

Original Research Article

Synthesis and applications of new aminothienopyridazines disperse dyes on polyester fabric

Alya Al-Etaibi^{1*}, Magda M. Kamel² and Morsy Ahmed El-Asasery²

¹Natural Science Department, College of Health Science, Public Authority for Applied Education and Training, Fayha, 72853, Kuwait

²Dyeing, Printing and Textile Auxiliaries Department, Textile Research Division, National Research Centre, 12622, Dokki, Giza, Egypt

*Corresponding author

ABSTRACT

Keywords

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Aminothienopyridazine coupled with aromatic diazonium salts to give the corresponding 7-(4'-Amino-2'-aryloxy)-4-[benzotriazol-1-yl]-2-p-tolyl-2H-thieno[3,4-d]pyridazin-1-one disperse dyes. Fastness properties of the reported dyes were intensively examined against light, perspiration and washing fastness, exhibiting fair, very good and excellent fastness levels, respectively.

Introduction

The past decade has 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 (Ashkar *et al.*, 2013). Heterocyclic based azo dyes are not only important for their excellent properties as disperse dyes for polyester textiles; they have also been utilized in non-textile applications such as lasers, photodynamic therapy, functional dye applications and non-linear optical systems (Singh *et al.*, 2002). Disperse dyes are substantially water-insoluble non-ionic dyes which are applied to hydrophobic fibres (polyester, cellulose acetate, nylon) from aqueous dispersions. Disperse dyes are characterized by the absence of solubilizing groups and low molecular weight.

A number of researchers have studied aminothiophene derivatives as azo disperse dyes in the dyeing of synthetic fibers (Maradiya *et al.*, 2002a,b; Naik and Halkar, 2006; Sabnis and Rangnekar, 1989; Abd-El-Aziz, *et al.*, 2006). In spite of the large number of reports on the utility of these compounds in the dye industry, to our knowledge, their corresponding arylazothienopyridazines have never been reported as potential monoazo disperse dyes. In continuation of the increasing interest in the synthesis of arylazothienopyridazines derivatives (Al-Mousawi *et al.*, 2006), this paper reports the synthesis of some arylazothienopyridazines using a conventional method and their application as disperse dyes on polyester fabrics.

Materials and Methods

Instrumentation

Melting points were recorded on a Gallenkamp apparatus. IR spectra were recorded using KBr pellets on a JASCO FTIR-6300 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Bruker DPX 400 MHz super-conducting NMR spectrometer with proton spectra measured at 400, and carbon spectra at 100 MHz. Mass spectra were measured on a high resolution GC/MS DFS-Thermo, of an electron ionization property (EI, 70 EV). Microanalyses were performed on Elemental-Vario Micro cube Analyzer.

General procedure for the synthesis of azo disperse dyes (4a-d)

A solution of aryldiazonium chloride 2 (prepared from the corresponding aromatic amine (0.01 mol) and the appropriate quantities of both hydrochloric acid and sodium nitrite) (10 mmol) at 0 °C was added to a solution of compound 1 (10 mmol) in acetic acid (50 ml) containing sodium acetate (0.60 g). The reaction mixture was stirred at room temperature for 1 hr and the solid product was collected by filtration and crystallized from DMF/ethanol (3:1). Compounds 4a, 4c and 4d have been confirmed by reported spectroscopic data (Al-Mousawi *et al.*, 2006)

7-(4'-Aminophenylazo)-4-[benzotriazol-1-yl]-2-p-tolyl-2H-thieno[3,4-d]pyridazin-1-one (4a)

Red crystals (75%), mp. >300 °C; IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 3326 and 3215 (NH₂), 1655 (CO); ^1H NMR (DMSO-*d*₆): δ_{H} 2.38 (s, 3H, CH₃), 6.49 (d, 2H, J = 8.7 Hz, 4-tolyl-H), 7.16 (d, 2H, J = 8.7 Hz, 4-tolyl-H), 7.30-7.32 (m, 2H, benzotriazolyl-H), 7.38 (s, 1H, thienyl-

H), 7.49-7.60 (m, 4H, phenyl-H), 7.76 (br, 2H, NH₂, D₂O exchangeable), 7.90 (d, 1H, J = 8 Hz, benzotriazolyl-H). 8.28 (d, 1H, J = 8 Hz, benzotriazolyl-H). Ms: m/z 478 [M⁺]. C₂₅H₁₈N₈OS: C, 62.74; H, 3.79; N, 23.41; S, 6.70. Found C, 62.63; H, 3.79; N, 23.18; S, 6.86.

7-(4-Amino-2-methylphenylazo)-4-benzotriazol-1-yl-2-p-tolyl-2H-thieno[3,4-d]pyridazin-1-one (4b)

Red crystals (78%), mp. 212 °C; IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 3310 and 3230 (NH₂), 1675 (CO); ^1H NMR (DMSO-*d*₆): δ_{H} = 2.24 (s, 3H, CH₃), 2.35 (s, 3H, CH₃), 6.38 (d, 2H, J = 8.4 Hz, 4-tolyl-H), 6.95 (d, 2H, J = 8.4 Hz, 4-tolyl-H), 7.28-8.29 (m, 2H, arom-H), 7.76 (s, 1H, thienyl-H), 7.28-8.29 (m, 5H, arom-H), 9.17 (br, 2H, NH₂, D₂O exchangeable), Ms: m/z 492 [M⁺].

7-(4'-Amino-2'-chlorophenylazo)-4-[benzotriazol-1-yl]-2-p-tolyl-2H-thieno[3,4-d]pyridazin-1-one (4c)

Red crystals (76%), mp. >300 °C; IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 3325 and 3220 (NH₂), 1655 (CO); ^1H NMR (DMSO-*d*₆): δ_{H} = 2.38 (s, 3H, CH₃), 6.43 (d, 2H, J = 8.8 Hz, 4-tolyl-H), 7.20 (d, 2H, J = 8.8 Hz, 4-tolyl-H), 7.30-7.32 (m, 2H, benzotriazolyl-H), 7.37 (s, 1H, thienyl-H), 7.54 (d, 2H, J = 8.6 Hz, 4-chlorophenyl-H), 7.60 (d, 2H, J = 8.6 Hz, 4-chlorophenyl-H), 7.76 (br, 2H, NH₂, D₂O exchangeable), 7.89 (d, 1H, J = 8 Hz, benzotriazolyl-H), 8.31 (d, 1H, J = 8 Hz, benzotriazolyl-H).

Ms: m/z 512 [M⁺]. C₂₅H₁₇N₈OSCl: C, 58.53; H, 3.34; N, 21.84; S, 6.25. Found C, 59.10; H, 3.49; N, 21.89; S, 6.32.

7-(4'-Amino-2'-nitrophenylazo)-4-[benzotriazol-1-yl]-2-p-tolyl-2H-thieno[3,4-d]pyridazin-1-one (4d)

Red crystals (78%), > 300°C; IR: $\nu_{\max}/\text{cm}^{-1}$ 3323 and 3218 (NH₂), 1666 (CO); ¹H NMR (DMSO-*d*₆): $\delta_{\text{H}} = 2.37$ (s, 3H, CH₃), 6.53 (d, 2H, J = 8.8 Hz, 4-tolyl-H), 7.33 (d, 2H, J = 8.8 Hz, 4-tolyl-H), 7.36 (s, 1H, thienyl-H), 7.55-7.62 (m, 5H, benzotriazolyl-H and arom-H), 7.90 (d, 1H, J = 8 Hz, benzotriazolyl-H). 7.96 (br, 2H, NH₂, D₂O exchangeable), 8.38 (d, 1H, J = 8 Hz, benzotriazolyl-H). Ms: m/z 523 [M⁺]. C₂₅H₁₇N₉O₃S: C, 57.35; H, 3.27; N, 24.07; S, 6.12. Found C, 57.33; H, 3.36; N, 23.79; S, 5.88.

High temperature dyeing method (HT)

Materials

Polyester 100% was used. The fabric was treated before dyeing with a solution containing non-ionic detergent 5 g/L (Hostapal CV, Clariant, Egypt) and sodium carbonate (2 g/L) in a ratio of 50:1 at 60°C for 30 min, thoroughly washed with water, and air dried at room temperature.

Dyeing

A dispersion of the dye was produced by dissolving the appropriate amount of dye (1% shade) in 2 mL DMF and then added drop wise with stirring to the dye bath (Liquor ration 50:1) containing sodium lignin sulfonate as dispersing agent. The ratio of dispersing agent to dyestuff is 1:1. The pH of the dye bath was adjusted to 4.5 using aqueous acetic acid and the wetted-out polyester fabrics were added. Dyeing was performed by raising the dye bath temperature to 130°C under pressure in a dyeing machine at a rate of 15°C/min, holding at this temperature for 60 min and then cooling to 50°C. After dyeing, the fabrics were thoroughly washed and subjected to surface reduction clearing ((2 g NaOH + 2 g sodium hydrosulphite)/L and soaped with 2% nonionic detergent to

improve washing fastness). The samples were heated in this solution for 45 min at 70 °C and then thoroughly washed and air-dried.

Colour measurements and analyses

Colour measurements

The colorimetric parameters of the dyed polyester fabrics were determined on a reflectance spectrophotometer. The colour yields of the dyed samples were determined by using the light reflectance technique performed on UV-Vis spectrophotometer. The colour strengths, expressed as K/S values, were determined by applying the Kubelka-Mink equation (Al-Mousawi *et al.*, 2013a,b).

$$K/S = [(1 - R)^2/2R] - [(1 - R_o)^2/2R_o]$$

where R = decimal fraction of the reflectance of the dyed fabric; R_o = decimal fraction of the reflectance of the undyed fabric; K = absorption coefficient; S = scattering coefficient.

Fastness tests

Fastness to washing

After washing using 5 g/L of the non-ionic detergent (Hostapal CV, Clariant, Egypt) and 2 g/L of sodium carbonate, the dyed fabrics were tested by using ISO standard methods (Chrysler *et al.*, 1990). A specimen of dyed polyester fabric was stitched between two pieces of undyed cotton and wool fabrics, all of equal length, and then washed at 50 °C for 30 min. The changes in color were assessed according to the gray scale (Al-Qalaf *et al.*, 2013).

Fastness to perspiration

The samples were prepared by stitching a piece of dyed polyester fabric between two pieces of cotton and wool fabrics, all of

equal length, and then immersed in the acid or alkaline solution for 30 min. The acid solution (pH = 4.5) contains sodium chloride (10 g/L), sodium dihydrogen orthophosphate (1 g/L) and histidine monohydrochloride (0.25 g/L). The alkaline solution (pH = 8.7) contains sodium chloride (10 g/L), disodium orthophosphate (1 g/L) and histidine monohydrochloride (0.25 g/L). The changes in color were assessed according to the gray scale (Al-Etaibi *et al.*, 2014).

Fastness to light

Light fastness was determined by exposing the dyed polyester on a Xenotest 150 (Original Hanau, chamber temperature 25–30°C, black panel temperature 60°C, relative humidity 50–60%, and dark glass (UV) filter system) for 40 h. The changes in color were assessed according to the blue scale (Al-Etaibi *et al.*, 2014).

Results and Discussion

The synthesis of some disperse dyes based on aminothienopyridazines moiety has been reported (Al-Mousawi *et al.*, 2006). Herein, in an attempt to evaluate their dyeing behaviour, the reactivity of aminothienopyridazines towards nitrogen electrophiles was investigated. The coupling take place at amino group rather than thienyl-H, this may be attributed to the steric effect due to the presence of bulky group, benzotriazolyl group, at position-4.

Thus compound 1 reacts with benzenediazonium salt in acidic medium afforded the disperse dyes 4a-d. The obtained dyes are believed to be formed through the non-isolated intermediates 3a-d, which undergoes rearrangement to give the final isolated dyes 4a-d. The structures 4a-d were supported by ¹H NMR spectra that displayed a singlet at δ_H ca. 7.4 ppm

assigning for thienyl-H along with downfield aromatic protons and NH₂ signals (Scheme 1).

Disperse dyes 4a-d were applied to polyester fabrics at 1% (dye shade), using high temperature dyeing method (HT) at 130 °C. Reddish-orange to violet colour shades were obtained. The dyeing properties on the polyester fabrics were evaluated in terms of their fastness properties (e.g., fastness to washing, perspiration and light). The colour of dyeing on polyester fabrics is expressed in terms of CIELAB colour space values (Table 1), and the following CIELAB coordinates were measured: lightness or darkness (L^*); brightness or dullness (chroma (C^*)); hue angle (h) from 0 to 360°; a^* , whose value represents the degree of redness (positive) and greenness (negative); and b^* , whose value represents the degree of yellowness (positive) and blueness (negative). The surface colour yield K/S was used to explain the amount of dye absorbed on the surface of the fibre. The K/S values listed in Table 1 which shows that dyes 4a-d showed high affinity for the polyester fabrics and the K/S were all generally satisfactory. The results listed in Table 1, demonstrate that the introduction of electron-withdrawing groups at the benzene ring improved the lightness and brightness; in contrast, the introduction of electron-donating decreased the lightness and brightness so dyes 4c was lighter and brighter than the 4b. The dyeing obtained using dye 4b was red (as shown by the higher a^* values, higher b^* values) and brighter (as shown by the higher C^* values) than the dye 4a. The h values in Table 1, show that almost all of the dyed polyester samples expressed the same hue, except dye 4d as a violet color. In general, the color hues of the disperse dye 4d on the polyester fabric shifted to the bluish directions; this was indicated by the negative value of $b^* = -16.25$ (yellow–blue axis).

The fastness ratings are recorded in Table 2, shows that the disperse dyeing displayed very good fastness levels to washing and excellent fastness levels to perspiration. In general, these dyes are characteristically hydrophobic, high washing and perspiration fastness ratings are expected. The light fastness of the dyes 4a-d on polyester displayed fair fastness on polyester fabrics. It is of value to mention here that light

fastness was obtained by the dye 4d containing a nitro group in the diazonium component, the nitro group increases the polarity of the dyes (Metwally *et al.*, 2004; Al-Mousawi *et al.*, 2014), which may link them more strongly to the fabric and it opens an extra way for the energy dissipation after light absorption which decreases the chances for photo-fading.

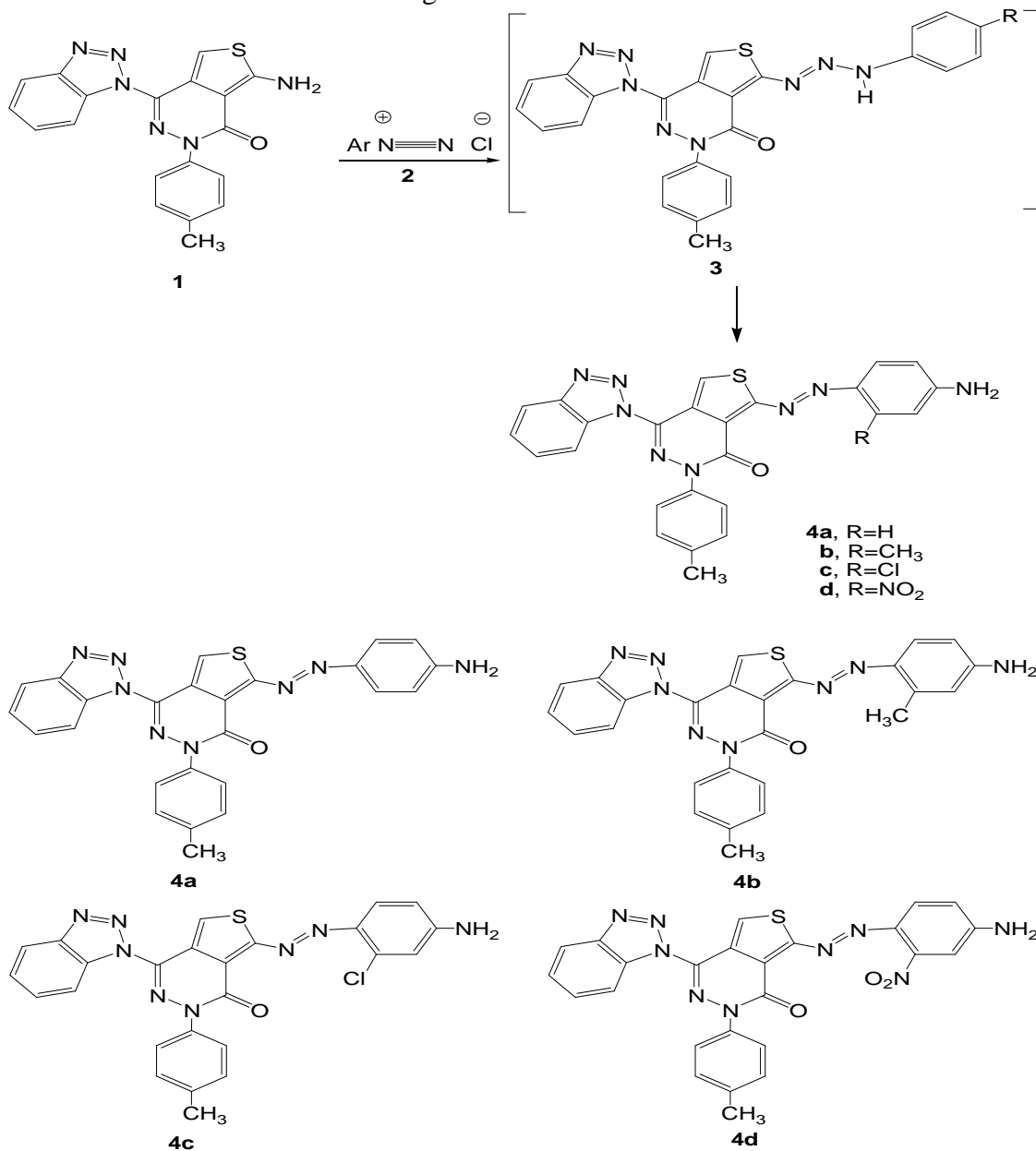


Table.1 Shade and optical measurements of the azo disperse dyes on the polyester fabrics

Dye no	Colour shade on polyester	Absorption (λ_{\max} (nm))	L^*	a^*	b^*	C^*	h^*	K/S
4a	Reddish-orange	505	42.34	37.11	13.96	39.47	20.79	10.05
4b	Red	520	39.05	45.68	18.28	49.32	22.07	16.03
4c	Pink	520	45.50	42.14	7.91	47.89	11.13	7.84
4d	Violet	550	33.37	25.63	-16.25	31.42	327.43	9.79

Table.2 Fastness properties of azo disperse dyes on polyester fabrics*

Dye no	Wash fastness			Perspiration fastness						Light fastness
				Acid			Alkaline			
	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW	
4a	5	5	5	5	5	5	5	5	5	3-4
4b	4-5	4	4	5	5	5	5	5	5	4
4c	5	5	5	5	5	5	5	5	5	3-4
4d	5	5	5	5	5	5	5	5	5	4

* Alt = alteration; SC = staining on cotton; SW = staining on wool.

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