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1-Morpholino- and 1,8-Dimorpholino-naphthalene: Coupling Components for New Azo Disperse Dyes†

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SUMMARY

Azo dyes have been prepared by diazotisation of aniline, 2-chloroaniline, 4-nitroaniline, 2-chloro-4-nitroaniline, 2,4-dinitroaniline, 5-methoxy-2-nitroaniline, 6-bromo-2,4-dinitroaniline and 6-cyano-2,4-dinitroaniline, and coupling with 1-morpholino- and 1,8-dimorpholino-naphthalene. The dyes obtained from the latter coupling component show hypsochromic shifts in their absorption maxima compared with analogues having only one morpholino group in the coupling residue. The dyes have been evaluated as disperse dyes on polyester fibre.

1. INTRODUCTION

Our investigations into the synthesis of disperse dyes having good all-round fastness properties indicated the value of *N*-phenyl- and *N*-naphthylmorpholines as coupling components. Thus, dyes derived from *N*-phenylmorpholine are stated to give dyeings of very good fastness properties.[1,2] Compared with the dialkylaminobenzene-based coupling components, the use of naphthylamine coupling components in the synthesis of azo disperse dyes is less common and the navy-blue dyeings obtained from the dye **6**, derived from the use of β-hydroxyethylaminonaphthalene as a coupling component,[3] have low lightfastness. With the object of overcoming the limitations in the use of such coupling

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components we investigated the possibility of using 1,4-diheterocyclohexylnaphthylamines as coupling components. Generally, dyes derived from coupling components of type **3**, i.e. containing saturated cyclic ring systems, show bathochromic shifts in their absorption maxima compared with analogous dyes derived from the *N*-dialkyl- and *N*,*O*-alkyl-aminobenzenes **1** and **2**.[4]

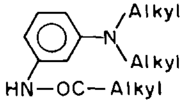
The use of 1,8-bis(dialkylamino)naphthalenes as a 'proton sponge' has been described.[5] The methods[6–8] reported for the synthesis of 1,4-diheterocyclohexylnaphthalenes, such as 1-morpholinonaphthalene **4**, are not very satisfactory and we report here an improved synthesis of 1-morpholino- and 1,8-dimorpholino-naphthalene (**5**) starting from 1- and 1,8-diaminonaphthalenes.[9] Recent publications[5,10] report the unusually high basicity $[\mathrm{p}K_a(\mathrm{BH}^+) = 7{\cdot}51 \pm 0{\cdot}01]$ of 1,8-dimorpholinonaphthalene.

We have previously synthesised dyes from *N*-sulphonyl(aminophenyl)-morpholine and *N*-methylene(aminophenyl)morpholine as diazo components.[11] The presence of *N*-sulphonyl- and *N*-methylene-phenylmorpholine groups in the diazo components did not enhance the tinctorial strength of dyes. The outstanding basicity displayed by 1,8-dimorpholinonaphthalene prompted us to study the dyes derived from 1-morpholino- and 1,8-dimorpholino-naphthalene as new coupling components.

2. RESULTS AND DISCUSSION

Earlier workers reported the synthesis of 1-morpholinonaphthalene from 1-naphthylamine and bis(2-chloroethyl) ether in 30–35% yields. We have now obtained 1-morpholinonaphthalene (**4**) in much higher yield (70%) by reacting 1-naphthylamine with a tenfold molar excess of bis(2-chloroethyl) ether in the presence of 10% NaOH. 1,8-Dimorpholinonaphthalene was prepared by using 1,8-diaminonaphthalene and bis(2-chloroethyl) ether in the ratio 1:10 as reported in our earlier Indian patent specifications.[9] Both compounds were purified by chromatography, followed by crystallisation from methanol.

The ^{1}H-NMR spectrum of **4** in $AsCl_3$ showed two multiplets (A_2B_2 pattern) at 3·08 and 4·09 for the N—CH_2 and O—CH_2 groups in morpholine. The seven aromatic protons appeared centred at 7·65 as a



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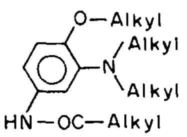

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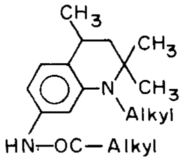

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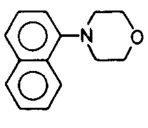

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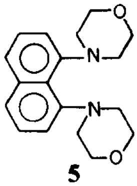

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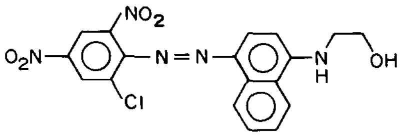

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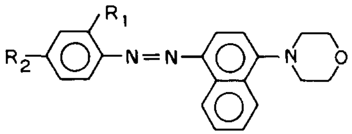

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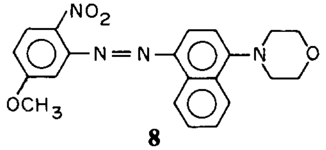
a $R_1 = R_2 = H$; b $R_1 = Cl, R_2 = H$; c $R_1 = H, R_2 = NO_2$

d $R_1 = Cl, R_2 = NO_2$; e $R_1 = R_2 = NO_2$



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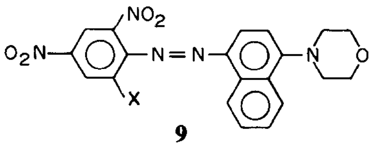

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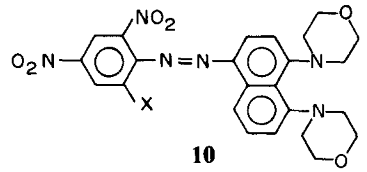

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a $X = Br$

b $X = CN$

multiplet. The ^{1}H-NMR spectra of morpholine and *N*-phenylmorpholine in CCl_4 gave N—CH_2 and O—CH_2 protons at 2·73 and 3·55 for morpholine and at 2·97 and 3·72 for *N*-phenylmorpholine, respectively.[12] The slight downfield shift in *N*-naphthylmorpholine (**4**) may be attributed to the highly polar acidic arsenic trichloride solvent. The N—CH_2 and O—CH_2 groups in 1,8-dimorpholinonaphthalene appeared at 3·1 and 4·1, respectively. The mass spectrum of compounds **4** and **5** showed the molecular-ion base peaks at *m/e* 213 and *m/e* 298, respectively. The ^{1}H-NMR spectra, mass spectra and elemental analysis of these compounds were thus consistent with the structures **4** and **5**. The structure of 1,8-dimorpholinonaphthalene has recently been studied by X-ray diffraction.[13]

Ten azo dyes were prepared by coupling diazotised aniline, 2-chloroaniline, 4-nitroaniline, 2-chloro-4-nitroaniline, 2,4-dinitroaniline, 5-methoxy-2-nitroaniline, 6-bromo-2,4-dinitroaniline and 6-cyano-2,4-dinitroaniline with **4** and **5** as coupling components. Yellow to orange dyes (**7a–e**) were obtained by coupling diazotised aniline, 2-chloroaniline, 4-nitroaniline, 2-chloro-4-nitroaniline and 2,4-dinitroaniline with **4**. With 5-methoxy-2-nitroaniline as diazo component, the reddish-orange dye **8**

TABLE 1
Electronic Spectra and Fastness Properties on Polyester of Dyes **7**–**10**

Dye	*Electronic spectra in DMF*		*Dyeings on polyester*		
	λ_{max} (*nm*)	ε	*Light fastness*	*Sublimation fastness*	*Hue*
7a	430	17 580	1–2	3	Pale yellow
7b	440	15 190	2	5	Yellow
7c	480	18 120	2–3	5	Orange
7d	486	16 120	2–3	5	Dark orange
8	478	18 760	2–3	5	Reddish-orange
9a	560	23 160	3–4	5	Bluish-violet
9b	630	22 480	3–4	5	Bluish-violet
10a	530	21 480	3	5	Reddish-violet
10b	610	20 890	3	5	Reddish-violet

Light and sublimation fastness are on 1–8 and 1–5 scales, respectively (8 and 5 represent maximum values).

was obtained. Blue dyes were obtained by coupling diazo components containing electron-attracting groups, such as 6-bromo-2,4-dinitroaniline and 6-cyano-2,4-dinitroaniline, with 1-morpholino- and 1,8-dimorpholinonaphthalene, and dyes **9** and **10** gave brilliant reddish-violet hues on polyester. Absorption characteristics and dyeing properties for dyes **7**–**10** on polyester fibre are summarised in Table 1. The dyeings were generally satisfactory with the exception of dye **7a**, which had poor tinctorial power and gave light yellow dyeings of poor light and sublimation fastness.

The use of 1,8-dimorpholinonaphthalene as coupling component results in dyes showing hypsochromic shifts in absorption maxima (Table 1) compared with analogous dyes from 1-morpholinonaphthalene. Thus, the dyes **10a** and **10b** absorb at 530 and 610 nm, whereas dyes **9a** and **9b** absorb at 560 and 630 nm, respectively. This may be attributed to steric effects in the 1,8-dimorpholino dyes.

3. EXPERIMENTAL

All melting points are uncorrected and are in °C. Visible spectra in DMF solution were recorded on a UV-vis 44069 spectrophotometer. Infrared spectra were recorded on a Perkin–Elmer 221 spectrophotometer (ν_{max} in cm^{-1}). PMR spectra were recorded on a Varian T-60 spectrophotometer and the chemical shifts are cited on a δ ppm scale using TMS as internal reference. The mass spectra were obtained on a CEC-21-110-B mass spectrometer at minimum source temperature.

3.1. 1-Morpholinonaphthalene (4)

Method A

To a mixture of morpholine (8·7 g, 0·1 mol) and sodium amide (4·72 g, 0·12 mol) in dry benzene (200 ml) externally cooled to -50°C was added 1-bromonaphthalene (20·7 g, 0·1 mol) portionwise with stirring over 2 h. The reaction mixture was stirred at -50 to -60° for a further 2 h and then poured on to ice and extracted with benzene (three × 200 ml). The benzene extract was dried over anhydrous sodium sulphate, filtered and solvent removed to give the crude product. This was chromatographed on silica gel using benzene–ethyl acetate (3:2) as eluent to give 1-morpholinonaphthalene which was recrystallised from methanol in fine colourless needles (1·93 g, 9%), m.p. 82° (Lit.[8] 81–83°).

Method B

A mixture of 1-aminonaphthalene (14·3 g, 0·1 mol), bis(2-chloroethyl) ether (142 g, 1 mol) and sodium hydroxide (50 ml, 10% solution) was stirred under reflux for 8 h. Excess bis(2-chloroethyl) ether was removed under vacuum and the amine isolated by extraction with benzene (300 ml). The crude product was recrystallised from methanol to yield white needles (15·1 g, 70%), m.p. 82°. (Found: C, 79·0; H, 7·1; N, 6·6. $C_{14}H_{15}NO$ requires C, 78·8; H, 7·1; N, 6·6%.) IR (Nujol): 1530, 1500, 1460, 1300, 1270, 1230, 1120, 1076, 1040, 1020, 940. PMR ($CDCl_3$): 3·08 (4H, $CH_2\alpha$ to N), 4·09 (4H, $CH_2\beta$ to N), 7·65 (7H, m). MS: *m/e* 213 ($M^{+\cdot}$, 100%), 182 (33%), 169 (27%), 155 (43%), 141 (67%), 127 (78%).

3.2. 1,8-Dimorpholinonaphthalene (5)

1,8-Diaminonaphthalene was obtained by reduction of 1,8-dinitronaphthalene with iron and acetic acid.[14] A mixture of 1,8-diaminonaphthalene (15·8 g, 0·1 mol), bis(2-chloroethyl) ether (142 g, 1 mol) and sodium hydroxide (50 ml, 10% solution) was stirred under reflux for 60 h. After reaction, excess bis(2-chloroethyl) ether (80 g) was removed under vacuum. The residue was extracted into chloroform and the extract washed initially with 1% sulphuric acid, then with water, and dried over anhydrous sodium sulphate. After removal of solvent, the product was crystallised from methanol to give colourless needles of **5** (2·95 g, 10%), m.p. 198°. (Found: C, 72·5; H, 7·5; N, 9·4. $C_{18}H_{22}N_2O_2$ requires C, 72·5; H, 7·4; N, 9·4%.) IR (Nujol): 1590, 1500, 1460, 1390, 1350, 1300, 1280, 1230, 1120, 1070, 1060, 1000. PMR ($CDCl_3$): 3·1 (8H, $CH_2\alpha$ to N), 4·1 (8H, $CH_2\beta$ to N), 7·5 (6H, m). MS: *m/e* 298 ($M^{+\cdot}$, 100%), 267 (25%), 239 (20%), 224 (18%), 212 (20%), 182 (60%), 154 (14%), 127 (14%).

3.3. 4-(Phenylazo)-1-morpholinonaphthalene (7a)

A solution of aniline (0·93 g, 0·01 mol) in hydrochloric acid (12·5 ml, 2M-HCl) was cooled to 0°C and diazotised by addition of sodium nitrite (10 ml, 1M solution). The diazo liquor coupled with a solution of 1-morpholinonaphthalene (2·13 g, 0·01 mol) in acetic acid (1·5 ml) at 0–5°C. After stirring the mixture overnight at 0–10°C, the separated dye was washed with water and recrystallised from chloroform (yield 82%), m.p. 100°. (Found: C, 75·8; H, 6·0; N, 13·1. $C_{20}H_{19}N_3O$ requires C, 75·7; H, 6·0; N, 13·1%).

The synthesis of other dyes was similarly effected.

3.4. 4-(2′-Chlorophenyl)azo-1-morpholinonaphthalene (7b)

Orange needles from chloroform (93·3%), m.p. 136°. (Found: C, 68·4; H, 5·1; N, 11·9. $C_{20}H_{18}ClN_3O$ requires C, 68·4; H, 5·1; N, 12·0%.) MS: *m/e* 351 ($M^{+\cdot}$).

3.5. 4-(4′-Nitrophenyl)azo-1-morpholinonaphthalene (7c)

Orange plates from chloroform (93%), m.p. 126°. (Found: C, 66·4; H, 5·0; N, 15·3. $C_{20}H_{18}N_4O_3$ requires C, 66·3; H, 5·0; N, 15·5%.) MS: *m/e* 363 ($M^{+\cdot}$).

3.6. 4-(2′-Chloro-4′-nitrophenyl)azo-1-morpholinonaphthalene (7d)

Reddish-orange needles from chloroform (90·5%), m.p. 166°. (Found: C, 60·6; H, 4·3; N, 14·1. $C_{20}H_{17}ClN_4O_3$ requires C, 60·6; H, 4·3; N, 14·0%.)

3.7. 4-(2′,4′-Dinitrophenyl)azo-1-morpholinonaphthalene (7e)

Reddish-orange needles from chloroform (93·4%), m.p. 178°. (Found: C, 58·9; H, 4·2; N, 17·2. $C_{20}H_{17}N_5O_5$ requires C, 59·0; H, 4·2; N, 17·2%.)

3.8. 4-(5′-Nitro-2′-methoxyphenyl)-1-morpholinonaphthalene (8)

Orange plates from chloroform (92·4%), m.p. 142°. (Found: C, 64·3; H, 5·3; N, 14·4. $C_{21}H_{20}N_4O_4$ requires C, 64·3; H, 5·4; N, 14·3%.)

3.9. 4-(6′-Bromo-2′,4′-dinitrophenyl)azo-1-morpholinonaphthalene (9a)

6-Bromo-2,4-dinitroaniline (2·62 g, 0·01 mol) was diazotised with nitrosylsulphuric acid (prepared from sodium nitrite (0·7 g) and conc. sulphuric acid (8·0 g)). Coupling with **4** gave **9a**, bluish-violet needles from chloroform

(94%), m.p. 143°. (Found: C, 49·8; H, 3·3; N, 14·3. $C_{20}H_{16}BrN_3O_5$ requires C, 49·7; H, 3·3; N, 14·4%.)

3.10. 4-(6′-Cyano-2′-dinitrophenyl)azo-1-morpholinonaphthalene (9b)

Following the procedure above, **9b** was obtained as violet plates from chloroform (88%), m.p. 171°. (Found: C, 58·2; H, 3·7; N, 19·3. $C_{21}H_{16}N_6O_5$ requires C, 58·3; H, 3·7; N, 19·4%.)

3.11. 4-(6′-Bromo-2′,4′-dinitrophenyl)azo-1,8-dimorpholinonaphthalene (10a)

A solution of 6-bromo-2,4-dinitroaniline (2·62 g, 0·01 mol) was diazotised with nitrosylsulphuric acid and coupled with 1,8-dimorpholinonaphthalene (2·48 g, 0·01 mol) to give a 75% yield of dye **10a**. It was crystallised from acetonitrile in bluish-violet plates (63·4%), m.p. 360°. (Found: C, 49·9; H, 4·2; N, 14·7. $C_{24}H_{23}BrN_6O_6$ requires C, 50·0, H, 4·0; N, 14·7%.)

3.12. 4-(6′-Cyano-2′,4′-dinitrophenyl)azo-1,8-dimorpholinonaphthalene (10b)

Bluish-violet prisms from acetone (73·5%), m.p. 360°. (Found: C, 58·1; H, 4·5; N, 18·9. $C_{25}H_{23}N_7O_6$ requires C, 58·0; H, 4·0; N, 18·9%.)

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