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Dyes Derived from Aminothiophenes. Part 5: Spectral Properties of Some Nitro-substituted Thiophene-based Azo Disperse Dyes

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ABSTRACT

The spectroscopic properties of a series of nitro-substituted thienyl-2- and thienyl-3-azo dyes in neutral and acidic solution were examined. In agreement with resonance theory and PPP-MO calculations, nitrothienyl-2-azo derivatives were found to be more bathochromic than analogues lacking nitro groups. Absorption intensities, half-band widths and positive solvatochromic shifts were also greater; additionally, the nitrothienyl-2-azo dyes exhibited negative halochromism. The nitrothienyl-3-azo dyes were hypso- and hypochromic relative to their thienyl-2-azo isomers. The spectra and halochromism of the 2,4-disubstituted dyes indicated the presence of steric hindrance. © 1997 Elsevier Science Ltd

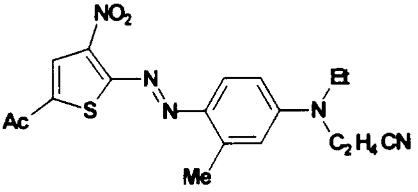
Keywords: Nitro-substituted aminothiophenes, heterocyclic azo dyes, PPP-MO calculations, solvatochromism, halochromism.

INTRODUCTION

Monoazo disperse dyes derived from 2-aminothiophenes containing nitro groups are prized for their bathochromism and high tinctorial strength relative to their carbocyclic analogues; these properties, which have aided the rise to prominence of such dyes as replacements for blue anthraquinone colorants,[1,2] were first reported by Dickey and co-workers nearly forty years ago.[3] Since then, however, only fragmentary data concerning the spectral properties of nitrothienyl-2-azo dyes have been disclosed.

The deep colours of these dyes can be explained by resonance theory; the sulphur atom acts as an electron sink and the thiophene ring system has less resonance stabilisation energy to lose on excitation than a benzenoid system.[4] However, PPP-MO and CNDO/S calculations suggest that the bathochromism is a consequence of the *cis*-diene structure of the heteroaromatic ring and that the presence of the sulphur atom is incidental.[5,6] Much less is known about the colour and constitution of nitro-substituted disperse dyes from 3-aminothiophenes; although the hues of a few examples of these colorants on polyester are quoted in the patent literature,[7,8] there are no published spectroscopic data concerning this type of dye.

The synthesis of some thienyl-2-, thiazolyl-2- and thienyl-3-azo dyes **1**–**5** containing nitro groups has been described previously.[9] This paper reports the spectroscopic properties of each dye in neutral and acidic solution and compares them with theoretical expectations and literature data.



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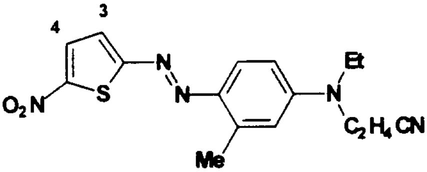

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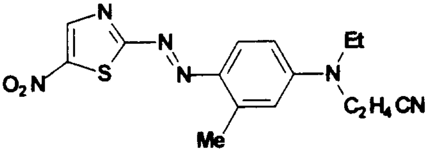
$3 = CO_2Me, CO_2Et, CO_2Bu, NO_2$
$4 = H, Me$



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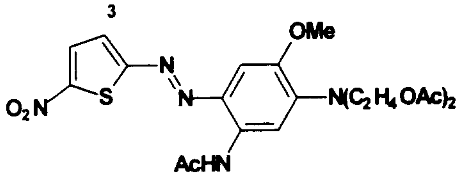

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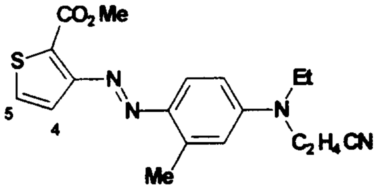

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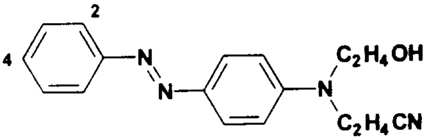
$4 = H, Me, NO_2$
$5 = H, NO_2$

RESULTS AND DISCUSSION

Spectroscopic properties in neutral solution

Data concerning the spectra of the dyes in DMF (λ_{max}, ϵ_{max}, $\Delta\lambda_{1/2}$), ethanol (λ_{max}) and toluene (λ_{max}) are listed in Table 1.

The figures are consistent with the observations of Dickey *et al.*[3] with respect to the bathochromism of nitrothienyl-2-azo dyes relative to aminoazobenzenes. For example, **1** is considerably more bathochromic and intense than **6** (2-NO_2-4-Ac), the latter having λ_{max} 463 nm and ϵ_{max} 29 900 in ethanol.[10]



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A consequence of the diene-like character of the thiophene ring of the dyes is that substituent effects are more efficiently transmitted than in aminoazobenzene analogues: the attachment of a nitro group to a thiophene-based diazo component will bring about a greater electronically driven bathochromic shift in the dye than the corresponding change for an aniline derivative. This can be illustrated by comparing the effect of the introduction of a nitro group into the 4-position of **6** (2-CO_2Et) and the 5-position of the analogous dye from 2-amino-3-methoxycarbonyl-5-methylthiophene to

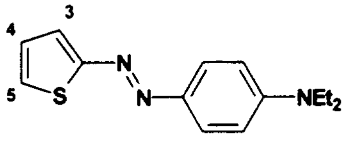
TABLE 1

Spectral Data (λ_{max} and $\Delta\lambda_{1/2}$ in nm, ϵ_{max} in $dm^3\ mol^{-1}\ cm^{-1}$) of the Dyes in Solution

Dye	λ_{max} (DMF)	ϵ_{max} (DMF)	$\Delta\lambda_{1/2}$ (DMF)	λ_{max} (EtOH)	λ_{max} (C_7H_8)
1	600.6 ± 0.4	43 900 ± 500	124	573	561
2 (3-CO_2Me)	607.8 ± 0.6	46 600 ± 900	123	579	562
2 (3-CO_2Me-4-Me)	589.1 ± 0.6	43 600 ± 1100	124	563	547
2 (3-CO_2Et)	606.5 ± 0.2	46 500 ± 700	124	579	559
2 (3-CO_2Bu^n)	607.1 ± 0.5	46 000 ± 500	123	578	561
2 (3-NO_2)	653.9 ± 0.8	54 000 ± 600	118	618	596
3	591.7 ± 0.5	50 200 ± 700	113	575	545
4 (3-CO_2Me)	651.2 ± 0.3	48 400 ± 300	119	626	635
4 (3-NO_2)	685.6 ± 0.2	64 500 ± 900	94	667	669
5 (4-Me-5-NO_2)	430.2 ± 0.8	22 900 ± 200	134	417	414
5 (5-NO_2)	478.5 ± 0.7	30 200 ± 600	121	459	452
5 (4-NO_2)	454.4 ± 0.5	21 600 ± 400	123	437	429

TABLE 2

Absorption Maxima (λ_{max} in nm) and Oscillator Strengths (f) Predicted by the PPP-MO Method for some *N*,*N*-Diethylaniline-based Nitrothienylazo Dyes



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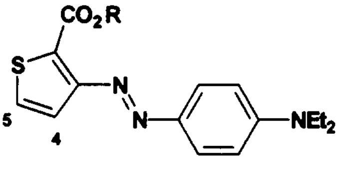

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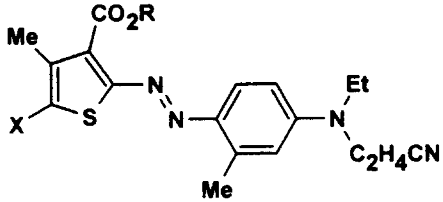
Dye	λ_{max} (calc.)	f (calc.)
7 (3-NO$_2$-5-Ac)	550	1.23
7 (3-CO$_2$R-5-NO$_2$)	559	0.92
7 (3-CO$_2$R-4-NO$_2$)	479	1.52
7 (3,5-NO$_2$)	581	0.73
8 (5-NO$_2$)	465	0.47
	423	1.01
8 (4-NO$_2$)	479	0.30
	443	0.79

create, respectively, **6** (2-CO$_2$Et-4-NO$_2$) and **2** (3-CO$_2$Me). In the former instance, the modification causes a red shift of 60 nm (to 465 nm) and an increase in ϵ_{max} of 2900 (to 30 100) for ethanol solutions.[10,11] However, a similar alteration (albeit not identical), in the latter instance, brings about greater differences: a bathochromic shift of 85 nm from 494 nm in ethanol occurs, as well as an increase in ϵ_{max} of 12 600 in DMF.[12] In a similar manner to the comparison of **1** and **6** (2-NO$_2$-4-Ac), **2** (3-CO$_2$Me) is *ca.* 110 nm more bathochromic and has an ϵ_{max} value around 15 000 greater than that of **6** (2-CO$_2$Et-4-NO$_2$).

The bathochromism of the thienyl-2-azo dyes is predicted by PPP-MO calculations performed for some *N*,*N*-diethylaniline-based analogues **7** (see Table 2).

Taking into consideration the slight structural differences between the synthesised toluidine-derived dyes, **1** and **2**, and the model dyes, **7**, as well as the fact that the parameters used were originally optimised for the estimation of the colour properties of compounds in cyclohexane solution, the calculated λ_{max} values correlate well with the observed figures for the dyes in toluene. It is recognised that the prediction of relative oscillator strengths within a series of azo dyes by the PPP-MO method is unsatisfactory;[13] the calculation of figures for the nitrothienylazo dyes was no exception (see Table 2).

TABLE 3
Influence of the 5-Substituent on the Spectra (λ_{max} and $\Delta\lambda_{1/2}$ in nm, ϵ_{max} in dm^3 mol^{-1} cm^{-1}) of some Related Thienyl-2-azo Dyes in DMF



X	R	λ_{max}	ϵ_{max}	$\Delta\lambda_{1/2}$	Ref.
Me	Et	499.9	33 900	103	12
CO_2Et	Et	529.6	39 100	107	12
Ac	Me	536.0	39 600	108	12
CN	Et	545.6	42 700	106	12
NO_2	Me	589.1	43 600	124	

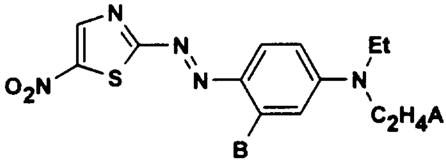
In accordance with the PPP-MO calculations and resonance theory, the dyes **1** and **2** are more bathochromic and hyperchromic than analogues lacking nitro-substitution. For example, **2** (3-CO_2Me-4-Me) is bluer and more intense than derivatives possessing substituents of lower electron-withdrawing strength in the 5-position (see Table 3).

Similarly, the dyes with 3-nitro substituents are more bathochromic and intense than the corresponding 3-alkoxycarbonyl dyes; for example, **1** has λ_{max} 600.6 nm and ϵ_{max} 43 900, whereas its 3-methoxycarbonyl analogue has values of 552.1 nm and 39 700.[12] A bathochromic shift of 46.1 nm and intensity increase of 7400 is exhibited by **2** (3-NO_2) relative to **2** (3-CO_2Me).

The nature of the alkyl ester type in **2** (3-CO_2R) has no significant effect on the absorption spectra of the dyes. However, the introduction of a methyl group into the 4-position of the thiophene ring of **2** (3-CO_2Me) produces a sizeable hypsochromic shift (19 nm); a similar effect was observed in the cases of the 5-methyl and 5-acetyl analogues.[12] This result was ascribed to the inductive effect of the 4-methyl group, as opposed to steric hindrance, since no reduction in ϵ_{max} or change in half-band width was observed. The hypsochromism of **2** (3-CO_2Me-4-Me) is also likely to have an electronic origin because of the relatively small changes brought about in ϵ_{max} and $\Delta\lambda_{1/2}$. As was noted with the 5-methyl and 5-acetyl derivatives, disruption of excited state solvation relative to ground state solvation by the methyl group (causing an increase in the energy gap between the states) can be discounted as a reason for the hypsochromic shift because of the significant difference in λ_{max} values (15 nm) between the 4-methyl derivative and its unsubstituted analogue in toluene.

TABLE 4

Spectral Data (λ_{max} in nm, ϵ_{max} in dm^3 mol^{-1} cm^{-1} and $\Delta\nu_{1/2}$ in cm^{-1}) of some 5-Nitrothiazolyl-2-azo Dyes in DMF



A	B	λ_{max}	ϵ_{max}	$\Delta\nu_{1/2}$	Ref.
H	H	595	54000	3310	16
H	$NHCOC_2H_4Cl$	605	59000	3250	16
CN	Me	592	50200	3320	

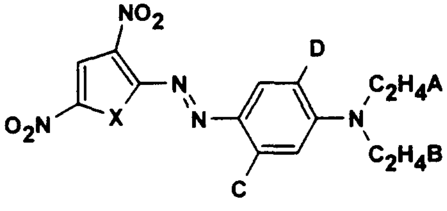
In line with data reported by Peters and Gbadamosi,[14] the figures in Table 1 indicate the C-CO_2R function to be a slightly better electron acceptor than a ring nitrogen atom as the thienyl-2-azo dyes **2** (3-CO_2R) are more bathochromic than the thiazole-based analogue **3**; however, the latter dye is more intensely absorbing (and brighter), having slightly higher ϵ_{max} values through a combination of lower molecular mass and reduced half-band width.

While relatively little has been published concerning half-band widths of carbocyclic dyes, even less information is available which pertains to heterocyclic structures. The half-band width of **3** (Table 4; A = CN, B = Me), is consistent with what appear to be the only $\Delta\nu_{1/2}$ values quoted in the literature for 5-nitrothiazole-based dyes; λ_{max} and ϵ_{max} values in DMF also correspond with that reported (see Table 4), the hypsochromic shift brought about by the cyano group seeming to just outweigh the bathochromic influence of the methyl group as revealed by the slight hypsochromism (3 nm) of the dye relative to (A = B = H). The acylamino group of (A = H, B = $NHCOC_2H_4Cl$) ensures that the dye is the brightest and most bathochromic of the three dyes as a result of intramolecular hydrogen-bonding.[15]

There would seem to be no information in the literature concerning the half-band widths of thienylazo dyes apart from that published recently by the authors.[12,17] A comparison of the 3,5-dinitrothienyl dyes with some carbocyclic analogues (see Table 5) shows the heterocyclic dyes to be brighter, the former having significantly smaller half-band widths, which partly explains their far higher ϵ_{max} values. As expected, the thiophene-derived dyes are also considerably more bathochromic, the shifts (*ca.* 100 nm) being of the same order as that found by Peters and Gbadamosi.[14]

TABLE 5

Spectral Data (λ_{max} in nm, ϵ_{max} in $dm^3\ mol^{-1}\ cm^{-1}$ and $\Delta\nu_{1/2}$ in cm^{-1}) of some 3,5-Dinitrothienyl-2-azo Dyes and their 2,4-Dinitrophenylazo Analogues in DMF



X	A	B	C	D	λ_{max}	ϵ_{max}	$\Delta\nu_{1/2}$	Ref.
CH=CH	OAc	OAc	NHAc	OMe	579	24 500	4700	18
S	OAc	OAc	NHAc	OMe	686	64 500	2080	
CH=CH	H	H	H	H	544	20 400	4400	18
S	CN	H	Me	H	654	54 000	2880	
S	OAc	OAc	Me	H	647	56 400	—	1
S	H	H	NHAc	H	644	87 400	—	1

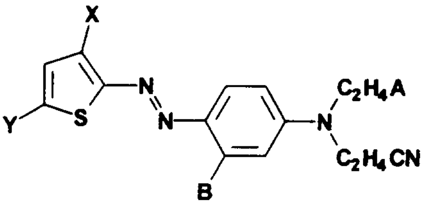
The spectral data of the dinitrothienyl dyes are consistent with figures reported by Annen *et al.* for two related dyes (see Table 5). Introduction of a methoxy group *para* to the acetylamino function of (X = S, A = B = D = H, C = NHAc) to give **4** (3-NO_2) produces bathochromic and hypochromic shifts as expected. The λ_{max} and ϵ_{max} values of the methyl-substituted dyes (C = Me) differ little, the cyanoethyl dye being more bathochromic (7 nm), its terminal amino nitrogen atom apparently experiencing less inductive electron withdrawal from its substituents than that brought about by the other dye's two acetyloxyethyl groups.

The data for **2** (3-CO_2Me) and **2** (3-NO_2) correspond reasonably well with figures reported for analogous dyes derived from *N*-cyanoethyl-*N*-hydroxyethylaniline (see Table 6).

The dyes of type **2**, i.e. where (A = H, B = Me), are bathochromic relative to the derivatives (A = OH, B = H) as would be anticipated for dyes with one fewer electron-withdrawing group and one extra electron-donor on the coupler residue.

The thienyl-3-azo dyes **5** are markedly hypso- and hypo-chromic relative to their isomers **2** (3-CO_2Me-4-H/Me) in accordance with PPP-MO calculations. The difference is most pronounced with the 4-methyl derivatives; the thienyl-3-azo dye **5** (4-Me-5-NO_2) is yellow (λ_{max} 430 nm in DMF) and only just over half as intense (ϵ_{max} 22 900) as its blue thienyl-2-azo isomer **2** (3-CO_2Me-4-Me), which has λ_{max} 589 nm and ϵ_{max} 43 600 in DMF.

TABLE 6
Comparison of the Spectral Data (λ_{max} in nm and ϵ_{max} in $dm^3\ mol^{-1}\ cm^{-1}$) of some Toluidine-based Thienyl-2-azo Dyes and with that of some Related Dyes in Ethanol

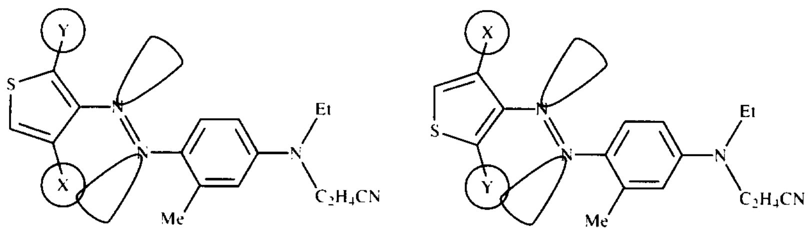


Substituents		A = H, B = Me		A = OH, B = H[14]	
X	Y	λ_{max}	ϵ_{max}*	λ_{max}	ϵ_{max}
CO_2Me	NO_2	579	46 600	560	38 000
NO_2	NO_2	618	54 000	596	40 700

*In DMF.

In addition to the alteration of the π-system, steric crowding would appear to have a hand in the hypso- and hypo-chromism as the former dye has two groups on its thiophene ring *ortho* to the azo link (see Fig. 1), leaving the dye unable to assume a conformation free of hindrance. Removal of the 4-methyl group to give **5** (5-NO_2) allows the dye the freedom to adopt a relatively unhindered conformation, **9a** ($X = H$, $Y = CO_2Me$), which is reflected in the consequent bathochromic shift (48 nm) and the increase in ϵ_{max} by almost one-third (see Table 1), as well as a narrowing of the absorption band ($\Delta\lambda_{1/2}$ decreased from 134 nm to 121 nm).

Steric crowding, brought about by the presence of both the ester and nitro groups *ortho* to the azo link, is presumably the reason for the low ϵ_{max} value



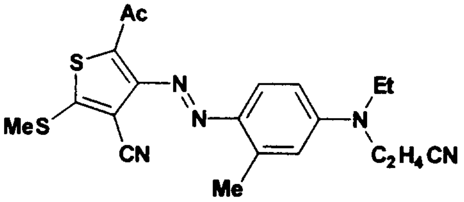
9a 9b

Fig. 1. Steric hindrance in 2,4-disubstituted-thienyl-3-azo dyes.

(21 600) of **5** (4-NO_2). PPP-MO calculations predict the 4-nitro derivative to be more bathochromic than its 5-nitro isomer (see Table 2), contrary to the observed order. The hypsochromism of the former dye appears to stem from the aforementioned steric hindrance, which is not taken into account in the calculations, hence the erroneous prediction.

The dye isomeric with **2** (3-CO_2Me) in which the nitro group is in the 4-position is predicted by PPP-MO calculations to absorb in roughly the same region as **5** (4-NO_2) and to be considerably hypsochromic relative to **2** (3-CO_2Me) (see Table 2). Switching the nitro group from the 5- to the 4-position would appear to effectively isolate it from the chromophore, the calculated data being little different from that of the analogue lacking nitro-substitution, **7** (3-CO_2R), whose predicted values were λ_{max} 479 nm and *f* 1.56.

While **10** has two *ortho* groups, the observed λ_{max} is not hypsochromic relative to the predicted value, suggesting that steric crowding is not a factor. It is well-known that a cyano group can be located *ortho* to the azo link on an aminoazobenzene derivative without causing crowding when the other *ortho* position is filled.[19,20] Analogously, **10** is able to adopt conformation **9a** (X = CN, Y = Ac), which, because of the nature of the cyano group, is hindrance-free.



10

λ_{max} = 510.1 ±0.5 nm, ε_{max} = 35300 ±900, $\Delta\lambda_{1/2}$ = 109 nm (DMF)

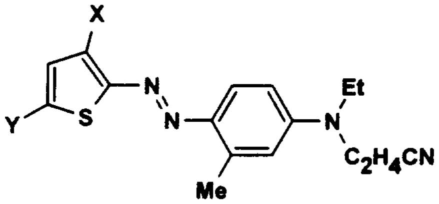
λ_{max} = 468 nm (toluene); λ_{max} = 450 nm (calculated)

Solvatochromism

All the toluidine-based dyes exhibit positive solvatochromism as expected for monoazo chromophores.[21] The typical trend whereby increased positive solvatochromic shifts are brought about by raising the total electron-withdrawing strength of the substituents on the diazo component was observed. For example, the introduction of nitro groups at the 3- and 5-positions of some thienyl-2-azo dyes leads to greater differences between λ_{max} values for their DMF and toluene solutions (see Table 7). As the nitro groups are

TABLE 7

Solvatochromism (λ_{max} in nm) of some Thienyl-2-azo Dyes with Various 3- and 5-Substituents



Substituents X	Substituents Y	λ_{max} (DMF)	$\Delta\lambda^a$	λ_{max} (EtOH)	$\Delta\lambda^b$	λ_{max} (C_7H_8)	$\Delta\lambda^c$	ΔD/debye
CO_2Me	Me	508.5	14.5	494	19	475	33.5	13.2
CO_2Me	Ac	552	17	535	17	518	34	14.2
NO_2	Ac	601	28	573	12	561	40	15.5
CO_2Me	NO_2	608	29	579	17	562	46	20.9
NO_2	NO_2	654	36	618	22	596	58	18.5

$\Delta\lambda^a = \lambda_{max}(DMF) - \lambda_{max}(EtOH)$; $\Delta\lambda^b = \lambda_{max}(EtOH) - \lambda_{max}(C_7H_8)$; $\Delta\lambda^c = \lambda_{max}(DMF) - \lambda_{max}(C_7H_8)$ in nm.

ΔD = difference in dipole moments of the ground and first excited states predicted by PPP-MO calculations for the analogous *N,N*-diethylaniline-derived dyes.

introduced, the gap between the polarity of the ground and excited states grows; the amount of stabilisation of the excited state relative to the ground state on increasing solvent polarity is raised and the solvatochromism becomes more marked, so, for example, the bathochromic shift for ($X = Y = NO_2$) is greater than that for ($X = CO_2Me$, $Y = Me$) on going from solution in toluene to DMF. However, this is a simplified picture of the complex interactions between dye and solvent and, while some comparisons show the trend (for example in Table 7, $\Delta\lambda^c$), others do not (for example, λ^b).

The thiazolyl dye **3** shows a similar solvatochromic shift (47 nm between DMF and toluene solutions) to its thienyl analogue **2** (3-CO_2Me), which displays a shift of 46 nm.

Both **4** (3-CO_2Me) and **4** (3-NO_2) have overall positive shifts (16 and 17 nm, respectively) between toluene and DMF solutions (see Table 1), although their ethanol solutions are slightly hypsochromic compared to those in toluene (2 and 9 nm). The overall shifts are much smaller than the corresponding shifts of 46 and 58 nm for the analogues **2** (3-CO_2Me) and **2** (3-NO_2), respectively.

TABLE 8
Spectral Data (λ_{max} and $\Delta\lambda$ in nm) for the Dyes **1–4** in Ethanol with and without Hydrochloric Acid

Dye	λ_{max} (EtOH)	λ_{max} (HCl/EtOH)	$\Delta\lambda$
1	573	540	−33
2 (3-CO_2Me)	579	546	−33
2 (3-CO_2Me-4-Me)	563	549	−14
2 (3-CO_2Et)	579	544	−35
2 (3-CO_2Bu^n)	578	544	−34
2 (3-NO_2)	618	529	−89
3	575	600	25
4 (3-CO_2Me)	626	538	−88
4 (3-NO_2)	667	529	−138

Also listed in Table 7 are the differences in dipole moments between ground and first excited states as calculated by the PPP-MO method. The expected relationship of increased difference being accompanied by greater solvatochromism does appear to hold reasonably well within the series, as has previously been observed for azoacetoacetanilide pigments.[22] However, the fact that the effect of the σ-framework on dipole moment has been neglected along with specific dye–solvent interaction may mean that the agreement is fortuitous, especially as the parameters have not been optimised with dipole moment calculations in mind. The correlation between thienyl-2- and thienyl-3-azo isomers is not good. While **2** (3-CO_2Me) has more marked solvatochromism compared to **5** (5-NO_2), the dyes having shifts of 46 and 27 nm, respectively, from toluene to DMF, the latter is predicted to have the greater difference in dipole moment between ground and excited states (20.9 and 35.0 D, respectively).

Spectroscopic properties in acidic solution

The halochromism of the thienyl-2-azo dyes was examined qualitatively. While red and violet thienyl-2-azo dyes, which lack nitro substitution, have been found to give positive halochromic shifts on addition of concentrated hydrochloric acid to ethanolic solutions,[12] the nitro-substituted dyes furnished negative shifts (see Table 8).

The observed values for **2** (3-CO_2Et) are similar to those reported for the analogous dye derived from *N*,*N*-diethylaniline (λ_{max} 594 nm and 531 nm, respectively, in ethanol and ethanol/hydrochloric acid).[23]

Increases (*ca.* 50 nm) in the size of the negative shifts were observed for the dyes **4** compared to their analogues **2** (3-CO_2Me) and **2** (3-NO_2).

In contrast to the thienyl-2-azo dyes, the thiazole-based dye, **3**, yielded a

TABLE 9
Spectral Data (λ_{max} in nm, ϵ_{max} in dm^3 mol^{-1} cm^{-1}) of the Thienyl-3-azo Dyes **5** in Ethanol and Ethanolic HCl

Dye	EtOH		EtOH/HCl		Equiv. HCl
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	(10^{-3})
5 (4-Me-5-NO_2)	417	25 000	503	39 000	70
5 (5-NO_2)	459	29 000	506	46 000	50
5 (4-NO_2)	437	—	498	—	—

positive shift, which can be ascribed to protonation at the ring nitrogen atom to form a diazahemicyanine cation.[24]

The thienyl-3-azo dyes were examined quantitatively in ethanol and in ethanolic hydrogen chloride in an attempt to probe the extent of steric crowding experienced by the molecules. Unsurprisingly, ϵ_{max} values in ethanol (see Table 9) correspond well with values obtained in DMF.

The azonium species of **5** (4-Me-5-NO_2) has a lower apparent ϵ_{max} than that of **5** (5-NO_2) which is presumably because, in the former dye, the two *ortho* groups inhibit protonation at the azo group. Unfortunately, the absence of any discernable ammonium peaks in both cases meant that tautomeric equilibrium constants (K_T = [azonium]/[ammonium])[25] for either dye could not be obtained; a lowering of this figure would have been expected on the introduction of the methyl group *ortho* to the azo link, since the steric hindrance produced would encourage an increase in the proportion of ammonium species present in the equilibrium relative to the azonium tautomer. In addition, an overall reduction in the basicity of the system would be expected; this was observed in that a higher acidity (70 000 equivalents acid) was required for optimum protonation in the methyl-substituted dye compared to the less hindered dye (50 000 equivalents).

EXPERIMENTAL

The synthesis and purification of the dyes **1–5** have been described previously.[9] The preparation of **10** from 2-acetyl-3-amino-4-cyano-5-(methylthio)thiophene (1.06 g, 0.005 mol), supplied by Maybridge Chemicals, using nitrosylsulphuric acid as with the other dyes, furnished a crude solid (1.93 g, 94% yield), which was recrystallised (2-ethoxyethanol, 2-ethoxyethanol/DMF, toluene twice) to give the pure dye as fine red needles (1.31 g, 64% pure yield, m.p. 221–221.5°C). Microanalysis found C, 58.4; H, 5.1; N, 16.95; S, 15.45% ($C_{20}H_{21}N_5OS_2$ requires C, 58.37; H, 5.14; N, 17.02; S, 15.58%).

The absorption spectra of the dye solutions were measured in quartz cells on a Philips PU8720 spectrophotometer (scan speed 50 nm min^{-1}). The acidic solutions were prepared either by addition of aqueous hydrochloric acid (36%) to an ethanolic solution of **1–4**, or by employing ethanolic hydrogen chloride for the dyes **5**. This solvent was prepared by bubbling hydrogen chloride, generated from the reaction between aqueous hydrochloric acid and sulphuric acid (98%),[26] through ethanol and standardising the resultant ethanolic hydrogen chloride by titration with aqueous potassium hydroxide using phenolphthalein as indicator. Ranges of dye solutions were prepared, containing known equivalents of hydrogen chloride, from stock solutions of dye and ethanolic hydrogen chloride, such that the optimum concentration for maximisation of the peak height of the azonium tautomer could be found.

PPP-MO calculations were performed as described previously.[17] In the case of thienyl-3-azo dyes with two substituents *ortho* to the azo link, predictions were made for both conformations and the results averaged.

CONCLUSIONS

In accordance with resonance theory and molecular orbital calculations, nitro substitution was found to cause pronounced bathochromism in a series of thienyl-2-azo dyes. Generally, red shifts in absorption were accompanied by increases in intensities, half-band widths and positive solvatochromic shifts analogously to aminoazobenzenes.

PPP-MO predictions were less successful for the nitrothienyl-3-azo derivatives, although their hypsochromism relative to the analogous thienyl-2-azo dyes was correctly forecast. Swapping the positions of the 3-ester and 2-azo functions of the thienyl-2-azo dyes to create the thienyl-3-azo isomers resulted in substantial decreases in absorption intensity and positive solvatochromic shifts. Deviations by the calculated λ_{max} figures of the 2,4-disubstituted thienyl-3-azo derivatives from the observed λ_{max} values can be ascribed to steric hindrance. Crowding appeared to be absent in a 2-acetyl-4-cyanothienyl-3-azo derivative owing to the ability of the cyano group to avoid any significant steric clash with the azo link, a well-known property that has been exploited for many years in the design of *o,o*-disubstituted carbocyclic monoazo dyes.

The bathochromicity and strong absorption of the nitrothienyl-2-azo dyes go some way to explaining the sizeable amount of commercial interest shown towards this colorant class. The lower intensities of the nitrothienyl-3-azo types account for the lack of industrial attention given to these dyes.

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REFERENCES

1. Annen, O., Egli, R., Hasler, R., Henzi, B., Jakob, H. & Matzinger, P., *Rev. Prog. Coloration*, **17** (1987) 72.
2. Egli, R., in *Colour Chemistry, The Design and Synthesis of Organic Dyes and Pigments*, eds A. T. Peters & H. S. Freeman. Elsevier, London (1991), p. 1.
3. Dickey, J. B., Towne, E. B., Bloom, M. S., Moore, W. H., Smith, Jr., B. H. & Hedberg, D. G., *J. Soc. Dyers Colour.*, **74** (1958) 123.
4. Gordon, P. F. & Gregory, P., *Organic Chemistry in Colour*. Springer, Berlin, 1983, p. 134.
5. Griffiths, J., *Colour and Constitution of Organic Molecules*. Academic Press, London, 1976, p. 186.
6. Kogo, Y., *Dyes and Pigments*, **6** (1985) 31.
7. ICI, British Patent 2 011 937, 1979.
8. BASF, European Patent 315 899, 1989.
9. Hallas, G. & Towns, A. D., *Dyes and Pigments*, in press. (DYPI 908).
10. Mehta, H. P. & Peters, A. T., *Dyes and Pigments*, **3** (1982) 71.
11. Mehta, H. P. & Peters, A. T., *Dyes and Pigments*, **2** (1981) 259.
12. Hallas, G. & Towns, A. D., *Dyes and Pigments*, in press. (DYPI 903)
13. Griffiths, J., *Dyes and Pigments*, **3** (1982) 211.
14. Peters, A. T. & Gbadamosi, A., *J. Chem. Tech. Biotechnol.*, **53** (1992) 301.
15. Ref. 4, p. 129.
16. Hu, J., Skrabal, P. & Zollinger, H., *Dyes and Pigments*, **8** (1987) 189.
17. Hallas, G. & Towns, A. D., *Dyes and Pigments*, **31** (1996) 273.
18. Wojciechowski, K., *Dyes and Pigments*, **12** (1990) 273.
19. Ref. 4, p. 154.
20. Ref. 5, p. 187.
21. Ref. 5, p. 76, 88.
22. Christie, R. M., Standring, P. N. & Griffiths, J., *Dyes and Pigments*, **9** (1988) 37.
23. Ref. 4, p. 144.
24. Hallas, G. & Marsden, R., *Dyes and Pigments*, **6** (1985) 463.
25. Liler, M., *Adv. Physical Org. Chem.*, **11** (1975) 267.
26. Vogel, A., *Textbook of Practical Organic Chemistry*, eds B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith & A. R. Tatchell, 4th edition. Longman, London, 1978, p. 297.