



Synthesis of Some New Disperse Dyes Derived from N-phenyl Naphthylamine

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ABSTRACT

Various mono azo disperse dyes have been synthesised by coupling reactions between N-phenyl naphthylamine and five diazo components. The dyes were applied on polyester and nylon fabrics and the fastness properties of the dyed fibres were evaluated. The chemical structures of the new dyes were confirmed using ¹H-NMR, ¹³C-NMR, FT-IR and UV-vis analyses. The results of the fastness tests of the dyed fabrics indicated that the dyes have affinity for polyester and nylon fibres.

Key words: Disperse dyes, N-phenyl naphthylamine, Diazotization, Fastness, Polyester, Nylon.

INTRODUCTION

Azo compounds are a very important class of compounds and have been and still receiving attention in scientific research. They are highly coloured and have been used as dyes and pigments for a long time^{1,2}. In addition, they have been studied extensively because of their excellent thermal and optical properties in applications such as optical recording medium^{3,6}, Toner^{7,8}, ink-jet printing^{9,10}, and oil-soluble light-fast dyes¹¹. Azo disperse dyes are a very useful class of polyester dyes whose potential utility has been extended to other fibres^{12,13}. In this present work, five new disperse dyes were synthesised by bringing together five important chemical compounds. Furthermore, the chemical structure of the disperse dyes were studied as well

as their fastness on polyester and nylon fibres for technical performance.

EXPERIMENTAL

All the reagents and solvents used in the research work were of reagent-grade quality and purchased from commercial suppliers. Melting points were determined on a Buchi SMP-20 melting point apparatus. Infrared spectra (in KBr pellets) were recorded on a Nicolet Averser 300 spectrometer; ¹H-NMR spectra were recorded on a mercury 200 BB MHz spectrometer. Chemical shifts are given in δ values (ppm) with tetramethylsilane (TMS) as internal reference and deuterated Chloroform, DMSO and Acetone as solvents. The UV-Vis spectra were measured in

1cm quartz cells on a Genesys IOS VL 200 series spectrophotometer.

Colour fastness tests

Rubbing fastness

Fastness to rubbing was determined according to AATCC Test Method¹⁴ 8-1993

Wash-fastness

Wash fastness was assessed by BS 1006-CO₂ Test¹⁵ 2 using soap solution (5g/l liquor ratio 50:1) for 45min at 50 ± 2°C

Light –fastness

Light fastness was determined by using the method¹⁶ based on the standard protocol issued by ISO. The dyed samples (2 × 6cm) were rated against standard blue wool samples¹⁻⁸.

Sublimation fastness

The sublimation fastness of the dyes on PET and nylon fabrics was evaluated according to ISO¹⁷ 105-POI: 1993. The test was carried out at 180°C for 30 seconds.

Synthesis of the Azo-dyes

Diazotisation of 2, 4 –dibromo-4-bromo-, 2, 4-dinitro-, 2, 4-dichloro-, and 4-chloro aniline

Aniline derivatives (4.0 mmol) was pasted with NaNO₂ (4.0 mmol) and water, 10mL to a smooth slurry and it was added to a well-stirred mixture of H₂SO₄ (d=1.84; 6ml) and ice (3.0g) at 0-5°C. The reaction mixture was stirred for 30 minutes.

Coupling reaction with N-Phenyl naphthylamine

The diazomium salt solution previously prepared (4.0 mmol) was added dropwise to the N-phenyl naphthylamine (4.0 mmol) dissolved in acetic acid (5mL). The combined solution was continuously stirred for 2 hours. After this time, the resulting precipitate was isolated by filtration and dried.

2, 4-dibromo-phenyl azo naphthylamine 5a

The crude product was recrystallized from hot CCl₄ to give a pink solid yield (67%), Mp: 252°C, UV (DMF): λ_{max} nm = 527. FT-IR, (nujol) V: 3395 (NH), 1596 – 1496 (-N=N-). 1626 (Ar-ring), 1463 (naphthalene-ring), 1238 (C-N) 656 cm⁻¹ (C-Br). 'H-NMR (199.96 MHz, DMSO-d₆) ppm: (s, 1H, NH), 6.95 (d, 6H, naphthalene-H) 7.75 (m, 5H, Ar-H).

¹³C-NMR (199.96MHz, MSO-d₆) ppm: 76.58, 77.86, 116.20, 118.15, 123.67, 126.68, 128.96, 130.11, 135.14, 137.84, 139.24.

4-Bromophenyl azonaphthylamine 5b

Recrystallization of the crude product from hot methanol gave a brown solid, yield (60%), Mp: 204°C, UV (DMF): λ_{max} nm = 385. FTIR (nujol) V: 3444 (NH), 1530-1481 (-N=N-) 1500 (Ar-ring), 1445 (naphthalene-ring) 1201 (C-N), 689 (C-Br), 'H-NMR (199.96 MHz, DMSO-d₆) ppm: 2.45 (s, IH, NH), 6.98 (d, 6H, naphthalene-H), 7.70 (m, 4H, Ar-H)¹³C-NMR (199.96 MHz, DMSO-d₆)b 110.30, 118.20, 120.76, 121.20, 122.86, 123.40, 124.22, 126.68, 127.76, 129.48, 129.90, 130.51, 131.56, 131.70, 206.18.

2, 4-Dinitrophenylazonaphthylamine 5c

Recrystallization of the crude compound from hot carbon tetrachloride gave a yellow-brown solid (42%). Mp: 243°C UV (DMF): λ_{max} nm=500 FTIR (nujol) V: 3424 (NH) 1546 (-N=N-) 1547, 1302 (NO₂), 1500 (Ar-ring), 1465 (naphthalene-ring), 1203 (C-N), 'H-NMR (199.96 MHz, DMSO-d₆) ppm: 2.50 (s, IH, NH), 6.98 (s, 6H, naphthalene-H), 7.20(m, 4H, Ar-H), 7.80(m, 3H, Ar-H). ¹³C-NMR (199.96 MHz DMSO-d₆) ppm: 76.56, 77.21, 77.76, 116.10, 118.00, 123.65, 126.66, 128.97, 130.10, 135.13, 137.83, 139.23.

2, 4-Dichlorophenylazonaphthylamine 5d

The crude product was purified by recrystallisation from CCl₄ to give a yellow- brown solid. (53%), Mp: 216-218°; UV (DMF); λ_{max} nm=500, FTIR (nujol) V: 3446 (NH), 1577 (-N=N-), 1500 (Ar-ring) 1459 (naphthalene-ring), 1213 (C-N) 735 (C-Cl), 'H-NMR (199.96 MHz, CDCl₃) ppm: 1.80(s, IH, NH), 7.50 (m, 4H, Ar-H), 8.84(d, 6H, naphthalene – H), 13.40 (s, 4H, Ar-H), ¹³C-NMR(199.96 MHz CDCl₃) ppm: 76.56, 77.22, 77.87, 116.00, 118.02, 123.67, 126.67, 128.96, 130.10, 130.07, 135.12, 137.82, 139.21.

4-chlorophenylazonaphthylamine 5e

Recrystallising the crude product of compound 5 gave a yellow-brown solid. (45%) Mp: 185°C UV(DMF) λ_{max} nm =500, FTIR (nujol) V:3444 (NH), 1598 (-N=N-), 1500 (Ar-ring) 1479 (naphthalene-ring), 1215 (C-N) 780 (C-Cl), 'H-NMR (199.96 MHz, Acetone-d₆) ppm: 2.05(s, IH, NH), 6.96 (d, 6H, naphthalene –H), 7.26(m, 5H, Ar-H), 7.68

(m, 4H, Ar-H), $^{13}\text{C-NMR}$ (199.96 MH_z , Acetone- d_6) ppm: 110.50, 118.73, 120.27, 121.18, 122.85, 123.31, 124.21, 126.57, 127.75, 129.47, 129.89, 130.49, 131.55, 131.69 206.17.

RESULTS AND DISCUSSION

The Azo disperse dye system having N-phenyl naphthylamine as coupler moiety are synthesised in this study. The synthetic pathway^{18,19}

used for the diazotisation reaction and subsequent coupling is shown in scheme 1. The FTIR spectral analysis carried out gave results that are in agreement with the proposed structures of the dyes and those of literature S^{20, 21}

The significant band at 3444-3395 cm^{-1} region is typical of the NH and water overlapping bands. At 1598-1576 cm^{-1} region, the absorption was assigned to the $-\text{N}=\text{N}-$ stretching vibration. The

Table 1: Fastness properties of PET fabric

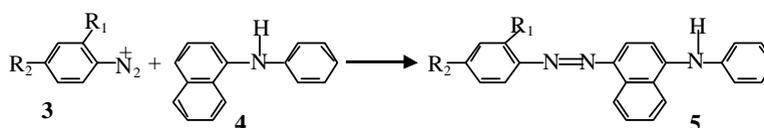
Dye	Wash fastness	Sublimation fastness	Rubbing fastness	Light fastness
5a	5	5	3-4	4
5b	5	5	4	5
5c	5	5	4	5
5d	5	5	4	5
5e	5	5	4	5

Table 2: Fastness properties of Nylon fabric

Dye	Wash fastness	Sublimation fastness	Rubbing fastness	Light fastness
5a	4	5	3-4	4
5b	5	5	4	5
5c	4	5	4	5
5d	4	4	4	4
5e	5	5	4	5

bands at 1479-1445 cm^{-1} region are typical of naphthalene rings. The COSY spectrum of dye 5d is shown in figure 2. The contours that are not on the cross peaks indicates pairs of protons that are splitting each other. Cross peak A for instance indicates that the H_a and H_b proton are coupled,

cross peak B shows that the H_d and H_g protons are coupled, cross peak C is indicative of the fact that H_c and H_i protons are coupled, cross peak D shows that the H_e and H_h protons are splitting each other. The spectral results agree with available experimental absorption spectra²².



- 5a $\text{R}_1, \text{R}_2 = 2,4$ -dibromo
 5b $\text{R}_2 = 4$ -bromo
 5c $\text{R}_1, \text{R}_2 = 2,4$ -dinitro
 5d $\text{R}_1, \text{R}_2 = 2,4$ -dichloro
 5e $\text{R}_2 = 4$ -chloro

Scheme 1.

Fastness properties

Wash fastness

The wash fastness test results of the dyes (Table 1 and 2) showed excellent rating of 5 on polyester. Substrate and also dyes 5b and 5a showed the same rating on nylon fabric. Dyes 5a, 5c and 5d gave a good rating of 4 on nylon. The

excellent wash fastness rating of the dyed polyester substrate is due to the high crystalline nature of the polyester fibre.

Light fastness

The light fastness testing results (Tables 1 and 2) showed the same variation in the ratings on

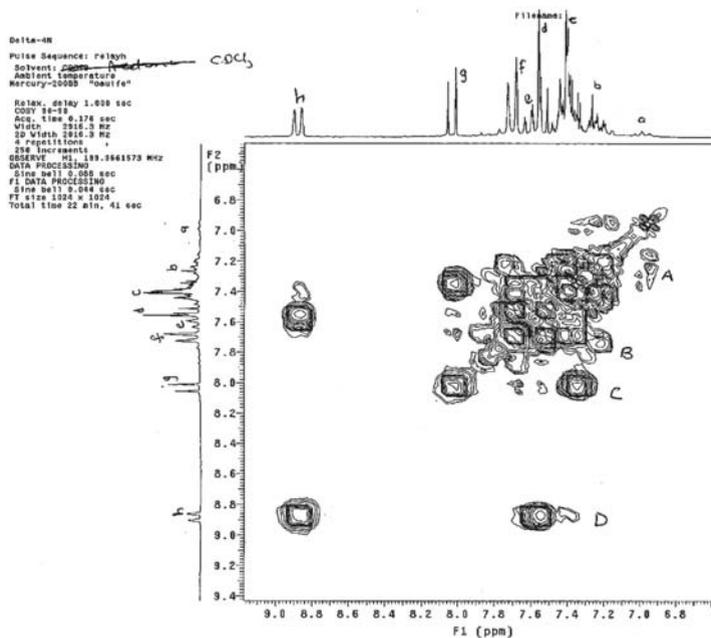


Fig. 1: COSY Spectrum of 5d

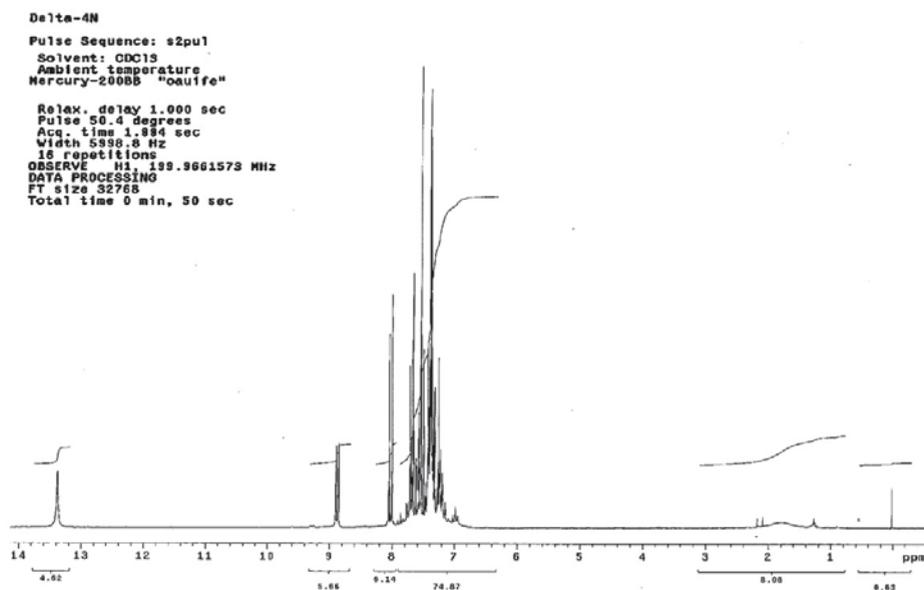


Fig. 2: ¹H-NMR of 5d

both polyester and nylon substrates. The light fastness changes in the diazo component as well as the position of the substituents in relation to the azo group²³. Thus, the decrease of light fastness of dye 5a is attributed to the presence of the o-bromo

substituent relative to the azo group. However, the high fastness of dyes 5b, 5c and 5e could be due to the electronegative para-substituent on the dye structure²⁴.

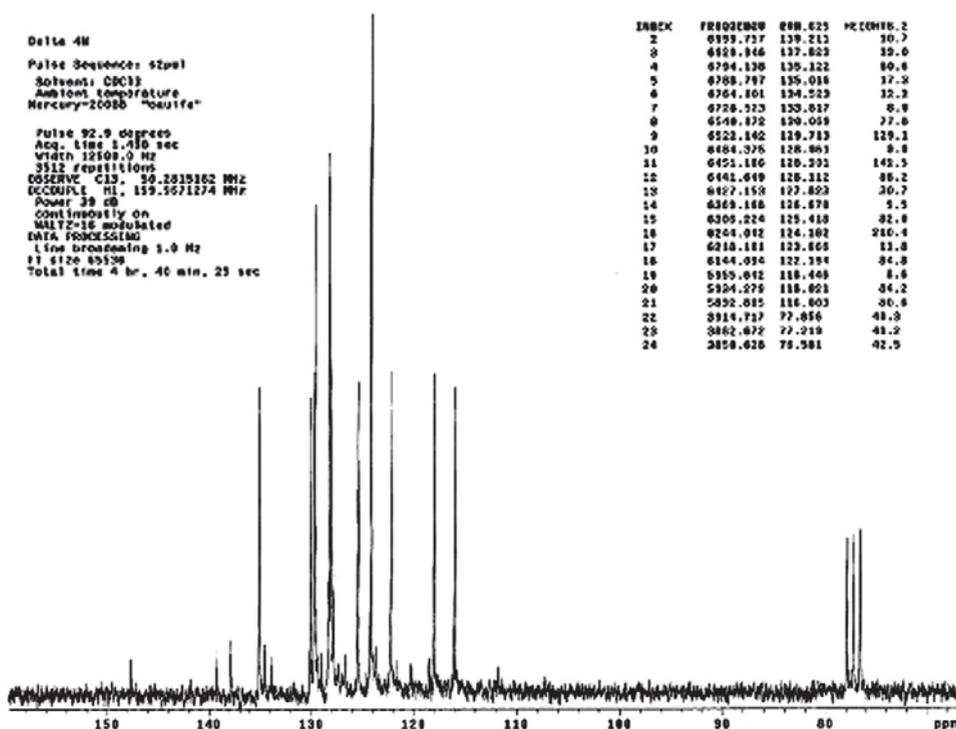


Fig. 3: ¹³C-NMR of 5d

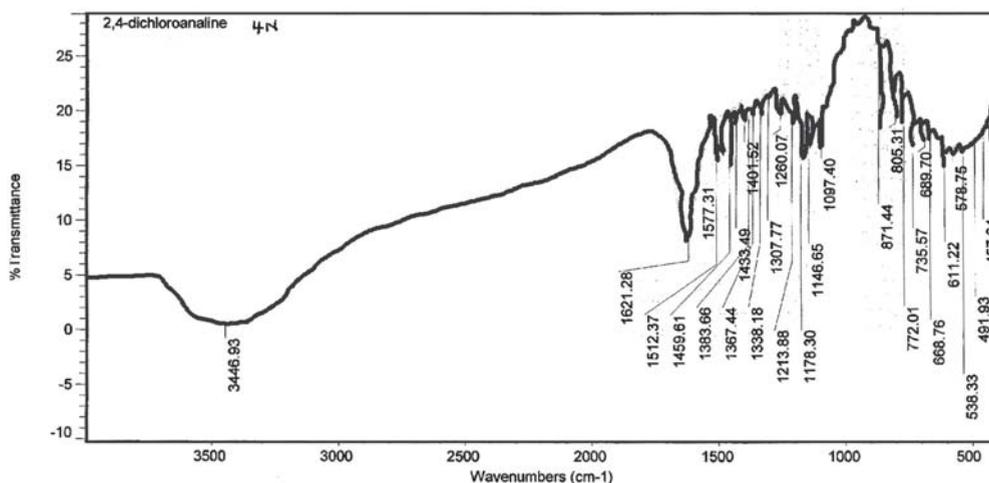


Fig. 4: UV-VIS Spectrum of 5d

Sublimation fastness

The result of the sublimation fastness testing (Tables 1 and 2) indicated that the dyes on the two fabrics are quite stable to heat. The heat stability of the dyes appears to be associated with the high molecular weight and polarity changes due to the presence of halogen atoms. This assertion is in agreement with that of literature²⁵.

Rubbing fastness

The rubbing fastness results showed that the dyes have similar rubbing fastness rating of 3-4 and 4 respectively on both polyester and nylon substrates.

CONCLUSIONS

In conclusion the azo-dyes having N-phenyl-naphthylamine moiety were prepared in this study. In general, it was observed from the results of the study that light fastness was highest in polyester substrate and lower in nylon substrate. This may be due to the regain of the fibres as access of water vapour to the dye particle is restricted in PET than in nylon. The high wash fastness of the dyed fabrics showed that the dyes have affinity for polyester and nylon fibres. The presence of halogen atoms in dyes 5a, 5b, 5c, and 5e has greatly enhanced their sublimation fastness ratings.

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