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Synthesis and properties of novel aziridinyl azo dyes from 2-aminothiophenes—Part 1: Synthesis and spectral properties

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Abstract

A series of yellow to greenish-blue aziridinyl azo dyes and their azo precursors containing a thienyl coupling moiety has been prepared from 2-aminothiophenes. The 2-aminothiophenes were readily obtained by using the Gewald reaction. It was found that cyclisation of the precursor dyes to the corresponding aziridinoazo dyes brought about bathochromic shifts in absorption maxima. Further spectral comparisons with *N*-phenylazo dyes derived from other terminal cyclic groups, such as four-, five-, six-, seven- and eight-membered rings, showed that the *N*-thienylaziridinoazo dyes are relatively bathochromic. From the viewpoint of solvatochromism, a clear contrast existed between λ_{max} values in different solvents; thus, a positive solvatochromism was observed in aprotic solvents, whereas a hypsochromic shift was brought about in polar protic solvents. PPP–MO calculations provided reliable predictions of absorption maxima for the various aziridinyl azo dyes and their precursor dyes.

Keywords: Aziridinyl azo dyes; 2-aminothiophene couplers; UV-VIS spectroscopy; Solvatochromism; PPP-MO calculations

1. Introduction

The basicity and electron donor capacity of the terminal nitrogen atom in dyes derived from 4-aminoazobenzene are of crucial importance in relation to colour [1–3]. In contrast to acyclic terminal groups, the characteristics of dyes derived from different cyclic terminal groups, such as heptamethyleneimine **3**, hexamethyleneimine **4**, piperidine **5**, pyrrolidine **6**, azetidine **7** and aziridine **8**, typically absorption spectra, halochromism and solvatochromism, vary dramatically according to ring size [2].

In neutral solution, the marginally greater electron-donating power of the heptamethyleneiminyl group confers a slightly longer absorption maxima in comparison with that of dyes **4** derived from *N*-phenylhexamethyleneimine, whereas monoazo dyes **5** containing a terminal piperidino group absorb hypsochromically compared with their pyrrolidinyl counterparts **6**. The lack of conjugative capacity of *N*-phenylaziridine among the series of *N*-phenyl cyclic amines is consistently

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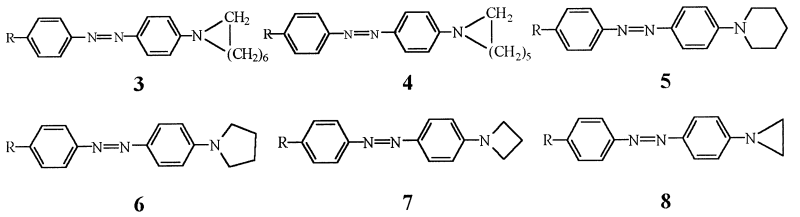
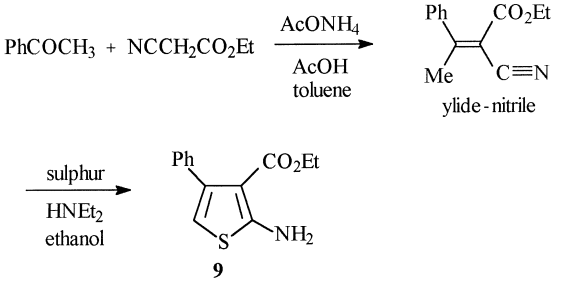


supported by other spectroscopic studies [4–6]. Thus, spectral data show that the electron-donor power of the terminal nitrogen atom decreases in the order heptamethyleneiminyl > hexamethyleneiminyl > pyrrolidinyl > piperidinyl > azetidinyl ≫ aziridinyl.

Despite the importance of thienylazo disperse dyes, preparative details corresponding to dyes derived from thienyl coupling components are scarce, and no information concerning aziridinyl azo dyes containing a thiophene ring has been reported.

This paper details the preparation of aziridinyl azo dyes **1** and their precursor dyes **2** starting from 2-aminothiophenes obtained directly by utilising the Gewald synthesis shown in Scheme 1.



Scheme 1. Preparation of 2-amino-3-ethoxycarbonyl-4-phenylthiophene **9** via anylide-nitrile.

2. Results and discussion

2.1. Preparation of the coupling components

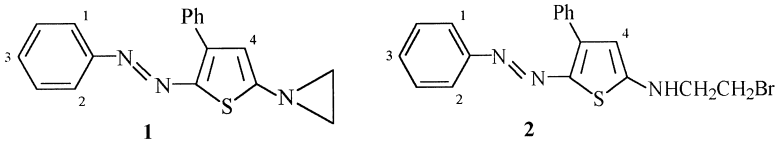
The first step in the preparation of the coupling components was the synthesis of the relevant 2-aminothiophenes using the Gewald reaction via an ylide-nitrile (see Scheme 1).

Gewald methods based on either an active methylene group or α-mercapto compounds for cyclisation into 2-aminothiophene derivatives have provided a number of crucial intermediates used as starting materials in this study, particularly those containing an electron withdrawing substitutent at the 3-position.

However, attempts to cyclise 2-aminothiophenes containing an electron donating substituent at the 3-position by Gewald methods have been ineffective, presumably due to the extreme difficulty of formation of an anion from the nitrile reagent.

In the case of 2-amino-3-ethoxycarbonyl-4-phenylthiophene **9**, a two-step cyclisation method [7] rather than a one-pot reaction was found to be more efficient in terms of a yield and purity.

The method involved an initial conversion of acetophenone and a nitrile component into the corresponding ylide-nitrile in the presence of ammonium acetate and acetic acid, followed by



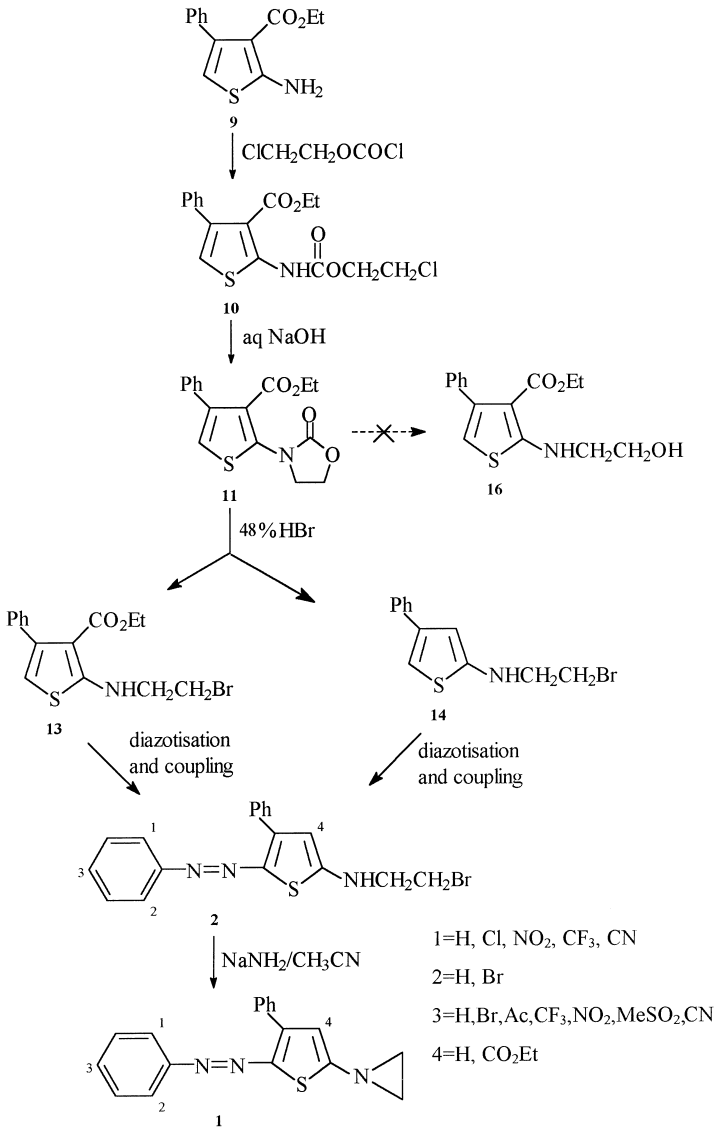
1 = H, Cl, NO_2, CF_3, CN 2 = H, Br

3 = H, Br, Ac, CF_3, NO_2, $MeSO_2$, CN 4 = H, CO_2Et

cyclisation with sulphur to give the desired thiophene **9** as shown in Scheme 1.

The formation of chloroethylcarbamates was first reported by Nemirowsky in 1885 [8], followed by the preparation of 2-chloroethylphenylcarbonates by reacting the corresponding anilines with 2-chloroethylchloroformate [9].

In general, to facilitate the condensation, a catalytic amount of pyridine can be used by adding in a suitable reaction solvent. However, for the synthesis of the targeted chloroethylcarbamate **10** (as shown in Scheme 2) starting from the corresponding 2-aminothiophene **9**, no basic catalyst was required to fulfil the reaction. The efficiency of the acylation was found to depend on both the reaction temperature and the solubility of the starting material in the solvent used for the reaction; thus, a high reaction temperature, usually under



Scheme 2. Synthetic routes to aziridinyl azo dyes from 2-aminothiophene.

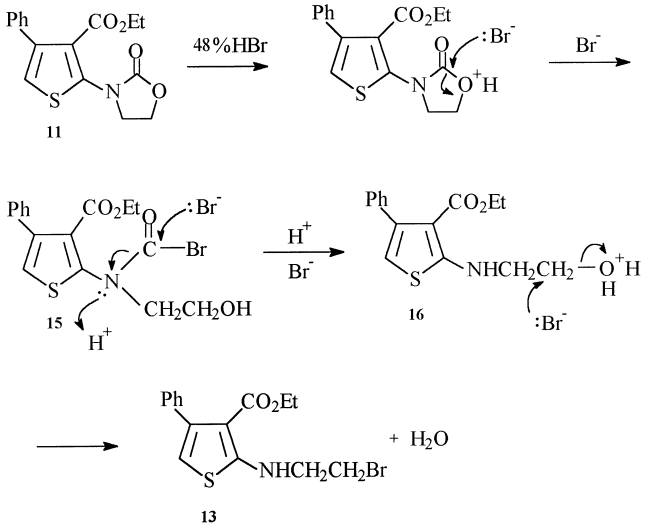
reflux, in an appropriate solvent, ethyl acetate for **9**, led to optimum yields.

In the next step, a two-stage synthesis of the desired β-hydroxyethylaminothiophene, starting from the chloroethylcarbamate **10**, was attempted using various alkalis. Chloroethylcarbamates can be cyclised to the corresponding oxazolidones by alkali treatment [8]; subsequent hydrolysis then leads to their conversion into 2-aminoethanols [9,10]. An intensive investigation into the cyclisation and hydrolysis of chloroethylcarbamate **10** revealed that conversion into 2-oxazolidone **11** is readily achieved at 90–95°C in the presence of an excess of aqueous sodium or potassium hydroxide. Reaction temperatures above 100°C led to the virtually exclusive formation of the corresponding carboxylic acid **12** with very little amount of the desired product **13** (Scheme 2).

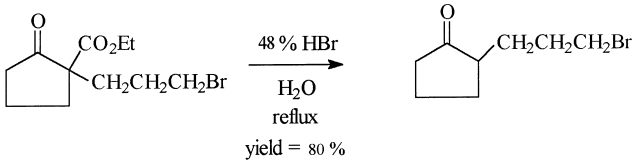
Formation of the aziridinyl ring can be best achieved by cyclising the relevant β-bromoethylamino group in the thiophene ring where bromide ion is utilised as a good leaving group. Treatment of compound **11** with 48% HBr solution eventually led to the formation of a β-bromoethylamino group via initial hydrolysis of the oxazolidone ring to a β-hydroxyethylamino group and displacement of the hydroxy group by a bromine atom. It seems likely that acidic hydrolysis of the oxazolidone ring, involving protonation and nucleophilic attack by bromide ion, is then followed by a further nucleophilic displacement in a two-step mechanism as outlined in Scheme 3.

As Scheme 3 depicts, the crucial ring-opening step can be facilitated by protonation at the oxygen atom in the oxazolidone ring, followed by cleavage of the C–O bond to form compound **15**. Subsequent nucleophilic attack by bromide leads to the formation of intermediate **16** which is not available by alkaline hydrolysis starting from compound **10**. Displacement of the hydroxy group by bromide takes place readily by expulsion of water. Thus, three equivalents of HBr are required to carry out this reaction sequence.

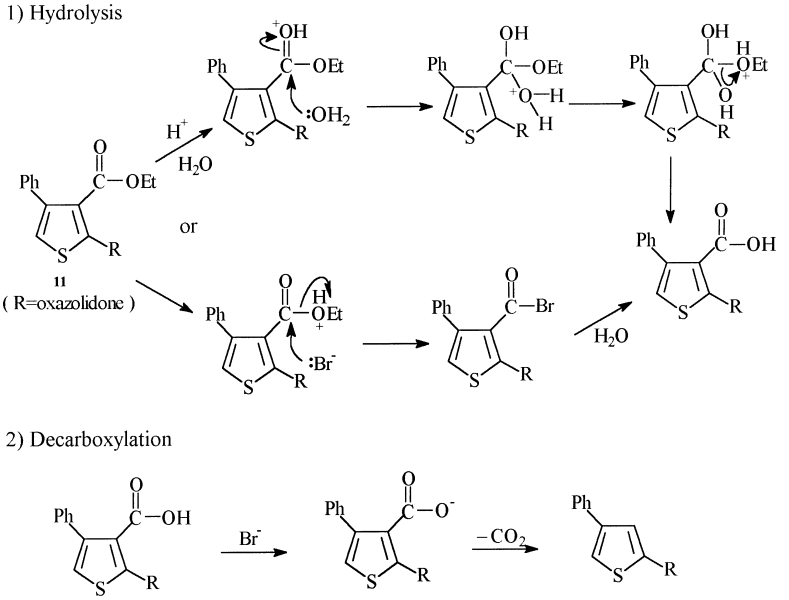
As well as acid hydrolysis, unexpected loss of the 3-ethoxycarbonyl group also took place to give compound **14** in appreciable amounts (Scheme 5). The hydrolysis of β-keto esters and subsequent decarboxylation are best accomplished with aqueous acid, such as HBr solution [11] (see Scheme 4). Even ethyl esters undergo an acid-catalysed cleavage in the presence of arenesulphonic acids [12] or the anhydride of boric acid [13]. Other methods used for cleavage of the ester function in β-keto esters involving hydrogenolysis of benzyl esters [14] and acid-catalysed cleavage of **t**-butyl esters [15,16] have been reported.



Scheme 3. Probable mechanism for hydrolysis and subsequent bromination.



Scheme 4. Acid-catalysed cleavage of a β-keto ester [11].



Scheme 5. Possible mechanism for the acid hydrolysis and decarboxylation of compound **11**.

Possible mechanisms for the formation of compound **14** involving sequential hydrolysis and decarboxylation in 48% HBr solution are illustrated in Scheme 5.

The formation of compounds **13** and **14** is competitive and depends largely on the reaction temperature. Above 100°C, formation of the decarboxylated compound **14** tends to be favoured, whereas in the range 90–100°C a mixture of the two compounds is obtained. Compound **13** can be removed from the crude precipitate by extraction into ethyl acetate.

2.2. Preparation of the precursor dyes

14 precursor azo dyes **2** have been prepared by coupling compound **13** with various diazotised anilines. Four more precursor dyes **2** were obtained from compound **14**.

Two types of nitrosating reagent, nitrosyl chloride from $NaNO_2$/HCl solution and nitrosylsulphuric acid from $NaNO_2$/conc H_2SO_4, were used for diazotisation of the variously substituted amines. Because of the mild acidity of $NaNO_2$/HCl solution resulting in relatively smaller amounts of by-products, most of the monosubstituted anilines were diazotised by this reagent where the basicity of the amines was sufficient to permit reaction with the nitrosyl chloride.

More weakly basic amines, such as 2,4-disubstituted and 2,4,6-trisubstituted anilines, except for 2-chloro-4-nitroaniline, required the use of nitrosylsulphuric acid. Although the optimum

reagent was used, a portion of unreacted 6-bromo-2,4-dinitroaniline remained after diazotisation, due to its lower nucleophilicity. Filtration of the coupling reaction mixture under strongly acidic conditions permitted the removal of unused amine from the product after coupling had finished.

It was necessary for the monosubstituted anilines and for 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.

In order to determine the end point of diazotisation, it was found useful to check for the presence of unreacted aniline on TLC by sampling the diazotisation mixture and extracting with ethyl acetate. Thus, when unreacted aniline no longer persisted on TLC, the diazotisation was ended.

Subsequent coupling reactions took place readily on adding the resulting diazonium salt continuously to an aqueous acetone solution of the coupling component. Frequent additions of ice flakes helped to keep the coupling temperature below 10°C and facilitated precipitation of the resulting dye.

To complete coupling, particularly for reactions using nitrosylsulphuric acid in the previous diazotisation, the pH of the reaction mixture was eventually adjusted to approximately 4. Thus, an appropriate amount of NaOH solution was slowly added below 10°C. At this stage, the presence of acetic acid, as a buffer, was very useful to prevent a sudden increase in pH. Physical properties of the dyes **2** have been summarised in Table 1.

2.3. Spectroscopic properties of the precursor dyes

As far as absorption maxima are concerned, λ_{max} values are directly proportional to the electronic power of the substituents in the benzenoid system. As Fig. 1 depicts, a reasonable linear correlation exists between the difference in wavelength ($\Delta\lambda_{max}$) relative to that of the unsubstituted dye and the Hammett substituent constants (σ_p) for relevant groups. A closer inspection of the visible spectral data for the *para*-substituted aminoazobenzene dyes shows that the 4-nitro group ($R = NO_2$) produces a more bathochromically shifted λ_{max} than that anticipated, whereas the 4-CF_3 substituent ($R = CF_3$), a less powerful electron acceptor, is less bathochromic than expected. The other *para*-substituents, Br, CN and CH_3CO, fall on or near the proportional line.

From the viewpoint of absorption maxima, electronic spectral data for the variously substituted

Table 1
Physical properties and synthetic data of the dyes **2** derived from coupling components **13** and **14**

Dye **2**	Molarity ($\times 10^{-3}$ mol)	% Crude yield (g)	Purification method	% Pure yield (g)	Appearance
a	1.93	83 (0.66)	F	65 (0.52)	Orange crystals
b	2.33	73 (0.82)	F	51 (0.57)	Orange needles
c	1.24	82 (0.48)	F	57 (0.33)	Orange powder
d	1.78	90 (0.72)	A	72 (0.58)	Scarlet powder
e	2.54	90 (0.98)	B	65 (0.71)	Dark red solid
f	1.95	86 (0.84)	B	63 (0.62)	Brown leaflets
g	1.56	89 (0.79)	C	61 (0.54)	Brown powder
h	1.60	79 (0.72)	C	58 (0.53)	Red-brown powder
i	1.69	77 (0.70)	B	60 (0.55)	Purple powder
j	2.18	90 (1.12)	F	57 (0.71)	Grey powder
k	1.57	88 (0.76)	B	66 (0.57)	Dark brown solid
l	2.85	87 (1.51)	F	62 (1.07)	Violet powder
m	1.75	83 (0.91)	F	56 (0.61)	Dark violet powder
n	1.66	87 (0.88)	C	71 (0.72)	Violet solid
o	1.46	81 (0.59)	B	66 (0.48)	Green powder
p	1.18	87 (0.55)	C	53 (0.34)	Dark green powder
q	1.43	86 (0.68)	G	61 (0.48)	Green solid
r	1.38	83 (0.52)	G	59 (0.37)	Dark green solid

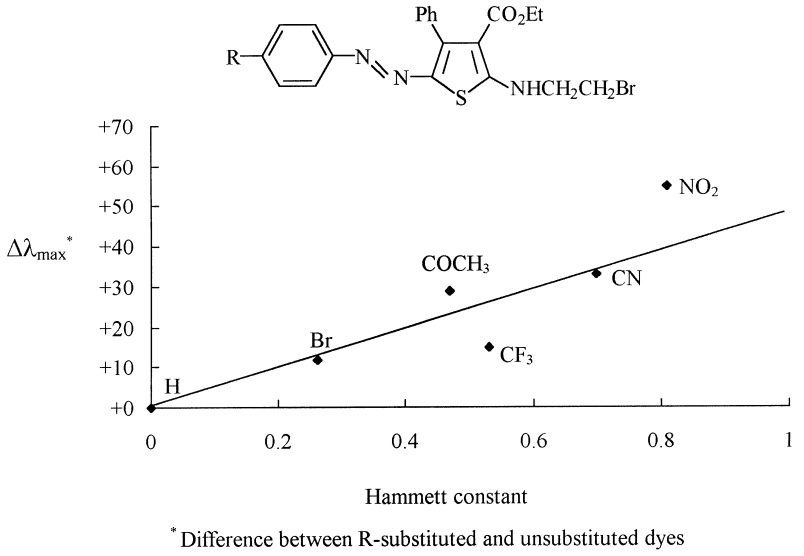


Fig. 1. Relation between Hammett constant (σ_p) and $\lambda_{DX}-\lambda_{DH}$ for azo dyes **2** derived from compound **13**.

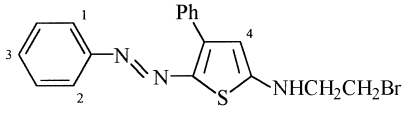
azo dyes show that there is a general tendency for the visible absorption band to move bathochromically as the electron withdrawing strength of substituents at the 4- or 2,4-positions increases, in accordance with the characteristics of donor-acceptor chromogens. As Table 2 shows, the λ_{max} values of some 2,4-disubstituted azo dyes shift towards the red in the order Cl < CF_3 < NO_2 < CN for substituents *ortho* to the azo linkage. The longer wavelength shown by the 2-cyano dye compared with that of the 2-nitro compound can be related to the smaller steric requirements of the rod-like cyano group. Exceptionally, however, the introduction of bromine *ortho* to the azo linkage in the 6-bromo-2,4-dinitro azo dye **2m**, produces a bathochromic shift of 11 nm relative to that of the 2,4-dinitro dye **2k**. Furthermore, this same dye **2m** also absorbs bathochromically compared with the 2-bromo-6-cyano-4-nitro counterpart **2l**. These red shifts can be explained in terms of stabilisation of the excited state by the bromine atom by conjugation with the *para*-nitro group.

A striking bathochromicity, in comparison with the visible spectra of the corresponding azo dyes **2a**–**2n**, is observed for some azo dyes **2o**–**2r** obtained from coupling component **14**. The colour shades of these dyes fall into blue to greenish-blue with λ_{max} values of 584–621 nm in acetone (see Table 2).

The bathochromic shifts exerted by azo dyes **2o**–**2r** can best be explained in terms of the inductive effect and the steric hindrance associated with a 3-substituent and the lone pair electrons of the terminal nitrogen atom. Thus, the absence of the 3-ethoxycarbonyl group permits a more polar excited state so that the migration of electrons towards the acceptor ring is facilitated. Also, more efficient conjugation of the terminal lone pair electrons with the adjacent π system is possible when only a hydrogen atom is present at the 3-position. Thus, as Table 2 shows, azo dyes **2o**–**2r** absorb bathochromically within the range 16–64 nm in comparison with the corresponding azo dyes **2a**–**2n**. In particular, these shifts are greatest in acetone.

Compared with the visible absorption spectra of azo dyes derived from *N*,*N*-dimethyl- and *N*,*N*-diethylaminoazobenzene, the azo dyes **2** prepared from the thiophenyl coupling component absorb maximally at longer wavelengths ranging from 13 to 40 nm in ethanol (see Table 3). The difference in λ_{max} ($\Delta\lambda_{max}$) between dyes **2** and the corresponding dyes **17** and **18** tends to decrease as the Hammett values increase. For instance, the parent azo dye **2a** absorbs at 446 nm in ethanol, whereas the

Table 2
Visible absorption spectra of the dyes **2** derived from coupling components **13** and **14**



2 (**2a~2n** : 4-CO_2Et, **2o~2r** : 4-H)

Dye	1	2	3	λ_{max} (nm) Toluene	$CHCl_3$	Acetone	EtOH	$10^{-4}\,\epsilon_{max}$ in EtOH
2a	H	H	H	447	448	453	446	1.95
2b	H	H	Br	460	461	465	459	1.60
2c	H	H	CF_3	463	462	468	462	1.70
2d	H	H	Ac	477	480	482	479	2.48
2e	H	H	CN	481	484	486	480	3.38
2f	H	H	NO_2	500	505	508	502	3.58
2g	Cl	H	$MeSO_2$	496	498	496	495	3.56
2h	NO_2	H	CF_3	490	–	497	492	2.04
2i	Cl	H	NO_2	520	525	530	524	1.90
2j	CF_3	H	NO_2	525	529	534	526	3.71
2k	NO_2	H	NO_2	531	539	540	538	2.49
2l	CN	Br	NO_2	534	551	548	558	2.23
2m	NO_2	Br	NO_2	538	548	551	545	1.92
2n	CN	H	NO_2	539	552	554	548	3.87
2o	CF_3	H	NO_2	–	549	584	584	4.24
2p	CN	Br	NO_2	581	589	612	560	3.17
2q	NO_2	Br	NO_2	573	580	606	567	2.99
2r	CN	H	NO_2	–	568	584	564	4.60

corresponding dyes **17c** and **18c** absorb at 416 and 408 nm, respectively. Judging from these results, it can be concluded that a five-membered thiophene ring is bathochromic in comparison with benzenoid coupling compounds when it is used as a coupling moiety, in the same way as its more traditional use as a diazo component.

Thus, the π-electrons in the thiophene ring are likely to migrate more easily by virtue of the greater diene character of the thiophene ring system [17]. But, in this case, the electron withdrawing CO_2Et group in the donor ring is responsible for the comparatively small increases in absorption maxima observed (up to 30 nm).

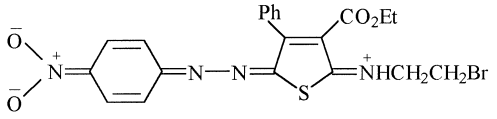
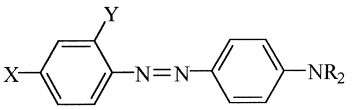


Table 3
Visible absorption spectra of some azo dyes **17** and **18** [18,24]



17 : R = Et, **18** : R = Me

Dye	X	Y	λ_{max} (nm)	$10^{-4}\epsilon_{max}$ EtOH	λ_{max} (nm)	$10^{-4}\epsilon_{max}$ Cyclohexane
17a	OCH_3	H	414	3.24	407 [d]	–
17b	CH_3	H	416	3.16	407 [e]	3.34 [e]
17c	H	H	416	2.88	408 [e]	3.23 [e]
17d	Br	H	427	3.31	418 [d]	–
17e	CF_3	H	434 [d]	–	425 [d]	–
17f	Ac	H	462	2.82	435 [d]	–
17g	CN	H	466 [b]	3.27 [b]	438	–
17h	NO_2	h	489	3.10 [f]	457 [f]	–
17i	NO_2	NO_2	530 [c]	4.70 [c]	496 [c]	–
18a	OCH_3	H	405 [h]	2.88 [h]	–	–
18b	CH_3	H	407	–	–	–
18c	H	H	408 [h]	2.75 [h]	–	–
18d	Br	H	419	–	–	–
18e	CF_3	H	427	–	–	–
18f	Ac	H	447 [h]	3.16	–	–
18g	NO_2	H	478 [h]	3.31	–	–
18h	NO_2	NO_2	516	–	–	–

[a] Ref. [18] unless otherwise stated.
[b] Ref. [19].
[c] Ref. [20].
[d] Ref. [21].
[e] Ref. [22].
[f] Ref. [23] for dyes **17**.
[g] Ref. [24] unless otherwise stated.
[h] Ref. [25] for dyes **18**.

For the series of dyes **2**, ϵ_{max} values tend to increase with increasing electron withdrawing capacity in the acceptor ring, in the absence of steric effects, with the exception of dyes containing 4-bromo **2b** and 4-CF_3 **2c** groups. A closer look reveals that the incorporation of a planar nitro group *ortho* to the azo linkage causes a reduction in ϵ_{max} value, whilst an equivalent CF_3 substituent does not. The 2,4,6-trisubstituted dyes **2l** and **2m** show dramatic decreases in colour strength due to the introduction of a further bulky substituent. Thus, dye **2m** produces only half the strength of ϵ_{max} compared with dye **2n** which is by far the deepest example.

There are no clear relationships between thermal stability and substituent effects in dye molecules **2a**–**2n** although the presence of a halogen atom tends to be associated with a decrease in decomposition temperature. Also, dyes **2a**–**2f** which contain only one *para*-substituent show quite similar heat stabilities. The presence of additional groups in *para*-nitro-substituted dyes **2i**–**2n** generally increases the sensitivity towards thermal decomposition, as revealed in Table 4.

2.4. Cyclisation to aziridinyl azo dyes

Cyclisation to the aziridinyl ring from either β-bromoethylamino or β-mesylethylamino groups requires a compromise between the reaction base and the solvent so as to minimise the amount of by-products which are inevitably formed, such as dimers and polymers. The terminal bromo or mesyl groups are highly susceptible to elimination in the presence of a strong base at a high reaction temperature.

Consequently, reaction conditions were optimised with $NaNH_2$ as base and CH_3CN as solvent so that the desired aziridinyl azo dyes **1** could be synthesised in reasonable yields by a simple procedure. However, by-products were always detected together with the main aziridinyl dye. Sodium ethoxide (NaOEt) can also be used as the base, but is less efficient.

Table 4
DSC data for some azo dyes **2**.

Dye	Substituents			Decomposition temperature (°C)
	1	2	3	
2a	H	H	H	196
2b	H	H	Br	190
2c	H	H	CF_3	207
2d	H	H	CH_3CO	203
2e	H	H	CN	214
2f	H	H	NO_2	210
2g	Cl	H	$MeSO_2$	188
2h	NO_2	H	CF_3	181
2i	CL	H	NO_2	182
2j	CF_3	H	NO_2	194
2k	NO_2	H	NO_2	183
2l	CN	Br	NO_2	193
2m	NO_2	Br	NO_2	293
2n	CN	H	NO_2	234

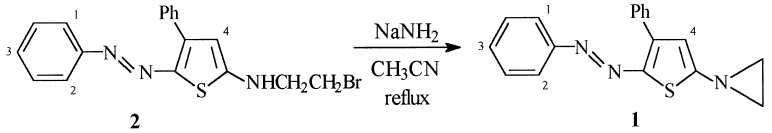
Optimum reaction times relate to the time taken for starting material to disappear completely (TLC). It is clear from Table 5 that precursors substituted by only one electron-accepting group tend to complete the reaction in shorter times than those possessing two or three such groups; the dinitro derivative **2k** is exceptional. Thus, the actual stabilities of the precursors towards the alkaline reaction medium at reflux temperature are approximately proportional to the reaction times for completion. The reaction mixture at completion contains cyclised material and by-products. Extended reaction times bring about decomposition of the aziridinyl dyes irrespective of the chemical stability of the precursors. Shorter reaction times were needed to cyclise precursors **2o**–**2r**, except for **2q**, compared with corresponding precursors prepared from coupling component **13**. Great care is required to prevent subsequent decomposition so that the optimum times to end the cyclisation, which range from 20 to 40 min, are crucial. The combination of the 4-phenyl and 3-CO_2Et groups in aziridinyl azo dyes **2** leads to improved resistance to alkaline hydrolysis as a result of conjugative effects.

2.5. Spectroscopic properties of the aziridinyl dyes

Consistent bathochromicity is observed when dyes **2** containing a β-bromoethylamino group are cyclised to the corresponding aziridinyl azo dyes **1**. Depending on the substituents, the extent of the shifts varies within the range 1–48 nm (see Table 6). For example, dye **11** absorbs maximally at 564 nm in $CHCl_3$, which is 13 nm longer than that of its precursor **2l**.

It is likely that the inductive effect induced from CH_2 groups in the aziridine ring on the lone pair electrons of the terminal nitrogen atom is somewhat greater than that induced by the ethyl group in the β-bromoethylamino chain in accordance with the order of electron release for simple alkyl groups connected to an unsaturated system: NEt_2 > NHEt > NH_2. More importantly, these bathochromic shifts strongly suggest that the aziridine ring of azo dyes **1** which has a great deal of angle strain, only incurs a small steric interaction with the adjacent thiophene ring system. Therefore,

Table 5
Optimum reaction times for the preparation of aziridinyl dyes **1**



Dye	1	2	3	4	Optimum reaction time (min)
1c	H	H	CF_3	CO_2Et	15
1d	H	H	Ac	CO_2Et	25
1e	H	H	CN	CO_2Et	15
1f	H	H	NO_2	CO_2Et	15
1g	Cl	H	$MeSO_2$	CO_2Et	20
1h	NO_2	H	CF_3	CO_2Et	20
1i	Cl	H	NO_2	CO_2Et	80
1j	CF_3	H	NO_2	CO_2Et	65
1k	NO_2	H	NO_2	CO_2Et	15
1l	CN	Br	NO_2	CO_2Et	45
1m	NO_2	Br	NO_2	CO_2Et	20
1n	CN	H	NO_2	CO_2Et	40
1o	CF_3	H	NO_2	H	25
1p	CN	Br	NO_2	H	30
1q	NO_2	Br	NO_2	H	40
1r	CN	H	NO_2	H	20

Table 6
Bathochromic shifts in absorption maxima arising from the cyclisation of azo dyes **2** to the aziridinyl dyes **1**

Dye	$\Delta\lambda$ (nm)[a]			
	Toluene	$CHCl_3$	Acetone	EtOH
1c	+9	+9	+7	+2
1d	+8	+7	+6	+5
1e	+7	+8	+5	+5
1f	+10	+11	+5	0
1g	+8	+9	+8	+6
1h	–	–	+1	+3
1i	+7	+9	+4	+2
1j	+10	+12	+7	+10
1k	–	+6	+2	+48
1l	+11	+13	+7	+30
1m	+7	+9	+4	+41
1n	+9	+5	+2	+28
1o	–	+15	+15	+18
1p	–	+13	+6	+28
1q	–	+14	+6	+18
1r	–	+7	+15	+24

[a] Relative to precursor dyes **2**.

the lone pair electrons of the terminal nitrogen atom are effectively conjugated with the π-electron system of the thiophene ring, giving rise to bathochromic shifts compared with the electrons of the nitrogen atom in the β-bromoethylamino group.

According to previous research work [5,26], the preferred conformation of *N*-phenylaziridine has the axis of the nitrogen lone pair perpendicular to the plane of the aromatic ring. The spectral characteristics [3] of the *N*-phenylaziridinyl dyes reveal that *N*-phenylaziridine is the least conjugated of the series of *N*-phenyl cyclic amines. Therefore, it is likely that the mesomeric interaction between the lone pair electrons of the terminal nitrogen atom and the aziridine ring will be more favoured than that with the adjacent benzene ring, and these findings account for the hypsochromic effect observed for the *N*-phenylaziridines.

By way of contrast, in this study, much longer λ_{max} values are found for the *N*-thienylaziridines **1c**–**1i** in comparison with those for the corresponding *N*-phenylaziridines **8** as shown in

Table 8. In all cases, $\Delta\lambda$ exceeds 100 nm, but there is a tendency for bigger increases in the absorption maxima as more powerful electron-attracting groups are introduced into the acceptor ring.

Further spectral comparisons with *N*-phenylazo dyes derived from other types of cyclic groups, four-, five-, six-, seven- and eight-membered rings, show clearly that azo dyes **1** containing an *N*-thienylaziridine group exhibit relatively bathochromic absorption spectra (Table 9). These shifts can best be explained by the increased sp^{λ} character of the nitrogen lone pair electrons of the aziridine ring, leading to more effective conjugation with the adjacent thiophene ring system due to diminished steric hindrance between the *ortho*-substituent of the thiophene ring and the nitrogen lone pair orbital.

Thus, the terminal nitrogen atom of *N*-thienylaziridine can accommodate a more coplanar conformation in contrast with that of *N*-phenylaziridine. Consequently, a preferred conformation for the *N*-thienylaziridine can be suggested as shown in Fig. 2.

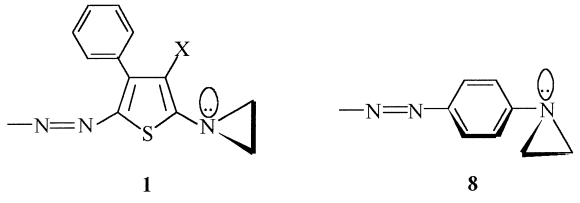
Comparison with some counterparts **1c**–**1n** possessing the 3-ethoxycarbonyl group emphasises the importance of the 3-substituent in relation to the absorption spectra. Unsubstituted aziridinyl dyes **1o**–**1r** absorb maximally at much longer wavelengths than the ethoxycarbonyl-substituted equivalent dyes **1c**–**1n**, as shown in Table 7. Dye **1p**, containing 2-bromo-6-cyano-4-nitro groups is the most bathochromic example in this series. In particular, the positive field-effect induced by the bromine atom in dye **1p** is clearly reflected in the longer λ_{max} values compared with those of dye **1r**.

From the viewpoint of solvatochromism, a clear contrast exists between λ_{max} values in the protic polar solvent, EtOH, and those in the aprotic solvents, $CHCl_3$ and acetone, as Table 7 summarises. Thus, a positive solvatochromism is found in the aprotic solvents in accordance with a more polar excited state being stabilised by polar solvents, whereas in the polar protic solvent intermolecular hydrogen bonding between the nitrogen lone pair electrons of the aziridine ring and the solvent (EtOH) is likely to stabilise the ground state of the dyes **1** leading to an increase in the electronic transition energy. This increase in energy is reflected in a hypsochromic shift.

Table 7
Visible spectral data for some aziridinyl azo dyes **1**

	λ_{max} (nm)				$10^{-4}\,\epsilon_{max}$
Dye	Toluene	$CHCl_3$	Acetone	EtOH	in EtOH
1c	472	471	475	464	1.85
1d	485	487	488	484	2.21
1e	488	492	491	485	3.44
1f	510	516	513	502	3.37
1g	504	507	504	501	3.63
1h	–	–	498	495	1.87
1i	527	534	534	526	3.20
1j	535	541	541	536	3.84
1k	–	545	542	586	2.37
1l	545	564	555	588	2.41
1m	545	557	555	586	1.88
1n	548	557	556	576	3.92
1o	–	564	599	602	3.88
1p	–	602	618	588	2.74
1q	–	594	612	585	2.45
1r	568	575	599	588	4.51

Comparisons of DSC data for dyes **1c**–**1n** with those of their precursors **2c**–**2n** reveal the relative stability of the aziridinyl dyes **1** to heat in the solid state except for dye **1m**, as illustrated in Table 10. The lower temperatures of decomposition observed for dyes **2c**–**2n** may be associated with the presence of a highly labile bromine atom in the terminal group.



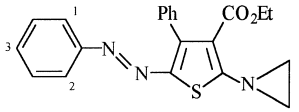
1 **8**

Fig. 2. Likely conformations for azo dyes **1** and dyes **8** derived from *N*-thienylaziridine and *N*-phenylaziridine, respectively.

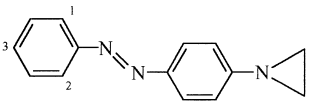
2.6. PPP–MO calculations

Both the Valence State Ionization Potential (VSIP) of each atom and the Electron Affinity (EA) of each relevant atom are crucial parameters for predicting reliable transition energies of dye molecules. Two sets of parameters for the terminal nitrogen atoms of the precursors and of the final

Table 8
Comparison of the absorption maxima of some azo dyes derived from *N*-phenylaziridine **8** and from *N*-thienylaziridine **1**



1



8

Dye	Substituent 1	2	3	λ_{max} (EtOH, nm)	$\Delta\lambda$[a] (EtOH, nm)
1c	H	H	CF_3	464	+106
1d	H	H	Ac	484	+116
1e	H	H	CN	485	+116
1f	H	H	NO_2	502	+117
1g	Cl	H	$MeSO_2$	501	+122
1i	Cl	H	NO_2	526	+130
8g	Cl	H	$MeSO_2$	379[b]	–
8i	Cl	H	NO_2	396[b]	–

[a] Relative to dye **8**.
[b] Ref. [27].

Table 9
Bathochromic shifts shown by *N*-thienylaziridines **1** compared with 4-aminoazobenzene dyes containing cyclic terminal groups

Dye	X	Y	Z	$\Delta\lambda^{EtOH}$ relative to Dye (**7**)	Dye (**6**)	Dye (**5**)	Dye (**4**)	Dye (**3**)
1c	CF_3	H	H	+44	+30	+41	+27	+26
1d	Ac	H	H	+48	+30	+48	+26	+24
1e	CN	H	H	+44	+25	+43	+23	+22
1f	NO_2	H	H	+33	+14	+32	+13	+13

Table 10
DSC data for some azo dyes **1**

Dye	Substituent 1	2	3	Decomposition temperature (°C)
1c	H	H	CF_3	228
1d	H	H	Ac	220
1e	H	H	CN	231
1f	H	H	NO_2	225
1g	Cl	H	$MeSO_3$	211
1h	NO_2	H	CF_3	198
1i	Cl	H	NO_2	199
1j	CF_3	H	NO_2	226
1k	NO_2	H	NO_2	245
1l	CN	Br	NO_2	218
1m	NO_2	Br	NO_2	239
1n	CN	H	NO_2	253

aziridinyl dyes have been appropriately modified herein as shown in Table 11.

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 indicates that CI 25 calculations are more likely to be reliable for dyes containing 4-nitro groups in the acceptor ring, whereas CI 9 calculations can be applied satisfactorily to the other dyes substituted by 4-CN, 4-Br or not substituted in the acceptor ring. For dyes **2a**–**2n** the PPP-MO method provides the most reliable predictions by far for absorption maxima (see Table 12), especially by CI 25 calculations. Generally good agreement is found except for **2i** and **2j** which show $\Delta\lambda$ values of 26 and 36 nm, respectively, being more bathochromic than predicted. Differences in λ_{max} values ranging from 19 to 41 nm have been observed for the dyes **2o**–**2r** which absorb at much longer wavelengths than dyes **2a**–**2n**. It may be assumed that the electronic effects associated with 3-substituents in the thiophene ring exert a profound influence on the absorption spectrum.

The small bathochromic shifts ranging from 7 to 11 nm observed in toluene for the aziridinyl dyes **1c**–**1n** obtained from precursors **2c**–**2n** can be

Table 11
Modified parameters for the terminal nitrogen atom of azo dyes **2** containing a β-bromoethylamino group in the thiophene ring and the corresponding aziridinyl azo dyes **1**

Parameters	Nitrogen atom of the β-bromoethylamino group	Nitrogen atom of the aziridinyl group
VSIP (eV)	19.2	18.2
EA (eV)	8.5	8.2
β_{X-Y}[a] (eV)	−2.75	−2.75
Bond length $_{X-Y}$[a] (A)	1.38	1.38

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

successfully calculated using 18.2 eV for VSIP and 8.2 eV for EA for the terminal nitrogen atom (see Table 11). Upon using these parameters, increases of 5–7 nm in the absorption maxima have been calculated by the PPP–MO method for the aziridinyl azo dyes **1c**–**1n**, and these results compare favourably with the experimental values.

Theoretically, the colour intensity termed the extinction coefficient (ϵ_{max}) is correlated to oscillator strength (f). Oscillator strength calculated by the PPP–MO method, is strictly related to the transition moment (M).

The results show that the PPP–MO method is a potential tool for the theoretical prediction of transition energies when it is applied to azo dyes involving a thiophene ring system, particularly for those dyes containing a 4-nitro-substituted acceptor ring. The accuracy of the predictions is improved by using CI 25 calculations.

Table 12
Calculated and observed (toluene) values of λ_{max} and ϵ_{max} and of f for dyes **2** and **1**

	λ_{max} (nm)			$10^{-4}\epsilon_{max}$	f
Dye	Obs.	Cal. (CI = 9)	Cal. (CI = 25)	(EtOH)	(CI = 25)
2a	447	453	459	1.95	1.093
2b	460	460	462	1.60	1.108
2c	463	453	459	1.70	1.090
2d	477	470	480	2.48	1.249
2e	481	474	485	3.38	1.206
2f	500	478	490	3.58	1.152
2g	496	486	497	3.56	1.124
2h	490	496	503	2.04	0.957
2i	520	482	494	1.90	1.121
2j	525	477	489	3.71	1.147
2k	531	526	541	2.49	0.747
2l	534	511	530	2.23	0.956
2m	538	531	539	1.92	0.965
2n	539	506	523	3.87	0.959
2o	549[a]	502	508	4.24	1.215
2p	581	525	539	3.17	1.052
2q	573	548	554	2.99	1.013
2r	568[a]	517	531	4.60	1.055
1c	472	453	459	1.85	1.092
1d	485	470	480	2.21	1.256
1e	488	474	485	3.44	1.215
1f	510	478	490	3.37	1.162
1g	504	486	497	3.63	1.135
1h	498[b]	496	503	1.87	0.952
1i	527	482	494	3.20	1.131
1j	535	477	489	3.84	1.157
1k	545[a]	526	541	2.37	1.017
1l	545	511	530	2.41	0.974
1m	545	531	539	1.88	0.972
1n	548	506	523	3.92	1.126
1o	564[a]	508	515	3.88	1.172
1p	602[a]	532	545	2.74	1.073
1q	594[a]	556	562	2.45	1.019
1r	568	523	537	4.51	1.078

[a] In $CHCl_3$.
[b] In acetone.

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, UK. 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, UK.

3.2. Preparative details of the coupling components

3.2.1. 2-Amino-3-ethoxycarbonyl-4-phenylthiophene

A reaction flask was fitted with a Dean-Stark trap, then acetophenone (20 g, 0.166 mol) was mixed with ethyl cyanoacetate (19.5 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 5 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 further stirring for an hour at room temperature. A pale orange solid of 2-amino-3-ethoxycarbonyl-4-phenylthiophene **9** was filtered off to provide a yield of 17% (7.0 g), lit. [28] m. p. 98°C, m. p. 97–98°C. ^{1}H NMR ($CDCl_3$, δ; 0.9 (3 H, t, CH_3), 4.0 (2 H, q, OCH_2), 6.0 (1 H, s, ArH), 6.1 (2 H, s, NH_2), 7.3 (5 H, s, PhH).

3.2.2. 2-(3-Ethoxycarbonyl-4-phenylthienyl)-N-β-chloroethyl carbamate

8.65 g (0.06 mol) of 2-chloroethyl chloroformate in 10 ml EtOAc was added slowly over 10 min to 10 g of 2-amino-3-ethoxycarbonyl-4-phenylthiophene **9** in 70 ml of EtOAc at room temperature. The mixture was then refluxed for 2 h. After the mixture was cooled, washed with 5% hydrochloric acid (50 ml), 5% sodium bicarbonate (50 ml), and water (50 ml), the solution was then dried over anhydrous sodium sulphate. EtOAc was removed by rotary evaporator and the resulting yellow oil allowed to stand overnight in a refrigerator. The crude product (13.6 g, 95% crude yield) solidified and was purified by column chromatography (eluent; hexane/EtOAc = 9/1) to provide 2-(3-ethoxycarbonyl-4-phenylthienyl)-*N*-*β*-chloroethyl carbamate **10** (10.8 g, 75% purified yield, off-white crystal), m. p. 53–55°C. Microanalysis: found C, 54.5; H, 4.6; N, 3.9; Cl, 10.1% ($C_{16}H_{16}ClNO_4S$ requires C, 54.3; H, 4.6; N, 4.0; Cl, 10.0%). ^{1}H NMR ($CDCl_3$, δ; 1.0 (3 H, t, $OCH_2\mathbf{CH_3}$), 3.7 (2 H, t, CH_2Cl), 4.4–4.6 (2×2 H, m, 2×OCH_2), 6.7 (1 H, s, ArH), 7.3 (5 H, s, PhH), 8.7 (1 H, s, NH).

3.2.3. 2-(3-Ethoxycarbonyl-4-phenylthienyl)-2-oxazolidone

Ten g (0.028 mol) of 2-(3-ethoxycarbonyl-4-phenylthienyl)-*N*-*β*-chloroethyl carbamate **10** were added to NaOH solution (NaOH 5.6 g, water 50 ml), and the mixture was then stirred for 1 h at 90–95°C. The resulting solid precipitate was filtered off and washed with water. The crude product was then added to ethanol (25 ml) with stirring for 2 h, filtered off, and dried at 50°C to give 2-(3-ethoxycarbonyl-4-phenylthienyl)-2-oxazolidone **11** as a pale yellow solid (6.6 g, 74% purified yield), m. p. 149–151°C. Mass: m/e = 317. Microanalysis: found C, 59.3; H, 4.8; N, 4.3% ($C_{16}H_{15}NO_4S$ requires C, 60.6; H, 4.8; N, 4.4%). ^{1}H NMR ($CDCl_3$, δ); 1.0 (3H, t, CH_3), 4.0–4.2 (2×2 H, m, 2×CH_2), 4.5 (2 H, t, OCH_2), 6.9 (1 H, s, ArH), 7.3 (5 H, s, PhH).

3.2.4. 2-(N-β-Bromoethylamino)-3-ethoxycarbonyl-4-phenylthiophene and 2-(N-β-bromoethylamino)-4-phenylthiophene hydrobromide

Five g (0.016 mol) of 2-(3-ethoxycarbonyl-4-phenylthienyl)-2-oxazolidone **11** were added portionwise to 50 ml of 48% hydrobromic acid with stirring. The mixture was then heated to 90–100°C, and stirred for 6 h. After 4–5 hours the mixture became a clear solution. The solution was cooled to room temperature, and poured into 500 ml of water containing ice, and the precipitate was filtered off to give the crude product, involving a mixture of *N*-2-bromoethylamino derivatives **13** and **14**. The crude solid was dried at room temperature overnight and was then added to 50 ml of EtOAc with stirring for 2 h. By filtering the mixture, only compound **13** remained dissolved in the filtrate, whereas the solid contained compound **14** as the main component. The filtrate was evaporated to remove EtOAc, then the crude product was purified by column chromatography (eluent: hexane/EtOAc = 9/1) to give 2.46 g (44% purified yield) of 2-(*N*-*β*-bromoethylamino)-3-ethoxycarbonyl-4-phenylthiophene (**13**, pale yellow powder). m. p. (**13**) 69–71°C. Microanalysis: found

C, 51.1; H, 4.7; N, 4.0; Br, 22.6; S, 9.3% ($C_{15}H_{16}BrNO_2S$ requires C, 51.0; H, 4.6; N, 4.0; Br, 22.6; S, 9.1%). ^{1}H NMR ($CDCl_3$, δ) ; 0.9 (3 H, t, CH_3), 3.55 (2 H, t, CH_2Br), 3.65 (2 H, t, NH**C**$\mathbf{H}_2$), 4.0 (2 H, q, OCH_2), 6.05 (1 H, s, ArH), 7.25 (5 H, s, PhH), 8.1 (1 H, b, NH). The crude solid 2-(*N*-β-bromoethylamino)-4-phenylthiophene hydrobromide **14** amounted to 1.9 g (43% yield, grey solid), m. p. (**14**) 162–164°C. Microanalysis: found C, 50.6; H, 4.4; N, 4.8; Br, 27.7% ($C_{12}H_{12}BrNS$ requires C, 51.1; H, 4.3; N, 5.0; Br, 28.3%). ^{1}H NMR (DMSO-d_6, δ); 3.7 (2 H, t, CH_2Br), 3.9 (2 H, t, NH**C**$\mathbf{H}_2$), 5.0 (1H, s, ArH), 7.4 (3 H, m, PhH), 7.5 (1 H, s, ArH), 7.7 (2 H, m, PhH).

3.3. Preparative details of the precursor dyes

The synthetic data and physical properties for each precursor dye are summarised in Table 1. Details of characterisation data are given in Tables 13 and 14 for azo dyes **2a**–**2n** and dyes **2o**–**2r**, respectively.

3.3.1. Diazotisation

The following general procedures of diazotisation were used.

3.3.1.1. General procedure for 4-substituted anilines and 2-chloro-4-nitroaniline using nitrosyl chloride. A finely ground powder of the 4-substituted aniline (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 $NaNO_2$ (2.1×10^{-3} mol) was added portionwise at 5–10°C, and the mixture was stirred for a further 1 h at the same temperature. The resulting clear solution was used immediately in the coupling reaction.

3.3.1.2. 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.

3.3.2. General procedure for coupling

Coupling component (1.8×10^{-3} mol) was dissolved in 20 ml of acetone, 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 **2**.

3.4. Cyclisation to aziridinyl dyes

The following general procedure was used for cyclising the precursor dyes to the corresponding aziridinyl dyes. Sodium amide (5.0×10^{-3} mol) was added to acetonitrile (20 ml), and the mixture was heated to reflux, then the β-bromoethylamino precursor **13** and **14** (1.0×10^{-3} mol) was added and stirring was continued under reflux. The reflux time varied depending on the substituents present (see Table 15). The completed reaction mixture was filtered hot and washed with acetonitrile (10 ml). The combined acetonitrile solution was evaporated, and the residue was column chromatographed to give aziridinyl dyes **1**. Details of the cyclisation conditions and characterisation data for some aziridinyl azo dyes **1** prepared are given in Tables 15 and 16, respectively.

3.5. Purification methods of the precursor dyes and aziridinyl dyes

Purification methods, as given in Table 1 and Table 15 have been detailed as follows; chromatography columns were prepared using silica 60 (70∼230 mesh ASTM).

(A) Column chromatography; hexane/EtOAc = 9/1 initially, then the portion of EtOAc was increased gradually.
(B) Column chromatography; hexane/EtOAc = 8/2 initially, then the portion of EtOAc was increased gradually.

Table 13
Characterisation data for some azo dyes **2** derived from 2-(*N*-β-bromoethylamino)-3-ethoxycarbonyl-4-phenylthiophene **13**

1. Microanalysis

Dye	m. p.	Elemental analyses									
		Reqires (%)					Found (%)				
	(°C)	C	H	N	Br	Other	C	H	N	Br	Other
2a	116–118	55.0	4.4	9.2	17.4		55.2	4.4	9.3	17.1	
2b	134–136	46.9	3.6	7.8	29.7		47.2	3.5	7.6	28.3	
2c	146–148	50.2	3.6	7.9	15.2	10.8 (F)	50.1	3.5	7.8	15.3	10.9 (F)
2d	183–184	55.2	4.4	8.4	16.0		54.6	4.4	7.9	15.9	
2e	197–198	54.7	3.9	11.6	16.5	6.6 (S)	54.4	3.8	11.5	16.7	6.8 (S)
2f	186–188	50.1	3.8	11.1	15.9	6.4 (S)	50.4	3.6	10.9	15.9	6.6 (S)
2g	166–167	46.3	3.7	7.3	14.0	11.2 (S)	46.2	3.5	7.0	13.8	10.8 (S)
2h	107–108	46.2	3.2	9.8	13.9		46.9	3.1	9.9	13.6	
2i	111–114	46.9	3.4	10.4	14.9	6.6 (Cl)	46.2	3.5	9.9	14.7	6.8 (Cl)
2j	179–180	46.2	3.2	9.8	14.0		46.4	3.1	9.7	13.8	
2k	163–166	46.0	3.3	12.8	14.6		45.6	3.2	13.1	14.8	
2l	174–176	43.5	2.8	11.5	26.3		44.0	2.8	11.0	25.9	
2m	191–194	40.2	2.7	11.2	25.5		41.0	2.7	10.7	24.7	
2n	223–225	50.0	3.4	13.3	15.1		50.6	3.5	13.1	15.2	

2. NMR spectra

Dye	Chemical shift ($CDCl_3$, δ)
2a	0.9 (3 H, t, CH_3), 3.55 (2 H, t, CH_2Br), 3.8 (2 H, t, $NHCH_2$), 4.0 (2 H, q, OCH_2), 7.3–7.5 (5H and 3 H, m, PhH and ArH), 7.7 (2 H, d of d, ArH), 9.1 (1 H, t, NH)
2b	0.9 (3 H, t, CH_3), 3.6 (2 H, t, CH_2Br), 3.8 (2 H, t, $NHCH_2$), 4.0 (2 H, q, OCH_2), 7.3 (5 H, s, PhH), 7.5 (4 H, s, ArH), 9.0 (1 H, t, NH)
2c	0.9 (3 H, t, CH_3), 3.6 (2 H, t, CH_2Br), 3.8 (2 H, t, $NHCH_2$), 4.0 (2 H, q, OCH_2), 7.35 (5 H, s, PhH), 7.55 (4 H, s, ArH), 9.1 (1 H, t, NH)
2d	0.9 (3 H, t, CH_3), 2.5 (3 H, s, $COCH_3$), 3.6 (2 H, t, CH_2Br), 3.8 (2 H, t, $NHCH_2$), 4.0 (2 H, q, OCH_2), 7.4 (5 H, s, PhH), 7.6 (2 H, d, ArH), 7.9 (2 H, d, ArH), 9.1 (1 H, t, NH)
2e	0.9 (3 H, t, CH_3), 3.6 (2 H, t, CH_2Br), 3.8 (2 H, t, $NHCH_2$), 4.0 (2 H, q, OCH_2), 7.4 (5 H, s, PhH), 7.55 (4 H, s, ArH), 9.16 (1 H, t, NH)
2f	0.9 (3 H, t, CH_3), 3.6 (2 H, t, CH_2Br), 3.82 (2 H, t, $NHCH_2$), 4.0 (2 H, q, OCH_2), 7.4 (5 H, s, PhH), 7.55 (2 H, d, ArH), 8.15 (2 H, d, ArH), 9.2 (1 H, t, NH)
2g	0.9 (3 H, t, CH_3), 3.0 (3 H, s, SO2CH_3), 3.6 (2 H, t, CH_2Br), 3.82 (2 H, t, $NHCH_2$), 4.0 (2 H, q, OCH_2), 7.25 (1 H, d, ArH), 7.4 (5 H, s, PhH), 7.6 (1 H, d of d, ArH), 7.92 (1 H, d, ArH), 9.3 (1 H, t, NH)
2h	1.0 (3 H, t, CH_3), 3.65 (2 H, t, CH_2Br), 3.9 (2 H, t, $NHCH_2$), 4.15 (2 H, q, OCH_2), 7.3 (1 H, d, ArH), 7.4 (5 H, s, PhH), 7.6 (1H, d, ArH), 8.4 (1 H, s, ArH), 9.3 (1 H, b, NH)
2i	0.9 (3 H, t, CH_3), 3.6 (2 H, t, CH_2Br), 3.7 (2 H, t, $NHCH_2$), 4.0 (2 H, q, OCH_2), 7.4 (5 H, s, PhH), 7.8 (1 H, d, ArH), 8.1 (1H, d, ArH), 8.3 (1 H, s, ArH), 9.35 (1 H, b, NH)
2j	0.9 (3 H, t, CH_3), 3.65 (2 H, t, CH_2Br), 3.9 (2 H, t, $NHCH_2$), 4.05 (2 H, q, OCH_2), 7.4 (5 H, s, PhH), 7.5 (1 H, d, ArH), 8.2 (1 H, d of d, ArH), 8.5 (1 H, d, ArH), 9.4 (1 H, t, NH)
2k	1.0 (3 H, t, CH_3), 3.8 (2 H, t, CH_2Br), 3.95 (2 H, t, $NHCH_2$), 4.1 (2 H, q, OCH_2), 7.3 (1 H, d, ArH), 7.4 (5 H, s, PhH), 7.5 (1 H, d, ArH), 8.2 (1 H, s, ArH), 9.0 (1 H, b, NH)
2l	0.9 (3 H, t, CH_3), 3.6 (2 H, t, CH_2Br), 3.85 (2 H, t, $NHCH_2$), 4.0 (2 H, q, OCH_2), 7.35–7.5 (5 H, m, PhH), 8.3 (1 H, d, ArH), 8.5 (1 H, d of d, ArH), 9.6 (1 H, t, NH)
2m	0.92 (3 H, t, CH_3), 3.7 (2 H, t, CH_2Br), 3.95 (2 H, t, $NHCH_2$), 4.1 (2 H, q, OCH_2), 7.4–7.6 (5 H, m, PhH), 8.6 (1 H, d, ArH), 9.1 (1 H, d, ArH), 9.7 (1 H, t, NH)
2n	0.92 (3 H, t, CH_3), 3.8 (2 H, t, CH_2Br), 3.95 (2 H, t, $NHCH_2$), 4.1 (2 H, q, OCH_2), 7.4 (5 H, s, PhH), 7.55 (1 H, d, ArH), 8.2 (1 H, d of d, ArH), 8.55 (1 H, d, ArH), 9.4 (1 H, t, NH)

Table 14
Characterisation data for some azo dyes **2** derived from 2-(*N*-β-bromoethylamino)-4-phenylthiophene **14**

1. Microanalysis and FT-IR

Dye	m. p. (°C)	Elemental analyses								FT-IR (KBr, cm^{-1})
		Requires (%)				Found (%)				
		C	H	N	Br	C	H	N	Br FT-IR	
2o	164–166	45.7	2.8	11.2	16.0	46.0	2.9	10.7	15.8	3284, ν (NH)
2p	186–188	42.6	2.5	13.1	29.9	44.3	2.6	13.1	29.1	3235, ν (NH); 2212, ν (CN)
2q	102–104	38.9	2.4	12.6	28.8	39.5	2.3	12.1	27.2	–
2r	173–175	50.0	3.1	15.3	17.5	50.7	3.1	14.9	17.2	–

2. NMR

Dye	Chemical shift (δ)
2o	$CDCl_3$; 3.7 (2 H, t, CH_2Br), 3.95 (2 H, t, $NHCH_2$), 7.0 (1 H, s, thiopheneH), 7.5 (3 H, m, PhH), 7.6 (1 H, d, ArH), 7.65 (2 H, m, PhH), 7.93 (1 H, s, NH), 8.3 (1 H, d of d, ArH), 8.4 (1 H, d, ArH)
2p	Acetone-d6 ; 3.9 (2 H, t, CH_2Br), 4.1 (2 H, t, $NHCH_2$), 7.2 (1 H, s, thiopheneH), 7.5 (3 H, m, PhH), 8.15 (2 H, m, PhH), 8.4 (1 H, s, ArH), 8.5 (1 H, s, ArH), 9.45 (1 H, b, NH)
2q	Acetone-d6 ; 3.9 (2 H, t, CH_2Br), 4.15 (2 H, t, $NHCH_2$), 7.2 (1 H, s, thiopheneH), 7.55 (3 H, m, PhH), 8.2 (2 H, m, PhH), 8.4 (1 H, s, ArH), 8.55 (1 H, s, ArH), 9.5 (1 H, b, NH)
2r	Acetone-d6 ; 3.6 (2 H, t, CH_2Br), 3.82 (2 H, t, $NHCH_2$), 6.85 (1 H, s, thiopheneH), 7.4 (3 H, m, PhH), 7.45 (1 H, d, ArH), 7.7 (2 H, m, PhH), 8.1 (1 H, d of d, ArH), 8.3 (1 H, d, ArH), 9.4 (1 H, b, NH)

Table 15
Experimental data for cyclisation of precursors **2** to aziridinyl dyes **1**

Dye	Molarity ($\times 10^{-4}$ mol)	% Crude yield (g)	Purification method	% Pure yield (g)	Appearance
1c	7.6	67 (0.23)	A	19 (0.07)	Orange leaflets
1d	8.0	75 (0.30)	A	17 (0.07)	Orange leaflets
1e	6.2	83 (0.21)	A	44 (0.11)	Red-orange solid
1f	6.0	66 (0.17)	A	41 (0.13)	Shiny brown powder
1g	5.3	62 (0.16)	A	33 (0.09)	Red powder
1h	5.3	70 (0.18)	A	39 (0.10)	Brown powder
1i	6.0	74 (0.19)	B	27 (0.07)	Red-brown solid
1j	5.3	59 (0.15)	A	36 (0.09)	Brown powder
1k	5.5	82 (0.21)	B	47 (0.12)	Dark brown powder
1l	4.9	68 (0.18)	A	41 (0.11)	Shiny brown leaflets
1m	4.8	69 (0.18)	A	35 (0.09)	Dark violet powder
1n	6.6	85 (0.25)	A	38 (0.11)	Shiny brown leaflets
1o	6.0	82 (0.21)	C	33 (0.08)	Dark brown solid
1p	5.6	77 (0.20)	C	36 (0.09)	Green powder
1q	5.4	85 (0.22)	C	42 (0.11)	Green powder
1r	6.6	73 (0.18)	B	31 (0.08)	Green-brown powder

Table 16
Characterisation data for some aziridinyl azo dyes **1**

1. Microanalysis and m. p.

Dye	m. p. (°C)	Elemental analyses							
		Requires %				Found %			
		C	H	N	Other	C	H	N	Other
1c	127—-130	59.3	4.1	9.4	12.8 (F)	58.1	4.0	9.0	13.2 (F)
1d	165—-168	65.9	5.0	10.0		64.3	4.9	10.3	
1e	179—-182	65.7	4.5	13.9		65.1	4.7	12.1	
1f	169—-172	59.7	4.3	13.2		60.0	4.4	13.0	
1g	160—-163	57.7	4.4	9.2	13.1 (S)	56.1	4.5	9.5	13.0 (S)
1h	157—-159	53.9	3.5	11.4		54.5	3.6	10.9	
1i	105—-108	55.2	3.8	12.3		56.2	3.8	12.7	
1j	170—-172	53.9	3.5	11.4		53.8	3.6	11.3	
1k	151—-153	54.0	3.7	15.0		52.8	3.8	13.9	
1l*	156—-157	50.2	3.0	13.3	15.2 (Br)	51.7	3.0	11.9	14.8 (Br)
1m	134—-136	46.2	2.9	12.8		39.5	2.9	12.6	
1n	197—-200	59.1	3.8	15.7		62.1	3.8	14.7	
1o	140—-144	54.5	3.1	13.4	13.6 (F)	53.2	3.2	13.1	12.9 (F)
1p	169—-172	50.2	2.7	15.4		50.7	2.7	14.9	
1q	98—-100	45.6	2.6	14.8	16.8 (Br)	46.0	2.7	13.9	17.3 (Br)
1r	158—-160	60.8	3.5	18.7		58.8	3.5	18.4	

2. NMR

Dye	Chemical shift ($CDCl_3$, δ)
1c	0.85 (3 H, t, CH_3), 1.5 (4 H, s, aziridine), 4.0 (2 H, q, OCH_2), 7.35 (5 H, s, PhH), 7.55 (4 H, s, ArH)
1d	0.85 (3 H, t, CH_3), 1.5 (4 H, s, aziridine), 2.1 (3 H, s, $COCH_3$), 4.0 (2 H, q, OCH_2), 7.4 (5 H, s, PhH), 7.5 (4 H, s, ArH)
1e	0.85 (3 H, t, CH_3), 1.5 (4 H, s, aziridine), 4.0 (2 H, q, OCH_2), 7.35 (5 H, s, PhH), 7.55 (4 H, s, ArH)
1f	0.9 (3 H, t, CH_3), 1.5 (4 H, s, aziridine), 4.0 (2 H, q, OCH_2), 7.4 (5 H, s, PhH), 7.6 (2 H, d, ArH), 8.2 (2 H, d, ArH)
1g	0.8 (3 H, t, CH_3), 1.4 (4 H, s, aziridine), 2.9 (3 H, s, SO_2CH_3), 3.9 (2 H, q, OCH_2), 7.3 (5 H, s, PhH), 7.4 (1 H, d, ArH), 7.6 (1 H, d of d, ArH), 7.9 (1 H, d, ArH)
1h	0.85 (3 H, t, CH_3), 1.5 (4 H, s, aziridine), 4.0 (2 H, q, OCH_2), 7.3 (1 H, d, ArH), 7.4 (5 H, s, PhH), 7.6 (1 H, d of d, ArH), 8.3 (1 H, d, ArH)
1i	0.9 (3 H, t, CH_3), 1.55 (4 H, s, aziridine), 4.1 (2 H, q, OCH_2), 7.4 (5 H, s, PhH), 7.5 (1 H, d, ArH), 7.95 (1 H, d of d, ArH), 8.3 (1 H, d, ArH)
1j	0.9 (3 H, t, CH_3), 1.6 (4 H, s, aziridine), 4.1 (2 H, q, OCH_2), 7.4 (5 H, s, PhH), 7.55 (1 H, d, ArH), 8.3 (1 H, d of d, ArH), 8.55 (1 H, d, ArH)
1k	DMSO-d_6: 1.0 (3 H, t, CH_3), 1.8 (4 H, s, aziridine), 4.05 (2 H, q, OCH_2), 7.2–7.6 (5H and 2×1 H, m, PhH and 2×ArH), 8.4 (1 H, d, ArH)
1l	0.9 (3 H, t, CH_3), 1.5 (4 H, s, aziridine), 4.05 (2 H, q, OCH_2), 7.35–7.5 (5 H, m, PhH), 8.35 (1 H, d, ArH), 8.4 (1 H, d, ArH)
1m	0.95 (3 H, t, CH_3), 1.5 (4 H, s, aziridine), 4.1 (2 H, q, OCH_2), 7.3–7.5 (5 H, m, PhH), 8.3 (1 H, d, ArH), 8.6 (1 H, d, ArH)
1n	0.85 (3 H, t, CH_3), 1.5 (4 H, s, aziridine), 4.05 (2 H, q, OCH_2), 7.2–7.4 (5 H, m, PhH), 7.5 (1 H, d, ArH), 8.2 (1 H, d of d, ArH), 8.5 (1 H, d, ArH)
1o	Acetone-d_6; 1.4 (4 H, s, Az), 7.1 (1 H, s, thiopheneH), 7.5 (3 H, m, PhH), 7.8 (1 H, d, ArH), 7.9 (2 H, m, PhH), 8.3 (1 H, d of d, , ArH), 8.45 (1 H, d, ArH)
1p	1.6 (4 H, s, Az), 7.1 (1 H, s, thiopheneH), 7.5 (3 H, m, PhH), 7.8 (2 H, m, PhH), 8.45 (1 H, d, ArH), 8.55 (1 H, d, ArH)
1q	Acetone-d_6; 1.4 (4 H, s, Az), 7.0 (1 H, s, thiopheneH), 7.3 (3 H, m, PhH), 7.6 (2 H, m, PhH), 8.4 (1 H, d, ArH), 8.5 (1 H, d, ArH)

(C) Column chromatography; hexane/EtOAc = 7/3 initially, then the portion of EtOAc was increased gradually.
(D) Column chromatography; hexane/EtOAc = 6/4 initially, then the portion of EtOAc was increased gradually.
(E) Column chromatography; hexane/EtOAc = 1/1 initially, then the portion of EtOAc was increased gradually.
(F) Recrystallisation from ethanol/cyclohexane.
(G) Recrystallisation from ethanol.

4. Conclusions

N-Thienylaziridinoazo dyes have been prepared from 2-amino-4-phenylthiophene coupling components using conventional diazo-coupling reactions and subsequent cyclisations in good yield; these dyes exhibited yellow to greenish-blue hues. The striking bathochromic shifts exerted by azo dyes without a 3-substituent in the thiophene ring, in comparison with 3-CO_2Et-substituted dyes, can best be explained by a more efficient conjugation of the terminal lone pair electrons with the adjacent π system. Cyclisation of the β-bromoethylamino group in the precursor dyes to the corresponding aziridine ring consistently gave rise to bathochromic shifts in absorption maxima. More importantly, much longer λ_{max} values were observed for the *N*-thienylaziridinoazo dyes compared with 4-aminoazobenzene derivatives containing other cyclic terminal groups, and could be correlated with a more coplanar conformation of the terminal nitrogen atom of *N*-thienylaziridine in contrast to that of *N*-phenylaziridine. With a few exceptions, the precursor and aziridinyl dyes exhibited positive solvatochromism in aprotic solvents, but showed hypsochromic shifts in polar aprotic solvents. PPP–MO calculations of absorption maxima provided reliable predictions, using modified parameters for the terminal nitrogen atom of the azo dyes.

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