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Monoazo disperse dyes—part 1: synthesis, spectroscopic studies and technical evaluation of monoazo disperse dyes derived from 2-aminothiazoles

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Abstract

Novel disperse dyes have been prepared from thiazolyl diazonium salts and coupling components based on *m*-aminoacetanilide derivatives. Depending upon various substituents incorporated into the chromophore, absorption maxima varied from 495 to 591 nm in various organic solvents. These dyes were chromophorically strong as evidenced both by molar extinction coefficient in solvent and by strength and build up on polyester.

Keywords: 2-Aminothiazole; Disperse dyes; Heterocyclic diazo components; *m*-Aminoacetanilide; Diazotization; Polyester

1. Introduction

The past three decades have witnessed considerable innovation in the field of azo dye chemistry based on heterocyclic systems and studies in the synthesis of such derivatives have been reported [1–5]. Heterocyclic based azo dyes are not only important for their excellent properties as dyes for polyester textiles; they have also been utilized [6–9] in non-textile applications such as photodynamic therapy, lasers, reprographic technology, functional dye applications and non-linear optical systems. Although a variety of heterocyclic systems have been employed for the synthesis of dyes there remains much scope for the design and development of new chromophores. Most of the recent research has focused on structural variations of existing types, for example variations in substituent, especially on the side chains of the coupling components. This approach has been adopted industrially partly because of the cost and availability of intermediates together with the consequential reduction in legislative formalities required for manufacture, product notification and testing. In one of our projects, on disperse dye, we were interested in the design, synthesis and evaluation of heterocyclic azo dyes with better fastness properties. This in turn might help dye houses to comply with increasing stringent limits being placed on the discharge of colored effluent. This paper deals with the preparation; characterization and evaluation of some new

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monoazo disperse dyes based on heterocyclic diazo components.

2. Experimental

The starting materials used in this study were of synthesis grade purchased from Aldrich chemical company or Merck India Ltd. and used as such. 3-*N*,*N*-di(methoxycarbonylethyl)amino acetanilide was generously gifted by BASF, Manchester, UK.

2.1. Preparation of intermediates

2.1.1. Preparation of 2-aminothiazoles

Resublimed iodine (7.6 g, 0.03 mol) was added to the slurry of appropriate carbonyl component (0.03 mol) [ethyl acetoacetate, acetophenone, *m*-nitro acetophenone or acetone (excess)] and thiourea (4.56 g, 0.06 mol) and the mixture was heated in an oil bath at 130–140 °C, overnight. After cooling the reaction mixture was diluted with water (ca. 50 ml) and heated to dissolve most of the solid, again cooled to ambient temperature and treated with 25% aqueous ammonium hydroxide (to pH 9–10). The precipitated thiazoles were collected and purified by crystallization from hot ethyl alcohol. Preparative, physical and ^{1}H NMR spectral details are shown in Table 1.

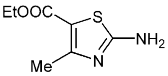
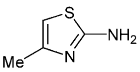
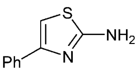
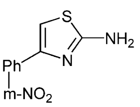
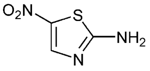
2.1.2. Nitration of 2-aminothiazole

Freshly prepared fuming nitric acid (3.47 g, 0.055 mol) was added, at below 12 °C and over 45 min, to a stirred solution of 2-aminothiazole (5.0 g, 0.05 mol) in conc. sulphuric acid (98%, 27.44 g, 0.28 mol). After stirring for 2 h at 0 °C and 12 h at 25 °C the resultant mixture was poured into ice-water [11]. The solid was removed and the filtrate was neutralized with a saturated aqueous solution of sodium bicarbonate to yield 2-amino-5-nitro thiazole (6.09 g, 84%) yield. The product was crystallised from ethyl alcohol. M.p. 202 °C [10].

*2.1.3. Preparation of 3-(*N,N*-diethyl)amino acetanilide*

Hydrochloric acid (36% w/w, 25.7 g, 0.25 mol) was added to a stirred, concentrated suspension of *m*-phenylenediamine (10.8 g, 0.1 mol) in water to

Table 1
Physical and spectroscopic data of 2-amino thiazole derivatives

Thiazole	m.p. (°C) [10,11]	Acetyl derivative m.p. (°C) [11]	Yield (%)	^{1}H NMR
	176	225	74	(CDCl$_3$) : δ 1.33 (t, J=8 Hz, 3H, Me), 2.52 (s, 3H, Me), 4.26 (q, J=8 Hz, 2H, CH$_2$), 5.2 (br, 2H, D$_2$O exchangeable, NH$_2$)
	42	136	75	(CDCl$_3$): δ 2.19 (s, 3H, C4-Me), 5.22 (br, 2H, D$_2$O exchangeable, NH$_2$), 6.03 (s, 1H, C5-H)
	151	214	70	(CDCl$_3$): δ 5.05 (br, 2H, D$_2$O exchangeable, NH$_2$), 6.72 (s, 1H, C5-H), 7.38 (m, 3H, ArH), 7.76 (d, 2H, ArH)
	188	308	64	(DMSO-d_6): δ 6.98 (s, 1H, C5-H), 7.0 (br, 2H, D$_2$O exchangeable, NH$_2$), 7.58 (t, 1H, ArH), 8.02 (d, 1H, Ar-H), 8.16 (d, 1H, Ar-H), 8.63 (s, 1H, Ar-H)
	202	> 360	84	–

give a solution of pH 1.0. This solution was cooled to 5 °C and acetic anhydride (20.4 g, 0.2 mol) was added to the mechanically stirred, cold solution over 2 h. The resultant solid, *m*-amino acetanilide hydrochloride (17.4 g, 93% yield) was collected, dried and used as such in a subsequent step. Diethyl sulphate (123 g, 0.8 mol) was added at room temperature, to a stirred mixture of *m*-amino acetanilide hydrochloride (37.4 g, 0.2 mol) and anhydrous potassium carbonate (82.8 g, 0.6 mol) in anhydrous acetonitrile (120 ml, dried over P_2O_5). The mixture was heated to reflux until complete, monitored by TLC (development with *p*-nitrobenzenediazonium tetrafluoroborate). The solid was removed, washed with acetonitrile (20 ml) and the combined filtrate was diluted with water and extracted with ethyl acetate (3×50 ml). The combined extract was washed with brine and dried over anhydrous sodium sulphate and finally the solvent was removed under reduced pressure. The residue was chromatographed over silica gel G (60–120 mesh). Elution with hexane/ethyl acetate furnished 3-(*N*,*N*-diethyl)amino acetanilide (37.0 g, 90%) m.p.: 82 °C; ^{1}H NMR (300 MHz): ($CDCl_3$) δ 1.38 (t, $J=7.0$ Hz, 6H, 2×Me), 2.35 (s, 3H, COMe), 3.55 (q, $J=7.0$ Hz, 4H, 2×CH_2), 6.62 (dd, $J_1=7.5$ Hz and $J_2=<1$Hz, 1H, ArH), 6.85 (d, $J=7.5$ Hz, ArH), 7.25 (br, 1H, ArH), 7.3 (t, $J=7.5$ Hz, 1H, ArH), 7.75 (br, 1H, NH, D_2O exchangeable); FAB MS (MNBA matrix) : 206 (M^+), 191 (M^+- Me), 177 ($M^+-2\times$Me), 163 (M^+-MeCO). Microanalysis : found C, 69.45; H, 8.63; N, 13.50% ($C_{12}H_{18}N_2O$ requires C, 69.90; H, 8.73; N, 13.59%).

2.2. Preparation of dyes

2.2.1. Diazotization

For all the diazo components except 2-amino-4-(*m*-nitro)phenyl thiazole, nitrosyl sulphuric acid was used for the diazotisation. It was prepared by adding sodium nitrite (0.83 g, 0.012 mol) to sulphuric acid (98%, 11.96 g, 0.12 mol) at 30 °C, heating the stirred mixture to 60–65 °C over 15 min and maintaining this temperature for 30 min to ensure complete dissolution of $NaNO_2$. The reaction mixture was cooled to 5 °C, acetic acid (5 ml) was added and stirring continued for 10 min. The temperature was then reduced to −5 °C, the appropriate amino thiazole (0.01 mol) was added over 30 min and the whole reaction mixture stirred at the same low temperature for at least 2 h. The completion of diazotisation was checked either through TLC monitoring of the ethyl acetate extract of the diazotisation reaction for any unreacted amino thiazole or, alternatively, by checking for the presence of excess nitrous acid using starch-iodide paper. 2-Amino-4-(*m*-nitro)-phenyl thiazole (2.21 g, 0.01 mol) was pasted with sodium nitrite (0.83 g, 0.012 mol) in small quantity of water and added to cooled conc. sulphuric acid (11.76 g, 0.12 mol) in portions, maintaining the temperature below −5 °C. After stirring for 15 min acetic acid (5 ml) was added and stirring was continued until completion of the diazotisation. The completion was judged by the usual methods.

2.2.2. Coupling procedure

A solution of the appropriate coupling component (0.015 mol) in acetic acid (15 ml) was added to an ice–water mixture (200 g) in a beaker equipped with a mechanical stirrer and pH meter. A pinch of sulphamic acid was added followed by the addition of the diazonium salt liquor (0.13 mol) at 0–5 °C over 1 h, the mixture was stirred for at least 3 h at ambient temperature. During the addition and stirring period the pH was adjusted to 1.5–2.0 by dropwise addition of aqueous sodium hydroxide to the coupling bath. Finally the pH was raised to 4.0–4.5 and the precipitated product was collected, washed with cold and hot water and dried. The product was either recrystallised from methylated spirits or, alternatively, purified by flash chromatography over silica gel G (60–120 mesh) using chloroform and chloroform:methanol (95:5) mixtures as eluent. The progress of the coupling reaction was checked by spotting on a filter paper a drop of the reaction mixture close to a spot of an alkaline aqueous solution of H-acid and detecting any color appearance at the interface of the two boundaries. The coupling reaction was adjudged complete when no color appeared at the interface indicating the absence of the diazonium salt.

2.3. Characterisation of dyes

Melting points were determined using a capillary melting point apparatus and are uncorrected.

Table 2
Physical and spectroscopic data of dyes 1–7

Dye 1	Yield: 70%; R_f: 0.75 (ethyl acetate:hexane 7:3); m.p. 145 °C; IR (KBr): ν 1360 [$(N{=}O)_2$ sym. str.], 1535 [$(N{=}O)_2$ asym str.], 1565 (amide-II), 1615 (C=C), 1690 (amide-I), 1740 (ester); ^{1}H NMR ($CDCl_3$): δ 1.23 (br, 1H, D_2O exchangeable, NH), 2.31 (s, 3H, NHCOMe), 2.74 (t, $J=6.99$ Hz, 4H, 2×CH_2), 3.70 (s, 6H, 2×Me), 3.84 (t, $J=6.96$ Hz, 4H, 2×CH_2), 6.50 (dd, $J=9.41$ Hz, $J=2.73$ Hz, 1H, ArH), 7.58 (s, 1H, C(5)H), 7.63 (d, $J=8.00$ Hz, 1H, ArH), 7.88 (d, $J=9.35$ Hz, 1H, ArH), 8.17 (m, 2H, ArH), 8.34 (d, $J=7.86$ Hz, 1H, ArH), 8.79 (br, 1H, ArH); MS : m/z 308 [M^+–N($CH_2CH_2CO_2Me$)$_2$, –COMe], 301 [(M^+–1) – $CH_2CH_2CO_2Me$, –COMe, –*p*-NO_2Ph], 285 [(M^+–2) –$CH_2CH_2CO_2Me$, –NHCOMe, –*p*-NO_2Ph], 269 [(M^+–2) –CO_2Me, –CO_2Me, –COMe, –*p*-NO_2Ph], 256 [M^+–$CH_2CH_2CO_2Me$, –NHCOMe, –*p*-NO_2Ph, –OMe], 241 [(M^+– 2) –$CH_2CH_2CO_2Me$, –$CH_2CH_2CO_2Me$, –*p*-NO_2Ph, –Me], 228 [M^+–*p*-NO_2Ph, –$CH_2CH_2CO_2Me$, –CO_2Me, –NHCOMe]; microanalysis: found: C, 54.05; H, 5.27; N, 14.66% ($C_{25}H_{26}N_6O_7S$ requires C, 54.5; H, 4.69; N, 15.16%)
Dye 2	Yield: 72%; R_f: 0.82 (ethyl acetate:hexane 7:3); m.p. 159 °C; IR (KBr) : ν 1340 [$(N{=}O)_2$ sym. str.], 1530 [$(N{=}O)_2$ asym. str.], 1570 (amide-II), 1610 (C=C), 1685 (amide-I); ^{1}H NMR ($CDCl_3$): δ 1.29 (t, $J=7.05$, 6H, 2×Me), 1.61 (br, 1H, D_2O exchangeable, NH), 2.31 (s, 3H, NHCOMe), 3.51 (q, $J=7.26$ Hz, 4H, 2×CH_2), 6.48 (dd, $J=9.49$ Hz, $J=2.70$ Hz, 1H, ArH), 7.35 (s, 1H, C(5)H), 7.80 (AA′BB′ system, $J=11.43$ Hz, $J=11.40$ Hz, 4H, ArH), 7.98 (m, 1H, ArH), 8.09 (s, 1H, ArH); MS: *m/z* 439 ($M^+ + 1$), 438 (M^+), 395 [M^+–COMe], 367 [M^+–N(Et)$_2$], 258 [($M^+ + 1$), –*p*-NO_2Ph, –NHCOMe]; microanalysis: found: C, 57.05; H, 5.20; N, 19.66% ($C_{21}H_{22}N_6O_3S$ requires C, 57.53; H, 5.02; N, 19.17%)
Dye 3	Yield: 80%; R_f: 0.73 (ethyl acetate:hexane 7:3); m.p. 98 °C; IR (KBr): ν 1560 (amide-II), 1610 (C=C), 1690 (amide-I), 1700 (ester); ^{1}H NMR ($CDCl_3$): δ 1.26 (t, $J=7.01$ Hz, 6H, 2×Me), 1.84 (br, 1H, D_2O exchangeable, NH), 1.35 (t, $J=7.10$ Hz, 3H, Me), 2.27 (s, 3H, NHCOMe), 2.73 (s, 3H, Me), 3.50 (q, $J=7.10$ Hz, 4H, 2×CH_2), .32 (q, $J=7.14$ Hz, 2H, CH_2), 6.48 (dd, $J=9.45$ Hz, $J=2.50$ Hz, 1H, ArH), 8.06 (m, 2H, ArH); MS: *m/z* 404 ($M^+ + 1$), 403 (M^+), 376 [($M^+ + 2$) –Et], 360 (M^+–COMe), 331 [M^+–N(Et)$_2$) or 360 - t], 288 [M^+–N(Et)$_2$, –COMe], 259 (288 – Et), 243 (288 – OEt). Microanalysis: found: C, 56.05; H, 6.30; N, 17.80% ($C_{19}H_{25}N_5O_3S$ requires C, 56.57; H, 6.20; N, 17.37%)
Dye 4	Yield: 83%; R_f: 0.78 (ethyl acetate:hexane 7:3); m.p. 140 °C; IR (KBr): ν 1562 (amide-II), 1605 (C=C), 1690 (amide-I), 1700 (ester), 1725 (ester); ^{1}H NMR ($CDCl_3$): δ 1.39 (t, $J=7.10$ Hz, 3H, Me), 1.59 (br, 1H, D_2O exchangeable, NH), 2.28 (s, 3H, NHCOMe), 2.72 (t, $J=6.99$ Hz, 4H, 2×CH_2), 2.78 (s, 3H, Me), 3.71 (s, 6H, 2×OMe), 3.85 (t, $J=6.95$ Hz, 4H, 2×CH_2), 4.36 (q, $J=7.12$ Hz, 4H, 2×CH_2), 6.52 (dd, $J=9.46$ Hz, $J=2.67$ Hz, 1H, ArH), 7.84 (d, $J=9.38$ Hz, 1H, ArH), 8.12 (br, 1H, ArH); MS : m/z 311 [(M^+– 2) - 2×CO_2Me, –CO_2Et, –Me], 302 [(M^+ – 1), –N($CH_2CH_2CO_2Me$), –Et], 296 (311 – Me), 285 [M^+–2) –$CH_2CH_2CO_2Me$, –$CH_2CH_2CO_2Me$, –Me, –NHCOMe], 284 [($M^+ + 1$) –$CH_2CH_2CO_2Me$, –NHCOMe, –OMe, –Me, –OEt] or [(M^+ – 1), –N($CH_2CH_2CO_2Me$)$_2$, –EtO], 268 (311 – NHCOMe), 253 (311 – NHCOMe), 242 (284 – NHCOMe), 240 (185 – OEt); Microanalysis: found: C, 53.65; H, 5.56; N, 12.99% ($C_{23}H_{29}N_5O_7S$ requires C, 53.18; H, 5.59; N, 13.49%)
Dye 5	Yield: 86%; R_f: 0.69 (ethyl acetate:hexane 7:3); m.p. 110 °C; IR (KBr): ν 1560 (amide-II), 1608 (C=C), 1700 (amide-I), 1735 (ester); ^{1}H NMR ($CDCl_3$): δ 1.64 (br, 1H, D_2O exchangeable, NH), 2.25 (s, 3H, NHCOMe), 2.48 (s, 3H, Me), 2.68 (t, $J=6.69$ Hz, 4H, 2×CH_2), 3.68 (s, 6H, 2×OMe), 3.80 (t, $J=6.98$ Hz, 4H, 2×CH_2), 6.45 (dd, $J=9.40$ Hz, $J=2.53$ Hz, 1H, ArH), 6.80 (s, 1H, C(5)H), 7.80 (d, $J=9.39$ Hz, 1H, ArH), 8.07 (m, 1H, ArH); MS: *m/z* 284 [(M^+–2) –Me, –NHCOMe, –$CH_2CH_2CO_2Me$]; Microanalysis: found: C, 53.19; H, 5.06; N, 15.24% ($C_{20}H_{25}N_5O_5S$ requires C, 53.69; H, 5.59; N, 15.66%)
Dye 6	Yield: 80%; R_f: 0.80 (ethyl acetate:hexane 7:3); m.p. 70 °C; IR (KBr): ν 1560 (amide-II), 1610 (C=C), 1710 (amide-I), 1735 (ester); ^{1}H NMR ($CDCl_3$): δ 1.62 (br, 1H, D_2O exchangeable, NH), 2.30 (s, 3H, NHCOMe), 2.71 (t, $J=6.95$ Hz, 4H, 2×CH_2), 3.70 (s, 6H, 2×OMe), 3.83 (t, $J=7.02$ Hz, 4H, 2×CH_2), 6.50 (dd, $J=9.45$ Hz, $J=2.50$ Hz, 1H, ArH), 7.43 (m, 5H, ArH), 7.90 (d, $J=9.36$ Hz, 1H, ArH), 7.99 (d, $J=7.08$ Hz, 2H, ArH), 8.10 (br, 1H, C(5)H); MS : *m/z* 306 [M^+–N($CH_2CH_2CO_2Me$), –Me], 301 [(M^+ – 1)–$CH_2CH_2CO_2Me$, –COMe, –Ph], 279 [(M^+ + 1)–COMe], 269 [(M^+ – 2) –Ph, –COMe, –2×CO_2Me], 242 [(M^+ – 2) –N($CH_2CH_2CO_2Me$)$_2$, –Ph], 241 [(M^+ – 2) –$CH_2CH_2CO_2Me$, –$CH_2CH_2CO_2Me$, –Ph, –Me]; Microanalysis: found: C, 59.19; H, 5.06; N, 13.24% ($C_{25}H_{27}N_5O_5S$ requires C, 58.94; H, 5.30; N, 13.75%)

(*continued on next page*)

Table 2 (*continued*)

Dye 7	Yield: 77%; R_f: 0.76 (methyl alcohol: ethyl acetate 1:2); m.p. 105 °C; IR (KBr): ν 1345 [$(N{=}O)_2$ sym. str.], 1530 [$(N{=}O)_2$ asym. str.], 1620 (amide-II), 1705 (amide-I), 1735 (ester); ^{1}H NMR ($CDCl_3$): δ 1.61 (br, 1H, D_2O exchangeable, NH), 2.34 (s, 3H, NHCOMe), 2.78 (t, $J=6.90$ Hz, 4H, 2×Me), 3.75 (s, 6H, 2×OMe), 3.94 (t, $J=6.91$ Hz, 4H, 2×CH_2), 6.49 (br, 1H C(5)H), 6.64 (m, 1H, ArH), 7.81 (m, 1H, ArH), 8.12 (br, 1H, ArH); MS : *m/z* 406 [$(M^+ + 1)$ –NHCOMe, –Me], 314 [$(M^+ + 1)$ –$CH_2CH_2CO_2Me$, –NO_2, –OMe], 327 [$(M^+{-}3)$ –CO_2Me, –NO_2, –COMe], 312 (M^+ –OMe, –OMe, –NO_2, –NHCOMe): Microanalysis : found: C, 47.19; H, 4.16; N, 17.24% ($C_{19}H_{22}N_6O_7S$ requires C, 47.70; H, 4.60; N, 17.57%)

^{1}H NMR spectra were obtained using a Bruker AC 200 MHz instrument using TMS as internal standard. Mass (70 eV) spectra were recorded on Shimadzu QP 2000A spectrometer. IR spectra were recorded on Pye UNICAM SP 3–300 or Shimadzu DR-8001 FT spectrophotometers. UV-VIS spectra were recorded on Shimadzu 1601 PC double beam spectrophotometer. Microanalytical data was recorded at the microanalytical laboratory RSIC, Panjab University, Chandigarh.

Preparative, physical and spectral details of dyes 1–7, which are synthesized using the above protocols, are listed in Table 2.

2.3.1. Examination of λ_{max} values

λ_{max} And ε_{max} values were recorded in four solvents of varying polarity (Table 3). Purified dyes were dissolved at ambient temperature using a shaker and the spectra recorded immediately.

2.4. Dyebath preparation and dyeing

Dyebath dispersions (0.5–1.0% w/v) were prepared by milling (Dyno-Mill), for 20 h, an aqueous suspension of the powdered dye with glass beads (4 mm diameter) in the presence of a dispersing agent (Zetex DA-N or sodium dispersol) of a mass equal to that of the dye. Dyeing was performed at 20:1 mass liquor ratio in sealed, stainless steel dye pots of 100 ml capacity using a Mathis LABOMAT M54 dyeing machine. An appropriate volume of the dye stock solution was placed in each pot so as to provide the desired quantity of dye (0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0% o.m.f.). Additional dispersing agent (1.0 g/l) was also added and the pH of the bath was set to 4.5 using glacial acetic acid. A pre-weighed, wetted-out polyester fabric (double jersey) was put in each pot and the dyeings performed by raising the dye bath temperature from 20 to 130 °C at 3 °C/min, holding at this temperature for 60 min and rapidly cooling (9.9 °C/min) to 50 °C as depicted in Fig. 1. The dyeings were then rinsed with cold water and reduction cleared [NaOH (2 g/l), $Na_2S_2O_4$ (1 g/l), Matexil DN-VL 200 (1 g/l)] at 60 °C for 10 min. After clearing the samples were rinsed successively with hot and cold water, detergent solution [(Akapon T (0.5 g/l)] at 70 °C for 3

Table 3
Absorption maxima, extinction coefficients and half-band widths (in nm) of the dyes 1–7 in solution

Dye	Toluene			Acetone λ_{max} nm	Acetonitrile λ_{max} nm	DMF λ_{max} nm	On polyester fabric (from the *K/S* data 0.5% shade) λ_{max} nm
	λ_{max} nm	ε_{max} $dm^3\ mol^{-1}\ cm^{-1}$	$\lambda_{1/2}$ (nm)				
Dye 1	507	56,485	91.0	511	511	529	520
Dye 2	513	59,414	87.4	517	520	526	530
Dye 3	531	54,550	91.0	536	539	547	550
Dye 4	520	48,815	94.6	525	527	536	530
Dye 5	495	43,529	94.6	497	498	505	510
Dye 6	504	48,630	94.6	508	509	516	520
Dye 7	561	55,142	94.6	576	575	591	580

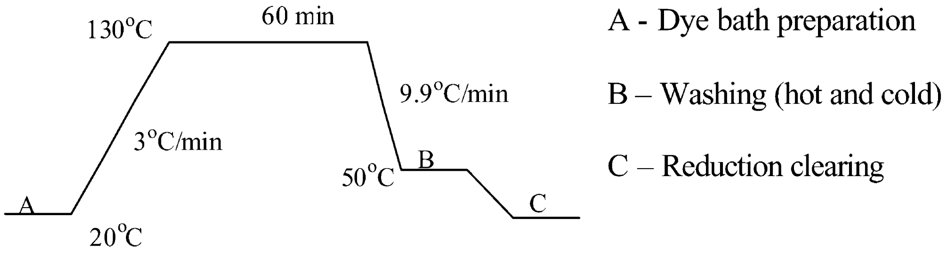


Fig. 1. HT dyeing profile of polyester used in this study.

min, and finally rinsed in cold water and air dried. The colorimetric properties of the dyeings (D_{65} illumination, 10° observer) were determined using a Spectraflash 600 colorimeter (Datacolor International).

2.5. Color fastness to washing

Fastness was assessed by the standard ISO CO6 C2S method test. A 10×4 cm dyed fabric strip stitched through the short end to SDC's multifibre test fabric was used. The washing was conducted on a Roaches washtec-P at 60 °C for 30 min, rinsed with cold water, air dried and analysed.

2.6. Light fastness measurements

Light fastness test ISO 105/B02 was performed on the xenon arc lamp using blue wool reference samples.

2.7. Color fastness to dry heat

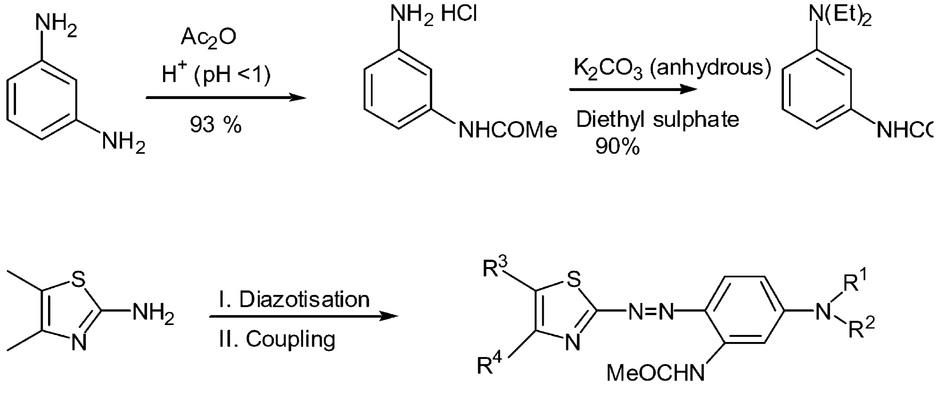
Color fastness to dry heat (excluding pressing) of the dyes was determined according to PO1 method (BS 1006:1990) using a composite sample (10×4 cm) sandwiched from each side by the undyed polyester, at 180 °C and 210 °C for 30 s on Roaches Crouzet Top 948 equipment. The treated samples were air dried for 4 h in air and analyzed.

3. Results and discussion

3.1. Structural characterization

The dyes used in this study were synthesized adopting the strategy outlined in Scheme 1 using intermediates as described (*vide experimental*). Thus, using differently substituted thiazoles, dyes were synthesized in excellent yields. The ^{1}H NMR data of the intermediates and the dyes is presented in Tables 1 and 2 respectively along with other physical data.

The absorption spectral characteristics of the dyes prepared in this study is summarized in Table 3 and corroborate well with similar dyes reported in literature [9,12–14]. The effect of substitution, in the thiazole ring of the diazo component and in the side chain of the coupling component, on the visible absorption spectrum and the color intensity, was also investigated. The wavelengths of maximum absorption, λ_{max}, of the dyes ranges from 495 to 561 nm in toluene (505 to 591 nm in dimethylformamide). Changes in λ_{max} and ε_{max} values can be brought about by varying the substituent either in the 4 or 5 position of the thiazole diazo component. As expected, the incorporation of an electron withdrawing group at C-5 of the thiazole moiety was found to give rise to bathochromic shifts: thus, the introduction of a ethoxycarbonyl group resulted in a 25 nm shift of λ_{max} to longer wavelength, (cf. dyes 5 and 4). As expected from the magnitude of the appropriate field and resonance components of the substituent effect (Hammett substituent constants, Table 4) [15,16], other dyes followed a similar pattern. The introduction of a more strongly electron withdrawing group in the 5 position provided much more bathochromic shades: thus the most bathochromic dye prepared was dye 7, λ_{max} 561 nm (R^3 = nitro, R^4 = hydrogen). Fairly modest bathochromic shifts were observed for the series comprising dyes 5, 6 and 1 where R^4 is methyl, phenyl and *m*-nitrophenyl respectively and R^3 is



Dyes	R^1	R^2	R^3	R^4
Dye 1	$CH_2CH_2CO_2Me$	$CH_2CH_2CO_2Me$	H	*m*-NO_2Ph
Dye 2	Et	Et	H	*m*-NO_2Ph
Dye 3	Et	Et	CO_2Et	Me
Dye 4	$CH_2CH_2CO_2Me$	$CH_2CH_2CO_2Me$	CO_2Et	Me
Dye 5	$CH_2CH_2CO_2Me$	$CH_2CH_2CO_2Me$	H	Me
Dye 6	$CH_2CH_2CO_2Me$	$CH_2CH_2CO_2Me$	H	Ph
Dye 7	$CH_2CH_2CO_2Me$	$CH_2CH_2CO_2Me$	NO_2	H

Scheme 1. Synthesis of thiazole based dyes 1–7.

hydrogen. In this series both the wavelength and the extinction coefficients increase in the order $5 < 6 < 1$. The introduction of electron withdrawing methoxycarbonyl groups at the β-position of the side chains of the coupling component results in a modest hypsochromic shift. Thus dye 2, $-(C_2H_5)_2$, $\lambda_{max} = 513$ nm absorbs at slightly longer wavelength than dye 1, $(CH_2CH_2COOCH_3)_2$, $\lambda_{max} = 507$ nm.

These dyes yield brighter shades (Fig. 2) in consonance with the similar dyes reported in the literature [5] and these findings are not surprising as the type of thiazole diazo components used herein might be expected to confer less steric hindrance at the azo linkage. This fact is further supported by the relatively narrow half band widths (<100 nm) of the absorption maxima of dyes 1–7; the possibility also exists of intramolecular hydrogen bonding of the *o*-acylamino substituent with the azo group. All these dyes have quite high ε_{max} values and show positive solvatochromism as the polarity of the solvent is increased (Table 4).

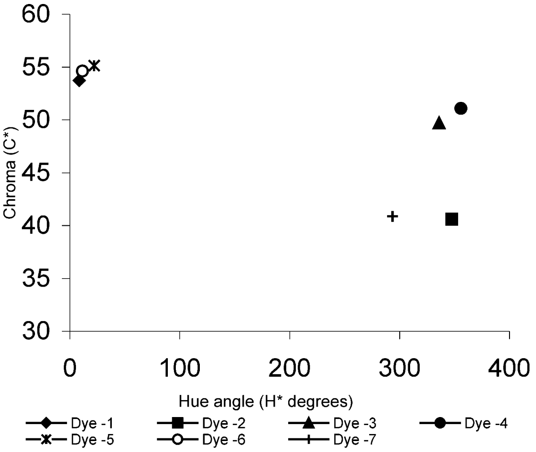


Fig. 2. Comparison of hue and chroma of the dyes 1–7.

3.2. Dyeing characteristics on polyester fabric

3.2.1. Color properties of the dyes on polyester

The dyes 1–7, when applied to polyester under the high temperature dyeing conditions furnished dyeings of red–violet–blue shades. There appears to be a general correlation between the hues of the dyeings on polyester with the absorption characteristics observed in solution. This contrasts with scant reports [13] especially in case of blue disperse dyes, of non compliance of such simple correlations. A comparison of the brilliance of the blue dye (dye 7) with reported [17] blue dyes based upon both anthraquinone and carbocyclic azo dyes reveals a fair degree of match (comparable C^* values). The comparison of the hue and chroma (Table 5) of these dyes are shown in Fig. 2.

Figs. 3 and 4 illustrate the build up properties of dyes 1–7 under high temperature dyeing conditions. Most of these dyes tend to saturate at a concentration slightly above 1.5% o.m.f., although there appears no direct correlation between the relative molecular mass of these dyes to the build up. This probably reflects the importance of other parameters such as dye solubility, which in turn are dictated by the types and a number of structural features within the dye. In the case of the pairs of dyes 1 and 2 the build up and strength on the fabric of the former, a bis (β-methoxycarbonylethyl) derivative, is a much inferior to that of the

Table 4
Field and resonance components of substituent effects

Constants	Me	Ph	NO_2	COOR
σ_{p}[a]	−0.14	0.05	0.81	0.44
σ_{m}[b]	−0.06	0.05	0.71	0.35
σ_{I}[c]	−0.05	0.10	0.65	0.20
σ_{R}[d]	−0.13	−0.10	0.15	0.16
F[e]	−0.01	0.25	1.0	0.47
R[f]	−0.41	−0.37	1.0	0.67

[a] Sum of resonance effects (*p*-position).
[b] Sum of resonance effects (*m*-position).
[c] Field effects.
[d] Resonance contribution.
[e] Fields effects contribution.
[f] Resonance contribution.

Table 5
Color coordinates at integ value 20 of the dyes 1–7 (light source D65/10° observer)

Dyes	L^*	a^*	b^*	C^*	H^*
Dye 1	44.66	53.11	08.14	53.73	008.72
Dye 2	34.50	39.63	−08.86	40.61	347.40
Dye 3	32.18	45.43	−20.19	49.71	336.04
Dye 4	33.29	50.78	−05.58	51.09	355.73
Dye 5	44.40	51.04	20.84	55.13	022.21
Dye 6	44.81	53.55	10.78	54.63	011.38
Dye 7	29.04	16.38	−37.49	40.87	293.64

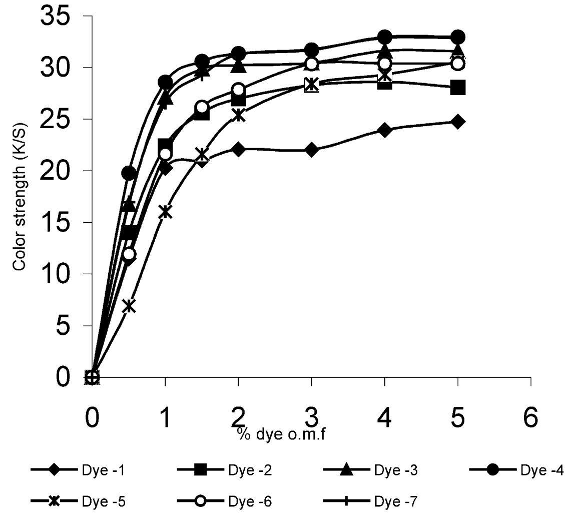


Fig. 3. Build-up curves of the dyes 1–7.

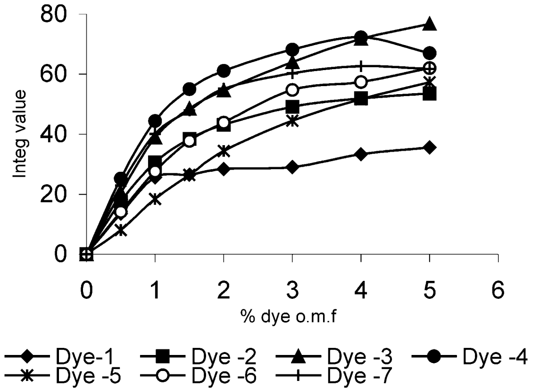


Fig. 4. Integ values of the dyes 1–7.

corresponding diethyl substituted dye. Conversely in the pair of dyes 3 and 4, the bis (β-methoxycarbonylethyl) derivative, dye 4, is the strongest at all but the heaviest depth of shade.

The excitation purity (P) (Table 6, Fig. 5) has been calculated from the placement of dyes 1–7 in the CIE chromaticity diagram (Fig. 6, *x*, *y* values for D65/10° observer). Also the dominant wavelengths for the spectrum colors and complimentary wavelengths for non-spectral colors have been indicated.

3.2.2. *Fastness properties of the dyed polyester*

All the fastness tests on the dyed and reduction cleared polyester samples have been performed at dyeing depth corresponding to *integ = 20* for each dye (Fig. 4). In *Integ method* each $(K/S)\lambda$ is weighted by the product of illuminant energy (El) and the sum of the CIE colour-matching functions $(\bar{x}_\lambda + \bar{y}_\lambda + \bar{z}_\lambda)$ at the relevant λ [18]. The major benefit of this technique is that it is associated with the colour map, a CIELAB a^*b^* diagram in which, by definition, all colours are shown at equal depth D_1 ($D_1 = 20$, say) [19].

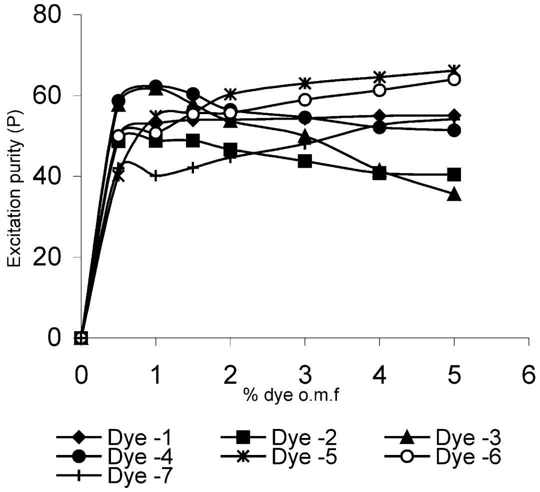


Fig. 5. Excitation purity (P) of the dyes 1–7.

3.2.2.1. *Wash fastness*.

The wash fastness of the dyed and reduction cleared polyester samples were determined by the standard ISO CO6 C2S test using a standard multifibre fabric as the adjacent fabric to monitor the change in color of the sample together with the staining of the individual components of the SDC multifibre strip. The fastness ratings are recorded in Table 7. In general these are good to excellent for fabrics which had

Table 6
Excitation purity (P), dominant wavelengths (λ_D) and color of the dyes 1–7

Dyes	Excitation purity ‘P’ at dye concentrations							Dominant wavelength[a] λ_D (nm)	Color
	0.5% owf	1.0% owf	1.5% owf	2.0% owf	3.0% owf	4.0% owf	5.0% owf		
Dye 1	50.00	53.03	53.95	54.03	54.36	54.96	55.06	498[b]	Bluish-red
Dye 2	48.72	48.78	48.84	40.66	43.75	40.82	40.46	508[b]	Dark maroon
Dye 3	57.70	61.70	57.89	53.66	50.00	41.51	35.59	514[b]	Reddish-violet
Dye 4	58.70	62.26	60.34	56.45	54.55	52.17	51.43	498[b]	Maroon
Dye 5	40.00	54.92	56.00	60.32	63.01	64.56	66.20	500[b]	Scarlet
Dye 6	50.00	50.70	55.41	55.70	58.97	61.32	64.00	660	Red
Dye 7	42.00	40.00	42.00	44.00	48.00	52.00	54.00	453	Blue

[a] Calculated from the CIE chromaticity diagram (Fig. 6).

[b] Complementary wavelength [λ_c (nm)].

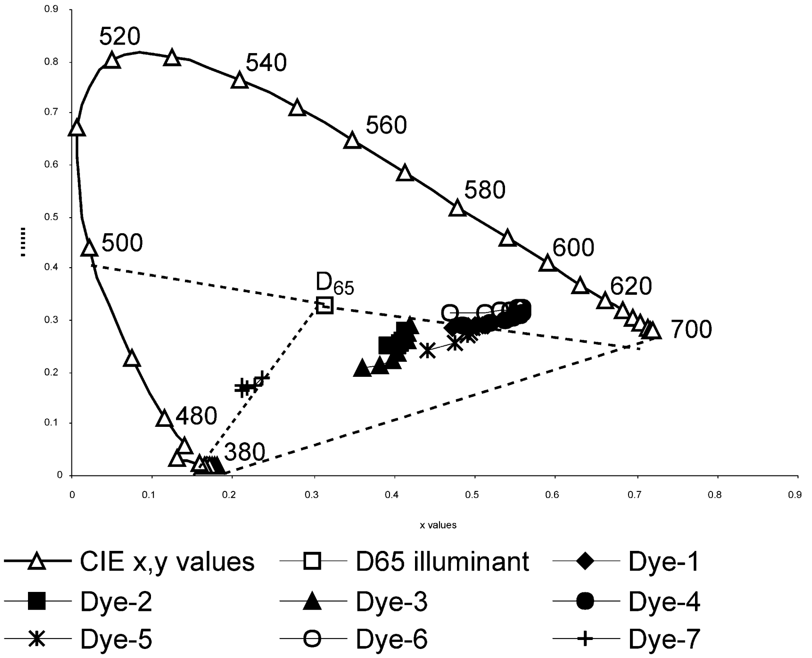


Fig. 6. CIE chromaticity diagram showing the position of the dyes 1–7 and dominant wavelength ($\lambda_D = 453$ nm) for dye 7 and complimentary wavelength ($\lambda_c = 498$ nm) for dye 1.

been subjected to the reduction clearing stage. However when the reduction clearing was omitted, marginally worse staining was observed. This indicated that reduction clearing is important for these dyeings. As these dyes are characteristically hydrophobic, high fastness ratings are expected. The dyes bearing an ester function, either in the diazo or coupling component, also displayed marginally better wash fastness; for example, the 5-nitro substituted dye (dye 7) also exhibited excellent fastness to washing.

3.2.2.2. Light fastness. Although in all the cases light fastness was poor (Table 8), the dyes 3, 4 and 7 were marginally superior to the others, again emphasizing the importance of appropriate substitutents. Attempts are in hand to improve the light fastness properties of these dyes.

Table 7
Wash fastness data of the dyes 1–7 (ISO CO6 C2S) 60° C/30 min

Dyes	Color fastness rating	Color staining rating					
		SCA	BUC	N	P	A	WW
Dye 1	5	5	4–5	4–5	5	5	4–5
Dye 2	4–5	4	4–5	3	4–5	5	4–5
Dye 3	5	4–5	5	4	5	5	4–5
Dye 4	5	4–5	5	4–5	5	5	5
Dye 5	4–5	4–5	5	4–5	5	5	5
Dye 6	4–5	4	4–5	4	5	5	4–5
Dye 7	5	4–5	5	5	5	5	4–5

SCA—secondary cellulose acetate; BUC—bleached unmercerised cotton; N—nylon 6,6; P—polyester; A—acrylic; WW—worsted wool.

Table 8
Light fastness of the dyes 1–7

	Dye 1	Dye 2	Dye 3	Dye 4	Dye 5	Dye 6	Dye 7
Light fastness	2	2	3–4	3–4	2	2	3–4

Table 9
Dry heat fastness (sublimation fastness) of the dyes 1–7

Dyes	180 °C		210 °C	
	Color staining on polyester	Color fastness	Color staining on polyester	Color fastness
Dye 1	5	4–5	4–5	3–4
Dye 2	4–5	4–5	3	3–4
Dye 3	3–4	3–4	2–3	2–3
Dye 4	4	3–4	2	4
Dye 5	3–4	4	2	3
Dye 6	4–5	4–5	3–4	3–4
Dye 7	4–5	4	3	3

3.2.2.3. Colour fastness to dry heat. Dry heat fastness was determined following PO1 method (BS 1006:1990). Generally fastness to heat was moderate to good (Table 9), consistent with the presence of polar groups on the chromophore.

4. Conclusions

This study describes the synthesis of some novel heterocyclic based monoazo disperse dyes using variously substituted 2-aminothiazoles as diazo components together with an evaluation of their spectral characteristics on polyester and in organic solvents. The wash fastness properties are generally good whereas the light fastness is poor although the incorporation of electron withdrawing substituents results in an improvement in light fastness. There appears, in most cases though not in all, to be a correlation between the color strength of the dyes in solution and on polyester.

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