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Unexpected Bathochromic Shifts in the Visible Absorption Spectra of Arylazo Dyes Containing the *ortho-N*-pyridinium–nitro Substituent Combination. Correlation of Solvatochromic Shifts with Kamlet–Taft Solvent Polarity Parameters

Michael G. Hutchings

ICI Specialties Research Centre, Blackley, Manchester M9 3DA, UK

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ABSTRACT

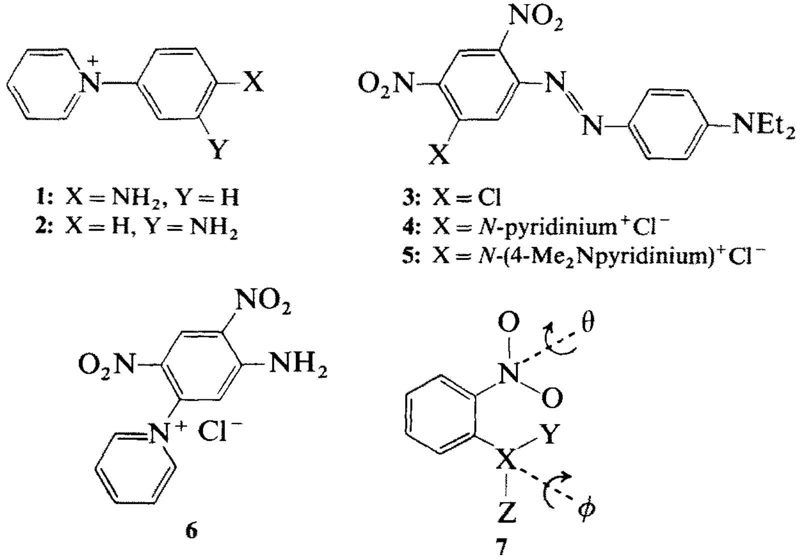
*A combination of 4-nitro and 5-*N*-pyridinium groups in a donor-substituted azobenzene leads to an unexpected bathochromic shift in visible absorption maximum compared with the 5-chloro precursor, despite increased steric interaction between the two substituents. This behaviour probably derives from an intramolecular polarisation effect of the cationic pyridinium group acting on the adjacent nitro group. Molecular orbital calculations support this conclusion. The visible spectra differences in various solvents can be related to solvent dipolarity as reflected by the Kamlet-Taft π^* solvent parameter. There is no relationship with H-bonding parameters.*

1 INTRODUCTION

If two substituents are present in a dyestuff molecule, it is frequently observed that their effect on the visible absorption maximum is the sum of the influence of each of the substituents individually. This additivity of substituent effects has been demonstrated in detail for chloro and sulpho substituents in five different azo chromogens.[1] More generally, a compilation of substituent increments has been deduced for a large variety of dyes based on the diphenylazo chromogen.[2] Exceptions to additivity usually derive from steric interaction between two substituents, or between a substituent and part of the chromogen. A common example is found in 2,6-disubstituted azobenzenes, where nonplanarity engendered by van der Waals' clash between the 6-substituent and azo-nitrogen leads to a hypsochromic shift in the absorption maximum and a decrease in extinction coefficient.[3,4] Other more subtle features deriving from steric interactions have been discovered in chlorosulpho-disubstituted azo systems.[1] Here again the resulting effects are hypsochromic shifts.

Far less common are examples of azobenzenes where steric interaction between two substituents results in a *bathochromic* shift in the absorption maximum, compared with simple additivity. Such a result is particularly interesting technically, since it is a frequent objective to drive a chromogen towards absorption in the red region of the visible spectrum.

Polyacrylonitrile (PAN) is usually dyed with cationic dyestuffs. These usually conform to two limiting types: either (a) the positive charge is fully delocalised and plays a significant role in the spectral properties of the chromogen, such as in cyanines or triarylcarbenium ions, or (b) the positive charge is appended to the chromogen via an insulating group, and thus exerts minimal influence on the absorption maximum. Our own past interest in this area led us to seek structures which are intermediate between these two types. In these the charge would not be formally delocalised into the chromogen but could nevertheless influence the colour of the molecule. An example of such an intermediate situation is that of diarylazo derivatives containing an *N*-pyridinium group in the diazo component.[5] Dyes based on **1** and **2** have colour properties very similar to analogues derived from the



1: $X = NH_2, Y = H$
2: $X = H, Y = NH_2$

3: $X = Cl$
4: $X = N$-pyridinium$^+Cl^-$
5: $X = N$-(4-Me_2Npyridinium)$^+Cl^-$

6

7

Scheme 1

corresponding nitroanilines. Thus the *N*-pyridinium group is affecting the colour of the molecule appreciably, despite the fact that the pendant cationic charge cannot be formally delocalised into the donor-substituted diarylazo chromogen.

In this paper results are presented for a new substituent combination in the common azobenzene chromogen, which leads to an appreciable—but unexpected—bathochromic shift in absorption. Naïve consideration of steric interactions might have been anticipated to predict the opposite.

This new system is a development of **2**, where nitro groups are now also present in the molecule **4**. These groups facilitate introduction of the *N*-pyridinium group by activating the aromatic chlorine atom in **3** towards nucleophilic displacement. The dye **4** gives a bright mid-blue shade on PAN. Possible underlying rationale are presented for the observed behaviour, as well as a correlation of the solvatochromism of dyes **3**, **4** and **5** with Kamlet–Taft solvent polarity parameters.

2 EXPERIMENTAL

Starting materials were available either commercially or from the ICI specimen collection. CAUTION: *Several of the chlorodinitro derivatives used in this study are skin sensitisers and extremely dermatitic.* Visible spectra were recorded on a Unicam SP8000 instrument in purified solvents. ^{1}H-NMR spectra were recorded on a Varian HA100 spectrometer using TMS as internal standard. IR spectra were taken as nujol mulls on a Perkin–Elmer 297 instrument. Statistical analyses were carried out using the commercial Statistical Analysis System (SAS) software.[6] Molecular orbital calculations were carried out using the ICI CNDOVSB semiempirical MO program, based on in-house parameterisation of the CNDO/S model.[7] Input structures were prepared on the ICI molecular modelling system VIKING.

2.1 2,4-Dinitro-5-*N*-pyridiniumaniline chloride hemihydrate (6)

2,4-Dinitro-5-chloroaniline (16·1 g) was heated with pyridine (50 ml) on an oil bath at 120°C for 6 h. After cooling, brown crystals were filtered off, washed and pumped. Recrystallisation from methanol gave a yellow product (18·1 g, 82%; m.p. >250°C). Found: C, 43·3%; H, 3·2%; N, 18·2%; $C_{11}H_9N_4O_4Cl \cdot 0{\cdot}5H_2O$ requires C, 43·20%; H, 3·30%; N, 18·33%. For ^{1}H-NMR data see Table 1. Attempts to diazotise and couple this product led only to complex mixtures of decomposition products, under all conditions tried.

2.2 Diazotisation of 2,4-dinitro-5-chloroaniline and coupling with *N,N*-diethylaniline

The aniline (21·8 g) was added portionwise to nitrosyl sulphuric acid ($NaNO_2$, 7·0 g, in H_2SO_4, 160 ml) at 20°C or lower, and allowed to stir for a further 1 h at 20°C. *N,N*-Diethylaniline (14·9 g), dissolved in aqueous HCl at 0 to 5°C, was treated with the diazonium salt solution, and stirred for 1 h after buffering with sodium acetate until neutral to Congo red. The azo dye (**3**) was filtered off, washed with water, recrystallised from butanol and dried (25·6 g, 70%; m.p. 164–164·5°C). Found: C, 51·3%; H, 4·1%; N, 18·6%; $C_{16}H_{16}N_5O_4Cl$ requires C, 51·13%; H, 4·26%; N, 18·64%. For ^{1}H-NMR data see Table 1.

2.3 Quaternisation of 2,4-dinitro-5-chloroaniline-derived dye with pyridine

The azo dye precursor (**3**) (100 mg) was heated in DMSO (7·5 ml) with pyridine (2 ml) for 2 h at 90°C. After cooling, the reaction mixture was poured into water and treated with ethyl ether or chloroform to remove traces of starting material. Precipitation of the product **4** was induced by addition of brine, and the product was filtered off and washed (85 mg, 70%; m.p. 145°C). For ^{1}H-NMR data see Table 1.

Dye **5** was prepared in analogous fashion (m.p. 184–186°C).

3 RESULTS AND DISCUSSION

The dye **4** was best prepared by reacting its chloro precursor **3** with pyridine in hot DMSO. A trace of unreacted starting material was the only impurity and could be removed by treatment of the product solution with a nonpolar organic solvent. Quaternisation in pyridine itself also succeeded, but water in the system caused the appearance of other impurities. This behaviour was particularly marked when dilute pyridine solutions of **4** were prepared for visible spectroscopy. Decomposition rapidly occurred, presumably due to base (pyridine)-catalysed hydrolysis via the small amount of water present in the dye, solvating the anion. The related dye **5** was prepared from 4-*N,N*-dimethylaminopyridine and **3** in an analogous manner. This appears to be more stable, although there is evidence for hydrolysis (see below).

Attempts to diazotise and couple the prequaternised aniline (**6**) led mainly to decomposition products, although TLC revealed the presence of a small amount of blue dye corresponding to the same product (**4**) obtained by postquaternisation of the chloro-substituted azo dye **3**.

TABLE 1
^{1}H-NMR Properties of Dinitro Derivatives

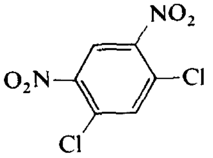
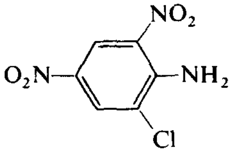
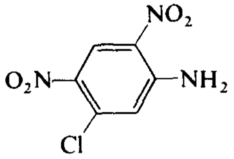
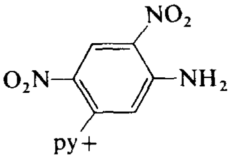
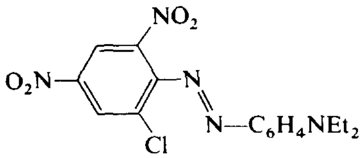
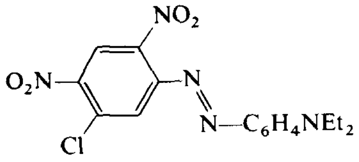
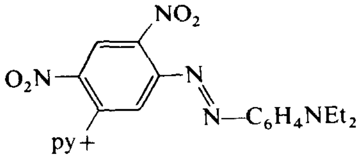
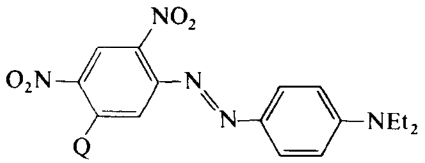
Compound	*Solvent*	*δ ppm (J Hz)*		
		A	*B*	*Others*
	d_6-DMSO	8·75 (0·0)	8·22 (0·0)	
	d_6-DMSO	8·61 (3·0)	8·23 (3·0)	8·06 (s, exch)
	d_6-DMSO	8·60 (0·0)	7·06 (0·0)	8·6 (s, exch)
	d_6-DMSO	9·15 (0·0)	7·35 (0·0)	8·9 (m, 5H) 8·2 (t, 1H)
	$CDCl_3$	8·35	8·35	7·73 (d, J = 9, 2H) 6·61 (d, J = 9, 2H) 3·45 (q, J = 7, 4H) 1·24 (t, J = 7, 6H)
	$CDCl_3$	8·27 (0·0)	7·74 (0·0)	7·66 (d, J = 9, 2H) 6·55 (d, J = 9, 2H) 3·44 (q, J = 7, 4H) 1·23 (t, J = 7, 6H)
	d_6-DMSO	9·07 (0·0)	8·36 (0·0)	9·37 (d, J = 6, 2H) 8·86 (m, 1H) 8·36 (m, 2H) 7·69 (d, J = 9, 2H) 6·86 (d, J = 9, 2H) 3·5 (m) 1·18 (t, J = 7, 6H)

TABLE 2
Solvent Influence on Absorption Maxima



Solvent	*Solvent parameters*				*Q = Cl* (**3**)			*Q* = N-*pyridinium* (**4**)				*Q = 4-dimethylamino*-N-*pyridinium* (**5**)			
	α	β	π^*	δ	λ_{max} (ε)	$\Delta\lambda^a$	*E* (*eV*)	λ_{max} (ε)	$\Delta\lambda^a$	$\Delta\lambda^b$	*E* (*eV*)	λ_{max} (ε)	$\Delta\lambda^a$	$\Delta\lambda^c$	*E* (*eV*)
MeOH	0·93	0·62	0·6	0	531 (35 200)	—	2·3352	587 (41 100)	—	56	2·1124	573 (48 200)	—	42	2·1641
Me_2CO	0·08	0·48	0·71	0	535	4	2·3178	588	1	53	2·1088	577	4	42	2·1491
DMF	0	0·69	0·88	0	546	15	2·2711	595	8	49	2·0840	583	10	37	2·1269
MeCN	0·19	0·31	0·75	0	538	9	2·3048	598	11	60	2·0736	581	8	43	2·1343
H_2O	1·17	0·18	1·09	0	Insoluble			618	31		2·0065	600	27		2·0667
$CHCl_3$	0·44	0·00	0·58	0·5	542	11	2·2878	619	32	77	2·0032	Insoluble			
NH_2CHO	0·71	0·55	0·97	0	565	34	2·1947	619	32	54	2·0032	601	28	36	2·0632
Cyclohexane	0	0	0	0	505	−26	2·4555	Insoluble				Insoluble			
Pyridine	0	0·64	0·87	1	550	19	2·2546	(524 decomposition)				600	27	50	2·0667
10% HOAc in H_2O								620 (28 500) and 490 (30 900)				600 (21 000) and 490 (39 300)			
2N HCl								488 (46 500)							

[a] λ(solvent) − λ(MeOH).
[b] λ(**4**) − λ(**3**).
[c] λ(**5**) − λ(**3**).

In the ^{1}H-NMR spectrum of molecule **4** the presence of two uncoupled singlets for the aromatic protons from the diazo component showed their continued presence in a 1,4-relationship. Data on closely related model species clearly revealed a coupling constant of 3 Hz for a *meta* orientation of protons (Table 1). The NMR spectra of dyes **4** and **5** also revealed the presence of water.

The visible spectral properties of dyes **3**, **4** and **5** in a variety of solvents, and associated data, are recorded in Table 2. The most striking observation central to this report is the bathochromic shift of the quaternary dyes **4** and **5**, which are blue in solution, compared with their chloro-precursor **3**, which is reddish-violet. This shift was particularly surprising. However, before developing the discussion, it is shown that the absorption maximum of **4** is indeed more bathochromic than expected on simple substituent additivity arguments. Absorption maxima data for systems relevant to estimation of the 'expected' absorption maximum of **4** in methanol are recorded in Table 3. The assumption of substituent additivity gives rise to the following:

(a) A 3-*N*-pyridinium substituent in isolation in the diazo component of dye **2** has a bathochromic effect of +41 nm compared with the unsubstituted dye.

(b) Thus, based on the value for the 2,4-dinitro derivative (Table 3), additivity of substituent influences leads to an estimated absorption maximum for **4** of 571 nm. This compares with the experimentally observed value of 587 nm, i.e. *+16 nm more bathochromic* than anticipated based on additivity.

(c) In fact, steric interactions between the 4-nitro and 5-*N*-pyridinium groups would be expected to lead to a decrease in planarity of the nitro group and a further resulting hypsochromic increment. The magnitude of this can be estimated as follows.

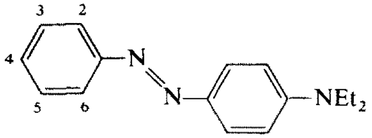
(d) A 3-chloro substituent in a simple 4′-diethylaminoazobenzene induces a bathochromic shift of +5 nm.

(e) The same substituent leads to a bathochromic shift of only +1 nm when introduced into the 5-position of the 2,4-dinitroaniline-derived dye. The difference of −4 nm is assumed to be lost through the 4-nitro group being forced out of plane by the adjacent 5-chloro-group. X-ray structural data show that chloro *ortho* to nitro causes torsion about the aryl-nitro C—N bond of 33–40° (three structures).[8,9] (This derivation assumes no difference in effect between chloro in the 3- and 5-positions of azobenzene. There is some indication that there might in fact be a small difference where these positions are rendered distinguishable by a 2-substituent, but this is only slight.[1])

(f) The steric influence of *N*-pyridinium adjacent to nitro is unknown.

TABLE 3

Experimental Absorption Maxima (nm) of Dyes Relevant to This Study



Substituents	λ_{max}	$\Delta\lambda^a$	*Reference*
—	415	—	2
2,4-$(NO_2)_2$	530	115	2
3-Cl	420	5	ICI data
2,4-$(NO_2)_2$-5-Cl	531	116	This work
3-py^+	456	41	5
2,4-$(NO_2)_2$-5-py^+	587	172	This work

[a] Difference between substituted and unsubstituted dyes.

Analysis of the structures of a variety of molecules of general structure **7** has shown that the main generalisation is that the sum of the torsion angles θ and ϕ is roughly constant at 90°.[10] However, a majority of structures have θ and ϕ values in the range 30–60°. It can, therefore, be hypothesised that the degree of torsion of the 4-nitro group in **4** is at least as much as in **3**, and would thus lead to a hypsochromic shift of 4 nm or greater.

Thus overall dye **4** is at least 20 nm more bathochromic than might be anticipated. Energetically, this value is quite small, but practically it results in a reddish-violet dye (**3**) being rendered blue, which is technically very useful.

Despite the possibly increased steric interactions present in **4** and **5** compared with **3**, and the resulting deplanarisation of the molecules' structures, the extinction coefficients are also increased compared with **3** (in methanol at least; see Table 2). Half-bandwidths are about the same. Again this points to some abnormal effect, since deplanarisation in such a chromogen normally leads to a decrease in extinction coefficient.[3,4]

Once it is accepted that the bathochromic effect of this substituent combination is higher than expected, it remains to suggest its origin. It is shown in the following section (3.1) that solvent effects are not responsible.

It is believed that the effect derives from some specific, if unanticipated, interaction between the *N*-pyridinium group and its *o*-nitro group. For example, the positive charge of the pyridinium group could exert a through-space pole–dipole electron-withdrawing effect on the nearby nitro group, rendering the latter even more electronegative than it already is. A more bathochromic effect would result. In effect, this mechanism is equivalent to the pyridinium group acting as an intramolecular solvating group on the nitro substituent.

A prediction of this simple analysis is that a donor-substituted pyridinium group such as 4-dimethylaminopyridinium would have a less bathochromic influence, since the cationic charge would be more delocalised and, on average, would be more remote from, and interact less with, the nitro group. In fact, for **5** the shift on quaternisation is about 12 nm less bathochromic than for **4** in all the solvents tried (Table 2), consistent with the model.

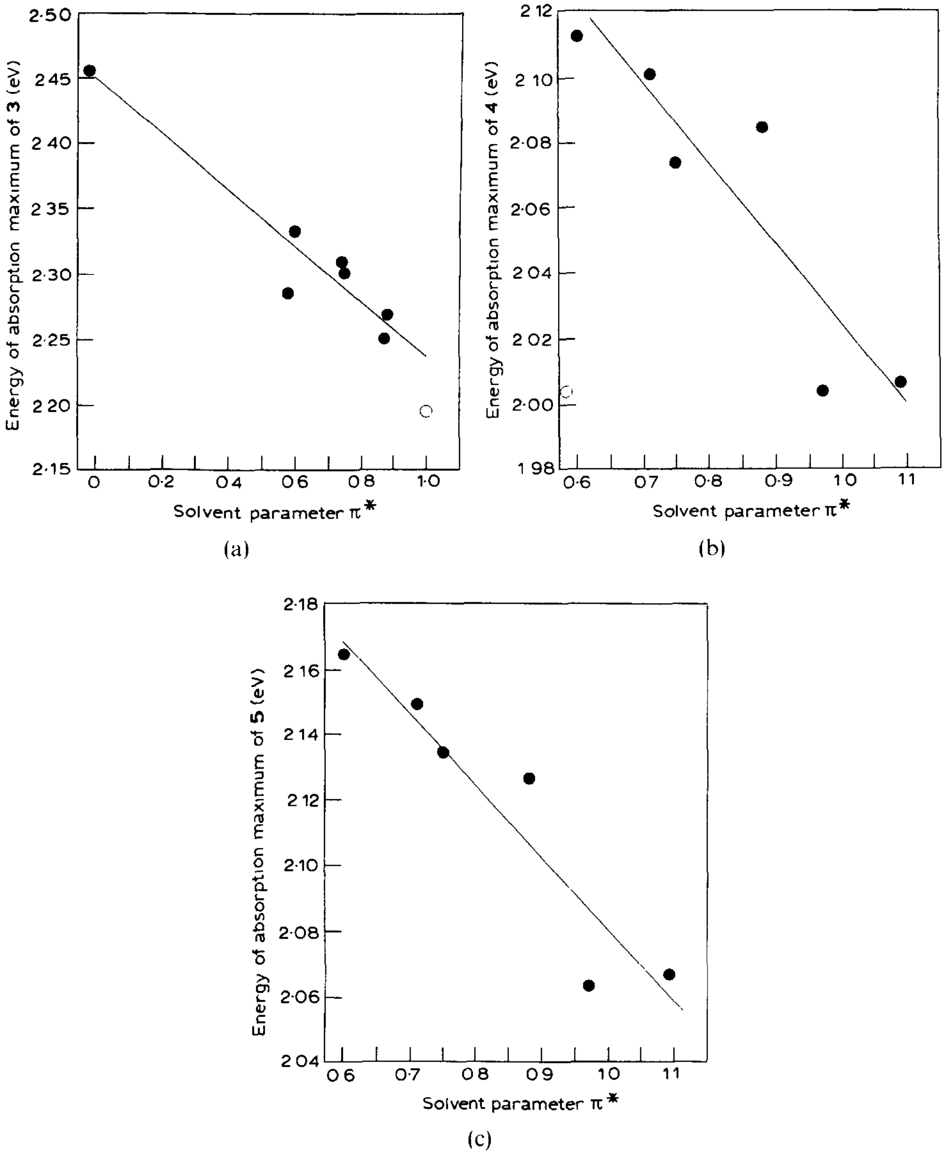
This mechanism was further investigated by means of molecular orbital (MO) calculations at the CNDO/S level (see Section 2). 4-Dimethylamino-4′-nitroazobenzene, protonated on a nitro oxygen atom with varying O—H bond lengths, was taken as a model of a nitroazobenzene interacting to varying degrees with a cationic centre. As the O—H bond length decreases from 2 to 0·96 Å, a bathochromic shift of 16 nm was calculated. This result is consistent with the observation that a cationic centre nearer to nitro leads to a more bathochromic shift.

A second explanation for the bathochromic effect was considered based on frontier orbital interactions between the pyridinium group and the adjacent nitro. However, no convincing explanation could be derived within the simple frontier orbital formalism adopted. Details are therefore not provided here. Further MO approaches are planned.

3.1 Solvatochromism

In order to understand better the shifts in absorption maxima for these three dyes in different solvents, correlations between the transition energies ($E(\mathrm{eV}) = 1240/\lambda(\mathrm{nm})$) and Kamlet-Taft solvent parameters have been carried out. The relevant parameters are also recorded in Table 2, and have the following meanings:[11,12] α is a reflection of the H-bond donor strength of the solvent (zero for those solvents with no acidic X-H groups); β quantifies the H-bond acceptor strength (basicity); π^* is the general dipolarity of the solvent (the higher the value, the more polar the solvent); and δ is a polarisability correction factor for aromatic solvents and those containing more than one chlorine atom.

A plot of E versus π^* for the neutral chloro dye **3** is given in Fig. 1(a). This shows a reasonable correlation between the two variables, confirmed by statistical analysis (entry 1; Table 4). Examination of Cook's D statistic[6] shows that the formamide result is influencing the correlation more than any other (high leverage), so a correlation was run omitting this value with some improvement (entry 2). Inclusion of the polarisability correction factor, δ, improved the correlation further (entry 3), but it is not clear whether this is



(a)

(b)

(c)

Fig. 1. Plot of absorption maximum energy against π^*. In each case the straight line fit is that given after selected solvents (○) have been deleted (see text). (a) Dye **3**; (b) dye **4**; (c) dye **5**.

reflecting a real effect or is purely statistical. (The δ parameter is not regarded as appropriate for positive solvatochromic molecules such as **3**.[11,12]) Inclusion of the H-bonding parameter α with π^* gave no improvement in correlation (entry 4). However, the H-bond acceptor (or basicity), parameter β, was statistically significant (entry 5). Again this is probably a statistical

TABLE 4

Coefficients and Statistics[a] for Correlation Analyses of the Form

$$E(\text{eV}) = C_0 + C_1\pi^* + C_2\delta + C_3\alpha + C_4\beta$$

Entry	C_0	C_1	C_2	C_3	C_4	n	R	s	F
Dye **3** (full data)									
1	2·460 (±0·024)	−0·235 (±0·034)				8	0·943	0·027	49·1
Dye **3** (less $HCONH_2$)									
2	2·450 (±0·021)	−0·211 (±0·030)				7	0·953	0·022	49·8
3	2·449 (±0·024)	−0·195 (±0·024)	−0·039 (±0·019)			7	0·978	0·017	43·5
4	2·452 (±0·024)	−0·211 (±0·033)		−0·005 (±0·029)		7	0·954	0·025	20·1
5	2·454 (±0·018)	−0·258 (±0·037)			0·065 (±0·038)	7	0·973	0·019	35·8
Dye **4** (full data)									
6	2·152 (±0·085)	−0·121 (±0·104)				7	0·46	0·049	1·3
Dye **4** (less $CHCl_3$)									
7	2·268 (±0·049)	−0·243 (±0·058)				6	0·904	0·023	17·9
8	2·261 (±0·049)	−0·221 (±0·061)		−0·023 (±0·022)		6	0·931	0·023	9·7
9	2·245 (±0·080)	−0·232 (±0·072)			0·026 (±0·067)	6	0·909	0·026	7·1
Dye **5** (full data)									
10	2·303 (±0·048)	−0·230 (±0·056)				7	0·88	0·023	16·7
Dye **5** (less pyridine)									
11	2·302 (±0·034)	−0·221 (±0·040)				6	0·940	0·016	30·5
12	2·298 (±0·036)	−0·209 (±0·045)		−0·014 (±0·016)		6	0·952	0·017	14·4
13	2·301 (±0·057)	−0·221 (±0·051)			0·002 (±0·048)	6	0·940	0·019	11·4

[a] n = number of data points; R = (multiple) correlation coefficient; s = root mean square error (eV); F = Fisher's F statistic.

artefact, since there are no H-bond donor sites in **3**, and it is difficult to see how solvent basicity should influence the spectra of **3** otherwise.

The main conclusion is that solvent dipolarity, as reflected by π^*, goes a long way to explaining quantitatively the solvatochromism observed for **3**. This result is what would be anticipated.

(The π^* parameter values were derived from the solvatochromic behaviour of a series of aromatic compounds, most bearing a nitro group. An alternative set of π^*_{azo} parameters has been derived more recently based on the solvatochromism of azo merocyanine dyes.[13] However, correlation of π^*_{azo} with E for **3** was inferior to that with π^*.)

At the outset it was not known if a similar treatment of the solvatochromism of dyes **4** and **5** would be appropriate, for three reasons. Firstly, the molecules are formally charged and this could influence interaction with solvent in an unpredictable manner. Secondly, interaction of the chloride counter anion with the cationic dye could be significant (e.g. close ion pairing in the less polar solvents). Thirdly, this anion is hydrated, and the presence of the small amount of water could mask the inherent effects of the bulk solvent. As will now be shown, a correlation with π^* is indeed possible for the visible spectra of **4** and **5**, if certain assumptions are allowed.

Figures 1(b) and (c) show plots for the absorption energies of **4** and **5**, respectively, against π^*. In these cases the insolubility of the dyes in anything other than quite polar solvents restricts the extent of the correlations. While it is apparent that the spectra of dye **5** correlate reasonably with π^* (entry 10; Table 4), the data for dye **4** correlate far less well (entry 6). In the case of dye **5** the statistics show that pyridine is the solvent most out of line. The adventitious presence of water in the solvent is suspected. Omission of this solvent point leads to improved statistics (entry 11). Furthermore, neither of the H-bonding parameters α or β makes a statistically significant improvement to the correlation (entries 12 and 13). Again solvent dipolarity (π^*) seems to give an acceptable rationalisation for the solvatochromism of **5**.

Given the small structural differences between dyes **4** and **5**, it was believed that the data for **4** should behave similarly to that for **5**, notwithstanding the initial poor correlation. In the case of dye **4** the absorption maximum recorded in chloroform is abnormally bathochromic. Several explanations for this behaviour are possible, all derived from the relatively nonpolar nature of chloroform compared with the other solvents used. Firstly, ion pairing could occur. This in itself might affect the absorption energetics of the dye. Moreover, if the chloride anion was in close proximity to the dye cation, so also would its associated solvent water. (^{1}H-NMR analysis of the dye indicates water of crystallisation—see above.) This in turn could simultaneously solvate the dye molecule, so that the local environment of the chromogen might be more nearly aqueous than chloroform. This explanation is particularly attractive, in that the absorption maxima of **4** in water and chloroform are almost the same. A third possibility is that the dye molecules might be aggregating (dimers or oligomers) in the relatively nonpolar chloroform. The spectrum would again be inconsistent with that expected for a monomeric molecule.

Whatever the underlying physical behaviour of **4** in chloroform, the datum point for this solvent could be justifiably omitted from the correlation analysis. A reasonable correlation with π^* then results (entry 7). As with the analogue **5**, inclusion of H-bonding parameters α and β led to no improvement in the correlation (entries 8 and 9).

To get a better understanding of the solvatochromism for these dyes it would be necessary to run spectra in more solvents. However, this was never the main goal of this short solvatochromic study. Rather it was to attempt to relate the visible spectral behaviour of the cationic dyes **4** and **5** to that of the neutral precursor **3**. This has been achieved with the data presented, leading to one main conclusion: the sensitivity of visible absorption energy to solvent dipolarity (π^*) is essentially the same for all three molecules (cf. coefficient of π^* for entries 2, 7 and 11 in Table 4). It is therefore concluded that the exceptional bathochromic absorptions of **4** and **5** compared with **3** are *not* due to specific solvation differences between the cationic and neutral dyes.

Both dyes **4** and **5** are largely protonated in 10% aqueous acetic acid, with a hypsochromic shift of −130 nm (**4**) or −110 nm (**5**) (Table 2) for the azo-protonated dyes. This species alone exists for **4** in 2N hydrochloric acid solution (Table 2).

4 CONCLUSION

The *N*-pyridinium substituent *ortho* to 4-nitro in a 4′-donor-substituted azobenzene has an unexpectedly high bathochromic effect. This is due to specific interaction between the two substituents, rather than any intermolecular solvation effect. Although this discussion has concentrated on the two molecules **4** and **5**, the same behaviour has been noted for nine other azo dyes which are constrained to exist in the azo tautomeric form. A single example of a hydrazo tautomer analogous to **3** and **4** (2-naphthol coupling component) showed no anomalous bathochromic shift when the *N*-pyridinium group was introduced.

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