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Ammonium–Azonium Tautomerism in Some *N*,*N*-Dialkylaminoazo Dyes. Part 1: General Considerations

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ABSTRACT

The UV–Vis properties in neutral and acid media of some N,N-*dialkylaminoazobenzenes containing electron donor substituents in the unsubstituted benzene ring are discussed. A redistribution of the individual vibronic band intensities within the long wavelength absorption* π–π^* *band due to specific solvation of the molecules in neutral media is observed and the corresponding vibrational sub-bands are assigned. In acid media, the increased positive halochromism is explained within the charge transfer (CT) models of the corresponding chromogenic systems. The tautomeric equilibrium constants,* K_T *and* pK_a *values of the ammonium and azonium tautomeric forms are evaluated. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

The structures of the conjugated acids of 4-aminoazo derivatives in acid media have been the subject of many discussions,[1–6] leading to the conclusion that a tautomeric equilibrium exists between the ammonium (AM) and azonium (AZ) forms (Scheme 1).

N,*N*-Dialkylaminoazo dyes (B) undergo a pronounced color change on addition of acid. This phenomenon, called halochromism, is of use in many applications, e.g. pH indicators,[5] optical sensors[7] and possibly photo- and radiochromic indicators. Since the tautomeric equilibrium depends on acid

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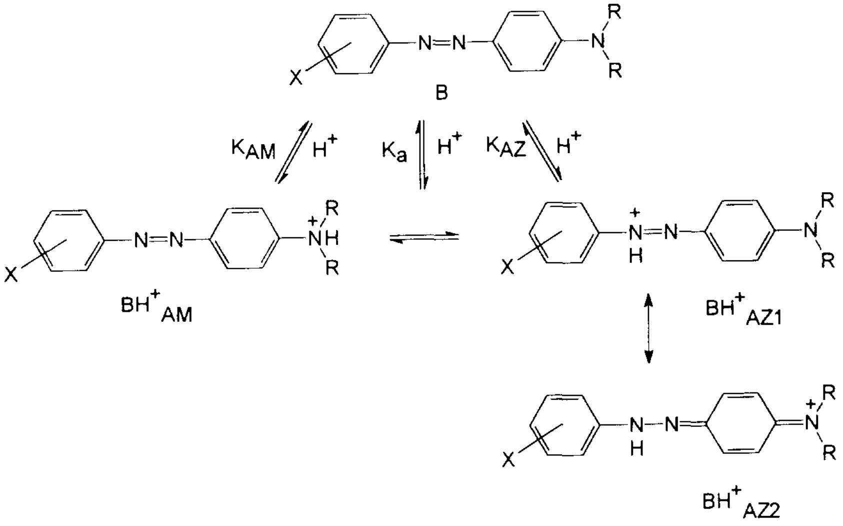


Scheme 1.

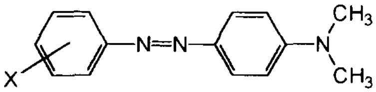
concentration, the nature of the solvent, and the relative basicities of the amino nitrogen (K_{AM}) and the β-azo nitrogen (K_{AZ}), it is difficult to estimate the true molar absorptivities of the corresponding bands, i.e. the A-band of the ammonium form at about 320 nm and the C-band of the azonium form at about 500 nm.[5,8,9]

Recently a quantitative approach for the analysis of the azo–quinonehydrazone tautomeric equilibrium of isomeric phenylazonaphthols was successfully applied.[10–13] The object of the present paper is to analyze the spectral properties in neutral and acid media of some *N*,*N*-dialkylaminoazo dyes in order to clarify the influence of structural factors such as the position and nature of the substituent in the unsubstituted phenyl ring on the ammonium–azonium tautomeric equilibrium.

MATERIALS AND METHODS

4-Aminoazobenzene (**I**) was obtained through purification of the commercially available dye (Aldrich). The 4-dimethylaminoazobenzene derivatives (**II–V**) were prepared by coupling the appropriate diazonium ion with *N*,*N*-dimethylaniline in buffered aqueous acetic acid. Purification methods and physical data are as supplied previously.[14] The compounds are shown in Scheme 2.

Solutions containing constant dye concentrations, but varying amounts of hydrochloric acid, were prepared in 50% v/v aqueous ethanol using a stock dye solution in ethanol. The absorption spectra of compounds **I–V** were



II X = H

III X = o-CH_3

IV X = m-CH_3

V X = p-CH_3

Scheme 2.

obtained on a Lambda 17 UV–Vis spectrophotometer (Perkin-Elmer) at constant temperature (25°C). Standard buffer solutions were used to calibrate the pH meter (Radelkis OP208/I) and the pK_a values were determined by a non-linear optimization procedure.

RESULTS AND DISCUSSION

The optimal water/ethanol ratio was checked initially in order to obtain correct and reproducible results from the absorption UV–Vis spectra. With the addition of water to alcoholic solutions of compounds **I–V** the intensity of the long wavelength shoulder at 440–450 nm increases considerably (Fig. 1) giving rise to a new absorption band in the visible region.

Two principle possibilities could explain such behavior, namely:

— formation of a hydrogen bond between the β-azo hydrogen and water;[15]

— the existence of vibrational fine structure within the long wavelength π–π^* band.[16,17]

In the case of compound **III**, where an o-OCH_3 substituent could possibly sterically hinder H-bond formation with the β-azo hydrogen atom, an even clearer picture is observed (Fig. 2). The spectral data (ν_{0-i}) for the vibrational sub-bands of the long wavelength π–π^* band of compound **II** in solvents of different polarity are presented in Table 1, where the corresponding values of ν_{0-i} are evaluated from the second and fourth derivative spectra.[17] It should be noted that in the most non-polar solvent (iso-octane) the vibronic nature of this band is clearly observed.

According to Mustroph[18] the 0–0 sub-band is due to a vibronic transition from the ground state to the planar singlet exited state, the 0–1 sub-band is connected with the N=N stretching vibronic transition, while the 0–2 sub-band is attributed to torsional vibrations around the Ph–N(=) bonds in the excited state.

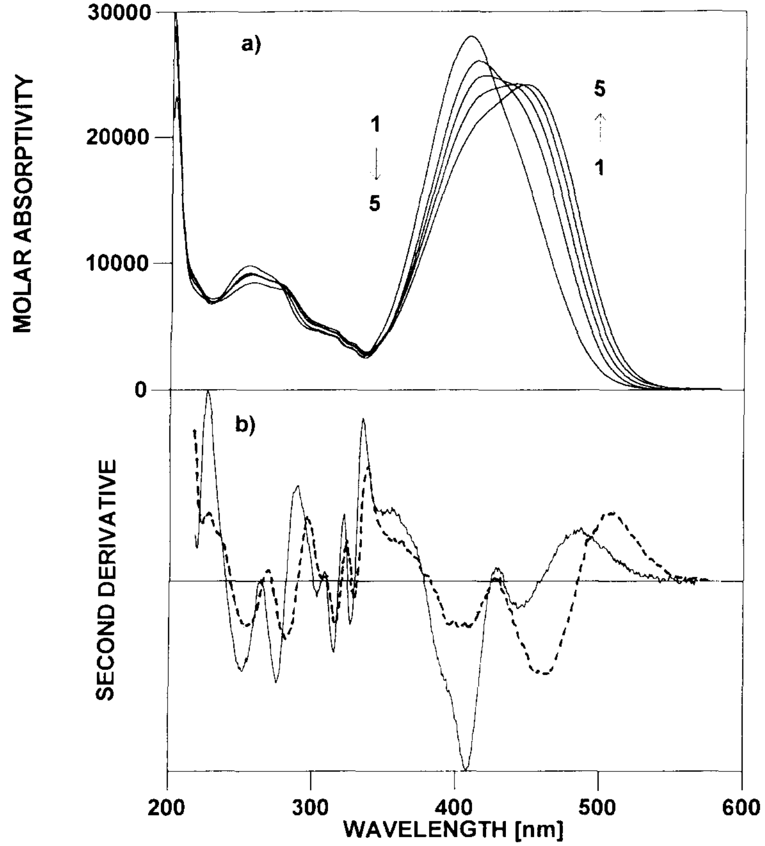


Fig. 1. (a) Absorption spectra of compound **II** at different v/v ethanol/water ratios: 1, 100% ethanol; 2, 70%; 3, 50%; 4, 40%; 5, 30% v/v ethanol/water. (b) Second derivative spectra of solutions 1 (———) and 5 (- - -).

Analysis of our data allows us to suggest that the spectral changes observed (Figs 1 and 2) are due to a redistribution of the vibrational intensities within the long wavelength π–π^* band in the compounds investigated.

The specific solvation caused by polar solvents like water forming a rigid solvent cage around the molecule, and the existence of electron donor substituents increasing the π-bond order of the C–N(=) bonds in the case of compounds **III–V**, are among the factors[18] favoring an increase in planarity. In all cases, when the water content is increased, the relative intensity of the 0–0 band increases and that of the 0–2 band decreases, confirming the assignment of the vibrational sub-bands.[18] It should be noted that even in a neutral medium the change of the solvent environment leads to a slight color change in these compounds due to the redistribution of the individual vibronic band intensities within the long wavelength absorption band.

The absorption spectra of compounds **II** and **V** in 50% v/v aqueous ethanol at different acidities are shown in Figs 3 and 4.

The observed spectral characteristics of the three main bands, i.e. the

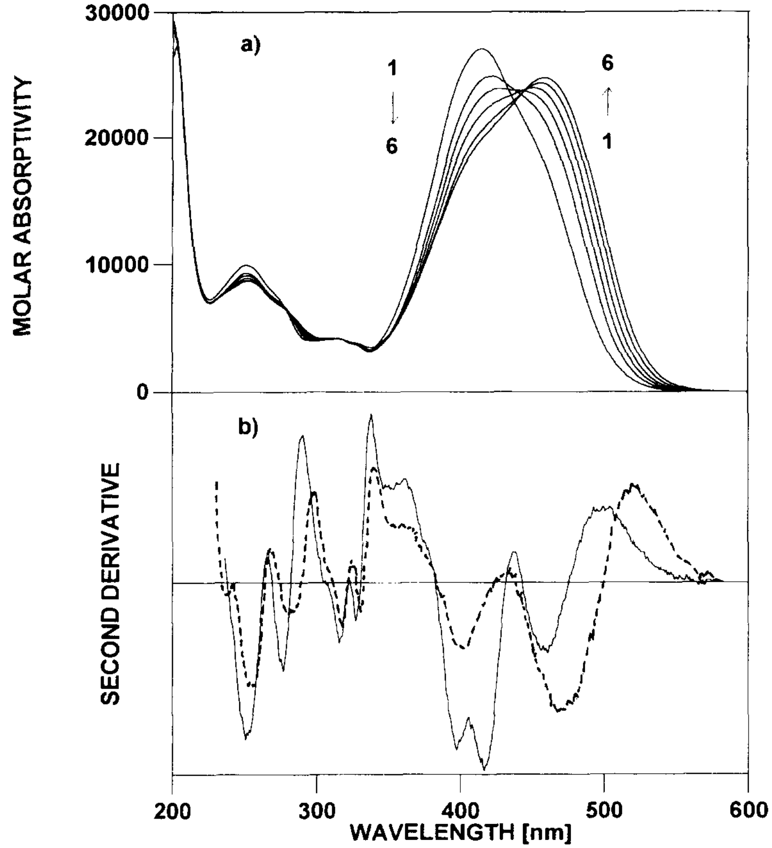


Fig. 2. (a) Absorption spectra of compound **III** at different v/v ethanol/water ratios: 1, 100% ethanol; 2, 70; 3, 50%; 4, 40%; 5, 30%; 6, 20% v/v ethanol/water. (b) Second derivative spectra of solutions 1 (———) and 6 (- - -).

TABLE 1

Positions (in cm^{-1}) of the Vibrational Sub-bands Within the Long Wavelength Absorption π–π^* Band of Compound **II** in Different Solvents

Solvent	D^a	ν_{0-4}	ν_{0-3}	ν_{0-2}	ν_{0-1}	ν_{0-0}
iso-Octane	1.94	29 410	27 650	26 205	24 850	23 580
Ethanol	24.3	28 800	27 410	25 880	24 410	22 520
Acetonitrile	36.2	28 680	27 290	25 770	24 320	22 400
Formamide	110	28 470	27 000	25 250	23 950	21 700

[a] Dielectric constant.

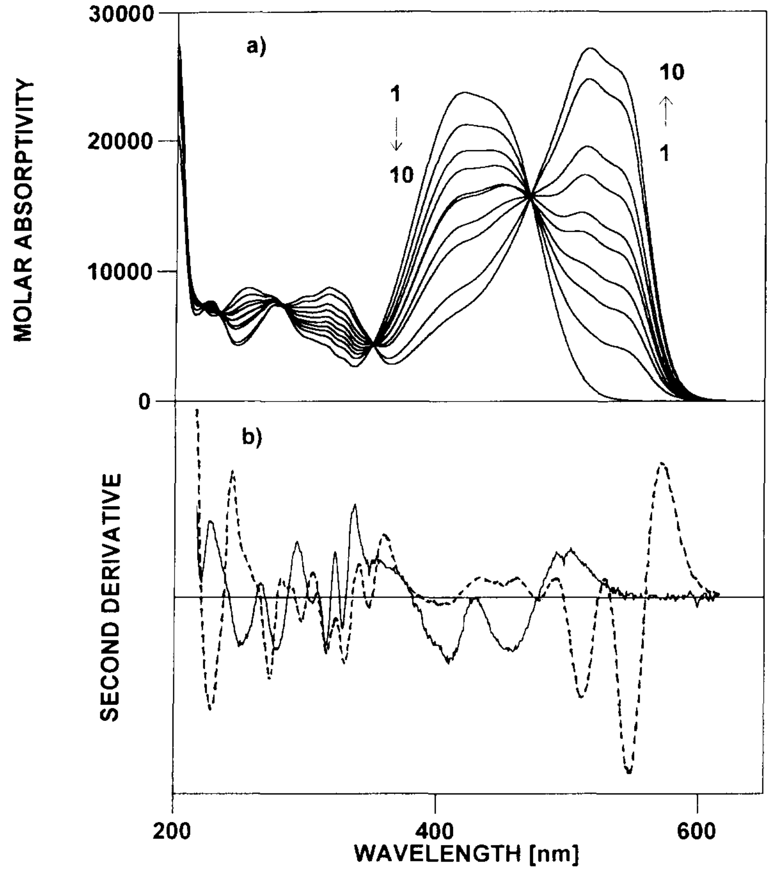


Fig. 3. (a) Absorption spectra of compound **II** in 50% v/v ethanol/water at different pH values: 1, without acid; 2, 2.91; 3, 2.63; 4, 2.50; 5, 2.33; 6, 2.26; 7, 2.12; 8, 2.04; 9, 1.77; 10, 1.63. (b) Second derivative spectra of solutions 1 (———) and 10 (- - -).

unprotonated B-, ammonium A- and azonium C-bands, according to Scheme 1, are presented in Table 2.

The influence of the structural (substituent effect) and environmental (solvent polarity) effects in the compounds investigated could be explained with the charge transfer (CT) model 1 (Scheme 3), where the substituted azobenzene chromophore system is classified as a donor (D)–acceptor (A) system.[19–22]

The azonium structure could be presented within the CT-model by system 2 (Scheme 4).[22]

It is worth nothing that the donor fragment in the azo form (CT-model 1) is acting in the azonium system (CT-model 2) as an acceptor, meaning that the same structural changes in a particular fragment could lead to different effects in the absorption bands determining their color. The introduction of

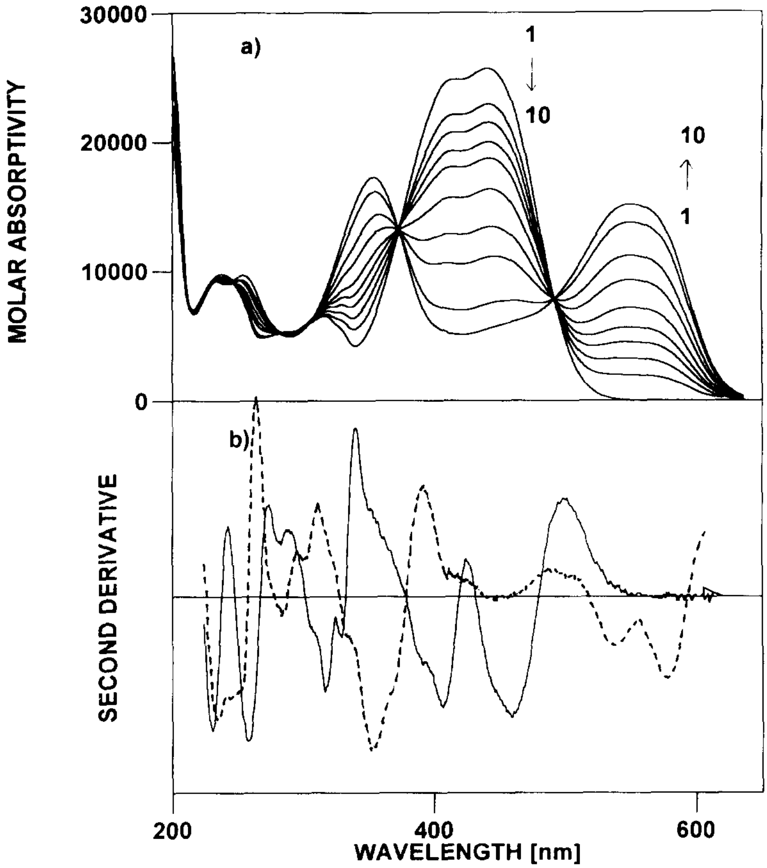
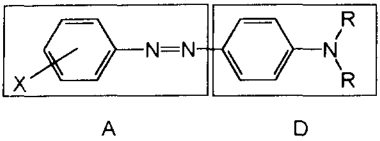


Fig. 4. (a) Absorption spectra of compound **V** in 50% v/v ethanol/water at different pH values: 1, without acid; 2, 3.10; 3, 2.83; 4, 2.65; 5, 2.52; 6, 2.35; 7, 2.13; 8, 1.98; 9, 1.68; 10, 1.49. (b) Second derivative spectra of solutions 1 (———) and 10 (- - -).

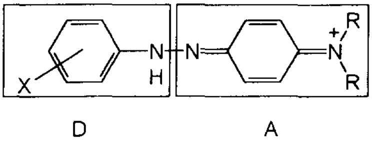
TABLE 2
Spectral Characteristics of the Unprotonated and Protonated (Ammonium and Azonium) Forms of Compounds I–V in 50% v/v Aqueous Ethanol

Dye	*Unprotonated form*				*Protonated forms*					
					Ammonium		*Azonium*			
	λ_{max}^{obs} *(nm)*	ϵ_{max}^{obs}	ν_{0-0} (cm^{-1})	ν_{0-1} (cm^{-1})	λ_{max}^{obs} *(nm)*	ϵ_{max}^{obs}	λ_{max}^{obs} *(nm)*	ϵ_{max}^{obs}	ν_{0-0} (cm^{-1})	λ_{0-1} (cm^{-1})
I	382	22 760	22 680	26 100	318	16 780	496	8410	19 190	20 160
II	420	23 790	21 830	24 270	317	8740	518	27 020	18 210	19 530
III	428	23 340	21 440	23 850	317	8220	530	19 450	17 530	18 490
IV	426	25 420	21 660	24 180	317	7820	522	29 660	18 090	19 350
V	442	25 690	21 660	24 550	354	17 250	554	15 160	17 270	18 460



CT-model 1

Scheme 3.



CT-model 2

Scheme 4.

stronger electron-donor $N(CH_3)_2$ substituents instead of NH_2 into the molecule of unprotonated **II** causes a bathochromic shift of about 18 nm (0–0 transition, in 50% v/v aqueous ethanol), while the introduction of the OCH_3 group in compounds **III–V** does not lead to significant color changes, in accordance with CT-model 1. The position of the A-band at 320–330 nm, associated with the ammonium tautomeric form BH^+_{AM}, closely corresponds to that of the compound without a protonated amino or dialkylamino group. The C-band of the azonium tautomeric form also has vibronic structure (Figs 3 and 4), and the electronic transition is associated with a charge transfer from the phenylamino fragment (D) to the quinoneimine one (A). The introduction of a relatively strong electron donor substituent, such as OCH_3 in the *o*- and *p*-positions (compounds **III** and **V**), leads to a pronounced bathochromic shift of the corresponding C-band, in accordance with CT-model 2. The net result is that electron donor substituents like the OCH_3 group significantly increase the difference in color of protonated and unprotonated species, which is an important factor for any specific 'hi-tech' application. In this respect, the color of the azonium form is deeper, more intense and brighter, since the average of its half-bandwidth is about 3000–3500 cm^{-1}, while in the unprotonated dyes this value is 5000–6000 cm^{-1}.

It is also of interest to note that the absorption spectra show that the protonation of the investigated compounds proceeds with relative increase of ammonium and azonium forms (Fig. 5, where the ϵ_C/ϵ_A ratio is plotted as a function of pH).

Evidently in all cases during the course of protonation, the increase in acidity leads to an increase in the ϵ_C/ϵ_A ratio in the following order **I** $<$ **V** $<$

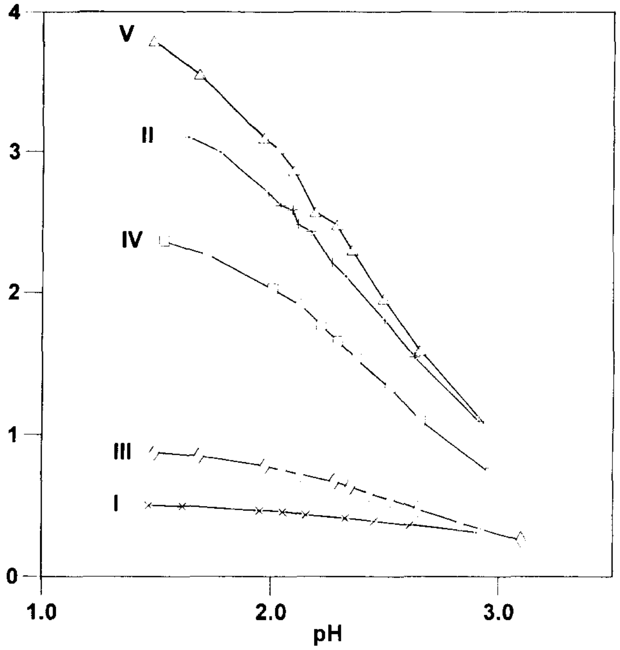


Fig. 5. The ϵ_C/ϵ_A ratio for compounds **I–V** as a function of pH.

III < **II** < **IV**, i.e. the amount of the azonium tautomeric form and the value of the tautomeric equilibrium constant K_T = [azonium]/[ammonium] also increases. After complete transformation of the first conjugated acid, any further increase in acid concentration (>2N HCl) to the point where the second protonation occurs is accompanied by an increase of ϵ_C and a decrease of ϵ_A. This means that the tautomeric equilibrium is gradually displaced toward the azonium form, in accordance with previous observations,[2,5,8,9] but the increasing order shown in Fig. 5 is not changed.

The tautomeric equilibrium constant K_T is a measure of the difference between the basicity of the β-azo nitrogen (pK_{AZ}) and that of the amino nitrogen (pK_{AM}).[5,23,24] One indication of the position of K_T could be the ratio ϵ_C/ϵ_A,[2,4,5,23] which is roughly proportional to K_T if the absorption of the azonium form at λ_{max} of the ammonium form is assumed to be zero, and vice versa:[5,9]

$$K_T = \frac{\epsilon_C}{\epsilon_A} \frac{\epsilon_{AM}^{\lambda_{AM}}}{\epsilon_{AZ}^{\lambda_{AZ}}} \qquad (1)$$

where ϵ_C and ϵ_A are apparent molar absorptivities of the C- and A- bands respectively, and $\epsilon_{AZ}^{\lambda_{AM}}$ and $\epsilon_{AM}^{\lambda_{AM}}$ are the corresponding true molar absorptivities.

However, the azonium form has some absorption ($\epsilon^{\lambda_{AM}}_{AZ} \sim 2000\ \mathrm{l\,mol^{-1}\,cm^{-1}}$) at the absorption wavelength (A-band) of the ammonium form,[9] while the ammonium form does not absorb at the absorption wavelength (C-band) of the azonium form. Therefore, K_T values for compounds **I–V** could be estimated using eqn (2):

$$K_T = \frac{\epsilon_C}{\epsilon^{\lambda_{AZ}}_{AZ} - \epsilon_C} \tag{2}$$

The values of K_{AZ}, K_{AM} and K_T are connected with eqns (3)–(5):[5,23]

$$K_T = \frac{K_{AM}}{K_{AZ}} \tag{3}$$

$$K_{AM} = K_a(1 + K_T) \tag{4}$$

$$K_{AZ} = K_a\left(1 + \frac{1}{K_T}\right) \tag{5}$$

The values of $\epsilon^{\lambda_{AZ}}_{AZ}$ and $\epsilon^{\lambda_{AM}}_{AM}$ were estimated to be $60\,400\ \mathrm{l\,mol^{-1}\,cm^{-1}}$ and $22\,900\ \mathrm{l\,mol^{-1}\,cm^{-1}}$, respectively, in the case of compound **II**[24] and similar values have also been reported.[9,25,26]

The estimated values of K_{AZ}, K_{AM} and K_T according to eqns (1)–(5), together with the values of $\mathrm{p}K^{obs}{}_a$ and ϵ_C/ϵ_A evaluated from the absorption spectra of compounds **I–V** are collected in Table 3. The introduction of the *o*- and *p*-OCH_3 group in compounds **III** and **V** leads to a decrease in the K_{AM} values and a corresponding increase in K_{AZ} values (Table 3). Following eqn (3), the net effect is evidently a decrease in K_T values and shift of the tautomeric equilibrium towards the ammonium form. The opposite effect is observed if the NH_2 group in compound **I** is replaced by the $N(CH_3)_2$ group in compound **II**. The values of K_{AZ}, K_{AM} and K_T in Table 3 should be con-

TABLE 3
Estimated ϵ_C/ϵ_A Ratios and Calculated Values of K_T, $\mathrm{p}K_{AM}$ and $\mathrm{p}K_{AZ}$ for Compounds **I–V**

Dye	$\mathrm{p}K_a^{obs}$	ϵ_C/ϵ_A	$K_T{}^a$	$\mathrm{p}K_{AM}{}^a$	$\mathrm{p}K_{AZ}{}^a$
I	2.07	0.501	0.162 (0.190)	2.00 (1.99)	1.21 (1.27)
II	2.00	3.092	0.809 (1.172)	1.74 (1.66)	1.65 (1.73)
III	2.06	2.366	0.475 (0.897)	1.89(1.78)	1.57 (1.73)
IV	1.94	3.793	0.965 (1.438)	1.65 (1.55)	1.63 (1.71)
V	2.10	0.879	0.335 (0.333)	1.97 (1.98)	1.50 (1.50)

[a] The values in parentheses are calculated according to eqn (1), the other values using eqn (2).

sidered as semi-quantitative, since the individual spectral characteristics of the tautomeric forms involved in the complex equilibria (Scheme 1) are not precisely determined. Using the recently developed approach for the quantitative analysis of tautomeric equilibria,[10–13] it is possible to solve such a non-trivial task. Preliminary results in this respect are promising and will be reported later.

ACKNOWLEDGEMENT

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REFERENCES

1. Badger, G. M., Buttery, R. G. & Lewis, G. M., *J. Chem. Soc.*, (1954) 1888.
2. Sawicki, E., *J. Org. Chem.*, **21** (1956) 605; **22** (1957) 365, 621, 743.
3. Si-Jung, Y. & Jaffe, H. H., *J. Am. Chem. Soc.*, **81** (1959) 3283.
4. Gerson, F. & Heilbronmer, E., *Helv. Chim. Acta*, **45** (1962) 42.
5. Bershtein, I. Ya & Ginsburg, O. F., *Russ. Chem. Rev.*, **41** (1972) 97.
6. Cox, R. A. & Buncel, E., In *The Chemistry of Hydrazo, Azo and Azoxy Groups*, ed. S. Patai. Interscience, New York, 1975, p. 18.
7. Mohr, G. J. & Wolfbeis, O. S., *Anal. Chim. Acta*, **292** (1994) 41.
8. Yamamoto, Sh., Tenno, Y. & Nishimura, N., *Austr. J. Chem.*, **32** (1979) 41.
9. Hepworth, D. J., Mason, D., Hallas, G. & Marsden, R., *Dyes & Pigments*, **6** (1985) 389.
10. Antonov, L. & Stoyanov, St., *Anal. Chim. Acta*, **314** (1995) 225.
11. Stoyanov, St., Antonov, L., Soloveytchik, B. & Petrova, V., *Dyes & Pigments*, **26** (1994) 149.
12. Anotonov, L., Stoyanov, St. & Stoyanova, T., *Dyes & Pigments*, **27** (1995) 133.
13. Antonov, L. & Stoyanov, St., *Dyes & Pigments*, **28** (1995) 31.
14. Stoyanov, St., Petrova, V., Antonov, L. & Petkov, I., *God. Sof. Univ., Khim. Fac. (Bulg.)*, **86** (1993) 33; *Chem. Abstr.*, **121** 204890s.
15. Brode, W., Seldin, I., Spoerr, P. & Wyman, G., *J. Am. Chem. Soc.*, **77** (1955) 2762.
16. Sueshi, Y., Asano, M., Yamamoto, Sh. & Nishimura, N., *Bull. Chem. Soc. Japan*, **58** (1985) 2729.
17. Antonov, L. & Stoyanov, St., *Anal. Chim. Acta*, in press; *Spectr. Lett.*, in press.
18. Mustroph, H., *Dyes & Pigments*, **15** (1991) 129.
19. Griffiths, J., *Colour and Constitution of Organic Molecules*. Academic Press, London, 1976, pp. 140–141.
20. Fabian, J., *Chimia*, **32** (1978) 323.
21. Mustroph, H. & Epperlein, J., *J. Prakt. Chem.*, **323** (1981) 755.
22. Mustroph, H., Haessner, R. & Epperlein, J., *J. Prakt. Chem.*, **326** (1981) 259.
23. Zenhäuserm, A. & Zollinger, H., *Helv. Chim. Acta*, **45** (1962) 1890.

24. Yamamoto, Sh., Nishimura, N. & Hasegawa, Sh., *Bull. Chem. Soc. Japan*, **46** (1973) 194.
25. Castelino, R. W. & Hallas, G., *J. Chem. Soc. B*, (1971) 793.
26. Cilento, G., Miller, E. C. & Miller, J. A., *J. Am. Chem. Soc.*, **78** (1956) 1718.