 28.8/196/265 | 153 | 39.2 | 3–4 | 3–4 | 4–5 | 4–5 | 4–5 | 4 | 4 | 3 |
| **2** (X = $CO_2Me$; Y = H) | yellow-orange | 19.1/139/191 | 144 | 69.3 | 4 | 4 | — | — | 4–5 | 4–5 | 4 | 3 |
| **2** (X = $CO_2Me$; Y = Cl) | golden yellow | 11.7/68.0/71.6 | 10.9 | 7.6 | 5 | 5 | — | — | 5 | 4–5 | 4–5 | 4 |
| **2** (X = $CO_2Me$; Y = $NO_2$) | yellow-orange | 15.6/117/137 | 25.2 | 23.7 | 4–5 | 4–5 | — | — | 5 | 5 | 4–5 | 4 |
| **2** (X = $CO_2Et$; Y = H) | yellow-orange | 19.7/134/193 | 140 | 50.1 | 4–5 | 4–5 | 5 | 5 | 4–5 | 4–5 | 4–5 | 3 |
| **2** (X = COPh; Y = H) | orange | 16.9/131/144 | 32.0 | 15.3 | 4–5 | 4 | — | — | 5 | 5 | 4–5 | 4 |
| **2** (X = Ac; Y = H) | red | 21.1/161/190 | 46.1 | 21.5 | 4–5 | 4 | — | — | 4–5 | 4 | 4 | 2–3 |
| **2** (X = CN; Y = H) | red | 21.9/169/238 | 79.2 | 26.0 | 4–5 | 4 | 5 | 5 | 5 | 4–5 | 4 | 2–3 |
| **2** (X = $NO_2$; Y = H) | dark violet | 36.7/243/351 | 64.8 | 33.2 | 4–5 | 4 | — | — | 5 | 4–5 | 4 | 3 |
| **4** (X = N) | orange | 25.3/166/227 | 136 | 153 | 4 | 4–5 | 4–5 | 4–5 | 4–5 | 4 | 3–4 | 2 |

P = Polyester; N = nylon; D = diacetate; C = cotton.

[a] 0.5% o.m.f.

[b] 0.05%/0.5%/1.0% o.m.f.

[c] Wash fastness (ISO 105 CO6 B2S) of polyester (0.5% o.m.f.); all samples had ratings of 5 for colour change and staining of polyester, cotton and acrylic.

[d] Perspiration fastness (ISO 105 E04) of polyester (0.5% o.m.f.); all samples had ratings of 5 for colour change and staining of polyester, cotton and acrylic.

[e] Sublimation fastness (ISO 105 PO1) of polyester (0.5% o.m.f.).

While analogous thienylazo dyes generally have been found to give much lower depths on nylon than polyester at 0.5% o.m.f. [39,40], the dyes **2** (X = $CO_2R$; Y = H) produced almost equal depths of shade on each substrate (*fk* 140–144 on nylon and 134–139 on polyester). The isomers **1** (X = C—$CO_2R$) did not quite achieve the depths on nylon attained on polyester, although **1** (X = N) gave similar colour yields (*fk* 184 on polyester at 0.5% o.m.f. compared to 191 on nylon). All of the dyes **1** built up to deeper shades than the corresponding tetramethylene derivatives **4** as was the case with polyester as substrate; for example, **1** (X = C—$CO_2Me$) produced a colour strength on nylon of *fk* 205 at 0.5% o.m.f., whereas **4** (X = C—$CO_2Me$) yielded a value of 68 [39]. The effects of bulky substituents and non-planarity were exaggerated with respect to those on polyester; the introduction of 4-substituents into **2** (X = $CO_2Me$; Y = H) transformed dyes of good substantivity into colorants with relatively low dyeability.

The benzothiazole-based derivatives built up well on diacetate, whereas the benzo[*b*]thienylazo dyes generally had poor substantivity for the substrate leading to pale, unlevel shades.

### 2.3.2 *Fastness properties of the dyeings*

*2.3.2.1 Wet fastness* The ratings of fastness to washing, and to perspiration for selected samples, of the polyester dyeings (0.5% o.m.f.) are given in Table 3. The poorer staining ratings of the polyester coloured with the series **1** relative to those of samples from **2** can be attributed to the heavier depths of the former dyeings. As expected, the fastness of the nylon and diacetate samples was inferior to that of the polyester dyeings after taking into account depth of shade. The ratings of the benzothiazolylazo dyes illustrate this finding well since these colorants yielded dyeings on each substrate of roughly the same strength (see Table 4).

**TABLE 4**

Wash Fastness of the (Tetrahydro)benzothiazolylazo Dyes on Various Substrates at 0.5% o.m.f.

| | | | *Staining* | | | | |
|---|---|---|---|---|---|---|---|
| *Dye* | *Fibre* | *Colour change* | *Diacetate* | *Cotton* | *Nylon* | *Polyester* | *Acrylic* |
| **1** (X = N) | polyester | 5 | 3–4 | 5 | 3–4 | 5 | 5 |
| | nylon | 5 | 2 | 4 | 2 | 4 | 4–5 |
| | diacetate | 5 | 2–3 | 4–5 | 2–3 | 4–5 | 4–5 |
| **4** (X = N) | polyester | 5 | 4 | 5 | 4–5 | 5 | 5 |
| | nylon | 5 | 2–3 | 4 | 2 | 4 | 4–5 |
| | diacetate | 4–5 | 4 | 5 | 4 | 5 | 5 |

*2.3.2.2 Light fastness* The light fastness ratings of the dyeings are listed in Table 5. The fastness of the dyes on polyester was relatively insensitive to the concentration of colorant on the fibre as has been noted with other thienylazo dye series [39, 40]. Therefore, despite the dyeings not being of standard depth, comparisons between the ratings of the samples were considered valid.

While the tetramethylene dyes **4** (X = C—$CO_2R$) have been observed to be very fugitive on polyester, nylon and diacetate (rating 1 on each substrate at 0.5% o.m.f.) [32], their fully aromatic counterparts had much improved light fastness with ratings of 5 on polyester and nylon, and 4 on diacetate, at 0.5% o.m.f. Similar increases occur in the case of the benzothiazolylazo dyes on making the alkylene ring of **4** (X = N) aromatic to create **1** (X = N) (see Table 5). The ratings of the latter colorant on polyester do not differ significantly from those of some analogues, **7**, based on closely-related coupling components; **7** (R = H) and **7** (R = Me) have fastness values of 4 and 3–4, respectively, at 0.5% o.m.f. [34, 41] compared to the rating of 4 for **1** (X = N). On diacetate, the ratings of **1** (X = N) and **7** (R = Me) are 4–5 and 5 at application levels of 0.5% and 0.4% o.m.f., respectively [41].

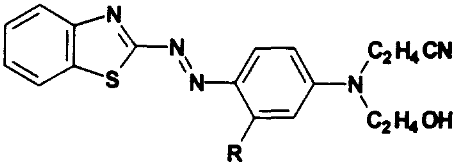

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**TABLE 5**
Light Fastness Ratings of the Dyeings

| | *Polyester* | | | *Nylon* | *Acetate* |
|---|---|---|---|---|---|
| *Dye* | *0.05%* | *0.5%* | *1.0%* | *0.5%* | *0.5%* |
| **1** (X = N) | 3 | 4 | 4 | 5 | 4–5 |
| **1** (X = C—$CO_2Me$) | 4–5 | 5 | 5 | 5 | 4 |
| **1** (X = C—$CO_2Et$) | 4–5 | 5 | 5 | 5 | 4 |
| **2** (X = $CO_2Me$; Y = H) | 5 | 5 | 5 | 4 | 3–4 |
| **2** (X = $CO_2Me$; Y = Cl) | 5 | 5 | 5–6 | 4 | 4 |
| **2** (X = $CO_2Me$; Y = $NO_2$) | 5 | 5 | 5 | 4 | 4 |
| **2** (X = $CO_2Et$; Y = H) | 5 | 5 | 5 | 4 | 4 |
| **2** (X = COPh; Y = H) | 4 | 4 | 4 | 3–4 | 3 |
| **2** (X = Ac; Y = H) | 4 | 4 | 4–5 | 4 | 3–4 |
| **2** (X = CN; Y = H) | 5 | 5 | 5–6 | 4 | 3–4 |
| **2** (X = $NO_2$; Y = H) | 2–3 | 2–3 | 3 | 1 | 1 |
| **4** (X = N) | 1 | 1 | 1–2 | 1 | 1 |

The photostabilities of dyes derived from 2-aminothiazole and 2-aminobenzothiazole on polyester have been found to be similar [34, 42]. These observations imply that the poor fastness of **4** (X = N) relative to **1** (X = N) is linked to the 4,5-tetramethylene group of the former colorant; thienyl-2-azo dyes possessing this substitution pattern or related alkylene functions have also been found to be fugitive [32, 39].

The light fastness ratings of the isomeric benzo[*b*]thienylazo dyes did not differ greatly from each other on any of the substrates (see Table 5); for example, **1** (X = C—$CO_2Et$) had ratings of 5, 5 and 4 on polyester, nylon and diacetate at 0.5% o.m.f., while **2** (X = $CO_2Et$; Y = H) displayed corresponding ratings of 5, 4 and 4.

As in the case of the dyes **1**, the members of series **2** showed little variation in stability with substrate type, the colorants generally having moderate to good fastness on each fibre (see Table 5); the 2-alkoxycarbonyl and 2-cyano derivatives possessed similar stabilities and those of the acyl analogues were slightly inferior. The 2-nitro derivative had the poorest ratings; its low light fastness on nylon is unsurprising in the light of findings with other nitrothienylazo dyes [40], but the fugitive nature of the polyester and diacetate dyeings is unexpected given that replacement of an alkoxycarbonyl function with a nitro group was not found to be deleterious to photostability in the case of other thiophene-based dyes [40]. In contrast, nitro substitution at the 4-position in **2** (X = $CO_2Me$; Y = $NO_2$) did not have an adverse effect on fastness on any of the substrates.

The light fastness of the dyes **2** on nylon and diacetate is consistent with that reported by Nishida *et al.* [26] for some related derivatives **6** (see Table 2). The generally higher ratings of the dyeings from the latter series are probably a consequence of the greater level of application employed.

*2.3.2.3. Sublimation fastness* For a particular sample, the staining of polyester produced by exposure to dry heat was found to be greater than that of cotton at a given temperature (see Table 3) in line with previous observations concerning the heat fastness of dyeings from thienylazo dyes [39, 40].

The polyester coloured with the dyes **1** had fastness ratings similar to those of samples produced with the more saturated analogues **4**; for example, **4** (X = C—$CO_2Et$) had ratings of 4–5 and 4 for the staining of cotton and polyester, respectively, at 180°C and ratings of 4 and 2 for the same materials at 210°C [39], whereas **1** (X = C—$CO_2Et$) yielded corresponding values of 4–5, 4, 4 and 3. The fastness of the thiophene-derived dyes did not differ much from that of their benzothiazolylazo analogues.

Swapping the position of the azo link and ester group of the benzo[*b*]thienyl-2-azo dyes **1** (X = C—$CO_2R$) to give the isomers **2** (X = $CO_2R$;

Y = H) did not significantly alter fastness (see Table 3). The slightly superior ratings of **2** (X = COPh; Y = H) relative to those of its 2-acetyl counterpart may be partly related to the increased mass of the former colorant.

## 3. EXPERIMENTAL

Chromatography and analysis were performed as described previously [32].

### 3.1 Preparation of the diazo components

2-Amino-3-ethoxycarbonylbenzo[*b*]thiophene was prepared by the method of Gewald and Neumann [30], upon which the procedure for the methyl ester analogue was also based (see Section 3.1.1). The 3-amino-2-methoxycarbonylbenzo[*b*]thiophene derivatives [23] were synthesised in a similar fashion to 3-amino-2-ethoxycarbonylbenzo[*b*]thiophene (see Section 3.1.2). 3-Amino-2-cyanobenzo[*b*]thiophene [22] was obtained in an analogous manner to its 2-acetyl analogue (see Section 3.1.3). 2-Amino-4,5-tetramethylenethiazole was prepared by a literature method [43].

#### *3.1.1 2-Amino-3-methoxycarbonylbenzo[*b*]thiophene*

A solution of 2-amino-3-methoxycarbonyl-4,5-tetramethylenethiophene [32] (18.11 g, 0.086 mol) in hot acetic anhydride (40 ml) was refluxed with stirring for 10 min, cooled and placed in a refrigerator to crystallise overnight. A cream crystalline solid (19.49 g, 89% crude, m.p. 118–119°C) was filtered off, washed neutral and dried; more product, yellow solid (1.71 g, 8% crude yield, m.p. 109–116.5°C), was obtained from hydrolysis of the filtrate. Recrystallisation (methanolic DMF) gave 2-acetylamino-3-methoxycarbonyl-4,5-tetramethylenethiophene as analytically-pure, cream-coloured crystals (m.p. 119–119.5°C). Microanalysis found C, 56.7; H, 5.9; N, 5.4; S, 12.85% ($C_{12}H_{15}NO_3S$ requires C, 56.9; H, 6.0; N, 5.5; S, 12.7%).

A mixture of 2-acetylamino-3-methoxycarbonyl-4,5-tetramethylenethiophene (14.44 g, 0.057 mol), sulphur (3.65 g, 0.114 mol) and dimethyl phthalate (17 ml) was stirred under nitrogen and heated to 200–220°C for 3.25 h by which time $H_2S$ gas evolution had ceased. Ethanol (12 ml) was added after cooling, the mixture filtered and the collected material washed with ethanol to give crude 2-acetylamino-3-methoxycarbonylbenzo[*b*]thiophene as a light brown powder (8.72 g, 61% crude yield). The crude product was suspended in ethanol (35 ml), heated to boiling and a solution of KOH (2.1 g) in water (5 ml) added over 7–8 min, before boiling for a minute longer. Drowning in water (200 ml) produced a brown suspension which was filtered off and water-washed neutral to give crude 2-amino-3-methoxycarbonylbenzo[*b*]thiophene as a brown solid (6.06 g, 84% crude yield) which was recrystallised (80–100° ligroin) as pale yellow needles (m.p. 99–109°C) and used without further purification. IR(nujol) ($cm^{-1}$): 3400, 3300 (NH), 1660 (C=O).

### *3.1.2 3-Amino-2-ethoxycarbonylbenzo[*b*]thiophene*

A solution of 2-nitrobenzonitrile (7.41 g, 0.05 mol) in ethyl thioglycolate (97%, 6.2 g, 0.05 mol) and DMF (100 ml) was cooled in ice and treated with potassium hydroxide (5.0 g) dissolved in water (25 ml) over 50 min at 0–5°C before stirring for 1 h under 5°C. The dark liquid was poured with stirring into an ice/water mix (600 ml) and allowed to stand overnight; the deposited cream-coloured solid (7.50 g, 68% crude yield, m.p. 82–84°C) was filtered off and water-washed. Recrystallisation (aqueous ethanol) furnished cream-coloured needle-like crystals (6.91 g, 62% purified yield, m.p. 86–87°C, lit. [22] 86.5–87°C).

### *3.1.3 3-Amino-2-acetylbenzo[*b*]thiophene*

*o*-(Benzylthio)benzoic acid [44] (70.0 g, 0.29 mol), toluene (1.2 l) and thionyl chloride (35.8 g, 0.30 mol) were stirred and heated to reflux for 2.5 h under nitrogen. The mixture was allowed to cool and aqueous ammonia (*d*=0.88, 140 ml) was added, causing precipitation of a white solid. The suspension was stirred for 1 h before filtering and washing the collected solid neutral with water. The white powder (56.3 g, 81% crude yield) was recrystallised (ethanol) to yield off-white translucent rods (53.9 g, m.p. 153–154°C, lit. [45] 152–153°C, lit. [46] 157–158°C) of *o*-(benzylthio)benzamide.

*o*-(Benzylthio)benzamide (51.7 g, 0.21 mol) and phosphorus oxychloride (99%, 89.1 g, 0.58 mol) were stirred and refluxed for 30 min, allowed to cool to room temperature and poured with stirring onto ice (*ca* 1 kg) to instantly precipitate a yellow solid. The suspension was neutralised (aqueous NaOH), filtered and water-washed to give a bright yellow powder (46.4 g, 97% crude yield, m.p. 60–63°C) which was recrystallised (methanol) to furnish *S*-benzyl-*o*-cyanothiophenol (44.2 g, m.p. 62–64°C, lit. [45] 65–66°C, lit. [47] 62–64°C).

To a suspension of finelypowdered aluminium chloride (96%, 38.3 g, 0.28 mol) in toluene (340 ml) under nitrogen, a solution of *S*-benzyl-*o*-cyanothiophenol (41.9 g, 0.19 mol) in toluene (340 ml) was added over 30 min. The red-brown mixture was stirred in a nitrogen atmosphere at room temperature for 48 h and then ice/water (150 ml) added. The toluene phase was isolated and washed with aqueous NaOH (1.2 M, 400 ml twice) and the extracts acidified with HCl (36%), whereupon a yellow oil separated out. Extraction of the oil (dichloromethane), water-washing of the combined extracts, drying with sodium sulphate overnight and rotary evaporation yielded *o*-cyanothiophenol as a pale yellow oil (23.4 g, 93% crude yield, lit. [48]

90% yield) which was used without further purification. IR(neat) (cm$^{-1}$): 2560 (SH), 2220 (C≡N); lit. [48] 2555, 2217.

*o*-Cyanothiophenol (2.70 g, 0.02 mol) was dissolved in aqueous NaOH (1.2 M, 20 ml) and chloroacetone (95%, 2.05 g, 0.021 mol) added dropwise over 5 min with stirring; a yellow precipitate formed within a few seconds of the start of the addition accompanied by an exotherm. The suspension was stirred for 10 min, cooled to 0°C, filtered and water-washed neutral to give a lemon-yellow powder (3.15 g, 82% crude yield). Recrystallisation (aqueous ethanol, ethanol) furnished 3-amino-2-acetylbenzo[*b*]thiophene as yellow crystals (2.62 g, m.p. 146–147°C, lit. [24] 147–149°C, lit. [48] 145.5–147°C).

### *3.1.4 3-Amino-2-nitrobenzo[*b*]thiophene*

*o*-Cyanothiophenol (2.70 g, 20 mmol) was dissolved in aqueous NaOH (1.2 M, 17 ml) and ethanol (28 ml) and treated, under nitrogen, over 20 min with bromonitromethane (3.27 g, 21 mmol) in ethanol (28 ml). The mixture was stirred for 15 min and the dark yellow suspension poured into water (60 ml). The deep yellow solid (2.62 g, 68% crude yield) was collected, water-washed neutral, dried, washed several times with chloroform and recrystallised from aqueous 2-ethoxyethanol to give dark yellow needles (1.15 g, m.p. 217.5–218°C, lit. [22] 217–218°C, lit. [49] 218–218.5°C).

### *3.1.5 3-Amino-2-benzoylbenzo[*b*]thiophene*

Phenacyl chloride (98%, 1.66 g, 10.5 mmol) dissolved in ethanol (20 ml) was added over 10 min to a solution of *o*-cyanothiophenol (1.35 g, 10.0 mmol) in aqueous NaOH (1.2 M, 7 ml) and ethanol (20 ml) at 40–45°C under a nitrogen blanket. Stirring at 40–45°C for 15 min gave an intense yellow solution, which was stirred into water (100 ml) and left overnight. Filtering and water-washing neutral gave a bright yellow solid (2.29 g, 91% crude yield, m.p. 99–101°C). Recrystallisation (aqueous ethanol, toluene/60–80°ligroin) furnished a yellow solid of m.p. 104–105°C, lit. [22] 103–104°C.

### *3.1.6 S-(Methylbenzoyl)-o-cyanothiophenol (3)*

*o*-Cyanothiophenol (2.70 g, 20 mmol) was dissolved in ethanol (27 ml) and aqueous NaOH (1.2 M, 15 ml) and, under a nitrogen atmosphere, phenacyl chloride (98%, 3.31 g, 21 mmol) in ethanol (27 ml) added over 10 min giving rise to a weak exotherm and precipitation of lemon-yellow solid. The suspension was stirred for 15 min, poured into water (60 ml), left to stand for several hours and filtered. The water-washed solid (4.58 g, 90% crude yield) was recrystallised four times in ethanol furnishing white needles of m.p. 128–129°C. Microanalysis found C, 71.4; H, 4.2; N, 5.45; S, 12.45% ($C_{15}H_{11}NOS$ requires C, 71.1; H, 4.3; N, 5.5; S, 12.7%). FTIR(nujol)/cm$^{-1}$: 2214 (C≡N); 1681 (C=O). PMR($CDCl_3$): 4.38 (2 H, s, $CH_2$), 7.26–7.97 (9H, *m*, $H_{ring}$).

**TABLE 6**

Methods of Synthesis and Purification of the Dyes

| *Dye* | *Method/ molarity* | *Crude yield (g/%)* | *Purification method* | *Pure yield (g /%)* | *%s* | *Appearance* | *m.p. (°C)* |
|---|---|---|---|---|---|---|---|
| **1** (X = N) | A/20 | 5.12/73 | ααα | 0.65/9 | 65/48 | shiny dark purple leaflets | 160–161 |
| **1** (X = C—$CO_2Me$) | B/8.0 | 2.70/83 | Δββ | 1.52/47 | 56 | shiny blue-green leaflets | 151 |
| **1** (X = C—$CO_2Et$) | B/8.0 | 2.87/85 | Δβ | 0.74/22 | 37/32 | dark crystalline powder | 137.5–138.5 |
| **2** (X = $CO_2Me$; Y = H) | A/10 | 2.49/61 | Δϵθθ | 0.68/17 | 27 | dark red crystals | 120.5–121 |
| **2** (X = $CO_2Me$; Y = Cl) | C/5.0 | 2.05/93 | μγδ | 1.32/60 | 64 | dull orange powder | 179–180 |
| **2** (X = $CO_2Me$; Y = $NO_2$) | C/4.0 | 1.17/65 | θθ | 0.38/21 | 33 | red crystals | 164–164.5 |
| **2** (X = $CO_2Et$; Y = H) | C/5.0 | —/— | Δαα | 1.05/50 | — | shiny dark red crystals | 112–113 |
| **2** (X = COPh; Y = H) | C/3.5 | 1.50/95 | Θ Δλ | 0.49/31 | 47/44 | red-purple needles | 149.5–150 |
| **2** (X = Ac; Y = H) | C/5.0 | 1.64/84 | μμμ | 1.09/56 | 66 | shiny green crystals | 178.5–179 |
| **2** (X = CN; Y = H) | C/3.5 | 1.10/84 | Θ ϵϵ | 0.57/44 | 70/59 | red crystals (green reflex) | 156–156.5 |
| **2** (X = $NO_2$; Y = H) | C/3.5 | 0.76/55 | Γϵ | 0.24/17 | 33/18 | fine green needles | 171.5–172 |
| **4** (X = N) | A/10 | —/— | ηβ | 1.75/50 | — | red needles and leaflets | 158.5–159 |

Method—diazotisation procedure (see Section 3.2); molarity—amount of amine used in mmol.
Purification method—column chromatography: Γ (silica/toluene), Δ (silica/95:5 toluene:ethyl acetate), Θ (silica/85:15 toluene:ethyl acetate).Recrystallisation: α (ethanol), β (aqueous ethanol), γ (ethanol/DMF), δ (2-ethoxyethanol), ϵ (aqueous 2-ethoxyethanol), η (acetone), θ (60–80°ligroin/ethyl acetate), λ (60–80° ligroin/toluene), μ (toluene).%*s*—Percentage yield of purification process, i.e. the percentage amount of pure dye obtained from the crude dye used in the purification (a second figure represents the theoretical pure yield, i.e. the percentage amount of pure dye obtained if all the crude sample had been used in the purification process, extrapolated from the percentage yield of the purification process).

### 3.2 Preparation of the dyes

The methods of diazotisation for each amine are indicated in Table 6; the procedures (A, aqueous sodium nitrite in 35% sulphuric acid, 3.9 ml per mmol amine; B, as A except 4.9 ml per mmol amine; C, nitrosylsulphuric acid in acetic and propionic acids), as well as coupling to *N*-(2-cyanoethyl)-*N*-ethyl-*m*-toluidine, were carried out as detailed elsewhere [32]. The majority of the crude products were isolated as solids and purified by column chromatography and recrystallisation, as described in Table 6, to microanalytical standard ($\leq \pm 0.3\%$ for C, H, N and S, as well as Cl where appropriate).

### 3.3. Analysis and application of the dyes

PPP-MO calculations and computer modelling were performed as described elsewhere [32]; in the case of dyes 2 ($X = CO_2Me$; $Y = Cl$ and $NO_2$), molecular modelling indicated the structure **5a** to be more energetically favourable than **5b** and only the former conformation was considered in the computation of data. The effect of a chlorine atom was simulated by modifying the valence state ionisation potential and electron affinity parameters of the adjacent carbon atom to 12.00 and 0.61 eV, respectively [50]. The procedures for the milling and application of the dyes to polyester, nylon 6,6 and diacetate as well as the measurement of the colour and fastness properties of the resultant dyeings have been described previously [32,39].

## 4. CONCLUSIONS

Benzo[*b*]thienylazo dyes have been synthesised by conventional methods and their colour properties examined in solution, and applied to hydrophobic fabric.

In agreement with resonance theory and PPP-MO calculations, the benzo[*b*]thienyl-2-azo dyes were bathochromic and hyperchromic relative to their tetramethylene analogues. The corresponding benzothiazole-based dyes were slightly hypsochromic and possessed higher $\epsilon_{max}$ values, presumably because of their narrower absorption bands. The benzo[*b*]thienyl-3-azo dyes were hypsochromic and less intensely absorbing than the benzo[*b*]thienyl-2-azo derivatives in line with PPP-MO predictions; the bathochromic shifts in $\lambda_{max}$ resulting from an increase in electron-withdrawing strength of the 2-substituent were replicated accurately although, owing to the presence of steric hindrance, the effects of 4-substitution were not anticipated by the calculations. Spectral characteristics were generally consistent with data reported in the literature.

Of the three substrates, application of the dyes to polyester was most satisfactory in terms of colour yield and fastness. The benzo[*b*]thienyl-2-azo dyes appear to offer no advantage over the analogous benzothiazolylazo derivative on polyester apart from slightly higher fastness to light. However, the former dyes were more promising than their tetramethylene analogues contrary to the view stated by Sabnis and Rangnekar [51]. These workers claimed that "the hydrophobic nature of tetrahydrobenzo structure is useful for better dyeability and dispersability" (*sic*) and that such dyes were superior to analogous benzo[*b*]thiophene-based colorants, although they presented no evidence. The results of this investigation contradict their findings and indicate that the planar ring system of the latter dyes is actually more favourable towards diffusion than the non-planar tetramethylene ring. In addition, the benzo[*b*]thienyl-2-azo dyes had much improved light fastness on polyester and the other substrates compared to their more saturated analogues.

The benzo[*b*]thienyl-3-azo dyes had reasonable fastness on polyester apart from the dye derived from 3-amino-2-nitrobenzo[*b*]thiophene which built up to very deep shades that were, unfortunately, fugitive towards light.

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