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Relationships Between the Structure of Nitrodiphenylamine Derived Monoazo Acid Dyes and their Spectroscopic and Fastness Properties

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SUMMARY

Fourteen monoazo acid dyes derived from 4-nitrodiphenylamine and 2-nitrodiphenylamine have been synthesized Relationships between the position of nitro and sulphonic groups and the wavelength of the visible absorption band and also the lightfastness on polyamide fibres have been examined. It is suggested that the colour of the dyes and their lightfastness depend on the possibility of formation of intramolecular hydrogen bonding The existence of such bonding was shown by the IR and UV–vis spectra of the investigated dyes and model derivatives of diphenylamine

1. INTRODUCTION

It is apparent from the literature that of the yellow dyes for polyamide fibres a high proportion are monoazo acid dye derivatives of nitrodiphenylamine.[1-3] Typically it is found that the 2-nitrodiphenylamine derivatives[4,5] are recommended despite the fact that suitable

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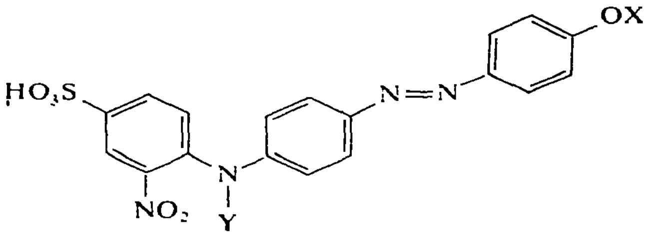
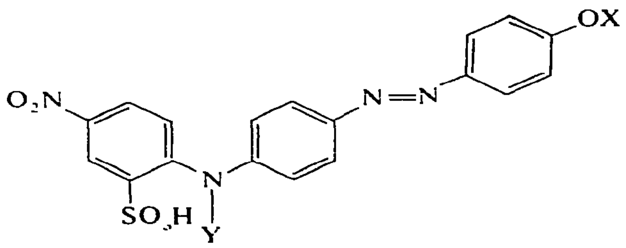
intermediates are less readily available than for the isomeric 4-nitrodiphenylamines. Many well known acid dyes have been prepared from 4'-amino-4-nitrodiphenylamine-2-sulphonic acid.[6,7] Investigations of nitrodiphenylamine derivatives used as disperse dyes[8-10] have shown a considerably higher lightfastness in the case of 2-nitrodiphenylamine dyes than has been observed with the 4-nitroisomers. Consequently (almost exclusively) the 2-nitrodiphenylamine derivatives are used now as disperse dyes. Recently they have found use also in azo acid dyes for polyamide,[1-5] but relationships between their structure and application properties have not been examined thoroughly. It seemed useful, therefore, to investigate relationships between the type and location of substituents in monoazo acid dye derivatives of nitrodiphenylamine (**I** and **II**) and their colour and fastness behaviour.



I



II

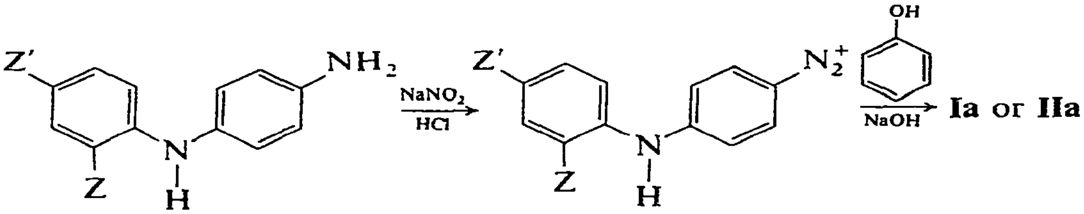
	X	Y
a	H	H
b	CH_3	H
c	C_2H_5	H
d	$SO_2C_6H_5$	H
e	$SO_2C_6H_4CH_3$	H
f	CH_3	C_2H_5
g	C_2H_5	C_2H_5
h	$SO_2C_6H_5$	C_2H_5

2 RESULTS AND DISCUSSION

Two series of dyes, **I** and **II**, were synthesized and their properties examined. These differed in the arrangement of NO_2 and SO_3H substituents in the diphenylamine residue and in the type of substituent Y attached to the amine group (H or C_2H_5), as well as in the substituent X attached to the hydroxy group (H, alkyl or acyl).

The syntheses of most of the dyes have been described in the literature or were carried out by standard procedures.

The parent dyes **Ia** and **IIa** were prepared according to Scheme 1.



Scheme 1. Z and Z' = NO_2 or SO_3H.

Alkylation of the hydroxyl group in dyes **Ia** and **IIa** was carried out with ethyl chloride[11] or methyl benzenesulphonate in 70% alcohol or water solution.

Esterification of the hydroxyl group in the above dyes was carried out with benzene sulphonyl chloride or *p*-toluenesulphonylchloride in aqueous alkaline media.

Based on previous examination of electronic absorption spectra of nitroderivatives of diphenylamine, Asquith and co-workers[8-10] and Luckij and co-workers[12,13] have suggested that *o*-nitrodiphenylamine and its derivatives exist in the *o*-quinonoid structure containing strong intramolecular hydrogen bonding (Fig. 1). The existence of such a bond could account for the considerable differences in physical and lightfastness properties of disperse dye derivatives of diphenylamine.[8-10] The existence of intramolecular hydrogen bonding in the *o*-nitrodiphenylamine system is also confirmed by the IR spectra of compounds used as models for acid dyes **I** and **II** (Table 1).

Due to the formation of hydrogen bonding, the band associated with the stretching frequency of free NH groups, which is 3430 cm^{-1} for solutions of diphenylamine and 4-nitrodiphenylamine in CCl_4, is shifted in the case of the *o*-nitro isomers to the region 3300–3380 cm^{-1}. Intramolecular interactions in the crystalline state result in two bands

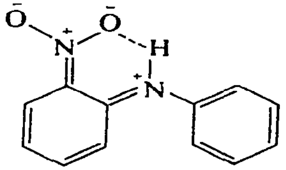
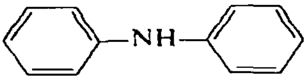
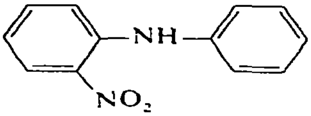
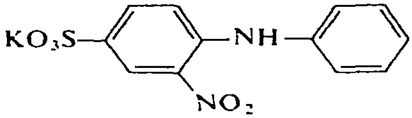
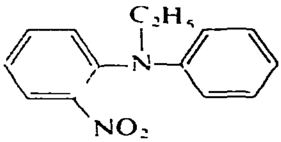
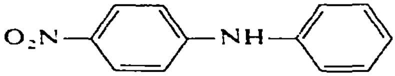
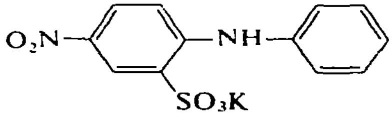


Fig. 1. Intramolecular hydrogen bonding in *o*-nitrodiphenylamine.

TABLE 1
IR Spectra of Diphenylamine and Nitrodiphenylamine Derivatives

Compound	*Medium*	*NH*		*NO_2*	
		Free	*H-bonded*	*Asym*	*Sym*
	KBr	3 410 m	3 383 m		
	CCl_4	3 430 w			
	KBr		3 355 m	1 507 s	1 330 m
	CCl_4		3 355 m	1 507 s	1 328 m
	KBr		3 325 m	1 515 s	1 342 m
	KBr			1 528 s	1 355 s
	CCl_4			1 530 s	1 355 s
	KBr		3 342 s	1 498 s	1 333 s
	CCl_4	3 430 s			1 355 s
	KBr		3 305 m	1 500 s	1 340 s

observed in the spectrum of diphenylamine in KBr: 3410 cm^{-1} (free NH) and 3383 cm^{-1} (associated NH). In the 4-nitrodiphenylamine spectrum in KBr, there is only one band characteristic of the associated NH group (3342 cm^{-1}), while in the 2-nitrodiphenylamine spectrum, strong intramolecular bonding brings about a shift of the NH band to a frequency of 3355 cm^{-1} both in the crystalline state and in CCl_4. The existence of intramolecular hydrogen bonding in 2-nitrodiphenylamine is additionally confirmed by the fact that there is no change in the position and intensity of this band when the CCl_4 solution is diluted.

As expected, the spectrum of *N*-ethyl-2-nitrodiphenylamine shows no absorption band in the range 3300–3450 cm^{-1} In the spectrum of the potassium salt of 2-nitrodiphenylamine-4-sulphonic acid, the NH band is observed at 3325 cm^{-1}. This is the result of intramolecular hydrogen bonding However, the band at 3305 cm^{-1} in the spectrum of the potassium salt of 4-nitrodiphenylamine-2-sulphonic acid can only be ascribed to intermolecular hydrogen bonding existing in the crystalline state. The existence of intramolecular hydrogen bonding in 2-nitrodiphenylamine is also supported by the presence of bands characteristic for asymmetric stretching vibration and symmetric vibration of the NO_2 group. In the case of the asymmetric vibration, the frequency is shifted from about 1530 cm^{-1} for *N*-ethyl-2-nitrodiphenylamine to about 1507–1515 cm^{-1} for the *N*-unsubstituted derivatives. In the case of symmetric vibration of the NO_2 group, however, the formation of an intramolecular hydrogen bond results in a shift from 1355 cm^{-1} to about 1330–1340 cm^{-1}.

Relationships between the arrangement of substituents and the colour of the dyes under investigation were obtained by comparison of the electronic absorption spectra of methanol solutions of the investigated dyes with those of model compounds (Figs 2, 3 and 4).

The spectrum of 2-nitrodiphenylamine-4-sulphonic acid (Fig 2) is very similar to that of 2-nitrodiphenylamine. According to Asquith and coworkers,[8-10] the 424 nm band ($\log \varepsilon = 3{\cdot}82$) of 2-nitrodiphenylamine, which is responsible for the colour, can be ascribed to the dominant contribution of the *o*-quinonoid to the molecular structure. These authors suppose that the polar quinonoid structure is stabilized by the intramolecular hydrogen bond and the intensity of the absorption band is related to the contribution of this resonance form to the molecule. The intensity of this band for 2-nitrodiphenylamine-4-sulphonic acid is almost the same as that for 2-nitrodiphenylamine (422 nm; $\log \varepsilon = 3{\cdot}79$)

For the series of monoazo acid dyes derived from 2-nitrodiphenylamine, **Ia–e**, two absorption bands (*ca* 370 nm and 425 nm) are observed (Fig. 2). The band at 425 nm ($\log \varepsilon = 3{\cdot}80$–$3{\cdot}95$) suggests a high contribution from the *o*-quinonoid structure, stabilized by the intramolecular hydrogen bond, similar to that in the model compounds. This band shows virtually no change in comparison with 2-nitrodiphenylamine and 2-nitrodiphenylamine-4-sulphonic acid despite the electron acceptor character of the arylazo residue in the dye molecule. The second absorption band, within the region 367–371 nm, can be ascribed to the *p*-hydroxyazobenzene system, or its *O*-substituted derivative, isolated from

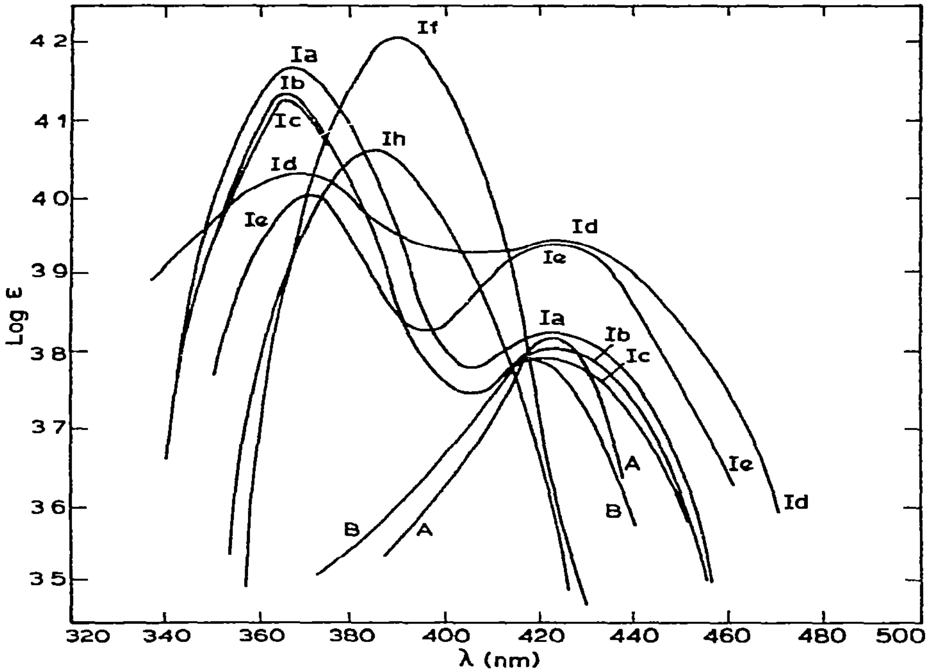


Fig. 2. UV–vis spectra of 2-nitrodiphenylamine derivatives and dyes **I** in methanolic solution A, 2-nitrodiphenylamine, B, 2-nitrodiphenylamine-4-sulphonic acid

the remaining part of the dye molecule. Absorption by this chromogen takes place beyond the visible range, and thus it is the nitrodiphenylamine band at 425 nm which determines the colour of the dye.

In the *N*-ethyl derivatives of the dyes based on 2-nitrodiphenylamine, **If–h**, there is no possibility of forming intramolecular hydrogen bonding, so the polar *o*-quinonoid structure is not stabilized. Therefore, the absorption intensity within the region 420–430 nm is very low compared with analogous *N*-unsubstituted compounds (**Ia–e**). However, more precise analysis of the spectra of the *N*-ethyl derivatives (Fig. 3) shows an inflexion near 430 nm suggesting a possible share of the *o*-quinonoid structure in the excited state in these dyes as well, which is in agreement with the literature data concerning similar compounds.[9,13 14]

The colour of the *N*-ethyl derivatives of the monoazo dyes is affected to a great extent by the band associated with the *p*-hydroxyazo chromophore system, which in this case is shifted bathochromically from about 370 nm to 390–395 nm. This bathochromic shift is probably due to

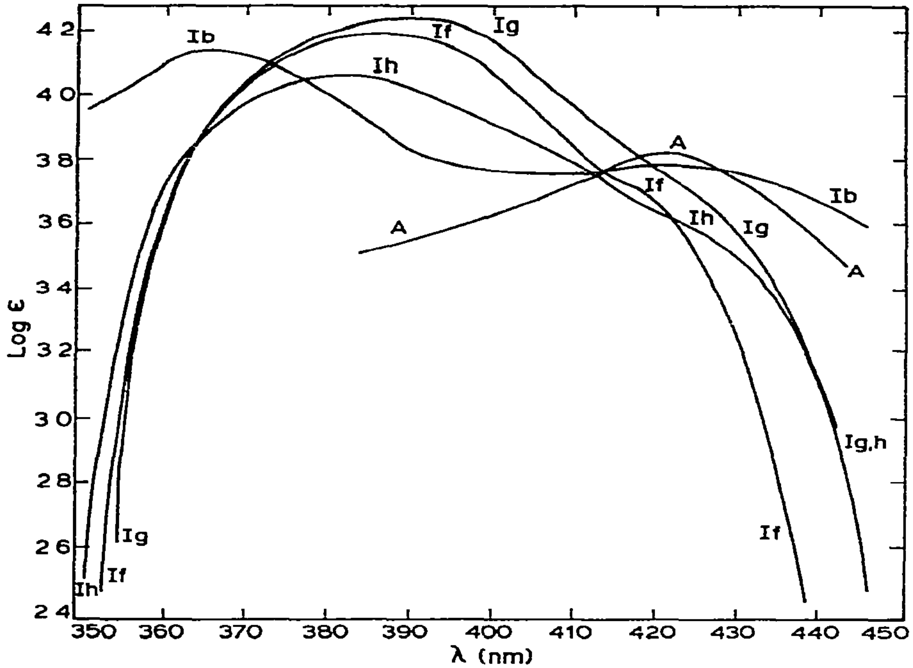


Fig. 3. UV–vis spectra of *N*-ethyl derivatives of dyes **I** in methanolic solution. A, 2-nitrodiphenylamine

the lack of intramolecular hydrogen bonding, and consequently to undisturbed electron acceptor interaction of sulphonic and nitro groups with the whole chromophore and with the change in the spatial structure of the molecule. Nevertheless, the *N*-ethyl dyes (**If–h**) in solution and on polyamide fibres show a distinct hypsochromic shift in comparison with the *N*-unsubstituted 2-nitrodiphenylamines (**Ia–e**). This is because the two absorption bands are within the visible region of the spectrum to any significant extent only in the case of the *N*-substituted derivatives.

The electronic absorption spectra of 4-nitrodiphenylamide, 4-nitrodiphenylamine-2-sulphonic acid and monoazo dyes (**II**) based on the latter structure showed that when the nitro group is in the *para* position, two chromophoric systems are not formed (Fig. 4) In the spectra of all these compounds, one intense band is observed. For 4-nitrodiphenylamine the maximum is at 392 nm ($\log \varepsilon = 4{\cdot}44$). In the case of 4-nitrodiphenylamine-2-sulphonic acid, hypsochromic and hypochromic effects are observed ($\lambda_{max} = 377$ nm; $\log \varepsilon = 4{\cdot}08$). In all the dyes **IIa–h**

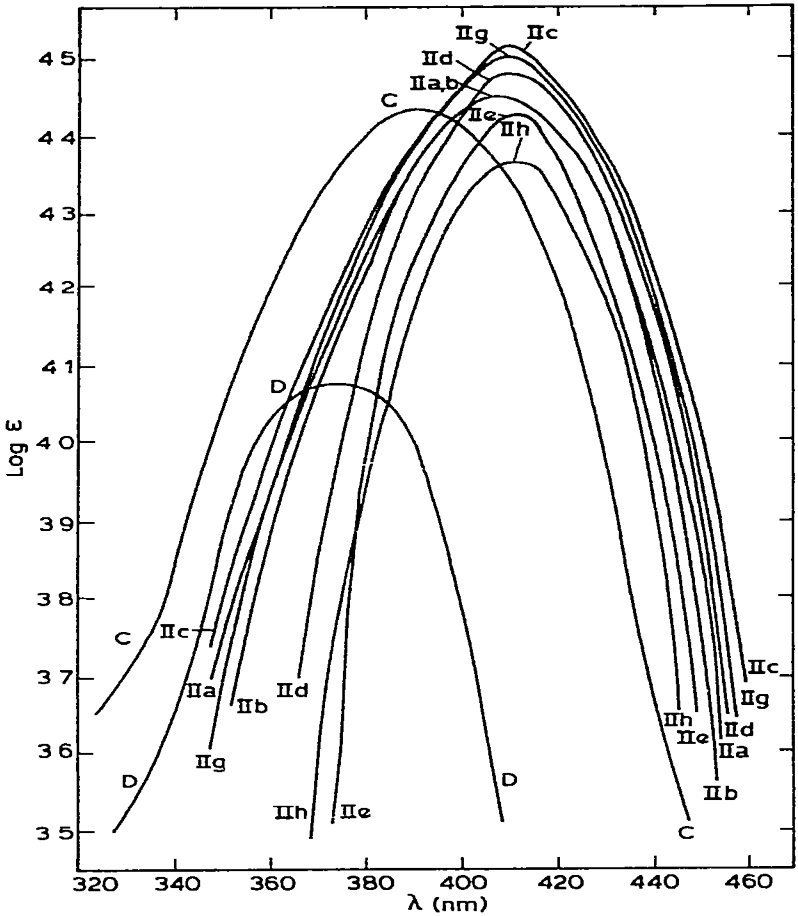


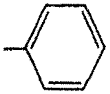
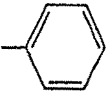
Fig. 4. UV–vis spectra of 4-nitrodiphenylamine derivatives and of dyes **II** in methanolic solution C, 4-nitrodiphenylamine, D, 4-nitrodiphenylamine-2-sulphonic acid

derived from 4-nitrodiphenylamine, one absorption band of considerable intensity is observed at about 410 nm ($\log \varepsilon = 4{\cdot}37$–$4{\cdot}51$). Substitution at the amino group with an ethyl group as in **IIg, h** causes no significant change in the spectrum. The 4-nitrodiphenylamine dyes provide virtually identical dyeings on polyamide fibres, the colour being a bright intense yellow.

The nature of substituents attached to the hydroxyl group of the dyes **I** and **II** does not significantly affect their colour. However, such substituents do affect other physical properties, for instance, solubility.

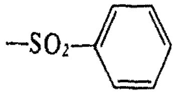
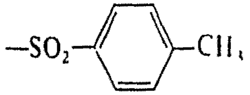
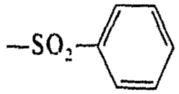
TABLE 2

Fastness Properties of Dyeings of **I** on Polyamide

Dye	*Y*	*X*	*Water*			*Washing (40°C)*			*Rubbing*		*Perspiration*						*Light (Xenotest)*
			a	*b*	*c*	*a*	*b*	*c*	*Wet*	*Dry*	*Acid*			*Alkaline*			
											a	*b*	*c*	*a*	*b*	*c*	
Ia	H	H	4–5	3–4	4–5	4	4–5	5	5	5	4–5	4	4–5	4–5	3	4–5	7
Ib	H	CH$_3$	4–5	4	4–5	4	4	5	5	5	4–5	4	4–5	4–5	4	4–5	6–7
Ic	H	C$_2$H$_5$	4–5	4	4–5	4–5	4	5	4–5	5	4–5	4	4–5	4–5	4	4–5	7
Id	H	--SO$_2$--	5	4–5	5	4–5	4–5	5	4–5	4–5	4–5	4	4–5	4–5	4	4–5	7
Ie	H	—SO$_2$——CH$_3$	5	5	5	4–5	4–5	5	4–5	5	4–5	4	4–5	4–5	4	4–5	7
If	C$_2$H$_5$	CH$_3$	4	4	4–5	4	4	5	4–5	5	3–4	3–4	4	4	3–4	4	4
Ig	C$_2$H$_5$	C$_2$H$_5$	4	4	4–5	4	4	5	5	4–5	4	3–4	3–4	4	3–4	4	4
Ih	C$_2$H$_5$	—SO$_2$—	4–5	4	5	4–5	4–5	5	5	5	4	3	3–4	4	3	3–4	4–5

a, Change; *b*, staining of polyamide, *c*, staining of wool

TABLE 3
Fastness Properties of Dyeings of **II** on Polyamide

Dye	*Y*	*X*	*Water*			*Washing (40°C)*			*Rubbing*		*Perspiration*						*Light (Xenotes)*
											Acid			*Alkaline*			
			a	*b*	*c*	*a*	*b*	*c*	*Wet*	*Dry*	*a*	*b*	*c*	*a*	*b*	*c*	
IIa	H	H	4-5	3	4-5	4	3-4	5	5	5	4	3-4	4-5	4-5	2-3	4-5	5-6
IIb	H	CH_3	4-5	3	4-5	4	3	5	5	5	4-5	4	5	4-5	3-4	4	5
IIc	H	C_2H_5	4-5	3	4-5	4	3	5	5	5	4-5	4	5	4-5	4	4	5
IId	H		4	4	5	4	4	5	5	5	4-5	4	5	4-5	4	4-5	5
IIe	H		4	4	5	4	4	5	5	5	4-5	4	5	4-5	4	4-5	5
IIg	C_2H_5	C_2H_5	4-5	3-4	5	4	3-4	5	5	5	4-5	4	5	4-5	4	4	5
IIh	C_2H_5		4	4	4-5	4	4	5	5	5	4-5	4	5	4-5	4	4-5	5

a, Change, *b*, staining of polyamide, *c*, staining of wool

Comparing the colour properties of monoazo dyes derived from 2-nitrodiphenylamine (**I**) and 4-nitrodiphenylamine (**II**), it may be concluded that the use of 4-nitrodiphenylamine derivatives would be more advantageous because of their intensity and brightness of hue. However, by analogy with previously investigated disperse dyes based on isomeric nitrodiphenylamines,[8–10] a considerably lower fastness to light might be expected for these dyes whose *o*-quinonoid structure is not stabilized by intramolecular hydrogen bonding, i.e. all derivatives of 4-nitrodiphenylamine (**IIa–h**) and *N*-ethyl derivatives of 2-nitrodiphenylamine (**If–h**). Examination of the lightfastness properties (Tables 2 and 3) showed that according to expectation the highest lightfastness for dyeings on polyamide fibres (7 in the 8-grade scale) was obtained with derivatives of *N*-unsubstituted 2-nitrodiphenylamine, **Ia–e**. For the *N*-ethyl derivatives **If–h**, where the *o*-quinonoid structure is not stabilized with intramolecular hydrogen bonding, the stability to photochemical degradation drops and the lightfastness of the dyeings decreases to 4 and 4–5. On polyamide these dyes (**If–h**) also show a slight decrease in fastness to acid and alkaline perspiration.

The monoazo dyes derived from 4-nitrodiphenylamine, **II**, show a lightfastness of about 5 because of the absence of intramolecular hydrogen bonding. The decrease in their fastness to light is notable in comparison with the 2-nitrodiphenylamine derivatives **I**, but is not as great as would be expected from the behaviour of 2- and 4-nitrodiphenylamine disperse dyes, for which the lightfastness decreases from 7–8 to 2.[8–10] In addition, in the case of the acid dyes, no decrease in the lightfastness of 4-nitro-*N*-ethyldiphenylamine (**IIg, h**) was observed in comparison with the *N*-unsubstituted compounds, **IIa–e**. This could be explained in terms of possible stabilization of the 4-nitrodiphenylamine residue by conjugation with the azo group of the molecule.

3. CONCLUSIONS

Spectrophotometric and lightfastness studies of the two series of monoazo acid dyes, **I** and **II**, demonstrate that strong intramolecular hydrogen bonding is present in the derivatives of *N*-unsubstituted 2-nitrodiphenylamines of type A (dyes **Ia–e**). This noticeably increases the photochemical stability of the dyes and ensures a very high lightfastness of dyeings on polyamide fibres. Dyes of type B containing an *N*-substituted amine group (**If–h**, and **IIg, h**) and derivatives of 4-nitrodiphenylamine (**IIa–e**), are unable to develop such intramolecular hydrogen bonds, and consequently show poorer fastness to light. The differences, however, are not as great as those observed in the case of analogous non-azo nitrodiphenylamine disperse dyes used for acetate and polyester fibres

From the colour point of view the presence of intramolecular hydrogen bonding in dyes of type A establishes two independent chromophoric systems This consequently causes a decrease in the colour intensities of solutions and dyeings as compared with dyes of type B. However, since only one of the chromophoric systems causes absorption within the visible range, the other absorbing within the UV range, a bathochromic effect is observed visually with a small hypochromic effect Thus durable reddish yellow dyes are obtained

Thus it becomes understandable why monoazo acid dyes (**Ia–e**) based on *N*-unsubstituted 2-nitrodiphenylamine are recommended for dyeing polyamide fibres. An important factor is the possibility of obtaining dyeings of very high fastness to light, which makes the reddish yellow acid dye derivatives of 2-nitrodiphenylamine so popular even though such dyes lack the purity and brightness of the 4-nitrodiphenylamine yellows.

4 EXPERIMENTAL

4.1. Preparation of model compounds

Diphenylamine and its derivatives were analysed by thin-layer chromatography (DC-Cellulose 5563 Merck) In the case of compounds not containing sulphonic groups, a mixture of cyclohexane, CH_3COOH and H_2O (40 39 1 by vol) was used as eluent, while in the case of sulphonic acids, a mixture of lauryl alcohol, dioxane and 25% aq. NH_3 (2 5:1 by vol) was used. The samples were prepared as 2% solutions in ethanol.

Diphenylamine

Industrial diphenylamine was purified by repeated crystallization from ethanol and then from cyclohexane Colourless flakes, m p. 54°C, were obtained. (Found: N = 8 2%. Required: N = 8·3%.)

2-Nitrodiphenylamine

The crude product prepared by condensation of *o*-nitrochlorobenzene and aniline[15] was recrystallized from 75% ethanol and then from cyclohexane. Orange flakes, m.p. 75·5–76°C, were obtained. (Found: N = 13·0%. Required: N = 13·1%.)

2-Nitro-N-ethyldiphenylamine

A mixture of 4·28 g (0·02 mol) of 2-nitrodiphenylamine, 5·6 g (0·1 mol) of KOH and 15·6 g (0·1 mol) of ethyl iodide was kept at 20°C for 10 days, then heated at the boiling point for 4 h. After cooling, dilution with water gave an oily product which was separated by decantation and was recrystallized successively from ethanol, benzene and cyclohexane. Golden yellow needles, m.p. 48·5–49·5°C, were obtained. (Found: N = 11·5% Required: N = 11·6%.) No bands characteristic of the NH group were found in the IR spectrum.

2-Nitrodiphenylamine-4-sulphonic acid

The crude product was prepared by condensation of 2-nitrochlorobenzene-4-sulphonic acid with aniline.[16] It was recrystallized from ethanol acidified with HCl, then from pure ethanol and cyclohexane Greenish yellow crystals, infusible up to 360°C, were obtained. (Found: N = 9·3% Required: N = 9·5%)

4-Nitrodiphenylamine

This was prepared by condensation of *p*-nitrochlorobenzene with aniline in the presence of Cu_2I_2[17] The crude product was purified by recrystallization from 75% ethanol and then from CCl_4. Greenish-yellow plates with m.p. 135–136°C were obtained. (Found: N = 13·0% Required: N = 13·1%.)

4-Nitrodiphenylamine-2-sulphonic acid

The crude product, prepared by condensation of 4-nitrochlorobenzene-2-sulphonic acid with aniline,[16] was crystallized from ethanol (acidified with HCl) and pure ethanol, then it was washed with cyclohexane. Olive-green rods of m.p. 283–284°C were obtained. (Found: N = 9·4%. Required: N = 9·5%)

4.2. Preparation of dyes

The dyes were analysed by paper chromatography (Whatman 3) or TLC

(DC-Cellulose 5563 Merck). A mixture of lauryl alcohol, dioxane and 25 % aq. NH_3 (2:5:1 by vol.) was used as eluent. The samples were prepared as 2 % solutions in a mixture of water and pyridine (2:1 by vol.). The progress of the etherification reactions was monitored by paper chromatography (Whatman 3), using 25 % aq. NH_3 as eluent.

Dyes **Ia** *and* **IIa**[2–4]

A solution of 30·9 g (0·1 mol) of 4′-amino-2-nitrodiphenylamine-4-sulphonic acid or 4-amino-4-nitrodiphenylamine-2-sulphonic acid in 500 cm^3 of water containing 4·4 g (0·11 mol) of NaOH and 7·25 g (0·105 mol) of $NaNO_2$ was added dropwise to a mixture of 34·5 g (0·28 mol) of 30 % aqueous HCl, maintaining the temperature at 10 °C. After 2 h, the dispersion of diazonium salt was added dropwise to a solution of 9·4 g (0·1 mol) of phenol in 150 cm^3 of water containing 4 g (0·1 mol) of NaOH and 20 g (0·2 mol) of Na_2CO_3 at 0 °C. After completion of the coupling process, the dispersion of dye was heated to 50 °C and salted out by adding 5 % of NaCl. The precipitated dye was filtered off and dried at 80 °C, giving 44·2 g in the case of dye **Ia** (94·5 % purity by vanadometric analysis, 95·7 % yield). In the case of dye **IIa**, 45·6 g of the Na salt was obtained (92·1 % purity; 96·3 % yield). The crude product was recrystallized from ethanol acidified with HCl, and then from pure ethanol.

The microanalytical data are given in Table 4

Dyes **Ib** *and* **IIb**[1]

To a solution of 20·7 g (0·05 mol) of dye **Ia** or **IIa** in 250 cm^3 of water adjusted with NaOH to pH 10 at 50 °C, 39 g (0·22 mol) of methyl benzenesulphonate was added dropwise. After 3 h, the mixture was heated to 90 °C and the precipitated dye filtered off. The crude dye was purified by washing with diluted NaOH solution, and then by crystallization as described previously. The purified product was analysed by chromatography and showed no starting material. Microanalytical data are given in Table 4.

Dyes **Ic** *and* **IIc**[11]

A mixture of 20·7 g (0·05 mol) of dye **Ia** or **IIa**, 4 g (0·1 mol) of NaOH, 50 cm^3 of water, 124 g of ethanol, 17·5 g (0·17 mol) of Na_2CO_3 and 12·9 (0·2 mol) of ethyl chloride was heated in an autoclave at 108–112 °C for 20 h. After dilution with twice the volume of water, the precipitated crude

TABLE 4
Microanalytical Data for Dyes I and II

Dye	*Analysis (%)*	
	Found	*Required*
Ia	13 3	13 5
Ib	12 8	13 1
Ic	12 5	12 7
Id	9 8	10 1
Ie	9 6	9 8
If	12 0	12·3
Ig	11 7	11 9
Ih	9 4	9 6
IIa	13 3	13 5
IIb	12 8	13 1
IIc	12 5	12 7
IId	9 9	10 1
IIe	9 6	9 8
IIg	11 7	11 9

dye **Ic** or **IIc** was filtered off Crude dyes were purified as described previously. The purified dye was analysed by chromatography and showed no impurities. Microanalytical data are given in Table 4.

Dyes **Id** *or* **Ie** *and* **IId** *or* **IIe**

To a solution of 20·7 g (0·05 mol) of dye **Ia** or **IIa** in 250 cm^3 of water containing 4 6 g of NaOH (0·115 mol), was added (for dyes **Id** and **Ie**) 10 5 g (0 06 mol) of benzenesulphonyl chloride at 50 °C during 0·5 h. In the cases of dyes **Ie** and **IIe** 11·4 g (0·06 mol) of *p*-toluenesulphonyl chloride at 80 °C was added After confirming the absence of starting material by chromatography, the dispersion was heated to 85 °C and the product salted out at pH 11. Crude dyes were purified as described previously. Microanalytical data are given in Table 4.

Dyes **If**, **Ig** *and* **IIg** *or* **Ih** *and* **IIh**

A mixture of 0 02 mol of dye (**Ib–e**) or (**IIb–e**), 5 6 g (0·1 mol) of KOH and 15 6 g (0·1 mol) of ethyl iodide in 75 g of dimethylformamide was left at 20 °C for 10 days. The solution was then heated at the boil for 2 h, diluted with water after cooling and the product filtered off. Crude dyes were purified as described previously. No starting materials were found by chromatographic analysis of the purified products. No bands characteristic of NH groups were present in the IR spectra Microanalytical data are given in Table 4.

Spectrophotometric studies within the UV–vis range were carried out with a Beckman DK-2A spectrophotometer, using methanolic solutions of dyes in the concentration range 0·004–0 008 g/dm^3 IR analyses were performed with a UR-10 spectrophotometer (Zeiss–Jena) Samples in the form of KBr discs of concentration 0 4–0·7 mg dye/300 mg KBr or as solutions in CCl_4 of concentration 1·2 g/100 cm^3 CCl_4 were used.

The lightfastness measurements on polyamide knitted fabric (Elastil) were made according to Polish Standards which correspond ISO Standards

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