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Ammonium–Azonium Tautomerism in some *N,N*-Dialkylaminoazodyes—II. Compounds Containing more than Two Protonation Sites[1]

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ABSTRACT

The UV–vis properties in neutral and acidic media of some N,N-*dialkylaminoazo dyes containing strong electron donor substituents or an extended conjugated system, leading to more than two protonation sites, are investigated in order to clarify the influence of these structural changes on the position of the ammonium–azonium tautomeric equilibrium. The observed absorption maxima associated with the colour changes of neutral and protonated molecules are assigned within the charge-transfer (CT) model. The tautomeric equilibrium constants K_T and pK_a values of the ammonium and azonium tautomeric forms of* N,N-*dialkylaminoazobenzenes containing strong electron donor substituents are evaluated. Copyright © 1996 Elsevier Science Ltd*

1. INTRODUCTION

N,N-dialkylaminoazo dyes and their derivatives undergo a pronounced colour change on addition of acid and this phenomenon, halochromism, is used in their application as pH indicators,[2] optical sensors[3] and possibly as photo- and radiochromic indicators. Unprotonated dyes of this type can be represented by the donor–acceptor chromogenic system 1 (Scheme 1).[4–7]

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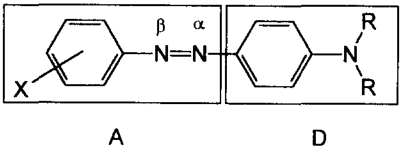
[1] For Part I see Ref. 1.



CT-model 1

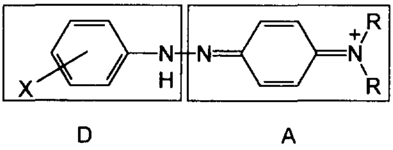
Scheme 1.

On protonation, a tautomeric equilibrium between the ammonium (AM) and azonium (AZ) forms exists;[2,4,8] two absorption bands are associated with these tautomeric structures; namely,

(a) the C-band at about 500–560 nm, assigned to the azonium cation, in which the β-azo nitrogen atom is protonated, and is responsible for the colour changes.

(b) the A-band at about 320 nm, associated with the protonated terminal nitrogen of the NR_2 group (ammonium form), and in which the protonation prevents mesomeric interaction of the terminal lone pair with the π-electronic system.

The azonium structure can be represented within the CT-model[2] (Scheme 2).[4,5,7]



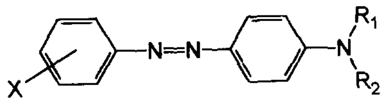
CT-model 2

Scheme 2.

The donor fragment in Scheme 1 acts, in the azonium system shown in Scheme 2, as an acceptor, i.e. structural changes in the system result in different effects in the absorption bands of each configuration. The object of this present paper is to evaluate the spectral properties in neutral and acidic media of some *N,N*-dialkylaminoazo dyes containing strong electron-donating substituents or an extended conjugated system, and which contain more than two protonation sites, in order to clarify the influence of these structural changes on the position of the ammonium–azonium tautomeric equilibrium.

2. MATERIALS AND METHODS

The compounds studied are as shown in Scheme 3. The *N,N*-dialkylaminoazo



where $X = p\text{-}NH_2$; $R_1 = R_2 = CH_3$	I
$X = p\text{-}NH_2$; $R_1 = R_2 = C_2H_5$	II
$X = p\text{-}NH_2$; $R_1 = C_2H_5$; $R_2 = C_2H_4OH$	III
$X = p\text{-}N(C_2H_5)$; $R_1 = R_2 = C_2H_5$	IV
$X = p\text{-}N{=}N\text{-}Ph$; $R_1 = R_2 = CH_3$	V
$X = p\text{-}N{=}N\text{-}Ph$; $R_1 = R_2 = C_2H_5$	VI
$X = H$, $R_1 = R_2 = H$	VII
$X = H$, $R_1 = R_2 = CH_3$	VIII
$X = p\text{-}OCH_3$, $R_1 = R_2 = CH_3$	IX

Scheme 3.

dyes I–III were prepared by coupling diazotised 4-nitroaniline with the appropriate *N,N*-dialkylaniline in an acetate buffer, followed by reduction of the resulting dye with $Na_2S_2O_4$ or $Na_2S{\cdot}H_2O$ in an alkaline medium.[9] Compounds IV[10] and V and VI[11] were prepared as previously described. pK_a determinations and UV–vis measurements were carried out as in a previous investigation.[1]

3. RESULTS AND DISCUSSION

It has been previously noted[1] that the addition of water to an ethanolic solution of *N,N*-dialkylaminoazo dyes is accompanied by distinct spectral changes due to the redistribution of the individual vibronic band intensities within the longwavelength π–π* absorption band. Solvation, forming a rigid solvent cage around the molecule, and the presence of electron-donor substituents which increase the π-bond orders of the C-N(=) bonds, are among the factors[12] favoring increase of planarity. The absorption spectra

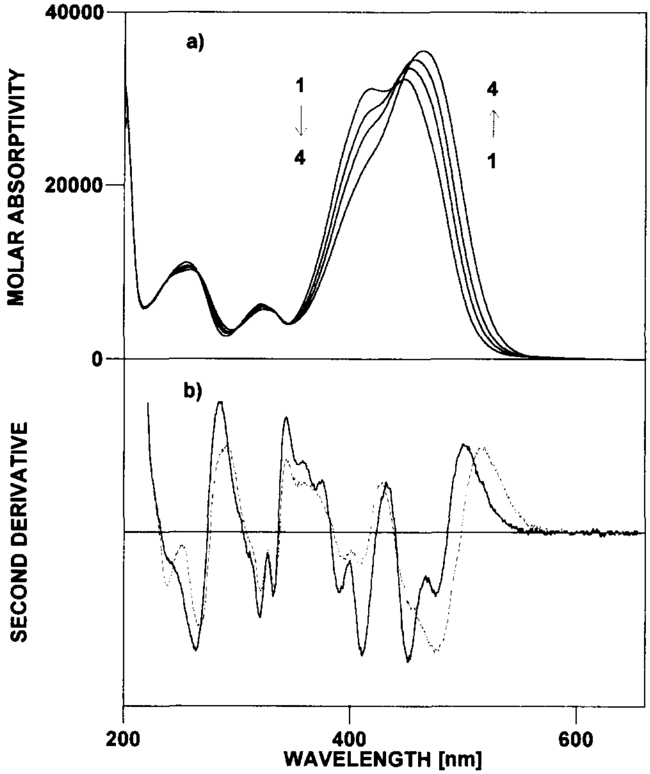


Fig. 1. (a)Absorption spectra of I in different v/v ratio of ethanol/water: 1—100% ethanol; 2—70%; 3—50%; 4—30% v/v ethanol/water. (b) Second derivative spectra of 1 (——) and 4 (- - - -).

of I (Fig. 1) in different water/ethanol mixtures confirms these conclusions, showing a relative increase of the 0–0 band intensity, while that of the 0–2 band decreases with increase of water content, in accord with the assignment of the vibrational sub-bands.[12]

The vibrational structure of the longwavelength π–π* band is even more distinct in the case of the symmetrical compound IV in isooctane (Fig. 2).

The position of the vibronic bands 0–i for compounds I–VI in isooctane are given in Table 1, together with those for 4-aminoazobenzene (VII), 4-*N*,*N*-dimethylaminoazobenzene (VIII) and 4′-methoxy-4-*N*,*N*-dimethylaminoazobenzene (IX) as reported in our previous study.[1]

According to Mustroph,[12] the intense υ_{0-1} band represents the N–stretching vibronic transition between the ground state and a planar vibrational excited state. This interpretation is supported when comparing the differences between the υ_{0-0} and υ_{0-1} values shown in Table 1, and also the resonance Raman vibrational frequencies of the NN stretching vibration

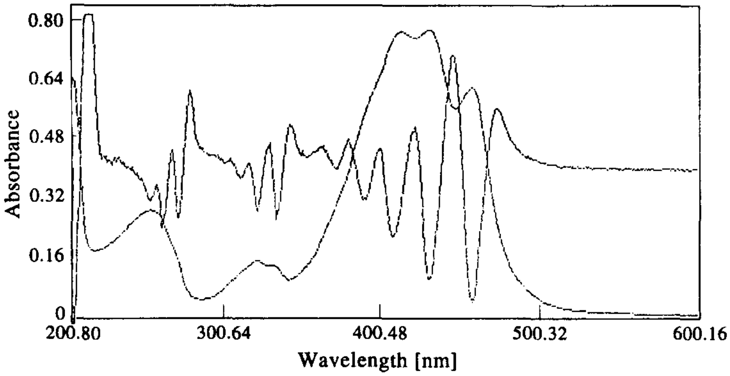


Fig. 2. Absorption and second derivative spectra of IV in isooctane.

($\bar{\upsilon} \approx 1400\ \mathrm{cm}^{-1}$).[12–14] The effect of the extended conjugation resultant from the electron acceptor—N=NPh group can be evaluated, from the values of the υ_{0-0} transitions in V and VIII, to be about 2800 cm^{-1} (~60 nm), while replacement of the H-atoms in the NH_2 group (VII) by a CH_3 group (as in VIII) leads to a bathochromic shift of about 3076 cm^{-1} (~50 nm) in the corresponding 0–0 transition. Introduction of a second electron-donor OCH_3 (IX) and NH_2 (I) group in VIII cause insignificant changes in the position of the 0–0 vibronic transitions (2 and 10 nm, respectively) in accordance with the charge-transfer model.[4,7]

The presence of the additional protonation sites resultant from the introduction of a second $N(R)_2$ group into the azobenzene conjugated system (I–IV), or of a second -NN group (as in V and VI), gives the possibility for considerable colour changes in acid media.

TABLE 1
Position of the Vibronic Bands for Compounds I–IX in Isooctane

Compound	υ_{0-3} [cm^{-1}]	υ_{0-2} [cm^{-1}]	υ_{0-1} [cm^{-1}]	υ_{0-0} [cm^{-1}]	$\upsilon_{0-1}-\upsilon_{0-0}$ [cm^{-1}]
I	27,778	25,773	24,510	22,978	1532
II	27,660	25,720	24,320	22,810	1510
III	27,716	26,096	24,752	23,105	1647
IV	25,720	24,510	23,280	21,890	1390
V	24,800	23,670	22,360	20,730	1630
VI	24,655	23,364	21,930	20,358	1572
VII	31,726	29,904	28,027	26,596	1431
VIII	27,650	26,205	24,850	23,520	1330
IX	27,720	26,210	24,900	23,450	1450

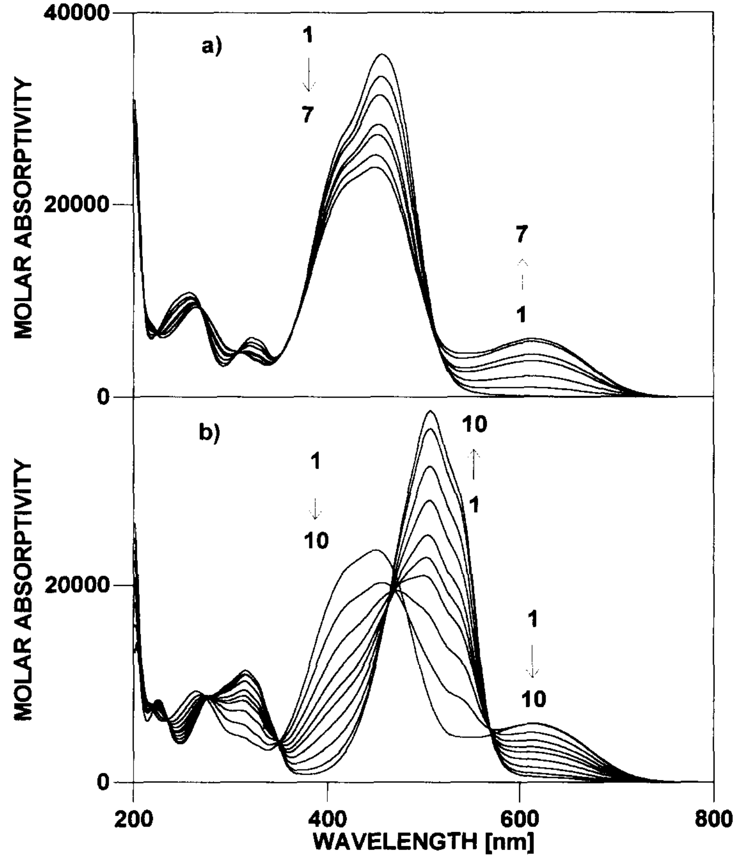
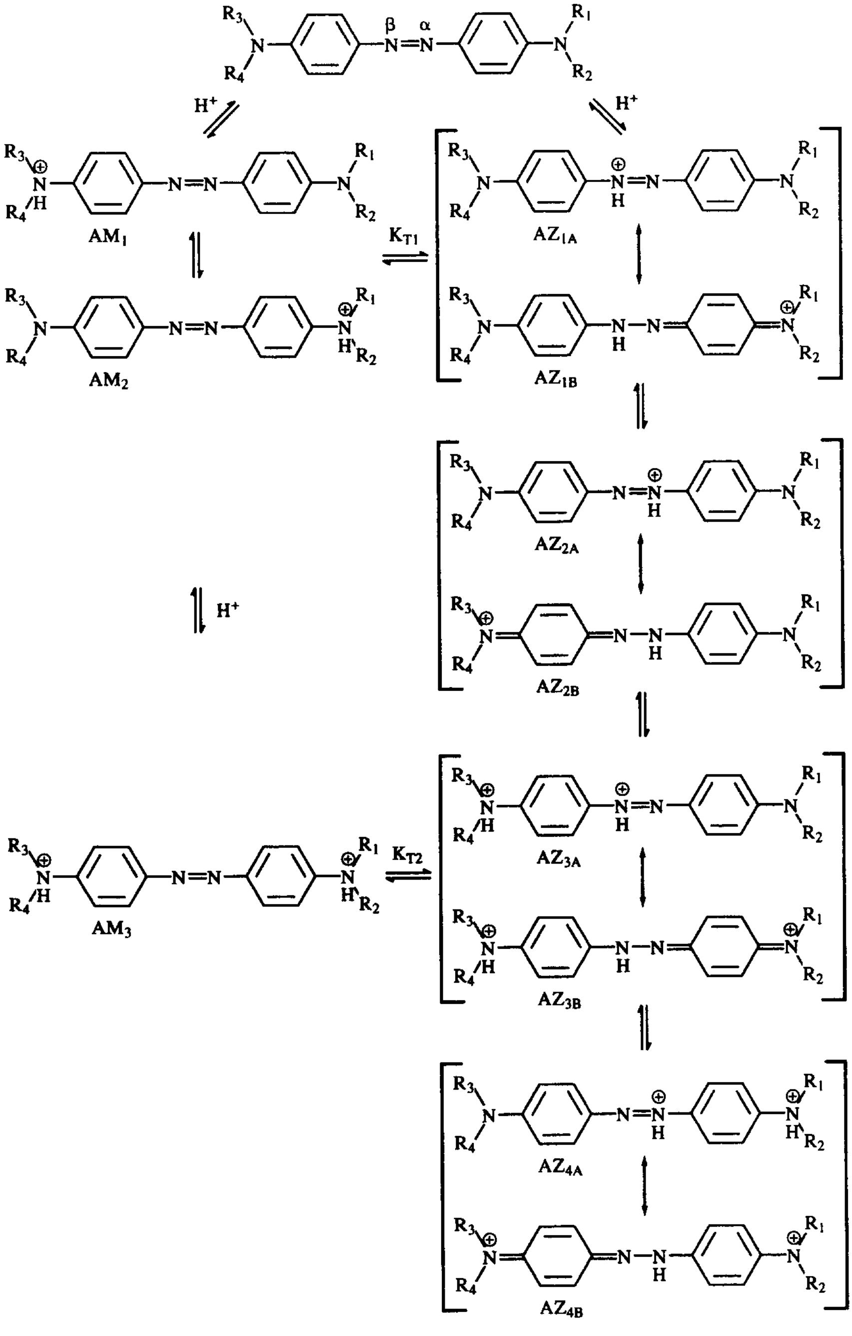


Fig. 3. (a) Absorption spectra of III in 50% v/v ethanol/water at different pH values: 1—without acid; 2—3.96; 3—3.49; 4—3.06; 5—2.89; 6—2.5; 7—2.39. (b) Absorption spectra of III in 50% v/v ethanol/water containing increasing amounts of HCl: 1—1 ml 0.1 N HCl; 2—0.4 ml 1 N HCl; 3—0.8 ml 1 N HCl; 4—1.2 ml 1 N HCl; 5—1.6 ml 1 N HCl; 6—2 ml 1 N HCl; 7—3 ml 1 N HCl; 8—5 ml 1 N HCl; 9—5 ml 2 N HCl; 10—10 ml 2 N HCl.

The absorption spectra of III in 50% v/v ethanol/water at different pH values, containing increasing amount of HCl are presented in Fig. 3.

The observed spectral changes and the origin of the absorption bands could be described adequately using Scheme 4, in which the possible tautomeric equilibria between the corresponding ammonium and azonium forms for the first and second protonation of compounds I–IV are included.

Spectral data for the absorption bands assigned to the corresponding unprotonated, monoprotonated and diprotonated structures of I–IV, according to Scheme 4, are shown in Table 2.


R3
R4
β
α
R1
R2
H+
H+
AM1
AM2
KT1
AZ1A
AZ1B
AZ2A
AZ2B
H+
AM3
KT2
AZ3A
AZ3B
AZ4A
AZ4B

Scheme 4.

TABLE 2

Absorption Bands Assigned to the Unprotonated, Monoprotonated and Diprotonated Structures of I–IV in 50% v/v Aqueous Ethanol

Dye	Unprotonated form		Monoprotonated form Azonium		Diprotonated forms			
					Ammonium		Azonium	
	λ_{max}^{obs} [nm]	ε_{max}^{obs}	λ_{max}^{obs} [nm]	ε_{max}^{obs}	λ_{max}^{obs} [nm]	ε_{max}^{obs}	λ_{max}^{obs} [nm]	ε_{max}^{obs}
I	452	30,130	600	5770	312	12,440	506	34,150
II	460	34,700	616	2430	315	14,112	499	31,390
III	456	35,690	613	6060	314	8540	509	45,600
IV	482	47,890	678	2880	315	16,472	507	30,500

In the case of IV, because of the symmetry of the molecule, the complex equilibrium shown in Scheme 4 is much more simplified, since structures AM1 and AM2, $AZ_{1A} \leftrightarrow AZ_{1B}$ and $AZ_{2A} \leftrightarrow AZ_{2B}$, respectively, are equivalent. Therefore, in the azonium mesomeric structure AZ_{1B}, the positive charge is completely delocalized, leading to the experimentally observed bathochromic shift of about 200 nm in comparison with the neutral form, this shift being the highest one observed, in accord with the colour rules[4,5] for the charge-transfer system 2. However, its intensity is very low, suggesting that the amount of the ammonium form is much higher. Evidently the absorption maximum corresponding to the AM1 form should be close to that of unprotonated 4-*N*,*N*-diethylaminoazobenzene ($\lambda_{max} = 440$ nm; $\varepsilon_{max} = 29{,}000$ litre mol^{-1} cm^{-1})[15] and indeed, in the spectrum of the monoprotonated IV, another absorption maximum at ~ 450 nm ($\varepsilon \sim 36{,}000$) closely overlapped with those of unprotonated IV, is observed.

The behavior of I–III in acidic medium is similar (Fig. 3a,b), and the corresponding absorption maxima for the azonium form are shifted hypsochromically to about 600–620 nm, but a considerable bathochromic shift is observed in comparison with VIII and IX,[1] again in accord with the chromogenic system 2. Since the electron-donor influence of the NR_1R_2 group on the basicity of the β-nitrogen atom of the azo group can be expected to be higher than that of the NH_2 group, it is most probable that the azonium structure $AZ_{1A} \leftrightarrow AZ_{1B}$ in the case of I–III is responsible for this low intensity transition. Again, a separate maximum for the ammonium form is not observed (Fig. 3a), and its position is, therefore, most probably at approximately the same absorption range at which the unprotonated form absorbs.

The absorption spectra of II in acetonitrile, with addition of increasing amounts of $HClO_4$, are shown in Fig. 4 and show that the intensity of the

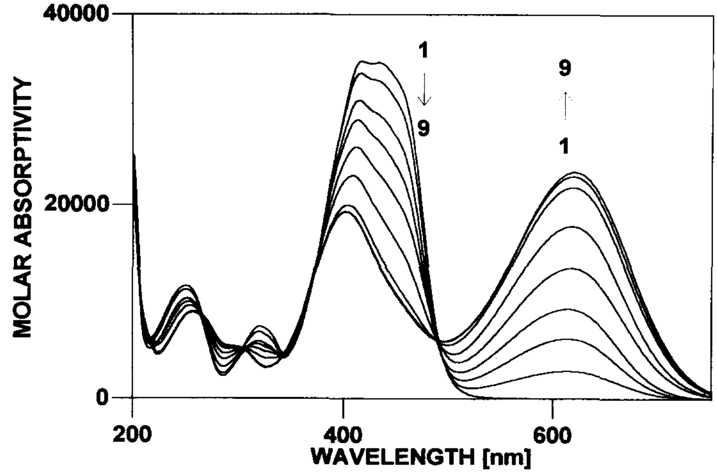


Fig. 4. Absorption spectra of II in CH_3CN containing increasing amounts of 0.02 M $HClO_4$: 1—without acid; 2—0.1 ml; 3—0.13 ml; 4—0.16 ml; 5—0.19 ml; 6—0.22 ml; 7—0.24 ml; 8—0.26 ml; 9—0.28 ml.

absorption maximum assigned to the azonium form increases considerably. Evidently the lower specific solvation ability of CH_3CN causes a shift of the tautomeric equilibrium towards the azonium form.

The value of the tautomeric equilibrium constant $K_T = [\text{azonium}]/[\text{ammonium}]$ is a measure of the relative basicities of the β-azo nitrogen atom (pK_a^{AZ}) and of the amino nitrogen atom (pK_a^{AM}) is related by eqns (1)–(3):[16–18]

$$K_T = K_{AM}/K_{AZ} \tag{1}$$

$$K_{AM} = K_a(1 + K_T) \tag{2}$$

$$K_{AZ} = K_a(1 + 1/K_T) \tag{3}$$

Since the ammonium form does not absorb at the azonium maximum (Fig. 4) K_T values can be determined using equation (4):[1,18]

$$K_T{}^i = \frac{\epsilon^i_{AZ}}{\epsilon^0_{AZ} - \epsilon^i_{AZ}} \tag{4}$$

where $\epsilon_{AZ}{}^i$ is the observed apparent molar absorptivity of the *i*th solution and $\epsilon_{AZ}{}^0$ is the true (individual) molar absorptivity of the azonium form.

The $\epsilon_{AZ}{}^0$ values can be estimated[19] by plotting the $\epsilon_{AZ}{}^i$ values vs the $\epsilon^i_{\lambda_{416}}$ values (Fig. 5), and this relationship should be linear if the following two conditions are fulfilled:

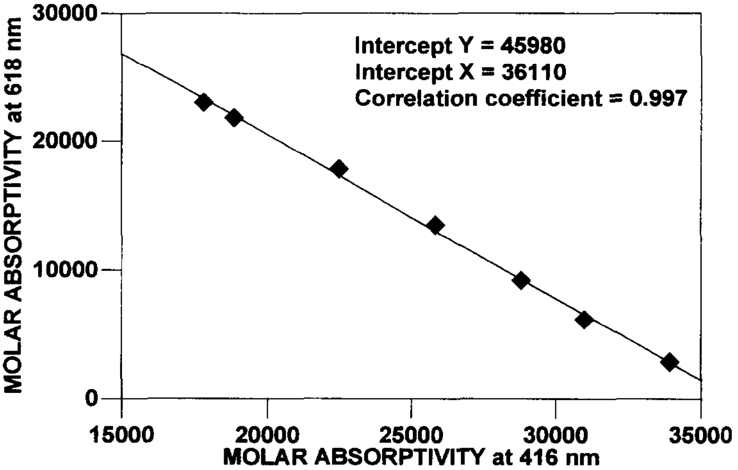


Fig. 5. Linear relation between the $\epsilon_{AZ}{}^{i}$ and $\epsilon^{i}_{\lambda_{416}}$ values for compound II in $CH_3CN/HClO_4$ solutions.

(a) the azonium form has no absorbance at the wavelength of neutral (ammonium) form

(b) the spectral characteristics of the neutral form are equal to that of the first protonated ammonium form.

The first of these conditions seems probable, or at least the absorbance is very small, as is evident from Fig. 4.

In the case of II, the spectral data for the neutral form in acetonitrile are $\lambda_{max} = 418$ nm and $\epsilon_{max} = 35{,}200$, while the corresponding values for the monoprotonated ammonium form in acetonitrile are $\lambda_{max} = 420$ nm and $\epsilon_{max} = 33{,}000$,[20] i.e. the second condition is also probable.

Similar spectral behavior in $CH_3CN/HClO_4$ is observed also for compounds I, III and IV. The values of $\epsilon_{AZ}{}^{0}/\epsilon_{AM}{}^{0}$ and $\epsilon_{AZ}{}^{0}$ are evaluated from the slope and intercept of the linear eqn (5):

$$\epsilon^{i}_{AZ} = a.\epsilon^{i}_{\lambda_{416}} + b \qquad (5)$$

where $a = \epsilon_{AZ}{}^{0}/\epsilon_{AM}{}^{0}$ and $b = \epsilon_{AZ}{}^{0}$.

The calculated values of K_T, K_{AZ} and K_{AM} for the first protonation in 50% v/v ethanol/water according to eqns (1)–(3) together with the values of $pK_a{}^{obs}$, $\epsilon_{AZ}{}^{0}$ and $\epsilon_{AZ}{}^{0}/\epsilon_{AM}{}^{0}$ are collated in Table 3.

The values of K_T, K_{AZ} and K_{AM} (Table 3) should be considered as semi-quantitative, since the individual spectral characteristics of the tautomeric forms involved in the complex equilibrium (Scheme 4) cannot precisely be determined.

TABLE 3
Estimated $\epsilon_{AZ}{}^0$ Values, $\epsilon_{AZ}{}^0/\epsilon_{AM}{}^0$ Ratio and Calculated Values of K_T, pK_{AM} and pK_{AZ} for Compounds I–IV

Dye	pK_a^{obs}	$\epsilon_{AZ}{}^0$	$\epsilon_{AZ}{}^0/\epsilon_{AM}{}^0$	K_T	pK_{AM}	pK_{AZ}
I	2.15	55,550	1.575	0.116	2.102	1.166
II	3.07	45,980	1.273	0.055	3.047	1.787
III	2.41	51,200	1.410	0.129	2.357	1.468
IV	>3 (3.2)[a]	63,770	1.486	0.047	3.180	1.852

[a] Value in brackets is for 4,4′-*N*,*N*-dimethylaminoazobenzene.

Further increase in the acidity (Fig. 3b) leads in all cases to a second protonation, although the first process is not fully complete. The absorption maxima for the diprotonated azonium and ammonium forms at about 500–510 nm and 310–315 nm are clearly apparent. While the AM_3 structure is the only possible one and its maximum corresponds to those of unprotonated azobenzene (λ_{max} ~315 nm), two mesomeric structures $AZ_{3A} \leftrightarrow AZ_{3B}$ and $AZ_{4A} \leftrightarrow AZ_{4B}$ are possible. The site of the second protonation is difficult to determine precisely, since the values of the absorption maxima (Table 2) lie in between those of the monoprotonated azonium form of VII (λ_{max} ~496 nm) and VIII (λ_{max} ~516 nm). From the shape and position of the

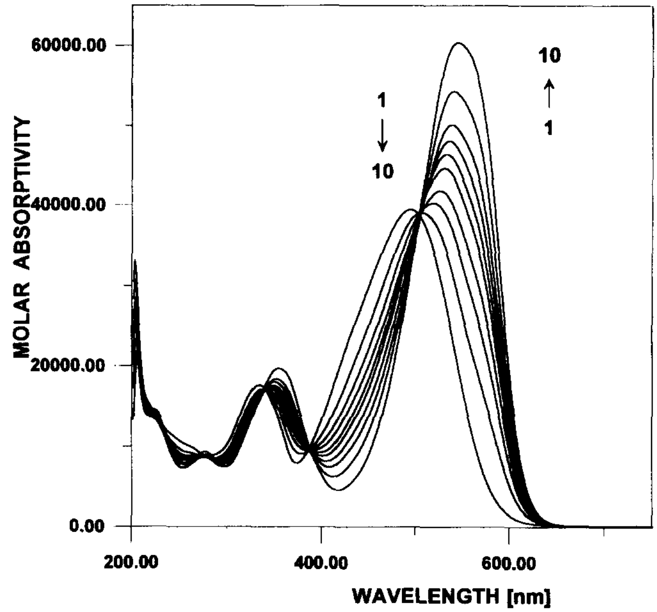


Fig. 6. Absorption spectra of V in 50% v/v ethanol/water at different pH values: 1—without acid; 2—2.40; 3—2.08; 4—1.91; 5—1.78; 6—1.70; 7-1.54; 8-1.41; 9-1.21; 10—5 ml 1 N HCl.

absorption bands, and considering the lower solvation of the $N(Alk)_2$ group,[21] it could be suggested that the mesomeric azonium structures $AZ_{3A} \leftrightarrow AZ_{3B}$ are the more reasonable, i.e. the second protonation occurs at the NH_2 group.[9,22,23]

In this respect, *ab initio* quantum-chemical methods, taking into account the solvent environment, could possibly help in solving this problem. In the case of the *p*-*N*-dialkylaminodisazobenzene dyes V and VI, five possible sites are available for the first protonation. The absorption spectra of V at different acidities are presented in Fig. 6.

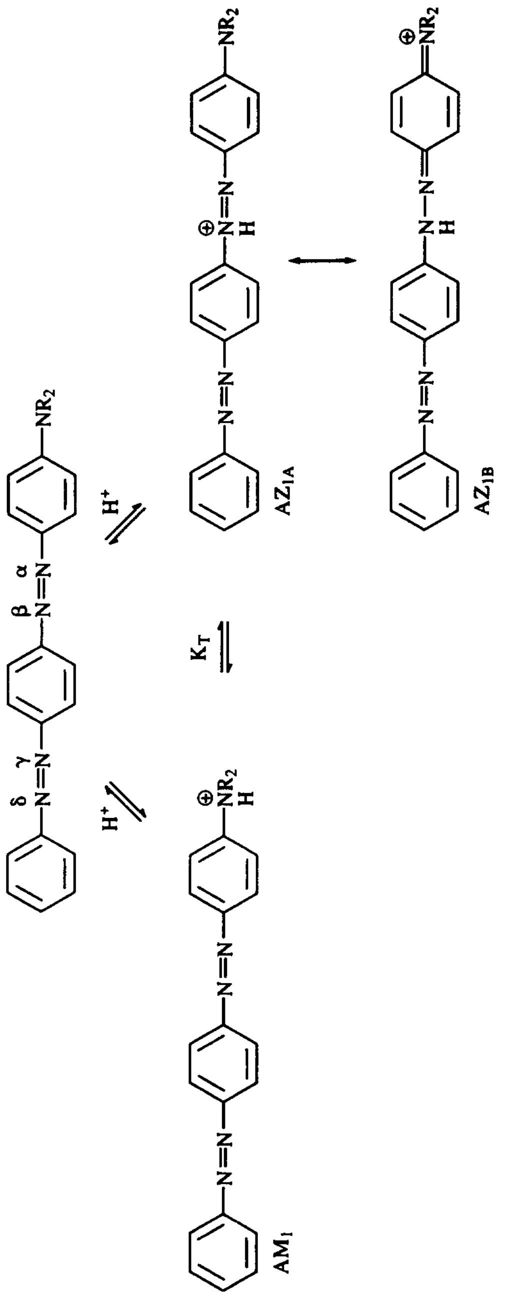
The most probable tautomeric structures of V and VI[11,23] are shown in Scheme 5, where the dialkylamino and β-nitrogen atoms are the chief competitors for the first proton.

The observed spectral characteristics (λ_{max} and ϵ_{max}) of the unprotonated, mono- and diprotonated ammonium and azonium tautomeric forms and of the triprotonated form, assigned according to Scheme 4 and literature data,[11,23,24] and also assuming that the second proton adds to the δ-azo nitrogen and that the dialkylamino, β- and δ-azo nitrogens are the three protonation sites, are presented in Table 4.

The AM_1 form absorbs at about 360 nm, a region in which the corresponding disazobenzene absorbs ($\lambda_{max} \sim 359$ nm),[24] while the $AZ_{1A} \leftrightarrow AZ_{1B}$ is batho-chromically shifted (~50 nm) in comparison with the unprotonated form. This positive halochromism is much smaller than in the case of I–IV since the electron acceptor -N=NPh group is substituted in the D-fragment (Scheme 2). On the other hand, the absorbance of the biprotonated azonium form, associated with the β- and δ-azo nitrogens, is even more batho-chromically shifted (~130 nm) towards the absorption maximum of the unprotonated dye. The molar absorptivity is very high ($\epsilon_{max} \geq 100{,}000$ litre mol^{-1} cm^{-1}), suggesting that increasing acid concentration leads to an increase of azonium ion concentration.[5,8] The first absorption band in both

TABLE 4
Spectral Characteristics of the Unprotonated, Monoprotonated Azonium and Ammonium Forms, Diprotonated Azonium Form and Triprotonated Form of Compounds V and VI

R	Unprotonated form		First protonation				Second protonation		Third protonation	
			Ammonium form		Azonium form					
	λ_{max} [nm]	ϵ_{obs}	λ_{max} [nm]	ϵ_{obs}	λ_{max} [nm]	ϵ_{obs}	λ_{max} [nm]	ϵ_{obs}	λ_{max}	ϵ_{obs}
CH_3	494	39,507	354	19,700	544	60,420	627	116,480	498	58,030
C_2H_5	504	37,853	360	33,190	544	21,090	630	94,576	496	50,770



Scheme 5.

cases (unprotonated and double protonated) is associated with a migration of electron density from the D-fragment towards the β- and δ-azo nitrogen atoms (see Scheme 1), which is strongly enhanced when the β- and δ-azo nitrogens are protonated. The triprotonated structure of V and VI absorbs at ~500 nm and its position and molar intensity closely corresponds to that of diprotonated disazobenzene ($\lambda_{max} = 502$ nm and $\epsilon_{max} = 55{,}000$).[24]

Thus, the use of the CT-models 1 and 2 facilitates the assignment of the protonated tautomeric forms of compounds containing more than two protonation sites, but the separate molar parts of the species involved can only be determined quantitatively if their individual spectral characteristics are known. This complex factor is still unsolved, and will be the subject of further investigations.

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