ELSEVIER

Dyes and Pigments 50 (2001) 93–97

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Synthesis, characterisation and application of disperse dyes derived from *N*-2-hydroxyethyl-1-naphthylamine

K.L. Georgiadou, E.G. Tsatsaroni*

Department of Chemistry, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

Received 30 June 2000; received in revised form 18 July 2000; accepted 3 March 2001

Abstract

The synthesis and characterisation of a series of disperse dyes obtained by diazotisation of heterocyclic arylamines and coupling of these compounds with *N*-2-hydroxyethyl-1-naphthylamine are reported. The dyes were applied to cellulose acetate and their dyeing and fastness properties were assessed and summarised. The absorption spectra of the dyes are discussed, with regard to structure and substitution of the heterocyclic diazo component. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Benzothiazole; Benzoisothiazole; Thiophene; *N*-2-Hydroxyethyl-1-naphthylamine; Cellulose acetate; Light fastness; Wash fastness; Rate of dyeing

1. Introduction

In recent years, efforts have been made to replace certain anthraquinone dyes with technically equivalent azo dyes, for both environmental and economic reasons [1]. In this regard, azo dyes based on heterocyclic amines have been developed, and the resultant dyes have higher tinctorial strength and give brighter dyeings than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, isothiazole, thiophene compounds afford very electronegative diazo components and, consequently, provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds [2–4]. Moreover, it is well known that ring systems of this type are useful for providing blue and green azo dyes.

Azo disperse dyes containing *N*-substituted-1-naphthylamines as coupling components have also been described as having blue colors in various publications [5–7]. As a continuation of our previous work in this area [7], we report herein the synthesis of the dyes **I**–**IV** having *N*-2-hydroxy ethyl-1-naphthylamine as the coupling component (Fig. 1).

The colour and fastness properties of dyes **I**–**IV** were determined, along with the effects of their structure on dye uptake.

2. Experimental

2.1. Materials and apparatus

2-Amino-6-methoxybenzothiazole, 2-amino-6-nitrobenzothiazole, 3-amino-5-nitro[2,1]benzisothiazole, 2-amino-3,5-dinitrothiophene were obtained from Zhejiang Company and were used without

---

* Corresponding author. Tel.: +30-31-997855; fax: +30-31-997769.

E-mail address: tsatsaro@chem.auth.gr (E.G. Tsatsaroni).

PII: S0143-7208(01)00034-1

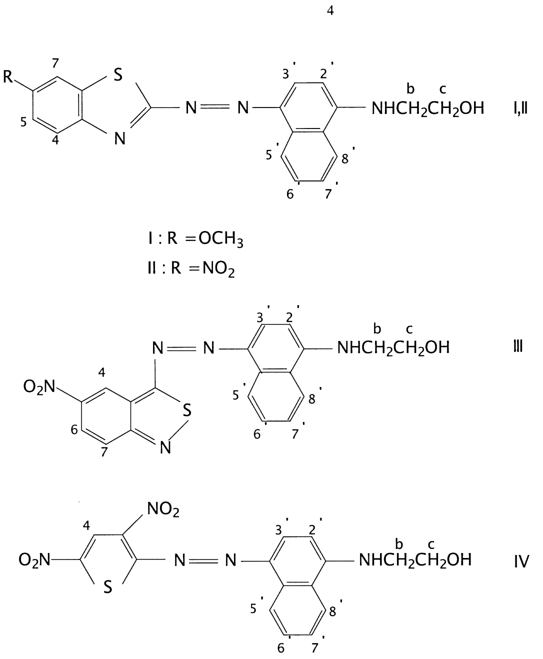

Fig. 1. Structures of dyes **I–IV**.

further purification. Melting points were determined with a Kofler hot stage apparatus and are uncorrected. UV–visible spectra were recorded with a Shimadzu UV 2101 spectrometer, using methanol as the solvent. ^{1}H-NMR data were obtained with a Bruker 300 AM spectrometer, using $CDCl_3/d_6$-DMSO as the solvent and TMS as the internal standard. Mass spectra were obtained with a VG-TS 250 spectrometer, and elemental analyses were obtained by using a Perkin-Elmer 2400-II Element Analyzer.

2.2. Synthesis of N-2-hydroxyethyl-1-naphthylamine

A mixture of 1-naphthol (144 g, 1 mol), sodium bisulphite (44 g, 0.4 mol) and 2-aminoethanol (92.5 g, 1.5 mol) in water (100 ml) was stirred at 115–125 °C and 1.2–2 bar for 22 h. The reaction mixture was cooled to 60–70 °C, basified with sodium hydroxide (80 g, 50%) until the naphthol component disappeared from the TLC, and then stirred with carbon activated (2.6 g) for 5–10 min at 70 °C. The mixture was filtered, the filtrate was allowed to stand for 20 min, and the sodium salt of unreacted 1-naphthol was separated by filtration. The filtrate containing *N*-2-hydroxyethyl-1-naphthylamine was used in dye syntheses without further purification.

*2.3. Synthesis of dyes **I–IV***

The four dyes were prepared by diazotisation of the heterocyclic amines followed by coupling with *N*-2-hydroxyethyl-1-naphthylamine.

2.3.1. Diazotisation

6-Methoxy-2-aminobenzothiazole (20.4 g, 0.1 mol) was added over 1 h at 5 °C to sulphuric acid (45 ml, 98%) with stirring. Nitrosylsulphuric acid (34.2 g. 0.11 mol, 40% in sulphuric acid) was added over 30 min at −10 °C, and diazotisation was continued for 1 h at −5 °C to give diazo liquor 1.

2-Amino-6-nitrobenzothiazole (19.9 g, 0.1 mol) was dissolved in phosphoric acid (242 ml, 279.2 g, 85%) by heating at 55 °C and stirring overnight. The solution was cooled and stirred at −8 °C as sodium nitrite (7.4 g, 0.1 mol) was added. Diazotization was continued for 3 h to give diazo liquor 2.

3-Amino-5-nitro[2,1]benzoisothiazole (19.9 g, 0.1 mol) was added with stirring to a mixture of phosphoric acid (41 ml, 85%), glacial acetic acid (10 ml) and sulphuric acid (70 ml, 98%). Nitrosylsulphuric acid (34.2 g, 0.1085 mol, 40% in sulphuric acid) was added over 30 min and diazotisation was continued for 3 h at 5 °C to give diazo liquor 3.

2-Amino-3,5-dinitrothiophene (19.5 g, 0.1 mol) was added over 45 min at 5–7 °C to a mixture of acetic acid (300 ml), propionic acid (50 ml), and nitrosylsulphuric acid (33.3 g, 0.105 mol, 40% in sulphuric acid). Diazotisation was continued for 2 h and urea (6 g, 0.1 mol) was added to the reaction mixture to destroy excess nitrosylsulphuric acid and to afford diazo liquor 4.

2.3.2. Coupling

Diazo liquors 1–4 were added slowly into a solution containing *N*-2-hydroxyethyl-1-naphthylamine (0.11 mol, 20.6 g) in a mixture of sulphuric acid (diazo liquor 1), hydrochloric acid (diazo liquors 2 and 4), or acetic acid–phosphoric acid (7:1, diazo liqour 3), sulfamic acid (1 g, 0.01 mol), and an ionic (0.1 g) or/and non-ionic (0.6 g) surfactant, using internal cooling. After stirring at 0 °C for 60 min, sodium hydroxide (600–1650 ml, 14%) was added to give pH 3, and the reaction mixture was stirred overnight and filtered.

2.3.2.1. Dye ***I***. The crude yield was 87.5% and the dye was purified by recrystallisation from ethanol, to give a purple solid having m.p. 201–203 °C. λ_{max} (nm, CH_3OH): 561; ε_{max} (CH_3OH): 54,650; ^{1}H-NMR (δ, $CDCl_3/d_6$-DMSO): 3.26 (broad *s*, 1H, *OH*), 3.74 (*t*, 2H, *J* = 5.9 Hz, *H-b*), 3.89 (*s*, 3H, CH_3O), 4.41 (*t*, 2H, *J* = 5.9 Hz, *H-c*), 6.94 (*d*, 1H, *J* = 9.1 Hz, *H-2′*), 7.09 (*dd*, 1H, *J* = 8.8 and 2.2 Hz, *H-5*), 7.29 (*d*, 1H, *J* = 2.2 Hz, *H-7*) 7.50–7.76 (*m*, 3H, *H-6′-8′*), 7.86 (*d*, 1H, *J* = 9.1 Hz, *H-3′*), 7.96 (*d*, 1H, *J* = 8.8 Hz, *H-4*), 8.08 (*d*, 1H, *J* = 9.1 Hz, *H-5′*); MS (*m*/*e*, %): 201.8 (8.3), 197.8 (12.2), 179.8 (83.3), 164.8 (81.4), 139.3 (25.1), 44.0 (100); Anal. (calc. found). C: 63.47, 62.80; H: 4.79, 4.72; N: 14.81, 14.24.

2.3.2.2. Dye ***II***. The crude yield was 99% and the dye was purified by recrystallisation from ethanol to give a blue solid having m.p. 212–214 °C. λ_{max} (nm, CH_3OH) 597; ε_{max} (CH_3OH): 43,860; ^{1}H-NMR (δ, $CDCl_3/d_6$-DMSO): 3.27 (broad *s*, 1H, *OH)*, 3.90 (*t*, 2H, *J* = 5.3 Hz, *H-b*), 4.50 (*t*, 2H, *J* = 5.3 Hz, *H-c*), 6.91 (*d*, 1H, *J* = 8.9 Hz, *H-2′*), 7.56–7.72 (*m*, 3H, *H-6′–8′*), 7.97 (*d*, 1H, *J* = 8.9 Hz, *H-3′*), 8.27 (*d*, 1H, *J* = 8.1 Hz, *H-5′*), 8.39 (*d*, 1H, *J* = 8.7 Hz, *H*-4), 8.53 (*dd*, 1H, *J* = 8.7 and 2.2 Hz, *H-5*), 8.73 (*d*, 1H, *J* = 2.2 Hz, *H-7*); MS (*m*/*e*, %): 197.0 (31.7), 195.0 (87.8), 79.0 (14.0), 60.1 (21.1), 45.1 (43.9), 28.1 (100); Anal. (calc. found). C: 58.00, 57.26; H: 3.84, 3.64; N: 17.80, 17.12.

2.3.2.3. Dye ***III***. The crude yield was 97.9% and the dye was purified by column chromatography (silica gel, 10–90% ethyl acetate in toluene) to give a blue solid having m.p. 236–237 °C. λ_{max} (nm, CH_3OH): 652; ε_{max} (CH_3OH): 27,700; ^{1}H-NMR (δ, $CDCl_3/d_6$-DMSO): 3.27 (broad *s*, 1H, *OH*), 3.82 (*t*, 2H, *J* = 5.1 Hz, *H-b*), 4.49 (*t*, 2H, *J* = 5.1 Hz, *H-c*), 6.82 (*d*, 1H, *J* = 9.1 Hz, *H-2′*), 7.53–7.71 (*m*, 3H, *H-6′–8′*), 8.09 (*d*, 1H, *J* = 8.5 Hz, *H-5′*), 8.16 (*d*, 1H, *J* = 9.1 Hz, *H*-3′), 8.44 (*d*, 1H, *J* = 8.8, Hz, *H-7*), 8.88 (*dd*, 1H, *J* = 8.8 and 2.2 Hz, *H-6*), 9.16 (*d*, 1H, *J* = 2.2 Hz, *H-4*); MS (*m*/*e*, %): 393.8 (22.8, M^+), 186.1 (45.3), 90.1 (100), 60.1 (8.7), 45.0 (15.7); Anal. (calc. found). C: 58.00, 57.55; H: 3.84, 3.86; N: 17.80, 17.37.

2.3.2.4. Dye ***IV***. The crude yield was 78.2% and the dye was purified by recrystallisation from ethanol to give a greenish-blue solid having m.p. 195–197 °C. λ_{max} (nm, CH_3OH): 684; ε_{max} (CH_3OH): 22,935.8; ^{1}H-NMR (δ, $CDCl_3/d_6$-DMSO): 3.27 (broad *s*, 1H, *OH*), 3.81 (*t*, 2H, *J* = 5.1 Hz, *H-b*), 4.48 (*t*, 2H, *J* = 5.1 Hz, *H-c*), 6.85 (*d*, 1H, *J* = 9.1 Hz, *H-2′*), 7.52–7.71 (*m*, 3H, *H-6′–8′*), 8.10 (*d*, 1H, *J* = 8.5 Hz, *H-5′*), 8.15 (*d*, 1H, *J* = 9.1 Hz, *H-3′*), 9.36 (*s*, 1H, *H-4*); MS (*m*/*e*, %): 355.0 (7.0), 280.8 (24.2), 206.9 (85.8), 199.0 (7.4), 143.0 (100.0), 115.0 (57.7); Anal. (calc. found). C: 49.6, 50.08; H: 3.38, 3.71; N: 18.08, 17.32.

2.4. Preparation of dye dispersions

In a typical dyeing experiment, the crude dye (25 g), a dispersing agent (TAMOL NN 9104, NNOK/Vultamol, sodium salt of polycondensated naphthalenesulphonic acid, MW > 7000, 25 g), a non-ionic surfactant (0.1 g) and water (250 ml) were added to a grinding mill (Sussmeyer) and the mixture was stirred for 20 min. Glass ottawa type balls were added and the subsequent grinding of the dye was monitored until the particle size reached 0.1–1 μ. The pH was adjusted to 7–8 with phosphoric acid (85%). A Practical Analyser, Microtrac X100P was used for measuring the particle size distribution.

2.5. Dyeings

Cellulose acetate fabric (2.9 g) was pretreated with an AATCC Standard anionic detergent WOB (1 g/l) at 60 °C for 20 min prior to being used for the dyeings. Dyeings were carried out in a Rotadyer apparatus (John Jeffreys Ltd, Rochdale, Banbury) using a liquor ratio of 20:1, pH 5.4 (sodium acetate–acetic acid buffer solution), and the volume of the dye dispersion required to obtain shade depths of 0.25, 0.5, 1.0% (owf). The dyebath temperature was raised to 85 °C over 1 h and maintained at that level for 1 h. The dyebath was cooled to 40 °C over 20 min and the dyed fabrics were washed with an AATCC Std anionic detergent (1 g/l, 200 ml) at 50 °C for 10 min. The fabric was rinsed well with water and dried at 100 °C.

2.6. Determination of dye uptake

Samples of the dyed fabrics were extracted with methanol (250 ml) in a Soxhlet apparatus and the absorbance of each extract was recorded at the λ_{max} of the dye. Using the appropriate calibration curve the dye concentration of each extract (mg dye/1000 ml) was obtained. Dye uptake was established from this value.

2.7. Rate of dyeing (i) and temperature range (ii) tests [8]

These experiments were carried out at a target shade depth of 0.5% (owf). In the first set of experiments, dyeings were conducted at 85 °C for 5, 10, 20, 80 and 160 min. The resultant data were analysed by comparing results of dyeings after 5, 10, 20 and 80 min with the results after 160 min [8a]. In the second set of experiments, dyeings were carried out at 50, 60, 70, 80 and 90 °C for 1 h. Result from the dyeing at 90 °C was compared with those from dyeings at the lower temperatures [8b]. Pretreatment and posttreatment of fabric samples were carried out as described in Section 2.5.

2.8. Wash and light fastness tests

These studies were carried out according to standard methods (BS 1006: 1992 C02 [9a] and B02 [9b]). A Suntest Hanau (Heraeus) apparatus equipped with a Xenon lamp (black panel temperature 50 ± 2 °C) was used for the light fastness assessment. Colour change was estimated against the blue wool standard scale 1–8 with the aid of a Verivide Colour Cabinet (Leslie Hubble) equipped with a D_{65} lamp.

Table 1
Electronic spectra data of dyes **I**–**IV**

Dye	**I**	**II**	**III**	**IV**
λ_{max} (nm)	561	597	652	684
Log ε	4.73	4.64	4.44	4.36
Colour	Violet	Dark blue	Deep blue	Greenish-blue

3. Results and discussion

3.1. Colour of dyes

The UV–visible absorption data for dyes **I**–**IV** are given in Table 1. As expected [3,4], heteroaryl-based azo dyes **I**–**IV** were characterised by significant bathochromic shifts compared to their phenyl analogues. For example, dye **II**, which contains a nitro-benzothiazole moiety as the acceptor ring, had $\lambda_{max} = 597$ nm (ethanol/water or methanol) while the corresponding dye derived from 4-nitroaniline had $\lambda_{max} = 530$ nm [7]. This 67 nm bathochromic shift was similar in magnitude to that obtained from the use of 6-chloro-2,4-dinitroaniline, which gave $\lambda_{max} = 596$ nm (ethanol/water) [7]. The benzoisothiazole and thiophene systems also gave strong bathochromic shifts, providing blue to blue-green dyes. Although the introduction of a methoxy group into the benzothiazole system instead of a nitro group lessened the bathochromic effect of the heterocycle, λ_{max} of dye **I** was nonetheless comparable to that of the dye obtained from 6-chloro-4-nitroaniline ($\lambda_{max} = 551$ nm, in ethanol/water) [7].

3.2. Dyeing and fastness properties

Dyes **I**–**IV** gave low to moderate uptake on cellulose acetate (Table 2), with the lowest colouration level observed using the thiophene-based dye **IV**. Similar results were obtained in a previous study involving dyes derived from *N*-2-hydroxyethy-l-naphthylamine [7], which exhibited low stability under certain dyeing conditions. In that study, the level of dye degradation varied with the structure of the diazo component. In the case of dye **II** almost 50% was found to undergo degradation at 125 °C and pH 4, while the level of degradation for the unsubstituted homolog was almost 80% under the same conditions [7].

Table 2
Dyeing and fastness properties of dyes **I–IV** on cellulose acetate

Dye	Mg dye/g fibre (% dye absorbed			Wash fastness									Light fastness			Rate of dyeing	Temperature range
				Colour change			Staining										
							Acetate			Nylon							
	Shade depth (% owf)																
	0.25	0.5	1.0	0.25	0.5	1.0	0.25	0.5	1.0	0.25	0.5	1.0	0.25	0.5	1.0	0.5	0.5
I	0.44 (17.6)	0.65 (13.0)	1.04 (10.4)	5	5	5	4–5	4	4	3–4	3	3	2	2	2	E	E
II	1.37 (54.8)	1.82 (36.4)	3.43 (34.3)	4–5 (B1)[a]	4–5 (B1)	4–5 (B1)	4–5	4–5	4–5	2–3	2	2	2–3	2–3	2–3	E	E
III	1.71 (68.4)	2.59 (51.8)	4.21 (42.1)	5	5	5	5	4	3–4	3–4	3	2–3	4–5	4–5	4	E	E
IV	0.25 (10.0)	0.45 (9.0)	0.83 (8.3)	5	5	55	5	5	5	4	3–4	3	6	5–6	5–6	E	E

The wash fastness properties of dyes **I–IV** expressed as colour change of the fabric samples was excellent, while light fastness was moderate to low (Table 2). Incorporation of a nitro-group into the 6-position of the benzothiaze moiety (cf. dye **II**) resulted in a modest improvement in light fastness, compared to dye **I**. Similar differences were observed for analogous dyes on polyester fibre [3]. The benzoisothiaze-based dye **III** showed moderate light fastness, while the thiophene-based dye **IV** exhibited the best light fastness of the four dyes studied.

The dyeing behaviour of dyes **I–IV** was estimated with regard to their dyeing rates and the effect of temperature on dye uptake. Data from both sets of experiments were qualitative. It was determined that these dyes had a rating of E, which designated them as ‘‘very slow’’ with regard to their adsorption vs. time behavior on cellulose acetate (rate-of-dyeing test) [8a] and ‘‘poor’’ with regard to their temperature range properties [8b]. Poor temperature range properties indicated slow dyeing, as the equilibrium exhaustion for all dyes was much higher at lower temperatures.

4. Conclusions

N-2-Hydroxyethyl-1-naphthylamine can be produced via a Bucherer reaction and then used as a coupler to make violet to greenish blue azo dyes when coupled certain heterocyclic amines. The resultant dyes obtained give low to moderate colouration of cellulose acetate, good wash fastness, and low to moderate light fastness depending on the choice of heterocyclic moiety.

Acknowledgements

We wish to thank Professor A.H. Kehayoglou for helpful discussions and Dr. L. Kyriazis and Dr. N. Damianos, VIOCHROM S.A. for providing the amines used in this investigation and for technical assistance.

References

[1] Annen O, Egli R, Hasler R, Henzi B, Jacob H, Matzinger P. Rev Prog Coloration 1987;17:72–85.
[2] Stead CV. Rev Prog Coloration 1970;1:23–30.
[3] Hallas G. J Soc Dyers Col 1979;95:285–94.
[4] Griffiths J. Rev Prog Coloration 1981;11:37–57.
[5] Peters AT, Sener ME. Dyes and Pigments 1987;8:99–118.
[6] Peters AT. J Soc Dyers Col 1988;104:344–8.
[7] Tsatsaroni EG. Dyes and Pigments 1996;31:301–7.
[8] Report of the Committee on the Dyeing Properties of Disperse Dyes—Disperse Dyes on Secondary Cellulose Acetate, Proceedings of the Society, J Soc Dyers Col, 1964;80:237–42; 8a: Rate-of-Dyeing Test; 8b: Temperature Range Test.
[9] Standard Methods for the Determination of the Colour Fastness of Textiles and Leather, 5th ed., 1990: British Standard 1006: 1990; [9a] C06: Colour fastness to washing; [9b] B02: Colour fastness to artificial light: Xenon arc fading lamp test, The Society of Dyers and Colourists, Bradford, 1990.