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Spectral Properties of Disperse Dyes, Derivatives of *N*-Methylnaphthalimidoazobenzene

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ABSTRACT

The UV–Vis spectra in DMF of a series of disperse dyes, derivatives of N-*methyl-4-(*N,N-*dialkylamino*-p-*phenylazo)naphthalimide are compared with analogous derivatives of phenylazobenzene. It was found that the Hammett σ-constant value of the naphthalimide residue is comparable with that of 2,4-dinitroaniline.*

1 INTRODUCTION

It has been previously reported[1] that benzeneazonaphthalimide dyes prepared from 4-aminonaphthalimide have a very intense colour due to the polar forms which occur under normal conditions. The proportion of the different forms of the dye structure depends on the type of dialkylamino group in the coupling component. Polyester fibres can be dyed with these dyes to give reddish-blue shades, while the 3-isomers give orange hues. Good performance properties and thermal stability of the dyes result from self-association of the naphthalimide derivatives, which however brings about lower water solubility, low diffusion coefficients and low value of the Nernst constant.[2]

Replacing the naphthalimide group ($R = H$) in the dye molecule by *N*-methylnaphthalimide ($R = CH_3$; **1**) does not detrimentally affect the properties of the dyes and it makes their application easier because of improvement in solubility (Wojciechowski, K., unpublished).[2,3] Structural influences on the colour of these dyes has not as yet been thoroughly

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TABLE 1
Characterization Data for Naphthalimides **1a–1w**

Dye	*X*	*Y*	R^1	R^2	*M.p. (°C)*	R_f[a]	*IR absorption* (cm^{-1})						
							N=N	*C—N*	*C—H*	*O—H*	*C=O*		
											Amide	*Ester*	
1a	H	H	H	H	217–219	0·75	1 603	1 358, 1 157	1 391, 820, 783		1 700, 1 668		
1b	NO_2	H	H	H	55–58	0·62	1 614	1 335	754		1 710, 1 670		(N—O) 1 531, 1 325
1c	NHAc	OEt	H	H	223–225	0·66	1 590	1 358	778		1 700, 1 661		(N—H) 1 513
1d	OH	H	H	H	186–189	0·68	1 597	1 368	785		1 706, 1 670		
1e	H	H	H	OH	199–202	0·57	1 594	1 363, 1128	1 402, 779	1 288, 1 040	1 700, 1 661		
1f	H	H	OH	OH	189–191	0·33	1 600	1 366	786	1 274, 1 044	1 708, 1 670		
1g	Me	H	OH	OH	227–230	0·37	1 591	1 354	1 379, 775	1 218, 1 038	1 694, 1 650		
1h	Cl	H	OH	OH	250–252	0·29	1 597	1 360	1 391, 783, 759	1 231, 1 044	1 698, 1 658		
1i	H	H	H	OAc	169–171	0·70	1 591	1 360	1 360, 779, 762		1 702, 1 663	1 744, 1 228, 1 037	
1j	H	H	OAc	OAc	149–152	0·67	1 600	1 368	786		1 709, 1 670	1 750, 1 234, 1 045	
1k	NHAc	H	OAc	OAc	141–145	0·29	1 598	1 370	828, 788, 760		1 655, 1 628	1 704, 1 230, 1 043	
1l	Me	H	OAc	OAc	205–206	0·68	1 600	1 357	1 382, 778		1 697, 1 659	1 751, 1 225, 1 044	
1m	Cl	H	OAc	OAc	198–200	0·65	1 596	1 360	1 386, 784		1 703, 1 663	1 745, 1 224, 1 041	
1n	NHAc	OMe	OAc	OAc	169–170	0·62	1 594	1 359	782		1 701, 1 663	1 747, 1 230, 1 045	
1o	H	H	ON	OAc	193–195	0·55	1 604	1 363	785, 759		1 704, 1 666	1 750, 1 234, 1 046	(C—N) 2 280
1p	H	H	ON	OH	214–216	0·50	1 598	1 360, 1 125	1 392, 780, 753		1 697, 1 661		(C—N) 2 270
1r	H	H	ON	H	178–181	0·65	1 594	1 358, 1 124	1 393, 779, 750		1 700, 1 664		(C—N) 2 250
1s	H	H	ON	ON	174–177	0·50	1 605	1 362, 1 130	1 398, 784, 752		1 702, 1 665		(C—N) 2 270
1t	NHAc	H	ON	ON	234–236	0·38	1 610	1 352, 1 108	773, 748		1 692, 1 658		(C—N) 2 250
1u	H	H	Cl	H	143–145	0·66	1 600	1 360, 1 126	1 395, 782, 764		1 704, 1 668		
1w	H	H	Cl	Cl	198–201	0·68	1 604	1 364, 1 132	1 397, 788, 759		1 705, 1 669		

[a] TLC (Silufol UV 254), eluant toluene/pyridine, 3·1 (v/v).

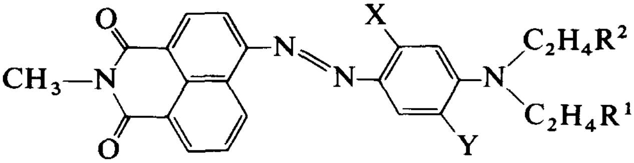
TABLE 2

Characterization Data for Disperse Dyes **2**, **3**, **4** (**a**, **d**, **g**, **k**, **n**)

Dye	*X*	*Y*	*R^1*	*R^2*	*Z*	*W*	*M.p. (°C)*	*R_f*[a]	*IR absorption (cm^{-1})*						
									N=N	*C—N*	*C—H*	*C=O Amide*	*C=O Ester*	*N–O*	
2a	H	H	H	H	Br	H	97–100	0·86	1 597	1 348, 1 130	1 382, 810				
2d	OH	H	H	H	Br	H	88–91	0·78	1 605	1 365, 1 142	1 389, 830, 794				
2g	Me	H	OH	OH	Br	H	123–125	0·53	1 598	1 349, 1 090	823, 805				(O—H) 1 223, 1 060
2k	NHAc	H	OAc	OAc	Br	H	321–325	0·36	1 570		795	1 695	1 647		
2n	NHAc	OMe	OAc	OAc	Br	H	55–58	0·73	1 609	1 369	822	1 743	1 663, 1 239		
3a	H	H	H	H	NO_2	H	149–152	0·76	1 599	1 338, 1 132	1 383, 846, 813			1 509, 1 322	
3d	OH	H	H	H	NO_2	H	153–155	0·67	1 600	1 331, 1 109	846, 830, 792			1 510 1 309	
3g	Me	H	OH	OH	NO_2	H	163–164	0·46	1 600	1 354, 1 092	845			1 507, 1 330	(O—H) 1 219, 1 050
3k	NHAc	H	OAc	OAc	NO_2	H	78–82	0·60	1 595	1 339, 1 107	853	1 740	1 620	1 512, 1 300	
3n	NHAc	OMe	OAc	OAc	NO_2	H	61–63	0·69	1 595	1 335, 1 099	855	1 740	1 678, 1 607	1 513	
4a	H	H	H	H	NO_2	NO_2	148–150	0·77	1 607	1 340, 1 140	1 385, 828			1 535, 1 312	
4d	OH	H	H	H	NO_2	NO_2	105–107	0·71	1 610	1 333, 1 121	820, 785			1 520, 1 315	
4g	Me	H	OH	OH	NO_2	NO_2	151–154	0 30	1 603	1 342, 1 100	834			1 534	(OH) 1 230, 1 063
4k	NHAc	H	OAc	OAc	NO_2	NO_2	107–110	0·67	1 603	1 331, 1 110	820	1 724	1 615	1 529, 1 320	
4n	NHAc	OMe	OAc	OAc	NO_2	NO_2	113–116	0·68	1 597	1 333, 1 112	822	1 735	1 690, 1 610	1 510	

[a] TLC (Silufol UV 254); eluant toluene/pyridine, 3:1 (v/v).

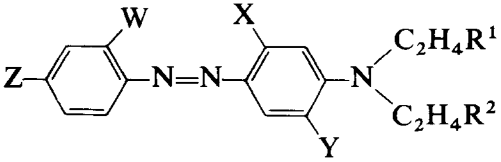
examined. It seemed, therefore, of value to synthesize a series of dyes **1** ($R = CH_3$) and to study how the replacement of the imide group by alkylimide and substitution into the phenyl ring would affect the spectral properties of these dyes. A series of dyes **1** was prepared using 4-amino-*N*-methylnaphthalimide as diazo component and various derivatives of *N*,*N*-dialkylaniline as coupling components (**1a–1w**).



$R^1, R^2 = H, OH, OAc, CN, Cl$
$X, Y = NO_2$, NHAc, OEt, OMe, Me, Cl, OH

1a–1w

For the purpose of comparison, analogous aminoazobenzene dyes were also examined; these were prepared using as diazo components: *p*-bromoaniline (dyes **2a**, **2d**, **2g**, **2k**, **2n**), *p*-nitroaniline (dyes **3a**, **3d**, **3g**, **3k**, **3n**) and 2,4-dinitroaniline (dyes **4a**, **4d**, **4g**, **4k**, **4n**).



$R^1, R^2 = H, OH, OAc; X, Y = H, OH, Me, NHAc, OMe$
$Z, W = H, Br, NO_2$

2, 3, 4 (a, d, g, k, n)

Detailed structures of the dyes and some of their physical and chemical properties are shown in Tables 1 and 2.

2 EXPERIMENTAL

Dyes **1a–1w** were prepared by diazotization of *N*-methyl-4-aminonaphthalimide with nitrosylsulphuric acid and coupling with the appropriate amine.[3] Acetyl derivatives were obtained by the method previously described[4] (**1k–1p**). UV–Vis spectra of dyes **1a–1w** and of the reference dyes were measured at room temperature using a Specord UV–Vis (Zeiss—Jena). Samples were stored for 24 h in darkness before measurement. The concentrations of dyes **1a–1w** were (1·47–3·98) × 10^{-5} mol litre^{-3} and those of the reference dyes [**2**, **3**, **4** (**a**, **d**, **g**, **k**, **n**)], (3·09–5·36) × 10^{-5} mol litre^{-3}; 1% dyeings on polyester fabrics were made by a bath process using a carrier.

3 DISCUSSION

Visual evaluation of the dyeings on polyester fabrics showed that the nature of the alkyl residue in the amine group of the coupling component affects both the intensity of dyeings and their shade. The highest intensity is shown by the dyeings of dyes **1a**–**1h**, which contain *N*,*N*-diethyl groups (R^1, R^2 = H) and *β*-hydroxyethyl groups (R^1, R^2 = H, OH and OH, OH). These substituents bring about an increase in the nucleophilic character of the tertiary nitrogen atom and of the stability of polar forms,[5] especially when there are no substituents in phenyl rings causing steric effects. The dyeings are violet or red with a blue hue. The lowest intensity of colour is observed in dyes **1o**–**1t**, where R^1 = CN, R^2 = OAc, OH, H, CN. These groups cause a considerable decrease in the colour intensity and also have a hypsochromic effect (rose, and orange) due to the decreased basicity of the nitrogen of the dialkylamine group. The substituents in the phenyl ring of the coupling components also considerably affect the colour of the dyeings, especially those in an *ortho* position to the azo bond (**1b**–**1d**, **1g**, **1h**, **1k**–**1n**, **1t**). The dyes with acetylamino, methyl and hydroxyl groups (NHAc, CH_3, OH) are bathochromic with respect to the unsubstituted derivatives (**1a**, **1f**, **1j**, **1s**), whilst acceptor substituents (Cl, NO_2) cause hypsochromic effects (**1b**, **1h**, **1m**) compared with dyes **1a**, **1f**, **1j**. In most cases substituents *ortho* to the dialkylamino group impart a considerable bathochromic effect (**1c**, **1n**) and make the shades dull, particularly when substituents such as OMe and OEt are also present in the 2-position relative to the azo bond. Reasons for these observations were investigated using UV–Vis spectra of the dyes in *N*,*N*-dimethylformamide solutions over the range 270–650 nm. The dyeings on polyester fabrics with the reference dyes, in which *p*-bromoaniline (dyes **2**), *p*-nitroaniline (dyes **3**) and 2,4-dinitroaniline (dyes **4**) were used as azo components, are yellow, red and blue or violet, respectively, thus showing in most cases a significant hypsochromic effect in relation to the naphthalimide dyes (**1a**–**1w**).

3.1 UV–Vis absorption maxima

Many of the dyes **1a**–**1w** usually show two absorption maxima which are characteristic for benzeneazonaphthalene derivatives. An exception is dye **1d** in which the hydroxyl group can result in the dye existing also in a

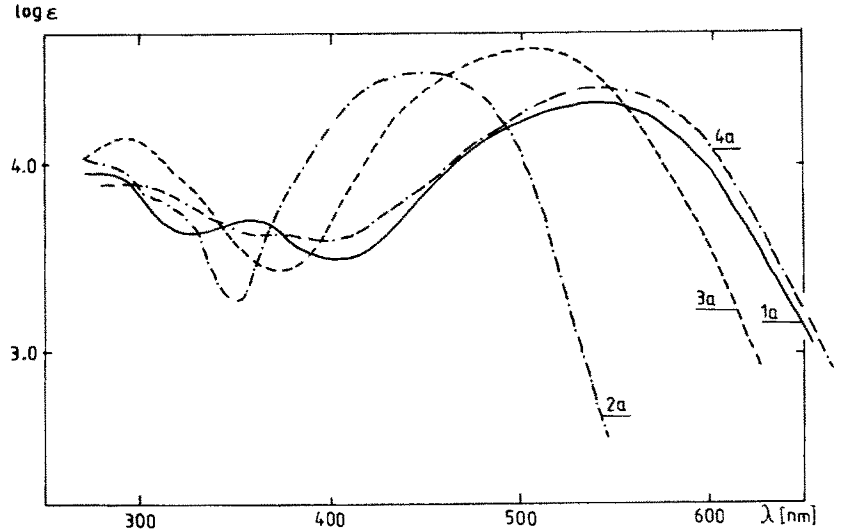


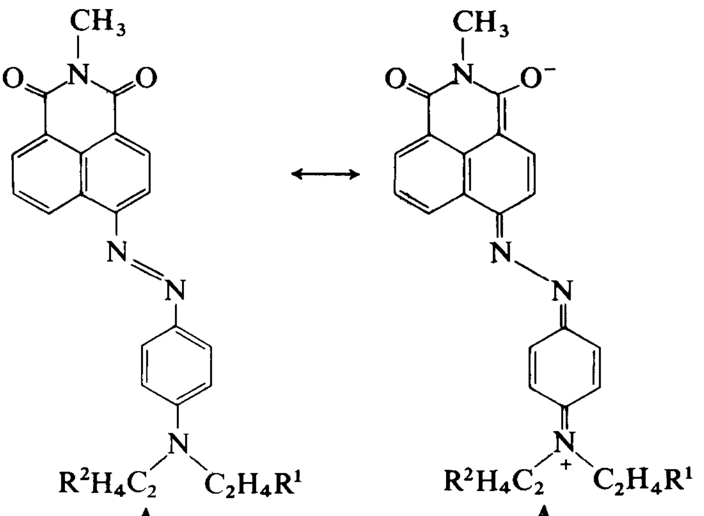
Fig. 1. Spectra of dyes derived from *N*,*N*-diethylaniline and *N*-methyl-4-aminonaphthalimide (**1a**), *p*-bromoaniline (**2a**), *p*-nitroaniline (**3a**) and 2,4-dinitroaniline (**4a**).

quinone form (this is the reason for the occurrence of a third absorption band within the long-wavelength range of absorption; see below).

In the UV range are observed 'naphthalene' bands which are ascribed to the absorption of the benzeneazonaphthalene (BAN) chromophore in the 349–370 nm range, and in the visible range the K-band appears in the region 492–573 nm, characteristic for azo dyes.[1,6,7] The spectral properties of the dyes are affected both by dialkylamino groups and by the substituents in the phenyl ring of the coupling component (Fig. 1).

The colour of naphthalimide dyes depends on the delocalization of electrons through the conjugated azo chromophore and depends on the energy difference between structures A_1 and A_2. The lower this difference, the higher is the bathochromic effect of the basic absorption band.[8] The contribution of the higher energy stabilized dipolar structure A_2 is enhanced by the presence of a conjugated electron acceptor (naphthalimide residue) and electron donor (dialkylamino group) and this results in a considerable bathochromic shift.

The presence of electron-acceptor substituents has been shown[3,4,5,8–14] to give the largest bathochromic shifts in benzeneazonaphthalenes and in benzeneazobenzene. In simple azobenzene derivatives the $\Delta\lambda$ value is in the order of 70 nm when the substituent in the diazo component is a nitro group (dyes **3**) and about 80 nm when there are two nitro groups (2,4-dinitroaniline dyes, **4**).[10] In the case of the reference dyes **2**–**4** these differences are 70–107 nm and, on the basis of these values, one can evaluate the acceptor 'force' of the *N*-methylnaphthalimide group. *N*,*N*-Dialkylaminoazobenzene



A$_1$ **A**$_2$

(DAA) was taken as the reference system, and the naphthalimide derivative was considered as DAA with an additional cyclic substituent. Application of the formula for the spectroscopic Hammett constant[15-17] allows the value of σ_0 to be calculated, viz.,

$$\sigma_0 = \sigma_1 . \frac{\nu_0 - \nu_2}{\nu_1 - \nu_2} + \sigma_2 . \frac{\nu_1 - \nu_0}{\nu_1 - \nu_2}$$

where σ_1, σ_2 are known constant of Br ($\sigma_1 = 0{\cdot}23$) and NO_2 substituents ($\sigma_2 = 0{\cdot}78$); ν_1, ν_2 are the absorption frequencies of the reference dyes, ν_0 is the absorption frequency of the naphthalimide dye and σ_0 is the calculated Hammett constant for the naphthalimide group. The values of σ_4 for the 2,4-dinitrophenyl residue were calculated in the same way (Table 3).

TABLE 3

Hamett Constants of Naphthalimide (σ_0) and 2,4-Dinitrophenyl (σ_4) Groups in Dyes **1**, **2** and **3**

Dye	$\nu_0 \times 10^{-3}$ **1**	$\nu_1 \times 10^{-3}$ **2**	$\nu_2 \times 10^{-3}$ **3**	σ_0	σ_4
a	1·86	2·23	1·98	1·05	1·10
d	1·80	2·23	1·93	1·03	1·03
g	1·86	2·11	1·94	1·04	1·26
k	1·79	2·07	1·86	0·97	1·12
n	1·74	2·13	1·92	1·26	1·12
			$\bar{\sigma} =$	1·07	1·12

Calculations made for dyes **1a, 1d, 1g, 1k, 1n** gave an average value $\bar{\sigma}_0 = 1{\cdot}07$. Thus, the electron-acceptor capacity of the *N*-methylnaphthalimide moiety is higher than that of the 4-nitrophenyl group and is of a similar order to that of the 2,4-dinitrophenyl residue, which has a $\bar{\sigma}_4$ value of 1·12. Thus, purely on considerations of colour, the *N*-methylnaphthalimido residue may be used in azo dyes as an alternative to 2,4-dinitrophenyl.

Colour shifts resultant from changes in the nature of the substituents R^1 and R^2 in the *N*,*N*-dialkylamino residue gives colour shifts which are bathochromic in the order [R^1, $R^2(\Delta\lambda_{max})$].

$$\text{CN, CN (0{\cdot}0)} < \text{Cl, Cl (12)} < \text{CN, OAc (14)} < \text{OAc, OAc (20)} < \text{CN, H (22)} < \text{CN, OH (29)} < \text{H, OAc (33)} < \text{H, Cl (40)} < \text{OH, OH (42)} < \text{H, OH (44)} = \text{H, H (44)}$$

The hypsochromic effect increases with the electron acceptor nature of R^1 and R^2 and is the highest for dyes containing CN groups. When one —CN group is replaced by —H, a bathochromic shift of 22 nm is observed and when replaced by —OH, a shift of 29 nm occurs. Acylation of the —OH decreases the shift to 14 nm. A similar effect is observed when $R^1 = Cl$, and after replacing by a hydrogen atom, the absorption maximum is shifted 27 nm towards longer wavelength. The highest bathochromic effect is shown by the β-hydroxyethyl derivatives or unsubstituted ethyl derivatives (R^1, $R^2 = H$ or OH) where $\Delta\lambda_{max} = 42\text{–}44$ nm. Acetylation decreases the electron-donor capacity of the *N*,*N*-dialkylamino group and this results in a lowering of the shifts to 20 (**1j**) or 33 nm (**1i**).

These results are relatable to the effect of the substituted alkylamino residues on the stability of the polar form A_2. The direction of the shift is as expected from the values of the inductive constants σ_I for R^1, R^2 ($\sigma_{CN} = 0{\cdot}61$, $\sigma_{Cl} = 0{\cdot}51$, $\sigma_{OAc} = 0{\cdot}44$, $\sigma_{OH} = 0{\cdot}31$).[18]

The naphthalimide dyes are characterized by two bands at about 350 nm (band B) and above 500 nm (band K).[1] In dyes **1a**–**1w**, b and B occurs almost in the visible region and hence this band noticeably affects the hue of the dye. This feature is described quantitatively by the ratio of extinction coefficients α of bands K and B:*

$$\alpha = \frac{E_2}{E_1}$$

where E_1 is the absorption at $\lambda_{max} \simeq 350$ nm and E_2 is the absorption at

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* In the reference dyes **2, 3, 4 (a, d, g, k, n)**, band B appears within the range below 300 nm; at 350 nm these dyes show minimum absorption. Hence, the presence of this band does not affect the colour.

$\lambda_{max} \simeq 500$ nm. The value of this constant varies from 1·29 to 4·17. It may be assumed that it is dependent on the effectiveness of the conjugation of the dialkylamino residue with the dye chromophore system and is associated with the nature of the substituents R^1 and R^2.

It has been previously found that conversion of the *N,N*-dialkylamino group into the quaternary or protonated form prevents electron delocalization and the spectrum of such dyes becomes similar to that of BAN.[1,8–10] In the dyes under investigation, the highest value of α is observed with dyes in which R^1 and R^2 have similar characters, the values decreasing in the order (R^1, R^2):

$$\text{H, H} > \text{Cl, Cl} > \text{CN, OAc} > \text{CN, OH} > \text{CN, CN} > \text{OAc, H} > \text{OH, H} > \text{OH, OH} = \text{OAc, OAc} > \text{CN, H} > \text{Cl, H}$$

In practice this means that dyes with such substituents possess the highest purity of shade. One may assume that a decisive part is played here by steric effects associated with the spatial configuration of the *N,N*-dialkylamino group. Values of the oscillator strength, *f*, being the true measure of the colour intensity, were calculated for the dyes under investigation from the following formula:[9]

$$f = 4{\cdot}32 \times 10^{-9} \times \Delta\nu_{1/2} \times \varepsilon_{max}$$

where $\Delta\nu_{1/2}$ is the width of the absorption band in cm^{-1} at $\varepsilon_{max}/2$. These values varied from 0·36 to 0·58 and the half-band width varied from 4700 to 5400 cm^{-1} (within the visible region from 492 to 537 nm) and are within the general range of values calculated for other disperse azo dyes.

In order to examine the effect of phenyl ring substituents on the colour of dyes, several derivatives were prepared where

X = NHAc, OH, OMe, Me, Cl, NO_2
Y = OEt, OMe
R_1, R_2 = H, OH, $OCOCH_3$, CN

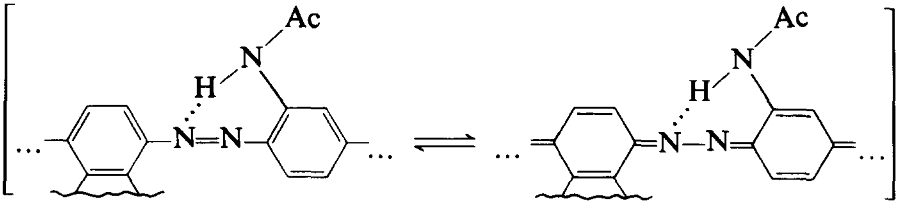
Spectroscopic data for these compounds are given in Table 4. It is apparent that substituents in the 2-position considerably affected the molar absorption in both the visible and UV range. The value of α is also changed. In most cases this coefficient increases considerably, in the extreme case up to 5·92 (**1m**), i.e. it is about 3·8 times higher than that for the dyes without additional substituents (**1j**). Such a high increase in the colour intensity is not observed in dyes **1b**–**1d**, where α is about unity, whilst for dye **1a** (without additional substituents) it is as high as 4·15. In the extreme case, when $X = NO_2$ (**1b**), the absorption in the visible range disappears. The decrease in the α value for dyes **1b**–**1d** is brought about by the high increase in the UV absorption ascribed to that of the chromophore of BAN.

TABLE 4
UV–Vis Spectroscopic Data for Derivatives of *N*-Methyl-4-aminonaphthalimide

Dye	$\lambda_{max}(log\,\varepsilon_{max})$			E_2/E_1	f	$\Delta\nu_{1/2}$
1a	357 (3·68)	536 (4·30)		4·17	0·41	4700
1b	370 (4·25)	527 (3·78)		0·38		
1c	350 (4·00)	573 (4·14)		1·02		
1d	351 (4·04)	537 (4·14)	661 (3·48)	1·26	0·42	7000
1e	351 (4·02)	537 (4·36)		2·18	0·47	4700
1f	350 (4·07)	534 (4·26)		1·55	0·39	5000
1g	360 (3·72)	553 (4·47)		5·67	0·66	5200
1h	360 (3·76)	544 (4·52)		5·76	0·69	4800
1i	351 (3·96)	525 (4·37)		2·57	0·49	4900
1j	350 (4·03)	512 (4·22)		1·55	0·38	5300
1k	356 (3·79)	573 (4·55)		5·76	0·65	4200
1l	358 (3·82)	532 (4·53)		5·14	0·74	5000
1m	359 (3·71)	508 (4·48)		5·92	0·69	5300
1n	351 (4·02)	558 (4·28)		1·82	0·46	5600
1o	352 (3·86)	506 (4·36)		3·16	0·53	5400
1p	352 (3·90)	521 (4·39)		3·09	0·54	5100
1r	350 (4·06)	514 (4·18)		1·32	0·36	5400
1s	349 (3·73)	492 (4·21)		3·02	0·38	5400
1t	364 (3·82)	527 (4·52)		5·76	0·73	5100
1u	354 (4·08)	531 (4·19)		1·29	0·36	5400
1w	354 (3·83)	504 (4·41)		3·80	0·58	5200

The absorption in the visible range 508–573 nm, the so-called K-band, results from the electron transition π–π^*, and is shifted bathochromically in relation to the absorption of dyes without additional substituents in the phenyl rings.

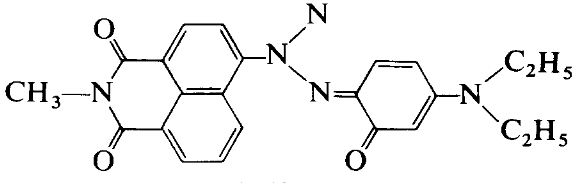
The largest shift of the K-band is exerted by electron-donor substituents, particularly by the acetylamino group (—NHAc). This results from the fact that this group can form intramolecular hydrogen bonds, which increase the coupling effectiveness without any simultaneous effect on the electron density of the coupled system.



An acetylamino group in the 2-position **1** causes bathochromic shifts from about 35 (**1t**) to 61 nm (**1k**) depending on the type of dye and other substituents producing steric hindrance. A methyl group in the 2-position

(**1l**), because of the increased electron density of the coupled system, gives a bathochromic shift of about 10–22 nm in relation to the electron acceptor substituted chloro derivative (**1m**), this value also being dependent on the nature of the dialkylamino group. Such a small bathochromic effect can be explained by the fact that, as has been found by other authors,[19,20] the chlorine atom does not cause any steric hindrance and the dye molecule possesses essentially a planar structure. This promotes the hydrazone form of the dye, with the absorption maximum bathochromically shifted in relation to the azo form. Both the substituents (CH_3, Cl) exert an advantageous effect on the absorption intensity and purity of shade. The value of $\log \varepsilon_{max}$ is 4·47 and 4·53, respectively, while α is 5·14 and 5·92, respectively. The latter is about 3.3–3.8 times higher than that of the reference dyes **1f**, **1j** without substituents in the 2-position.

The electron donor hydroxy group in an *ortho*-position to the azo bond (dye **1d**) brings about an additional band shifted bathochromically in relation to the band in the visible range at 537 nm. This band occurs at 661 nm, shows a low intensity ($\log \varepsilon_{max} = 3{\cdot}48$) and results from the quinone–hydrazone tautomerism. Dye **1d**, under the measurement conditions, occurs not only in the azo form but also in the quinone form (A_3).[9,10,21-23] Additional substituents in the phenyl ring, in most cases, influence also the increase in the oscillator strength, *f*. These values are 1·48 times (for dyes **1g**, **1h**) and 2·18 times (for dyes **1k**–**1m**) higher than those of unsubstituted dyes **1f**, **1j**, **1s**. The increase in the oscillator strength, in this case, is mainly due to the increased molar absorption of the dyes (ε_{max}). The coefficient *f* is affected to a lesser extent by the half bandwidth $\Delta\nu_{1/2}$, the values of which are similar in all dyes examined.



A_3 (dye **1d**)

3.2 Spectra of reference dyes

In order to evaluate the character of the naphthalimide group in the dyes under investigation, comparative examinations were carried out with azo dyes derived from *p*-bromo, *p*-nitro- and 2,4-dinitroaniline as diazo components. The derivatives for which the naphthalimide dyes showed the strongest bathochromic effect were used as coupling components (Table 5).

TABLE 5
UV–Vis Spectroscopic Data for Some Aminoazobenzene Disperse Dyes

Dye		$\lambda_{max}(log\ \varepsilon_{max})$		f	$\Delta\nu_{1/2}$
2a		448 (4·48)		0·64	5 000
2d	292 (3·84)	474 (4·36)	576 (3·00)	0·42	4 100
2g	291 (4·10)	448 (4·54)		0·78	5 200
2k	298 (4·00)	470 (4·45)		0·69	5 700
2n	297 (4·13)	484 (4·34)		0·52	5 500
3a	292 (4·13)	505 (4·59)		0·81	4 800
3d		514 (4·39)	658 (3·11)	0·58	5 500
3g	297 (4·06)	519 (4·53)		1·38	4 700
3k		521 (4·43)		0·66	5 700
3n	296 (4·12)	539 (4·32)		0·50	5 500
4a	294 (3·91)	544 (4·39)		0·40	4 400
4d		475 (4·06)	558 (4·01)	0·62	12 600
4g	296 (3·98)	556 (4·43)		0·52	4 500
4k		558 (4·32)		0·17	3 800
4n	296 (4·07)	579 (4·31)		0·41	4 700

It was found that the naphthalimide group corresponded to the 2,4-dinitroaniline.

The reference dyes (**2**, **3**, **4**), like most azobenzene derivatives, do not show distinct bands within the UV range above 300 nm. The values of f calculated for them are higher than those for analogous naphthalimide dyes. Only the

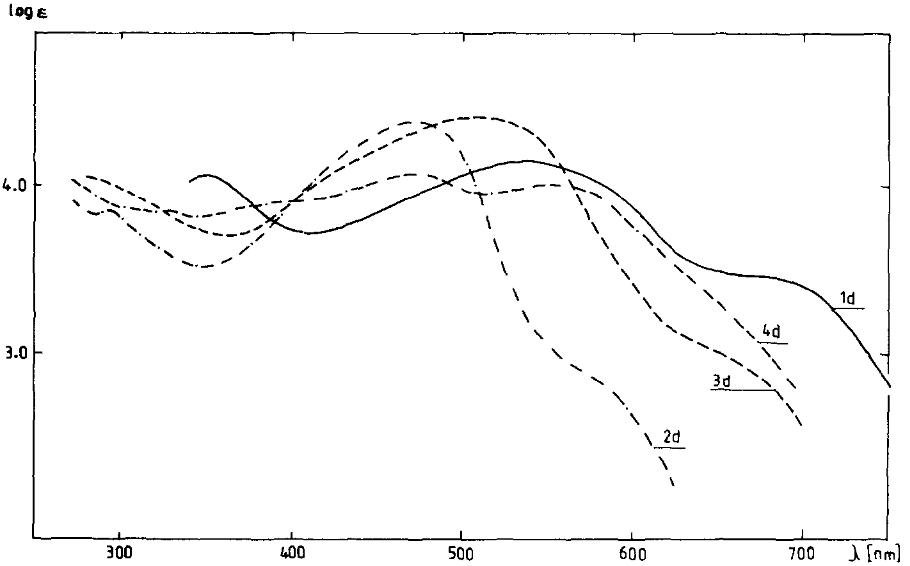


Fig. 2. Spectra of dyes derived from 3-hydroxy-N,N-diethylaniline and N-methyl-4-aminonaphthalimide (**1d**), p-bromoaniline (**2d**), p-nitroaniline (**3d**) and 2,4-dinitroaniline (**4d**).

derivatives of 2,4-dinitroaniline dyes (**4**) have values of *f* equal or lower, which may be the result of steric hindrance associated with the presence of substituents in an *ortho*-position to the azo bond.[24]

The dyes with OH groups in the 2-position (**2d, 3d, 4d**) have spectra similar to those of dye **1d**, due to the fact that the dyes are in the quinone–hydrazone form (A_3)[9,12] in addition to the polar form A_2. This results in the occurrence of an additional band in the long-wavelength Vis range and a distinct decrease in the absorption intensity of particular bands and makes the shade dull. The values of $\Delta\lambda_{max}$ in the Vis range for the quinone–hydrazone forms of dyes **2d, 3d** and **4d** are 102, 144 and 83 nm, respectively, while for dye **1d** $\Delta\lambda_{max}$ is 124 nm (Fig. 2). The considerably lower $\Delta\lambda_{max}$ value for dye **4d** (R^1, $R^2 = H, H$; X, Y = H, OH) suggests a higher contribution of the polar structure A_2 (λ_{max} for dye **4a**, in which X, Y = H, is 544 nm). It may be assumed that the quinone form dominates in the remaining dyes with substituents such as Br, NO_2 (**2d, 3d**) and naphthalimide dyes (**1d**).

4 CONCLUSIONS

Dyes derived from 4-amino-*N*-methylnaphthalimide were red, blue or violet, depending on the type of substituent in the coupling component. They are suitable for dyeing polyester and polyamide. An especially advantageous effect is given by coupling components containing electron donor substituents such as OMe, Me, Cl and NHAc in positions *ortho* to the azo bond, these producing considerable bathochromic shifts of the long-wavelength absorption bands. The most useful is the acetylamino substituent, with which the formation of a hydrogen bond helps to increase the effectiveness of colour coupling of the phenylazonaphthalene system. In the naphthalimide dyes, the coefficient α plays an important role, affecting especially the shade purity since a lower share of the B-band in the spectrum (a higher value of α) shows that the absorption of the chromophore system of the whole dye (K-band) predominates over BAN.

4-Amino-*N*-methylnaphthalimide is a useful diazo component for the synthesis of azo disperse dyes. Its acceptor ‘force’ is comparable with that of 2,4-dinitroaniline and its use in addition ensures high-performance properties of the dyes.[2,3]

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