



Disperse Dyes Based on Pyrazolopyrimidinones I: Their Dyeing Applications and Antimicrobial Activities

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Abstract : The goal of this study is to synthesize a series of disperse dyes based on pyrazolopyrimidinones. These dyes were synthesized by reaction of arylhydrazonopyrazolones with enamines under acidic condition. Their structures were established by using Elemental analysis, FTIR, Mass, UV and NMR spectroscopy. These disperse dyes were applied to polyester fabrics, their fastness properties were tested. In addition, their biological activities against Gram negative and Gram positive bacteria were conducted.

Introduction

Disperse dyes are non-ionic dyes with sparing solubility in water. Disperse dyes are capable to retain comparatively better selectivity for hydrophobic fabrics, such as acetate, nylon and polyester. Moreover, disperse dyes have excellent tinctorial value. Azo disperse dyes are considered as class of organic colorants which consist of at least a conjugated chromophore azo group in association with one or more aromatic or heteroaromatic ring system ¹. They are capable of producing high intensity color and have excellent technical properties^{2,3}. The disperse dyes based on pyrazolopyrimidines and its derivatives have biological activities ⁴ and applicable for dyeing polyesters^{5,6,7,8}. In continuation of our interest in synthesis of condensed pyrazolopyrimidinones new dyestuffs ^{9,10,11}, the present study deals with efficient synthesis of condensed arylazopyrazolopyrimidinones disperse dyes and studying their dyeing properties on polyester fabrics. The antibacterial activity of pyrazolopyrimidinones disperse dyes against Gram negative and Gram positive bacteria was investigated.

Experimental

General

All melting points were determined on an electrothermal digital melting point apparatus and are uncorrected. The infrared spectra were recorded on IR-470 infrared spectrophotometer, Shimadzu; and Pye Unicam SP3-100 spectrophotometer using KBr pellet technique at Assiut University. ¹H-NMR spectra were measured on a Varian 300 MHz in deuterated dimethylsulphoxide (DMSO-d₆) using tetramethylsilane (TMS) as internal reference and the chemical shifts are expressed in ppm at Cairo University. Mass spectra were performed on HP model MS-5988 at Cairo University. Microanalyses for C, H, N and halogen were performed on a Vario El Elemental analyzer at Cairo University.

General Procedure for the Synthesis of azo Disperse Dyes 3a-e

A mixture of arylhydrazonopyrazolones (4.1, 0.02 M) and enamionones (3.5 g, 0.02 M) was dissolved in glacial acetic acid 5 mL and refluxed for 3 h. the formed solid was collected and crystallized from DMF/water to give dyes 3a-e.

7-Phenyl-3-phenylazo-pyrazolo[1,5-a]pyrimidin-2-one (3a)

Yield 3.3 g (51.4%), m.p. 206-208 °C. IR (KBr): $\nu = 3435 \text{ cm}^{-1}$ (NH), 3025 cm^{-1} (CH-arom.), 1632 cm^{-1} (C=O of amid group), 1592 cm^{-1} (C=C). UV(DMSO) $\lambda_{\text{max}} = 425 \text{ nm}$. MS: m/z = 315 (M+, 88%), 238 (100%), 210 (36%), 128 (30%). ¹H-NMR (DMSO-d₆) 7.37 -7.78 (m, 10H, arom-H), 8.07 (d, 2H, *J* = 3.6 MHz, arom-H), 8.73 (d, 1H, *J* = 4.8 MHz, NH). Anal. Calcd. For C₁₈ H₁₃ N₅ O (315): C 68.57; H 4.13, N 22.22. Found: C 68.20; H 3.59; N 22.10.

7-Phenyl-3-p-tolylazo-pyrazolo[1,5-a]pyrimidin-2-one (3b).

Yield 4.2 g (67.14%), m.p. 235-237 °C. IR (KBr): $\nu = 3493 \text{ cm}^{-1}$ (NH), 3035 cm^{-1} (CH-arom.) , 2930 cm^{-1} (CH-aliph.), 1632 cm^{-1} (C=O of amid group), 1578 cm^{-1} (C=C). UV(DMSO) $\lambda_{\text{max}} = 428 \text{ nm}$. MS: m/z = 328 (M+, 94%), 315 (14%), 252 (75%), 224 (33%). ¹H-NMR (DMSO-d₆) 2.35 (s, 3H, CH₃), 7.29 (d, 2H, *J* = 8.1MHz, arom-H), 7.45 (d, 2H, *J* = 4.8 MHz, arom-H), 7.56-7.68 (m,5H,arom-H), 8.05 (d, 2H, *J* = 8.4 MHz, arom-H), 8.70 (d, 1H, *J* = 4.8 MHz, NH). Anal. Calcd. for C₁₉H₁₅ N₅O (328): C 69.30; H 4.56, N 21.27. Found: C 68.80; H 4.05; N 21.20.

3-(4-Chloro-phenylazo)-7-phenyl-pyrazolo[1,5-a]pyrimidin-2-one (3c).

Yield 5.4 g (77.8%), m.p. 246-248 °C. IR (KBr): $\nu = 3443 \text{ cm}^{-1}$ (NH), 3061 cm^{-1} (CH-arom.), 1633 cm^{-1} (C=O of amid group), 1601 cm^{-1} (C=C). UV(DMSO) $\lambda_{\text{max}} = 423 \text{ nm}$. MS: m/z = 349.5 (M+, 73%), 238 (100%), 210 (34%), 128 (58%). ¹H-NMR (DMSO-d₆) 7.46 (d, 2H, *J* = 4.8 MHz, arom-H), 7.54-7.64 (m, 5H, arom-H), 7.79 (d, 2H, *J* = 8.7 MHz, arom-H), 8.06 (d, 2H, *J* = 8.4, arom-H), 8.73 (d, 1H, *J* = 4.8 MHz, NH). Anal. Calcd. for C₁₈H₁₂ N₅OCl (349.5): C 61.80; H 3.43, N 20.03. Found: C 61.51; H 3.15; N 20.25.

3-(4-Bromo-phenylazo)-7-phenyl-pyrazolo[1,5-a]pyrimidin-2-one (3d).

Yield 6.4 g (81.6%), m.p. 267-269 °C. IR (KBr): $\nu = 3446.43 \text{ cm}^{-1}$ (NH), 3054 cm^{-1} (CH-arom.) , 1645 cm^{-1} (C=O of amid group), 1621 cm^{-1} (C=C).UV(DMSO) $\lambda_{\text{max}} = 417 \text{ nm}$. MS: m/z = 394 (M+, 36%), 238 (94%), 210 (32%), 182 (28%). ¹H-NMR (DMSO-d₆) 7.47 (d, 2H, *J* = 4.8 MHz, arom-H), 7.61 (d, 2H, *J* = 5.10 MHz, arom-H), 7.67-7.74 (m, 5H, arom-H), 8.05 (d, 2H, *J* = 7.8MHz, arom-H), 8.73 (d, 1H, *J* = 4.8 MHz, NH). Anal. Calcd. for C₁₈H₁₂ N₅OBr (394): C 54.82; H 3.05, N 17.77. Found: C 55.00; H 2.75; N 17.40.

3-(4-Nitro-phenylazo)-7-phenyl-pyrazolo[1,5-a]pyrimidin-2-one (3e).

Yield 3.4 g (61.4%), m.p. > 300 °C. IR (KBr): $\nu = 3415 \text{ cm}^{-1}$ (NH), 3067 cm^{-1} (CH-arom.) , 1644.21 cm^{-1} (C=O of amid group), 1606 cm^{-1} (C=C). UV(DMSO) $\lambda_{\text{max}} = 425 \text{ nm}$. MS: m/z = 360 (M+, 49%), 238 (56%), 210 (18%), 182 (14%). ¹H-NMR (DMSO-d₆) 7.67 (m, 5H, arom-H), 7.91 (d, 2H, *J* = 8.70 MHz, arom-H), 8.07 (d, 2H, *J* = 4.8 MHz, arom-H), 8.33 (d, 2H, *J* = 7.8 MHz, arom-H), 7.78 (d, 1H, *J* = 4.2 MHz, NH). Anal. Calcd. for C₁₈H₁₂ N₆O₃ (360): C 60.00; H 3.34, N 23.34. Found: C 59.39; H 2.90; N 23.50.

Fabrics

Scoured and bleached 100% polyester fabric was supplied by El-Mahalla El-Kobra Company, Egypt. The fabrics were scoured in aqueous solution having a liquor ratio of 1:50 and containing 2 g/L of nonionic detergent solution (Hostapal; Clariant, Swiss) and 2 g/L of Na₂CO₃ at 50 °C for 30 min to remove waxes and impurities, then rinsed thoroughly in cold tap water, and dried at room temperature. The dyeing was carried out in an IR laboratory scale dyeing machine at National Research Centre.

Dyeing process

All dyes were used as pure powder in the same form as prepared without milling. Fabric samples (2 g) were introduced into a flask containing a dyebath of 2% (o.w.f) dye shade and Matexil DA-N (supplied by ICI Company, UK) as dispersing agent at 130 °C with a 1:50 liquor ratio; during dyebath preparation, the dye was

mixed with 10 drops of DMF and then mixed with dispersing agent, and water was added to prepare a homogeneous dispersion of the dye. The pH was adjusted to 4.5 by using acetic acid. At the end of the dyeing process, the dyed samples were removed, rinsed in warm water, and subjected to reduction clearing in a solution comprising 2 g/L of sodium hydrosulphite and 2g/L of sodium hydroxide (caustic soda) for 10 min at 60 °C, with a liquor ratio of 1:40, and the reduction-cleared sample was rinsed thoroughly in water. The dyed samples were removed, rinsed in tap water, and allowed to dry in the open air.

Color Measurements

The colorimetric parameters of the dyed polyester fabrics were determined on a reflectance spectrophotometer. The color yields of the dyed samples were determined by using the light reflectance technique performed on an UltraScan PRO D65 UV/VIS Spectrophotometer. The color strengths, expressed as K/S values, were determined by applying the Kubelka-Mink equation¹⁰.

$$K/S = [(1 - R)^2 / 2R] - [(1 - R_0)^2 / 2 R_0]$$

Where, R is the reflectance of colored samples and K and S are the absorption and scattering coefficients, respectively. R₀ = decimal fraction of the reflectance of the undyed fabric.

CIE Lab Difference

$$\Delta E = [\Delta L^2 + \Delta a^2 + \Delta b^2]^{1/2}$$

ΔE : the total color difference between the sample and the standard: (*L*) represents the white-black axis, (*a*) represents the red-green axis and finally (*b*) represents the yellow-blue axis.

Color Fastness

Color fastness to washing

The color fastness to washing was determined according to the ISO 105-C02:1989 method¹². The composite specimens were sewed between two pieces of bleached cotton and wool fabrics, and then immersed into an aqueous solution containing 5 g/L of nonionic detergents at a liquor ratio of 1:50. The bath was thermostatically adjusted to 60 °C for 30 min. After the desired time, samples were removed, rinsed twice with occasional hand squeezing, and then dried. Evaluation of the wash fastness was established using the grey scale for color change.

Color fastness to rubbing

Color fastness to rubbing was determined according to the ISO 105-X12:1987 test method¹³. The test is designed for determining the degree of color that may transfer from the surface of the colored fabrics to another surface by rubbing. The current test can be carried out on dry and wet fabrics.

Dry crocking test

The test specimen was placed flat on the base of the crockmeter. A white testing cloth was mounted. The covered finger was lowered onto the test specimen and caused to slide back and forth 20 times. The white test sample was then removed for evaluation using the grey scale for staining.

Wet crocking test

The white test sample was thoroughly (65%) wetted with water. The procedure was run as before. The white test samples were air dried before evaluation.

Color fastness to perspiration

Two artificial perspiration solutions (acidic and alkaline) were prepared as follows according to the ISO 105-E04:1989 test method¹⁴. The acidic solution was prepared by dissolving L-histidine monohydrochloride monohydrate (0.5 g), sodium chloride (5 g), and sodium dihydrogen orthophosphate dihydrate (2.2 g) in one liter of distilled water. Then, the pH was finally adjusted to 5.5 using 0.1 N NaOH. To prepare the alkaline

solution, L-histidine monohydrochloride monohydrate (0.5 g), sodium chloride (5 g), and disodium hydrogen orthophosphate dihydrate (2.5 g) were all dissolved in one liter of distilled water. The pH was adjusted to 8 using 0.1 N NaOH. The fastness test was performed as follows. The 5 cm × 4 cm colored specimen was sewn between two pieces of uncolored specimens to form a composite specimen. The composite samples were immersed for 15-30 min in both solutions with well agitation and squeezing to ensure complete wetting. The test specimens were placed between two plates of glass or plastic under a force of about 4-5 kg. The plates containing the composite specimens were then held vertically in an oven at 37 ± 2 °C for 4 h. The effect on the color of the tested specimens was expressed and defined by reference to the grey scale for color change.

Color fastness to light

The light fastness test was carried out in accordance with the ISO 105-B02:1988 test method¹⁵, using a carbon arc lamp and continuous light for 35 h. The effect on the color of the tested samples was recorded by reference to the blue scale for color change.

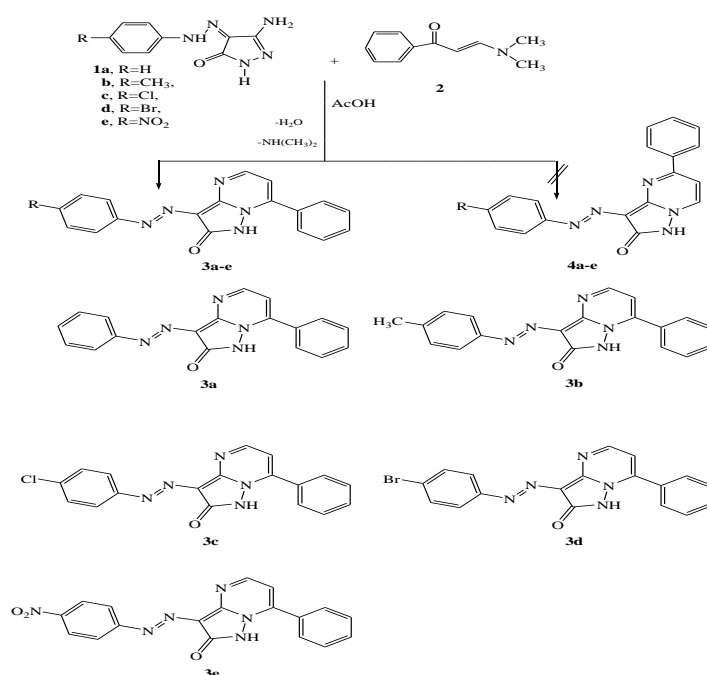
Antimicrobial Activities Test

All prepared disperse dyes were screened in vitro for their antibacterial activities against *Escherichia coli*, *Pseudomonas aeruginosa* and *Serratia marcescens* as Gram negative bacteria and *Bacillus cereus*, *Micrococcus luteus* and *Staphylococcus aureus* as Gram positive bacteria by the agar diffusion technique¹⁶. 1 mg/ml solution in dimethylformamide (DMF) was used. The bacteria are maintained on nutrient agar. DMF showed no inhibition zones. The agar media were inoculated with different microorganism's culture tested after 24 hours of inoculated at 37 °C for bacteria. The diameter of inhibition zone (mm) was measured. The data obtained is summarized in Table 3 (These tests conducted at Assiut University).

Results and Discussion

Synthesis and Characteristics

Our designed strategy for the synthesis of some azo disperse dyes based on pyrazolopyrimidinone is displayed in Scheme 1. Arylhydrazonopyrazolones **1a-e** react with enaminone **2** to yield the corresponding pyrazolo[1,5-a]pyrimidinones disperse dyes **3a-e** whose identities were elucidated by using elemental analysis, mass spectral data, ¹H-, ¹³C-NMR spectroscopy as well as the IR, and UV. The possible formation of regioisomers **4a-e** in reactions of **1a-e** with enaminone **2** is ruled out based not only on 2D NMR experiments⁹, but also on X-ray crystallographic structure that performed by one of us for such dyes^{10,11}.



Scheme 1: Synthesis of arylazopyrazolopyrimidinones disperse dyes.

Dyeing and Fastness Properties

Arylazopyrazolopyrimidinones dyes **3a-e** were applicable for dyeing polyester fabrics as a substrate (2% shade). The obtained data given in Table 1, reveals that the dyeing substrate have diverse K/S and total color difference ΔE . The difference in K/S and ΔE depends on the substitutes existence or its position in the dye molecules¹⁷. The data outlined in Table 1 reveals that the K/S of the dye **3b** (29.80) is much higher than the K/S of dyes **3d** and **3e** (21.90 and 9.41). Also, the total color difference ΔE of dye **3b** (93.26) is much higher than the ΔE of dyes **3d** and **3e** (86.43 and 74.33). We used CIELAB coordinates to express the dyeing color of the substrate as measured: lightness (L); (a) (red–green axis), (b) (yellow-blue axis); chroma (c); hue angle from 0 to 360° (h). Generally, The positive values of (b) = 80.24, 78.36 and 78.85 revealed that the hues of the pyrazolopyrimidinones disperse dyes **3a-c** on the substrate moved to the yellowish trend. The hues of the disperse dye **3e** on the substrate moved to the greenish trend; this was elucidated by the small value of (a) = 4.20.

Table 1. Optical measurements of azo disperse dyes on the polyester fabrics.

Dye No	K/S	λ_{\max}	L	a	b	C	h	ΔE
3a	32.13	460	61.34	22.96	80.24	83.72	74.04	92.93
3b	29.80	460	60.13	27.31	78.36	83.78	70.79	93.26
3c	26.76	445	61.56	19.71	78.85	84.22	75.97	93.28
3d	21.90	440	65.29	12.73	65.29	77.75	80.55	86.43
3e	9.41	445	66.98	4.20	63.11	64.92	86.19	74.33

Fastness Properties

Washing fastness

The washing fastness increase when electron-attracting groups exist in the dye structure, it may be due to these dyes under investigate are clearly diffused into the pores of the substrate and engaged in their positions by a variety of forces as Van der Waal. Electron-withdrawing substituents permit hydrogen bonding and Van der Waal forces with the dyed fabrics consequently, increases their washing fastness, as shown in Table 2.

Rubbing and Perspiration fastness

The obtained data outlined in Table 2 showed that dyed substrate have very good rubbing fastness and excellent perspiration fastness, these results may be attributed to excellent intra-fiber diffusion of the dye molecules inside the substrate and the dye molecule particle size is assumed comparatively enormous.

Light fastness

Several reports demonstrate fading in dyes is a result of disintegration of azo group as photolysis, oxidation, or reduction^{18, 19}. The rates photolysis, oxidation, or reduction should be sensitive to conditions treatment, the type of substrate and the dyes structure. Since utilized substrate is polyester fabrics, fading probably takes place by oxidation²⁰. Oxidation of $-N=N-$ linkages supposed to be a component of electron density henceforth; electron attracting groups supposed to decrease the rate of fading, in contrast, electron donating substituent will increase the rate of fading. This is in concurrence with the obtained data that show the existence of NO_2 substituent in the dye **3e** increases fastness to light to very good (6). Alternatively, the fading is slowly increased for dye **3b** to (4), this may be attributed to presence of a CH_3 group.

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

Dye Number	Fastness to Rubbing		Wash fastness			Fastness to Perspiration						Fastness to Light	
	Dry	Wet	Alt	SC	SW	Acidic			Alkaline				
						Alt	SC	SW	Alt	SC	SW		
3a	5	5	5	5	5	5	5	5	5	5	5	5	4-5
3b	5	5	4-5	4-5	4-5	5	5	5	5	5	5	5	4
3c	5	5	5	5	4-5	5	5	5	5	5	5	5	4-5
3d	4-5	4-5	5	5	4-5	5	5	5	5	5	5	5	4-5
3e	5	5	4-5	4-5	4-5	5	5	5	5	5	5	5	6

Where: Alt = Alteration, SC = Staining on cotton, SW = Staining on wool.

Antimicrobial Activity

The obtained results listed in Table 3 showed that dyes **3a** and **3e** have moderate activities against *Escherichia coli* and *Staphylococcus aureus*, respectively. In contrast dyes **3a-e** showed no activities against of *Serratia marcescens*. Disperse dyes **3a** and **3d** showed positive antimicrobial activities against four microorganisms, while dyes **3b**, **3c** and **3e** showed positive antimicrobial activities against three microorganisms. Hence, the prepared dyes illustrated promising results concerning its possibility to be used in medicinal fields.

Table 3. Antimicrobial activities of the azo disperse dyes.

Dye No	G ⁻ (inhibition zone in mm)			G ⁺ (inhibition zone in mm)		
	<i>Escherichia coli</i> (cont.26)	<i>Pseudomonas aeruginosa</i> (cont.42)	<i>Serratia marcescens</i> (cont.28)	<i>Bacillus cereus</i> (cont.18)	<i>Micrococcus luteus</i> (cont.24)	<i>Staphylococcus aureus</i> (cont.34)
3a	9	8	0	7	0	9
3b	7	7	0	0	8	0
3c	7	0	0	0	7	8
3d	8	8	0	7	0	7
3e	10	8	0	0	0	8

Conclusions

A pyrazolopyrimidinones disperse dyes were synthesized. These dyes were applied to polyester fabrics. The dyed substrate displayed excellent perspiration fastness and very good fastness levels to rubbing, light and washing, respectively. Moreover, the antimicrobial activities of these dyes against Gram negative and Gram positive bacteria were discussed.

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