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Structure–stability Relationships in some Azo Disperse Dyes

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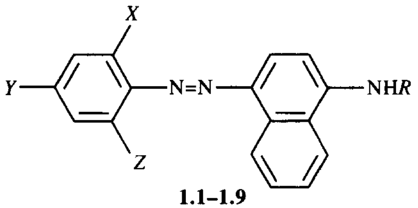
ABSTRACT

The synthesis of a series of dyes derived from N-*substituted 1-naphthylamines as coupling components is reported. The effect of substituents in the diazo and coupling residues on the colour and the dye stability at pH 4, 7 and 9 is discussed. The main degradation product of one member of the series was identified. Copyright © 1996 Elsevier Science Ltd*

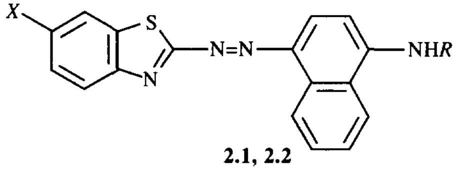
INTRODUCTION

The synthesis and fastness properties of azo disperse dyes derived from *N*-substituted 1-naphthylamines as coupling components has been reported,[1,2] as have substituent effects on the colour and fastness properties of these and similar dyes.[1–8] Some data relevant to the influence of various factors (pH, temperature, water, dye structure) on the photodegradation of some 4-aminoazobenzene disperse dyes have also been reported.[9,10] There are, however, no published data on the pH sensitivity and degradation during dyeing of azo dyes derived from *N*-substituted 1-naphthylamine as coupling component, although pH control during dyeing is necessary to minimize dye degradation, as is reported in many patents.

In this work the effect of pH and dye structure on the stability of a series of dyes of type **1** and **2** is reported. The degradation product of one member of the series was identified and a possible degradation mechanism is proposed.



1.1–1.9



2.1, 2.2

EXPERIMENTAL

Materials

N-2-hydroxyethyl-1-naphthylamine, *N*-3-methoxypropyl-1-naphthylamine (YCL Ltd) and the substituted amilines (YCL Ltd, Aldrich Chemicals, BDH) were technical samples and were used without further purification.

Methods and apparatus

Diazotization and coupling reactions were carried out by procedures already reported.[1,24]

2′,6′-Dicyano-4-nitro-phenylazo-*N*-2-hydroxyethyl-1-naphthylamine **1.5** was prepared from the corresponding dibromo compound **1.4** by heating with cuprous cyanide in N,N′-dimethyl formamide.[4]

Acetylation of 2′,4′-dinitro-6′-chloro-phenylazo-*N*-2-hydroxy ethyl-1-naphthylamine **1.6** was carried out in pyridine with acetic anhydride; benzoylation of **1.6** was carried out with benzoyl choride in tetrahydrofuran in the presence of triethylamine.[11]

Dyes were purified by column chromatography on Silica Gel 60 (Merck) using toluene containing up to 10% ethyl acetate as eluant. Dyes were extracted from the appropriate zones with ethanol and were allowed to crystallize from the extract liquor.

UV–visible spectra were recorded in a PYE UNICAM SP 800 spectrophotometer using ethanol/water 9/1 as reference.

Stability tests were carried out in a Roaches Engineering Ltd dyeing machine at pH 4, 7 and 9 using dye dispersions of 0.004, 0.02 and 0.1% dye concentration in buffer solutions of pH 4, 7 and 9, which were heated at 125°C for 1 h. After neutralization and evaporation of the liquor (at ambient temperature), the absorbance of residue was measured in ethanol/water 9/1.

The main degradation product of 2′,4′-dinitro-6′-chloro-phenylazo-*N*-2-hydroxyethyl-1-naphthylamine **1.6** was identified by its spectral data and elemental analysis. The IR (Nujol), NMR (TMS, d_6-acetone) and mass spectra were recorded on Perkin Elmer 157, JEOL JNX-GX 270 HT and Hitachi Perkin Elmer RMU-GL spectrophotometers, respectively.

RESULTS AND DISCUSSION

The percentage of dye degraded at the three pH values mentioned above, and the λ_{max} of the corresponding dyes, are given in Table 1. From the data in Table 1, the following conclusions can be drawn.

Most dyes were degraded completely at pH 9 under the dyeing conditions used, whereas at pH 7 the percentage degradation was the lowest. Different results were obtained by irradiation of 4-aminoazobenzene dyes at different pH values.[10] In that case, increased stability in alkaline media and a considerably decreased stability in acidic media were observed. The percentage dye degraded also reduced with increasing dye concentration. Similar results are reported[9] for the photochemical degradation of azo disperse dyes. Introduction of electron acceptor substituents in the diazo component results in an increased dye degradation at the three pH values studied and in bathochromic shifts of λ_{max} of the corresponding dyes due to electron delocalization from the hydroxyethylamino group of the coupler. Thus dye **1.1**, with no substituents in the diazo component, has the minimum degradation, with λ_{max} 440 nm. Introduction of the electron acceptor 4-nitro substituent into the diazo component results in a significant bathochromic shift (λ_{max} 530 nm), and this compound is completely degraded at pH 9 and pH 4, and at low concentrations (Table 1).

By introducing a 2′-chloro substituent as a second electron acceptor group, a further bathochromic shift and a higher percentage dye degradation is observed. In contrast, the presence of two bulky substituents *ortho* to the azo group (dye **1.4**) has a smaller effect on the colour and stability of the compound, which has λ_{max} 492 nm and a stability comparable to that of the unsubstituted dye **1.1**, in agreement with similar data in the literature.[6]

The presence of a second nitro group in the 2′-position in the diazo component causes a significant bathochromic shift of the corresponding dye **1.6** compared with dye **1.3** which has one nitro group (Table 1). Dye **1.6** is completely degraded at the three pH values and concentrations studied. *O*-Acetylation or benzoylation of dye **1.6** is advantageous with respect to the stability of the resulting dyes (**1.7** and **1.8**, respectively), with a slight alteration in λ_{max} of the dyes compared with **1.6** (594, 590 and 596 nm, respectively).

The highest bathochromic shift was observed for dye **1.5** (Table 1) with a 4′-NO_2 group and two cyano substituents in positions *ortho* to the azo linkage. The stability of this dye was very low; it was degraded completely at pH 7 and pH 9, but at pH 4 had a medium to low stability, expressed as percentage dye degraded (Table 1).

Although the nitro group has a stronger electron accepting character than the cyano group, the bathochromic shift of dye **1.6** is less than that of **1.5**.

TABLE 1

λ_{max} (ethanol/water 9/1) and stability of dyes **1.1–1.9** and **2.1–2.2** at pH 4, 7 and 9

Dye	*X*	*Y*	*Z*	*R*	λ_{max} *(nm)*	*Percentage of dye degraded*		
						pH 4	*pH* 7	*pH* 9
1.1	H	H	H	C_2H_4OH	444	58.75	42.50	42.50[a]
						37.50	25.00	30.00[b]
						33.75	23.40	25.00[c]
1.2	H	NO_2	H	C_2H_4OH	530	d^{470}	50.00	d^{470}
						42.00	32.00	d^{470}
						25.00	22.00	42.00
1.3	Cl	NO_2	H	C_2H_4OH	551	d^{625}	57.00	d^{625}
						d^{675}	45.00	d^{540}
						15.00	22.50	61.25
1.4	Br	NO_2	Br	C_2H_4OH	492	68.75	40.00	55.00
						43.75	38.75	35.00
						37.50	32.50	35.00
1.5	CN	NO_2	CN	C_2H_4OH	615	d^{632}	70.00	$d^{420,630}$
						d^{632}	56.00	$d^{420,630}$
						d^{632}	55.00	$d^{420,630}$
1.6	NO_2	NO_2	Cl	C_2H_4OH	596	d^{612}	d^{628}	d^{628}
						d^{612}	d^{628}	d^{628}
						d^{612}	d^{628}	d^{628}
1.7	NO_2	NO_2	Cl	$C_2H_4OCOCH_3$	594	42.50	20.00	d^{628}
						20.00	17.50	d^{628}
						15.00	13.90	d^{628}
1.8	NO_2	NO_2	Cl	$C_2H_4OCOC_6H_5$	590	50.00	37.00	d^{628}
						30.00	22.00	d^{628}
						26.80	95.00	d^{628}
1.9	NO_2	NO_2	Cl	$C_3H_6OCH_3$	604	30.00	32.50	d^{628}
						21.50	15.00	d^{628}
						7.50	12.50	d^{628}
2.1	H				555	87.50	85.00	90.00
						85.00	81.00	81.00
						80.00	82.50	81.00
2.2	NO_2				597	d^{582}	d^{582}	d^{582}
						55.00	d^{582}	d^{582}
						48.10	58.00	d^{582}

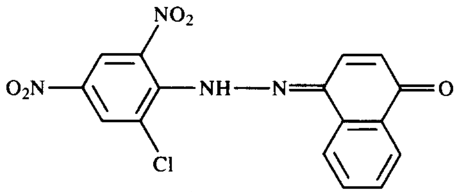
[a, b, c] Amounts of dye in 0.004, 0.02 and 0.1 g per 100 ml buffer solution, respectively.
d indicates degradation product at particular λ_{max}.

This may be attributed to some steric inhibition of charge delocalization in the 2′-nitro derivative, which does not exist in the case of the planar 2′-cyano group.[6,7]

Replacement of the *N*-2-hydroxyethylamino group in the naphthalene coupler by the *N*-3-methoxypropylamino group, which has a stronger electron donor character, results in dye **1.9**, with a slight bathochromic shift and higher stability (Table 1).

The use of benzothiazole based diazo components is not advantageous compared with aniline derivatives. Thus, the unsubstituted dye **2.1**, which had a significant bathochromic shift compared with the unsubstituted dye **1.1**, has a very low stability at the three pH values studied, whereas introduction of a nitro substituent in the benzothiazole ring produces a dye with a deep blue colour which is completely degraded at low concentrations at the three pH values studied.

Finally, the structure of the main degradation product of dye **1.6** was identified by established spectral data, namely IR, NMR, MS and elemental analysis (see Table 2). This product was assigned the following structure.



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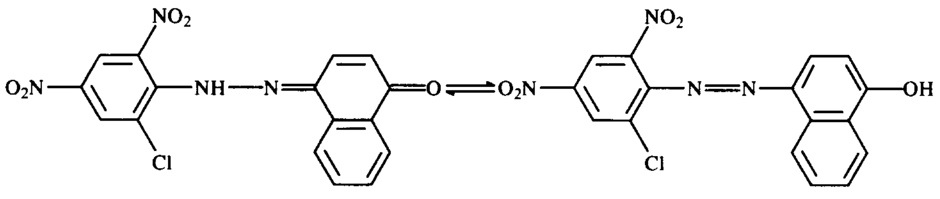
The results in Table 2 indicate that the degradation could proceed via the following steps: dealkylation of the amino group of the coupler, followed by oxidation of the amino group, and nucleophilic substitution of the resultant moiety by a hydroxy group in the strongly alkaline medium. An equilibrium exists between the two forms **3a** and **3b**, characteristic for these compounds, which is confirmed by the colour change from yellow in non-polar solvents (toluene, chlorobenzene) to greenish blue in polar solvents (acetone, ethanol).



3a **3b**

TABLE 2 Melting Point, Spectral Data and Elemental Analysis of Compound 3

Melting point (°C)	Visible spectrum (λ_{max}, solvent)	IR (cm^{-1}, Nujol)	NMR (δ, d_6-acetone)	MS (*m/e*, %)	Elemental analysis		
					N(%)	C(%)	H(%)
214-216	440nm, toluene 628nm, ethanol	3250 (NH) 1640 (CO) 1590 (C=C)	6.94(d), 8.17(d) 8.2(d), 8.35(d) 7.74(t), 7.63(t) 8.63(s), 8.69(s)	372(53)$M^{+\cdot}$ 217(9) 143(100) 115(39)	Calculated: 15.05	51.61	2.42
					Found: 14.98	51.57	2.60

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REFERENCES

1. Peters, A. T. & Sener, M. E., *Dyes and Pigments*, **8** (1987) 99.
2. Peters, A. T., *J. Soc. Dyers Col.*, **104** (1988) 344.
3. Hallas, G., *J. Soc. Dyers Col.*, **95** (1979) 285.
4. Peters, A. T., *J. Soc. Dyers Col.*, **101** (1985) 361.
5. Dawson, J. F., *J. Soc. Dyers Col.*, **107** (1991) 395.
6. Mehta, H. P. & Peters, A. T., *Dyes and Pigments*, **3** (1982) 71.
7. Mehta, H. P. & Peters, A. T., *Dyes and Pigments*, **8** (1987) 99.
8. Peters, A. T., *Text. Res. J.*, **44** (1974) 719.
9. Bridgeman, I. & Peters, A. T., *Text. Res. J.*, **44** (1974) 639.
10. Bridgeman, I. & Peters, A. T., *Text. Res. J.*, **44** (1974) 645.
11. Al-Kassim, S. & Peters, A. T., *J. Soc. Dyers Col.*, **89** (1973) 359.