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Disperse Dyes Derived from 4-Phenylazo-1-naphthylamine and 4-Phenylazo-5-hydroxy-1-naphthylamine

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SUMMARY

Application of the Bucherer reaction between 1-naphthol and alkylamines gave a satisfactory synthesis of N-substituted 1-naphthylamines. A method avoiding the use of pressurised reaction vessels, i.e. reaction of 1-naphthol with alkylamines in the presence of zinc chloride and hydrochloric acid, is reported. Coupling of diazotised 6-chloro-2,4-dinitroaniline to the above intermediates affords blue dyes which colour synthetic-polymer fibres in deep shades of generally good fastness to light and sublimation. Similar use as coupling components of 5-hydroxy-1-naphthylamines enables blue dyes to be obtained without the use of trisubstituted anilines as diazo component. Dyes thus derived from 2-chloro-2-nitroaniline absorb at longer wavelength than those from 6-chloro-2,4-dinitroaniline with analogous 1-naphthylamine-based couplers. Similar bathochromic shifts are observed in dyes derived from 2-methoxy-1-naphthylamines as coupling components, but these dyes have poor stability. Relationships between colour and dye structure are reported, and the use of 4-amino-1,8-naphthalimides as diazo components was additionally investigated. These give, with N-substituted 1-naphthylamines as coupling components, deep bluish-violet dyes of good fastness properties.

1 INTRODUCTION

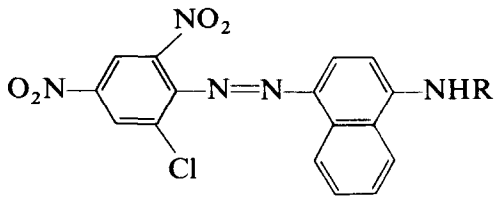
Azo disperse dyes utilising *N*-substituted 1-naphthylamines as coupling components were extensively described during the 1930s as blue dyes for cellulose secondary acetate. One of the simplest of such dyes is that obtained by diazotisation of 6-chloro-2,4-dinitroaniline and coupling to 1-naphthylamine,[1] and similar dyes resulted from the use of *N*-substituted couplers, e.g. *N*-2-hydroxyethyl,[2] *N*-3-methoxy-2-hydroxypropyl,[3] *N*-2,3-dihydroxypropyl,[4-7] *N*-3-chloro-2-hydroxypropyl,[8] and *N*-2-ethoxyethyl.[9] These *N*-substituted 1-naphthylamine coupling components could be replaced by 1-amino-5-naphthol and its *N*-substituted derivatives[10-16] or by ring-closed analogues based either on 1,2,3,4-tetrahydrobenzoquinolines with[17,18] or without[20-22] an additional hydroxy substituent in the naphthalene ring or on 1,2,3,4-tetrahydroquinoline.[23-28] Dyes derived from such ring-closed couplers were introduced to enable the production of blue colourations which were both dischargeable and fast to burnt gas fumes, properties not readily attainable with the more widely used blue disperse dyes based on aminoanthraquinones, e.g. Celliton Discharge Blue 5G (CI Disperse Blue 15, CI 11435); Celliton Discharge Blue 3G (CI Disperse Blue 38, CI 11430); Celliton Blue RRF (CI Disperse Violet 7, CI 11410), and Celliton Discharge Blue BG (CI 11420).

Fastness properties of these dyes, particularly to light, were not high, but later developments in the use of heterocyclic diazo components resulted in much faster dischargeable azo blue dyes derived from 5-nitro-2-amino-thiazoles as diazo component.[29-31] Following the introduction of polyester fibres, blue azo dyes building up to deep navy-blue hues on this substrate were developed and coupling components utilised in such dyes were based mainly on 2-alkoxy-5-acylamino-*N*-substituted anilines, although the use of *N*-substituted 1-naphthylamines also gave industrially viable dyes. One of the earliest patent specifications for the latter was for the deep dyeing blue from 6-chloro-2,4-dinitroaniline and *N*-2-hydroxyethyl-1-naphthylamine[32] (CI Disperse Blue 85) and subsequently a variety of *N*-substituents was described, exemplified by *N*-cyclohexyl and *N*-benzyl,[33] *N*-2,3-bis-carboethoxyethyl,[34] *N*-2-carboethoxyethyl,[35] *N*-2-acetoxyethyl,[36] *N*-3-methoxypropyl,[37] *N*-2,3-bisacetoxypropyl,[38] *N*-2-(2-acetoxyethoxy)ethyl,[39,40] *N*-2,3-epoxypropyl,[41] *N*-aryl,[42] and *N*-2-hydroxy-1-phenylethyl.[43]

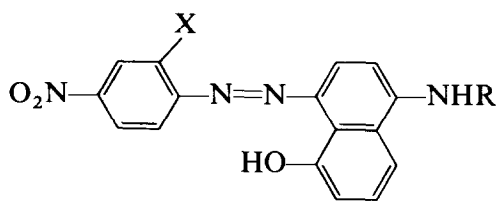
Whilst one of the principal routes to many coupling components of the above type involves the alkylation or arylation of 1-naphthylamine, the use of an alternative synthesis is important in view of the potential toxicological problems associated with naphthylamines. 1-Naphthylamine is a controlled substance and 2-naphthylamine is a carcinogen and may be present in

amounts up to 10% in 1-naphthylamine produced by nitration and reduction of naphthalene. One of the simplest alternative syntheses of substituted 1-naphthylamines avoiding the use of the amine is the Bucherer reaction from 1-naphthol.

We describe here the synthesis of a series of dyes of general formulae **I** and **II** and an evaluation of structural modifications in these dyes on their colour and fastness properties.



I



II (X = H or NO_2)

2 RESULTS AND DISCUSSION

2.1 Synthesis of dyes and intermediates

N-2-Hydroxyethyl-1-naphthylamine, a coupling component used in industrial blue azo disperse dyes (e.g. CI Disperse Blue 85), can be obtained by reaction of 1-naphthylamine with ethylene oxide. Resultant condensates tend to be of a dark brown viscous material containing unreacted 1-naphthylamine and the use of such products as coupling components enables dyes of outstanding build-up to be obtained, probably due to the 'mixture effect' often observed in non-homogeneous disperse dyes. The use of the potentially hazardous 1-naphthylamine can be obviated by use of the Bucherer reaction, involving interaction of 1-naphthol wth alkylamines in the presence of aqueous sulphite or bisulphite. This reaction, initially reported in 1904,[44] has been extensively reviewed,[45,46] and proceeds via ketonic intermediate stages.

In this present study, the reaction of 1-naphthol with various

alkylamines gave almost quantitative conversion to the appropriately *N*-substituted 1-naphthylamines, but reaction failed with aniline and 4-toluidine. This is consistent with previous observations[45] that reaction with arylamines is specific to 2-naphthols; claims have however been made[47–49] for the successful reaction of both 1- and 2-naphthols with anilines substituted in the *para* position by strongly electron-donating substituents, suggesting that the poor reactivity of aniline with 1-naphthol may be in part relatable to its lower basicity.

N-Aryl-1-naphthylamines are readily obtained from 1-naphthylamine and an excess of arylamine in the presence of catalytic amounts of sulphanilic acid, hydrochloric acid, ammonium iodide[50] and 4-toluenesulphonic acid.[51] The latter was used in this present study and gave satisfactory reaction with aniline, 4-toluidine and 4-(2-hydroxyethyl)-aniline. 1-Naphthylamine condensed readily with styrene oxide in the presence of acetic acid,[52] giving *N*-[(2-hydroxy-1-phenyl)ethyl]-1-naphthylamine, which has been described as a useful coupling component in azo disperse dyes.[43] Similar conditions have been used in the condensation of styrene oxide with 1,4-diaminoanthraquinone,[53] and the use of catalytic amounts of boron trifluoride ethyl etherate in the absence of solvents has also been stated[54] to be equally effective. The presence of the phenyl group in the 1-position of the 2-hydroxyethyl residue has been established[43] by NMR data, amending the previously assigned orientation[52] in the 2-position.

N-[2-(2-carboethoxy)ethyl]-1-naphthylamine[35] was prepared as previously described, and 3-hydroxybenzo[*h*]-1,2,3,4-tetrahydroquinoline was prepared from the arylamine and 1-chloro-2,3-epoxypropane using established methods.[55,56]

The possibility of synthesising *N*-alkylamino-1-naphthylamines without the use of pressurised reaction vessels was investigated and it was found that reaction of 1-naphthol with a two-molar excess of 2-aminoethanol in presence of a molar equivalent of zinc chloride gave complete conversion after 9 h at 160°C. Vacuum distillation yielded 86% of *N*-2-hydroxyethyl-1-naphthylamine. Modification to the above to obtain a crude reaction liquor which could satisfactorily be used directly in the coupling process was investigated. In the presence of 10% excess of 2-aminoethanol and 0·025 mol of zinc chloride, reaction proceeded readily to about 75% conversion and then ceased. Addition of a little hydrochloric acid was then found to result in completion of the reaction. On this basis, a satisfactory method (see Section 3.2) was developed. Using this procedure, but omitting the hydrochloric acid, gave only 60% reaction after 36 h. The use of other combinations of metal salts and acids was investigated, but without any significant improvement, although replacing the hydrochloric acid by

similar amounts of orthophosphoric acid or 4-toluenesulphonic acid was equally effective. Replacing the zinc chloride by stannous chloride resulted in a slower and less complete reaction. When using secondary amines such as 2-(2-hydroxyethyl)aminoethanol, no *N*,*N*-bis-substituted derivative could be detected, the major product being the *N*-mono-substituted derivative. The process was found to be equally useful in the synthesis of mono-aminated derivatives of 1,5-dihydroxynaphthalene.

2.2 Colour of dyes

Replacement of the aniline coupling residue in 4-aminoazobenzenes by naphthylamines results in a shift in the visible absorption maxima to longer wavelength. Thus, whilst 4-aminoazobenzene has λ_{max} 385 nm in ethanol,[57] 4-phenylazo-1-naphthylamine absorbs at 438 nm,[58] the shift of 53 nm being of a similar order to that resulting from introduction of a 4′-nitro group into 4-*N*-2-hydroxyethyl-*N*-2-cyanoethylaminoazobenzene.[59] Introduction of a second naphthyl residue gives further bathochromic shifts in absorption maxima. 4-(1-Naphthylazo)-1-naphthylamine, for example, absorbs at 465 nm,[60] a value attained in 4-*N*-2-hydroxyethyl-4-*N*-2-cyanoethylaminoazobenzene by 2′-nitro-4′-methylsulphonyl (λ_{max} 467 nm) or 4′-nitro-2′-carboethoxy (λ_{max} 465 nm) substitution.[61] Orientation of the naphthalene residues influences the colour; thus, whilst 4-(2-naphthylazo)-1-naphthylamine absorbs at the same wavelength as the above isomer,[62] the 2-(2-naphthylazo)- and 2-(1-naphthylazo)-1-naphthylamines absorb at 476 nm[62] and 490 nm[60] respectively.

The bathochromic shifts between analogous 4-aminoazobenzenes and 4-phenylazo-1-naphthylamines increase as the donor–acceptor interaction in the chromogen is enhanced. Thus, in comparing the effect of additional substitution into the diazo component of dyes derived from *N*-2-hydroxyethylaniline and *N*-2-hydroxyethyl-1-naphthylamine couplers (Table 1, λ_{max} data in ethanol, from Section 3 and from ref. 63), it is seen that $\Delta\lambda$ values between the aniline- and naphthylamine-based dyes increase with increasing substitution in the diazo component, in the cases shown by 47 nm, 67 nm, 70 nm and 80 nm. Additionally, the $\Delta\lambda$ values within each series are greater in the naphthylamine dyes than in the aniline analogues: progressing from aniline to 6-chloro-2,4-dinitroaniline, $\Delta\lambda$ values are 85 nm, 21 nm and 47 nm in the naphthylamine dyes and 65 nm, 18 nm and 37 nm in the aniline dyes. The overall colour shift between dyes derived from aniline and 6-chloro-2,4-dinitroanilines is 120 nm with the aniline coupler and 153 nm for the naphthylamine coupler, further demonstrating the influence of the naphthyl residue on colour development.

To attain a similar colour to that of naphthylamine derivatives, the

presence of additional electron-donor substituents is necessary in dyes derived from aniline-based couplers. Thus the dye 4-nitroaniline → *N*-2-hydroxyethyl-1-naphthylamine has absorption maxima (522 nm) in a region between that of 4-nitroaniline → 3-acetamido-*N*,*N*-diethylaniline (511 nm) and 4-nitroaniline → 3-acetylamino-5-methoxy-*N*,*N*-diethylaniline (530 nm), although the colour of the latter dyes has been related[64] more to intramolecular hydrogen-bonding between the azo and acylamino groups rather than to the electron-donating character of the acylamino group.

TABLE 1

Diazo component	λ_{max} (*nm*)	
	Coupling component	
	N-2-hydroxyethyl-aniline	*N-2-hydroxyethyl-1-naphthylamine*
Aniline	398	445
4-Nitroaniline	463	530
2-Chloro-4-nitroaniline	481	551
6-Chloro-2,4-dinitroaniline	518	598

The phenylazo-1-naphthylamine dyes **I** absorb generally in the 600 nm region (Table 2). Presence of the hydroxy group in the alkyl side chain of the coupler generally results in small hypsochromic shifts due to the $-I$ effect of the substituent; compare dye **I.2** with dyes **I.3**, **I.15**, **I.16** and **I.18**. The effect is particularly apparent in the 2-hydroxy-1-phenylethyl derivative **I.19**, presumably due to steric effects of the phenyl ring. This latter dye absorbs in a similar region to the *O*-acylated and related derivatives **I.4**–**I.10**, the hypsochromic shifts in which (10–12 nm) are of a similar order to those resulting from *O*-acylation of 2′-chloro-4′-nitro-4-*N*-2-hydroxy-4-*N*-2-cyanoethylaniline,[65] and in which similar small colour shifts result from differences in the polar nature of the acylating residue; for example, the isocyanate derivatives are bathochromic with respect to the chloroformate derivatives (compare **I.6** and **I.8**; **I.7** and **I.9**).

Introduction of a hydroxy substituent into the 5-position of the coupling residue results in significant bathochromic shifts (Table 3) and allows the synthesis of blue dyes from less extensively substituted diazo components than in dyes **I**. The shifts are typified by comparison of the dyes **III.5**, **II.2**, **I.3** and **II.7** (Table 4). Thus, introduction of a 5-hydroxy group into the coupling residue of **III.5** results in a bathochromic shift of 61 nm, compared with the 47 nm shift arising from additional 6′-nitro substitution into the

TABLE 2
Characterisation and Fastness Data for 1-Naphthylamine Derivatives I

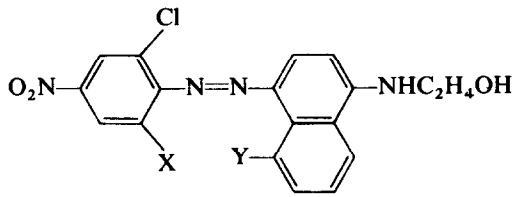
Dye	*R*	*M.p.* (°C)	*Absorption in ethanol*		*Fastness on polyester*			
			λ_{max} (*nm*)	*log e*	*Lightfastness*			*Sublimation* (°C) (*2·5% dye*)
					0·1%	*0·5%*	*2·5%*	
I.1	H	229–230	608	4·52	4	4	4–5	160
I.2	C_2H_5	209–210	600	4·49	5	5	5	160
I.3	C_2H_4OH	189–190	598	4·50	4–5	5	5	170
I.4	$C_2H_4OCOCH_3$	219–220	586	4·39	5	5	5	170
I.5	C_2H_4OCOPh	199–200	587	4·38	5	5	5–6	180
I.6	$C_2H_4O.COOEt$	196–197	585	4·41	5	5	5–6	170
I.7	$C_2H_4O.COOPh$	198–199	586	4·37	5	5	5–6	180
I.8	$C_2H_4O.CONHEt$	199–200	590	4·46	5	5	5	170
I.9	$C_2H_4O.CONHPh$	188–189	588	4·53	5	5–6	5–6	180
I.10	$C_2H_4O.CONHC_{10}H_8$-α	150–152	585	4·31	5	5–6	5–6	190
I.11	$C_2H_4OCH_3$	157–158	599	4·40	5	5	5–6	160
I.12	C_3H_6OH	153–154	601	4·52	4–5	4–5	5	170
I.13	$C_3H_6OCH_3$	163–164	600	4·54	5	5	5–6	160
I.14	$CH_2CHOH.CH_2OH$	175–176	598	4·52	4–5	4–5	5	180
I.15	$C_2H_4OC_2H_4OH$	194–195	598	4·56	4–5	5	5	160
I.16	C_2H_4COOEt	196–197	589	4·44	5	5	5–6	160
I.17	$CH_2CH(OH)CH_3$	190–191	595	4·54	5	5	5	170
I.18	$CH(Ph)CH_2OH$	155–156	585	4·31	5	5–6	5–6	180
I.19	C_6H_{11}	203–204	606	4·39	5	5	5–6	170
I.20	CH_2Ph	187–188	593	4·42	5	5–6	5–6	170
I.21	Ph	212–213	595	4·20	5	5	5–6	180
I.22	$C_6H_4CH_3$-*p*	228–229	598	4·36	5	5–6	5–6	180
I.23	$C_6H_4C_2H_4OH$-*p*	175–176	599	4·48	5	5–6	5–6	180

TABLE 3
Characterisation and Fastness Data for 5-Hydroxy-1-naphthylamine Derivatives **II**

Dye	*X*	*R*	*M.p.* (°C)	*Absorption in ethanol*		*Fastness on polyester*			
				λ_{max} (*nm*)	*log e*	*Lightfastness*			*Sublimation* (°C) (*2·5% dye*)
						0·1%	*0·5%*	*2·5%*	
II.1	H	H	196–197	618	4·38	4	4	4	180
II.2	H	C_2H_4OH	192–193	612	4·48	4–5	5	5	190
II.3	H	$C_2H_4OCH_3$	158–159	610	4·51	5	5	5	180
II.4	H	$C_3H_6OCH_3$	162–163	619	4·50	5	5	5	190
II.5	H	$C_2H_4OC_2H_4OH$	173–174	614	4·46	5	5	5	180
II.6	NO_2	H	>360	629	4·36	[a]			
II.7	NO_2	C_2H_4OH	176–177	631	4·44	4–5	4–5	5	180
II.8	NO_2	$C_2H_4OC_2H_4OH$	164–165	630	4·46	4–5	4–5	5	190

[a] Dye degraded (see Section 2.3).

TABLE 4



	X	*Y*	λ_{max} (*nm*)
III.5	H	H	551
II.2	H	OH	612
I.3	NO_2	H	598
II.7	NO_2	OH	631

diazo component. Similar shifts are apparent in related dyes with other *N*-substituents in the coupler residue, e.g. *N*-$C_2H_4OCH_3$, dyes **III.6**, **II.3** and **I.11**; *N*-$C_3H_6OCH_3$, dyes **III.8**, **II.4** and **I.13**. Such large colour shifts seem unlikely to result from the additional electron delocalisation from the 5-hydroxy group since the extended conjugation is lateral, rather than longitudinal. The bathochromic shifts are more probably relatable to H-bonding between the 5-hydroxy and azo residues; compare the 2-acylamino-4-aminoazobenzenes referred to above. In hydroxy-substituted dyes in which the hydroxy group cannot undergo H-bonding with the azo group, colour shifts are much less, for example **II.1**, 2-chloro-4-nitroaniline → 1-amino-5-naphthol, λ_{max} 618 nm; **III.9**, 2-chloro-4-nitroaniline → 1-amino-7-naphthol, λ_{max} 569 nm. The 7-hydroxy group does however influence the colour, dye **III.9** absorbing at a wavelength 18 nm longer than the hydroxyl free analogue, **III.5** (λ_{max} 551 nm).

The effect of introduction of the methoxy group *ortho* to the amino group of the coupling component is also one of marked bathochromicity. Thus, dye **III.16**, 2-chloro-4-nitroaniline → 2-methoxy-1-naphthylamine absorbs at 587 nm, a wavelength 36 nm longer than **III.5**, 2-chloro-4-nitroaniline → *N*-2-hydroxyethyl-1-naphthylamine (551 nm), and a similar shift (34 nm) is observed between analogous dyes derived from 6-chloro-2,4-dinitroaniline as diazo component (**I.1**, λ_{max} 608 nm; **III.17**, λ_{max} 642 nm). This similarity of $\Delta\lambda$ value between the pairs of dyes derived from 2-chloro-4-nitroaniline and 6-chloro-2,4-dinitroaniline as diazo component contrasts with the comparative effect of 5-hydroxy substitution in the coupling component. Thus, whilst $\Delta\lambda$ between 2-chloro-4-nitroaniline → *N*-2-hydroxyethyl-1-naphthylamine (**III.5**, λ_{max} 551 nm) and the 5-hydroxy analogue (**II.2**, λ_{max} 612 nm) is 61 nm, the corresponding $\Delta\lambda$ for dyes derived

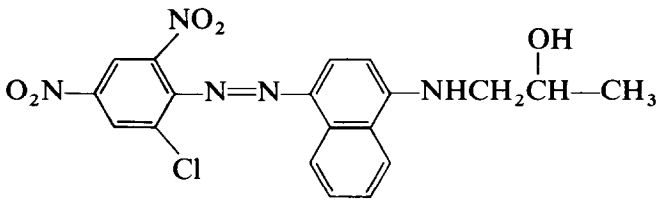
from 6-chloro-2,4-dinitroaniline is only 33 nm (**I.3**, λ_{max} 598 nm; **II.7**, λ_{max} 631 nm).

This would indicate that the effect of the 2-methoxy group on the colour of the dyes is not solely resultant from additional electron delocalisation through the conjugated system, and in this orientation it is not conjugated with the azo group. The effect of such 2-methoxy substitution cannot thus be rationalised purely in terms of valence bond theory, a conclusion also reached[64] in a comparison of 4-*N*,*N*-diethylaminoazobenzenes and their 3-methoxy derivatives, although the decreased absorbance from possible steric crowding noted in the aminoazobenzene derivatives is not so consistently apparent in the naphthylamine dyes.

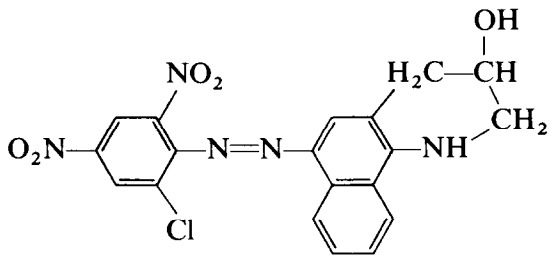
The 2-methoxy substituted dyes **III.16** and **III.17** were found to be unstable under certain purification processes in the dye synthesis. Thus, 2-chloro-4-nitroaniline → 2-methoxy-1-naphthylamine (**III.16**) contained a yellow impurity of higher R_f value than the main violet zone, but the latter changed rapidly (5–10 nm) to yellow when the developed silica gel tlc sheet was exposed to light or left in the dark. Attempted purification by column chromatography on silica gel gave a good separation of the two zones but the violet zone turned yellow on standing for 1–2 h or on immediate attempted extraction from the silica with boiling ethanol or acetone. The initial yellow contaminant, and the yellow degradation product of the violet-coloured **III.16**, gave superimposable IR spectra, had identical m.p. (no depression in admixture) and λ_{max} (461 nm in ethanol). Mass spectrometry indicated a molecular weight of one mass unit higher than that of **III.16** purified by recrystallisation from chlorobenzene. Fragmentation patterns confirmed the additional mass unit to be in the coupling component fragment and NMR data were consistent with the absence of an amino group but the presence of a hydroxy group.

The 6-chloro-2,4-dinitroaniline derivative **III.17** behaved similarly, but degradation was not as facile. Relevant NMR spectral data on this dye hydrolysis reaction will be reported separately.

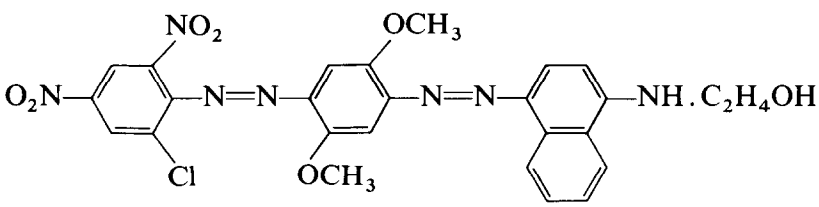
Bathochromic shifts were also apparent in the ring-closed 3-hydroxybenzo[*h*]-1,2,3,4-tetrahydroquinoline derivative **III.13**. The ring closure in **III.13** gives an additional donor residue *ortho* to the amino group, the resultant increased electron mobility in the dye leading to a bathochromic shift of 34 nm relative to **I.18**, i.e. of a similar order to that resulting from the presence of the donor methoxy substituent *ortho* to the amino group. The bathochromic shifts are lower than those observed in cyclisation of 4-aminoazobenzene derivatives,[66] but the additional electron delocalisation in **III.13** is similar to that resulting from the presence of a further phenylazo residue in the dye system, the disazo dye **III.15** having the same absorption maxima.



I.18, λ_{max} 595 mm



III.13, λ_{max} 629 nm



III.15, λ_{max} 629 nm

2.3 Colouration and fastness properties

The dyes **I.1**–**I.23** (Table 2) all gave excellent colouration of polyester; at 0·5% depth of shade, the colourations corresponded approximately to the ISO 1/1 standard depth. Build-up of the dyes was generally very good, giving deep reddish-blue (acylated derivatives **I.5**–**I.11**) to navy-blue colourations at 2·5% depth of shade. The 5-hydroxy substituted dye **II.1**–**II.5** derived from 2-chloro-4-nitroaniline as diazo component afforded intense dark blue dyeings with a greenish tint, 2·5% depth of shade dyeings tending to a blue-black hue. The greenness of hue was more apparent in the 6-chloro-2,4-dinitroaniline derivatives, dyes **II.7** and **II.8** building up to very deep colourations. Fastness to light and sublimation of both **I** and **II** on polyester was of a generally good order, dyes without aliphatic hydroxy groups in the *N*-substituent tending to have the better lightfastness.

The primary amino derivative **II.6** was unsatisfactory on polyester, giving, as did the corresponding dyes from 6-bromo-, 6-fluoro- and 6-iodo-2,4-dinitroaniline,[67] dull greyish-blue dyeings, presumably due to dye degradation under high-temperature application conditions. Bright blue

dyeings were given however by these dyes on cellulose secondary acetate, although lightfastness of the dyeings was poor (2, 2, 2–3 respectively).

The 2-methoxy derivatives **III.16** and **III.17** degraded during polyester colouration, giving yellowish-green and green dyeings respectively; extraction of the dyeings and tlc evaluation of the extract indicated the formation of a yellow degradation product of similar R_f value to the yellow component formed during dye purification. On cellulose secondary acetate, bright violet and blue dyeings respectively were obtained, of good build-up, but poor lightfastness (2).

Selected dyes (**I.3**, **I.4**, **I.13**, **I.14**, **I.19** and **I.21**; **II.2**, **II.4**) were applied to cellulose secondary acetate and all gave good colouration of this substrate, building up to deep hues similar to those observed on polyester; lightfastness was generally much lower (2–3) than on polyester. The dyeings in several instances were of brighter hue than corresponding dyeings on polyester, particularly those of **II.2** and **II.4**, indicating that the dye degradation noted for the 2-methoxy-1-naphthylamine-derived dyes on polyester was to some extent pertinent to other dyes also. The pH sensitivity and degradation during dyeing of dyes of type **I** and **II** has been noted in many patent specifications and careful pH control during colouration is essential to obviate dye degradation. Investigations into the relationships between dye structure and stability of **I** and **II** will be reported later.

The dyes **III.10**–**III.12** derived from 4-amino-1,8-naphthalimides as diazo component were deep violet in colour, absorption maxima being in the region of 100 nm more bathochromic relative to similar dyes from *N*-2-cyanoethyl-*N*-2-hydroxyethylaniline as coupling component.[68] Thus, dye **III.10** absorbs (λ_{max} 574 nm) at a wavelength 98 mm longer than the dye 4-amino-*N*-3-methoxypropyl-1,8-naphthalimide → *N*-2-cyanoethyl-*N*-2-hydroxyethylaniline. This $\Delta\lambda$ value is considerably greater than that observed between the dyes from aniline and *N*-2-cyanoethyl-*N*-2-hydroxyethylaniline (λ_{max} 397 nm)[59] or *N*-2-hydroxyethyl-1-naphthylamine (**III.3**, λ_{max} 445 nm), i.e. $\Delta\lambda$ 48 nm, but is the same as that between the corresponding dyes from more electronegatively substituted anilines, e.g. 6-chloro-2,4-dinitroaniline, which have λ_{max} 500 nm[69] and 598 nm (**I.3**) respectively. The advantageous use of 4-amino-1,8-naphthalimides as diazo component in assisting colour development in azo disperse dyes is thus confirmed in these dyes from typical 'blue' coupling components, as was observed[68] when using simpler aniline-based 'red' couplers. With *N*-2-hydroxyethyl-1-naphthylamine, *N*-3-methoxypropyl-1,8-naphthalimide gives a dye (**III.10**) of absorption maximum (λ_{max} 574 nm) midway between that of the dyes derived from 2-chloro-4-nitroaniline (**III.5**, λ_{max} 551 nm) and 6-chloro-2,4-dinitroaniline (**I.3**, λ_{max} 598 nm) as diazo component.

Colouration of cellulose secondary acetate by **III.10–III.12** was very poor, but the dyes built up to deep bluish-purple hues on polyester. The dyeings had generally good fastness to both light (5, 5–6, 5–6) and sublimation (initial mark off at 2·5% depth, 190°C).

3 EXPERIMENTAL

3.1 *N*-2-Hydroxyethyl-1-naphthylamine: typical synthesis by Bucherer reaction

A mixture of 1-naphthol (35 g, 0·25 mol), 40% w/v sodium bisulphite solution (30 ml) and 2-aminoethanol (30·5 g, 0·5 mol) made up to 200 ml with water was heated at 135–140°C for 18 h in a rotating autoclave. The reaction mixture was cooled, acidified with hydrochloric acid and boiled until evolution of sulphur dioxide had ceased. The solution was filtered (Norit) and the filtrate basified with 20% aq. sodium hydroxide to pH 8 and left to stand overnight, during which time the slightly resinous product solidified. Vacuum distillation afforded a pale grey solid (41·5 g, 91·4%) which crystallised from 20% aq. ethanol in off-white platelets, m.p. 54–55°C, of *N*-2-hydroxyethyl-1-naphthylamine.

By replacing the 2-aminoethanol with other amines, a series of *N*-substituted-1-naphthylamines was obtained. These were isolated either as the free base as above or as the hydrochloride salt, by dissolving the crude dried reaction product in toluene, filtering (Norit) and passing dry HCl gas through the solution. Thus prepared were *N*-3-hydroxypropyl- (89·4%, b.p. 180°C at 1 mm); *N*-2-hydroxypropyl- (84·7%, m.p. 77–78°C); *N*-2-methoxyethyl- (81·3%, m.p. 73–74°C); *N*-3-methoxypropyl- (86·8%, hydrochloride m.p. 142–144°C); *N*-cyclohexyl- (77·8%, m.p. 53–54°C); *N*-benzyl- (80·4%, m.p. 75–76°C); *N*-2-(2-hydroxyethoxy)ethyl- (90·7%, hydrochloride m.p. 128–130°C); and *N*-2,3-dihydroxypropylamino-1-naphthylamine (86·5%, m.p. 112–113°C).

3.2 Alternative synthesis of *N*-substituted-1-naphthylamines

A mixture of 1-naphthol (28·8 g, 0·2 mol), 2-aminoethanol (13·4 g, 0·22 mol) and anhydrous zinc chloride (1·36 g, 0·01 mol) was heated slowly, with stirring, until a melt was obtained (appox. 60°C). Conc. hydrochloric acid (0·5 ml) was added slowly and the temperature raised to 150–155°C and maintained for 30 h under a nitrogen atmosphere; a test sample showed all the 1-naphthol to have reacted.

The liquor on cooling gave a honey-coloured viscous mass (the

darkening of which on prolonged air exposure was minimised by addition of 0·01 g sodium borohydride). The reaction mass was almost totally soluble in 5% aq. hydrochloric acid and contained *N*-2-hydroxyethyl-1-naphthylamine and inorganic residues. It was used directly in azo coupling reactions to give **I.2**, but isolation of the pure coupler was readily effected as the hydrochloride (85% isolation).

In a similar manner were obtained *N*-3-hydroxypropyl- (82%, as hydrochloride); *N*-2,3-dihydroxypropyl- (97%, liquor used without isolation); and *N*-3-methoxypropyl-1-naphthylamine (86%, as hydrochloride).

Increasing the molar ratios of reactants in the above to 1-naphthol (0·1 mol), 2-aminoethanol (0·2 mol) and zinc chloride (0·1 mol) resulted in reaction being complete in 9 h.

3.3 *N*-Substituted 5-hydroxy-1-naphthylamines

A mixture of 1,5-dihydroxynaphthalene (16 g, 0·1 mol), water (85 ml) and sodium metabisulphite (4·5 g) was refluxed for 24 h with 2-aminoethanol (9·15 g, 0·15 mol). The mixture was cooled, basified to pH 14 with 20% aq. sodium hydroxide and filtered to give, as insoluble material, 1,5-bis-*N*-2-hydroxyethylaminonaphthalene (6·2 g), m.p. 182–183°C (ethanol). The filtrate was treated with charcoal, filtered, cooled in ice, acidified to pH 1 with conc. hydrochloric acid and stirred for 40 min prior to filtering the residue of unreacted 1,5-dihydroxynaphthalene (1·4 g). The filtrate was again charcoaled, cooled in ice and the pH adjusted to 7 with ice-cold 15% aq. sodium hydroxide. After stirring for 4 h, the cream-coloured *N*-2-hydroxyethyl-5-hydroxy-1-naphthylamine (12·7 g, 62·4%) was collected, m.p. 138–140°C (10% aq. ethanol).

In a similar manner were prepared *N*-3-methoxypropyl-5-hydroxy-1-naphthylamine (64·3%, m.p. 82–83°C) and *N*-2-(2-hydroxyethoxy) ethylamino-5-hydroxy-1-naphthylamine (56·7%, oil used without further purification).

3.4 *N*-Aryl-1-naphthylamines

A mixture of 1-naphthylamine (14·3 g), *p*-toluidine (22 g) and toluene-4-sulphonic acid (2 g) was refluxed for 24 h in nitrobenzene (50 ml). Solvent was removed by steam distillation, the residue filtered, digested in 2N-hydrochloric acid (200 ml) (Norit), filtered and the filtrate neutralised to give *N*-4-toluidino-1-naphthylamine (12·8 g, 54·9%), off-white prisms, m.p. 77–79°C (10% aq. ethanol).

Similarly were prepared *N*-phenyl-1-naphthylamine (74·6%, off-white platelets, m.p. 61–62°C from 20% aq. ethanol) and *N*-4-(2-hydroxyethyl-) phenyl-1-naphthylamine (47·8%, cream plates, m.p. 99–100°C from

ethanol) ($C_{18}H_{17}NO$ requires: C, 82·1; H, 6·5; N, 5·3. Found: C, 82·0; H, 6·2; N, 5·1%).

3.5 *N*-(2-Hydroxy-1-phenylethyl)-1-naphthylamine (cf. ref. 52)

A mixture of 1-naphthylamine (4·3 g, 0·03 mol) and styrene oxide (6·6 g, 0·055 mol) was stirred for 8 h at 90°C in xylene (25 ml) and glacial acetic acid (0·5 ml). Xylene was distilled off, glacial acetic acid (15 ml) added and the mixture warmed to 50°C. The resultant solution was run slowly into boiling water (100 ml) and the liquor boiled to remove styrene oxide. The liquor on cooling deposited a grey solid (7·6 g, 86%) which crystallised from 50% aq. ethanol in off-white needles of *N*-(2-hydroxy-1-phenylethyl)-1-naphthylamine, m.p. 64–66°C.

3.6 *N*-(2-Carboethoxy)ethyl-1-naphthylamine

This was prepared from 1-naphthylamine and ethyl acrylate following the procedure described in Example 2 of ref. 35. The reaction liquor was added to water, stirred at 50–60°C for 2 h and the product extracted with toluene. The resultant dark brown viscous oil (78·6% yield) was used without further purification.

3.7 2-Methoxy-1-naphthylamine

A solution of 2-methoxynaphthalene (10·5 g) in methylene chloride (25 ml) was nitrated at 0°C by dropwise addition over 3 h of conc. nitric acid (3·5 ml). The liquor was then stirred for 1 h at 0°C and then at room temperature overnight. Excess acid was removed by aqueous extraction, solvent distilled off *in vacuo* and the residue (12·5 g, 92·6%) recrystallised from toluene in yellow platelets of 2-methoxy-1-nitronaphthalene, m.p. 124–126°C.

A mixture of 2-methoxy-1-nitronaphthalene (20 g), water (20 ml), conc. hydrochloric acid (0·5 ml) and iron powder (30 g) was stirred at 90°C for 5 h, with addition of 2 × 0·5 ml conc. hydrochloric acid. The cooled liquor was basified with 40% aq. sodium hydroxide and extracted with toluene; the organic layer was separated, dried and treated with dry hydrogen chloride gas to precipitate the amine hydrochloride (18·1 g, 87·7%). This, dissolved in dilute hydrochloric acid and neutralised, gave 2-methoxy-1-naphthylamine, off-white needles, m.p. 52–54°C (ethanol) ($C_{11}H_{11}NO$ requires: C, 76·3; H, 6·4; N, 8·1. Found: C, 76·0; H, 6·1; N, 7·9%).

3.8 3-Hydroxybenz[*h*]-1,2,3,4-tetrahydroquinoline

A mixture of 1-naphthylamine (10 g) and 1-chloro-2,3-epoxypropane (30 g) in 1-pentanol (35 ml) was stirred while heating over 1 h to 125–130°C; the

mixture was stirred at 125–130°C for a further 10 h, cooled, filtered and the residue crystallised from ethanol in off-white prisms (mass spectrum, p^+ at *m/e* 199).

3.9 Synthesis of azo dyes

Finely ground 6-chloro-2,4-dinitroaniline (2·17 g) was added over 30 min at 5–10°C to a mixture of glacial acetic acid (8 ml) and nitrosylsulphuric acid prepared from sodium nitrite (0·72 g) and conc. sulphuric acid (8 ml). Diazotisation was continued at 10–15°C for a further 3 h and the diazo liquor run slowly into a solution of the appropriate coupling component (0·01 mol) in a mixture of 10% aq. hydrochloric acid (30 ml) and glacial acetic acid (15 ml) internally cooled with ice. After stirring at 0–5°C for 90 min, a solution of sodium acetate (5 g) in water (50 ml) was added, the liquor stirred a further 30 min and filtered. The resultant dyes were purified by recrystallisation from ethanol (Norit), or, where appropriate, by column chromatography on Kieselgel 60 (Merck) using toluene:ethyl acetate (95:5) as eluant.

In this manner were prepared the dyes **I.1–I.3** and **I.11–I.23** (Table 1) and **II.6–II.8** (Table 2). The acylated and related dyes **I.4–I.10** were prepared as described[65] for similar derivatives of 2′-chloro-4′-nitro-*N*-2-hydroxyethyl-*N*-2-cyanoethylaniline.

Dyes **II.1–II.5**, together with the dyes listed in Table 5, were prepared by diazotisation and coupling methods previously described for mono-,[59] di-,[61] and tri-substituted anilines[69] and for 4-amino-1,8-naphthalimides[68] as diazo components.

Dyes derived from the use of 2-methoxy-1-naphthylamine as coupling component could not readily be purified by the above chromatographic method. Thus, dye **III.16**, obtained in 87% yield as a violet solid from the azo coupling reaction, showed on tlc a major purple component and a higher R_f yellow component; the purple zone rapidly turned yellow on exposure to light (the change occurring more slowly in the dark). Column chromatography on silica gel separated the components, but the purple zone turned yellow on standing (6–8 h) or on immediate attempted extraction with ethanol. The yellow degradation product was found to be identical with the yellow component [m.p. 265–266°C, λ_{max} in ethanol, 461 nm (log *e* 4·27)] initially present in the crude dye. Recrystallisation of the crude product from toluene gave dark purple needles of **III.16**, free from the yellow impurity. The crystals after several months of exposure to daylight showed no further degradation but, when readsorbed onto silica, rapidly degraded to the yellow compound. This was shown (see Section 2.2) to correspond to 4-(2′-chloro-4′-nitroazophenyl)-2-methoxy-1-naphthol. Similar degradation was observed in the isolation of **III.17.**

TABLE 5
Miscellaneous Dyes

	Diazo component	*Coupling component*	*M.p.* (°C)	λ_{max} (*nm*) (*in ethanol*)	*log e*
III.1	2-Chloro-4-nitroaniline	*N*-2-Hydroxyethylaniline	156–157	481	4·51
III.2	6-Chloro-2,4-dinitroaniline	*N*-2-Hydroxyethylaniline	172–173	518	4·42
III.3	Aniline	*N*-2-Hydroxyethyl-1-naphthylamine	187–188	445	4·29
III.4	4-Nitroaniline	*N*-2-Hydroxyethyl-1-naphthylamine	126–128	525	4·36
III.5	2-Chloro-4-nitroaniline	*N*-2-Hydroxyethyl-1-naphthylamine	210–211	551	4·40
III.6	2-Chloro-4-nitroaniline	*N*-2-Methoxyethyl-1-naphthylamine	198–199	552	4·37
III.7	Aniline	*N*-3-Hydroxypropyl-1-naphthylamine	141–142	451	4·38
III.8	2-Chloro-4-nitroaniline	*N*-3-Methoxypropyl-1-naphthylamine	168–169	556	4·52
III.9	2-Chloro-4-nitroaniline	1-Amino-7-naphthol	200–201	569	4·30
III.10	*N*-3-Methoxypropyl-4-amino-1,8-naphthalimide	*N*-2-Hydroxyethyl-1-naphthylamine	228–229	574	4·53
III.11	*N*-(3-*n*-Butoxypropyl)-4-amino-1,8-naphthalimide	*N*-2-Hydroxyethyl-1-naphthylamine	184–185	571	4·55
III.12	*N*-(3-*n*-Butoxypropyl)-4-amino-1,8-naphthalimide	*N*-3-Methoxypropyl-1-naphthylamine	176–177	575	4·55
III.13	6-Chloro-2,4-dinitroaniline	3-Hydroxybenzo[*h*]-1,2,3,4-tetrahydroquinoline	188–189	629	4·24
III.14	6-Chloro-2,4-dinitroaniline	2,5-Dimethoxyaniline	246–247	566	4·28
III.15	**III.14**	*N*-2-Hydroxyethyl-1-naphthylamine	176–177	629	4·51
III.16	2-Chloro-4-nitroaniline	2-Methoxy-1-naphthylamine	234–235	587	4·49
III.17	6-Chloro-2,4-dinitroaniline	2-Methoxy-1-naphthylamine	245–246	642	4·18

3.10. Dye characterisation and fastness tests

The dyes were characterised by satisfactory elemental analysis, tlc and mass spectrometry. Electronic spectra were recorded on a Unicam SP800 spectrophotometer from solution in absolute ethanol, dye solutions being kept in the dark for 72 h prior to recording of spectra. Dyes **I** and **II** were applied to synthetic-polymer fibres and the light and sublimation fastness of the dyeings assessed as previously described.[65]

4. CONCLUSIONS

N-Substituted 1-naphthylamines, readily obtainable by conventional Bucherer reaction or by use of zinc chloride in presence of hydrochloric acid at atmospheric pressure, afford deep dyeing blue to navy-blue dyes when coupled with 6-chloro-2,4-dinitroaniline. Fastness to light and sublimation of the dyes were of generally good order. The use of *N*-substituted-1-amino-5-naphthol as coupling components facilitates the synthesis of blue dyes without the use of tri-substituted anilines as diazo component, but whilst the use of 2-methoxy-1-naphthylamine also results in large bathochromic shifts, resultant dyes are prone to hydrolysis, with replacement of the amino group by hydroxy. Satisfactory deep bluish-violet dyes are obtained when 4-amino-1,8-naphthalimides are used as diazo components.

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