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Synthesis and spectral properties of azo dyes derived from 2-aminothiophenes and 2-aminothiazoles

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Abstract

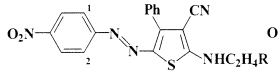
A series of thienylazo and thiazolylazo disperse dyes has been prepared from their corresponding coupling components, 2-aminothiophenes and 2-aminothiazole. Depending on the various substituents present in the diazo component, absorption maxima varied from 437 to 534 nm in toluene. The spectroscopic properties of the azo dyes were examined with respect to the effects of 3- and 4-substituents present in the coupling component. Thus, the appropriate Hammett substituent constants could be related to the observed bathochromic shifts in the order $CONH_2 < < CN < CO_2Et < < H$ at the 3-position of the thiophene ring. However, the resonance effect of the 4-phenyl group contributed to the red shifts observed, unlike the corresponding 4-methyl group. PPP–MO gave reliable predictions of absorption maxima by using new modified parameters for the terminal nitrogen atom in the coupling component.

Keywords: Monoazothiophenes; Gewald reaction; Monoazothiazoles; PPP–MO calculations

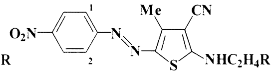
1. Introduction

Azo dyes with heterocyclic diazo components have been intensively investigated to produce bright and strong colour shades ranging from red to greenish blue on synthetic fabrics. These results led to commercial products to replace the conventional azobenzene disperse dyes [1–6]. Nitro substituted aminothiophenes and aminothiazoles were primarily of importance as diazo components. Although heterocycles have rarely been reported as coupling components for blue disperse dyes, some examples obtained from the coupling moieties of 2-aminothiophenes and 2-aminothiazoles were distinguished by their high colour strength and brilliant shades [7,8].

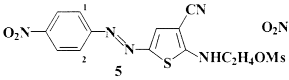
In the present study, we report the synthesis of the various coupling components and the subsequent monoazo disperse dyes **1–6**, **7** and **8** starting from 2-aminothiophenes and 2-aminothiazole as well as the spectral properties of the dyes prepared. The PPP–MO method was used to calculate the energies of the excited states of the dyes.



1 (R = OMs), **2** (R = Br)



3 (R = OMs), **4** (R = Br)



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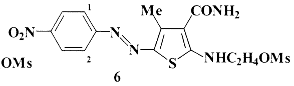

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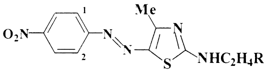

7 (R = OMs), **8** (R = Br)

1 = Cl, CF_3, CN, NO_2, Br, 2 = H, Br

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2. Results and discussion

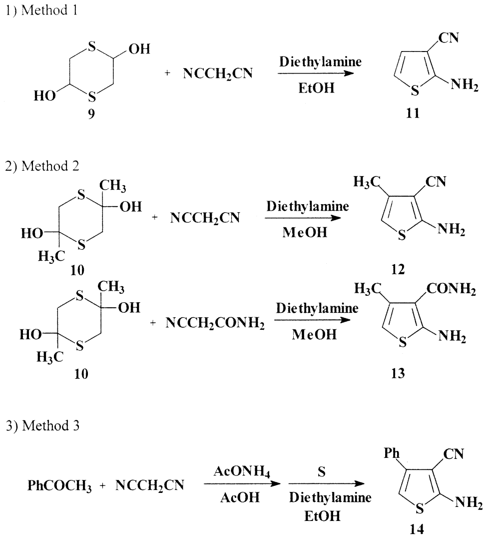
2.1. Preparation of the coupling components

Four different starting materials based on 2-aminothiophene have been prepared by using the Gewald reaction, as shown in Scheme 1, while 2-amino-4-methylthiazole **15** was available at laboratory grade.

In the next step, the relevant chloroethyl carbamates were readily prepared by reacting the corresponding 2-aminothiophenes and 2-aminothiazole with 2-chloroethyl-chloroformate in an appropriate solvent in the presence of pyridine to facilitate the condensation. Optimum reaction conditions for the synthesis of acylated aminothiophenes and aminothiazole are shown in Table 1.

Cyclisation and subsequent hydrolysis of the 2-chloroethylcarbamates were attempted in order to synthesise the corresponding 2-aminoethanols in the presence of an excess of aqueous sodium hydroxide while leaving the nitrile group intact. Reaction temperatures and times were varied for each of the starting materials **11–15**. Table 2 details the reaction conditions optimised in this study.

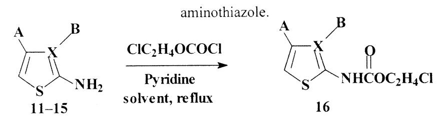
As it was intended to investigate the effects of the terminal group in the coupling component, the 2-aminoethanols were converted into either the corresponding 2-mesylamino or 2-bromoethylamino analogues.



Scheme 1. Preparation of the coupling components based on 2-aminothiophene.

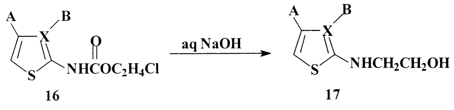
Nucleophilic substitution of alcohols by CH_3SO_2Cl (mesyl chloride) is quite similar to that by RCOCl but with lower reactivity. The likely mechanism of nucleophilic substitution at a sulphonyl sulphur atom, even though it is not identical, resembles the usual S_N2 mechanism involving a trigonal pyramidal transition state as shown below [9]. However, there is some evidence that the reaction takes place by an elimination-addition mechanism via a sulfene intermediate **21** when an α-hydrogen atom is present in the substrate [9], as with CH_3SO_2Cl.

Table 1
Optimum reaction conditions for the acylation of 2-aminothiophenes and 2-aminothiazole

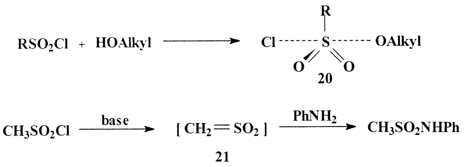


A	B	X	Solvent
H	CN	C	CH_2Cl_2
Me	CN	C	EtOAc
Me	$CONH_2$	C	MeOH
Ph	CN	C	EtOAc
Me	–	N	EtOAc

Table 2
Optimum reaction conditions for the cyclisation and subsequent hydrolysis of 2-chloroethylcarbamates



Starting material	A	B	X	Reaction temperature (°C)	Reaction time (h)
16a	H	CN	C	80–85	1
16b	Me	CN	C	90–100	1
16c	Me	$CONH_2$	C	70–75	1.5
16d	Ph	CN	C	100	1
16e	Me	–	N	60–70	1



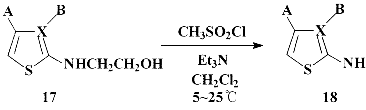
It has now been found that compounds containing a 3-cyano substituent are very suitable for mesylation, with acceptable reaction yields ranging from 73 to 94%. However, the presence of a 3-amide group tends to retard the substitution reaction, resulting in significantly lower yields.

The reaction time needed to complete the mesylation of starting material derived from 2-aminothiazole was similar to those of 2-aminothiophenes, taking less than 3 h. Details of the optimised reaction conditions and reaction times are tabulated in Table 3.

Two methods have been used to introduce a bromine atom into the terminal 2-ethylamino group in thiophene and thiazole systems.

The first method involves displacement of the hydroxy group by a bromine atom under strongly acidic conditions. Thus, the hydroxy group of compounds **17c** and **17e** is easily replaced by a bromine atom to give the corresponding 2-bromoethylamino products **19c** and **19e** in the presence of 48% HBr solution. A nucleophilic catalyst, such as LiBr, was used for compound **17e**. However, the reactivity of compound **17c** was not satisfactory in comparison with compound **17e**, giving a yield of only 50%. Alternatively, the poor reaction yield for the conversion of compound **17c** into the product **19c** was dramatically improved by replacing the mesyloxy group (OSO_2Me) with bromide, leading to a yield of about 90%. Table 4 gives the optimum reaction conditions for the preparation of 2-bromoethylamino derivatives of thiophene and thiazole.

Table 3
Optimum reaction conditions for mesylation



Starting material	A	B	X	Reaction time (h)
17a	H	CN	C	1
17b	Me	CN	C	3
17c	Me	$CONH_2$	C	6
17d	Ph	CN	C	2
17e	Me	–	N	2

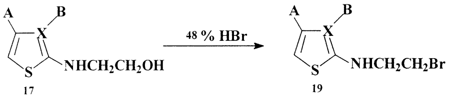
2.2. *Preparation of the azo dyes*

2.2.1. *Diazotisation and coupling*

Some azo dyes were prepared by coupling the intermediates with relevant diazotised anilines. More weakly basic amines, such as 4-nitro-2-substituted and 4-nitro-2,6-disubstituted anilines, except for 2-chloro-4-nitroaniline, required the use of nitrosylsulphuric acid. It was necessary for the 2-chloro-4-nitroaniline to be first stirred in HCl solution for a sufficient time, normally 10 h at room temperature, prior to the addition of $NaNO_2$, so that the formation of by-product arising from a coupling reaction between the free aniline and the diazonium salt could be minimised.

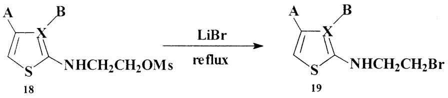
Table 4
Optimum reaction conditions for the preparation of 2-bromoethylamino derivatives

a.



Starting material	A	B	X	Catalyst	Reaction temp. (°C)	Reaction time (h)
17c	Me	$CONH_2$	C	–	95–100	3
17e	Me	–	N	LiBr	90–95	10

b.



Starting material	A	B	X	Solvent	Reaction time (h)
18b	Me	CN	C	Acetone	3
18c	Me	$CONH_2$	C	EtOH	2

Physical properties of the dyes are summarised in Table 5.

2.2.2. *Bromination of mesylated azo dyes*

Displacement of the mesyloxy group in the 2-ethylamino substituent of the various dyes **1**, **3** and **7** by a bromine atom was achieved effectively for dyes **2**, **4** and **8**, except dye **8c**, as shown in Table 6. LiBr readily brought about nucleophilic substitution in acetone at reflux by displacement of the good leaving group, $^{-}OSO_2CH_3$.

2.3. *Spectroscopic properties of the azo dyes*

2.3.1. *Absorption maxima of some azo dyes* **1** *and* **2** *derived from coupling components* **18d** *and* **19d**

Absorption maxima obtained for some 4-nitro-substituted azo dyes indicate that 2,6-disubstituted

Table 5
Physical properties and synthetic data for dyes **1**, **3**, **5**, **6**, **7** and **8** derived from coupling components **18** and **19**

Dye	Molarity ($\times 10^{-3}$ mol)	% Crude yield (g)	Purification method	% Pure yield (g)	Appearance
1a	1.24	87 (0.55)	C	68 (0.43)	Brown powder
1b	1.26	79 (0.54)	C	59 (0.40)	Dark brown solid
1c	1.23	79 (0.48)	C	63 (0.38)	Dark brown solid
1d	1.24	81 (0.58)	C	69 (0.49)	Navy powder
1e	1.22	83 (0.60)	E	60 (0.43)	Navy powder
3a	0.87	76 (0.29)	B	59 (0.23)	Scarlet powder
3b	1.27	85 (0.52)	C	67 (0.41)	Red–brown solid
3c	1.27	85 (0.47)	C	72 (0.40)	Violet leaflets
3d	1.18	94 (0.57)	E	71 (0.43)	Brown powder
3e	1.26	81 (0.54)	D	63 (0.42)	Dark brown solid
3f	1.27	86 (0.62)	E	57 (0.41)	Dark brown solid
5a	1.16	72 (0.36)	B	61 (0.31)	Red leaflets
5b	0.97	86 (0.39)	C	68 (0.31)	Red–brown solid
5c	1.00	89 (0.37)	C	72 (0.30)	Brown powder
5d	1.00	91 (0.45)	E	73 (0.36)	Red–brown solid
5e	1.00	87 (0.45)	E	63 (0.33)	Brown powder
6a	1.19	53 (0.31)	F	34 (0.20)	Red–brown solid
6b	1.13	74 (0.38)	F	49 (0.25)	Yellow–red powder
6c	1.13	81 (0.49)	F	53 (0.32)	Scarlet powder
7a	3.06	70 (0.88)	E	47 (0.59)	Red–brown solid
7b	3.06	74 (1.11)	E	55 (0.83)	Scarlet powder
7c	4.66	61 (1.45)	E	43 (1.02)	Dark brown solid
8c	3.82	77 (1.45)	E	58 (1.09)	Dark brown solid

Table 6
Experimental data for the replacement of mesyloxy

Dye	Molarity ($\times 10^{-3}$ mol)	% Crude yield (g)	Purification method	% Pure yield (g)	Appearance
2a	0.35	77 (0.13)	A	43 (0.07)	Brown solid
2b	0.37	83 (0.16)	A	65 (0.12)	Dark red powder
2c	0.37	75 (0.13)	B	51 (0.09)	Dark brown powder
2d	0.35	83 (0.16)	B	68 (0.13)	Red–brown powder
2e	0.34	72 (0.14)	C	53 (0.10)	Brown powder
4a	0.42	78 (0.15)	A	60 (0.12)	Red leaflets
4b	0.46	83 (0.16)	A	61 (0.12)	Brown powder
4c	0.35	73 (0.13)	D	46 (0.08)	Dark brown solid
8a	0.49	55 (0.11)	C	34 (0.07)	Dark red powder
8b	1.63	68 (0.53)	B	47 (0.37)	Brown powder

dyes **1d** and **1e** possessing electron withdrawing groups generally absorb bathochromically compared with the 2-monosubstituted dyes **1a–1c**. These findings emphasise the importance of electronic effects on the visible absorption spectrum. The most red-shifted spectrum was observed with dye **1e** which contains two *ortho* groups subject to crowding effects. Thus, azo dye **1e** absorbs at 547 nm in acetone, whereas the analogous dye **1c** possessing an *ortho*-cyano group absorbs at 543 nm in the same solvent, as shown in Table 7.

Direct comparison between dye **1c** and its counterpart **1d** also confirms that the further introduction of a bromine atom into an *ortho*-position adjacent to the azo linkage has but little effect on the λ_{max} value. The electronic effect of a substituent in the 3-position of the thiophene ring (see Table 9) can be seen to relate to λ_{max} when some azo dyes **22**, which contain a 3-CO_2Et group, are compared with the corresponding azo dyes **2**. The CN group is a more powerful electron acceptor than the CO_2Et group and consistent hypsochromic shifts are observed for dyes **2** as shown in Table 9 [10]. The nitrile group in the 3-position of the thiophene ring in **1** and **2** decreases the electron-donating power of the terminal nitrogen atom in the 2-aminoethyl group. Although the resultant values of the hypsochromic shift can vary according to the solvent used in measuring the spectra, all the dyes **2** absorb maximally at shorter wavelengths than the corresponding ethoxycarbonyl dyes **22** in the range 1–20 nm. The greatest differences in λ_{max} generally appear in $CHCl_3$ as solvent. Relevant data are given in Tables 7, 8 and 10. Various physical constants for CO_2Et and CN groups are given in Table 9.

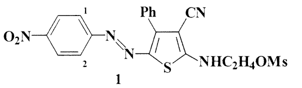
2.3.1.1. Solvatochromism. Both dyes **1** and **2** also show bathochromic shifts as the solvent polarity is increased. Very similar results are found in toluene and in $CHCl_3$.

From the viewpoint of ε_{max} values, 4-nitro-2-substituted dyes, such as **1b**, **1c**, (Scheme 2) **2b** and **2c** with CF_3 or CN groups, and the 4-nitro-2-bromo-6-cyano-substituted dyes **1d** and **2d**, show exceptionally high tinctorial strength in ethanol. Comparatively lower values of ε_{max} are found for dyes **1a** and **2a** containing a 2-chloro substituent.

Table 7
Absorption maxima of some azo dyes derived from coupling components **18d** and **19d**

a.

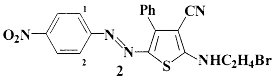
19d.



1

Dye	1	2	λ_{max} (nm) Toluene	$CHCl_3$	Acetone	EtOH	$10^{-4}\varepsilon_{max}$ (EtOH)
1a	Cl	H	515	509	526	626	4.85
1b	CF_3	H	518	513	529	619	7.17
1c	CN	H	533	533	543	604	7.47
1d	CN	Br	533	534	547	606	7.38
1e	NO_2	Br	534	532	547	605	3.91

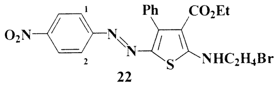
b.



2

Dye	1	2	λ_{max} (nm) Toluene	$CHCl_3$	Acetone	EtOH	$10^{-4}\varepsilon_{max}$ (EtOH)
2a	Cl	H	–	–	526	627	4.35
2b	CF_3	H	517	514	533	619	7.37
2c	CN	H	533	533	545	606	7.21
2d	CN	Br	532	531	547	607	7.15
2e	NO_2	Br	532	533	550	606	3.54

Table 8
Absorption maxima of some azo dyes **22** containing a 3-CO_2Et group [11]



22

Dye	1	2	λ_{max} (nm) Toluene	$CHCl_3$	Acetone	EtOH	$10^{-4}\varepsilon_{max}$ (EtOH)
22a	Cl	H	520	525	530	524	1.90
22b	CF_3	H	525	529	534	526	3.71
22c	CN	H	539	552	554	548	3.87
22d	CN	Br	534	551	548	558	2.23
22e	NO_2	Br	538	548	551	545	1.92

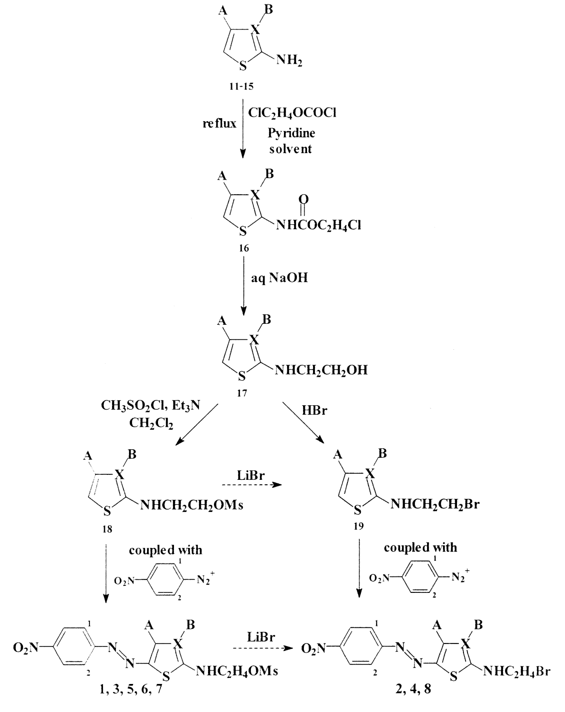
Table 9
Physical constants for CO_2Et, CN, phenyl and methyl groups [10]

Constants	CO_2Et	CN	C_6H_5	CH_3
$\sigma_p{}^a$	0.44	0.70	0.05	−0.14
σ_m	0.35	0.62	0.05	−0.06
$\sigma_I{}^b$	0.20	0.56	0.10	−0.05
σ_R	0.16	0.08	−0.10	−0.13
F^c	0.47	0.90	0.25	−0.01
R^d	0.67	0.71	−0.37	−0.41

[a] Represents the sum of resonance and field effect.
[b] Represents the field effect.
[c] Represents the field-effect contribution.
[d] Represents the resonance contribution.

Table 10
Spectral shifts of dyes **2** in absorption maxima relative to those of dyes **22**

			$\Delta\lambda_{max}$ (nm)			
Dye	1	2	Toluene	$CHCl_3$	Acetone	EtOH
2a	Cl	H	–	–	−4	+103
2b	CF_3	H	−8	−15	−1	+93
2c	CN	H	−6	−19	−9	+58
2d	CN	Br	−2	−20	−1	+49
2e	NO_2	Br	−6	−15	−6	+61



Scheme 2. Synthetic routes to some azo dyes from 2-aminothiophenes and 2-aminothiazole.

However, the introduction of both NO_2 and Br produces a significant decrease in tinctorial strength due to steric crowding (see Table 7).

Dramatic increases in λ_{max} values are observed in ethanol in contrast to the behaviour of the corresponding dyes **22** (Table 8). Thus, intermolecular hydrogen bonding between dye molecules **1** and **2** and ethanol, which is capable of stabilising the ground state of the dyes leading to a resultant blue shift, does not operate. Presumably, in these dyes there is no appropriate site for hydrogen bonding with ethanol to occur, in contrast to the presence of a CO_2Et group in dyes **22**. Consequently, the effect of small amounts of water contained in ethanol has a significant effect on colour in this solvent.

2.3.2. *Absorption maxima of some azo dyes* 3 *and* 4 *derived from coupling components* 18b *and* 19b

The role of a 4-methyl substituent in the thiophene ring of dyes **3** and **4** in relation to the visible absorption spectrum and the colour intensity has also been investigated. Although a methyl group can be regarded as a marginally better electron donor than a phenyl group, as shown by the physical constants reported in Table 9, most of dyes **3** and **4** absorb maximally at shorter wavelengths than the corresponding dyes **1** and **2** which possess a 4-phenyl group. Presumably, the resonance effect induced by an electron-rich phenyl group is more favoured than the slightly stronger field effect of a methyl group. Thus, all the 4-methyl dyes absorb hypsochromically compared with their 4-phenyl analogues, as shown in Tables 12 and 13.

As for the previous series, the 2-bromo-6-cyano-4-nitro derivative **3d** is by far the most bathochromic, again emphasising the positive role of the 6-bromo substituent in moving the visible absorption spectrum bathochromically with a negligible steric effect. However, the presence of two bulky bromine atoms in the dye **3f** gives rise to a marked hypsochromic effect (see Table 11). Absorption spectral data for **3** and **4** are given in Table 11, and comparisons between dyes **3**, **4**, **1** and **2** are given in Tables 12 and 13.

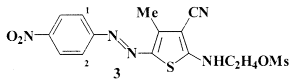
Both dyes **3** and **4** are also sensitive to small amounts of water present in ethanol, leading to large bathochromic shifts. As with dyes **1** and **2**, no intermolecular hydrogen bonding occurs when the dyes **3** and **4** are dissolved in ethanol, so that significant bathochromic shifts are measured consistently in this system. In accordance with the previous results, increasing electron withdrawal at X or Y in the acceptor ring is correlated with relatively smaller shifts of λ_{max}.

Dyes **3b** and **3c** possess by far the deepest hues and show high values of ε_{max} being almost twice that of the crowded dye **3e**. Similarly, comparatively weaker tinctorial strength is obtained from the analogous dibromo dye **3f** in ethanol (see Table 11).

Table 11
Absorption maxima of some azo dyes derived from coupling components **18b** and **19b**

a.

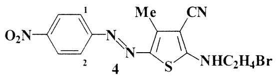
19b.



3

Dye	1	2	λ_{max} (nm) Toluene	CHCl$_3$	Acetone	EtOH	$10^{-4}\varepsilon_{max}$ (EtOH)
3a	Cl	H	–	–	515	599	4.71
3b	CF$_3$	H	512	501	521	602	6.03
3c	CN	H	519	516	535	584	6.34
3d	CN	Br	531	528	553	584	4.40
3e	NO$_2$	Br	522	518	543	586	3.10
3f	Br	Br	485	485	503	600	4.65

b.



4

Dye	1	2	λ_{max} (nm) Toluene	CHCl$_3$	Acetone	EtOH	$10^{-4}\varepsilon_{max}$ (EtOH)
4a	CF$_3$	H	505	501	518	598	5.54
4b	CN	H	519	520	535	583	5.70
4c	NO$_2$	Br	521	519	547	586	3.20

Table 12
Hypsochromic shifts of dyes **3** relative to the corresponding dyes **1**

Dye	1	2	$\Delta\lambda_{max}$ (nm) Toluene	CHCl$_3$	Acetone	EtOH
3a	Cl	H	–	–	−11	−27
3b	CF$_3$	H	−6	−12	−8	−17
3c	CN	H	−14	−17	−8	−20
3d	CN	Br	−2	−6	+6	−22
3e	NO$_2$	Br	−12	−14	−4	−19

2.3.3. Absorption maxima of some azo dyes 5 *derived from coupling components* 18a

Dyes **5** do not contain an electron donating group in the 4-position so that λ_{max} is hypsochromic in comparison with the corresponding dyes **1** and **3** containing 4-phenyl and 4-methyl groups, respectively. Stabilisation of the excited state by electron donation at the 4-position does not occur in **5**, thereby accounting for the relative hypsochromic shifts. A comparison between dyes **5** and **3** reveals that 2,4,6-tri-substitution in the acceptor ring, such as in dyes **5d** and **5e**, brings about bigger shifts of λ_{max} than the 2,4-di-substituted dyes, due to the different electrical strengths of the acceptor ring (Table 15). Exceptionally, 2-bromo-6-nitro substituents incur somewhat decreased absorption at 518 nm in dry acetone (Table 14). As previously, sensitivity to the water contained in acetone or ethanol solvents is apparent, with a dramatic increase in both λ_{max} and ε_{max} values. Comparison with the visible spectrum of the dyes **3** containing a 4-methyl group suggests that the water effect on the

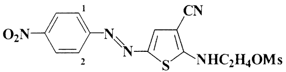
Table 13
Hypsochromic shifts of dyes **4** relative to the corresponding dyes **2**

Dye	1	2	$\Delta\lambda_{max}$ (nm) Toluene	CHCl$_3$	Acetone	EtOH
4a	CF$_3$	H	−12	−13	−15	−21
4b	CN	H	−14	−13	−10	−23
4c	NO$_2$	Br	−11	−14	−3	−20

absorption maxima for dyes **5** is slightly greater than that for dyes **3** to the extent of 2–9 nm red-shifted in ethanol, respectively, as illustrated in Table 15.

Dye **5c** containing 2-cyano-4-nitro substituents exhibits by far the highest ε_{max} value of 7.53×10^{-4} in ethanol. The 2-chloro-4-nitro dye **5a** also displays relatively stronger intensity in colour depth compared with its counterpart dyes. Furthermore, a consistently high value for ε_{max} appeared for dye **5b** having a 2-CF_3 group in the acceptor ring, Thus, the CF_3 group apparently enhances the tinctorial strength when it is introduced into an *ortho*-position unless a second *ortho*-substituent is incorporated. Undoubtedly, two bulky *ortho* groups, NO_2 and Br, decrease the ε_{max} value dramatically due to steric crowding.

Table 14
Absorption maxima of some azo dyes **5**



5

			λ_{max} (nm)				$10^{-4}\varepsilon_{max}$
Dye	1	2	Toluene	$CHCl_3$	Acetone	EtOH	(EtOH)
5a	Cl	H	–	–	507	606	5.20
5b	CF_3	H	499	489	509	604	7.23
5c	CN	H	515	510	524	592	7.53
5d	CN	Br	515	511	534	593	5.98
5e	NO_2	Br	510	489	518	591	2.95

Table 15
Hypsochromic shifts of some azo dyes **5**

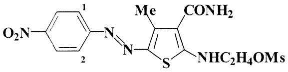
			$\Delta\lambda_{max}$ (nm)			
Dye	1	2	Toluene	$CHCl_3$	Acetone	EtOH
a. Comparison with the corresponding dyes **3**						
5a	Cl	H	–	–	−8	+7
5b	CF_3	H	−13	−12	−12	+2
5c	CN	H	−4	−6	−11	+8
5d	CN	Br	−16	−17	−19	+9
5e	NO_2	Br	−12	−29	−25	+5
b. Comparison with the corresponding dyes **1**						
5a	Cl	H	–	–	−19	−20
5b	CF_3	H	−19	−24	−20	−15
5c	CN	H	−18	−23	−19	−12
5d	CN	Br	−18	−23	−13	−13
5e	NO_2	Br	−24	−43	−29	−14

2.3.4. Absorption maxima of some azo dyes 6 *derived from coupling components* 18a

Judging from the visible absorption spectral data in Table 16, there is strong evidence to indicate the existence of intramolecular hydrogen bonding between the 3-amido group and a hydrogen atom in the 2-ethylamino group of the thiophene ring. Subsequent stabilisation of the ground state of the dye molecule by hydrogen bonding is probably responsible for the exceptional hypsochromic shifts observed for the amido dyes **6** (Table 17).

Although relevant physical constants for the $CONH_2$ group, such as the Hammett constant, resonance contribution value and field effect contribution value, differ somewhat from those of CO_2Et and CN groups (Table 9), the 3-amido

Table 16
Absorption maxima of some azo dyes **6** derived from coupling component **18c**



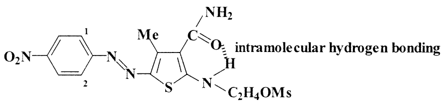
6

			λ_{max} (nm)				$10^{-4}\varepsilon_{max}$
Dye	1	2	Toluene	$CHCl_3$	Acetone	EtOH	(EtOH)
6a	CF_3	H	437	427	434	440	1.03
6b	CN	H	463	451	462	460	1.85
6c	CN	Br	474	464	474	480	2.23

Table 17
Hypsochromic shifts shown by dyes **6** relative to dyes **3**

			$\Delta\lambda_{max}$ (nm)			
Dye	1	2	Toluene	$CHCl_3$	Acetone	EtOH
6a	CF_3	H	−75	−74	−87	−162
6b	CN	H	−56	−65	−73	−124
6c	CN	Br	−57	−64	−79	−104

group is likely to have a bathochromic effect on λ_{max} from an electronic point of view. However, the significant hypsochromic shifts observed for dyes **6** emphasise the dramatic effect caused by intramolecular hydrogen bonding.



6

The decreases in λ_{max} range from 73 to 87 nm in acetone compared with dyes **3**. These values are relatively less sensitive to the polarity of the solvent. Since strong hydrogen bonding exists within the dye molecule, it is not surprising that water is no longer able to interact significantly with dye molecules to produce large shifts in the absorption band, in contrast to the other types of azo dyes previously mentioned.

As well as very large shifts toward shorter wavelengths, the dyes **6** also exhibit comparatively weak tinctorial strength (see Table 16). It is likely that the increased sp^3 character of the nitrogen atom in the 2-ethylamino group, caused by the intramolecular hydrogen bonding, may reduce the conjugation between the lone pair of electrons and the adjacent π-electron system, leading to a reduction in the tinctorial strength. The presence of an *o*-bromine atom in dye **6c** leads to an increase in ε_{max}.

2.3.5. *Absorption spectra of some azo dyes* 7 *and* 8 *derived from coupling components* 18e *and* 19e

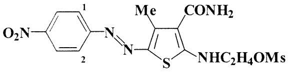
The absorption maxima of some azo dyes obtained from various 2-aminothiazole intermediates fall into the range 509–523 nm in dry acetone, as summarised in Table 18. In particular, both dyes **7c** and **8c** are exceptionally hypsochromic, indicating a significant steric interaction between the *ortho*-substituents and the (-electrons in the adjacent azo group. Furthermore, comparison with the corresponding 2-aminothiophene derivatives shows clearly that the thiophene ring system acts as a better electron donor than the thiazole ring. The thiazole ring, being more electron deficient, is accordingly a poor electron donor. Table 19 shows comparative λ_{max} values for the two ring systems.

2.4. *PPP–MO calculations [12]*

New modified parameters for the terminal nitrogen atom of the mesylated dyes are shown in Table 20. Both the Valence State Ionization Potential (VSIP) of each atom and the Electron Affinity (EA) of each relevant atom are crucial parameters for calculating theoretical transition energies of dye molecules.

The number of CI to refine the calculation result is also one of the important parameters to be considered. Comparison of the calculated energy for the transitions between CI 9 and CI 25 generally

Table 18
Visible spectral data for some azo dyes derived from 2-aminothiazole derivatives



6

	Substituents			λ_{max} (nm)		
Dye	1	2	R	Toluene	$CHCl_3$	Acetone
7a	CN	H	OMs	–	503	510
8a	CN	H	Br	–	501	509
7b	CN	Br	OMs	508	512	523
8b	CN	Br	Br	509	514	523
7c	NO_2	Br	OMs	496	498	511
8c	NO_2	Br	Br	497	500	510

Table 19
Comparison between dyes based on 2-aminothiazoles and analogous dyes derived from 2-aminothiophenes

	Substituents			$\Delta\lambda_{max}$ (nm)		
Dye	1	2	R	Toluene	$CHCl_3$	Acetone
7a[a]	CN	H	OMs	–	−13	−25
8a[b]	CN	H	Br	–	−19	−26
7b[c]	CN	Br	OMs	−22	−16	−30
7c[d]	NO_2	Br	OMs	−26	−20	−32
8c[e]	NO_2	Br	Br	−24	−19	−37

[a] Relative to dye **3c**.
[b] Relative to dye **4b**.
[c] Relative to dye **3d**.
[d] Relative to dye **3e**.
[e] Relative to dye **4c**.

Table 20
Modified parameters for the terminal nitrogen atom of azo dyes containing a $NHCH_2CH_2OMs$ group in the thiophene ring

Parameters	Nitrogen atom of the substituted ethylamino group
VSIP (eV)	19.2
EA (eV)	8.5
$\beta_{X\text{–}Y}$[a] (eV)	−2.75
Bond length $_{X\text{–}Y}$[a] (A)	1.38

[a] X–Y represents the bond connecting a terminal nitrogen atom and the 2-carbon atom of the thiophene ring.

indicates that CI 25 calculations are more likely to be reliable for dyes containing 4-nitro groups in the acceptor ring.

The PPP–MO calculations with CI 25 for dyes **1** containing a 3-cyano group in the thiophene ring provide closer results to the observed λ_{max} values in toluene. In this case, shorter wavelengths are calculated by the PPP–MO method for dyes **1a** and **1b** as well.

In contrast, the effect of a methyl substituent at the 4-position of the thiophene ring instead of a phenyl group in the analogous dyes **1** is more difficult to calculate accurately, since no π-electrons are involved in the PPP–MO calculation. Thus, with some exceptions calculated for the dyes **3e** and **3f**, the calculated absorption maxima appear at much shorter wavelengths than those observed in toluene (see Table 21).

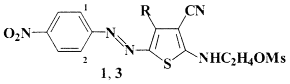
Calculations for dyes **5a**, **5b** and **5c**, involving relatively less bulky substituents, consistently predict smaller λ_{max} values (see Table 22). Calculated results for dyes possessing a 3-amido substituent in the thiophene ring are unlikely to be precise because the parameters for a nitrogen atom in the 2-ethylamino group are assumed as a free-form (see Table 22).

3. Experimental

3.1. General information

Melting points were determined on an Electrothermal melting point apparatus and also by differential scanning calorimetry using a DuPont Instruments Analyser 2000 with a DuPont DSC 10 Cell base. The NMR spectra were obtained with a JEOL JNM-FX 200 at 200 MHz for solutions in an appropriate deuterated solvent. IR absorption spectra were recorded on a Perkin–Elmer 1740 Infrared Fourier Transform Spectrometer. Visible absorption spectra were measured in a Perkin–Elmer Lambda 15 UV/VIS Spectrophotometer. Mass spectra were obtained with a VG AutoSpec Mass Spectrophotometer by Electron Ionisation (EI) in the School of Chemistry, University of Leeds.

Table 21
Calculated and observed values of λ_{max} for dyes **1** and **3**



1, 3

	Substituents			λ_{max} (nm)		
Dye	1	2	R	Observed^{tol}	Calculated (CI = 9)	Calculated (CI = 25)
1a	Cl	H	Ph	515	482	490
1b	CF_3	H	Ph	518	474	485
1c	CN	H	Ph	533	503	518
1d	CN	Br	Ph	533	508	524
1e	NO_2	Br	Ph	534	526	533
3a	Cl	H	Me	515[a]	467	477
3b	CF_3	H	Me	512	465	476
3c	CN	H	Me	519	490	499
3d	CN	Br	Me	531	494	502
3e	NO_2	Br	Me	522	508	516
3f	Br	Br	Me	485	473	484

[a] In acetone.

Table 22
Calculated and observed values of λ_{max} for dyes **5** and **6**

	λ_{max} (nm)		
Dye	Observed^{tol}	CI = 9	CI = 25
5a	507[a]	457	467
5b	499	454	464
5c	515	478	489
5d	515	483	492
5e	510	500	507
6a	437	462	469
6b	463	482	493
6c	474	484	498

[a] In acetone.

Microanalyses were carried out on a Carlo Erba Elemental Analyser 1108 for C, H, N and an Oxygen Flask Combustion, followed by titration for Br, F, Cl and S in the School of Chemistry, University of Leeds.

3.2. Preparative details of the coupling components

3.2.1. Preparation of 2-aminothiophenes

3.2.1.1. 2-Amino-3-cyanothiophene. 2,5-Dihydroxy-1,4-dithiane (10.1 g, 0.065 mol) and ethanol (60 ml) were cooled to 10°C and a solution of malononitrile (8.7 g, 0.131 mol) and ethanol (10 ml) was added at 10°C for 10 min. A solution of diethylamine (9.5 g, 0.073 mol) in ethanol (10 ml) was then added dropwise at 10°C. The temperature was raised to 35–40°C and then reaction mixture was stirred for 2 h. The reaction mixture was poured into water (300 ml) and the resulting brown solid 2-amino-3-cyanothiophene 11 was filtered off and dried at 50–60°C to give a yield of 72% (11.8 g), m.p. [13]. 104–105°C, m.p. 103–105°C, ^{1}H NMR ($CDCl_3$, δ); 5.2 (2H, b, NH_2), 6.5 (^{1}H, d, ArH), 6.8 (^{1}H, d, ArH). FT–IR (KBr, cm^{-1}); 3414, 3331, ν (NH) for NH_2, 2208, ν (CN), 1626, δ (NH_2).

3.2.1.2. 2-Amino-3-cyano-4-methylthiophene. 2,5-Dihydroxydimethyl-1,4-dithiane (4 g, 0.022 mol) was dissolved in methanol (40 ml), then cooled to 5°C. A solution of malononitrile (2.9 g, 0.044 mol) and methanol (4 ml) was added at 5°C for 10 min, then a methanol solution (4 ml) containing diethylamine (3.54 g, 0.048 mol) was added dropwise at 5°C for 20 min. The mixture was warmed to 35–40°C, and stirred further 1.5 h before pouring into water (300 ml). Filtration of the solidified product, an off-white coloured powder, and drying at 50-60°C gave 2-amino-3-cyano-4-methylthiophene **12** (5.0 g, 81%), m.p. [13] 119–120°C, m.p. 118–120°C, ^{1}H NMR ($CDCl_3$, δ); 2.25 (3H, s, CH_3), 4.9 (2H, b, NH_2), 6.2 (^{1}H, s, ArH), FT-IR (KBr, cm^{-1}); 3418, 3324, ν (NH) for NH_2, 2204, ν (CN), 1628, δ (NH_2).

3.2.1.3. 2-Amino-3-carbamyl-4-methylthiophene. This derivative was prepared by the same procedure as 3.2.1.2 starting from 3.73 g (0.044 mol) of 2-cyanoacetamide instead of malononitrile to give 3.2 g (yield 46%) of 2-amino-3-carbamyl-4-methylthiophene **13** as an off-white powder, m.p. [13] 176–178°C, m.p. 175–178°C. Microanalysis: found C, 45.8; H, 5.0; N, 17.7% ($C_6H_8N_2OS$ requires C, 46.1; H, 5.2; N, 17.9%). ^{1}H NMR (DMSO-d_6, δ); 2.3 (3H, s, CH_3), 6.3 (1H, s, ArH), 6.5 (2H, b, NH_2), 6.7 (2H, b, $CONH_2$).

3.2.1.4. 2-Amino-3-cyano-4-phenylthiophene. A reaction flask was fitted with a Dean-Stark trap, then *p*-acetophenone (20 g, 0.166 mol) was mixed with malononitrile (11.4 g, 0.172 mol), acetic acid (4 g) and ammonium acetate (2.6 g, 0.034 mol) in toluene (120 ml). The reaction mixture was stirred under reflux for 6 h with removal of the condensed water. The excess of toluene was evaporated and the brown liquid residue was mixed with ethanol (100 ml) and sulphur (3.4 g). After the mixture was cooled to 10°C a solution of diethylamine (8.6 g, 0.118 mol) in ethanol (10 ml) was added dropwise at 10°C, and stirred for 3 h at 50°C. Evaporation of ethanol gave the crude product which was added to ethanol (40 ml), followed by a further stirring for an 1 h at room temperature. Orange solid 2-amino-3-cyano-4-phenylthiophene **14** was filtered off to provide a yield of 15% (5.0 g), m.p. [13] 100–102°C, m.p. 101–103°C, ^{1}H NMR ($CDCl_3$, δ); 5.0 (2H, s, NH_2), 6.4 (1H, s, ArH), 7.3–7.6 (5H, m, PhH).

3.2.2. Acylation of 2-aminothiophenes and 2-aminothiazole

*3.2.2.1. 2-(3-Cyanothienyl)-*N*-β-chloroethyl carbamate.* 12 g (0.084 mol) of 2-chloroethyl chloroformate in 15 ml CH_2Cl_2 was added slowly over 10 min to 7 g (0.056 mol) of 2-amino-3-cyanothiophene **11** with a catalytic amount of pyridine in 90 ml of CH_2Cl_2 at room temperature; the mixture was then refluxed for 2 h. The mixture was then cooled, washed with 5% hydrochloric acid (50 ml), 5% sodium bicarbonate (50 ml) and water (50 ml), and dried over anhydrous sodium sulphate. CH_2Cl_2 was removed by rotary evaporator and the resulting crude product, as yellow oil, was purified by column chromatography (eluent: hexane/EtOAc = 8/2) to provide 6.8 g of 2-(3-cyanothienyl)-*N*-β-chloroethyl carbamate **16a** (52%, off-white powder), m.p. 110–111°C. Microanalysis: found C, 41.8; H, 3.1; N, 12.2; Cl, 15.4% ($C_8H_7ClN_2O_2S$

requires C, 41.7; H, 3.1; N, 12.1; Cl, 15.4%). ^{1}H NMR ($CDCl_3$, δ); 3.7 (2H, t, CH_2Cl), 4.4 (2H, t, OCH_2), 6.8 (^{1}H, d, ArH), 7.3 (1H, d, ArH), 8.2 (1H, s, NH).

*3.2.2.2. 2-(3-Cyano-4-methylthienyl)-*N*-β-chloroethyl carbamate.* This derivative was prepared by the same procedure as 3.2.2.1, starting from 6 g (0.042 mol) of 2-chloroethyl chloroformate in 6 ml EtOAc and 4 g (0.028 mol) of 2-amino-3-cyano-4-methylthiophene **12** with a catalytic amount of pyridine in 30 ml EtOAc. The residue, after evaporation, was added to 15 ml of ethanol and the precipitate was then filtered off. The yield of 2-(3-cyano-4-methylthienyl)-*N*-β-chloroethyl carbamate **16b** was 72% (5.1 g, off-white powder), m.p. 141–143°C. Microanalysis: found C, 44.5; H, 3.7; N, 11.4; Cl, 14.3% ($C_9H_9ClN_2O_2S$ requires C, 44.2; H, 3.7; N, 11.4; Cl, 14.5%). ^{1}H NMR ($CDCl_3$, δ); 2.35 (3H, s, CH_3), 3.8 (2H, t, CH_2Cl), 4.65 (2H, t, OCH_2), 6.65 (1H, s, ArH), 8.4 (1H, s, NH).

*3.2.2.3. 2-(3-Carbamyl-4-methylthienyl)-*N*-β-chloroethyl carbamate.* This derivative was prepared by the same procedure as 3.2.2.1, starting from 2.8 g (0.0195 mol) of 2-chloroethyl chloroformate in 3 ml methanol and 2 g (0.013 mol) of 2-amino-3-carbamyl-4-methylthiophene **13**, with a catalytic amount of pyridine in 20 ml of methanol. The mixture was added to 50 ml water and the precipitate was then filtered off to give 2.8 g of carbamate **16c** (83%, off-white solid), m.p. 178–181°C. Microanalysis: found C, 40.5; H, 4.3; N, 10.5% ($C_9H_{11}ClN_2O_3S$ requires C, 41.1; H, 4.2; N, 10.7%). ^{1}H NMR (DMSO-d_6, δ); 2.45 (3H, s, CH_3), 3.75 (2H, t, CH_2Cl), 4.3 (2H, t, OCH_2), 7.0 (1H, s, ArH), 7.2 (2H, b, $CONH_2$).

*3.2.2.4. 2-(3-Cyano-4-phenylthienyl)-*N*-β-chloroethyl carbamate.* This derivative was prepared by the same procedure as 3.2.2.1, starting from 2.1 g (0.015 mol) of 2-chloroethyl chloroformate in 3 ml EtOAc and 2 g (0.01 mol) of 2-amino-3-cyano-4-phenylthiophene **14**, with a catalytic amount of pyridine in 25 ml EtOAc. The crude product was added to 10 ml of ethanol with stirring and then filtered to give 2.33 g of carbamate **16d** (76%, off-white powder), m.p. 143–145°C. Microanalysis: found C, 54.9; H, 3.6; N, 9.1; Cl, 11.6% ($C_{14}H_{11}ClN_2O_2S$ requires C, 54.8; H, 3.6; N, 9.1; Cl, 11.6%). ^{1}H NMR ($CDCl_3$, δ); 3.8 (2H, t, CH_2Cl), 4.6 (2H, t, OCH_2), 6.95 (1H, s, ArH), 7.4–7.7 (5H, m, PhH), 8.3 (1H, s, NH).

*3.2.2.5. 2-(4-Methylthiazolyl)-*N*-β-chloroethyl carbamate.* This derivative was prepared by the same procedure as 3.2.2.1, starting from 37.5 g (0.26 mol) of 2-chloroethyl chloroformate in 40 ml EtOAc and 20 g (0.175 mol) of 2-amino-4-methylthiazole **15**, with a catalytic amount of pyridine in 200 ml of EtOAc. The mixture was then evaporated to remove EtOAc and the residue was poured into water (200 ml) and filtered to give 22.5 g of carbamate **16e** (58%, white powder), m.p. 146–148°C. Microanalysis: found C, 38.3; H, 4.1; N, 12.5% ($C_7H_9ClN_2O_2S$ requires C, 38.1; H, 4.1; N, 12.7%). ^{1}H NMR ($CDCl_3$, δ); 2.4 (3H, s, CH_3), 3.8 (2H, t, CH_2Cl), 4.5 (2H, t, OCH_2), 6.55 (1H, s, ArH).

3.2.3. Cyclisation and subsequent hydrolysis

*3.2.3.1. 2-(*N*-β-Hydroxyethylamino)-3-cyanothiophene.* 5 g (0.022 mol) of carbamate **16a** were added to NaOH solution (NaOH 4.4 g, water 40 ml) and the mixture was then stirred for 1 h at 80–85°C. The crude product was then extracted by 70 ml of EtOAc and was column chromatographed (eluent; hexane/EtOAc = 7/3) to give 2-(*N*-β-hydroxyethylamino)-3-cyanothiophene **17a** as a yellow sticky oil (2.2 g, 62%). Microanalysis: found C, 48.9; H, 4.7; N, 16.6% ($C_7H_8N_2OS$ requires C, 50.0; H, 4.8; N, 16.7%).

*3.2.3.2. 2-(*N*-β-Hydroxyethylamino)-3-cyano-4-methylthiophene.* 5 g (0.02 mol) of carbamate **16b** were added to NaOH solution (NaOH 4.4 g, water 40 ml) and the mixture was then stirred for 1 h at 90–100°C. The mixture was cooled to 10°C and neutralised to pH 6 by adding dilute H_2SO_4. The crude product was filtered off and column chromatography (eluent; hexane/EtOAc = 1/1) provided 2.2 g of product **17b** (59%, pale red crystal), m.p. 75–77°C. Microanalysis: found C, 52.7; H, 5.5; N, 15.3% ($C_8H_{10}N_2OS$ requires C, 52.7; H, 5.5; N, 15.4%). ^{1}H NMR ($CDCl_3$, δ); 2.25 (3H, s, CH_3), 3.3–3.7 (1H and 2H, m, OH and NH**CH_2**), 4.0 (2H, t, **CH_2**OH), 5.9 (^{1}H, b, NH), 6.1 (1H, s, ArH). FT–IR (KBr, cm^{-1}); 3392, ν (OH), 3204, ν (NH), 2195, ν (CN).

*3.2.3.3. 2-(*N*-β-Hydroxyethylamino)-3-carbamyl-4-methylthiophene.* 2 g (7.6×10^{-3} mol) of carbamate **16c** were added to NaOH solution (NaOH 1.7 g, water 25 ml) and the mixture was then stirred for 1.5 h at 70–75°C. The mixture was cooled to 5°C and acidified to pH 5–6 with dilute HCl. The fibrous off-white powder was filtered to give 1.0 g of product **17c** (66%), m.p. 231–233°C. Microanalysis: found C, 48.6; H, 5.8; N, 14.3% ($C_8H_{12}N_2O_2S$ requires C, 48.0; H, 6.0; N, 14.0%). ^{1}H NMR (DMSO-d$_6$, δ); 2.45 (3H, s, CH_3), 3.7–4.0 (2×2H and 1H, m, 2×CH_2 and NH), 5.2 (1H, b, OH), 6.9 (1H, s, ArH).

*3.2.3.4. 2-(*N*-β-Hydroxyethylamino)-3-cyano-4-phenylthiophene.* 2 g (6.5×10^{-3} mol) of carbamate **16d** were added to NaOH solution (NaOH 1.5 g, water 20 ml) and the mixture was then stirred for 1 h at 100°C. Ether (50 ml) and water (50 ml) were added to the reaction mixture, the ether fraction was collected, dried over sodium sulphate, and the solvent was removed by rotary evaporation to give a yield of 94% (**17d**, 1.5 g, off-white powder), m.p. 52–55°C. Microanalysis: found C, 64.5; H, 4.9; N, 11.2% ($C_{13}H_{12}N_2OS$ requires C, 63.9; H, 5.0; N, 11.5%). ^{1}H NMR (CDCl$_3$, δ); 2.9 (^{1}H, b, OH), 3.45 (2H, t, NH**CH$_2$**), 3.9 (2H, t, **CH$_2$**OH), 5.9 (^{1}H, t, NH), 6.4 (1H, s, ArH), 7.4–7.6 (5H, m, PhH).

*3.2.3.5. 2-(*N*-β-Hydroxyethylamino)-4-methylthiazole.* 7 g (0.032 mol) of carbamate **16e** were added to NaOH solution (NaOH 7.3 g, water 70 ml) and the mixture was then stirred for 1 h at 60–70°C. The product was extracted with 150 ml of EtOAc and the EtOAc layer was dried over sodium sulphate. The solvent was then removed by rotary evaporation to give a pale brown sticky oil **17e** (4.15 g, 83%). Microanalysis: found C, 45.6; H, 6.4; N, 17.9; S, 19.8% ($C_6H_{10}N_2OS$ requires C, 45.5; H, 6.4; N, 17.7; S, 20.3%).

3.2.4. Mesylation of 2-hydroxyethylamino groups

*3.2.4.1. General procedure for the preparation of N-β-methanesulphonyloxyethylamino derivatives **18**.* 1 g (4.1×10^{-3} mol) of *N*-β-hydroxyethylamino derivative **17d** in 10 ml of methylene chloride was cooled to 0°C. 0.56 g (4.9×10^{-3} mol) of methanesulphonyl chloride in 1 ml of methylene chloride was added at 0°C over 10 min and 0.91 g (9.0×10^{-3} mol) of triethylamine in 1 ml of methylene chloride was then added dropwise at 0–10°C. The mixture was stirred for a further 2 h, during which time the temperature was allowed to rise to room temperature. 50 ml of methylene chloride were added and the whole was washed with 50 ml of water, 50 ml of 10% HCl, 50 ml of 10% NaHCO$_3$, and then with 50 ml of water. The methylene chloride layer was dried over sodium sulphate and then the solvent was removed by rotary evaporation. The crude product was column chromatographed (eluent; hexane/EtOAc = 7/3) to give 0.96 g of 2-(*N*-β-methanesulphonyloxyethylamino)-3-cyano-4-phenylthiophene (**18d**, 73%, pale grey powder), m.p. 75–76°C. Microanalysis: found C, 51.3; H, 4.2; N, 8.4; S 19.8% ($C_{14}H_{14}N_2O_3S_2$ requires C, 52.2; H, 4.4; N, 8.7; S, 19.9%). ^{1}H NMR (CDCl$_3$, δ); 3.1 (3H, s, CH$_3$), 3.7 (2H, m, NH**CH$_2$**), 4.6 (2H, t, CH$_2$O), 5.7 (^{1}H, b, NH), 6.4 (^{1}H, s, ArH), 7.4–7.7 (5H, m, PhH).

The reaction conditions, yields and characterisation data for some *N*-β-methanesulphonyloxyethylamino derivatives **18**, those prepared by the general procedure 3.2.4, are given in Table 23.

3.2.5. Preparation of 2-bromoethylamino groups

3.2.5.1. 2-(N-β-Bromoethylamino)-3-carbamyl-4-methylthiophene. 1 g (3.6×10^{-3} mol) of β-methanesulphonyloxyethylamino compound **18c** was mixed with 2.2 g (26.4×10^{-3} mol) of lithium bromide in 30 ml of ethanol and was refluxed for 2 h. During the reaction, an off-white solid precipitated and was then filtered off to give 0.85 g of bromide **19c** (90%, pale grey powder), m.p. 244–246°C. Microanalysis: found C, 36.8; H, 4.1; N, 10.3; Br, 29.9% ($C_8H_{11}BrN_2OS$ requires C, 36.5; H, 4.2; N, 10.6; Br, 30.4%). ^{1}H NMR (DMSO-d$_6$, δ); 2.4 (3H, s, CH$_3$), 3.9 (2H, t, CH$_2$Br), 4.1 (2H, t, NH**CH$_2$**), 7.0 (^{1}H, s, ArH).

*3.2.5.2. 2-(*N*-β-Bromoethylamino)-4-methylthiazole.* 2 g (0.013 mol) of 2-hydroxyethylamino compound **17e** with 1.2 g (0.014 mol) of lithium

Table 23
Experimental and characterisation data for some *N*-β-methanesulphonyloxyethylamino derivatives **18**
a.

Compound	Molarity (10^{-3} mol)	% Yield (g)	Appearance	m.p. (°C)	NMR (δ)
18b	11.0	73 (2.1)	White solid	94–97	$CDCl_3$:2.25 (3H, s, CH_3), 3.15 (3H, s, SO_2CH_3), 3.8 (2H, m, NH**CH_2**), 4.5 (2H, t, CH_2OSO_2), 5.7 (1H, b, NH), 6.2 (1H, s, ArH)
18a	11.9	73 (0.97)	Off-white crystals	103–104	–
18c	9.9	55 (1.5)	White powder	167–169	DMSO-d_6: 2.5 (3H, s, CH_3), 3.2 (3H, s, SO_2CH_3), 3.8 (1H, s, NH), 4.3 (2H, m, NH**CH_2**), 4.7 (2H, t, CH_2OSO_2), 7.0 (1H, s, ArH)
18e	12.6	60 (1.8)	Pale orange crystals	117–119	$CDCl_3$: 2.3 (3H, s, CH_3), 2.7 (3H, s, SO_2CH_3), 4.4 (2×2H, s, 2×CH_2), 6.3 (1H, s, ArH)

b.

	Elemental analyses								
	Requires (%)				Found (%)				
Compound	C	H	N	S	C	H	N	S	FT–IR (KBr, cm^{J1})
18b	41.5	4.6	10.8	24.6	40.6	4.5	10.4	24.2	3260, ν (NH); 2210, ν (CN); 1352, 1171, ν (SO_2)
18a	39.0	4.1	11.4	26.0	39.0	4.0	11.1	25.9	3354, ν (NH); 2205, ν (CN); 1339, 1172, ν (SO_2)
18c	38.8	5.1	10.1	23.0	39.2	5.0	10.5	22.7	3423, 3370, ν (NH) for NH_2; 3169, ν (NH) for NH; 1351, 1180, ν (SO_2)
18e	35.6	5.1	11.9	27.1	35.4	5.2	12.0	26.8	–

bromide in 7 ml of hydrobromic acid stirred for 10 h at 90–95°C. The mixture was then poured into 40 ml of cold water and basified with aqueous $NaHCO_3$ (pH 7∼8) before EtOAc (100 ml) was added to extract the product. The EtOAc layer was dried and the solvent was removed by rotary evaporation to give 1.9 g of 2-bromoethylamino product **19e** (70%, off-white powder), m.p. 222–223°C. found C, 32.9; H, 4.1; N, 12.4; Br, 35.9% ($C_6H_9BrN_2S$ requires C, 32.6; H, 4.1; N, 12.7; Br, 36.1%).

3.3. Diazotisation

3.3.1. Procedure for 2-chloro-4-nitroaniline using nitrosyl chloride

A finely ground powder of 2-chloro-4-nitroaniline (0.35 g, 2×10^{-3} mol) was added to a mixture of concentrated hydrochloric acid (2 ml) and water (15 ml), and stirred overnight at room temperature. The mixture was cooled to 5°C, a fine powder of $NaNO_2$ (0.14 g, 2.1×10^{-3} mol) was added portionwise at 5–10°C and the mixture was then stirred for a further 1 h at the same temperature. The resulting clear solution was used immediately in the coupling reaction.

3.3.2. General procedure for 2,4-disubstituted and 2,4,6-trisubstituted anilines using nitrosylsulphuric acid

Sodium nitrite (2.1×10^{-3} mol) was added portionwise to 5 ml of concentrated sulphuric acid at 10°C and stirred for 1 h at 60–70°C. The solution was cooled to below 5°C, then the finely ground aniline derivative (2×10^{-3} mol) was slowly added and the mixture was stirred for a further 1 h at 5–10°C to give a clear solution. The resulting diazonium solution was used immediately in the coupling reaction.

3.4. Coupling

3.4.1. General procedure for coupling

Coupling component (1.8×10^{-3} mol) was dissolved in 20 ml of acetone and then cooled to 0°C by adding ice. The diazonium solution previously prepared was added dropwise over 20 min with vigorous stirring and with frequent addition of ice flakes. The mixture was stirred for a further 1 h at 5–10°C, then 1 ml of acetic acid was added and 10% sodium hydroxide solution was dropped in slowly until the pH became 3–4. The product was then filtered off, washed with hot water and with cold water, and dried at 60–70°C to give azo dye.

Details of characterisation data are given in Tables 24–27 for azo dyes prepared by general procedure 3.4.

3.5. Replacement of methanesulphonate group in azo dyes by a bromine atom

3.5.1. General procedure for replacement

6.9×10^{-3} mol of mesylated dye and 7.0×10^{-3} mol of lithium bromide were refluxed for 4 h in 20 ml of acetone. The mixture was filtered hot and the filtrate was poured into 40 ml of water. The precipitate was filtered off to give the bromo derivative.

Table 28 summarises the characterisation data.

3.6. Purification methods for the azo dyes

Purification methods, as given in Table 5 and Table 6, are detailed as follows; chromatography columns were prepared using silica 60 (70–230 mesh ASTM).

A: Column chromatography; hexane/EtOAc = 8/2 initially, then the portion of EtOAc was increased gradually.
B: Column chromatography; hexane/EtOAc = 7/3 initially, then the portion of EtOAc was increased gradually.
C: Column chromatography; hexane/EtOAc = 6/4 initially, then the portion of EtOAc was increased gradually.

Table 24
Characterisation data for some azo dyes derived from 2-(*N*-β-methanesulphonyloxyethylamino)-3-cyano-4-phenylthiophene **18d**

		Elemental analyses								
		Requires (%)				Found (%)				
Dye	m.p. (°C)	C	H	N	Other	C	H	N	Other	Decomposition temperature (°C)
1a	188–189	47.5	3.2	13.8	12.7 (S)	48.3	3.3	13.7	12.5 (S)	209
1b	236–238	46.8	3.0	13.0	11.9 (S)	46.9	2.9	12.8	11.2 (S)	252
1c	230–231	50.8	3.2	16.9	12.9 (S)	51.3	3.2	16.7	13.1 (S)	243
1d	198–199	43.8	2.6	14.6		43.5	2.6	14.2		222
1e	159–161	40.3	2.5	14.1	13.4	40.0	2.5	13.1	13.8 (Br)	230

Table 25
Characterisation data for some azo dyes derived from 2-(*N*-β-methanesulphonyloxyethylamino)-3-cyano-4-methylthiophene **18b**

		Elemental analyses								
		Requires (%)				Found (%)				
Dye	m.p. (°C)	C	H	N	Other	C	H	N	Other	FT–IR (KBr, cm^{-1})
3a	178–179	40.6	3.2	15.8	14.4 (S), 8.0 (Cl)	41.1	3.1	15.5	14.2 (S), 8.0 (Cl)	3310, ν (NH); 2215, ν (CN)
3b	219–221	40.3	2.9	14.7	13.4 (S)	40.7	2.9	14.5	12.9 (S)	3230, ν (NH); 2216, ν (CN)
3c	219–221	44.2	3.2	19.3	14.8 (S)	44.0	3.2	19.0	14.8 (S)	3230, ν (NH); 2214, ν (CN)
3d	189–191	37.4	2.6	16.4	12.5 (S)	38.2	2.7	16.1	12.7 (S)	3220, ν (NH); 2213, ν (CN)
3e	162–165	33.8	2.5	15.8	12.0 (S)	33.2	2.5	15.7	12.2 (S)	3333, ν (NH); 2213, ν (CN)
3f	199–201	31.8	2.3	12.3	11.3 (S), 28.2 (Br)	31.9	2.2	12.1	11.3 (S), 28.4 (Br)	3225, ν (NH); 2213, ν (CN)

Table 26
Characterisation data for some azo dyes derived from 2-(*N*-β-methanesulphonyloxyethylamino)-3-cyanothiophene **18a** and from 2-(N-*β*-methanesulphonyloxyethylamino)-3-carbamyl-4-methylthiophene **18c**

		Elemental analyses								
		Requires (%)				Found (%)				
Dye	m.p. (°C)	C	H	N	Other	C	H	N	Other	FT–IR (KBr, cm^{-1})
5a	202–204	39.1	2.8	16.3	8.2 (Cl)	39.1	2.6	16.2	8.0 (Cl)	–
5b	214–215	38.9	2.6	15.1	13.8 (S) 12.3 (F)	38.8	2.6	14.6	13.8 (S) 12.4 (F)	3235, ν (NH); 2218, ν (CN)
5c	208–210	42.9	2.9	20.0	15.3 (S)	41.8	2.9	20.4	15.7 (S)	–
5d	204–206	36.1	2.2	16.8	16.0 (Br) 12.8 (S)	35.8	2.0	16.2	16.3 (Br) 12.2 (S)	– –
5e	172–175	32.4	2.1	16.2	12.3 (S)	33.0	2.2	16.1	11.9 (S)	3327, ν (NH); 2217, ν (CN)
6a	170–173	38.8	3.3	14.1	11.5 (F)	37.9	3.4	14.4	11.2 (F)	3417, 3370, ν (NH) for NH$_2$; 3099, ν (NH)
6b	176–178	42.5	3.6	18.6	14.2 (S)	43.2	3.7	18.7	14.6 (S)	3168, ν (NH); 2233, ν (CN); 1710, ν (CO)
6c	203–205	36.2	2.8	15.8	12.1 (S)	37.0	2.7	15.6	12.4 (S)	3428, 3338, ν (NH) for NH$_2$; 3075, ν (NH) for NH; 2225, ν (CN)

Table 27
Characterisation data for some azo dyes derived from β-methanesulphonyloxyethylaminothiazole derivatives.

		Elemental analyses							
		Requires (%)				Found (%)			
Dye	m.p. (°C)	C	H	N	Other	C	H	N	Other
7a	157–160	41.0	3.4	20.5	15.6 (S)	41.9	3.5	20.2	15.8 (S)
7b	172–175	34.4	2.7	17.2	16.3 (Br)	34.7	2.5	17.8	15.7 (Br)
7c	131–133	30.7	2.6	16.5	12.6 (S)	31.7	2.7	16.1	13.2 (S)
8c	123–125	29.2	2.0	17.0	32.3 (Br)	28.7	2.1	17.4	33.6 (Br)

Table 28
Characterisation data for some azo dyes **2**, **4** and **8**

		Elemental analyses								
		Requires (%)				Found (%)				
Dye	m.p. (°C)	C	H	N	Br	C	H	*N*	Br	Decomposition temperature (°C)
2a	109–110	46.5	2.7	14.3	16.3	46.2	2.8	14.7	16.2	221
2b	233–234	45.8	2.5	13.4	15.2	46.3	2.4	13.1	15.8	242
2c	216–218	50.0	2.7	17.5	16.6	49.6	2.7	18.2	17.0	241
2d	154–156	42.9	2.2	15.0	28.5	42.4	2.4	14.6	28.3	225
2e	199–201	39.3	2.1	14.5	27.5	40.1	2.0	14.3	26.8	214
4a	215–217	39.0	2.4	15.2	17.3	38.7	2.3	15.4	17.7	228
4b	200–201	43.0	2.6	20.0	19.1	43.5	2.8	20.3	19.6	213
4c	172–175	32.5	1.9	16.2	30.8	31.7	2.0	16.1	29.7	189
8a	179–181	39.5	2.8	21.3	20.2	39.2	2.7	21.6	20.7	–
8b	175–178	32.9	2.1	17.7	33.7	32.4	2.2	17.9	33.0	–

D: Column chromatography; hexane/EtOAc = 1/1 initially, then the portion of EtOAc was increased gradually.
E: Recrystallisation from ethanol/cyclohexane.
F: Recrystallisation from ethanol.

4. Conclusions

Monoazo disperse dyes containing a heterocyclic coupling moiety have been prepared from 2-aminothiophenes and 2-aminothiazoles and their spectral properties investigated. The 2-aminothiophenes were readily obtained by using the Gewald reaction. From the point of view of the 3-substituent present in the thiophene ring, λ_{max} values of the variously substituted dyes shift towards the red in the order $CONH_2 << CN < CO_2Et <<$ H, in line with the appropriate Hammett substituent constant. All 4-phenyl dyes absorb bathochromically compared with their 4-methyl analogues, due to the resonance effect of the electron-rich phenyl group. The absorption maxima of some azo dyes obtained from 2-aminothiazole intermediates were found to be hypsochromic compared to those of the corresponding dyes prepared from 2-aminothiophenes. PPP–MO calculations provided reliable predictions in absorption maxima for the dyes prepared by using modified parameters for the terminal nitrogen atom.

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