Dyes and Pigments **18** (1992) 227–235

Properties of Azo Dyes Derived from 2-(*N*-substituted alkyl-*N*-arylamino)ethyltrimethyl-ammonium Salts. Part I: Phenylamino Derivatives

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(Received 17 July 1991; accepted 8 October 1991)

ABSTRACT

*Results are presented on the properties of azo dyes derived from 2-(*N*-2-hydroxyethyl-, allyl- or benzyl-*N*-phenylamino)ethyltrimethyl-ammonium salts as coupling components and 3-nitro-, 4-nitro-, 2-chloro-4-nitro- and 2,6-dichloro-4-nitroanilines as diazo components.*

The electronic spectra of the dye are discussed and a qualitative evaluation is given of their pH-stability and acid-base equilibria. It is shown that with the conjugated acids obtained, the tautomeric equilibrium is shifted almost entirely to the azonium tautomer. The nature of the substituent at the nitrogen atom of the coupling component is of importance for the combination characteristics and reserving capacity of the dyes. The compatibility value, the rate of dye-bath exhaustion and reserving capacity decrease in the order benzyl, allyl, hydroxyethyl. The colour, light-fastness and other fastness properties are not significantly influenced by the substituent.

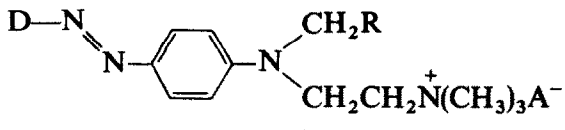
1 INTRODUCTION

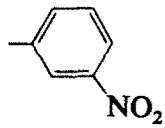
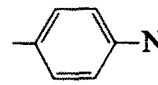
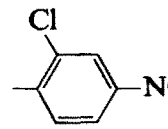
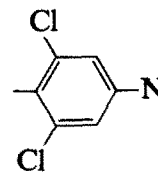
Azo dyes based on 2-(*N*-alkyl-*N*-arylamino)ethyltrimethylammonium salts have found practical application[1] and some of them are amongst the most frequently used cationic dyes. Published data pertaining to analogous dyes containing *N*-substituted alkyl moieties in the coupling component are more limited. It could be expected that the properties of such dyes would depend

Dyes and Pigments 0143-7208/92/$05.00

to a large extent on the nature of the substituent at the nitrogen atom linking the side chain to the chromophore system. By varying this substituent, dyes with different properties could be synthesized.

We have described a method for the synthesis of a series of 2-(*N*-substituted alkyl-*N*-arylamino)ethyltrimethylammonium salts[2] and in a continuation of these studies,[3] we report here on the influence of substituents such as 2-hydroxyethyl, -allyl and -benzyl on the properties of the derived azo dyes.



	D	R
1a–1c		—CH_2OH—$CH{=}CH_2$—C_6H_5
2a–2c		—CH_2OH—$CH{=}CH_2$—C_6H_5
3a–3c		—CH_2OH—$CH{=}CH_2$—C_6H_5
4a–4c		—CH_2OH—$CH{=}CH_2$—C_6H_5

2 RESULTS AND DISCUSSIONS

Electronic spectra data for the dyes is given in Table 1. It is apparent that the colour of the dyes is not significantly influenced by the nature of the substituent at the nitrogen atom of the coupling component. The band maxima are flat, relatively wide (half-band-width $\Delta\nu_{1/2}$ 5500–6200 cm^{-1}) and asymmetrical (assymetry factor $\rho = 0{\cdot}56$–$0{\cdot}80$), a character which influences the purity and intensity of the dye colour. The dyes from 3-nitroaniline (1a–1c, yellow) and 2,6-dichloro-4-nitroaniline (4a–4c, yellowish-brown) have similar λ_{max} and differ mainly in their asymmetry factor. In the case of 1a–1c ρ is 0·64–0·75 while this value is 0·78–0·80 for

TABLE 1
Spectral Characteristics of the Dyes

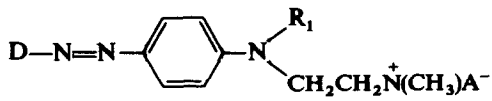
Dye	$H_2O:C_2H_5OH$ 4:1				H_2SO_4 *0·1 mol/litre*		H_2SO_4 *4 mol/litre*		
	λ_{max} (*nm*)	ε_{max} ($\times 10^{-3}$)	$\Delta\nu_{1/2}$ ($\times 10^{-3}\,cm^{-1}$)	σ	λ_{max} (*nm*)	ε_{max} ($\times 10^{-3}$)	λ_{max} (*nm*)	ε_{max} ($\times 10^{-3}$)	$\Delta\nu_{1/2}$ ($\times 10^{-3}\,cm^{-1}$)
1a	439	23·4	5·9	0·64	428s	16·6	521s	61·5	3·1
					459	21·2	541	60·0	
					508s	14·7			
					536s	11·3			
1b	435	24·3	6·0	0·70	451	21·5	523s	60·5	3·0
					536s	10·3	537	61·7	
1c	431	21·7	6·0	0·75	437	21·0	523s	57·8	3·1
					539s	6·0	543	54·8	
2a	475	26·6	5·5	0·62	517	34·7	527s	69·3	2·8
					543s	29·7	551	74·7	
2b	465	27·1	6·2	0·56	465	27·4	521s	77·4	3·0
							534	78·9	
2c	469	25·1	5·6	0·63	504	29·2	530	66·9	3·0
							549s	65·9	
3a	486	31·8	5·6	0·63	490	30·1	534	72·1	3·2
3b	485	27·1	5·5	0·63	488	27·3	532	30·4	3·0
3c	479	22·5	5·6	0·67	480	24·1	532s	52·5	3·1
							541	52·8	
4a	439	23·1	5·7	0·78	442	24·1	490	41·4	3·9
4b	438	23·6	5·7	0·79	439	24·4	488	36·0	3·8
4c	437	23·6	5·7	0·8	437	24·4	492	29·7	4·3

4a–4c. Despite the relatively close values of the absorption maxima (431–439 nm), the higher ρ values are the reason for the pronounced brownish hue of the dyes from 2,6-dichloro-4-nitroaniline compared with those from 3-nitroaniline. For dyes having the same diazo components, quite narrow ranges of variation of their absorption maxima occur (viz., from 2 nm in the case of 4a–4c to 10 nm for 2a–2c), these ranges shifting slightly to shorter wavelength in the order hydroxyethyl, allyl, benzyl (except for dye 2b). On the other hand, it was observed that a higher asymmetry factor corresponds to bands situated in the shorter wavelength region. Thus opposite effects on the colour are mutually compensated to some extent, and dyes having the same diazo component and differing solely in the type of substituent at the nitrogen atom of the coupling component have similar shades even when the difference in λ_{max} reaches 10 nm.

For the same substituent *R*, the asymmetry factor decreases for the diazo component in the order 2,6-dichloro-4-nitroaniline, 3-nitroaniline, 2-chloro-4-nitroaniline, 4-nitroaniline.

Table 2 shows data for dyes having H, CH_3 or C_2H_5 as substituents at the

TABLE 2
Spectral Characteristics[a] of other Azo Dyes



D	R_1	*A*	λ_{max} (*nm*)	ε_{max} ($\times 10^{-3}$)	$\Delta\nu_{1/2}$ ($\times 10^{-3}$ cm^{-1})	ρ
3-Nitrophenyl	H	Cl	407 440s	21·6	6·4	1·13
3-Nitrophenyl	CH_3	CH_3SO_4	436	23·2	5·8	0·65
3-Nitrophenyl	C_2H_5	I	453	21·5	6·0	0·48
4-Nitrophenyl	H	Cl	456	25·2	5·9	0·75
4-Nitrophenyl	CH_3	Cl	473	26·9	5·7	0·61
4-Nitrophenyl	C_2H_5	I	478	35·2	5·6	0·58
2-Chloro-4-nitrophenyl	H	Cl	460	26·1	6·0	0·71
2-Chloro-4-nitrophenyl	CH_3	I	485	27·0	5·6	0·60
2-Chloro-4-nitrophenyl	C_2H_5	I	485	22·3	6·1	0·56

[a] Data from own studies.

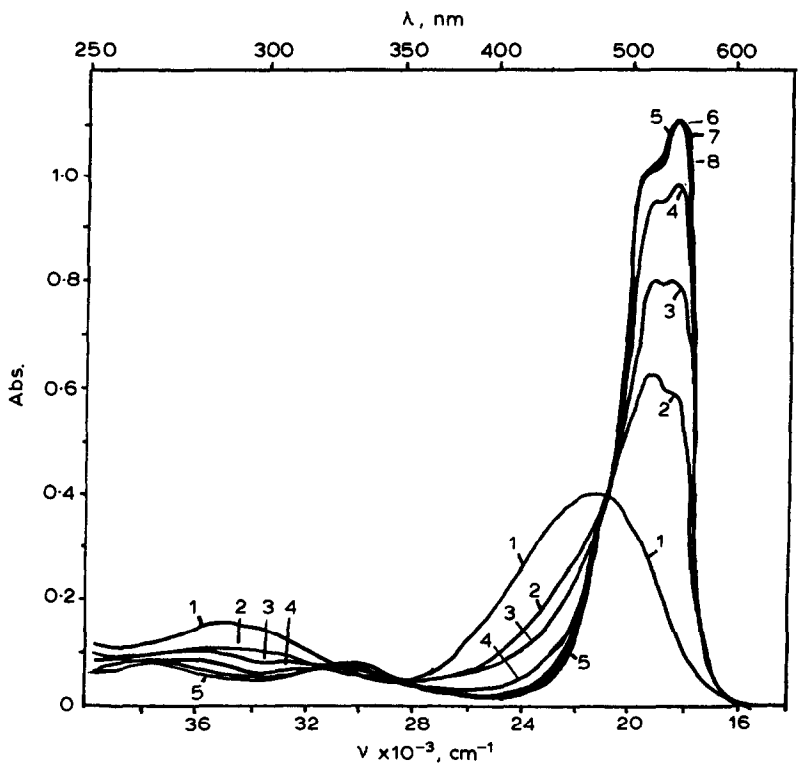
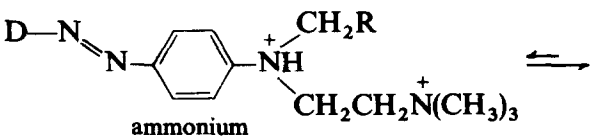


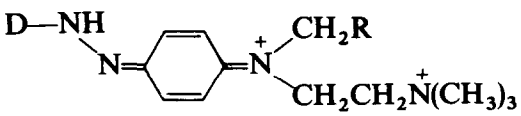
Fig. 1. Absorption spectra of dye 2a (c = 3·08 mol/litre) in sulphuric acid. 1—0, 2—0·1, 3—0·2, 4—0·49, 5—0·99, 6—1·97, 7—3·95, 8—6·02 mol/litre H_2SO_4.

nitrogen atom. It is seen that the bathochromic shift in dyes containing hydroxyethyl, allyl and benzyl substituents is almost the same as that in the methyl analogues and smaller than that in the ethyl derivatives. The other characteristics, i.e. half-bandwidth and asymmetry factor show the same trend. Thus, with respect to their shade, the dyes 1–4 are more similar to the *N*-methyl rather than the *N*-ethyl derivatives.

The dyes show a relatively good pH stability. Changes in the spectra are observed at acidity higher than $0{\cdot}5–1{\cdot}10^{-3}$ mol/litre sulphuric acid. The nature of these changes in solutions with different acidity is the same, as shown for dye 2a in Fig. 1. It is seen that a bathochromically shifted band appears as a result of proton addition and this is attributed to the azonium tautomer in the possible azonium–ammonium equilibrium.[4]



ammonium



azonium

The spectrum does not show a band at about 320 nm due to the ammonium tautomer, and is influenced substantially by the acid concentration. The tautomeric equilibrium in these dyes is thus shifted almost completely to the azonium form.

As seen from the data in Table 1, the protonation of the dyes is practically complete in solutions containing 4 mol/litre sulphuric acid. At sulphuric acid concentration of about 0·1 mol/litre the dyes 1a–1c and 2a–2c are protonated to a considerable extent, while the less basic dyes 3a–3c and 4a–4c (having a chlorine atom as second and third electron acceptor show protonation only at an initial stage. The bands of the protonated dyes are narrower (half-width $\Delta\nu_{1/2} = 2800–4200\,\text{cm}^{-1}$), symmetrical and more intensive (up to 2·9 times) than those of nonprotonated dyes. Most of the dyes show a complex spectral profile composed of strongly overlapping intensive bands with maxima separated by 10–24 nm. The prevalance of one or other maximum, as shown for dye 2a, does not depend on the acid concentration. The intensity is independent of the dye concentration (Fig. 2), and hence aggregation does not take place.

Results obtained on the coloration of the polyacrylonitrile fibre Bulana, staining of other fibres during conjoint dyeing of polyacrylonitrile, and the

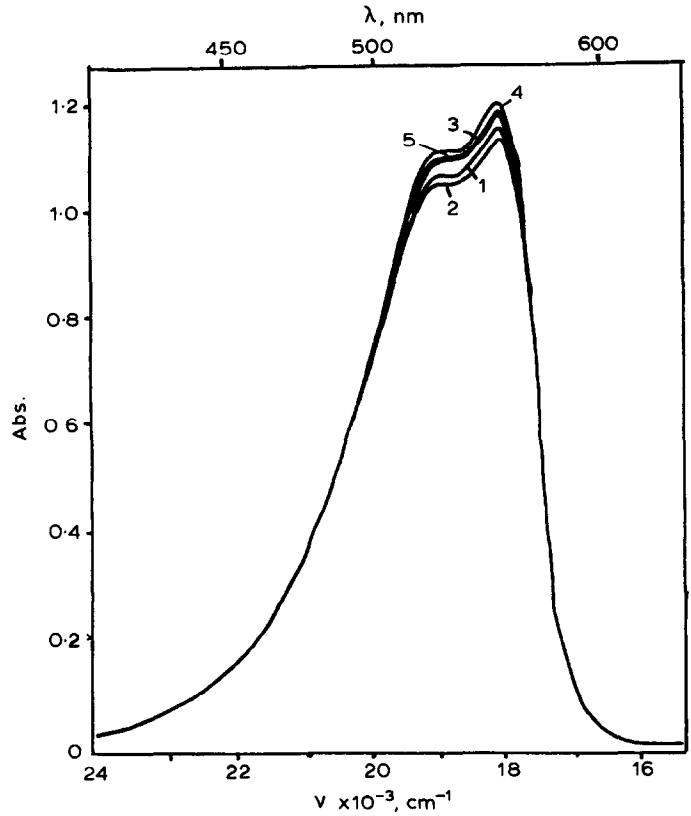


Fig. 2. Long-wave bands in the absorption spectra of dye 2a in sulphuric acid solution 2·35 mol/litre H_2SO_4. Dye concentration (mol/litre), cell thickness (cm). 1—$7{\cdot}37 \times 10^{-5}$ (0·2), 2—$2{\cdot}95 \times 10^{-5}$ (0·5), 3—$1{\cdot}47 \times 10^{-5}$ (1), 4—$0{\cdot}74 \times 10^{-5}$ (2), 5—$0{\cdot}30 \times 10^{-5}$ (5).

compatibility value (k-value) characterising the rates of dye uptake are presented in Table 3.

The dyes show good light fastness, which is characteristic of this type of dye; fastness to washing, perspiration, rubbing and dry cleaning is also excellent. Coloration of natural and acetate silk does occur and, with some exceptions, cotton, viscose and polyester fibres are well reserved. Substantial differences are observed in the behaviour of the dyes with respect to wool and polyamide. Their reserving capacity is influenced by the type of substituent at the N atom and is highest in the case of benzyl, followed by allyl and hydroxyethyl. The diazo component also influences the reserving capacity. The dyes from 2-chloro-4-nitroaniline show a lower reserving capacity than those from other diazo components and particularly those from 3-nitro- and 4-nitroaniline.

In contrast to similar dye with an *N*-methyl or *N*-ethyl substituent which

TABLE 3
Coloristic Properties of the Dyes on Bulana Fibre

Dye	*Fastness properties*					*Coloration of accompanying fibres*[a]							*K value*
	Light	*Washing 60°*	*Perspiration-acidic basic*	*Friction dry wet*	*Dry cleaning*	*C*	*AR*	*PA*	*W*	*R*	*VR*	*PE*	
1a	6	5	5	5	5	−	++	++	+	++	+	−	5
1b	6	5	5	5	5	−	++	+	+	++	−	−	3·5
1c	7	5	5	5	5	−−	++	−	−−	++	−−	−−	3
2a	7	5	5	5	5	−	++	++	++	++	+	−	5
2b	7	5	5	5	5	−	++	+	−	++	−	−	3
2c	6–7	5	5	5	5	−	++	++	−	++	−−	−−	3
3a	7	5	5	5	5	−	++	++	++	++	−	+	5
3b	6	5	5	5	5	−	++	+	+	++	−	+	3·5
3c	6	5	5	5	5	+	++	+	+	++	+	+	2
4a	6–7	5	5	5	5	−	++	+	+	++	−	−	5
4b	6–7	5	5	5	5	−	++	+	+	++	−	+	3·5
4c	6–7	5	5	5	5	−	++	−	+	++	−	−	2

[a] C, cotton; AR, acetate rayon; PA, polyamide; W, wool; R, rayon; VR, viscose rayon; PE, polyester. ++, good; +, slight; −, noticeable; −−, resist.

are characterised by a medium rate of dye uptake the dyes 1–4 have ratings varying from 2 to 5. A relationship between the compatibility value and the nature of the substituent at the N atom is apparent. Dyes with the same substituent have the same or very similar *k*-values, irrespective of the nature of the diazo component. The compatibility value drops and the rate of dye uptake increases in the order hydroxyethyl, allyl, benzyl. Dyes with a hydroxyethyl substituent have a compatibility value of 5 and are exhausted slowly. Dyes with an allyl substituent have a medium exhaustion rate (*k*-value 3·5, 3 for dye 2b) while those with a benzyl substituent show medium to rapid exhaustion (*k*-value 2–3). The hydrophilic character decreases in the same order and the hydrophobicity of the substituents is increased

TABLE 4
Melting Points and Elemental Analysis Data

Dye	*MP* (°C)	*Molecular formula*	*Analysis*[a] *found/calc.* (%)		
			C	*H*	*N*
1a	220–223	$C_{19}H_{26}N_5O_3I$	45·97	5·76	14·22
			45·70	5·25	14·02
1b	215–218	$C_{20}H_{26}N_5O_2I$	48·66	5·90	13·96
			48·49	5·29	14·14
1c	221–222	$C_{24}H_{28}N_5O_2I$	52·91	5·48	13·18
			52·85	5·17	12·84
2a	232–235	$C_{19}H_{26}N_5O_2I$	45·77	5·49	13·82
			45·70	5·25	14·02
2b	243–245	$C_{20}H_{26}N_5O_2I$	48·86	5·78	13·85
			48·49	5·29	14·14
2c	234–237	$C_{24}H_{28}N_5O_2I$	52·99	4·94	12·57
			52·85	5·17	12·84
3a	250–254	$C_{19}H_{25}ClN_5O_3I$	43·40	5·02	13·10
			42·75	4·72	13·12
3b	233–237	$C_{20}H_{25}ClN_5O_2I$	46·18	5·16	13·31
			45·34	4·76	13·22
3c	198–199	$C_{24}H_{27}ClN_5O_2I$	49·31	4·93	11·82
			49·71	4·69	12·08
4a	230–232	$C_{19}H_{24}Cl_2N_5O_3I$	40·24	4·50	12·22
			40·16	4·26	12·32
4b	240–246	$C_{20}H_{24}Cl_2N_5O_2I$	43·25	4·49	12·13
			42·50	4·28	12·39
4c	267–269	$C_{24}H_{26}Cl_2N_5O_2I$	46·92	4·59	11·21
			46·92	4·27	11·40

[a] Solvents used for recrystallization: 1a–1c, ethanol; 2a, 2b, ethanol/water; 2c, 3a–3c, 4a–4c, ethanol.

accordingly. Thus, while the k-values are almost independent of the nature of the diazo component, the nature of the substituent at the nitrogen atom is of prime importance for the compatibility characteristic of the dyes. By changing the substituent, this characteristic can be altered in a desired direction without significantly influencing the colour.

3 EXPERIMENTAL

The coupling components[2] and the dyes[3] were obtained as previously described. Purification of the dyes was carried out by dissolution in hot water and precipitation as iodides with KI. Relevant data is shown in Table 4. Dyeings on polyacrylonitrile fibres were carried out from a dye bath containing (o.w.f.) 0·75% dye, 5% acetic acid and 10% sodium sulphate at 100°C in a 100–150:1 liquor ratio. Mixed substrate evaluations were similarly effected using polyacrylonitrile and other fibre (Table 4) in a 1:1 ratio. Compatibility values were determined according to Beckmann[5] using a standard series of blue dyes.

4 CONCLUSIONS

The results show that the substituent at the nitrogen atom influences the rate of dye-bath exhaustion and the compatibility characteristics of the dyes, as well as their reserving capacity. The compatibility value increases, while the exhaustion rate and the reserving capacity decreases in the order benzyl, allyl, hydroxyethyl. The λ_{max} are bathochromically shifted in the same order; the same order holds with respect to decreasing asymmetry factor. The colour, light-fastness and other fastness properties are relatively unaffected.

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