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Thermodynamic Study of Solvent and Substituent Effects on 4-Substituted Aminoazobenzenes

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SUMMARY

Proton dissociation equilibria of various 4-substituted aminoazobenzenes have been studied as a function of temperature. The corresponding thermodynamic functions ΔG^0, ΔH^0, and ΔS^0 have been calculated. Azonium–ammonium tautomeric equilibria of the monoprotonated dyes have also been investigated. The experimental data have been interpreted in terms of linear free energy relationships. Analysis of the solvatochromism of these dyes has led to the determination of some specific interactions with solvents, which, together with electronic factors, can well rationalize many aspects of the behaviour of these molecules.

1 INTRODUCTION

The widespread interest in azo dyes is due to many factors. They are valuable dyes for polyesters in view of their ready availability, cheapness and good stability towards both light and oxidation; they find extensive application in analytical chemistry as acid–base, redox and metallochromic indicators and they are of interest from a theoretical aspect in view of the sensitivity of their physical and chemical properties to changes in the substituents and in the environment, as well as to other perturbing agents.[1,2]

We have studied the behaviour of 4-diethylaminoazobenzenes, especially in relation to their interactions with the medium. In particular, our investigations have been carried out on acid–base and tautomeric equilibria,[3] solvent and substituent effects on electronic spectra[4] and on

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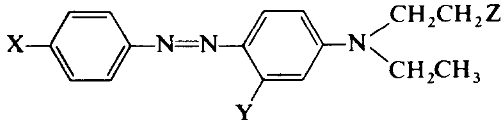
TABLE 1
Dyes of General Formula



Dye	*Substituent*		
	X	*Y*	*Z*
I	H	H	H
II	OCH_3	H	H
III	CO_2H	H	H
IV	CN	H	H
V	NO_2	H	H
VI	H	H	OH
VII	OCH_3	H	OH
VIII	CO_2H	H	OH
IX	CN	H	OH
X	NO_2	H	OH
XI	H	OC_2H_5	H
XII	OCH_3	OC_2H_5	H
XIII	CO_2H	OC_2H_5	H
XIV	CO_2H	CH_3	H
XV	CO_2H	H	$OCOCH_3$
XVI	H	H	$OCOCH_3$
XVII	H	H	CN
XVIII	OCH_3	H	CN
XIX	CN	H	CN
XX	NO_2	H	CN

thermal *cis–trans* isomerization of these compounds,[5] in order to establish general structure–reactivity patterns.

In this paper we have extended our previous studies on model compounds to a larger group of these dyes involving compounds of more direct commercial interest. The compounds studied, together with, for comparison, compounds from our previous studies, are shown in Table 1. Their acid–base properties and solvent effects on their electronic spectra have been evaluated.

2 EXPERIMENTAL

2.1 Materials

All the products were kindly supplied by ACNA S.p.A. and purified by repeated crystallization from 1-butanol. Spectrograde solvents were used and, if necessary, purified by standard techniques.[6]

2.2 Measurements

pK_a values were determined by absorption spectroscopy in the visible region, according to a standard technique.[7] A Perkin–Elmer model 552S spectrophotometer, equipped with a thermostated cell compartment ($\pm 0{\cdot}05$°C), was used. Dye concentrations were 3×10^{-5}–5×10^{-5} M and the linearity of the absorbance–concentration plot for each species was verified over the concentration range 5×10^{-6} to 5×10^{-3} M. In the pH range 0–10 the solvent adopted for pK_a measurements was 20 wt% aqueous methanol, whilst measurements at higher acidities were carried out in aqueous sulphuric acid solutions (up to 96 wt% H_2SO_4). In aqueous methanol the difference between the measured pH and pa_H^* ($= -\log_{10} a_H^*$, a_H^* being the activity of hydrogen ions referred to the standard state in the mixed solvent[8]) was considered to be $-0{\cdot}06$ pH units at 298·15 K;[8] H_0 values were taken from the literature.[9] Buffers at different pa_H^* and at constant ionic strength ($I = 0{\cdot}045$ M) were prepared by mixing, in appropriate ratios, aqueous alcoholic solutions (i) and (ii) [(i) 0·025 M-NaOAc–0·025 M-KCl; (ii) 0·05 M-KCl–0·1 M-HCl] with an aqueous methanol solution of the substrate. Mean ionic activity coefficients, $\gamma_\pm$, were estimated from the Debye–Hückel approximation

$$-\log \gamma_\pm = \frac{1{\cdot}8123 \times 10^6 I^{1/2}}{(DT)^{1/2}[1 + 50{\cdot}288 \times 10^8 (DT)^{-1/2} a_i I^{1/2}]} \qquad (1)$$

where D is the dielectric constant of the solvent, T is absolute temperature, and a_i is the distance of closest approach of ions (taken as 4·5Å). Ionic activity coefficients of uncharged species were assumed to be unity. Electronic spectra of the dyes were measured in various solvents at 298·2 K. Each solution was kept in the dark for a time long enough to avoid the presence of *cis*-isomers. Small amounts of diethylamine (less than 0·5 wt%) were added to each solution to ensure the presence of only unprotonated species. This procedure was assumed not to modify noticeably the spectra in a pure solvent.

3 RESULTS AND DISCUSSION

3.1 Acid–base properties

The complex pattern of proton transfer processes shown by the dyes studied in this work is reproduced in Scheme 1. Equilibrium data of reaction (1) were measured in aqueous sulphuric acid solutions, while the solvent used in the determination of pK_a of reactions (2) and (3) was 20 wt% aqueous methanol. pK_a values and their standard deviations, in the temperature range 293·2–323·2 K, are reported in Table 2.

TABLE 2

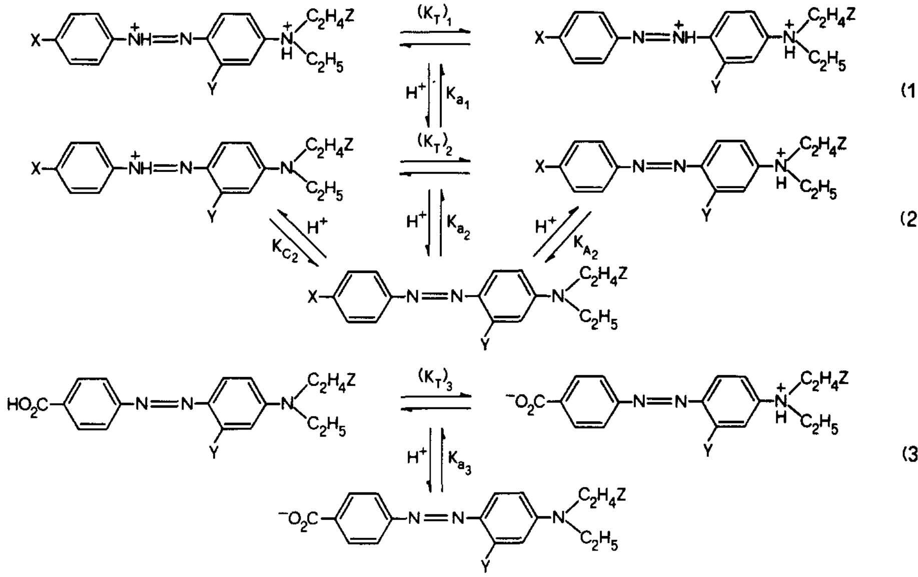
pK_a (K_a(M)) Values for Proton Dissociation Reactions (1)–(3) (Scheme 1) as a Function of Temperature T (K)

T (K)	Dye IV		Dye VI		Dye VIII		
	$-pK_{a_1}$	pK_{a_2}	$-pK_{a_1}$	pK_{a_2}	$-pK_{a_1}$	pK_{a_2}	pK_{a_3}
293·2	5·22 ± 0·01	1·94 ± 0·01	3·98 ± 0·01	1·86 ± 0·01	5·49 ± 0·01	1·63 ± 0·01	6·04 ± 0·01
298·2		1·90 ± 0·01		1·84 ± 0·01		1·57 ± 0·01	6·0 ± 0·1
303·2		1·86 ± 0·01		1·82 ± 0·01		1·54 ± 0·01	6·13 ± 0·07
308·2		1·83 ± 0·01		1·80 ± 0·01		1·51 ± 0·01	6·12 ± 0·07
313·2		1·80 ± 0·01		1·78 ± 0·01		1·51 ± 0·01	6·17 ± 0·05
318·2		1 79 ± 0·01		1·75 ± 0·02		1·53 ± 0·02	6·20 ± 0·06
323·2		1·78 ± 0·01		1·73 ± 0·02		1·58 ± 0·04	6·26 ± 0·05

T (K)	Dye IX		**Dye XI**[a]	Dye XII[a]	Dye XIII		
	$-pK_{a_1}$	pK_{a_2}	pK_{a_2}	pK_{a_2}	$-pK_{a_1}$	pK_{a_2}	pK_{a_3}
293·2	6·00 ± 0·01	1·48 ± 0·07	4·17 ± 0·01	3·89 ± 0·01	5·3 ± 0·1	4·41 ± 0·02	5·64 ± 0·02
298·2		1·48 ± 0·05	4·12 ± 0·01	3·82 ± 0·01		4·40 ± 0·09	5·63 ± 0·05
303·2		1·46 ± 0·06	4·06 ± 0·01	3·76 ± 0·01		4·38 ± 0·08	5·60 ± 0·04
308·2		1·46 ± 0·06	4·00 ± 0·01	3·72 ± 0·01		4·35 ± 0·09	5·67 ± 0·02
313·2		1·47 ± 0·08	3·95 ± 0·01	3·67 ± 0·01		4·34 ± 0·09	5·66 ± 0·03
318·2		1·44 ± 0·07	3·88 ± 0·01	3·64 ± 0·01		4·32 ± 0·09	5·64 ± 0·02
323 2		—	3·82 ± 0·01	3·61 ± 0·01		4·30 ± 0·09	5·62 ± 0·02

T (K)	Dye XV			Dye XVI		Dye XVII	
	$-pK_{a_1}$	pK_{a_2}	pK_{a_3}	$-pK_{a_1}$	pK_{a_2}	$-pK_{a_1}$	pK_{a_2}
293·2	5·31 ± 0·01	1·13 ± 0·01	5·51 ± 0·05	3·96 ± 0·01	1·28 ± 0·01	4·33 ± 0·02	0·67 ± 0·04
298·2		1·11 ± 0·01	5·54 ± 0·01		1·25 ± 0·01		
303·2		1 09 ± 0·01	5·54 ± 0·02		1·23 ± 0·01		
308·2		1·05 ± 0·02	5·52 ± 0·04		1·21 ± 0·01		
313·2		1·02 ± 0·03	5·50 ± 0·03		1·19 ± 0·01		
318·2		0·98 ± 0·06	5·45 ± 0·04		1·16 ± 0·02		
323·2		0·99 ± 0·06	5·4 ± 0·1		—		

[a] This dye undergoes irreversible degradation in concentrated sulphuric acid.



Scheme 1.

It is evident that substitution on the parent structure significantly influences the acid–base properties of these molecules. Electron-withdrawing groups in the 4′-position markedly increase proton dissociation constants and both pK_{a_1} and pK_{a_2} show good linear correlations with Hammett σ_p values[10,11] (pK_{a_1}: $r = 0{\cdot}989$, $\rho = -3{\cdot}45$; pK_{a_2}: $r = 0{\cdot}999$, $\rho = -1{\cdot}13$, where r is the correlation coefficient and ρ is the slope of the corresponding Hammett plot), if dye **II** is excluded from the linear regression. However adoption of the σ_p value of CO_2^- instead of that corresponding to CO_2H makes possible the insertion of **II** in the Hammett plot (pK_{a_2}: $r = 0{\cdot}998$, $\rho = -1{\cdot}12$), suggesting a zwitterionic structure for the neutral form of this molecule. The general acidity increase by substitution of electron-acceptor groups in the 4′-position may be explained on the basis of the consequent lower availability for protonation of the lone pairs of the azo and amino nitrogen atoms.

If we consider dyes which have substituents on the diethylamino group, such as **VI**, **VIII**, **IX**, **XV**, **XVI**, **XVII**, both pK_{a_1} and pK_{a_2} are greater than the corresponding values for the unsubstituted dyes. This effect works in the same direction as 4′-substitution, but it appears to be of an inductive nature; in fact pK_{a_2} values correlate well with the σ_I parameter[12] ($r = 0{\cdot}9996$, $\rho = -3{\cdot}85$, for dyes **I**, **VI**, **XVI**, **XVII**, which carry no substituent in the 4′-position). On the other hand, 4′-groups operate in a parallel way both for the 4-(*N*-hydroxyethyl-*N*-ethyl)aminoazobenzenes (pK_{a_2} vs σ_p: $r = 0{\cdot}996$, $\rho = -0{\cdot}57$) and for the 4-*N*,*N*-diethylaminoazobenzenes, even if with somewhat lower efficiency.

TABLE 3

Thermodynamic Functions (ΔG^0, ΔH^0, ΔS^0) for Proton Dissociation Reactions (2) and (3) (Scheme 1)

	Dye ***IV***	*Dye* ***VI***	*Dye* ***VIII***		*Dye* ***IX***	*Dye* ***XI***
	reaction (2)	*reaction (2)*	*reaction (2)*	*reaction (3)*	*reaction (2)*	*reaction (2)*
$\Delta G^0_{298\cdot2}$, kJ mol^{-1}	10·82 ± 0·13	10·51 ± 0·13	9·03 ± 0·12[a]	34·58 ± 0·13	8·40 ± 0·12	23·50 ± 0·13
$\Delta H^0_{298\cdot2}$, kJ mol^{-1}	11·1 ± 1·1	8·0 ± 1·0	13·4 ± 1·1[a]	−13·9 ± 2·0	1·8 ± 1·1	21·2 ± 2·0
$\Delta S^0_{298\cdot2}$, kJ mol^{-1} K^{-1}	1·0 ± 4·0	−8·0 ± 4·0	15·0 ± 4·0[a]	−163·0 ± 8·0	−22·0 ± 4·0	−7·0 ± 4·0

	Dye ***XII***	*Dye* ***XIII***		*Dye* ***XV***		*Dye* ***XVI***
	reaction (2)	*reaction (2)*	*reaction (3)*	*reaction (2)*	*reaction (3)*	*reaction (2)*
$\Delta G^0_{298\cdot2}$, kJ mol^{-1}	21·81 ± 0·12	25·12 ± 0·14	32·14 ± 0·14	6·33 ± 0·12	31·54 ± 0·13	7·16 ± 0·13
$\Delta H^0_{298\cdot2}$, kJ mol^{-1}	17·8 ± 1·1	6·9 ± 1·5	0 ± 2	10·8 ± 1·1	1·1 ± 1·2	8·2 ± 1·2
$\Delta S^0_{298\cdot2}$, kJ mol^{-1} K^{-1}	−14·0 ± 4·0	61·0 ± 8·0	−108·0 ± 8·0	15·0 ± 4·0	−102·0 ± 4·0	4·0 ± 4·0

[a] Values calculated in the temperature range 293·2–313·2 K.

The presence of an ethoxy group in position Y (see Table 1) shifts $\mathrm{p}K_{\mathrm{a}_2}$ towards values comparatively higher than for all the other X- and Y-substituted dyes. This effect does not appear to be relatable purely to simple electrostatic factors, as in the cases discussed above. The effect is much stronger than that expected on the basis of linear free energy relationships. The further stabilization of the protonated form apparent in the ethoxy-substituted compound could be tentatively attributed to hydrogen-bonding of the ethoxy-oxygen to the proton on the azo-group (see Scheme 1), with a consequent increase of the basicity of this group.

In most cases, $\mathrm{p}K_{\mathrm{a}}$ vs $1/T$ plots were linear, thus allowing the determination of the mean reaction enthalpies (ΔH^0) and entropies (ΔS^0) from the van't Hoff equation. The values of these functions, as well as free energy changes (ΔG^0) for reactions (2) and (3), are shown in Table 3. ΔG^0, ΔH^0 and ΔS^0 are quite complex functions of structural, electronic and solvation factors, not easy to separate, but some general trends can be observed. Entropy and enthalpy values of reaction (3) are consistent with the corresponding data of benzoic acids, and, in the case of reaction (2), a ΔH^0-lowering effect of the electron-withdrawing 4′-groups is clearly apparent. This can be attributed to the better solvation in water of strongly dipolar dyes in the unprotonated form and is consistent with results on solvent effects on the electronic spectra of these molecules (see Section 3.2).

The monoprotonated dye exists in two tautomeric forms (ammonium and azonium), as shown in Scheme 1. Therefore, due to the fact that spectrophotometric determinations of protonated dye give experimentally only the sum of the concentrations of the two forms, $\mathrm{p}K_{\mathrm{a}_2}$ values reported in Table 2 are to be considered as only 'apparent' values. The equilibrium ratio between the ammonium and azonium form concentrations is given by the tautomerism constant $(K_{\mathrm{T}})_2$; knowledge of this parameter leads easily to the determination of the real proton dissociation microconstants K_{A_2} and K_{C_2} (see Scheme 1).

The problem of measuring $(K_{\mathrm{T}})_2$ has been studied by many authors (an exhaustive review is given in ref. 2) and is complicated by the fact that physical separation of the two tautomeric species is not possible. In general the band at *ca* 300nm is ascribed to the ammonium form and that at *ca* 510 nm to the azonium tautomer.[2] In Table 4 spectral data of the various forms of the dyes studied here are reported. We have adopted the extrapolation method of Bershtein and Ginzburg,[13] which makes use of the fact that the tautomeric equilibrium is invariably shifted to the azonium form with increase in acidity. If the absorption spectra of solutions of different acid content, but of constant total dye concentration, are recorded, it may be easily shown[13] that a linear relationship exists between the absorbances of these solutions at the two wavelengths at which each species

TABLE 4
Maximum Absorption Wavelengths λ_{max} (nm) of Some of the Dyes Under Investigation and Their Conjugated Acids in 20 wt% Aqueous Methanol Solutions

	λ_{max} (nm)							
	IV	*VI*	*VIII*	*IX*	*XI*	*XII*	*XV*	*XVI*
$XC_6H_4\overset{+}{N}H{=}NC_6H_3Y\overset{+}{N}HC_4H_9Z$	410[a]	411[a]	412[a]	408[a]	[b]	[b]	410[a]	413[a]
$XC_6H_4N{=}NC_6H_3Y\overset{+}{N}HC_4H_9Z$	317	318	320	319	320	303	320	326
$XC_6H_4\overset{+}{N}H{=}NC_6H_3YNC_4H_9Z$	504	516	512	508	478	502	512	514
$XC_6H_4N{=}NC_6H_3YNC_4H_9Z$	475	418		470	431	456	445	413
$^{-}O_2CC_6H_4N{=}NC_6H_3YNC_4H_9Z$			435				426	

[a] In concentrated sulphuric acid solution.
[b] This dye undergoes irreversible degradation in concentrated sulphuric acid.

typically absorbs. The molar extinction coefficients of the tautomers can thus be determined and $(K_T)_2$ calculated.

As expected,[14] $\log(K_T)_2$ is, in all cases, a linear function of H_0, according to the following equation.

$$\log(K_T)_2 = aH_0 + b \tag{2}$$

It is only in very strong acid solutions that linearity breaks down and a saturation effect is observed. $(K_T)_2$ values and the experimental a and b parameters of eqn (2) are collated in Table 5. The acid–base microconstants pK_{A_2} and pK_{C_2} (see Scheme 1), calculated by means of K_{a_2} and $(K_T)_2$, are shown in Table 6.

Even if solvation effects are responsible for the acid shift of the tautomeric equilibrium to the azonium form, the exact nature of this effect is not clear. It has been suggested[15] that, when the concentration of water molecules available for solvation of the azo and amino nitrogen atoms decreases, the

TABLE 5
Values of $(K_T)_2$ (see Scheme 1) at $H_0 = -1$, $T = 293{\cdot}2$ K, and the Parameters a and b of Eqn (2)

Dye	$(K_T)_2$	a	b
IV	0·90	0·19	0·15
VI	0·84	0·22	0·15
VIII	0·31	0·26	0·02
IX	0·26	0·19	−0·41
XV	0·07	0·16	−1·01
XVI	0·32	0·38	−0·12
XVII	0·14	0·23	−0·62

TABLE 6
Ammonium and Azonium Form Proton Dissociation Equilibrium Constants, pK_{A_2} and pK_{C_2} Respectively, at 293·2 K

Dye	pK_{A_2}	pK_{C_2}
IV	1·6	1·7
VI	1·5	1·6
VIII	1·0	1·5
IX	0·8	1·4
XV	−0·05	1·10
XVI	0·66	1·2
XVII	−0·24	0·61

most important factor in the stabilization of the cationic dye is the coulombic interaction with the counter-ion. This effect should favour the species protonated on the azo group in more acid medium because anion approach to the azonium form is easier than to the ammonium form, because of the better water solvation of the latter. Our data do not support this hypothesis. Firstly, our investigations were concerned with dyes containing the diethylamino group rather than the amino group. Solvation of the ammonium form should be smaller, but nevertheless the tautomeric equilibrium of the dyes shows the same behaviour to that of the corresponding 4-aminoazobenzenes.[15] Secondly, inspection of Table 5 shows that $(K_T)_2$ values are strongly influenced by substituents on the diethylaminogroup; however, this effect may be completely ascribed to electronic effects, as the good correlations of $p(K_T)_2$ with σ_p^- [12] for dyes **I**, **II**, **III**, **IV**, **V** ($r = 0{\cdot}98$; $\rho = -0{\cdot}51$) and with σ_I for dyes **I**, **VI**, **XVI**, **XVII** ($r = 0{\cdot}988$; $\rho = -2{\cdot}14$) reveal.

Here again, as in the case of the pK_{a_2} vs σ_I correlation for these dyes, a remarkably high ρ value is observed. This is a good indication that the inductive effect is probably mainly due to a direct through-space polarization of the reaction site by the substituent dipole.

Moreover, the parameter a of eqn (2) expresses quantitatively the sensitivity of the tautomeric equilibrium to acidity changes and is related to the different dependence of the activity coefficients of the two tautomers on acid concentration. However, as is shown in Table 5, a is only weakly modified by the presence on the diethylamino group of substituents such as OH, $OCOCH_3$ or CN, which are characterized by very different steric, hydrogen-bonding and electronic properties and, consequently, would be expected to modify strongly the solvation of the diethylamino group.

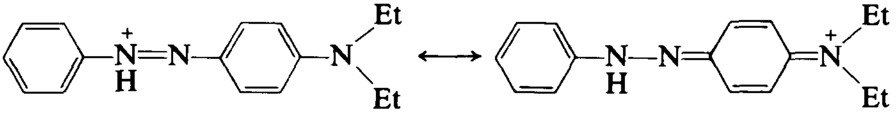
In our opinion, the better stabilization of the azonium form at high acidities, where water molecules available from hydrogen bonding are less concentrated, may be attributed mainly to the greater charge delocalization

TABLE 7

Transition Energies E_T (kcal mol^{-1}) of the Visible Absorption Bands of Some Azo Dyes and Taft's Solvent Polarity Parameter π^* [16]

Solvent	π^*	*Dye*								
		VI	*VII*	*VIII*	*IX*	*X*	*XV*	*XVI*	*XVIII*	*XX*
Cyclohexane	0·000	71·50	71·50	—	66·50	64·27	62·65	64·41	72·96	66·20
Tetrachloromethane	0·294	70·97	71·14	67·14	66·05	64·71	61·57	63·98	72·22	65·75
1-Butanol	0·503	70·44	70·44	66·82	63·56	59·09	62·11	62·72	71·68	65·90
2-Propanol	0·505	70·62	70·79	66·51	64·27	60·21	62·31	62·45	—	—
1-Propanol	0·534	—	—	—	—	—	62·45	62·45	—	—
Toluene	0·535	70·10	70·44	67·77	65·00	61·37	—	—	—	—
Ethanol	0·540	69·76	70·79	68·42	63·56	59·58	62·17	62·31	71·50	61·63
Ethyl acetate	0·545	69·76	70·44	66·05	64·27	60·21	59·95	61·90	71·50	63·27
Methanol	0·586	69·76	70·10	67·14	63·00	59·58	61·57	62·31	71·50	63·27
Benzene	0·588	69·76	70·10	67·77	64·71	60·85	—	—	—	—
Acetone	0·683	69·42	69·76	65·00	62·72	58·97	60·98	62·24	70·97	62·17
Acetonitrile	0·713	69·42	69·76	65·00	63·00	59·58	—	—	70·97	62·17
Chloroform	0·760	70·62	70·62	65·9	64·27	60·21	—	—	—	—
Dichloromethane	0·802	—	—	—	—	—	60·85	62·31	71·50	63·27
N,*N*-Dimethylformamide	0·875	68·10	68·75	64·41	60·85	57·20	—	—	—	—
Diethylene glycol	0·932	65·00	63·98	60·96	59·71	56·75	—	—	—	59·96
1,1,2,2-Tetrachloroethane	0·948	69·93	70·10	65·00	63·56	58·97	60·21	61·51	71·50	62·72
Dimethyl sulphoxide	1·000	67·29	67·29	62·86	60·08	56·08	58·73	59·89	69·42	59·58
Nitrobenzene	1·029	67·29	66·51	68·10	60·85	57·20	—	—	—	—
Water	1·090	63·56	62·85	61·51	59·55	57·20	59·03	60·92	69·59	—
Formamide	1·118	68·10	65·00	64·27	60·21	56·63	—	—	—	—

possible in the azonium tautomer, as indicated by the resonance forms (eqn 3) and the consequent stronger dipolar interactions with the solvent.


(3)

3.2 Solvent effect on electronic spectra

Transition energies (E_T kcal mol^{-1}) of the visible absorption band in various solvents of some of the dyes shown in Table 1 are collated in Table 7. The general marked bathochromic shift in polar solvents is a clear indication of the CT nature of the transition here considered. In a previous study[4] on 4′-substituted 4-diethylaminoazobenzenes, spectral data were found to be well correlated with the Kamlet–Taft π^* scale of solvent dipolarity–polarizability,[16] but only if different classes of solvents, namely non-hydrogen-bonding solvents (NHB), amphiprotic solvents (HBD/A) and hydrogen-bonding acceptor solvents (HBA), are considered separately. Dipole–dipole dipole-induced dipole interactions were shown to play a predominant role in the solvatochromism of these dyes but also more specific interactions could be detected in HBD/A and HBA solvents, such as hydrogen bonding to the diethylamino group or solvation interactions of the azo-group nitrogen lone pairs with solvent carbonyl groups.

In this work, we have extended our investigation to dyes characterized by the presence of substituents in the Z-position (see Table 1), following substantially the same approach used in ref. 4. Here again, by considering different classes of solvents, linear correlations of transition energies (E_T) with π^*, corresponding to eqn (4), could be obtained;

$$E_T = E_0 + s\pi^* \qquad (4)$$

E_0 and s parameters are reported in Table 8.

It is evident that introduction of hydroxy and cyano groups in the Z-position leads almost invariably to a hypsochromic shift with respect to the parent compound.

On the other hand, as observed in the case of proton dissociation equilibria, fundamentally the same factors are operative in determining the solvatochromism both of 4-(*N*-hydroxyethyl-*N*-ethyl)aminoazobenzenes and of 4-*N*,*N*-diethylaminoazobenzenes, as revealed by the good linear correlations existing between E_T values of each couple of corresponding dyes, at least in HBD/A and NHB solvents. For example a plot of E_T(**VI**) as a function of E_T(**I**) gives a correlation coefficient of 0·990 and a slope of 0·93, indicating direct proportionality between the respective transition energies.

TABLE 8
E_0 and s Values (see Eqn (4)) of the Investigated Compounds in Different Classes of Solvents

Dye	*NHB*		*HBA*		*HBD/A*	
	E_0	s	E_0	s	E_0	s
	(*kcal mol*$^{-1}$)		(*kcal mol*$^{-1}$)		(*kcal mol*$^{-1}$)	
VI	71·49	−1·47	73·01	−5·64	78·50	−15·02
VII	71·54	−1·39	74·46	−7·18	78·17	−14·47
VIII	68·12	−3·16	69·54	−6·4	73·38	−13·33
IX	66·70	−3·22	69·19	−9·31	67·86	−8·06
X	64·29	−5·52	65·17	−9·1	62·56	−5·61
XV	62·50	−2·32	—	—	65·10	−5·59
XVI	64·61	−3·05	—	—	63·92	−2·76
XVIII	72·83	−1·54	74·07	−4·63	73·53	−3·63
XX	66·48	−3·90	67·70	−8·12	73·39	−16·0

This behaviour may be attributed mainly to the inductive electron-withdrawing properties of these groups, which lead to a lower availability of the amino nitrogen lone pair for intramolecular charge transfer. Moreover, in the case of 4′-substituted 4-(*N*-hydroxyethyl-*N*-ethyl)aminoazobenzenes, hydrogen bonding to the hydroxyethyl group in HBD/A and HBA solvents leads to s values markedly lower than those of 4-*N*,*N*-diethylamino analogues. As suggested by the authors who introduced this parameter,[16] s is a convenient indicator of the interaction of a chromophore with its environment and is related to the relative change in polarity of excited and ground states. The extended hydrogen bonding interactions brought about by the hydroxyethyl group in HBD/A and HBA solvents are still operative, at least partially, in the excited state, with a consequently greater excited-state charge delocalization than in the case of 4-diethylaminoazobenzenes, justifying the experimental low s values. As observed in the case of 4′-nitro-4-diethylaminoazobenzene, the strong electron-withdrawing action of the nitro-group limits the availability of nitrogen lone pairs for specific interactions with the solvent and leads to values of E_0 and s very similar in all classes of solvents, making polarity–polarizability effects predominant. On the other side, solute–solvent specific interactions are particularly important in 4′-methoxy-substituted derivatives.

4 CONCLUSION

Colour and tinctorial properties, as well as lightfastness of disperse dyes, are complex functions of electronic structural factors and of specific interactions with the matrix. In this paper acid–base equilibria and solvent effects on the electronic spectra of a range of azo dyes have been studied, in attempts to discriminate among the various factors relevant to the properties of these dyes. pK_a, K_T (see Scheme 1), ΔH^0 and ΔS^0 have been measured and interpreted on the basis of linear free energy relationships. Analysis of the solvatochromism of these dyes has led to the determination of some specific interactions with the solvent.

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