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Properties of Azo Dyes Derived from 2-(*N*-substituted alkyl-*N*-arylamino)ethyltrimethyl-ammonium Salts: Part II. 3-Toluidino and 3-Anisidino Derivatives

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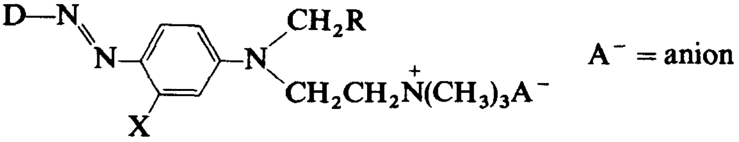
ABSTRACT

*The influence of 2-hydroxyethyl, allyl and benzyl substituents at the nitrogen atom of the arylamino group on the properties of azo dyes derived from 2-(3-toluidino-, or 3-anisidino)ethyl-*N,N,N*-trimethylammonium salts as coupling components and 3-nitro-, 4-nitro-, 2-chloro-4-nitro- and 2,6-dichloro-4-nitroaniline as diazo components was studied. Electronic spectra data for the dyes in 20% ethanol and in sulphuric acid (0·1 and 4 mol litre*$^{-1}$*), together with some coloristic properties, are reported. Relationships previously established for dyes derived from 2-phenylaminoethyl-*N,N,N*-trimethylammonium salts with respect to the effect of the substituent at the nitrogen atom and dye properties are valid for these dyes also. Methyl and methoxyl substituents in the azo component (in an* ortho *position with respect to the azo group) affect not only the colour, but also the rate of dyebath exhaustion, and thus the dyebath exhaustion properties of these dyes can be varied for specific end-use by appropriate structural modifications of the dyes.*

1 INTRODUCTION

Previous studies of the effect of 2-hydroxyethyl, allyl and benzyl substituents at the nitrogen atom of the phenylamino group on the properties of azo dyes derived from 2-phenylaminoethyl-*N*,*N*,*N*-trimethylammonium salts[1] are here extended to structural analogues containing methyl and methoxyl groups (**1a**–**1f**, **2a**–**2f**, **3a**–**3f**, **4a**–**4f**).



Dye nos	*D*	*X*	*R*
1a–1c	3-Nitrophenyl	CH_3	$CH_2OH, CH{=}CH_2, C_6H_5$
1d–1f	3-Nitrophenyl	OCH_3	$CH_2OH, CH{=}CH_2, C_6H_5$
2a–2c	4-Nitrophenyl	CH_3	$CH_2OH, CH{=}CH_2, C_6H_5$
2d–2f	4-Nitrophenyl	OCH_3	$CH_2OH, CH{=}CH_2, C_6H_5$
3a–3c	2-Chloro-4-nitrophenyl	CH_3	$CH_2OH, CH{=}CH_2, C_6H_5$
3d–3f	2-Chloro-4-nitrophenyl	OCH_3	$CH_2OH, CH{=}CH_2, C_6H_5$
4a–4c	2,6-Dichloro-4-nitrophenyl	CH_3	$CH_2OH, CH{=}CH_2, C_6H_5$
4d–4f	2,6-Dichloro-4-nitrophenyl	OCH_3	$CH_2OH, CH{=}CH_2, C_6H_5$

The preparation of 2-(3-toluidino- and 3-anisidino)ethyl-*N*,*N*,*N*-trimethylammonium salts, and of the dyes derived from them, has been previously reported.[2,3]

2 RESULTS AND DISCUSSION

Table 1 shows the electronic spectra characteristics of the dyes; the shape of the absorption band is broad ($\Delta\nu_{1/2} = 5400–6900\,cm^{-1}$) and asymmetrical (assymetry factor 0·41–1·07) with a flat maximum, thus resulting in the brownish hue inherent in the colour of these dyes.

The nature of the substituent at the nitrogen atom does not significantly affect the position of the absorption maximum. Such influences are most pronounced in the dyes derived from 4-nitroaniline, except for dyes **2a** (which shows a bathochromically shifted maximum, with a considerably lower asymmetry factor) and **4a** (which shows a hypsochromic shift accompanied by a higher asymmetry factor). The relationship between the nature of the substituent at the nitrogen atom and the absorption maxima for similar dyes in which X = H[1] is considerably decreased in these present dyes. Possibly the substituent X causes changes in the geometry of the excited and ground states, leading to more complex electronic transitions, as suggested by the larger half band widths of these dyes compared with those where X = H.

Unlike the case where X = H[1], the nitroaniline-based dyes in which X is CH_3 or OCH_3 show a complex long-wavelength absorption band, with two

TABLE 1
Spectral Characteristics of the Azo Dyes

Dye no.	*20% C_2H_5OH*				*0·1 mol litre^{-1} H_2SO_4*		*4 mol litre^{-1} H_2SO_4*			
	λ_{max} (*nm*)	ε_{max}	$\Delta\nu_{1/2}$ $\times 10^{-3}$ (*cm*$^{-1}$)	*Asymmetry factor*	λ'_{max} (*nm*)	ε_{max}	λ''_{max} (*nm*)	ε_{max}	$\Delta\nu_{1/2}$ $\times 10^{-3}$ (*cm*$^{-1}$)	$\Delta\lambda^a$ (*nm*)
1a	429	22 500	6·2	1·07	512	37 600	512s	59 100	3·0	+80
	454s	21 300			534s	36 400	534	59 500		
1b	430	23 800	6·1	1·03	512	40 700	519s	60 200	3·0	+75
	459s	22 600			530s	39 700	534	60 800		
1c	432	19 600	6·0	0·97	514	27 200	523s	55 600	3·0	+82
	448s	18 800			541s	26 000	541	56 400		
1d	432s	22 600	5·9	0·42	488	54 300	488	37 600	3·4	+39
	461	24 600			500s	53 400	500s	34 200		
1e	434s	23 100	5·9	0·41	480	37 900	486	45 400	3·3	+35
	465	25 100					500s	44 600		
1f	431s	24 300	6·1	0·42	484	58 100	484	63 500	3·2	+41
	459	25 600			500s	56 600	500s	62 400		
2a	504	29 100	5·8	0·43	516s	60 300	516s	68 200	3·0	+42
					546	61 200	546	72 700		
2b	483	26 000	5·8	0·54	523s	58 900	527s	69 100	2·9	+60
					539	59 400	543	72 800		
2c	480	23 800	5·8	0·67	517	49 300	506s	67 000	2·7	+66
							546	72 500		
2d	496	30 600	5·4	0·51	488	54 300	488	37 600	3·5	+4
					500	53 400s	500	34 200s		
2e	500	24 300	5·4	0·55	497	80 500	494	81 700	3·6	+6
2f	490	32 200	5·5	0·54	491s	73 300	491s	77 300	3·0	+21
					511	75 100	511	79 900		
3a	493	24 600	5·7	0·65	510	33 900	525	61 700	3·2	+32
3b	495	23 100	5·8	0·59	506	26 400	523	56 900	3·1	+28
3c	492	24 000	5·8	0·66	490	24 200	536	62 400	3·1	+44
3d	506	27 100	5·4	0·57	497	62 900	497	45 700	3·5	0
					515s	62 400	515s	45 600		
3e	498	28 200	5·7	0·56	486	67 900	493	69 400	3·2	−5
3f	504	29 700	5·4	0·52	500	67 200	500s	71 200	3·1	+17
					521s	66 500	521	71 900		
4a	431	19 500	6·9	0·83	439	18 600	431	19 500	6·6	0
4b	451	21 500	6·0	0·67	451	23 000	451	22 600	6·1	0
4c	450	20 300	6·1	0·74	450	20 400	496	47 200	3·5	+46
4d	450	25 000	6·0	0·75	463	32 000	453	25 200	6·0	+3
4e	447	23 800	6·0	0·80	457	30 000	446	25 500	5·9	−1
4f	447	24 100	6·2	0·72	456	27 900	488	52 100	4·2	+44

[a] $\Delta\lambda = \lambda''_{max} - \lambda_{max}$; in the case of complex bands the long-wavelength maxima are used in the calculation.

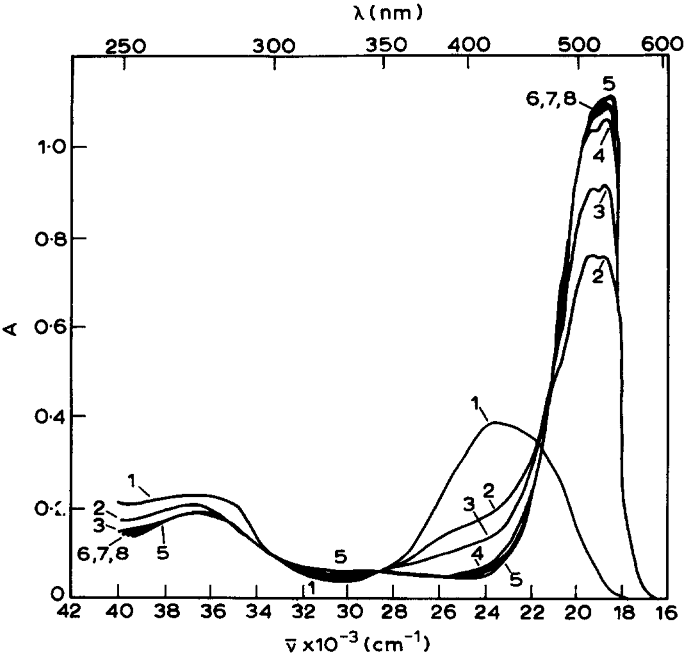


Fig. 1. Absorption spectra of dye **1c** ($c = 4{\cdot}03 \times 10^{-5}$ mol litre^{-1}) in sulphuric acid solution at the following concentrations (mol litre^{-1}): 1, 0; 2, 0·10; 3, 0·20; 4, 0·49; 5, 0·99; 6, 1·97; 7, 3·95; 8, 6·02.

maxima differing by up to 30 nm. Due to overlapping, one of these maxima appears as a shoulder. Where X is CH_3, the maximum in the shorter-wavelength range at 429–432 nm is predominant, whereas where X is OCH_3 that in the longer-wavelength range (458–465 nm) is the more resolved. This is the reason for the great differences in the asymmetry factors (0·97–1·07) of

TABLE 2

Shifts of λ_{max} of the Dyes Caused by CH_3 and OCH_3 Substituents, $\Delta\lambda = \lambda_{max(X)} - \lambda_{max(H)}$[a]

D	Δλ (*nm*)					
	$R = CH_2OH$		$R = CH{=}CH_2$		$R = C_6H_5$	
	$X = CH_3$	$X = OCH_3$	$X = CH_3$	$X = OCH_3$	$X = CH_3$	$X = OCH_3$
3-Nitrophenyl	−10/+15s	−7s/+22	−5/+24s	−1s/+30	+1/+17s	0s/+28
4-Nitrophenyl	+29	+21	+18	+35	+11	+21
2-Chloro-4-nitrophenyl	+7	+20	+10	+13	+13	+25
2,6-Dichloro-4-nitrophenyl	−8	+11	+13	+9	+13	+10

[a] The $\lambda_{max(H)}$ data are according to Ref. 1.

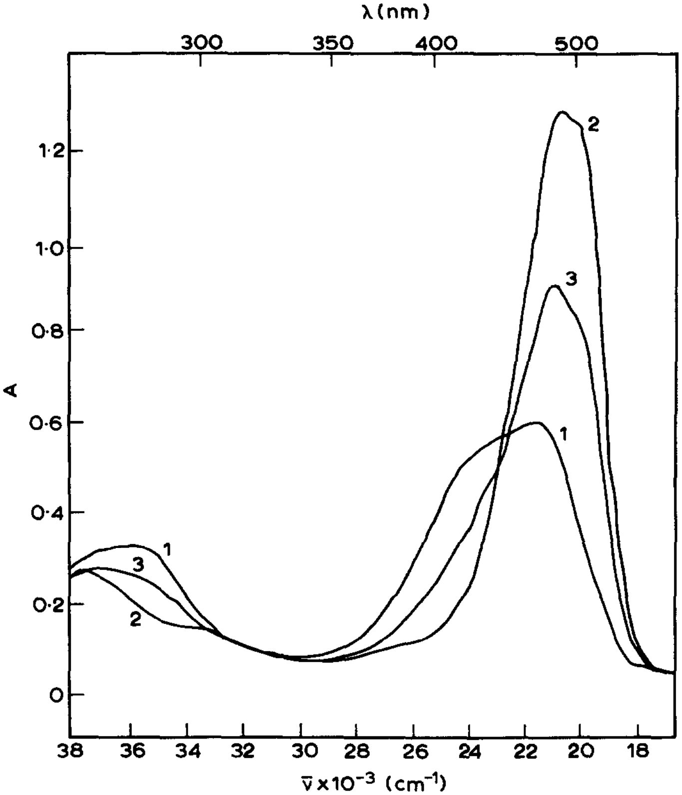


Fig. 2. Absorption spectra of dye **1d** ($c = 2{\cdot}3 \times 10^{-5}$ mol litre^{-1}) in sulphuric acid solution at the following concentrations (mol litre^{-1}): 1, 0; 2, 0·1; 3, 4.

dyes **1a–1c**, in which X is CH_3, and of dyes **1a–1f** (0·41–0·42) in which $X = OCH_3$, as calculated using the more resolved band maximum.

Shifts in the absorption maxima resultant from the CH_3 and OCH_3 substituents are shown in Table 2. The maxima of the long-wavelength bands of most of the dyes derived from 4-nitro- and 2-chloro-4-nitroaniline as diazo-components are in the bluish-green region and these dyes are red. The effect of X is the least in the dyes with 2,6-dichloro-4-nitroaniline as diazo component. Regardless of whether X is CH_3 or OCH_3, the maxima appear at practically the same wavelength (447–451 nm, except for **4a**). It is also evident that where two chlorine atoms are in the *ortho* position with respect to the azo group, steric effects are dominant.

Data on the long-wavelength bands of the dyes in 0·1 and 4 mol litre^{-1} sulphuric acid solutions are shown in Table 1. Comparison of their intensities (in 0·1 mol litre^{-1} H_2SO_4) with those of dyes in which $X = H$[1] suggests their stronger basicity due to the electron-donor nature of the CH_3

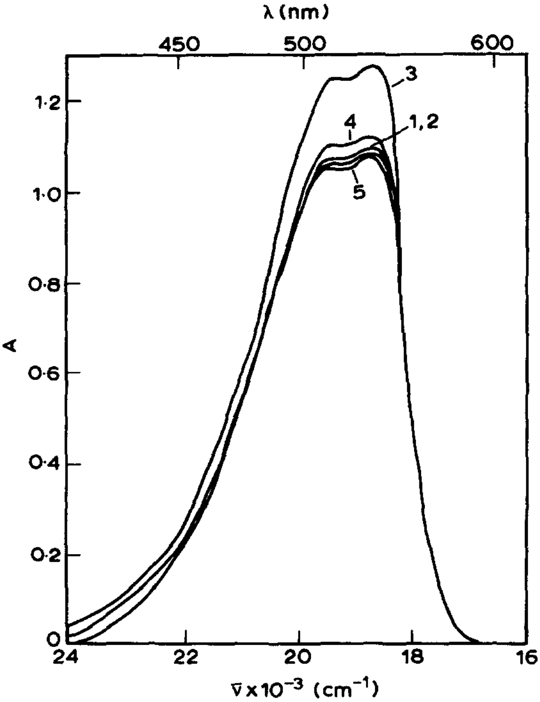


Fig. 3. Long-wavelength band in the absorption spectra of dye **1c** in sulphuric acid solution (2·35 mol litre^{-1}). Dye concentration, mol litre^{-1} and (cell thickness, cm) are as follows: 1, 10·08 × 10^{-5} (0·2); 2, 4·03 × 10^{-5} (0·5); 3, 2·32 × 10^{-5} (1); 4, 1·01 × 10^{-5} (2); 5, 0·40 × 10^{-5} (5).

and OCH_3 groups. The conjugated acids obtained are in the azonium form. The ammonium–azonium equilibrium is the same in stronger H_2SO_4 solutions (4 mol litre^{-1} and higher, Fig. 1). Only with dyes **1d, 2d** and **3d** in 4 mol litre^{-1} H_2SO_4 is a decrease of the absorption coefficient of long-wavelength bands observed, together with a slight increase of the absorption in the region 280–300 nm (Fig. 2). This is an indication that the equilibrium is somewhat shifted to the ammonium tautomer. The dyes from 2,6-dichloro-4-nitroaniline as diazo component behave in a different manner and the changes observed require additional studies.

The long-wavelength bands of the azonium tautomers are similar to those of the dyes where X = H; they are narrower and more intense than those of the non-protonated dyes. In these cases also, the two maxima of the bands are unaffected by the concentrations of acid and of the dye in the solution (Figs 1 and 3). Thus, aggregation does not occur in these cases.

The data in Table 3 demonstrate the influence of the electron-donor substituents X on the colour of the azonium tautomers; this has an effect opposite to that in the non-protonated dyes, and is most apparent where

TABLE 3

Shifts of λ_{max} of the Azonium Tautomers of the Dyes Caused by the Substituent $X = CH_3$ or OCH_3, $\Delta\lambda'' = \lambda''_{max(X)} - \lambda''_{max(H)}$[a]

D	*Δλ″ (nm)*					
	$R = CH_2OH$		*$R = CH = CH_2$*		*$R = C_6H_5$*	
	$X = CH_3$	*$X = OCH_3$*	*$X = CH_3$*	*$X = OCH_3$*	*$X = CH_3$*	*$X = OCH_3$*
3-Nitrophenyl	−7	−41	−3	−37	−2	−43
4-Nitrophenyl	−5	−51	+9	−40	−3	−38
2-Chloro-4-nitrophenyl	−9	−19	−9	−39	−5	−20

[a] The $\lambda''_{max(H)}$ data are according to Ref. 1; in the case of complex bands the long-wavelength are used in the calculation.

TABLE 4

Coloration Properties of the Dyes

Dye no.	*Fastness properties*					*Coloration of accompanying fibres*[a]							*K-value*
	Light	*Washing*	*Perspiration*	*Rubbing*	*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	6	5	5	5	5	−−	++	−	−	++	−−	−−	2
1d	6	5	5	5	5	−−	++	+	+	++	−−	−−	5
1e	5–6	5	5	5	5	−−	++	−	+	++	−	−	5
1f	6	5	5	5	5	−−	++	−	−	++	−−	−−	3·5
2a	7	5	5	5	5	−	++	+	+	++	+	−	5
2b	7	5	5	5	5	−	++	+	+	++	−	+	3
2c	6–7	5	5	5	5	+	++	−	+	++	−	−	2
2d	6	5	5	5	5	−	++	++	++	++	+	+	5
2e	5–6	5	5	5	5	−	++	+	+	++	−	−	3·5
2f	6–7	5	5	5	5	−	++	+	+	++	−	+	3·5
3a	7	5	5	5	5	+	++	++	++	++	+	+	5
3b	6	5	5	5	5	−	++	+	+	++	−	+	3
3c	7	5	5	5	5	+	++	+	+	++	+	+	1·5
3d	5–6	5	5	5	5	−	++	++	+	++	−	++	5
3e	7	5	5	5	5	−	++	+	+	++	−	+	3·5
3f	6	5	5	5	5	+	++	−	+	++	+	+	3
4a	7	5	5	5	5	−	++	+	++	++	−	−	5
4b	7	5	5	5	5	−	++	+	+	++	−	+	3·5
4c	7	5	5	5	5	+	++	+	+	++	−	−	1
4d	7	5	5	5	5	−	++	++	+	++	−	+	5
4e	6–7	5	5	5	5	−	++	+	+	++	−	+	5
4f	6	5	5	5	5	−	++	−	+	++	−−	−	3

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

TABLE 5
Melting Points and Elemental Analysis Data

Dye no.	*M.p. (°C)*[a]	*Molecular formula*	*Analysis (%): Found calcd*		
			C	*H*	*N*
1a	227–230	$C_{20}H_{28}N_5O_3I$	46·4	5·6	13·5
	(A)	(513·4)	46·8	5·5	13·6
1b	217–219	$C_{21}H_{28}N_5O_2I$	49·6	5·6	14·0
	(C)	(509·4)	49·5	5·5	13·75
1c	235–237	$C_{25}H_{30}N_5O_2I$	54·0	5·7	12·2
	(A)	(559·5)	53·7	5·4	12·5
1d	211–215	$C_{20}H_{28}N_5O_4I.H_2O$	44·2	5·5	12·6
	(A)	(547·4)	43·9	5·55	12·8
1e	221–225	$C_{21}H_{28}N_5O_3I$	48·0	5·6	13·4
	(A)	(525·4)	48·0	5·4	13·3
1f	219–221	$C_{25}H_{30}N_5O_3I$	52·5	5·6	11·5
	(B)	(598·5)	52·2	5·4	11·7
2a	253–255	$C_{20}H_{28}N_5O_3I$	46·8	5·7	13·3
	(B)	(513·4)	46·8	5·5	13·6
2b	239–243	$C_{21}H_{28}N_5O_2I$	49·7	5·9	13·8
	(A)	(509·4)	49·5	5·5	13·7
2c	253–255	$C_{25}H_{30}N_5O_2I$	53·8	5·5	12·6
	(B)	(559·5)	53·7	5·4	12·5
2d	254–256	$C_{20}H_{28}N_5O_4I$	45·4	5·4	13·3
	(A)	(529·4)	45·4	5·3	13·2
2e	218–223	$C_{21}H_{28}N_5O_3I$	—	—	13·4
	(A)	(525·4)			13·3
2f	257–259	$C_{20}H_{27}ClN_5O_3I$	52·5	5·0	12·35
	(B)	(575·5)	52·2	5·25	12·2
3a	243–244	$C_{20}H_{27}ClN_5O_3I$	43·6	5·0	12·35
	(A)	(547·9)	43·85	5·0	12·8
3b	231–235	$C_{21}H_{27}ClN_5O_2I$	46·6	5·3	12·7
	(A)	(543·9)	46·4	5·0	12·9
3c	232–233	$C_{25}H_{29}ClN_5O_2I$	50·35	5·2	11·4
	(A)	(593·9)	50·55	4·9	11·8
3d	241–244	$C_{20}H_{27}ClN_5O_2I$	43·3	5·2	12·6
	(B)	(563·9)	42·6	4·8	12·4
3e	227–230	$C_{21}H_{27}ClN_5O_3I$	—	—	12·7
	(B)	(559·9)			12·5
3f	255–257	$C_{25}H_{29}ClN_5O_3I$	48·9	4·4	11·4
	(B)	(609·9)	49·2	4·8	11·5
4a	236–238	$C_{20}H_{26}Cl_2N_5O_3I$	41·0	4·5	11·9
	(B)	(588·3)	40·8	4·45	11·9
4b	234–238	$C_{21}H_{26}Cl_2N_5O_2I$	43·4	4·3	12·2
	(A)	(578·3)	43·6	4·5	12·1
4c	202–203	$C_{25}H_{28}Cl_2N_5O_2I$	48·0	4·8	10·7
	(A)	(627·14)	47·8	4·5	11·15
4d	243–247	$C_{20}H_{26}Cl_2N_5O_4I$	40·3	4·5	11·6
	(A)	(604·3)	39·75	4·35	11·6
4e	170–174	$C_{21}H_{27}Cl_2N_5O_3I$	42·7	4·45	11·4
	(A)	(594·3)	42·4	4·4	11·8
4f	241–242	$C_{25}H_{28}Cl_2N_5O_3I$	47·4	4·7	10·7
	(B)	(644·4)	46·6	4·4	10·9

[a] Solvents used for recrystallization are indicated in parentheses: A, ethanol; B, ethanol/water; C, acetone/water.

$X = OCH_3$. Negative halochromism, characteristic of the azonium tautomers of *p*-aminobenzenes with an electron-donor substituent at the *meta* position with respect to the amino group, is only observed with some of the dyes (Table 1). However, for the majority of the dyes where $X = CH_3$ or for dyes where 3-nitroaniline is the diazo component, the halochromism is clearly positive.

The results from studies on the stability of the dyes, their behaviour during combined dyeing with other fibre types, and the dyebath exhaustion rates as characterized by the compatibility values, are shown in Table 4. The dyes exhibit very good resistance to light and other factors. The results of the combined dyeings are in good agreement with conclusions on the reserve properties of similar dyes where X = H, and are dependent on the nature of the substituent at the nitrogen atom and on the diazo component.[1] It follows that the introduction of a methyl or methoxy group at the *ortho* position in the azo component does not substantially affect the reserve properties of the dyes. Similar to the dyes in which X = H[1], these dyes also show a clear relationship between the compatibility value (*K*-value) and the nature of the substituent at the nitrogen atom. Dyes with an *N*-(2-hydroxyethyl) substituent are exhausted slowly. A medium exhaustion rate is observed with *N*-allyl-substituted dyes (except for dyes **1e** and **4e**) and a moderate-to-rapid exhaustion is typical for dyes with *N*-benzyl substituents. The *K*-value is, however, also dependent to some extent on other substituents. This is apparent with *N*-allyl-substituted dyes, where, for $X = OCH_3$ *K*-values are higher than for $X = CH_3$. This additional influence of the substituent X on the exhaustion rate is particularly evident in the dyes with an *N*-benzyl substituent, their *K*-values differing by 1·5–2 units. Rapid exhaustion is typical of the dyes where $X = CH_3$ (*K*-value 1–2), whilst where $X = OCH_3$, a medium exhaustion rate is observed (*K*-value 3–3·5). It follows, therefore, that the type of diazo component does not significantly affect the exhaustion rate of these dyes; the substituent on the nitrogen atom of the phenylamino group is of major importance for the *K*-value. The latter can, however, vary within certain limits on changes in the nature of the electron donor in the *ortho* position with respect to the azo group.

3 EXPERIMENTAL

The dyes were prepared following the procedure described in Ref. 3; coupling components were obtained according to the method given in Ref. 2. Data for the dyes are given in Table 5. Purification of the dyes, the determination of their melting points, fastness properties, dyeing of other fibres, *K*-value, and electronic spectra are as described in Ref. 1.

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