Dyes and Pigments 92 (2012) 902-908

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

New azodisperse dyes with thiazole, thiophene, pyridone and pyrazolone moiety for dyeing polyester fabrics

M.A. Metwally*, Ebrahim Abdel-Galil, Amira Metwally, Fathy A. Amer

Department of Chemistry, Faculty of Science, Mansoura University, 35516 Mansours, Egypt

A R T I C L E I N F O

Article history: Received 26 March 2011 Received in revised form 13 July 2011 Accepted 16 July 2011 Available online 30 July 2011

Keywords: Azodisperse dyes Thiazole Thiophene Pyridone Pyrazolone Polyester fabrics

1. Introduction

Disperse dyes are very popular and important class of dyes for dyeing polyester fabrics owing to their brilliancy, wide range of hue, excellent fastness properties, in addition to the environmental and economic reasons [1]. Especially useful in this respect are azo dyes derived from coupling of diazonium salts with sulfur and/or nitrogen heterocyclic compounds as coupling components. These sulfur and/or nitrogen heterocyclic azo dyes provide bright strong shades that range from yellow, orange, red, and blue to green colors [2–5].

Moreover, the aminopyrazole compounds are very useful as precursors for the synthesis of fused heterocyclic ring systems, which play an important role in biological and pharmacological activities [6,7], and they can also be used as intermediates in the dyestuff industry [8,9].

In view of these findings, and in continuation of our previous studies [10–13] on the synthesis of a variety of thiazole and thiophene derivatives from the readily obtainable cheapest starting materials for dyeing of polyester fabrics, we now report on the successful synthesis of several new 5-antipyrinylazo-thiazoles, 4-antipyrinylazo-thiophenes, 5-antipyrinylazo-pridindiones, and 4-antipyrinylazo-pyrazoles and their applications as disperse dyes for dyeing polyester fabrics.

ABSTRACT

New antipyrinylazo dyes were prepared by diazocoupling of 4-antipyrinyl diazonium chloride with a variety of coupling components e.g. thiazole, thiophene, pyridone, and pyrazole moieties. The synthesized dyes were characterized by UV–visible absorption, IR, ¹H NMR, and MS spectroscopy. These dyes were applied as disperse dyes for dyeing polyester fabrics and their fastness properties were evaluated. Also the position of color in CIELAB coordinates (L^* , a^* , b^* , H^* , C^*) was assessed.

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2. Experimental

General: All melting points (uncorrected) are in degree centigrade and were determined on Gallenkamp electric melting point apparatus. Elemental analyses were carried out in the microanalytical unit, Faculty of Science, University of Mansoura. UV/Vis spectra were recorded with a Perkin-Elmer Lambda 551 S spectrometer. IR spectra were recorded (KBr) with on a Mattson 5000 FTIR spectrometer. ¹H NMR spectra were measured on a Bruker WP 300 in CDCl₃, DMSO-d₆ or CF₃COOD as solvent, using TMS as an internal standard. Mass spectra were recorded on a Finnigan MAT 212 instrument. Polyester fabric was used to assess the dyeing behavior of the compounds under investigation. It was produced by Kafr El-Dawar Spinning and Weaving Company (Egypt). All applications and fastness properties of the dyes were studied in Laboratories and Research sector in Misr Beida Dyers Company, Alexandria, Egypt. The color parameters of the dyed fibers were determined on a GretagMacbeth CE 7000a spectrophotometer in Laboratories and Research sector in Misr Beida Dyers Company, Alexandria, Egypt.

2.1. Synthesis

2.1.1. Synthesis of N-(5-antipyrinylazo-4-methyl-thiazol-2-yl)-N'-(1-aryl-ethylidene)-hydrazine dyes **4**

To a cold solution $(0-5 \,^{\circ}\text{C})$ of the thiazole derivatives **3** (0.005 mol) in pyridine (30 ml), a cold solution of freshly prepared



^{*} Corresponding author. Tel.: +20 101645979. E-mail address: mamegs@mans.edu.eg (M.A. Metwally).

^{0143-7208/\$ –} see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2011.07.009

antipyrinyl diazonium chloride (0.005 mol) was added with continuous stirring. The reaction mixture was allowed to stand in cold for 2 h, diluted with water and then filtered. The antipyrinylazo-thiazole dyes **4** thus obtained, were dried and recrystallized from ethanol.

2.1.1.1. N-(5-Antipyrinylazo-4-methylthiazol-2-yl)-N'-(1-phenylethy lidene)-hydrazine (**4a**). m.p. = $160-162 \degree$ C. Yield = 67%. IR ($\overline{\nu}/cm^{-1}$): 3143 (NH), 1653 cm⁻¹ (CO). MS (M⁺; EI): m/z (%) = 445 (74). Found: C, 61.78; H, 5.12; N, 22.09%. C₂₃H₂₃N₇OS (445.54) requires C, 62.00; H, 5.20; N, 22.01%.

2.1.1.2. N-(Cyclohexylidene-N'-(5-antipyrinylazo-4-methylthiazol-2-yl)-hydrazine (**4b**). m.p. = 145–145 °C. Yield = 65%. IR ($\bar{\nu}/cm^{-1}$): 3135 (NH), 1664 cm⁻¹ (CO). Found: C, 59.77; H, 5.82; N, 23.08%. C₂₁H₂₅N₇OS (423.53) requires C, 59.55; H, 5.95; N, 23.15%.

2.1.2. Synthesis of ethyl 2-antipyrinylhydrazono-2-phenylthiocarbamoyl acetate (**6**)

The freshly prepared antipyrinyl diazonium chloride (0.01 mol) was added with continuous stirring to a cold $(0-5 \degree C)$ solution of the thiocarbamoyl derivative 7 (0.01 mol) in ethanol (50.0 ml) and sodium acetate (4.0 g). The reaction mixture was allowed to stir at $(0-5\degree C)$ for 2 h, and then the solid was collected by filtration. The obtained precipitate was dried and recrystallized from ethanol.

$$\begin{split} \text{m.p.} &= 165 - 166 \ ^\circ\text{C}, \text{ lit. m.p.} = 165 \ [15]. \ \text{Yield} = 84\%. \ \text{IR} \ (\overline{\nu}/\text{cm}^{-1}): \\ 3274 \ (\text{NH}), \ 1668 \ \text{cm}^{-1} \ (\text{CO}). \ ^1\text{H} \ \text{NMR} \ (\text{CDCI}_3): \ \delta/\text{ppm} = 1.38 \ (t, \ 3\text{H}, \ \text{CH}_3), 2.60 \ (s, \ 3\text{H}, \ \text{CH}_3), 3.08 \ (s, \ 3\text{H}, \ \text{CH}_3), 4.30 \ (q, \ 2\text{H}, \ \text{CH}_2), 7.25 - 7.62 \\ (\text{m}, \ 5\text{H}, \ \text{Ar-H}), \ 12.70 \ (s, \ \text{H}, \ \text{NH}), \ 15.87 \ (s, \ 1\text{H}, = \text{N}-\text{NH}). \ \text{Found: C}, \\ 60.25; \ \text{H}, \ 5.36; \ \text{N}, \ 16.08\%. \ \text{C}_{22}\text{H}_{23}\text{N}_5\text{O}_3\text{S} \ (437.51) \ \text{requires C}, \ 60.39; \ \text{H}, \\ 5.30; \ \text{N}, \ 16.01\%. \end{split}$$

2.1.3. Synthesis of 5-anilino-4-antipyrinylazo-3-hydroxythiophene dyes **8a**-**d**

To a solution of **6** (0.005 mol) in ethanolic sodium ethoxide (prepared by dissolving 0.12 g sodium metal in 30 ml absolute ethanol), the appropriate α -halogenated reagent e.g. chloroacetone, phenacyl chloride, ethyl chloroacetate or chloroacetonitrile (0.005 mol) was added. The reaction mixture was heated under reflux for 2 h. The reaction mixture was poured into cold water, neutralized with dilute HCl, and the solid product that formed was filtered off and recrystallized from ethanol or DMF-ethanol (1:2) mixture to afford the corresponding thiophene dyes **8a–d**.

2.1.3.1. 2-Acetyl-5-anilino-4-antipyrinylazo-3-hydroxythiophene (**8a**). m.p. = 234–235 °C. Yield = 83%. IR ($\bar{\nu}/cm^{-1}$): 3221, 3142 (NH and OH), 1635 (CO), 1594 cm⁻¹ (CO). Found: C, 61.82; H, 4.79; N, 15.58%. C₂₃H₂₁N₅O₃S (447.51) requires C, 61.73; H, 4.73; N, 15.65%.

2.1.3.2. 5-Anilino-4-antipyrinylazo-2-benzoyl-3-hydroxythiophene (**8b**). m.p. = 237–239 °C. Yield = 80%. IR ($\bar{\nu}$ /cm⁻¹): 3258, 3138 (NH and OH), 1662 (CO), 1589 cm⁻¹ (CO). ¹H NMR (CDCl₃): δ /ppm = 2.78 (s, 3H, CH₃), 3.32 (s, 3H, CH₃), 7.13–7.84 (m, 15H, Ar-H), 13.25 (s, H, NH), 15.22 (s, 1H, OH). Found: C, 65.84; H, 4.69; N, 13.82%. C₂₈H₂₃N₅O₃S (509.58) requires C, 66.00; H, 4.55; N, 13.74%.

2.1.3.3. 5-Anilino-4-antipyrinylazo-2-ethoxycarbonyl-3-hydroxythio phene (**8c**). m.p. = 130–132 °C. Yield = 78%. IR ($\bar{\nu}$ /cm⁻¹): 3266, 3152 (NH and OH), 1655 (CO), 1591 cm⁻¹ (CO). ¹H NMR (CDCl₃): δ /ppm = 1.35 (t, 3H, CH₃), 2.72 (s, 3H, CH₃), 3.32 (s, 3H, CH₃), 4.32 (q, 2H, CH₂), 7.08–7.52 (m, 10H, Ar-H), 11.21 (s, H, OH), 13.65 (s, 1H, NH). Found: C, 60.49; H, 4.89; N, 14.76%. C₂₄H₂₃N₅O₄S (477.54) requires C, 60.36; H, 4.85; N, 14.67%.

2.1.3.4. 5-Anilino-4-antipyrinylazo-2-cyano-3-hydroxythiophene (**8d**). m.p. = 158–160 °C. Yield = 87%. IR ($\bar{\nu}$ /cm⁻¹): 3230, 3174 (NH and OH), 2179 (CN), 1652 cm⁻¹ (CO). MS (M⁺; EI): *m*/*z* (%) = 430 (100). Found: C, 61.20; H, 4.32; N, 19.60%. C₂₂H₁₈N₆O₂S (430.48) requires C, 61.38; H, 4.21; N, 19.52%.

2.1.4. Synthesis of 2-antipyrinylhydrazono-thioacetoacetanilide (10)

The freshly prepared antipyrinyl diazonium chloride (0.01 mol) was added with continuous stirring to a cold (0-5 °C) solution of the thiocarbamoyl derivative **9** (0.01 mol) in ethanol (50.0 ml) and sodium acetate (4.0 g). The reaction mixture was allowed to stir at (0-5 °C) for 2 h, and then the solid was collected by filtration. The obtained precipitate was dried and recrystallized from ethanol.

 $\begin{array}{ll} m.p.=200-202\ ^{\circ}C. & Yield=89\%. & IR \quad (\overline{\nu}/cm^{-1}): & 3254 \quad (NH), \\ 1653\ cm^{-1} \ (2\ CO). \ ^{1}H \ NMR \ (CDCl_{3}): \ \delta/ppm=2.15 \ (s, \ 3H, \ CH_{3}), \ 2.60 \\ (s, \ 3H, \ CH_{3}), \ 3.15 \ (s, \ 3H, \ CH_{3}), \ 7.20-7.60 \ (m, \ 5H, \ Ar-H), \ 12.25 \ (s, \ H, \ NH), \ 14.65 \ (s, \ 1H, = N-NH). \ Found: \ C, \ 61.96; \ H, \ 5.16; \ N, \ 17.23\%. \\ C_{21}H_{21}N_{5}O_{2}S \ (407.49) \ requires \ C, \ 61.90; \ H, \ 5.19; \ N, \ 17.19\%. \end{array}$

2.1.5. Synthesis of 5-anilino-4-antipyrinylazo-3-hydroxythiophene dyes **12a**–**d**

To a solution of **10** (0.005 mol) in ethanolic sodium ethoxide (prepared by dissolving 0.12 g sodium metal in 30 ml absolute ethanol), the appropriate α -halogenated reagent e.g. chloroacetone, phenacyl chloride, ethyl chloroacetate or chloroacetonitrile (0.005 mol) was added. The reaction mixture was heated under reflux for 2 h. The reaction mixture was poured into cold water, neutralized with dilute HCl, and the solid product that formed was filtered off and recrystallized from ethanol to afford the corresponding thiophene dyes **12a**–**d**.

2.1.5.1. 2-Acetyl-5-anilino-4-antipyrinylazo-3-methylthiophene (**12a**). m.p. = 272–273 °C. Yield = 84%. IR ($\bar{\nu}$ /cm⁻¹): 3254 (NH), 1664 cm⁻¹ (2 CO). Found: C, 64.64; H, 5.28; N, 15.80%. C₂₄H₂₃N₅O₂S (445.54) requires C, 64.70; H, 5.20; N, 15.72%.

2.1.5.2. 5-Anilino-4-antipyrinylazo-2-benzoyl-3-methylthiophene (**12b**). m.p. = 255–256 °C. Yield = 88%. IR ($\bar{\nu}$ /cm⁻¹): 3272 (NH), 1664 cm⁻¹ (2 CO). ¹H NMR (CDCl₃): δ /ppm = 2.50 (s, 3H, CH₃), 2.68 (s, 3H, CH₃), 3.28 (s, 3H, CH₃), 7.02–7.77 (m, 15H, Ar-H), 13.50 (s, H, NH). Found: C, 68.74; H, 4.89; N, 13.86%. C₂₉H₂₅N₅O₂S (507.61) requires C, 68.62; H, 4.96; N, 13.80%.

2.1.5.3. 5-Anilino-4-antipyrinylazo-2-ethoxycarbonyl-3-methylthio phene (**12c**). m.p. = 226–227 °C. Yield = 76%. IR ($\bar{\nu}$ /cm⁻¹): 3278 (NH), 1691 (CO), 1665 cm⁻¹ (CO). ¹H NMR (CDCl₃): δ /ppm = 1.35 (t, 3H, CH₃), 2.70 (s, 6H, 2CH₃), 3.26 (s, 3H, CH₃), 4.35 (q, 2H, CH₂), 7.06–7.56 (m, 10H, Ar-H), 13.49 (s, 1H, NH). Found: C, 63.29; H, 5.38; N, 14.81%. C₂₅H₂₅N₅O₃S (475.56) requires C, 63.14; H, 5.30; N, 14.73%.

2.1.5.4. 5-Anilino-4-antipyrinylazo-2-cyano-3-methylthiophene (**12d**). m.p. = 269–270 °C. Yield = 81%. IR ($\bar{\nu}$ /cm⁻¹): 3248 (NH), 2196 (CN), 1653 cm⁻¹ (CO). MS (M⁺; EI): m/z (%) = 428 (82). Found: C, 64.38; H, 4.72; N, 19.68%. C₂₃H₂₀N₆OS (428.51) requires C, 64.47; H, 4.70; N, 19.61%.

2.1.6. Synthesis of 5-antipyrinylazo-3-cyano-4-methylpyridin-2,6dione (**14**)

A mixture of ethyl 2-antipyrinylhydrazono-acetoacetate **(13)** (0.01 mol), cyanoacetamide (0.01 mol), and potassium carbonate (1.38 g) in acetone (50 ml) was stirred and refluxed until the reaction was completed (about 3–4 hours). The reaction mixture

was poured into ice-water and the crude product was filtered, dried and recrystallized from ethanol to give **14** as red crystals.

m.p. > 300 °C. Yield = 92%. IR ($\bar{\nu}/cm^{-1}$): 3424 (NH), 3112 (OH), 2198 (CN), 1627 cm⁻¹ (broad, CO). ¹H NMR (DMSO): δ /ppm = 2.40 (s, 3H, CH₃), 2.60 (s, 3H, CH₃), 3.25 (s, 3H, CH₃), 7.20–7.55 (m, 5H, Ar-H), 7.95 (s, 1H, NH), 10.70 (s, 1H, OH). Found: C, 59.28; H, 4.46; N, 23.13%. C₁₈H₁₆N₆O₃ (364.36) requires C, 59.34; H, 4.43; N, 23.07%.

2.1.7. 4-Antipyrinylazo-3-methyl-5-hydroxypyrazole-1-carbothioic acid amide (15)

A mixture of ethyl 2-antipyrinylhydrazono-acetoacetate **(13)** (0.01 mol), thiosemicarbazide (0.01 mol), and sodium acetate (1.00 g) in ethanol (50 ml) was refluxed for 4 h. During the reaction, the red product precipitated. The crude product was filtered, washed with water, dried and recrystallized from ethanol to afford the antipyrinylazo-pyrazole **15** as red crystals.

m.p. = 228–230 °C. Yield = 88%. IR ($\bar{\nu}/cm^{-1}$): 3340, 3192, 3162 (NH₂ and OH), 1659 cm⁻¹ (CO). ¹H NMR (DMSO): $\delta/ppm = 2.50$ (s, 3H, CH₃), 2.60 (s, 3H, CH₃), 3.25 (s, 3H, CH₃), 7.20–7.55 (m, 5H, Ar-H), 7.85 (s, 2H, NH₂), 13.20 (s, 1H, OH). Found: C, 51.80; H, 4.68; N, 26.35%. C₁₆H₁₇N₇O₂S (371.42) requires C, 51.74; H, 4.61; N, 26.40%.

2.1.8. Synthesis of 5-amino-4-antipyrinylazo-1-benzenesulfonyl-1H-pyrazol-3-ol (**18**)

The freshly prepared antipyrinyl diazonium chloride (0.005 mol) was added with continuous stirring to a cold (0-5 °C) solution of the benzenesulfonyl-2-cyanoacetic acid hydrazide **16** (0.005 mol) in pyridine (50.0 ml). The reaction mixture was allowed to stir at (0-5 °C) for 2 h, diluted with water, and then the solid product was collected by filtration. The obtained precipitate was dried and recrystallized from ethanol–DMF mixture (3:1).

m.p. = 205–206 °C. Yield = 57%. IR ($\bar{\nu}/cm^{-1}$): 3461, 3432, 3293 (NH₂ and OH), 1658 cm⁻¹ (CO). ¹H NMR (DMSO): δ /ppm = 2.60 (s, 3H, CH₃), 3.20 (s, 3H, CH₃), 7.20-7.50 (m, 10H, Ar-H), 10.15 (s, 2H, NH₂), 12.35 (s, 1H, OH). MS (M⁺; EI): m/z (%) = 453 (12). Found: C, 52.83; H, 4.28; N, 21.71%. C₂₀H₁₉N₇O₄S (453.47) requires C, 52.97; H, 4.22; N, 21.62%.

2.1.9. Synthesis of 5-amino-4-(antipyrinylazo)-3-hydroxypyrazole-1-carbothioic acid phenylamide (**21**)

The freshly prepared antipyrinyl diazonium chloride (0.005 mol) was added with continuous stirring to a cold (0-5 °C) solution of the thiourea derivative **19** (0.005 mol) in pyridine (50.0 ml). The reaction mixture was allowed to stir at (0-5 °C) for 2 h, diluted with cold water, and then the solid product was collected by filtration. The obtained precipitate was dried and recrystallized from ethanol–DMF mixture (5:1).

m.p. = 274–275 °C. Yield = 63%. IR ($\bar{\nu}$ /cm⁻¹): 3430, 3295 (NH₂ and OH), 1652 cm⁻¹ (CO). MS (M⁺; EI): *m*/*z* (%) = 448 (7). Found: C, 56.38; H, 4.54; N, 24.90%. C₂₁H₂₀N₈O₂S (448.50) requires C, 56.24; H, 4.49; N, 24.98%.

2.2. Dyeing procedure and fastness determinations

2.2.1. Dyeing of polyester fabrics

A dispersion of the dye was produced by dissolving the appropriate amount of dye (2% shade) in 1 cm³ acetone and then added dropwise with stirring to the dyebath (liquor ration 20:1) containing 1% Setamol WS (sodium salt of a condensation product of naphthalene sulfonic acid and formaldehyde) as anionic dispersing agent of BASF. The pH of the dyebath was adjusted to 5.5 using aqueous acetic acid and the wetted-out polyester fabrics were added. Dyeing was performed by raising the dyebath temperature to 130 °C at a rate of 3 °C/min, holding at this temperature for

60 min and rapidly cooling to 50 °C. The dyed fibers was rinsed with cold water and reduction cleared (1 g dm⁻³ sodium hydroxide, 1 g dm⁻³ sodium hydrosulfite, 10 min, 80 °C). The samples were rinsed with hot and cold water and finally air-dried.

2.2.2. Color fastness tests

Fastness to washing, perspiration, rubbing, sublimation, and light was tested according to the reported methods [14].

2.3. Color assessment

The colorimetric parameters (Table 2) of the dyed polyester fabrics were determined on a reflectance spectrophotometer (Gretag-Macbeth CE 7000a), equipped with a D65/10° source and barium sulphate as standard blank, UV excluded, specular component included and three repeated measurements average settings.

3. Results and discussion

3.1. Discussion of the synthetic strategy

Condensation of bromoacetone (1) with thiosemicarbazone derivatives 2 by reflux in ethanol containing a catalytic amount of sodium acetate afforded the corresponding 4-substituted-2-thiazolylhydrazones of ketones 3 [15] (Scheme 1). The thiazole C-5 position in derivatives 3 is highly reactive toward diazocoupling with the antipyrinyl diazonium chloride to furnish the corresponding antipyrinylazo-thiazole dyes 4 (Scheme 1). The structure of the highly functionalized thiazolyl dyes 4 was assigned on the basis of their elemental analyses and spectral data. The IR spectra of the dyes 4 clearly indicate the presence of NH absorption band at 3143–3135 cm⁻¹ and CO absorption band at 1664–1653 cm⁻¹. The mass spectrum of 4a (for example) showed the molecular ion peak at m/z = 445 (intensity 74%) corresponding to the molecular weight of the molecular formula C₂₃H₂₃N₇OS.

Treatment of ethyl α -phenylthiocarbamoylacetoacetate (**5**) [16] with the antipyrinyl diazonium chloride in ethanol containing sodium acetate effected acetyl group cleavage (Japp–Klingmann reaction) with the formation of the corresponding thiocarbamoyl intermediate **6**. The versatile ethyl 2-antipyrinylhydrazono-2-phenylthiocarbamoyl acetate derivative **6** underwent heterocyclization with several α -halogenated reagents e.g. chloroacetone, phenacyl chloride, ethyl chloroacetate and chloroacetonitrile in the presence of sodium ethoxide to furnish the corresponding 4-antipyrinylazo-3-hydroxy-2-substituted-thiophene dyes **8a–d**.

The formation of thiophene derivatives **8a**–**d** from the reaction of **6** with the appropriate alkylating agent such as chloroacetone,



Scheme 1.

phenacyl chloride and ethyl chloroacetate seems to follow the sequence outlined in Scheme 2. It is suggested that the reaction starts through nucleophilic attack of the thiolate group to form the nonisolable S-alkylated intermediate **7** which via nucleophilic substitution and intramolecular cyclocondensation by ethanol elimination gave the corresponding polyfunctionally 3-hydroxy-substituted-thiophenes **8a**–**d**.

The structures of the highly functionalized 3-hydroxythiophene dyes **8a**–**d** were elucidated on the basis of their elemental analyses and spectral data. The IR spectrum of the dye **8a** showed absorption peaks at 3142 and 1594 cm⁻¹ due to the presence of hydroxyl group and conjugated carbonyl group, respectively. The strong decrease in the carbonyl and hydroxyl absorption frequencies is attributed to the intramolecular H-bond structure. The ¹H NMR spectrum of **8b** (as an example) showed singlet signals at 2.78 and 3.32 ppm due to methyl protons and a multiplet signal in the region 7.13–7.84 corresponding to the aromatic protons. The presence of a broad singlet at 13.25 ppm was attributed to the presence of NH group, while the hydrogen bonded OH group is downfield shifted to 15.22 ppm. The mass spectrum of **8d** (for example) showed the molecular ion peak at m/z = 430 (intensity 100%) corresponding to the molecular weight of the molecular formula C₂₂H₁₈N₆O₂S.

Treatment of α -phenylthiocarbamoyl-acetylacetone (9) with the antipyrinyl diazonium chloride in ethanol containing sodium acetate effected one acetyl group cleavage (Japp–Klingmann reaction) with the formation of the corresponding thiocarbamoyl intermediate **10**. The versatile 2-antipyrinylhydrazono-thio-acetoacetanilide (**10**) underwent heterocyclization with several α -halogenated reagents e.g. chloroacetone, phenacyl chloride, ethyl chloroacetate and chloroacetonitrile in ethanol-sodium ethoxide solution to furnish the corresponding 4-antipyrinylazo-3-methyl-2-substituted-thiophene dyes **12a–d** (Scheme 3).

The formation of thiophene derivatives **12a**–**d** from the reaction of **9** with the appropriate alkylating agent such as chloroacetone, phenacyl chloride, ethyl chloroacetate and chloroacetonitrile seems to follow the sequence outlined in Scheme 3. It is suggested that the reaction starts through nucleophilic attack of the thiolate group to form the nonisolable S-alkylated intermediate **11** which via nucleophilic addition and intramolecular cyclocondensation by water elimination gave the corresponding 3-methyl-substitutedthiophenes **12a**–**d**.



Scheme 2.



The structures of the highly functionalized 3-methylthiophene dyes **12a**–**d** were elucidated on the basis of their elemental analyses and spectral data. The IR spectrum of the dye **12a** showed an absorption peak at 3254 cm^{-1} corresponding to NH and a broad absorption peak at 1664 cm^{-1} corresponding to the carbonyl groups. The ¹H NMR spectrum of **12b** (as an example) showed singlet signals at 2.50, 2.68 and 3.28 ppm due to methyl protons and a multiplet signal in the region 7.02–7.77 corresponding to the aromatic protons, in addition to a singlet signal at 13.50 ppm due to the presence of NH group. The mass spectrum of **12d** showed the molecular ion peak at m/z = 428 (intensity 82%) corresponding to the analysis of the molecular weight of the molecular formula C₂₃H₂₀N₆OS.

Pyridones and pyrazolones as coupling components have been shown to be important colorants for yellow to orange dyes in industrial applications. Moreover, N-substituted pyridone azo disperse dyes, which were derived from benzenoid derivatives as coupling components, show good color strength, luminous colors and excellent light fastness [17–19]. It is further reported that pyrazolones derivatives as coupling component can be used to synthesize yellow 4-arylazo pyrazolones dyes [20].

5-Antipyrinylazo-3-cyano-4-methylpyridin-2,6-dione (14) (Scheme 4) was synthesized by cyclization of ethyl 2-anti pyrinylhydrazono-acetoacetate (13) with cyanoacetamide in hot acetone containing potassium carbonate. The chemical structure of 14 was elucidated on the basis of its elemental and spectroscopic analysis. The IR spectrum displayed absorption bands at 3424 corresponding to NH, 3112 for the hydroxyl group, 2198 the nitrile group (CN) and 1627 cm⁻¹ corresponding to the carbonyl groups. The ¹H NMR spectrum revealed a singlet signal at δ 2.40 due to methyl protons (pyridone-CH₃), a singlet signals at δ 2.60 and 3.25 due the methyl protons, a singlet signal at δ 7.95 for NH proton and a singlet signal at δ 10.70 due to OH proton.

On the other hand, cyclization of **13** with thiosemicarbazide by heating in ethanol containing sodium acetate afforded the antipyrinylazo-pyrazolone derivative **15** (Scheme 4). The IR spectrum of **15** showed the characteristic absorption bands for the NH₂ and OH groups at 3340, 3192, 3162 cm⁻¹ and absorption band at 1659 cm⁻¹ for the carbonyl group. The ¹H NMR spectrum revealed singlet signals at δ 2.50, 2.60 and 3.25 for the methyl protons, a multiplet at δ 7.20–7.55 for the aromatic protons, a singlet at



 δ 7.85 for the amino protons (NH₂), and a singlet at δ 13.20 due to OH proton.

The azo coupling between antipyrinyl diazonium chloride **1** and benzenesulfonyl-2-cyanoacetic acid hydrazide **16** did not stop at the antipyrinylhydrazono intermediate **17** but this cyclized directly to afford the corresponding 4-antipyrinylazo-1-benzenesulfonyl-1*H*-pyrazole **18** (Scheme 5). The pyrazole structure **18** was established on the basis of the elemental and spectroscopic data. The IR spectrum clearly indicates the lack of cyano group absorption and showed the amino group absorption at 3461 and 3293 cm⁻¹. Furthermore, the ¹H NMR spectrum revealed singlet signals at δ 2.60 and 3.20 for the methyl protons, a multiplet at δ 7.20–7.50 for the aromatic protons, a singlet at δ 10.15 for the amino protons (NH₂), and a singlet at δ 12.35 due to OH proton.

The azo coupling between antipyrinyl diazonium chloride and thiourea derivative **19** afforded the corresponding 4-antipyrinylazo-3-hydroxy-pyrazole-1-carbothioic acid phenylamide **21** through in situ heterocyclization of the antipyrinyl-hydrazono intermediate **20** (Scheme 6). The chemical structure of **21** was secured by the correct elemental and spectroscopic data.

The dyes **18** and **21** may exist in two tautomeric forms, namely the antipyrinylazopyrazolone form **A** and the antipyrinylazohydroxy-pyrazole form **B**.





3.1.1. Conclusion

Several antipyrinylazo dyes were prepared, e.g. thiazole, thiophene, pyridone, and pyrazole moieties. The newly synthesized dyes were applied as disperse dyes for dyeing polyester fabrics and their fastness properties were evaluated. Also the position of color in CIELAB coordinates (L^* , a^* , b^* , H^* , C^*) was assessed.

3.2. Absorption spectral characteristics

Generally, variation in color of these dyes results from the alternation in coupling components. Since the synthesized dyes obtained varied in color from yellow to reddish violet, a convenient method of measuring the color of the compound was to study the absorption spectra of their solutions. The visible absorption maxima for the synthesized dyes were measured in chloroform and are listed in Table 2. The absorption maxima of the synthesized dyes ranged from 415 to 480 nm. Within the series of antipyrinylazo dyes investigated, the relation between the shift observed in the absorption maxima, and polar characteristics of the coupling moieties, may be summarized as follows: (i) The dye **4a** ($\lambda_{max} = 454$) substituted with phenylethylidene group absorb maximally at longer wavelengths than the corresponding dye with cyclohexylidene group **4b** ($\lambda_{max} = 438$). (ii) The antipyrinylazo-3methylthiophene dyes 12 absorb maximally at longer wavelengths than the corresponding antipyrinylazo-4-hydroxythiophene dyes 8.

3.3. Dyeing and fastness properties

The development of disperse dyes "Dyes insoluble in water and applied from aqueous dispersion rather than from solution" was a revolutionary solution to the problem of coloration of synthetic fibers. The dyes were essentially insoluble in water and were prepared for application by being ground, in the presence of dispersing agents, to microscopically fine particles of the order of a few microns and, then, by pan drying the resultant suspension. The resulting readily dispersible solid could then dye the more hydrophobic acetate fiber by partitioning into the fiber from low dye bath concentrations. The synthesized disperse dyes under investigation **4**, **8**, **12**, **14**, **15**, **18** and **21**) were applied to polyester fabric at 2% shade by high-temperature pressure technique (130 °C) and gave generally deep and bright hues, ranging from yellow to reddish-violet. The dyeings on polyester fabrics were evaluated in terms of their fastness properties. The dyes gave excellent

Table 1				
Fastness properties of the synthesized	dyes 4 , 8 ,	12, 14, 15, 18	and 21 on p	olyester fabrics.

Dye Washing		Perspiration		Rubbing		Sublimation fastness		Light (40 h)
		Acid	Alkali	Dry	Wet	Staining at 180 °C	Staining at 210 °C	
4a	4-5	4-5	4-5	2-3	3	4-5	3–4	2-3
4b	4	4	4	4	4-5	4-5	3–4	2-3
8a	4-5	4-5	4-5	2-3	3-4	4-5	4-5	3-4
8b	4-5	4-5	4-5	2-3	3	4-5	4-5	4
8c	4-5	4-5	4-5	2-3	2-3	4-5	4-5	3-4
8d	4-5	4-5	4-5	4	3-4	4-5	4-5	4
12a	4-5	4-5	4-5	2-3	2-3	4-5	4-5	4
12b	4-5	4-5	4-5	2-3	2-3	4-5	4	4-5
12c	4	4	4	2-3	3	4	2-3	4
12d	4-5	4-5	4-5	3-4	3-4	4-5	4-5	3-4
14	4-5	4-5	4	2-3	3	4-5	4-5	3
15	4-5	4-5	4-5	3	3-4	4-5	4-5	3
18	4-5	4-5	4-5	4	4	4-5	4	2-3
21	4-5	4-5	4-5	4-5	4–5	4-5	4-5	2-3

uniformity of coloration on polyester fabrics and the overall fastness properties of the dyes are shown in Table 1.

3.3.1. Fastness to washing

The dyed polyester fabrics have very good fastness to washing according to the international geometric Grey scale. The rather good fastness properties to washing may be due to the absence of solubilizing groups, which renders solubility, and wash ability of the dye-out of the fabrics.

3.3.2. Fastness to perspiration: (acid and alkaline)

The results obtained in Table 1; show that the fastness to acid and alkaline perspiration is rather satisfactory ranging 4–5. Such results indicate the relative stability of the prepared antipyrinylazothiazole and/or antipyrinylazo-thiophene dyes in acid and alkaline medium, similar to the conditions used in this test.

3.3.3. Fastness to rubbing

The test is designed to determine the amount of color transferred from the surface of colored fabrics to another surface by rubbing. The rubbing fastness test was carried out using the AATCC crockmeter. Most of the dyes have a moderate (3) to good (4) rubbing fastness.

3.3.4. Fastness to sublimation

Sublimation fastness properties of synthesized dyes expressed as color staining on the undyed polyester piece ranged from good to very good. In most cases, the best sublimation fastness was obtained by the antipyrinylazo-thiophene dyes (e.g. dyes **8** and **12**).

Table 2

Color coordinates of the dyes 4, 8, 12, 14, 15, 18 and 21 (light source $= D65/10^\circ$ observer).

Dye	L^*	С*	H^*	<i>a</i> *	b*	K/S	UV λ_{max}
4a	63.90	16.40	63.00	7.40	14.60	0.72	454
4b	67.90	13.70	71.30	4.40	12.90	0.45	438
8a	57.10	46.60	65.30	19.40	42.30	3.30	468
8b	66.90	58.80	70.40	19.70	55.30	2.77	466
8c	71.10	52.30	68.30	19.30	48.50	1.70	474
8d	65.30	44.90	60.80	21.90	39.20	1.80	470
12a	72.20	37.50	51.70	23.20	29.40	0.81	478
12b	61.80	37.70	49.60	24.50	28.70	1.39	480
12c	61.80	51.30	50.60	32.50	39.70	2.90	480
12d	68.20	34.20	45.60	23.90	24.40	1.00	476
14	84.20	15.30	57.60	8.20	22.90	0.71	458
15	87.80	11.60	91.00	-0.20	21.60	0.66	444
18	76.00	17.60	69.10	6.30	26.50	0.58	424
21	83.80	15.50	82.00	2.17	25.40	0.68	415

3.3.5. Fastness to light

Light fastness of the synthesized dyes on polyester was moderate (according to the blue scale) and is significantly affected by the nature of the substituents in the coupling component. In most cases, the best light fastness (good, 4-5 of the blue wool standard scale 1-8) was obtained by the antipyrinylazo-thiophene dyes **8** and **12**.

3.4. Color assessment

The color parameters of the dyed polyester fabrics were measured using the GretagMacbeth CE 7000a spectrophotometer. The assessment of color-dyed fabrics was made in terms of tristimulus colorimetry. The following CIELAB coordinates are measured, lightness (L^*), chroma (C^*), hue angle from 0° to 360° (h), (a^*) value represents the degree of redness (positive) and greenness (negative) and (b^*) represents the degree of yellowness (positive) and blueness (negative).

The measured *K*/*S* value given by the reflectance spectrometer is directly correlated with the dye concentration on the dye substrate according to the Kubelka–Munk equation: $K/S = (1 - R)^2/2R$. Where K = absorbance coefficient, S = scattering coefficient, R = reflectance ratio.

The color of the synthesized dyes (4, 8, 12, 14, 15, 18 and 21) on polyester fabric was evaluated using the CIELAB system in terms of L^{*}, a^{*} and b^{*}. The color coordinates listed in Table 2 indicate that the dyes have good affinity to polyester fabric and tend to give the following conclusions: (i) The dyes under investigation showed good affinity toward polyester fabric at high temperature (130 °C) and gave generally deep and bright intense hues, ranging from yellow to reddish violet. (ii) The color hues of the dyes under investigation on polyester fabric are shifted to the yellowish direction on the yellow-blue axis according to the positive values of b^* . (iii) The color hue of the dye **15** on polyester fabric is shifted to the greenish direction on the red-green axis as indicated from the negative value of a^* (-0.20). While the color hues of the other synthesized dyes on polyester fabrics are shifted to the reddish direction on the red-green axis as according to the positive values of a^* for these dyes.

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