Dyes and Pigments, Vol. 31, No. 4, pp. 273–289, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
PII: S0143-7208(96)00004-6 0143-7208/96 \$15.00+0.00

A Comparison of the Properties of Some 2-Aminothiophene-derived Disperse Dyes

Geoffrey Hallas & Andrew D. Towns

Department of Colour Chemistry and Dyeing, University of Leeds, Leeds LS2 9JT, UK

(Received 20 November 1995; accepted 20 December 1995)

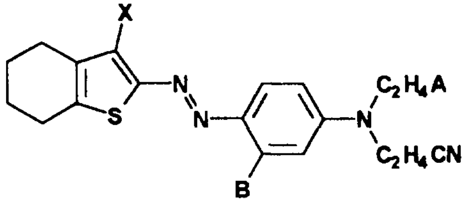
ABSTRACT

In the course of an investigation into the properties of monoazo disperse dyes synthesised from aminothiophene diazo components, significant discrepancies were observed between the spectroscopic and fastness data of some thienyl-2-azo dyes compared to that previously reported for closely related analogues. Considerable differences in λ_{max} *and* ε_{max} *values were noted; in some cases, light fastness ratings were at variance with previously disclosed figures.*

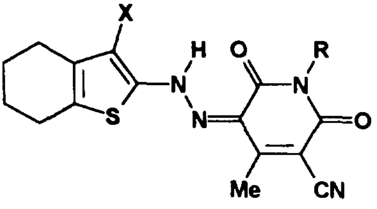
1. INTRODUCTION

There is much more information available on heterarylmonoazo disperse dyes outside of the patent literature than there was fifteen years ago. Papers concerning benzothiazolylazo dyes, for example, on chloro-[1–3] and nitrobenzothiazolylazo derivatives,[4,5] are appearing with increasing frequency; numerous reports on benzisothiazolylazo dyes, for example, 5-nitro derivatives,[6–8] have also been issued since Wippel[9] first shed light on the subject. However, while nearly forty years have passed since Dickey and co-workers[10] published their classic paper on thiophene-based disperse dyes, it is only within the last decade that studies of such dyes have appeared with any regularity. Recent reports mention thienylazo dyes as part of a general dye series,[11,12] as a series in their own right[13,14] and as intermediates.[15]

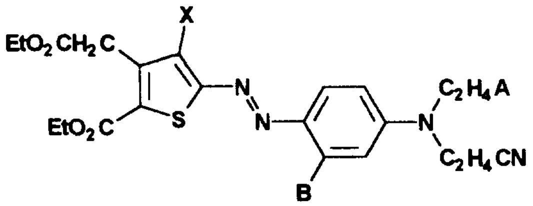
During studies on the synthesis and application of 2- and 3-aminothiophene-based disperse dyes, discrepancies were observed between the colour and fastness data obtained for the dyes **1**, **3** and **5** compared to figures disclosed for the respective analogues **2**, **4** and **6** by Sabnis and Rangnekar.[16–19]



1 A = H, B = Me
2 A = CN, B = H



3 R = Et
4 R = H



5 A = H, B = Me
6 A = CN, B = H

2. RESULTS AND DISCUSSION

A comparison of the absorption characteristics of DMF solutions of the dyes revealed several unexpectedly marked differences in λ_{max} and ε_{max} values, for example, in the tetramethylenethienyl-2-azo series **1** and **2** (see Table 1).

The influence of the 3-substituent was not very pronounced in series **1**. Of

TABLE 1
Colour properties of the thienyl-2-azo dyes **1** and **2**[16,19] in DMF solution (λ_{max} in nm, ε_{max} in $dm^3 \ mol^{-1} \ cm^{-1}$) and shade when applied to polyester at 1% o.m.f.

X	**1**			**2**		
	λ_{max}	ε_{max}	Shade	λ_{max}	ε_{max}	Shade
CN	531.1 ± 0.3	42 300 ± 200	Red	525	log 3.30	Red–violet
CO_2Me	504.1 ± 0.2	34 400 ± 500	Dark orange	–	–	–
CO_2Et	503.0 ± 0.4	34 000 ± 400	Orange–red	510	log 3.37	Red–violet
COPh	505.2 ± 0.4	33 400 ± 800	Orange–red	–	–	–
COTh-2	505.5 ± 0.1	34 100 ± 100	Orange–red	–	–	–
$CONH_2$	506.4 ± 0.6	33 700 ± 500	Red	581	30 900	Blue

the six derivatives, the dye with the cyano group was, as expected, the most bathochromic and intense in DMF. The λ_{max} and ε_{max} values of the other five analogues were similar (503–506 nm and 34 400–33 400 in DMF).

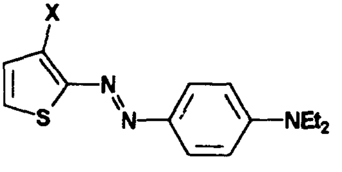
The λ_{max} value of (**1**; X = $CONH_2$) was not consistent with that reported by Sabnis and Rangnekar for the related dye (**2**; X = $CONH_2$), which was claimed to be blue on polyester;[19] the dye would be expected to be red and slightly hypsochromic compared to (**1**; X = $CONH_2$) as it has an extra electron-acceptor and no electron-donor on the coupler residue. The 3-cyano derivatives were consistent in this respect, (**2**; X = CN) being the more hypsochromic of the pair by 6 nm, although of the ethoxycarbonyl derivatives, (**2**; X = CO_2Et) appeared to be the more bathochromic against expectations. While the ε_{max} values of the 3-carbamyl derivatives were similar, Sabnis and Rangnekar reported those of the their other dyes in logarithmic form corresponding to values of less than 10 000, which are unusually low for azo dyes in general, and especially when compared to the analogues **1**.

Predicted λ_{max} data from PPP-MO calculations for the *N,N*-diethylaniline-based thienyl-2-azo dyes **7** are consistent with the values obtained from toluene solutions of the series **1** (see Table 2).

While the calculations predicted the cyano derivative to be more bathochromic than the alkoxycarbonyl derivatives, the greater intensity of the former was not anticipated. This result may be explained partly by the

TABLE 2

Calculated spectroscopic data for some *N,N*-diethylaniline-based thienyl-2-azo dyes **7** and observed data for their analogues **1**



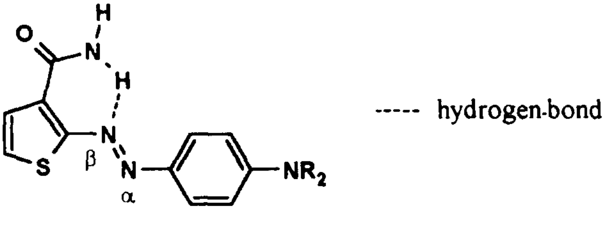
7

X	7		1	
	λ_{max}(calc.)/nm	*f*(calc.)	$\lambda_{max}(C_7H_8)$/nm	ε_{max}(DMF)/ $dm^3\ mol^{-1}\ cm^{-1}$
CN	494	1.48	501	42 300
CO_2Me	479	1.56	481	34 400
CO_2Et	479	1.56	474	34 000
COPh	479	1.43	487	33 400
COTh-2	482	1.39	488	34 100
$CONH_2$	473[a]	1.53	502	33 700

[a] 483 when hydrogen-bonding accounted for (see below).

narrower half-band width of the cyano derivative ($\Delta\lambda_{1/2}$ 94 nm) compared to the esters ($\Delta\lambda_{1/2}$ 105–107 nm). Alternatively, the bulkier ester groups may well be subject to steric crowding which is beyond the scope of the calculations. The poor correlation between oscillator strength (f) and ε_{max} is not unexpected, since it has been recognised that such relationships within a series of structurally similar chromogens are unsatisfactory because, in addition to steric factors and differing absorption band shape, the parameters used in the calculations have been optimised for prediction of λ_{max} rather than intensity.[20]

The λ_{max} values of the 3-aroyl derivatives were reproduced quite accurately, although there was a relatively large disagreement between calculated and observed values for the 3-carbamyl derivative (see Table 2). Anomalous solvatochromic behaviour may be partly responsible, the dye not exhibiting the typical positive solvatochromism shown by the other derivatives of type **1**. Interaction between the amide protons and the azo link could also be another reason; molecular modelling (geometry unoptimised) indicated that the formation of a six-membered ring, completed by a hydrogen-bond, would be likely in the configuration shown; the proton–β-nitrogen distance was found to be 1.93 Å.



Modelling revealed the alternative configuration (7-membered ring, interaction with α-nitrogen) to be less favourable, there being a large steric clash. The λ_{max} value obtained from the calculation performed using parameters for the six-membered ring conformation with the hydrogen-bonded azo (β-nitrogen) and amide (NH_2) groups showed a slight improvement (483 nm), although the shortfall from the observed figure was still relatively large (19 nm). However, the calculated λ_{max} data for this dye and the other analogues show clearly that the diazo components are not sufficiently powerful as electron-sinks to give blue dyes with simple aniline-derived coupling components. Even a 3-nitro group is not able to confer the required bathochromicity: (**7**; X = NO_2) is predicted to have λ_{max} 534 nm (f 1.18) which corresponds to a violet coloration in DMF solution and on polyester.

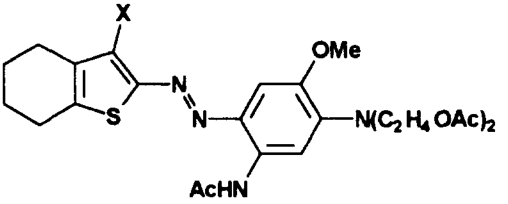
Further evidence contradicting the observation that (**2**; X = $CONH_2$) is blue comes from the use of *N,N*-di(2′-acetyloxyethyl)-5-acetylamino-2-methoxyaniline in making the dyes **8**. As in series **1** and **2**, the 3-cyano derivative

TABLE 3
Colour properties of the thiophene-based pyridone dyes **3** and **4**[16,19] in DMF solution (λ_{max} in nm, ε_{max} in dm^3 mol^{-1} cm^{-1}) and when applied to polyester at 1% o.m.f.

X	**3**			**4**		
	λ_{max}	ε_{max}	Shade	λ_{max}	ε_{max}	Shade
CN	514.4 ± 0.4	34 600 ± 600	Bright orange	515	log 3.64	Pale red
CO_2Et	498.2 ± 0.4	28 400 ± 100	Bright pink	497	log 3.76	Very bright pink
$CONH_2$	502[a]	–	–	484	20 000	Brilliant orange

[a] Value for crude dye.

was more bathochromic (λ_{max} of the crude dye 556 nm) than the 3-ethoxycarbonyl derivative (528 nm). However, even with this coupler, which tends to produce bathochromic dyes, the 3-carbamyl component still only gave a red dye (λ_{max} 522 nm), in contrast to the claim of Sabnis and Rangnekar concerning the colour of (**2**; X = $CONH_2$).



8

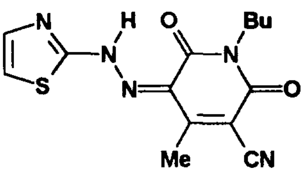
The λ_{max} values for the tetramethylenethiophene-derived pyridone dyes **3** accorded well with those of the dyes **4** prepared by Sabnis and Rangnekar (see Table 3), although again extinction coefficients for the latter were very low.

PPP-MO calculations correctly predicted the relative bathochromism of these dyes (see Table 4) compared to most pyridone dyes from carbocyclic diazo components which are yellow or orange.[21] The thiophene derivatives

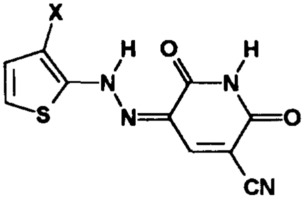
TABLE 4
Calculated spectroscopic data for the hydrazone and azo tautomers of some thiophene-based pyridone dyes **10** and observed data for their analogues **3**

X	**10** (Hydrazone)		**10** (Azo)		**3**	
	λ_{max}(calc.)/ nm	f(calc.)	λ_{max}(calc.)/ nm	f(calc.)	$\lambda_{max}(C_7H_8)$/ nm	ε_{max}(DMF)/dm^3 mol^{-1} cm^{-1}
CN	497	1.36	470	1.21	486	34 600
CO_2Et	496	1.40	480	1.15	499	28 400

are also significantly more bathochromic than a related thiazole derivative **9** which has λ_{max} (DMF) 436 nm.[22]



9



10

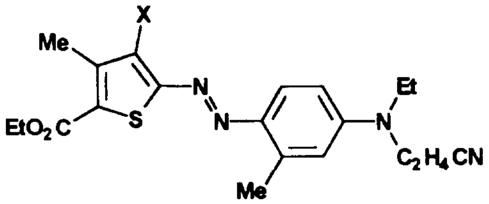
In line with a previous report[21] concerning pyridone dyes with carbocyclic diazo components, calculated figures served to confirm the preferential existence of the dyes in the hydrazone form as these were closer to the observed values than the corresponding data calculated for the azo tautomers (see Table 4).

Two papers[17,18] have been published concerning the use of 2-amino-4-ethoxycarbonylmethyl-5-ethoxycarbonylthiophene derivatives in the synthesis of disperse dyes, the disclosed data indicating that reasonably light-fast blue dyes, for example **6**, can be produced in conjunction with simple aniline-based coupling components (see Table 5).

This revelation, while interesting from a commercial perspective, was not observed for the dyes **5** prepared from *N*-2-cyanoethyl-*N*-ethyl-*m*-toluidine and the same diazo components. Dyes from this coupler are expected to be

TABLE 5

Colour properties of the thienyl-2-azo dyes **5**, **6** and **11** in DMF solution (λ_{max} in nm, ε_{max} in dm^3 mol^{-1} cm^{-1}) and shade when applied to polyester at 1% o.m.f.



11

Dye	X	λ_{max}	ε_{max}	Shade	Ref.
11	CN	560.8 ± 0.8	47 400 ± 500	Pale rubine	
5	CN	564.7 ± 0.3	48 600 ± 700	Red–violet	
6	CN	585	32 400	Sky-blue	17
11	CO_2Et	529.6 ± 0.5	39 100 ± 600	Red	
5	CO_2Et	535.5 ± 0.5	40 700 ± 400	Crimson	
6	CO_2Et	582	40 700	Blue	18

more bathochromic compared to those from *N*,*N*-di(2-cyanoethyl)aniline, i.e. dyes **6**, since the former possess an extra electron donor and one fewer electron acceptor on the coupler residue. The ε_{max} value of (**6**; X = CN) is surprisingly low when compared to the other 3-cyano-substituted thienyl-2-azo dyes of types **1**, **5** and **11**, which also have intensities greater than their corresponding 3-ethoxycarbonyl analogues, unlike the dyes **6**.

A comparison of the colour properties of the dyes **5** and **11** indicates that swapping the 4-methyl group for a 4-ethoxycarbonylmethyl group results in small bathochromic and hyperchromic shifts, as expected on slightly increasing the electron-withdrawing strength of the 4-substituent. PPP-MO calculations predict the *N*,*N*-diethylaniline analogues of (**11**; X = CN) and (**11**; X = CO_2Et) to absorb maximally at 518 nm and 506 nm, respectively, in non-polar solvents, close to the observed values of 530 nm and 495 nm for the toluidine-based dyes in toluene. Even accounting for the slight bathochromic shift caused by the 4-substituent in the dyes **5**, the calculations serve to refute the claim that dyes of this type, produced from simple aniline-derived couplers, are blue.

Another unexpected trend reported by Sabnis and Rangnekar is that (**6**; X = CN) and its *N*,*N*-di(2-hydroxyethyl)-*m*-chloroaniline analogue (λ_{max} 580 nm in DMF) are more bathochromic than the corresponding dye prepared from *N*,*N*-dimethylaniline (λ_{max} 540 nm in DMF);[17] the last dye is predicted to be the most bathochromic on the basis of it having fewer electron-accepting groups located on the coupling component compared to the other two dyes. While the converse trend is observed for the 3-ethoxycarbonyl-based dye series (i.e. the *N*,*N*-dimethylaniline-derived dye is the most bathochromic),[18] the data for these dyes are, curiously, very similar to those given for analogues prepared from 2-amino-3-carbamyl-4,5-tetramethylenethiophene:[19] the carbamyl-based diazo component has only one moderate electron-accepting substituent compared to the three present in the 3,5-di(ethoxycarbonyl)-4-ethoxycarbonylmethyl compound and, thus, the former is expected to produce dyes of considerable hypsochromism relative to the latter component, i.e. (**2**; X = $CONH_2$) should be hypsochromic relative to (**6**; X = CO_2Et), yet λ_{max} values are given as being the same to within a few nm. (Additionally, light and sublimation fastness ratings are listed as being identical.) However, within the toluidine-based dye series, the expected hypsochromism of (**1**; X = $CONH_2$) relative to (**5**; X = CO_2Et) was observed.

A relative insensitivity of the light fastness to change in concentration on polyester was shown. The maximum difference in fastness between the lightest and heaviest shades for a given dye was one point over a twenty-fold increase in application level (0.05–1.0% o.m.f.) to polyester; most of the dyeings had a smaller variation (see Table 6). A relative insensitivity over

TABLE 6
Light fastness of some thiophene-based disperse dyes applied to polyester at various depths of shade (% o.m.f.)

X	A	Light fastness of A			B	Fastness of B
		0.05%	0.5%	1.0%		1.0%
CN	**1**	1	2	2	**2**	4
CO_2Me	**1**	1	1	1–2		
CO_2Et	**1**	1	1	1	**2**	3
COPh	**1**	–	1	–		
COTh-2	**1**	–	1	–		
$CONH_2$	**1**	–	1	–	**2**	5
CN	**3**	–	2–3	–	**4**	3
CO_2Et	**3**	–	1	–	**4**	5
CN	**5**	5–6	5–6	6	**6**	4
CO_2Et	**5**	5	5	5–6	**6**	5–6
CN	**11**	5	5	5–6		
CO_2Et	**11**	4–5	5	5		

a 0.1–2.5% o.m.f. application range on polyester (and where reported on diacetate) is apparent in the results of Peters and co-workers with carbocyclic[23–26] and heterocyclic[1–3,11–27] monoazo dyes. For this reason, it was considered valid to compare the ratings of the dyeings despite the fact that they were not of a standard depth.

The ratings of the prepared dyes did not generally correspond well with those of Sabnis and Rangnekar[16–19] (see Table 6). Whilst the superior fastness of the dyes **2** over **1** could be anticipated by taking into account the effect of the additional cyano group located on the coupler residue,[28] the degree of difference is surprisingly large, especially between the carbamyl derivatives. The inconsistency may be a result of differing test methods, that of the Indian workers not being specified. In view of the relative insensitivity of the fastness to concentration on the fibre, the different application method used by Sabnis and Rangnekar (concerning preparation of the dyebath and the dyeing operation itself) is less likely to be a cause, as are the differences in substantivities of the dyes for polyester.

Similarly, the pyridone-derived dyes **3** from the same diazo components were found to have poorer stability than the related dyes **4** prepared by Sabnis and Rangnekar (see Table 6) in which the nitrogen atom of the pyridone ring was not alkylated.

The light fastness values of the series **5** and **6** were more consistent (see Table 6). The slight differences in the coupling components appear to have little effect: the addition of a cyano group onto the end of the alkylamino chain would be expected to have a beneficial effect on light fastness with polyester as the substrate,[28] although no significant changes are in evidence. The fastness of the derivative (**6**; X = CN) of Sabnis and Rangnekar is unexpectedly low; a value slightly above that of the corresponding 3-ethoxycarbonyl analogue is to be expected in the light of results obtained with other toluidine-derived thienyl-2-azo dyes, for example, the derivatives **11**. A comparison of the data of **5** and **11** suggests that the addition of an ester group onto the 4-methyl substituent produces a slight improvement in light fastness.

3. EXPERIMENTAL

Thin-layer chromatography was performed using aluminium-backed silica gel plates (DC Alufolien Kieselgel 60 F_{254}, Merck) and alumina plates (DC Alufolien Aluminiumoxid 150 F_{254} neutral Type T, Merck), both types having a layer thickness of 0.2 mm. Column chromatography (column diameters 4.5 cm and 5.5 cm) was performed with alumina (Al oxide 90 active neutral 0.063–0.2 mm, Merck; Al oxide active neutral Brockmann grade 1, BDH) or silica (silica gel 100 0.063–0.2 mm, Merck; 0.13–0.25 mm, BDH).

Melting points were determined using an electrothermal melting point apparatus and were uncorrected. Thermal analysis was performed on a DuPont 2000 differential scanning calorimeter. Infra-red absorption spectra were recorded using a Unicam SP1100 spectrophotometer in Nujol mull; Fourier-transform infra-red spectra were obtained with a Perkin-Elmer 1740 spectrophotometer in KBr discs. ^1H NMR spectra were acquired using a Perkin-Elmer 60 MHz machine. The UV–visible absorption spectra of the dye solutions were measured in quartz cells on a Philips PU8720 spectrophotometer (scan speed 50 nm min^{-1}).

3.1. Preparation of intermediates

The coupling components were industrial samples (Yorkshire Chemicals). *N*,*N*-Di(2′-acetyloxyethyl)-5-acetylamino-2-methoxyaniline was used without further purification, while *N*-2-cyanoethyl-*N*-ethyl-*m*-toluidine was double-distilled and *N*-ethyl-3-cyano-4-methylpyridin-2,6-dione was isolated from solution by neutralisation and recrystallised from ethanol.

The diazo components were obtained as commercial samples (2-amino-3,5-di(ethoxycarbonyl)-4-methylthiophene, Yorkshire Chemicals) or prepared via the Gewald synthesis: 2-amino-3-ethoxycarbonyl-4,5-tetramethylenethiophene[29,30] and 2-amino-3-carbamyl-4,5-tetramethylenethiophene[29] were prepared in a similar manner to the 3-cyano analogue as described below.

2-Amino-3-cyano-4,5-tetramethylenethiophene

Malononitrile (99%, 3.34 g, 0.05 mol), cyclohexanone (4.91 g, 0.05 mol), sulphur (1.60 g, 0.05 mol) and ethanol (10 ml) were stirred while diethylamine (5 ml) was added portionwise so the mixture temperature remained below 40°C, yellow solid precipitating before completion of the addition. The mixture was stirred for 3.5 h at 40–50°C, refrigerated and the solid collected. The brown solid (7.56 g, 85% crude yield) was recrystallised (ethanol twice, 100–120°C ligroin/ethyl acetate), producing pale beige needles of m.p. 145.5–147°C. Lit.[29] 86% yield, m.p. 147–148°C.

2-Amino-3-methoxycarbonyl-4,5-tetramethylenethiopene

Cyclohexanone (19.67 g, 0.20 mol), methyl cyanoacetate (99%, 20.02 g, 0.20 mol), sulphur (6.41 g, 0.20 mol) and methanol (40 ml) were stirred together and treated with diethylamine (20 ml) over 8 min below 30°C. The mixture was stirred for 3.5 h at 45–50°C, the suspension left overnight and made up to 200 ml with water, filtered and the collected solid water-washed to give a yellow powder (33.72 g, 80% crude yield, m.p. 128–130.5°C). Three recrystallisations from methanol gave the pure compound as white crystals, m.p. 130–131°C. Microanalysis found C, 56.9; H, 6.2; N, 6.65; S, 15.05% ($C_{10}H_{13}NO_2S$ requires C, 56.8; H, 6.2; N, 6.6; S, 15.2%). FTIR(KBr)/cm^{-1}: 3421, 3314 (NH); 1654 (C=O).

2-Amino-3-benzoyl-4,5-tetramethylenethiophene

Benzoylacetonitrile (99%, 5.72 g, 0.039 mol), cyclohexanone (3.83 g, 0.039 mol), sulphur (1.38 g, 0.043 mol) and ethanol (20 ml) were mixed and treated with morpholine (4.0 ml) in one portion. The mixture was heated to reflux with stirring for 3 h, the dark liquor allowed to stand for 2 days and the bright yellow–orange needles (7.78 g, 78% crude yield, m.p. 151–153°C) filtered off. Recrystallisation (ethanol/charcoal) produced yellow crystals (6.97 g, m.p. 153–154°C). Lit.[29] 40% yield, m.p. 155°C, lit.[31] 40% yield, m.p. 156°C.

2-Amino-3-(2′-thienoyl)-4,5-tetramethylenethiophene

Morpholine (4.0 ml) was added in one portion to a suspension of 2-thienoylacetonitrile (6.05 g, 0.040 mol), cyclohexanone (3.93 g, 0.040 mol) and sulphur (1.41 g, 0.044 mol) in ethanol (20 ml), before stirring and refluxing for 3 h. The dark mixture was allowed to stand overnight and filtered, the collected material consisting of an orange crystalline solid (8.02 g, 76% crude yield, m.p. 128–131°C). (Drowning the filtrate gave a dark red powder (1.81 g, m.p. < 110°C), total crude yield 93%.) Recrystallisation (ethanol/charcoal, then 100–120°C ligroin, followed by ethanol) gave analytically pure, bright yellow–orange crystals, m.p. 131–132°C. Microanalysis found C, 59.2; H, 4.85; N, 5.25; S, 24.15% ($C_{13}H_{13}NOS_2$ requires C, 59.3; H, 5.0; N, 5.3; S, 24.3%). FTIR(KBr)/cm^{-1}: 3375, 3254 (NH).

2-Amino-3,5-diethoxycarbonyl-4-ethoxycarbonylmethythiopene
A stirred mixture of diethyl acetone-1,3-dicarboxylate (95%, 10.64 g, 0.05 mol), sulphur (1.60 g, 0.05 mol), ethyl cyanoacetate (98%, 5.77 g, 0.05 mol) and ethanol (10 ml) was treated with diethylamine (5 ml) at 40°C and then stirred at 50–55°C for 5 h. After standing for 2 days, shiny red leaflets (5.34g, 32% crude yield) were filtered from the viscous clear red liquor. Recrystallisation (ethanol, twice) gave a cream crystalline solid (4.45 g, m.p. 113–114°C, lit.[18] 179°C, lit.[32] 115–116°C). Microanalysis found C, 51.2; H, 6.1; N, 4.25; S, 10.05% ($C_{14}H_{19}NO_6S$ requires C, 51.0; H, 5.8; N, 4.25; S, 9.7%). DSC suggested purity, showing a sharp endotherm at 115.6–116°C. IR(nujol)/cm^{-1}: 3420, 3320 ($-NH_2$); 1720 ($-CH_2COOEt$); 1680 ($-CO_2Et$). Lit.[18] (nujol) 3430, 3330, 1720, 1675. PMR(DMSO-d_6): 1.05–1.35 (9H, m, CH_3); 4.0–4.4 (6H, m, $CO_2CH_2CH_3$); 2.1 (2H, s, $HetCH_2$); 8.1 (2H, s, NH_2).

2-Amino-5-ethoxycarbonyl-3-cyano-4-ethoxycarbonylmethylthiopene
A stirred mixture of diethyl acetone-1,3-dicarboxylate (95%, 10.64 g, 0.05 mol), sulphur (1.60 g, 0.05 mol), malononitrile (99%, 3.34 g, 0.05 mol) and ethanol (10 ml) was treated with morpholine (5 ml) at 40°C and then stirred at 65–75°C for 1.5 h, complete dissolution of sulphur occurring after 1.25 h. The brown liquid was cooled in ice and crystallisation induced by stirring in a few small lumps of ice. The mixture was filtered after 1 h at 0°C, the solid sucked liquid-free and washed with water to give a buff product (11.40 g, 81% crude yield, m.p. 134–135°C). Two recrystallisations (ethanol) furnished off-white needles, m.p. 136–137°C, lit.[17] 141°C, lit.[32] 137°C.

2-Amino-5-ethoxycarbonyl-3-cyano-4-methylthiopene
To a stirred mixture of ethyl acetoacetate (13.02 g, 0.10 mol), sulphur (3.21 g, 0.10 mol), malononitrile (99%, 6.67 g, 0.10 mol) and ethanol (20 ml) at 35–45°C, morpholine (10 ml) was added over 5 min and the mixture stirred at 60–70°C for 3 h before placing the brown liquid in a fridge overnight. Filtration and washing the collected solid with cold ethanol yielded a brown powder (8.02 g, 38% crude yield). Recrystallisation (ethanol, ethanol/charcoal) produced pink crystals (m.p. 210–211°C, lit.[32] 209°C). FTIR(KBr)/cm^{-1}: 3402, 3314 (NH); 2205 ($C\equiv N$); 1675 ($C=0$). Lit.[32] (KBr): 3400, 3310, 2200, 1670.

3.2. Preparation of dyes

The methods of diazotisation for each amine (see Section 3.2.1) are given in Table 7 together with the molarity of the reaction in mmol. The coupling conditions used were specific to each coupler (see Section 3.2.2). Also given

TABLE 7
Methods of synthesis and purification of the thiophene-derived dyes

Dye	X	Method/ molarity	Crude yield (g/%)	Purification method	Pure yield (g/%)	%s	Appearance	M.p. (°C)
1	CN	A/5.0	1.50/79	$\Gamma\alpha$	0.85/45	57	Red–purple crystalline powder	160–162
1	CO_2Me	B/15	4.00/65	$\Theta\ \beta\beta$	0.21/3	7/5	Red fibrous solid	139–139.5
1	CO_2Et	B/20	5.69/67	$\Gamma\alpha\alpha\beta$	0.73/9	18/12	Shiny red leaflets	137.5–138.5
1	COPh	A/10	3.11/72	$\Lambda\Lambda\gamma\gamma\gamma$	0.13/3	4	Red crystals (green reflex)	158–159
1	COTh-2	C/8.0	2.66/72	$\Gamma\gamma\gamma\gamma$	0.10/3	4	Shiny green crystals	154–154.5
1	$CONH_2$	D/15	1.99/34	$\Pi\alpha\beta$	0.07/1	9/3	Red fibrous needles	215.5–216
3	CN	A/8.0	2.66/90	$\beta\beta\delta\delta\varepsilon$	0.08/3	10/9	Bronze–red crystals	234–236
3	CO_2Et	B/10	1.91/46	$\Sigma\delta$	0.15/4	15/7	Shiny dark red needles	268–269
5	CN	E/5.0	2.16/90	$\Lambda\beta$	0.87/36	40	Violet & green shiny crystals	155.5–156.5
5	CO_2Et	E/5.0	2.00/76	$\Lambda\gamma\gamma$	0.42/16	21	Shiny purple crystals	110–110.5
11	CN	E/5.0	1.86/91	$\eta\eta\varepsilon\varepsilon\lambda\varepsilon\varepsilon\varepsilon$	0.26/13	14	Shiny green crystals	234–235
11	CO_2Et	E/5.0	2.10/92	$\lambda\lambda\mu\mu\nu\nu\lambda$	1.25/55	60	Bronzy dark crystals	168–169

in Table 7 are the crude yields, purification methods (see Section 3.2.3) and pure yields of the dyes, '%s' being the 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).

3.2.1. Diazotisation

Conventional techniques were used as detailed in Table 7. The diazotisation methods are listed below. The presence of an excess of nitrous acid was tested for (after dilution of the sample if necessary) by starch–iodide paper; confirmation of the presence of diazonium ions was made by the formation of an intense coloration on addition of a sample to a solution of *N*-1-naphthylethylenediamine hydrochloride.

The following methods were used:

(A) The amine was dissolved by warming in aqueous sulphuric acid (35%, 3.9 ml per mmol amine). Sodium nitrite (5–10% excess) in water (1.0 ml per mmol amine) was added over 30 min at 0–5°C and the whole stirred at this temperature for 60 min.

(B) The amine was dissolved by warming in aqueous HCl (17%, 2.0 ml per mmol amine). Sodium nitrite (5–10% excess) in water (0.4 ml per mmol amine) was added over 30 min at 0–5°C and the whole stirred at this temperature for 30–60 min.

(C) As in A, except aqueous sulphuric acid (35%, 4.9 ml per mmol amine) was used.

(D) As in B, except aqueous HCl (11%, 5.0 ml per mmol amine) was used.

(E) Nitrosylsulphuric acid was prepared by adding sodium nitrite (10% excess) to sulphuric acid (98%, 0.4 ml per mmol amine) at 20–30°C, heating to 60–65°C over 10 min with stirring and maintaining this temperature for up to 5 min to ensure complete dissolution. After allowing the solution to cool, a mixture of acetic and propionic acids (5:1, 0.64 ml per mmol amine) was added under 30°C. The amine was added over 20–30 min under 5°C and the whole stirred at 0–5°C for 2–4 h.

3.2.2. Coupling

The procedures were determined by the coupling component and the method of diazotisation employed. (Sulphamic acid was added to the coupler solution before addition of the diazonium mixture if it had not been already added at the end of the diazotisation.)

For dyes derived from the toluidine coupler and from diazo components diazotised by methods A, C and E, a mixture of coupling component, water (4.9 ml per mmol amine), HCl (36%, 0.10 ml per mmol amine) and ice (5 g per mmol amine) was used. Addition of the diazonium mixture was made at 0–5°C and the whole stirred for at least 2 h before diluting or raising the pH to 4.5 (aqueous NaOH or sodium acetate) prior to filtering and water-washing neutral.

For dyes derived from the toluidine coupler using diazotisation methods B and D, the coupler was dispersed in a mixture of acetic acid (99%, 0.25 ml per mmol amine), water (0.5 ml per mmol amine) and sodium acetate (0.5 g per mmol amine), the mixture cooled below 5°C and the diazonium solution added below this temperature over 5–10 min. After stirring at 0–5°C for 2–4 h or overnight, the mixture was diluted, filtered and water-washed neutral.

The pyridone-based dyes were prepared by dissolving the pyridone in aqueous sodium hydrogen carbonate (15%, 20 ml per mmol amine). The diazonium solution was added under 5°C and the whole stirred for 2–3 h, adding ice to cool when necessary. The suspension was neutralised (dilute HCl) and the solid collected and water-washed.

The dyes derived from the 5-acetylamino-2-methoxyaniline-based coupler were prepared by dissolving the coupler in water (2.2 ml per mmol amine), sulphuric acid (98%, 0.1 ml per mmol amine) and ice (4.0 g per mmol amine). The diazonium mixture was added over 5–10 min under 5°C and stirred at this temperature for 1–2 h before diluting and/or raising the pH to 6. The suspension was stirred overnight, filtered and the collected solid water-washed neutral.

3.3. Purification

The crude products were isolated as solids and purified by a combination of column chromatography and recrystallisation. As detailed in Table 7, the chromatographic treatments correspond as follows: Γ (silica/95:5 toluene: ethyl acetate), Θ (as Γ except alumina), Λ (as Γ except 85:15), ∏ (alumina/ 85:15 toluene:ethyl acetate, gradually changing ratio to 1:1), Σ (alumina/ 1:1 dichloromethane:toluene, gradually changing to 1:1 dichloromethane: acetone).

Recrystallisation was performed with the following solvents: aqueous ethanol (α), ethanol (β), methanol (γ), ethyl acetate (δ), 2-ethoxyethanol (ε), toluene (η), toluene/ethyl acetate (λ), ethanol/DMF (μ) and aqueous 2-ethoxyethanol (ν).

The purified dyes were all found to have satisfactory ($\leqslant \pm$ 0.3%) elemental analyses (C, H, N and S).

3.4. Dye application

A sample of powdered dye (200 mg) in an aqueous solution (20 ml) of Diwatex 30FKP (0.10 g, Borregaard LignoTech) contained in a screw-top jar (60 ml capacity), holding a milling medium of zirconium oxide beads (40 g), was roll-milled for 72 h. Dispersions were obtained which examination by microscope revealed as containing primary particles of dye, the size of most being about 1 μm or less. The preparation was completed by removal of the milling medium and dilution to 100 ml. (In cases where the requisite amount of dye was unavailable, the amounts of materials were scaled down proportionally to the size of dye sample used.)

Each dye was applied to texturised polyester using a high-temperature method. A dyebath (liquor ratio 15:1) was prepared from distilled water, the appropriate amount of dye dispersion and enough Dyapol BD (Yorkshire Chemicals) to give a concentration of 1 g/litre. Its pH was adjusted to 4.5 by addition of aqueous disodium monohydrogen orthophosphate (2%) or acetic acid (2%), the fabric immersed and dyed (Mathis Labomat infra-red or Zeltex Polycolor equipment), raising the dyebath temperature to 130°C over 15 min and maintaining it for 1 h.

The fabric samples were rinsed well with cold water and reduction-cleared by heating in liquor containing NaOH (2 g/litre), sodium dithionite (2 g/litre) and Dyapol G (2 g/litre, Yorkshire Chemicals) at 70°C for 20 min. The samples were then rinsed with cold water, dried (80°C or below) and stentered at 180°C for 30 s.

The ISO 105 B02 test was used to assess the light fastness of every dyeing.[33]

3.5. Computational methods

PPP-MO calculations for the model dyes **7** and **10** were performed by means of a FORTRAN programme[34] on a personal computer equipped with a 486DX (33 MHz) central processing unit. The fixed β approximation was used and two-centre electron repulsion integrals determined by the Nishimoto–Mataga relationship.[35] A limited configuration interaction treatment was employed to refine the electronic excitation energies involving the nine singly excited singlet configurations obtained by promotion of an electron from the three highest occupied orbitals to the three lowest unoccupied orbitals.

Standard parameters, bond lengths and angles were used.[12,21,36] Structures were assumed to be planar. Thiophene rings were presumed to have equal internal bond angles (108°) and the geometry of the azo link to be such that steric interactions were minimised, i.e. conformations in which *ortho* substituents were oriented so as to avoid clashes with lone pairs on the azo link, as shown for the structures for **7** and **10** (see earlier). Where groups had two possible orientations, for example acyl and ester functions, results were obtained by averaging data calculated for both geometries.

Ester groups were simulated by employing parameters for an acetyl group and a methoxy function. For the latter, slightly better results were obtained using figures associated with methoxy groups, which were adjacent to a carbonyl group in a quinone, than for figures pertaining to such groups in isolation.

Spectral data were calculated for both the hydrazone and azo forms of the dyes **10**. In the former case, hydrogen-bonding between the relevant NH and carbonyl functions was assumed to occur; any interaction involving 3-substituents on the diazo component and the NH function was not accounted for.

Optimisation of the parameters to get a better correlation between calculated and observed data was not attempted since there were several influences outside the scope of the calculations. These included the use of toluene as the solvent for the spectroscopic measurements, instead of cyclohexane, as well as inductive effects from sources such as alkyl(ene) groups on the diazo or coupling components and the 2-cyanoethyl group of the toluidine-based dyes.

Molecular modelling was performed using the 'Hyperchem' software package.[37]

4. CONCLUSIONS

Thiophene-derived disperse dyes have been synthesised and their colour properties examined in solution and on polyester. A comparison of these properties with those of previously reported closely related analogues yielded some unexpected and marked differences.

Dyes prepared from 3-substituted tetramethylenethiophenes were found to have very poor light fastness on polyester, contrary to the ratings reported for structurally similar colorants by Sabnis and Rangnekar; additionally, their disclosure that blue 3-carbamyl derivatives can be produced from simple aniline-based couplers appears contentious in the light of the experimental data and PPP-MO calculations. Absorption intensities did not correspond well: the prepared dyes did not have the generally unusually low ε_{max} values attributed by Sabnis and Rangnekar to their dye series.

While the 4-ethoxycarbonylmethyl-5-ethoxycarbonylthiophene-based dyes were found to have reasonably good light fastness on polyester in line with published figures, experimental and PPP-MO calculation evidence contradicts the reports of such dyes being blue.

ACKNOWLEDGEMENTS

Yorkshire Chemicals plc are thanked for their financial and technical assistance.

REFERENCES

1. Peters, A. T. & Gbadamosi, N. M. A., *Dyes and Pigments*, **18** (1992) 115.
2. Peters, A. T., Tsatsaroni, E. & Xisai, Ma, *Dyes and Pigments*, **20** (1992) 41.
3. Peters, A. T., Taebi, A. & Yang, S. S., *J. Soc. Dyers Colour.*, **109** (1993) 397.
4. Peters, A. T., Yang, S. S. & Chisowa, E., *Dyes and Pigments*, **28** (1995) 151.
5. Malankar, U. V. & Desai, K. R., *Orient J. Chem.*, **10** (1994) 301; *Chem. Abs.*, **122** 293396w.
6. Kraska, J. & Sokolowska-Gajda, J., *J. Soc. Dyers Colour.*, **100** (1984) 316.
7. Kraska, J. & Sokolowska-Gajda, J., *Dyes and Pigments*, **7** (1986) 161.
8. Kraska, J. & Sokolowska-Gajda, J., *Dyes and Pigments*, **8** (1987) 345.
9. Wippel, H. G., *Melliand Textilberichte*, **50** (1969) 1090.
10. Dickey, J. B., Towne, E. B., Bloom, M. S., Moore, W. H., Smith, B. H. & Hedberg, D. G., *J. Soc. Dyers Colour.*, **74** (1958) 123.
11. Peters, A. T. & Gbadamosi, A., *J. Chem. Tech. Biotechnol.*, **53** (1992) 301.
12. Hallas, G. & Marsden, R., *Dyes and Pigments*, **6** (1985) 463.
13. Rangnekar, D. W. & Jhaveri, P. V., *Indian J. Fibre Text. Res.*, **15** (1990) 26.
14. Rangnekar, D. W. & Chitale, R. S., *Indian J. Fibre Text. Res.*, **15** (1990) 81.
15. Sabnis, R. W. & Rangnekar, D. W., *J. Het. Chem.*, **27** (1990) 417.
16. Sabnis, R. W. & Rangnekar, D. W., *Dyes and Pigments*, **10** (1989) 295.
17. Sabnis, R. W. & Rangnekar, D. W., *J. Chem. Tech. Biotechnol.*, **47** (1990) 39.
18. Sabnis, R. W., Kazemi, G. & Rangnekar, D. W., *Bull. Chem. Soc. Jpn*, **64** (1991) 3768.
19. Sabnis, R. W. & Rangnekar, D. W., *Indian J. Fibre. Text. Res.*, **17** (1992) 58.
20. Griffiths, J., *Dyes and Pigments*, **3** (1982) 211.
21. Lubai, C., Xing, C., Kunyu, G., Jrazhen, H. & Griffiths, J., *Dyes and Pigments*, **7** (1986) 373.
22. Ertan, N. & Eyduran, F., *Dyes and Pigments*, **27** (1995) 313.
23. Mehta, H. P. & Peters, A. T., *Dyes and Pigments*, **2** (1981) 259.
24. Mehta, H. P. & Peters, A. T., *Dyes and Pigments*, **3** (1982) 71.
25. Peters, A. T., *J. Soc. Dyers Colour.*, **101** (1985) 361.
26. Peters, A. T., *J. Soc. Dyers Colour.*, **104** (1988) 344.
27. Peters, A. T., *J. Soc. Dyers Colour.*, **85** (1969) 507.
28. Hallas, G., *J. Soc. Dyers Colour.*, **95** (1979) 285.
29. Gewald, K., Schinke, E. & Böttcher, H., *Chem. Ber.*, **99** (1966) 94.
30. Shvedov, V. I. & Grinev, A. N., *J. Org. Chem. USSR*, **1** (1965) 2269.
31. Gewald, K., *Z. Chem.*, **2** (1962) 305.
32. Wierzbicki, M., Cagniant, D. & Cagniant, P., *Bull. Soc. Chim. Fr.*, (1975) 1786.
33. Standard Methods for the Determination of the Colour Fastness of Textiles and Leather, 5th edn, SDC, 1990.
34. Griffiths, J., Lasch, J. G. & Schermaier, A. J., PPP.EXE, August 1987.
35. Nishimoto, K. & Mataga, N., *Z. Phys. Chem.*, **12** (1957) 335.
36. Griffiths, J., Lasch, J. G. & Schermaier, A. J., PPP.DOC, May 1988.
37. Hyperchem Release 3 For Windows, Autodesk Inc. (1992).