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Dyes and Pigments, Vol. 33, No. 3, pp. 205–213, 1997
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PII: S0143-7208(96)00047-2 0143-7208/97 $17.00+0.00

Dyes Derived from Aminothiophenes—Part 2. Spectroscepic Properties of some Disperse Dyes Derived from 2-Aminothiophenes

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(Received 11 March 1996; accepted 19 April 1996)

ABSTRACT

The colour properties of a series of red to violet thienyl-2-azo disperse dyes in solution have been investigated. As expected, the attachment of increasingly electron-withdrawing groups to the thiophene ring resulted in bathochromic and hyperchromic shifts. The shifts in absorption maxima were predicted quantitatively by PPP-MO calculations with reasonable accuracy. The solvatochromism and halochromic behaviour of the dyes were also examined. © 1997 Elsevier Science Ltd. All rights reserved

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

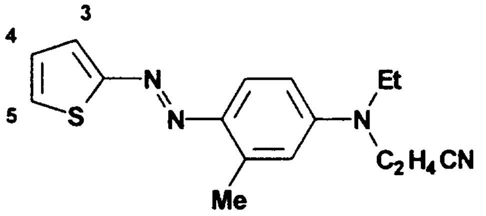
INTRODUCTION

The colours of hydrophobic monoazo dyes containing thiophene rings were investigated as long ago as 1949.[1] A decade later, a systematic study by Dickey *et al.*[2] was published which established the relative bathochromicity of thienyl-2-azo dyes over their carbocyclic counterparts and provided qualitative evidence of the higher absorption intensities of the former dye type.

Resonance theory gives two reasons for the bathochromism of such dyes.[3] The first concerns the role of the sulphur atom, which is said to act as an additional electron-withdrawing group; it has available, unoccupied 3*d*-orbitals that can accommodate transferred negative charge and stabilise the excited state, resulting in a bathochromic shift. The second factor relates to the loss of aromaticity of the heterocyclic ring on excitation: the ground state of a thienyl-2-azo dye has less resonance stabilisation energy than its benzenoid analogue and is closer in energy to its excited state. The lower energy gap equates to bathochromism. However, PPP-MO calculations suggest that the bathochromicity is a consequence of the *cis*-diene structure of the heteroaromatic ring and that the presence of the sulphur atom is incidental.[4] CNDO/S calculations which specifically include the 3*d* atomic orbitals of the sulphur atom indicate that the bathochromism is not attributable to them.[5]

Despite, or perhaps because of, the industrial interest generated by the bathochromism and intensity of thienyl-2-azo disperse dyes, a comprehensive modern investigation into the influence of diazo component substituent effects on colour properties within a sizeable dye series has not been published; the majority of the data on the spectroscopic behaviour of disperse dyes derived from 2-aminothiophenes have only appeared recently and have been of a fragmentary nature.[6–15]

This paper details the colour properties of the dyes **1** in neutral and acidic solution and compares them with theoretical expectations and literature data.



1

3 = CN, CO_2R, $CONH_2$
4 = H, Me
5 = R, Ph, Ac, CN
4,5 = (aryl)alkylene

RESULTS AND DISCUSSION

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, as are predicted values of λ_{max} and oscillator strengths (f), as given by PPP-MO calculations for related dyes performed as described earlier.[16] Taking into consideration the slight structural differences between the synthesised toluidine-derived dyes and the *N*,*N*-diethylaniline-based model dyes used in the calculations, as well as the fact that the parameters used were originally optimised for dye solutions in cyclohexane, the predicted λ_{max} values correlate well with those observed for the dyes in toluene. However, the calculated oscillator strengths do not correspond well with the intensities of the dyes: values of f fail to reflect the relative differences in the areas under the absorption curves of the dyes, which can be approximated to the product of ε_{max} and half-band width.

TABLE 1

Spectral Data (λ_{max} and $\Delta\lambda_{1/2}$ in nm, ε_{max} in dm^3 mol^{-1} cm^{-1}) for the Thienyl-2-azo Dyes **1** in DMF, Ethanol and Toluene

Substituents			λ_{max}	ε_{max}	$\Delta\lambda_{1/2}$	λ_{max}	λ_{max}	*PPP-MO*
3	*4*	*5*	*(DMF)*	*(DMF)*	*(DMF)*	*(EtOH)*	*(C_7H_8)*	λ_{max}, f
CN	$-(CH_2)_3-$		536.2 ± 0.6	41 900 ± 400	92	519	517	494, 1.48
CO_2Me	$-(CH_2)_3-$		517.6 ± 0.1	34 800 ± 500	113	502	495	479, 1.56
CO_2Et	$-(CH_2)_3-$		517.1 ± 0.1	34 600 ± 200	112	503	491	479, 1.56
CN	$-(CH_2)_5-$		530.5 ± 0.3	42 900 ± 500	94	513	505	494, 1.48
CO_2Me	$-(CH_2)_5-$		500.8 ± 0.3	37 000 ± 500	102	484	470	479, 1.56
CO_2Et	$-(CH_2)_5-$		500.5 ± 0.3	35 300 ± 200	101	484	469	479, 1.56
CN	$-(CH_2)_6-$		530.9 ± 0.6	41 700 ± 200	93	514	500	494, 1.48
CN	$-(CH_2)_{10}-$		531.9 ± 0.3	42 100 ± 400	95	514	500	494, 1.48
CN	$-PhC_2H_4-$		546.4 ± 0.3	47 100 ± 300	93	528	515	498, 1.35
CN	$-C_2H_4Ph-$		568.5 ± 0.3	50 600 ± 600	106	552	538	527, 1.62
CN	Me	Me	528.6 ± 0.2	41 500 ± 500	95	511	505	494, 1.48
CO_2Me	Me	Me	499.8 ± 0.3	34 000 ± 300	102	484	471	479, 1.56
CO_2Et	Me	Me	499.9 ± 0.6	33 900 ± 300	103	483	469	479, 1.56
CO_2Me	H	Me	508.5 ± 0.3	34 000 ± 600	108	494	475	479, 1.56
CO_2Me	H	Et	510.5 ± 0.3	33 400 ± 400	108	490	475	479, 1.56
CO_2Me	H	Bu^n	510.8 ± 0.4	34 600 ± 200	110	493	476	479, 1.56
CO_2Me	H	Ph	538.8 ± 1.0	40 900 ± 300	113	522	512	518, 1.24
CO_2Me	H	Ac	552.1 ± 0.4	39 700 ± 300	116	535	518	505, 1.39
CO_2Me	Me	Ac	536.0 ± 0.1	39 600 ± 400	108	522	506	505, 1.39
CO_2Et	Me	CN	545.6 ± 0.3	42 700 ± 900	106	528	514	513, 1.67
CN	Me	CN	573.9 ± 0.3	52 500 ± 800	99	558	543	532, 1.38
$CONH_2$	H	Ph	547.2 ± 1.6	45 200 ± 700	102	538	523	518, 1.30

PPP-MO—Calculated λ_{max} (in nm) and oscillator strengths (f) for analogous *N*,*N*-diethylaniline-derived dyes.

TABLE 2

Influence of the Interchange of Ethoxycarbonyl and Cyano Groups on the Spectral Data (λ_{max} and $\Delta\lambda_{1/2}$ in nm and ε_{max} in dm^3 mol^{-1} cm^{-1}) of some Thienyl-2-azo Dyes (**1**; 4-Me) in DMF

3	*5*	λ_{max}	$\Delta\lambda_{max}$	ε_{max}	$\Delta\varepsilon_{max}$	$\Delta\lambda_{1/2}$	*Ref.*
CO_2Et	CO_2Et	529.6	—	39 100	—	107	16
CO_2Et	CN	545.6	16.0	42 700	3600	106	
CN	CO_2Et	560.8	31.2	47 400	8300	100	16
CN	CN	573.9	44.3	52 500	13 400	99	

$\Delta\lambda_{max}$ and $\Delta\varepsilon_{max}$ are the differences in λ_{max} and ε_{max}, respectively, compared to that of $X = Y = CO_2Et$.

Factors contributing to this state of affairs may be the use of a polar solvent (DMF) in the determination of ε_{max} values and the parameters having been empirically optimised for the prediction of λ_{max} rather than absorption intensity.

Spectral data for the 4,5-alkylene dyes are consistent with those observed for the 4,5-tetramethylene analogues; for example, the derivatives **1** (3-CO_2R-4,5-$(CH_2)_4$-) have λ_{max} values of 503–504 nm and ε_{max} 34 000–34 400 in DMF,[16] close to the figures listed in Table 1 for the analogous dyes.

The ring size in the **1** (3-CN-4,5-$(CH_2)_n$-) series, where $n = 4$, 5, 6 and 10, has little effect on λ_{max}, which is unsurprising given that the increase in the inductive effect of an alkyl chain falls away rapidly as it is lengthened, or on ε_{max}, where the increase in mass with ring size would be predicted to cause a slight decrease in the values, yet they were the same within experimental error limits. Curiously, **1** (3-CN-4,5-$(CH_2)_3$-) is slightly more bathochromic (5 nm in DMF) than the other dyes with larger rings; the shift is even more pronounced (14–17 nm) for the 3-CO_2Me and 3-CO_2Et analogues relative to the other alkylene dyes.

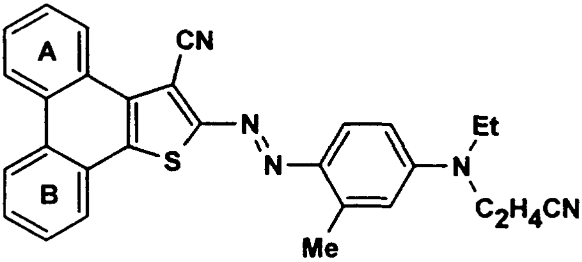
All the 3-cyano-4,5-alkylene dyes have smaller half-band widths than their corresponding 3-alkoxycarbonyl analogues (see Table 1) in agreement with the findings concerning the tetramethylene dyes;[16] however, there is little difference between the 5-cyano and 5-ethoxycarbonyl derivatives (see Table 2).

The two derivatives in which a benzene ring is fused onto **1** (3-CN-4,5-$(CH_2)_4$-) are bathochromic and hyperchromic relative to the parent dye as would be expected with an extension of conjugation (see Table 3).

The extension is most effective when the ring is connected directly to the thiophene system at the 5-position, in **1** (3-CN-4,5-C_2H_4Ph-), as opposed to the 4-position, in **1** (3-CN-4,5-PhC_2H_4-). While resonance theory is prone to error when applied to small molecules, it is more reliable when considering monoazo dyes and correctly predicts the bathochromicity of **1** (3-CN-4,5-C_2H_4Ph-) relative to its isomer on the basis of the former possessing

TABLE 3

Spectral Data in DMF (λ_{max} in nm and ε_{max} in dm^3 mol^{-1} cm^{-1}) of the Dyes Produced by Fusing Benzene Rings onto a 3-Cyano-4,5-tetramethylenethienyl-2-azo Dye



A	*B*	λ_{max}	ε_{max}	*Ref.*
x	x	531.1	42 300	16
√	x	546.4	47 100	
x	√	568.5	50 600	

more excited state canonicals than the latter; the extra forms represent the dispersal of negative charge on the benzenoid ring and consequent stabilisation of the excited state. However, PPP-MO calculations show there is virtually no charge transfer into the phenyl substituents in either derivative on excitation, although the λ_{max} values for each dye are predicted reasonably accurately.

Similarly, some closely related dyes (**1**; 3-CO_2Me-5-Ph and 3-$CONH_2$-5-Ph, respectively), albeit without the alkylene bridging, are bathochromic and hyperchromic compared to their tetramethylene analogues, in the same way as with **1** (3-CN-4,5-C_2H_4Ph-). PPP-MO calculations give reasonable predictions for the relative λ_{max} values of these phenyl-substituted derivatives (see Table 1). An allowance[16] for the interaction between the carbamyl and azo groups of **1** (3-$CONH_2$-5-Ph) did not bring about any improvement (λ_{max} 529 nm, *f* 1.34). The effect on λ_{max} of fusing benzene rings onto **1** (3-CN-4,5-$(CH_2)_4$-) is mimicked quite well despite the non-planarity of the resultant systems.

The expected general trend, predicted by resonance theory and by PPP-MO calculations, whereby bathochromism and hyperchromism result on increasing the total electron-withdrawing power of the substituents in the diazo component was observed; for example, the 3-cyano derivatives are bluer and more intense than their 3-alkoxycarbonyl analogues (see Table 1). A similar trend is shown on increasing the withdrawing strength of the 5-substituent; for instance, changing the 5-methyl group of **1** (3-CO_2Me-5-Me) to a 5-acetyl group results in a bathochromic shift in λ_{max} of 43.6 nm and intensity increase of 5600.

Additivity of substituent effects is evident in the series **1** (3-CO_2Et/CN-4-Me-5-CO_2Et/CN). Changing an ethoxycarbonyl group to a cyano group causes bathochromic shifts of 31.2 and 16.0 nm, respectively, for the 3- and 5-positions (see Table 2). The fact that a larger shift occurs when the swap is made at the 3-position suggests that there may be some relief from steric hindrance on replacing the ester function for a cyano group. Combining the replacements would be expected to result in a shift of 47.3 nm, close to the observed value of 44.3 nm. Also, within experimental error, ε_{max} values are additive.

The introduction of a methyl group into the 4-position of the thiophene ring causes a significant hypsochromic shift in the **1** (3-CO_2Me-4-R-5-Me and 3-CO_2Me-4-R-5-Ac) pairings (see Table 1); the origin of the effect would appear to be electronic as there is no reduction of ε_{max} (or significant change in half-band width) characteristic of steric hindrance. Gordon and Gregory came to the same conclusion with a carbocyclic system,[17] which would be more likely to suffer from overcrowding since the thiophene system has larger external bond angles. Hindrance between methyl groups would not be expected to affect colour as they do not exert a mesomeric effect, so the shift is likely to have an electronic origin. Another possibility may be that the presence of the methyl group brings about increased disruption of ground state solvation relative to excited state solvation; however, the fact that the differences between the derivative with the methyl subsituent and that without in each pairing remain significant in both polar (DMF, ethanol) and non-polar (toluene) solvents does not support this explanation.

A hypsochromic shift (6.7 nm) is also observed on the introduction of an alkyl substituent into the 4-position by joining the free end of the butyl group in **1** (3-CO_2Me-5-Bu^n) to the thiophene ring to create **1** (3-CO_2Me-4,5-$(CH_2)_4$-); again, ε_{max} was unaffected within experimental error, the dyes having values of 34 600 and 34 400, respectively. Reducing the +I effect of the 4-methyl substituent by addition of an ester group to create a 4-ethoxycarbonylmethyl substituent has been found to cause bathochromic shifts in line with theory.[16]

Solvatochromism

All the dyes exhibit positive solvatochromism as expected for monoazo chromophores.[18] 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 stronger electron acceptors 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 1). The dyes of type **1** (3-CO_2R) and **1** (3-CN) typically give shifts of *ca.* 30 nm in DMF compared to solutions in toluene within a range of 19–36 nm. There did not appear to be any correlation with the substituent pattern in the 4- and 5-positions (for example, in the 3-CN/CO_2R-4-Me-5-CN/CO_2R series) or any guarantee of a 3-cyano derivative having greater solvatochromic shifts than its 3-alkoxycarbonyl analogue.

Halochromism

Many of the thienyl-2-azo dyes display positive halochromism, i.e. an increase in λ_{max} of the ethanolic solution on addition of hydrochloric acid (see Table 4); those possessing just one moderately electron-withdrawing group give large shifts, for example, the 3-alkoxycarbonyl-(4,)5-alkyl(ene) derivatives, such as **1** (3-CO_2Me-5-Me) whose ethanolic solution turned from yellow–red (λ_{max} 494 nm) to blue (λ_{max} 592 nm) on addition of acid. The alkylene derivatives did not appear to be very stable in acidic solution: **1** (3-CO_2Me-4,5-$(CH_2)_4$-) and its ethyl ester analogue did give an observable azonium species, but only at a relatively high acidity which seemed to be detrimental to the chromophore, the solutions fading rapidly. However, closely related derivatives (for example, the 5-alkyl series) were more stable; these apparently minor changes having an effect on stability have also been noted in connection with the diazotisation of the corresponding diazo components.[20] No azonium species were identified in the **1** (3-CN-4,5-$(CH_2)_n$-) series; the formation of peaks at *ca.* 410–425 nm was noted at high acidities, the colour of the solutions fading rapidly. Marsden[19] also observed this behaviour with some *o*-substituted thienyl-2-azo dyes and ascribed the absorption bands to dicationic species. The other tetramethylene derivatives appeared not to give an azonium species, presumably because of steric hindrance making protonation energetically unfavourable in the cases of **1** (3-COPh-4,5-$(CH_2)_4$-) and its thienoyl analogue. The behaviour of the 3-carbamyl derivative (and its 5-phenyl analogue) may be a result of interaction between the amide protons and the relevant azo nitrogen atom.

Addition of a second moderately electron-withdrawing group into the 5-position considerably reduces the degree of halochromism. As the electron-accepting strength of the 5-substituent is increased, the size of the shift is lowered; for example, the introduction of a 5-ethoxycarbonyl group into **1** (3-CO_2Et-4,5-Me) produces a shift decrease of 78 nm.

Additivity of substituent effects is apparent in the **1** (3,5-CN/CO_2Et-4-Me) series (see Table 4). Exchanging a 5-carboxyethyl group for a cyano group reduces the halochromic shift by 27 nm, the same change at the 3-position resulting in a reduction of 38 nm. Both changes would be expected to cause a total decrease of 65 nm, so that the positive halochromism ($\Delta\lambda$ 49 nm) of **1** (3,5-CO_2Et-4-Me) should become the negative halochromism ($\Delta\lambda$ -16 nm) of **1** (3,5-CN-4-Me), which actually shows a shift of -17 nm.

TABLE 4
Spectral Data for the Thienyl-2-azo Dyes **1** in Ethanol with and without Hydrochloric Acid

Substituents 3	4	5	λ_{max} *(EtOH)/nm*	λ_{max} *(HCl/EtOH)/nm*	$\Delta\lambda$*/ nm*
CN	-$(CH_2)_4$-		514	—*	—
CO_2Me	-$(CH_2)_4$-		486	605**	119
CO_2Et	-$(CH_2)_4$-		490	605**	115
COPh	-$(CH_2)_4$-		490	—*	—
COTh	-$(CH_2)_4$-		490	—*	—
$CONH_2$	-$(CH_2)_4$-		507	—*	—
CO_2Et	Me	Me	483	610	127
CO_2Et	Me	CO_2Et	510	559	49
CO_2Et	Me	CN	528	550	22
CN	Me	CO_2Et	542	553	11
CN	Me	CN	558	541	-17
CO_2Et	CH_2CO_2Et	CO_2Et	518	551	33
CN	CH_2CO_2Et	CO_2Et	546	560	14
CO_2Me	H	Me	494	592	98
CO_2Me	H	Et	490	592	102
CO_2Me	H	Bu^n	493	595	102
CO_2Me	H	Ph	522	618	96
CO_2Me	H	Ac	535	553	18
CO_2Me	Me	Ac	522	553	31

*Azonium peak not observed; **colour faded quickly.

EXPERIMENTAL

The synthesis and purification of the thienyl-2-azo dyes **1** have been described previously.[16,20] The UV–visible absorption spectra of the dye solutions were measured in quartz cells on a Philips PU8720 spectrophotometer (scan speed 50 nm min^{-1}).

CONCLUSIONS

As increasingly electron-withdrawing groups are located onto the thienyl-2-azo dyes, blue shifts are obtained in agreement with resonance theory and PPP-MO calculations. Bathochromism is accompanied by hyperchromism; 3-cyano derivatives have larger ε_{max} values and smaller half-band widths than their 3-alkoxycarbonyl analogues. The dyes exhibit positive solvatochromism as anticipated by resonance theory. Increasing the electron-accepting strength of the thiophene residue results in the expected reduction in size of the positive halochromic behaviour of the dyes, the most strongly withdrawing component giving a negative halochromic shift.

ACKNOWLEDGEMENT

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

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