Dyes and Pigments 9 (1988) 401–417

Spectrophotometric Characteristics of *N,N*-dialkylamino-3- and -4-phenylazonaphthalimides

Krzysztof Wojciechowski

Institute of Dyes, Polytechnic University,
90–924 Łódź, Poland

(Received 14 July 1987; accepted 4 September 1987)

ABSTRACT

Azo disperse dyes derived from 3- and 4-aminonaphthalimides show large differences in colour when dyed on polyester fibres. The electronic spectra of the dyes have been examined and compared with reference compounds, viz. derivatives of phenylazonaphthalene. It was found that the 4-aminonaphthalimide derivatives, in 'neutral' solution, can exist also in a polar configuration to an extent dependent mainly on the type of N,N-dialkyl substituent in the coupling component.

1 INTRODUCTION

Monoazo dyes containing acetamide, benzamide, phthalimide and naphthalimide residues have been found to have good general properties, particularly with respect to thermal stability.[1–4] We have previously reported[5] the effect of amide groups on the spectral properties of such dyes and found that the naphthalimide dyes exhibited, in solvents with various acid contents, spectral characteristics difficult to predict.

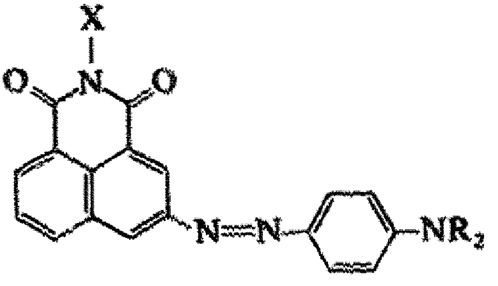
The azo naphthalimide dyes (I, II) have different physical and dyeing properties compared with related dyes containing acetamide, benzamide and phthalimide residues. The naphthalimide derivatives show exceptionally good thermal stability and their dyeings have good fastness properties,[3,4] but their water solubility is very poor and they have low diffusion coefficients and low values of the Nernst distribution constant (K.

Dyes and Pigments 0143-7208/88/$03·50

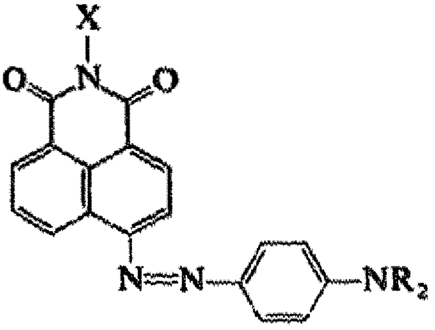
Wojciechowski, unpublished). These properties are brought about by a strong self-association of the naphthalimide derivatives due to hydrogen bonds. Large differences occur in the colour of dyeings obtained from dyes having the azo group in the 3-position (I) compared with the 4-substituted derivatives (II), and these differences are not apparent in similar azo derivatives of acetanilide, benzamide and phthalimide.[2]

In order to determine the factors causing such differences in the properties of the isomeric azo derivatives of naphthalimide, the spectra of dyes I and II in methanol and in methanolic 1M- and 10M-H_2SO_4 were recorded.

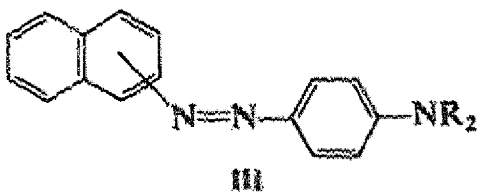
As reference standards, several derivatives of phenylazonaphthaline (III–V) were also prepared and their spectral properties were similarly examined to determine the effect of particular fragments of the dye molecules on their properties.



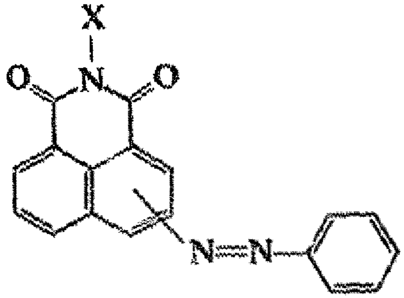
I



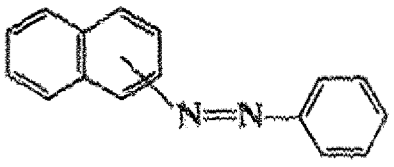
II



III



IV



V

$X = H, CH_3$
$R = CH_3; C_2H_5$

2 EXPERIMENTAL

The synthesis of dyes I and II has been described previously.[2] Dyes III were obtained by diazotization of 1- or 2-naphthylamine followed by coupling with a suitable *N*,*N*-dialkylamine using standard procedures.

Dyes **IVa**, **IVb**, and **IVd** were prepared by condensation of nitrosobenzene with 3- or 4-aminonaphthalimide.[6] The dyes were purified by prolonged washing with 5% HCl at 90°C and then with water until neutral. Dyes **IVc** were obtained by alkaline fusion of nitrobenzene and 4-aminophthalimide[7] and purification of the product by prolonged washing with 2% HCl followed by crystallization from 30% aqueous dioxan.

1-Benzeneazonaphthalene (**Va**) was prepared by coupling diazotized aniline with 1-naphthylamine followed by deamination through decomposition of the diazonium salt.[8] The product was purified by heating with boiling 5% NaOH (repeated five times) and twice with boiling 5% HCl. The product was then dissolved in acetic acid at 50°C and poured into water. The precipitate was filtered and washed with water until neutral. 2-Benzeneazonaphthalene (**Vb**) was prepared by condensation of nitrosobenzene and 2-naphthylamine.[6] The product was extracted with ether and crystallized from methanol.

UV–VIS spectra of dyes **I–V** were recorded at room temperature, using a SPECORD UV–VIS spectrophotometer (Zeiss–Jena), storing the samples before measurements for 24 h in darkness and those of dyes **Ia–Id**, **IIa–IId** for seven days. The spectra were taken for dyes **Ia–Vb** at the following dye concentrations: **Ia**, $1{\cdot}74 \times 10^{-4}\,\mathrm{m\,dm^{-3}}$; **Ic**, $1{\cdot}61 \times 10^{-4}\,\mathrm{m\,dm^{-3}}$; **Id**, $1{\cdot}55 \times 10^{-4}\,\mathrm{m\,dm^{-3}}$; **IIc**, $2{\cdot}23 \times 10^{-4}\,\mathrm{m\,dm^{-3}}$; **IId**, $6{\cdot}93 \times 10^{-4}\,\mathrm{m\,dm^{-3}}$; **IIIa**, $4{\cdot}4 \times 10^{-4}\,\mathrm{m\,dm^{-3}}$; **IIIb**, $3{\cdot}31 \times 10^{-4}\,\mathrm{m\,dm^{-3}}$; **IIIc**, $3{\cdot}99 \times 10^{-4}\,\mathrm{m\,dm^{-3}}$; **IIId**, $3{\cdot}99 \times 10^{-4}\,\mathrm{m\,dm^{-3}}$; **Va**, $1{\cdot}03 \times 10^{-4}\,\mathrm{m\,dm^{-3}}$. The spectra of the remaining dyes were recorded using saturated solutions in methanol, and the acidified methanol solutions were prepared by addition of a suitable amount of concentrated H_2SO_4.

3 RESULTS AND DISCUSSION

3.1 Spectral characteristics of dyes III–V

3.1.1 Spectra in methanol

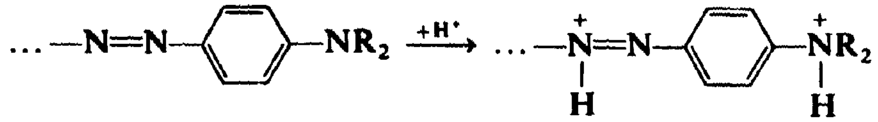
The reference dyes **IV** and **V** show, over 300 nm, characteristic K absorption bands ascribed to a $\pi \rightarrow \pi^*$ shift in the range 320–330 nm (2-isomers) or 360–390 nm (1-isomers, Figs 3 and 5).[9,10] The presence of the electron-donating *N,N*-dialkylamino group in dyes **III** brings about a considerable bathochromic effect. Corresponding values for λ_{max} of the K absorption bands are in this case in the region of 420–445 nm. The R bands, in the form of points of inflexion and corresponding to $n \rightarrow \pi^*$ shifts are bands of low intensity within the range 410–470 nm (dyes **IV** and **V**) and it is therefore not possible to identify them in dyes **III** since they are submerged by the nore intense K bands[11] (Fig. 4).

3.1.2 Spectra in 1M *and* 10M-H_2SO_4 *in methanol*

Replacing the neutral methanolic solvent by solutions acidified with H_2SO_4 leads to significant changes in the spectrum and to the appearance of new absorption bands in both the UV and the visible range (see Table 1). The dyes studied have different proton-accepting centres, viz. azo, dialkylamino, and the carbonyl groups of a heterocyclic amide system.

In 1M-H_2SO_4 the largest bathochromic shifts are observed with dyes **III** (Fig. 4). In these dyes, new, long-wavelength absorption bands at 523–532 nm, and particularly for dyes **IIIa**, and **IIIc**, are observed at 385–410 nm. These are associated with the existence of these dyes in the 'azonium' $\mathbf{B}_2$ and 'ammonium' **C** forms.[5,12–14]

On the other hand, the spectra of all the dyes in 10M-H_2SO_4 show distinct changes. In this medium, the nitrogen atoms in the azo band in dyes **IV** and **V** also undergo protonation (Figs 3 and 5). New, intense absorption bands at 425–525 nm, 440 nm and 541 nm appear in these compounds. Analogous absorption bands for dyes **III** are within the range 543–585 nm and 378–443 nm. Under these conditions, protonation of the azo band, as well as of *N*,*N*-dialkylamino groups or even of a carbonyl group, takes place (in dyes **IVa**–**IVd**), resulting in the above effect.

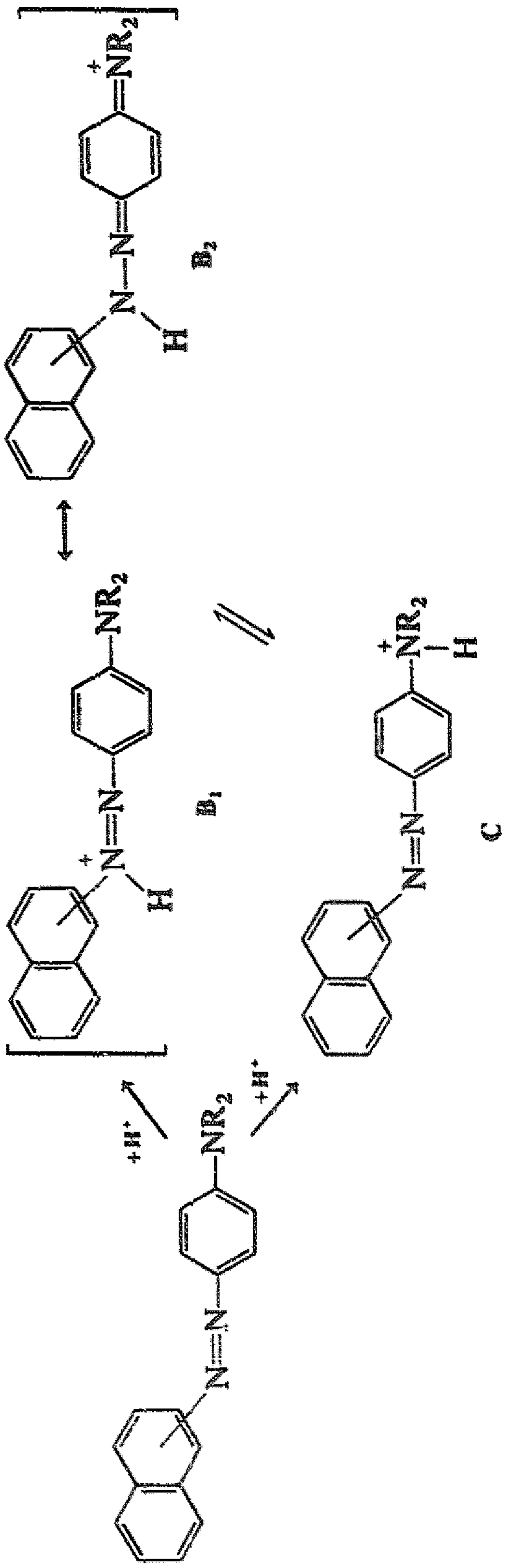


These results are helpful in the analysis of the spectra of the naphthalimide dyes **Ia**–**Id** (Fig. 1) and **IIa**–**IId** (Fig. 2) (see Section 3.2).

3.2 Spectral properties of dyes I and II

As noted above, the naphthalimide dyes **I**, **II** are characterized by very good properties and show significant differences in colour depending on the position of substitution of the azo group in the naphthalimide residue, i.e. the 3- and 4-isomers.[2] The differences in λ_{max} values between methanol and dimethylformamide solutions of 4- and 3-benzeneazonaphthalimide can be up to 60 nm in DMF (see Table 2) and in methanol some of the 4-substituted derivatives show a double absorption maximum in the long-wavelength region (dyes **IIa**-**IId**, Fig. 2).

The present considerations are limited to a discussion of bands within 270–600 nm, where the known K and R bands appear and which show


+H⁺
+H⁺
NR₂
N=N
H
B₁
B₂
C

characteristic changes depending on the solvent used.[14,15] In the UV range, there are only the 'naphthalene' bands, characteristic for simple naphthalene derivatives (Fig. 3 and 5) and in the visible range bands characteristic for azo dyes.[9,10,16,17] In view of the insolubility of some dyes, it was possible only to record their spectra in saturated solutions of unknown concentration. This has no influence however on comparisons of the spectra of the dyes.

TABLE 1
UV-VIS Electronic Spectral Data of Dyes III–V

Dye	*X*	*R*	*MeOH*		1M-H_2SO_4		10M-H_2SO_4	
			λ_{max}	*(log 10E)*	λ_{max}	*(log 10E)*	λ_{max}	*(log 10E)*
IIIa	—	Me	323·4	(1·30)	409·8	(1·61)	348·6	(1·34)
			432·5	(1·92)	525·2	(1·20)	584·1	(1·73)
			565·6	(0·91)~				
IIIb	—	Me	303·0	(1·50)~	431·0	(1·09)	443·2	(1·19)
			422·3	(1·82)	531·9	(1·50)	543·4	(1·35)
			454·5	(1·75)~	568·1	(1·35)~	576·0	(1·27)~
			531·9	(1·19)~				
IIIc	—	Et	320·9	(1·19)	280·6	(2·00)	352·1	(1·31)
			444·8	(2·04)	385·8	(1·77)	555·5	(1·62)
					523·0	(0·87)~		
IIId	—	Et	297·9	(1·64)~	434·0	(1·34)~	435·5	(1·23)~
			435·5	(1·96)	492·1	(1·46)	543·4	(1·57)
			531·9	(1·35)~	523·0	(1·40)~	568·2	(1·54)~
IVa	H	—	322·6	(1·43)	323·4	(1·51)	348·6	(1·49)
			345·8	(1·21)~	347·7	(1·28)~	436·3	(1·28)
			414·6	(0·61)	415·9	(0·66)		
IVb	Me	—	324·2	(1·76)	324·2	(1·76)	339·2	(1·81)
			354·6	(1·52)~	354·6	(1·50)~	425·9	(1·78)
			414·5	(0·89)	415·9	(0·87)		
IVc	H	—	386·9	(1·30)	303·0	(1·08)	353·1	(1·12)
			416·6	(0·98)~	384·6	(1·32)	490·2	(1·09)
IVd	Me	—	363·3	(1·04)	352·1	(1·04)	337·4	(1·02)
			390·6	(0·98)~	390·6	(0·95)~	525·2	(0·80)
			456·2	(0·73)~	468·1	(0·61)~		
					560·5	(0·36)~		
Va	—	—	273·8	(1·49)	273·8	(1·52)	278·7	(1·26)
			291·7	(1·42)	291·7	(1·42)	367·6	(1·37)
			372·0	(1·51)	372·0	(1·55)	541·1	(1·74)
			456·2	(0·55)~	461·2	(0·47)~		
Vb	—	—	333·8	(1·80)	289·0	(1·54)	440·1	(1·69)
			382·2	(1·59)~	331·1	(1·56)	502·0	(1·60)
			471·7	(0·97)~	366·5	(1·40)~		
					508·1	(0·84)		

~, Approximately estimated maxima or inflexions of absorption curve.

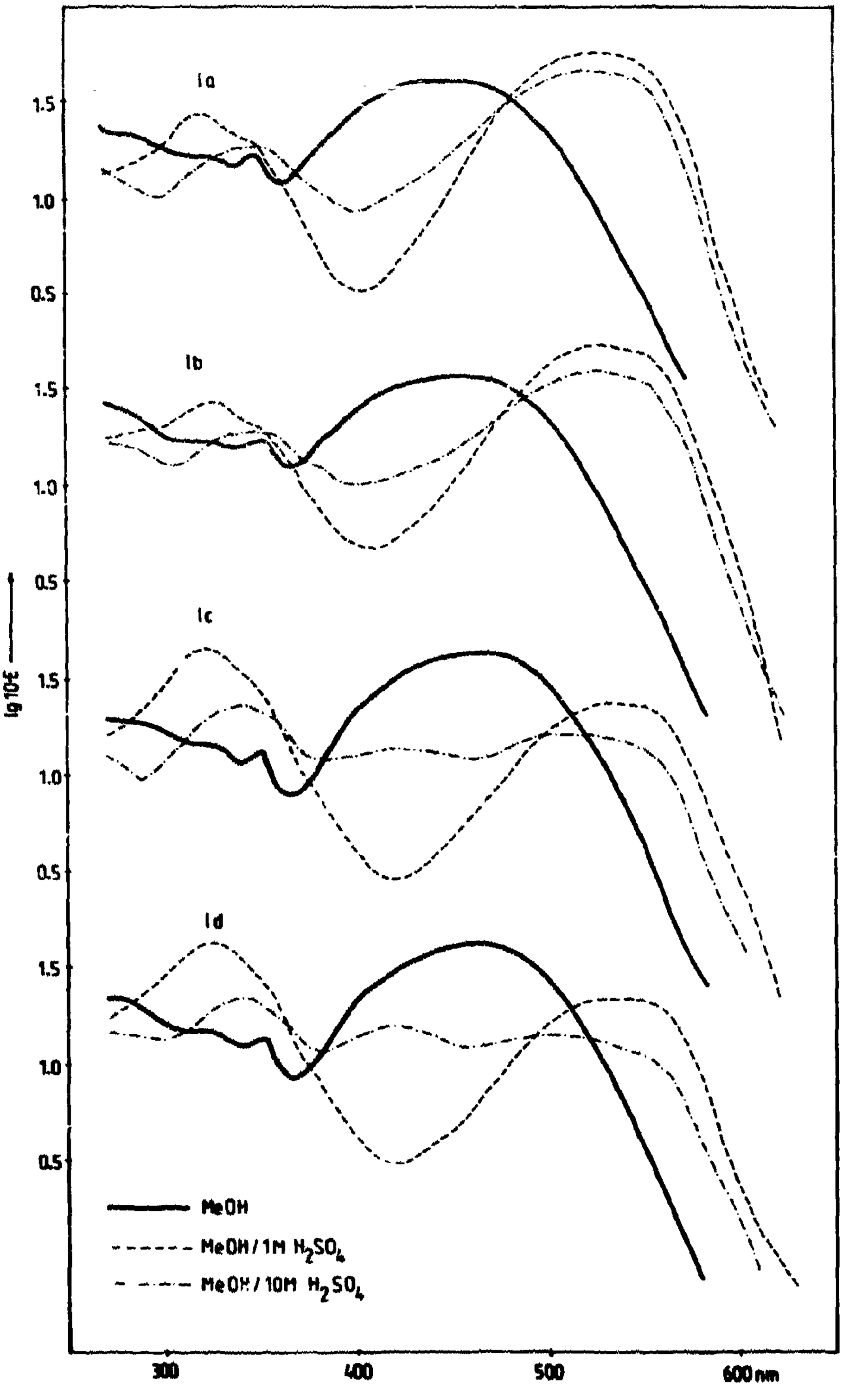


Fig. 1. The UV–VIS absorption spectra of 3-(*p*-*N*,*N*-dialkyl)aminophenylazonaphthalimides (Ia–Id).

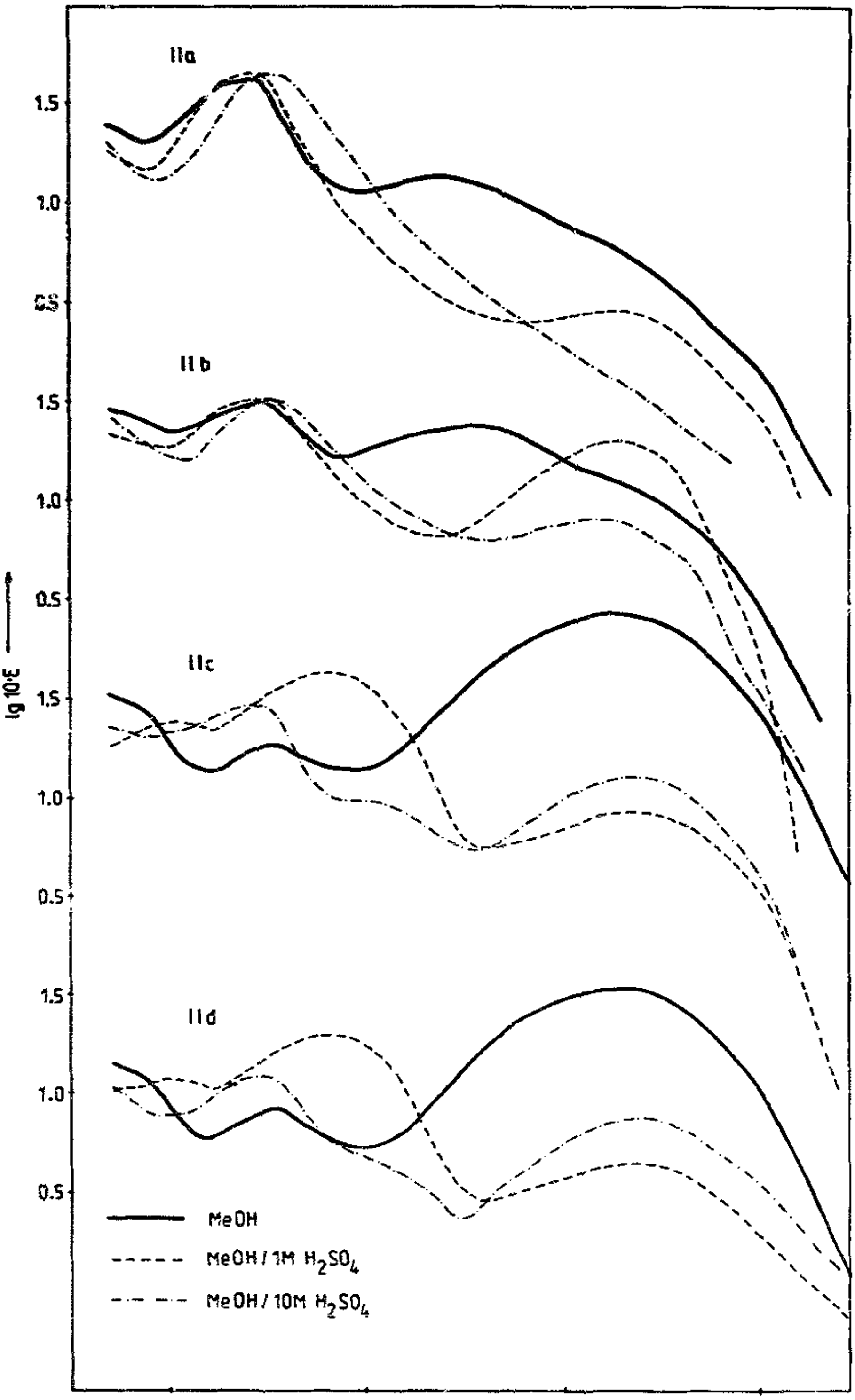


Fig. 2. The UV-VIS absorption spectra of 4-(*p*-*N*,*N*-dialkyl)aminophenylazonaphthalimides (**IIa**–**IId**).

TABLE 2
UV–VIS Electronic Spectral Data of Dyes **I** and **II**

Dye	*X*	*R*	*MeOH*		1M-H_2SO_4		10M-H_2SO_4	
			λ_{max}	*(log 10E)*	λ_{max}	*(log 10E)*	λ_{max}	*(log 10E)*
Ia	H	Me	350·1	(1·23)	322·6	(1·44)	350·1	(1·28)
			457·8	(1·62)	353·1	(1·33)~	381·1	(1·07)~
					525·2	(1·76)	520·8	(1·67)
					538·5	(1·74)~		
Ib	Me	Me	349·1	(1·25)	323·4	(1·44)	352·1	(1·29)
			457·8	(1·58)	349·1	(1·32)~	523·0	(1·61)
					529·7	(1·74)	538·8	(1·59)~
Ic	H	Et	319·3	(1·17)	323·4	(1·67)	339·2	(1·37)
			349·6	(1·13)	352·1	(1·43)~	418·1	(1·15)
			469·9	(1·64)	523·0	(1·38)	514·4	(1·23)
					541·1	(1·37)	545·8	(1·16)
Id	Me	Et	329·4	(1·18)	325·1	(1·64)	338·3	(1·36)
			348·6	(1·15)	348·2	(1·45)~	420·8	(1·22)
			469·9	(1·64)	523·0	(1·35)	512·3	(1·17)
					541·1	(1·34)~	545·8	(1·06)~
IIa	H	Me	344·8	(1·62)	345·8	(1·66)	354·1	(1·65)
			440·1	(1·13)	527·4	(0·46)		
			525·2	(0·80)~				
IIb	Me	Me	349·1	(1·49)	348·2	(1·51)	353·1	(1·51)
			454·5	(1·37)	529·6	(1·30)	518·6	(0·90)
			520·0	(1·27)~	543·4	(1·27)~	560·0	(0·75)~
IIc	H	Et	355·1	(1·02)	300·8	(1·25)	349·1	(1·25)
			531·9	(1·78)	389·4	(1·50)	405·8	(0·99)
					538·8	(0·75)	536·5	(1·20)
IId	Me	Et	352·1	(0·92)	300·8	(1·14)	347·7	(1·09)
			529·6	(1·54)	393·1	(1·29)~	400·6	(0·68)~
					534·2	(0·65)~	541·1	(0·88)

~, Approximately estimated maxima or inflexions of absorption curve.

Dyes **Ia–Id** have several absorption maxima with poorly distinguishable bands in the short-wavelength region of the spectrum, ('naphthalene' bands) and in the visible region (the phenylazonaphthalene chromophore) (Fig. 1). The effect of isolated substituents on the absorption was discussed in the initial part of the paper for the reference compounds **III–V**. In the UV range, dyes **Ia–Id** show absorption within the range 319–350 nm, i.e. close to the absorption of the reference compounds **IVa**, and **IVb** (Fig. 3). A small bathochromic shift is probably due to interaction between the dialkylamino and imide groups. Similarly, there is a displacement of these bands to the

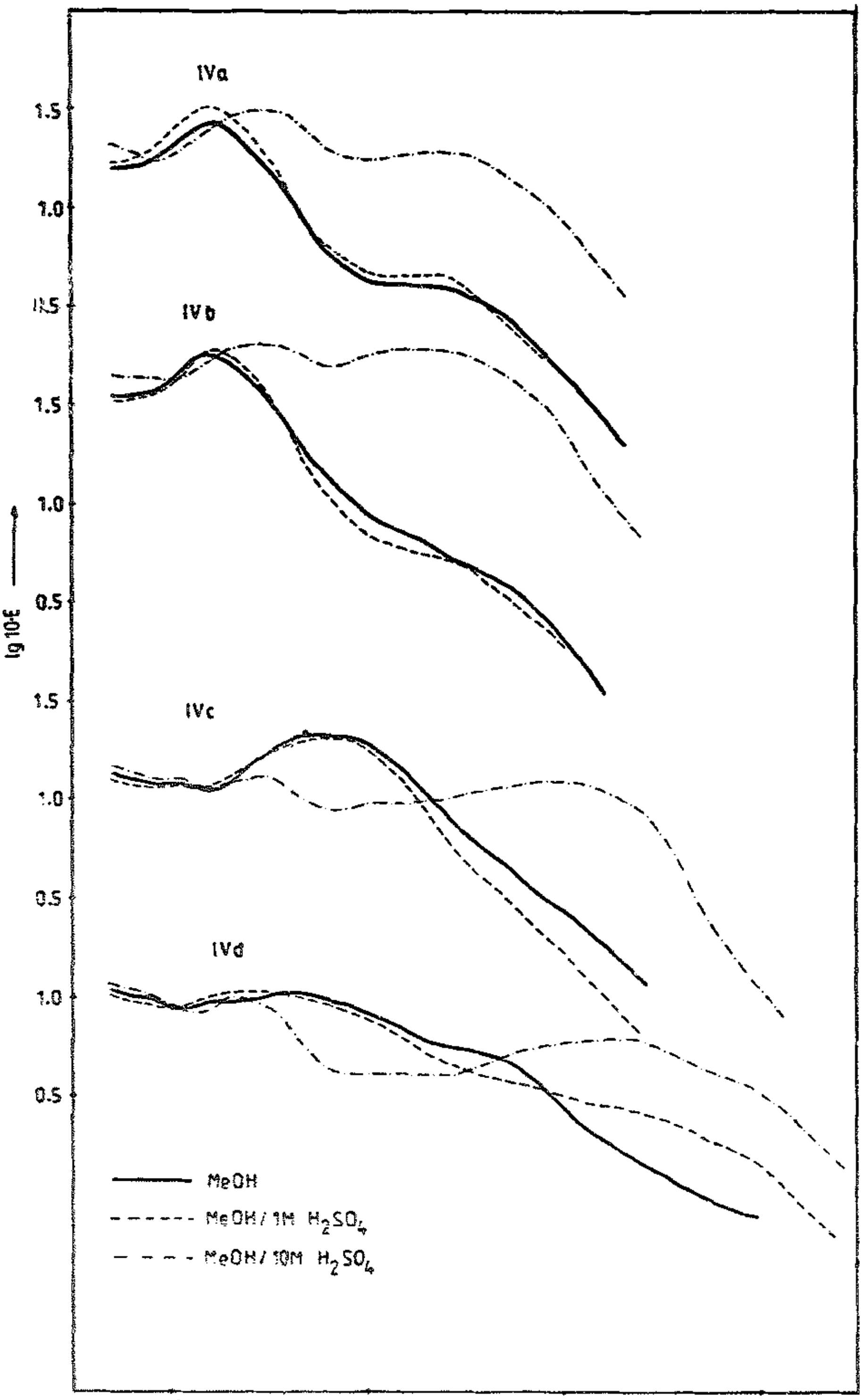


Fig. 3. The UV-VIS absorption spectra of 3- (IVa, IVb) and 4-phenylazonaphthalimides (IVc, IVd).

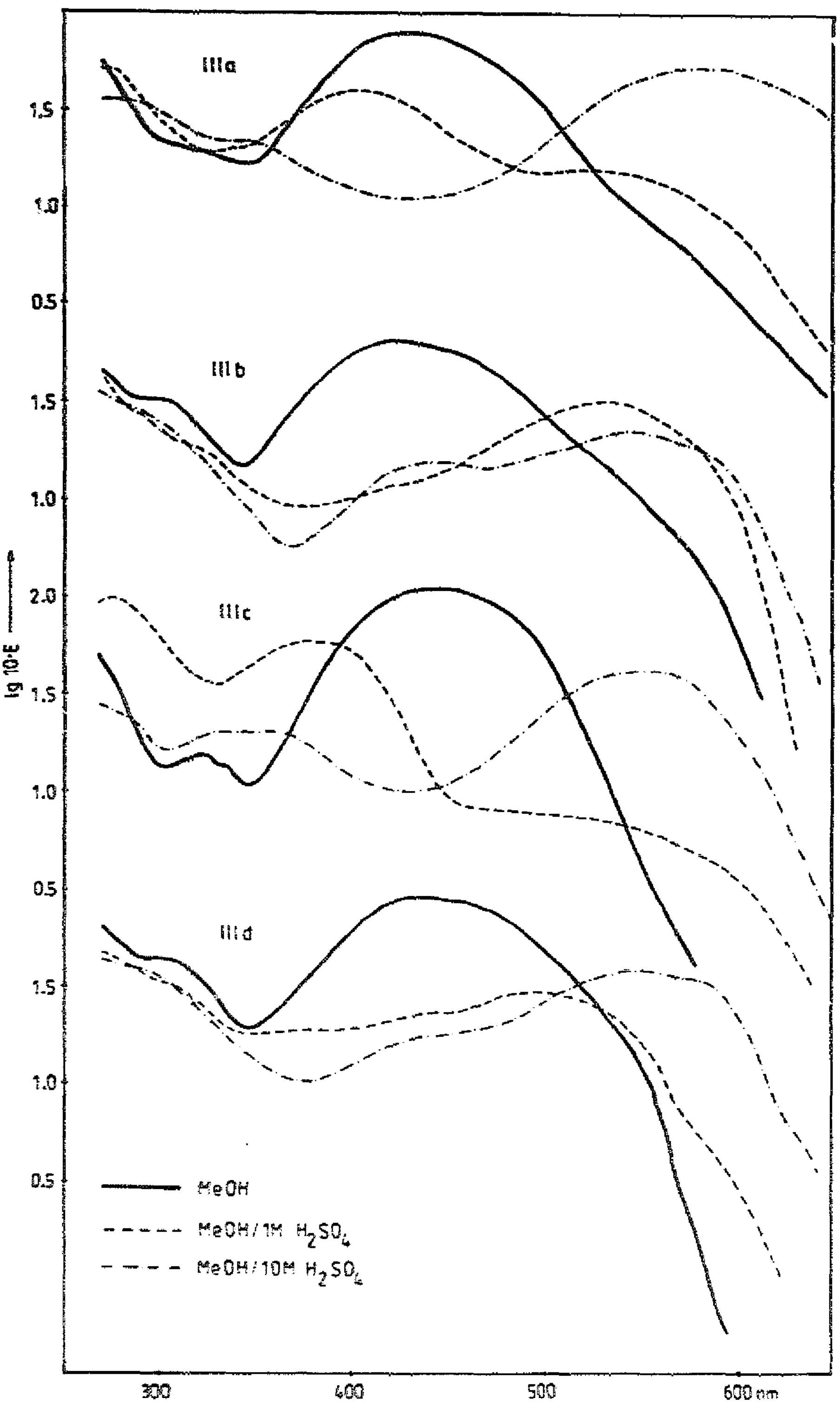


Fig. 4. The UV-VIS absorption spectra of 1- (**IIIa**, **IIIc**) and 2- (p-N,N-dialkyl)aminophenylazonaphthalenes (**IIIb**, **IIId**).

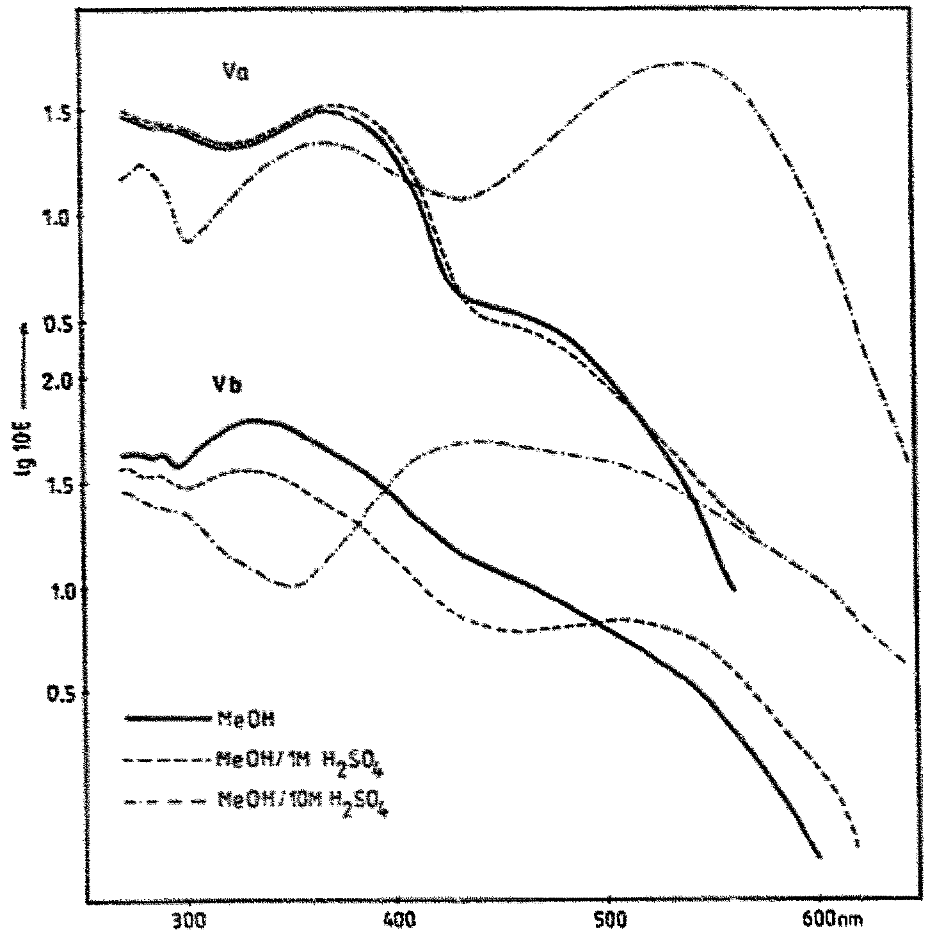


Fig. 5. The UV-VIS absorption spectra of 1- (Va) and 2-phenylazonaphthalene (Vb).

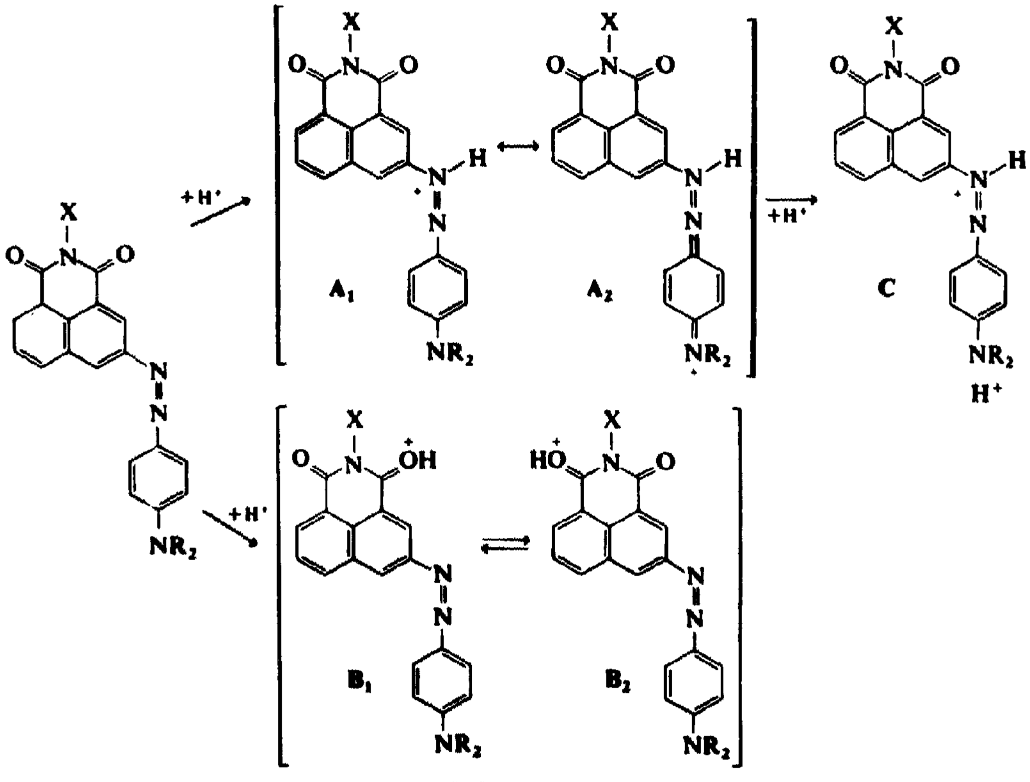
457–470 nm region, compared with the 422–445 nm absorptions for corresponding reference compounds (IIIb and IIId, Fig. 4). A general pattern can be observed, resulting from the use of the coupling component containing the diethylamino group, which results in a bathochromic shift of 12 nm in the VIS range compared with the dimethylamino derivatives (Fig. 1).

Very characteristic changes are observed in the spectra recorded in methanolic solutions of 1M- and 10M-H_2SO_4. In the more dilute 1M-H_2SO_4, there appear additional absorption bands, shifted to longer wavelength by about 60–70 nm compared with the spectra in methanol (Fig. 1).

At the same time, the characteristic band for these compounds at 457–470 nm disappears. In the short-wavelength region of the spectrum, there is a hypsochromic shift of bands by about 20–30 nm, associated probably with the more electron-accepting nature of the protonated imide group. Such a phenomenon is not observed in the reference compounds IVa, and **IVb** (Fig. 3), which suggests a simultaneous influence of the two forms A_2 and $[B_1 \leftrightarrows B_2]$ on the spectrum.

In methanolic 10M-H_2SO_4 solution, there is an increase of dye absorption within 400–450 nm and its intensity is similar to that of the main band. Also the bands ascribed to the protonated form $[A_1 \leftrightarrow A_2]$ are slightly changed depending on the nature of the dialkylamino group. It is possible that dyes **I** produce, in this more strongly acidic medium, some of the doubly protonated structure **C**, viz. at the azo group and at the *N,N*-dialkylamino group, the extent of which varies where R = Me or R = Et.

The changes taking place in the dye molecule depending on the proton concentration in solution can be illustrated by the general Scheme 1.



Scheme 1

Protonation of the terminal amino nitrogen atom of the coupler prevents delocalization of the nitrogen lone pair,[12,14] leading to absorption at lower wavelength, and this is evident in the spectra of the reference compounds **IVa** and **IVb** (Fig. 3), in which protonation can only occur at the azo group (the imide group affects the absorption mainly below 360 nm). The part played by the protonated imide group and its effect on the spectrum are not fully understood. This group is separated from the benzeneazonaphthalene system and its effect on the spectrum may be only a result of the inductive effect. Studies of the acidified solutions allow also the determination of the effect of dialkylamino groups on the spectral properties of 3-benzeneazonaphthalimide dyes. Dyes with the *N*,*N*-dimethylamino groups satisfy the general relationships discussed, but the nature of the observed changes is not so clear as in the case of the *N*,*N*-diethylamino derivatives.

Unexpected differences in the thermal and the dyeing properties of various dyes depending on the nature of alkyl substituents in the amino group have been reported previously.[3,18]

Dyes with the *N*,*N*-dimethylamino group (**Ia** and **Ib**), compared with dyes containing the *N*,*N*-diethylamino groups (**Ic** and **Id**), show a smaller increase in absorption within the 400–450 nm range in 10M-H_2SO_4 compared with the spectra in 1M-H_2SO_4. This is probably associated with the lower stability of the cation $-\overset{+}{N}H(CH_3)_2$. A similar behaviour was observed in the reference dyes **IIIb** and **IIId** (Fig. 4).

In the short-wavelength range, a hypsochromic shift of about 20–25 nm takes place, but only in 1M-H_2SO_4 solutions. In 10M-H_2SO_4, this phenomenon is much weaker and it may be assumed that in 10M-H_2SO_4 the prevailing form C, with a protonated azo group, effectively protects against further protonation of the imide group and formation of structures derived from $[B_1 \leftrightarrows B_2]$.

As has been previously noted,[2,18] the azo derivatives of 4-aminonaphthalimide (**IIa**–**IId**) show quite different physical, chemical and dyeing properties from the 3-substituted isomers (**Ia**–**Id**). The presence of an azo group in the 4-position creates an additional possibility of electron interaction between the cyclic 6-membered amide system and the *N*,*N*-dialkylamino group. The acceptor and donor character of these substituents should bring about a considerable bathochromic effect compared with the isomeric 3-arylazonaphthalimide dyes (**Ia**–**Id**).[20] Dyes **IIa**–**IId** in fact give blue or violet dyeings on polyester fibres, whilst the 3-isomers (**Ia**–**Id**) give orange hues.

A study of the absorption spectra in neutral and acidic H_2SO_4 solutions indicates the reasons for these results. Some dyes **II** show, in the visible range, double maxima, one around 440–454 nm, in a similar region to the absorption of the 3-isomers (457–470 nm) and a second in the 520–525 nm region (dyes **IIa** and **IIb**). Dyes **IIc**, and **IId** show essentially one long-wavelength band at about 530 nm. In addition, the new bands are not observed in the long-wavelength range of the spectra recorded in the acidified solutions, in contrast to the dyes **Ia**–**Id** (Fig. 1).

Due to conjugation, dyes **IIa**–**IId** can exist in the 'neutral' (D'_1) as well as in the polar forms (D'_2).[19] This is illustrated by the spectrum of dye **IIc** and that composed of the reference partial chromophores **IIIc** and **IVc** (Fig. 6). Dye **IIc** shows absorption in the visible at about 530 nm, whilst the absorption of

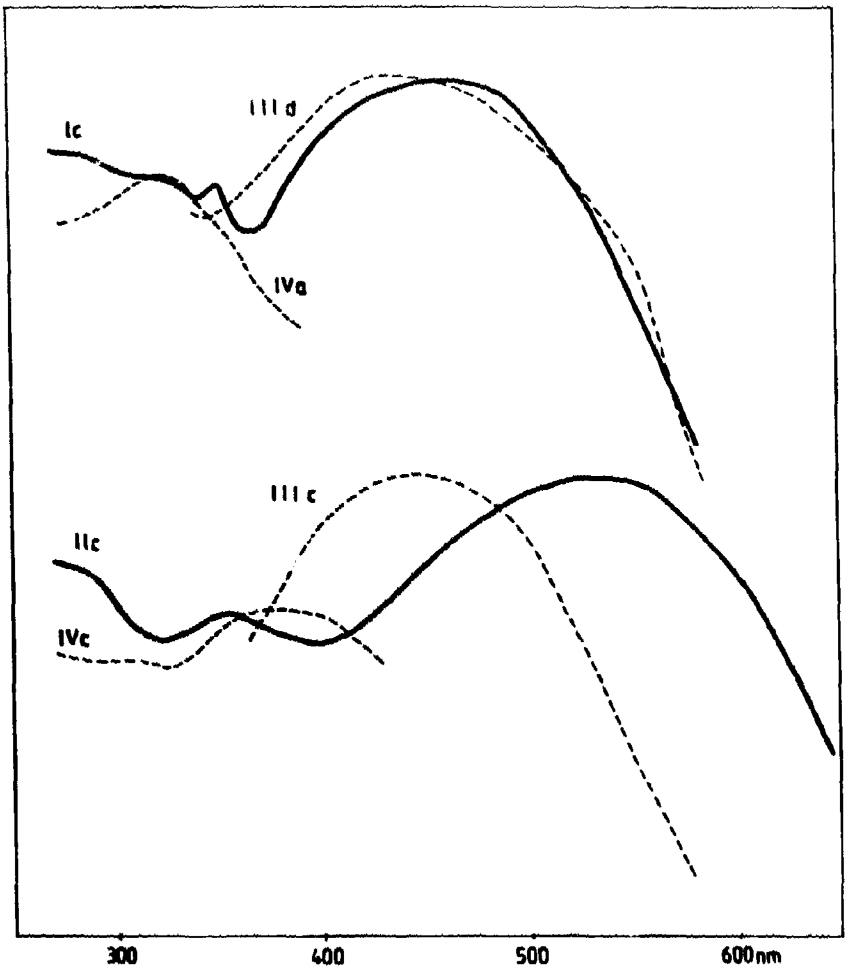
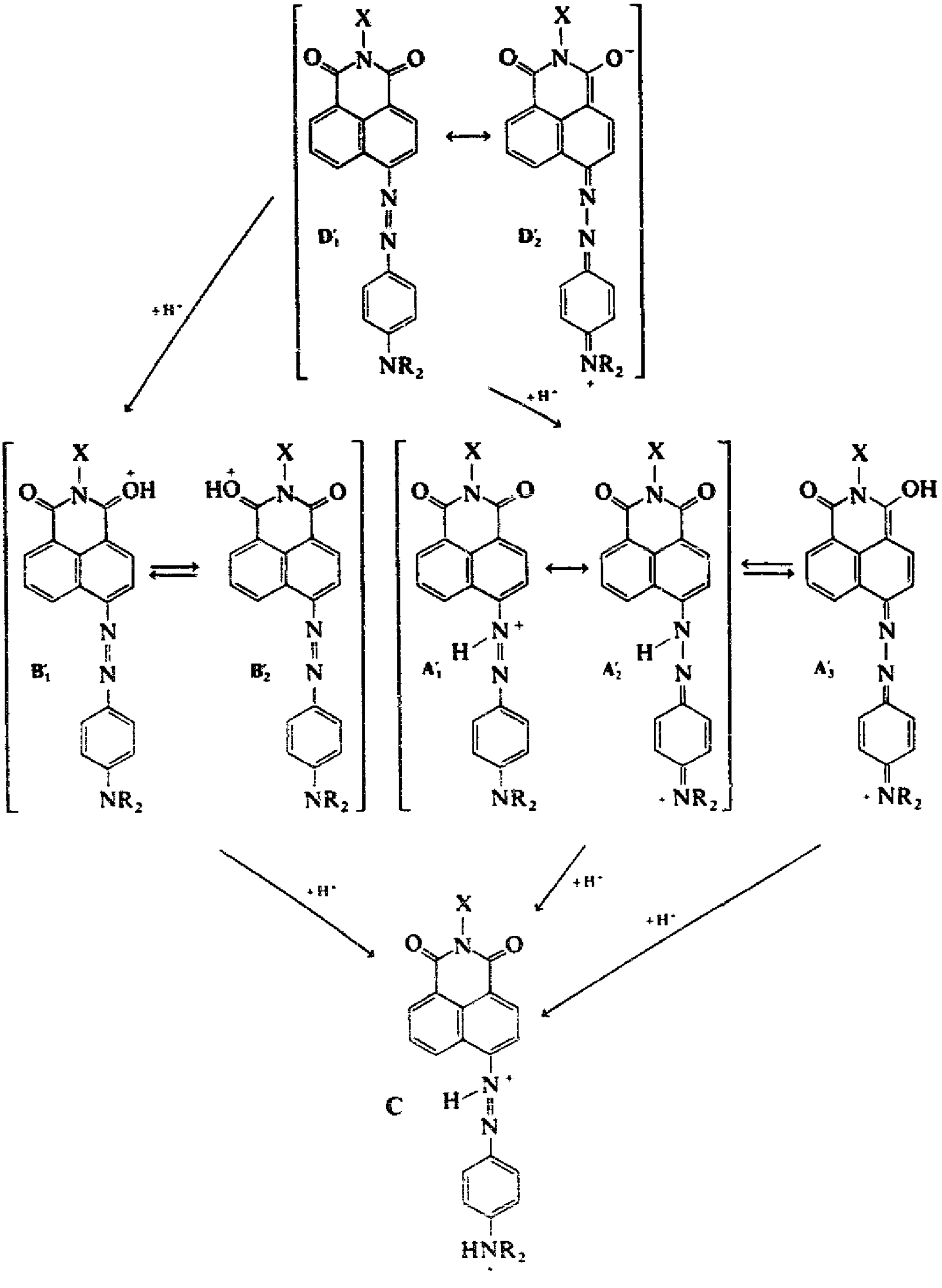


Fig. 6. Comparative spectra in methanol of dyes **Ic** and **IIc** and that composed of partial chromophores. For clarification, it is assumed that for dye **Ic**: *UV*: log $10E_{max}$(**IVa**) = log $10E_{max}$ (**Ic**); *VIS*: log $10E_{max}$ (**IIId**) = log $10E_{max}$(**Ic**) and for dye **IIc**, respectively: *UV*: log $10E_{max}$ (**IVc**) = log $10E_{max}$ (**IIc**); *VIS*: log $10E_{max}$ (**IIIc**) = log $10E_{max}$ (**IIc**).

the reference dye **IIIc**, which exists in the 'neutral' form, is at 445 nm. For comparison, the spectrum of dye **Ic**, a 3-arylazonaphthalimide derivative, is also shown. It consists of two partial chromophores of dialkylaminoazonaphthalene (**IIId**) and of benzenoazonaphthalimide (**IVa**), the slight deviation of absorption maxima being a result of the mutual interaction between substituents. In the range 344–355 nm, the absorption of the benzenoazonaphthalene chromophore is observed.

Similarly to dyes **Ia–Id**, the isomeric derivatives of 4-benzenoazonaphthalimides **IIa–IId** have 'basic' absorption bands within the range 440–454 nm (Fig. 2), and dyes **IIc–IId** appear probably mainly in the polar form (D'_2). The equilibria existing in 'neutral' and acidic solutions are illustrated in the general Scheme 2.



Scheme 2

The results obtained in the above show that the colour shifts observed in the 4-substituted isomers are due to the coexistence, even in unacidified solution, of the 'neutral' (D'_1) and polar (D'_2) forms which results in the bathochromic shift of the long-wavelength absorption bands. This can be attributed to the presence of an electron-donating substituent (*N*,*N*-dialkylamino) and an electron-accepting (cyclic amide) system in positions allowing mutual conjugation. This is not observed in the 3-isomers, where such interactions are not possible.

Whilst the contribution of such polar forms is observed in the naphthalimide derivatives, they are not observed in similar azo derivatives of acetamide, benzamide and phthalimide.[5]

REFERENCES

1. Szadowski, J., *Zesz. Nauk. PŁ*, **44** (1981) 19.
2. Szadowski, J., Wojciechowski, K. and Malinowski, W., *J. Soc. Dyers Colourists*, **101** (1985) 105.
3. Wojciechowski, K. and Szadowski, J., *J. Thermal. Anal.*, **31** (1986) 297.
4. Peters, A. T. and Bide, N. J., *Dyes and Pigments*, **7** (1986) 237.
5. Wojciechowski, K. and Szadowski, J., *Pol. J. Chem.*, **60** (1986) 797.
6. Ogata, Y. and Takagi, T., *J. Amer. Chem. Soc.*, **80** (1958) 3591.
7. Martynoff, M., *Bull. Soc. Chim. France*, (1951) 214.
8. Nietzki, R. and Zehner, R., *Ber*, **26** (1893) 143.
9. Skulski, L. and Urbański, T., *Bull. Acad. Polon. Sci.*, **10** (1960) 561.
10. Skulski, L. and Urbański, T., *Rocz. Chem.*, **36** (1962) 801.
11. Schulze, J., Gerson, F., Murrell, J. N. and Heilbronner, F., *Helv. Chim. Acta*, **44** (1961) 429.
12. Hallas, J., *J. Soc. Dyers Colourists*, **95** (1979) 285.
13. Korolew, B. A., Timowa, S. P. and Ufimcew, W. N., *Żurn. Org. Chim.*, **7** (1971) 1191.
14. Skulski, L. In *Wiazanie Wodorowe*, PWN, Warsaw, 1969, p. 33.
15. Skulski, L. and Maciejewska, D., *Pol. J. Chem.*, **59** (1985) 37.
16. Badger, G. M. and Buttery, R. G., *J. Chem. Soc.*, (1953) 2156. (1985) 37.
17. Bogusławskaja, N. A., Bogusławskij, B. N. and Jaworkij, B. M., *Żurn. Obszcz. Chimii*, **30** (1960) 112.
18. Szadowski, J., Přikryl, J. and Wojciechowski, K., *Chem. Stosowana*, **23** (1987) 415.
19. Izmailskij, V. A. and Smirnow, E. A., *Żurn. Obszcz. Chimii*, **26** (1956) 3042.