



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

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### 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,  $^1\text{H}$  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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## 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-pyridones, and 4-antipyrinylazo-pyrazoles and their applications as disperse dyes for dyeing polyester fabrics.

## 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.  $^1\text{H}$  NMR spectra were measured on a Bruker WP 300 in  $\text{CDCl}_3$ ,  $\text{DMSO}-d_6$  or  $\text{CF}_3\text{COOD}$  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 °C) of the thiazole derivatives **3** (0.005 mol) in pyridine (30 ml), a cold solution of freshly prepared

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antipyrynyl 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 antipyrynylazo-thiazole dyes **4** thus obtained, were dried and recrystallized from ethanol.

**2.1.1.1. N-(5-Antipyrynylazo-4-methylthiazol-2-yl)-N'-(1-phenylethylidene)-hydrazine (4a).** m.p. = 160–162 °C. Yield = 67%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3143 (NH), 1653  $\text{cm}^{-1}$  (CO). MS ( $M^+$ ; EI):  $m/z$  (%) = 445 (74). Found: C, 61.78; H, 5.12; N, 22.09%.  $\text{C}_{23}\text{H}_{23}\text{N}_7\text{OS}$  (445.54) requires C, 62.00; H, 5.20; N, 22.01%.

**2.1.1.2. N-(Cyclohexylidene)-N'-(5-antipyrynylazo-4-methylthiazol-2-yl)-hydrazine (4b).** m.p. = 145–145 °C. Yield = 65%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3135 (NH), 1664  $\text{cm}^{-1}$  (CO). Found: C, 59.77; H, 5.82; N, 23.08%.  $\text{C}_{21}\text{H}_{25}\text{N}_7\text{OS}$  (423.53) requires C, 59.55; H, 5.95; N, 23.15%.

**2.1.2. Synthesis of ethyl 2-antipyrynylhydrazono-2-phenylthiocarbonyl acetate (6)**

The freshly prepared antipyrynyl diazonium chloride (0.01 mol) was added with continuous stirring to a cold (0–5 °C) solution of the thiocarbonyl 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 °C) for 2 h, and then the solid was collected by filtration. The obtained precipitate was dried and recrystallized from ethanol.

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

**2.1.3. Synthesis of 5-anilino-4-antipyrynylazo-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  $\alpha$ -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-antipyrynylazo-3-hydroxythiophene (8a).** m.p. = 234–235 °C. Yield = 83%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3221, 3142 (NH and OH), 1635 (CO), 1594  $\text{cm}^{-1}$  (CO). Found: C, 61.82; H, 4.79; N, 15.58%.  $\text{C}_{23}\text{H}_{21}\text{N}_5\text{O}_3\text{S}$  (447.51) requires C, 61.73; H, 4.73; N, 15.65%.

**2.1.3.2. 5-Anilino-4-antipyrynylazo-2-benzoyl-3-hydroxythiophene (8b).** m.p. = 237–239 °C. Yield = 80%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3258, 3138 (NH and OH), 1662 (CO), 1589  $\text{cm}^{-1}$  (CO).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 2.78 (s, 3H,  $\text{CH}_3$ ), 3.32 (s, 3H,  $\text{CH}_3$ ), 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%.  $\text{C}_{28}\text{H}_{23}\text{N}_5\text{O}_3\text{S}$  (509.58) requires C, 66.00; H, 4.55; N, 13.74%.

**2.1.3.3. 5-Anilino-4-antipyrynylazo-2-ethoxycarbonyl-3-hydroxythiophene (8c).** m.p. = 130–132 °C. Yield = 78%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3266, 3152 (NH and OH), 1655 (CO), 1591  $\text{cm}^{-1}$  (CO).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 1.35 (t, 3H,  $\text{CH}_3$ ), 2.72 (s, 3H,  $\text{CH}_3$ ), 3.32 (s, 3H,  $\text{CH}_3$ ), 4.32 (q, 2H,  $\text{CH}_2$ ), 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%.  $\text{C}_{24}\text{H}_{23}\text{N}_5\text{O}_4\text{S}$  (477.54) requires C, 60.36; H, 4.85; N, 14.67%.

**2.1.3.4. 5-Anilino-4-antipyrynylazo-2-cyano-3-hydroxythiophene (8d).** m.p. = 158–160 °C. Yield = 87%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3230, 3174 (NH and OH), 2179 (CN), 1652  $\text{cm}^{-1}$  (CO). MS ( $M^+$ ; EI):  $m/z$  (%) = 430 (100). Found: C, 61.20; H, 4.32; N, 19.60%.  $\text{C}_{22}\text{H}_{18}\text{N}_6\text{O}_2\text{S}$  (430.48) requires C, 61.38; H, 4.21; N, 19.52%.

**2.1.4. Synthesis of 2-antipyrynylhydrazono-thioacetacetanilide (10)**

The freshly prepared antipyrynyl diazonium chloride (0.01 mol) was added with continuous stirring to a cold (0–5 °C) solution of the thiocarbonyl 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.

m.p. = 200–202 °C. Yield = 89%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3254 (NH), 1653  $\text{cm}^{-1}$  (2 CO).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 2.15 (s, 3H,  $\text{CH}_3$ ), 2.60 (s, 3H,  $\text{CH}_3$ ), 3.15 (s, 3H,  $\text{CH}_3$ ), 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%.  $\text{C}_{21}\text{H}_{21}\text{N}_5\text{O}_2\text{S}$  (407.49) requires C, 61.90; H, 5.19; N, 17.19%.

**2.1.5. Synthesis of 5-anilino-4-antipyrynylazo-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  $\alpha$ -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-antipyrynylazo-3-methylthiophene (12a).** m.p. = 272–273 °C. Yield = 84%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3254 (NH), 1664  $\text{cm}^{-1}$  (2 CO). Found: C, 64.64; H, 5.28; N, 15.80%.  $\text{C}_{24}\text{H}_{23}\text{N}_5\text{O}_2\text{S}$  (445.54) requires C, 64.70; H, 5.20; N, 15.72%.

**2.1.5.2. 5-Anilino-4-antipyrynylazo-2-benzoyl-3-methylthiophene (12b).** m.p. = 255–256 °C. Yield = 88%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3272 (NH), 1664  $\text{cm}^{-1}$  (2 CO).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 2.50 (s, 3H,  $\text{CH}_3$ ), 2.68 (s, 3H,  $\text{CH}_3$ ), 3.28 (s, 3H,  $\text{CH}_3$ ), 7.02–7.77 (m, 15H, Ar-H), 13.50 (s, H, NH). Found: C, 68.74; H, 4.89; N, 13.86%.  $\text{C}_{29}\text{H}_{25}\text{N}_5\text{O}_2\text{S}$  (507.61) requires C, 68.62; H, 4.96; N, 13.80%.

**2.1.5.3. 5-Anilino-4-antipyrynylazo-2-ethoxycarbonyl-3-methylthiophene (12c).** m.p. = 226–227 °C. Yield = 76%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3278 (NH), 1691 (CO), 1665  $\text{cm}^{-1}$  (CO).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 1.35 (t, 3H,  $\text{CH}_3$ ), 2.70 (s, 6H, 2 $\text{CH}_3$ ), 3.26 (s, 3H,  $\text{CH}_3$ ), 4.35 (q, 2H,  $\text{CH}_2$ ), 7.06–7.56 (m, 10H, Ar-H), 13.49 (s, 1H, NH). Found: C, 63.29; H, 5.38; N, 14.81%.  $\text{C}_{25}\text{H}_{25}\text{N}_5\text{O}_3\text{S}$  (475.56) requires C, 63.14; H, 5.30; N, 14.73%.

**2.1.5.4. 5-Anilino-4-antipyrynylazo-2-cyano-3-methylthiophene (12d).** m.p. = 269–270 °C. Yield = 81%. IR ( $\bar{\nu}/\text{cm}^{-1}$ ): 3248 (NH), 2196 (CN), 1653  $\text{cm}^{-1}$  (CO). MS ( $M^+$ ; EI):  $m/z$  (%) = 428 (82). Found: C, 64.38; H, 4.72; N, 19.68%.  $\text{C}_{23}\text{H}_{20}\text{N}_6\text{OS}$  (428.51) requires C, 64.47; H, 4.70; N, 19.61%.

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

A mixture of ethyl 2-antipyrynylhydrazono-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

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