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Synthesis, biological activity and dyeing performance of some novel azo disperse dyes incorporating pyrazolo[1,5-*a*]pyrimidines for dyeing of polyester fabrics

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ABSTRACT

Several novel pyrazolopyrimidine azo compounds were achieved from diazotization of 4-aminoacetanilide and coupling with malononitrile and then refluxed with hydrazine hydrate to furnish 3,5-diamino-4-(4-acetamidophenylazo)-1*H*-pyrazole. The later compound was diazotized and coupled with substituted α-cyanocinnamate, α-cyanocinnamonitrile, 2-cyano-3-ethoxyacrylic acid ethyl ester, chalcones and ethylacetoacetate to produce novel dyestuffs. Structures of the dyes were fully characterized by using FT-IR, ^{1}H NMR, mass spectroscopy and elemental analysis. The dyes were applied to polyester fiber, affording satisfactory results and showed biological activity towards various microorganisms.

1. Introduction

Simple nitrogen-containing heterocycles receive a large amount of attention in the literature, as a consequence of their exciting biological properties and their role as pharmacophores of considerable historical importance. It is well known that nitriles are widely used as intermediates for a large number of heterocyclic compounds. The aminopyrazole compounds have been easily obtained by the reaction of nitrile derivatives with hydrazine, and are very useful as precursors for the synthesis of fused heterocyclic ring systems [1,2].

Reactions of aminopyrazoles with electrophilic reagents give rise to various fused annulated heterocyclic systems, including pyrazolo[1,5-*a*]pyrimidines which are synthetic analogs of purines. These compounds exhibit a wide spectrum of biological activity, in particular enzymatic, antibacterial, antiphlogistic and antiparasitic activities [3,4]. They are also used as intermediates in the dyestuff industry [5–7].

In the present work, some new disperse dyes from pyrazolo[1,5-*a*]pyrimidine for dyeing polyester were synthesized. This is an extension research program in our laboratory, which based on the synthesis of novel azo-heterocyclic system. These compounds exhibit significant biological activities and show ability for dyeing of polyester fibers [8–13].

2. Experimental

Melting points reported were measured on a Stuart Scientific Co. Ltd. (UK) melting point apparatus. IR spectra (KBr) were recorded on FTIR/5300 spectrophotometers. The absorption in the visible region (700–325 nm) was measured by a recording Perkin Elmer Lambda-3B UV–Visible spectrophotometer using glass cells, having 1.0 cm optical path length. NMR spectra were measured on DMSO-d_6 solution using a Varian Mercury 300 (300 MHz ^{1}H NMR, 75 MHz ^{13}C NMR) spectrophotometer and chemical shifts are given in parts per million from TMS. Mass spectra were recorded on a GC–MS QP1000 EX (70 eV) or MS 5988 (15 eV) spectrometers. Elemental analyses were carried out at the Microanalytical Centre, Cairo University.

2.1. Synthesis of the dyes

2.1.1. Synthesis of 2-(4-acetamidophenylazo)malononitrile (**2**)

The diazonium salt solution was prepared by adding sodium nitrate (0.69 g, 0.01 mol) in water (20 mL) to a solution of 4-aminoacetanilide (**1**) (1.5 g, 0.01 mol) in HCl (1 M; 50 mL) at 0 °C. The reaction mixture was stirred for 10 min. The diazotized solution was then added to a well-stirred mixture of malononitrile

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(0.66 g, 0.01 mol), ethanol (15 mL) and water (50 mL). Sodium acetate was added in small portions to keep the reaction mixture alkaline to litmus. After 3 h of stirring at 0 °C, the crude product **2** was filtered, washed with water and air-dried as orange crystals, λ_{max} 481 in ethanol ($\log\varepsilon$4.0), yield (1.77 g, 78%) and m.p. 215–217 °C. IR (KBr) ν_{max}/cm^{-1}: 3545 (NH), 2984 (CH stretching), 2225 (CN), 1677 (C=O) and 1413 (N=N). ^{1}H NMR (DMSO-d_6) δ ppm: 2.04 (3H, s, $\underline{CH_3}CONH$), 3.42 (1H, s, CH), 7.41–7.60 (4H, m, Ar-H), 10.01 (1H, s, $CH_3CO\underline{NH}$) and 12.80 (1H, b, NH). Anal. Calcd. for $C_{11}H_9N_5O$ (227): C, 58.14; H, 3.99; N, 30.82. Found: C, 58.10; H, 4.00; N, 31.00.

*2.1.2. Synthesis of 3,5-diamino-4-(4-acetamidiophenylazo)-1H-pyrazole (**3**)*

A mixture of compound **2** (2.27 g, 0.01 mol), hydrazine hydrate (1 mL, 0.02 mol) and pyridine 0.5 mL in 30 mL ethanol was heated under reflux for 3 h. The reaction product was collected at room temperature. The separated solid was filtered, washed with water, dried and recrystallized from ethanol to give **3**; as yellow crystals, λ_{max} 452 in ethanol ($\log\varepsilon$3.6), yield (1.81 g, 70%) and m.p. 268–270 °C. IR (KBr) ν_{max}/cm^{-1}: 3395 (NH; broad) 3296, 3192 (NH_2), 2926 (CH stretching), 1665 (C=O), 1417 (N=N). ^{1}H NMR (DMSO-d_6) δ ppm: 2.05 (3H, s, $\underline{CH_3}CO$), 5.90 (2H, s, NH_2), 6.25 (2H, s, NH_2), 7.56–7.62 (4H, m, Ar-H), 9.90 (1H, s, NH) and 10.06 (1H, s, $CH_3CO\underline{NH}$). Anal. Calcd. for $C_{11}H_{13}N_7O$ (259): C, 50.96; H, 5.05; N, 37.82. Found: C, 51.00; H, 5.10; N, 38.00.

*2.1.3. Synthesis of 2-amino-3-(4-acetamidiophenylazo)-7-(substituted phenyl)-5-oxo-4H-pyrazolo[1,5-a]pyrimidine-6-carbonitrile (**4a–c**)*

A suspension of compound **3** (2.59 g, 0.01 mol) and ethyl α-cyanocinnamate derivatives (0.01 mol) in ethanol (30 mL) was treated with piperidine (1 mL). The reaction mixture was refluxed for 3 h. The solvent was then evaporated and the obtained product was recrystallized from ethanol to give **4a–c**.

*2.1.3.1. Compound **4a**.* This compound was obtained from reaction of compound **3** with ethyl 3-(2-chlorophenyl)-2-cyanoacrylate (2.59 g, 0.01 mol) as orange crystals, λ_{max} 485 in ethanol ($\log\varepsilon$3.2), yield (3.37 g, 75%) and m.p. 310–312 °C. IR (KBr) ν_{max}/cm^{-1}: 3415, 3284, 3186 (NH_2, NH), 2859 (CH stretching), 2212 (CN), 1623 (C=O), 1417 (N=N). ^{1}H NMR (DMSO-d_6) δ ppm: 2.02 (3H, s, CH_3CO), 6.51 (2H, s, NH_2), 7.27–7.62 (8H, m, Ar-H), 9.90 (1H, s, NH) and 10.09 (1H, s, $CH_3CO\underline{NH}$). Anal. Calcd. for $C_{21}H_{15}ClN_8O_2$ (447): C, 56.45; H, 3.38; N, 25.08. Found: C, 56.50; H, 3.40; N, 25.00.

*2.1.3.2. Compound **4b**.* This compound was obtained from reaction of compound **3** with ethyl 2-cyano-3-(4-fluorophenyl)acrylate (2.36 g, 0.01 mol) as brown crystals, λ_{max} 491 in ethanol ($\log\varepsilon$3.9), yield (3.23 g, 75%) and m.p. 320–322 °C. IR (KBr) ν_{max}/cm^{-1}: 3408 (NH), 3286, 3189 (NH_2), 2864 (CH stretching), 2218 (CN), 1624 (C=O), 1415 (N=N). ^{1}H NMR (DMSO-d_6) δ ppm: 2.05 (3H, s, CH_3CO), 6.82 (2H, s, NH_2), 7.43–7.82 (8H, m, Ar-H), 9.94 (1H, s, NH) and 10.09 (1H, s, $CH_3CO\underline{NH}$). Anal. Calcd. for $C_{21}H_{15}FN_8O_2$ (430): C, 58.60; H, 3.51; N, 26.04. Found: C, 59.00; H, 3.50; N, 26.00.

*2.1.3.3. Compound **4c**.* This compound was obtained from reaction of compound **3** with ethyl 2-cyano-3-(4-methoxyphenyl)acrylate (2.31 g, 0.01 mol) as orange crystals, λ_{max} 474 in ethanol ($\log\varepsilon$3.2), yield (3.76 g, 85%) and m.p. 240–242 °C. IR (KBr) ν_{max}/cm^{-1}: 3423 (NH, NH_2; broad), 2856 (CH stretching), 2214 (CN), 1605 (C=O), 1413 (N=N). ^{1}H NMR (DMSO-d_6) δ ppm: 2.04 (3H, s, CH_3CO), 3.83 (3H, s, OCH_3), 6.62 (2H, s, NH_2), 7.43–7.82 (8H, m, Ar-H), 9.92 (1H, s, NH) and 10.01 (1H, s, $CH_3CO\underline{NH}$). Anal. Calcd. for $C_{22}H_{18}N_8O_3$ (442): C, 59.72; H, 4.10; N, 25.33. Found: C, 60.00; H, 4.00; N, 25.00.

*2.1.4. Synthesis of 2,5-diamino-3-(4-acetamidiophenylazo)-7-(substituted phenyl)-pyrazolo[1,5-a]pyrimidine-6-carbonitrile (**5a–d**)*

A suspension of compound **3** (2.59 g, 0.01 mol) and α-cyanocinnamonitrile derivatives (0.01mole) in ethanol (30 mL) was refluxed with piperidine (1 mL) for 3 h. The solid product which formed after evaporation of the solvent was collected by filtration and recrystallized from ethanol to give **5a–d**.

*2.1.4.1. Compound **5a**.* This compound was obtained from reaction of compound **3** with 2-(4-chlorobenzylidene)malononitrile (1.88 g, 0.01 mol) as yellow crystals, λ_{max} 465 in ethanol ($\log\varepsilon$3.8), yield (3.21 g, 72%) and m.p. 330–331 °C. IR (KBr) ν_{max}/cm^{-1}: 3429, 3301 (NH_2, NH; broad), 2858 (CH stretching), 2213 (CN), 1605 (C=O), 1411 (N=N). ^{1}H NMR (DMSO-d_6) δ ppm: 2.04 (3H, s, CH_3CO), 6.89 (2H, s, NH_2), 7.55–7.98 (8H, m, Ar-H), 8.51 (2H, s, NH_2) and 10.01 (1H, s, $CH_3CO\underline{NH}$). Anal. Calcd. for $C_{21}H_{16}ClN_9O$ (445): C, 56.57; H, 3.62; N, 28.27. Found: C, 56.60; H, 3.60; N, 28.30.

*2.1.4.2. Compound **5b**.* This compound was obtained from reaction of compound **3** with 2-(4-fluorobenzylidene)malononitrile (1.72 g, 0.01 mol) as yellow crystals, λ_{max} 468 in ethanol ($\log\varepsilon$3.6), yield (3.13 g, 73%) and m.p. 308–309 °C. IR (KBr) ν_{max}/cm^{-1}: 3440, 3313, 3182 (NH_2, NH; broad), 2860 (CH stretching), 2214 (CN), 1605 (C=O), 1417 (N=N). ^{1}H NMR (DMSO-d_6) δ ppm: 2.05 (3H, s, CH_3CO), 7.06 (2H, s, NH_2), 7.38–7.97 (8H, m, Ar-H), 8.56 (2H, s, NH_2) and 10.12 (1H, s, $CH_3CO\underline{NH}$). Anal. Calcd. for $C_{21}H_{16}FN_9O$ (429): C, 58.74; H, 3.76; N, 29.36. Found: C, 58.70; H, 3.80; N, 29.40.

*2.1.4.3. Compound **5c**.* This compound was obtained from reaction of compound **3** with 2-(4-methoxybenzylidene)malononitrile (1.84 g, 0.01 mol) as orange crystals, λ_{max} 481 in ethanol ($\log\varepsilon$4.3), yield (3.49 g, 79%) and m.p. 302–304 °C. IR (KBr) ν_{max}/cm^{-1}: 3457, 3303, 3167 (NH_2, NH; broad), 2835 (CH stretching), 2211 (CN), 1605 (C=O), 1414 (N=N). ^{1}H NMR (DMSO-d_6) δ ppm: 2.07 (3H, s, $\underline{CH_3}CO$), 3.81 (3H, s, $O\underline{CH_3}$), 6.51 (2H, s, NH_2), 7.04–7.89 (8H, m, Ar-H), 8.50 (2H, s, NH_2) and 10.01 (1H, s, $CH_3CO\underline{NH}$). Anal. Calcd. for $C_{22}H_{19}N_9O_2$ (441): C, 59.86; H, 4.34; N, 28.56. Found: C, 60.00; H, 4.30; N, 29.00.

*2.1.4.4. Compound **5d**.* This compound was obtained from reaction of compound **3** with 2-(3,4-dimethoxy-benzylidene)malononitrile (2.14 g, 0.01 mol) as orange crystals, λ_{max} 480 in ethanol ($\log\varepsilon$3.1), yield (3.49 g, 74%) and m.p. 297–299 °C. IR (KBr) ν_{max}/cm^{-1}: 3449, 3323 (NH_2, NH; broad), 2843 (CH stretching), 2210 (CN), 1619 (C=O), 1417 (N=N). ^{1}H NMR (DMSO-d_6) δ ppm: 2.03 (3H, s, $\underline{CH_3}CO$), 3.83 (6H, s, 2x$O\underline{CH_3}$), 6.89 (2H, s, NH_2), 6.94–7.62 (7H, m, Ar-H), 8.50 (2H, s, NH_2) and 10.05 (1H, s, $CH_3CO\underline{NH}$). Anal. Calcd. for $C_{23}H_{21}N_9O_3$ (471): C, 58.59; H, 4.49; N, 26.74. Found: C, 59.00; H, 4.50; N, 27.00.

*2.1.5. Synthesis of 2-amino-3-(4-acetamidiophenylazo)-5-ethoxy-7-oxo-4H-pyrazolo[1,5-a]-pyrimidine-6-carbonitrile (**6**)*

A mixture of compound **3** (2.59 g, 0.01 mol) and 2-cyano-3-ethoxyacrylic acid ethyl ester (1.69 g, 0.01 mol) was refluxing in dimethylformamide (20 mL) and triethylamine (1 mL) for 1 h. The reaction product was collected and recrystallized from ethanol to give **6** as brown crystals, λ_{max} 487 in ethanol ($\log\varepsilon$3.7), yield (2.62 g, 69%) and m.p. 270–272 °C. IR (KBr) ν_{max}/cm^{-1}: 3439 (NH), 3326, 3270 (NH_2), 2854 (CH stretching), 2213 (CN), 1689 (C=O), 1415 (N=N). ^{1}H NMR (DMSO-d_6) δ ppm: 1.21 (3H, t, $\underline{CH_3}CH_2$), 2.02 (3H, s, $\underline{CH_3}CO$), 4.02 (2H, q, $CH_3\underline{CH_2}$), 6.51 (2H, s, NH_2), 7.21–7.60 (4H, d, Ar-H), 9.93 (1H, s, NH) and 10.09 (1H, s, $CH_3CO\underline{NH}$). Anal. Calcd. for $C_{17}H_{16}N_8O_3$ (380): C, 53.68; H, 4.24; N, 29.46. Found: C, 54.00; H, 4.20; N, 29.50.

*2.1.6. Synthesis of 2-amino-3-(4-acetamidiophenylazo)-5-substituted-7-substitutied-pyrazolo[1,5-a]pyrimidine (**7a–c**)*

A mixture of compound **3** (2.59 g, 0.01 mol) and chalcones (0.01 mol) was refluxed in piperidine (1 mL) and ethanol (30 mL) for 4 h. The resulting product was collected by filtration and recrystallized from acetic acid to give **7a–c**.

*2.1.6.1. Compounds **7a**.* This compound was obtained from reaction of compound **3** with 1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (2.38 g, 0.01 mol) as red crystals; λ_{max} 567 in ethanol (log ε 4.1), yield (3.58 g, 80%) and m.p. 320–322 °C. IR (KBr) ν_{max}/cm^{-1}: 3439 (NH), 3326, 3270 (NH_2), 2927 (CH stretching), 1659 (C=O), 1414 (N=N). ^{1}H NMR (DMSO-*d*6) δ ppm: 2.07 (3H, s, CH_3CO), 6.51 (2H, s, NH_2), 7.10–8.40 (14H, m, Ar-H and pyrimidine C—H) and 10.09 (1H, s, CH_3CONH). Anal. Calcd for $C_{27}H_{23}N_7O_2$ (477): C, 67.91; H, 4.85; N, 20.53. Found: C, 68.00; H, 5.00; N, 21.00.

*2.1.6.2. Compounds **7b**.* This compound was obtained from reaction of compound **3** with 3-(4-bromophenyl)-1-phenylprop-2-en-1-one (2.87 g, 0.01 mol) as reddish-violet crystals; λ_{max} 570 in ethanol (log ε 4.5), yield (4.20 g, 80%) and m.p. 220–222 °C. IR (KBr) ν_{max}/cm^{-1}: 3469 (NH, NH_2, broad), 2917 (CH stretching), 1654 (C=O), 1453 (N=N). ^{1}H NMR (DMSO-*d*6) δ ppm: 2.47 (3H, s, CH_3CO), 5.34 (2H, s, NH_2), 6.80–7.50 (13H, m, Ar-H and pyrimidine C—H) and 10.09 (1H, s, CH_3CONH). Anal. Calcd for $C_{26}H_{20}BrN_7O$ (525): C, 59.32; H, 3.83; N, 18.63. Found: C, 69.00; H, 4.00; N, 19.00.

*2.1.6.3. Compounds **7c**.* This compound was obtained from reaction of compound **3** with 1,3-bis(4-bromophenyl)prop-2-en-1-one (3.66 g, 0.01 mol) as reddish-violet crystals; λ_{max} 488 in ethanol (log ε 3.6), yield (4.52 g, 75%) and m.p. 308–310 °C. IR (KBr) ν_{max}/cm^{-1}: 3397 (NH), 3297, 3193 (NH_2), 2931 (CH stretching), 1668 (C=O), 1492 (N=N). ^{1}H NMR (DMSO-*d*6) δ ppm: 2.04 (3H, s, CH_3CO), 6.50 (2H, s, NH_2), 7.5–7.7 (13H, m, Ar-H and pyrimidine C—H) and 10.10 (1H, s, CH_3CONH). Anal. Calcd for $C_{26}H_{19}Br_2N_7O$ (603): C, 51.59; H, 3.16; N, 16.20. Found: C, 51.60; H, 3.20; N, 16.00.

*2.1.7. Synthesis of 2-amino-3-(4-acetamidiophenylazo)-7-methyl-4H-pyrazolo[1,5-a]-pyrimidin-5-one (**8**)*

A solution of compound **3** (2.59 g; 0.01 mol) in acetic acid (20 mL) was treated with ethyl acetoacetate (1.3 mL). The mixture solution was refluxed for 3 h and the obtained product **8** was recrystallized from ethanol as brown crystals; λ_{max} 496 in ethanol (log ε 3.5), yield (2.54 g, 78% and m.p. 286–288 °C. IR (KBr) ν_{max}/cm^{-1}: 3443, 3283 (NH_2, NH; broad), 2924 (CH stretching), 1624 (C=O), 1530 (N=N). ^{1}H NMR (DMSO-*d*6) δ ppm: 2.08 (3H, s, CH_3CO), 2.40 (3H, s, CH_3), 5.70 (1H, s, pyrimidine C—H), 6.51 (1H, s, pyrimidine NH), 7.61–7.82 (4H, m, Ar-H), 10.12 (1H, s, CH_3CONH) and 12.43 (2H, s, NH_2). Anal. Calcd for $C_{15}H_{15}N_7O_2$ (325): C, 55.38; H, 4.65; N, 30.14. Found: C, 55.40; H, 5.00; N, 30.20.

2.2. Dyeing procedures [14]

2.2.1. Materials used

The synthesized disperse dyestuffs **2–8** used in study is shown in Schemes 1 and 2.

Dekol-N (2 g/dm^3), an anionic dispersing agent of BASF.

Levegal PT (Bayer) as carrier.

Polyester fiber; 100% (PET): Woolen type, denier 1.4 mm, from Misr Rayon Co., Kafr El-Dawar, Egypt, which was scoured, bleached and dried under vacuum for 48 h at room temperature.

2.2.2. Dyeing of polyester fiber

The required amount of dye (2% shade) was dissolved in ethanol and added dropwise with stirring to a solution of Dekol-N (2 g/dm^3), an anionic dispersing agent of BASF, then the dye was precipitated in a fine dispersion ready for use in dyeing.

The dye bath (1:20 liquor ratio), containing 5 g/dm^3 Levegal PT (Bayer) as carrier, 4% ammonium sulphate, and acetic acid at pH 5.5, was brought to 60 °C, the polyester fabric was entered and run for 15 min. The fine dispersion of the dye (2%) was added, and the temperature was raised to boiling within 45 min, dyeing was continued at boiling temperature for about 1 h, then the dyed material was rinsed and soaped with 2% nonionic detergent to improve rubbing and wet fastness.

2.3. Assessment of color fastness [15–17]

Fastness to washing, perspiration, light, and sublimation was tested according to the reported methods.

2.3.1. Fastness to washing

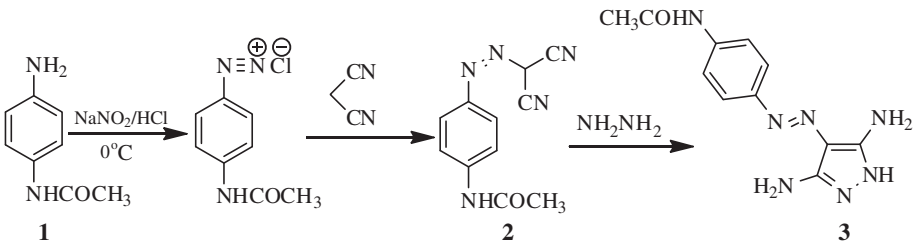
A specimen of dyed polyester fabric was stitched between two pieces of undyed cotton fabric (all fabric pieces had the same diameter) and then washed at 50 °C for 30 min. The staining of the undyed adjacent fabric was assessed according to the following grayscale: 1, poor; 2, fair; 3, moderate; 4, good; 5, excellent.

2.3.2. Fastness to perspiration

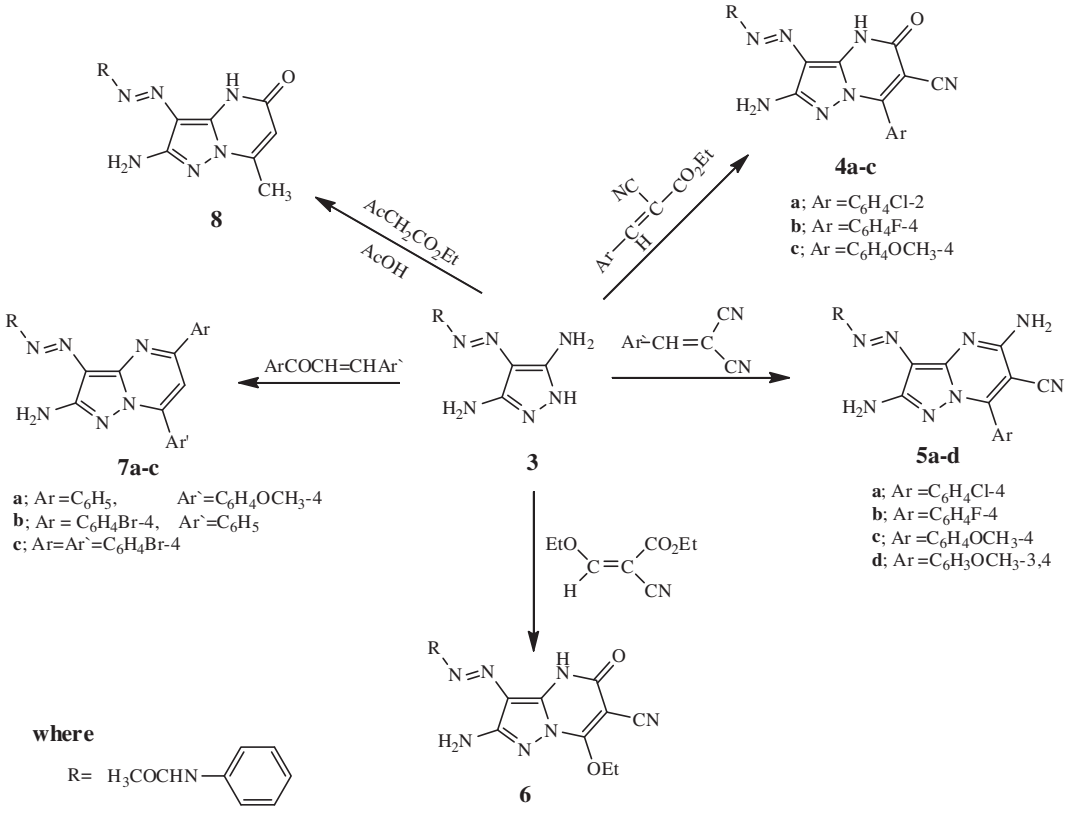
The samples were prepared by stitching pieces of dyed polyester fabric between two pieces of undyed cotton fabric (all fabric pieces had the same diameter) and then they were immersed in the acid medium for 30 min. The staining of the undyed adjacent fabric was assessed according to the following grayscale: 1, poor; 2, fair; 3, moderate; 4, good; 5, excellent. The acid solution (pH 3.5) contained sodium chloride 10 g dm^{-3}, lactic acid 1 g dm^{-3}, disodium orthophosphate 1 g dm^{-3}, and histidine monohydrochloride 0.25 g dm^{-3}.

2.3.3. Fastness to rubbing

The dyed polyester fabric was placed on the base of a crock meter (Atlas electronic type), so that it rested flat on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was forced to slide on the tested fabric back



Scheme 1. Synthesis of 3,5-diamino-4-(4-acetamidiophenylazo)-1*H*-pyrazole (**3**) as intermediate dyes.



Scheme 2. Synthesis of some disperse dyestuffs (**4**–**8**).

and forth twenty times by turning the crank ten complete turns. For the wet rubbing test, the test square was thoroughly wetted in distilled water. The rest of the procedure was the same as the dry test. The staining on the white testing cloth was assessed according to the grayscale: 1, poor; 2, fair; 3, moderate; 4, good; 5, excellent.

2.3.4. Fastness to sublimation

Sublimation fastness was measured with an iron tester (Yasuda No. 138). The samples were prepared by stitching pieces of dyed polyester fabric between two pieces of undyed polyester (all fabric pieces had the same diameter) and then treated at 180 and 210 °C for 1 min. Any staining of the undyed adjacent fabric or change in tone was assessed according to the following grayscale: 1, poor; 2, fair; 3, moderate; 4, good; 5, excellent.

2.3.5. 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 following blue scale: 1, poor; 3, moderate; 5, good; 8, very good.

2.3.6. Exhaustion isotherms [18]

The rate of exhaustion of the dyestuffs on polyester fiber was measured at equilibrium at 100 °C, according to previous methods. The rate of exhaustion was assessed by taking samples from the dyebath at different times during the dyeing process. The optical density of the dye bath samples was then measured using a UV–Visible spectrophotometer.

2.4. Microbiological investigations

Antimicrobial activity was carried out by Microbiology Lab., Faculty of Science, Al-Azhar University, Cairo, Egypt. The antibacterial activities of the synthesized compounds **2**–**8** were determined by the agar diffusion technique [19]. The organisms tested were *Staphylococcus aureus* (NCTC-7447) and *Serratia marcesens* (IMRU-70). The antimicrobial activities of compounds **2**–**8** at different concentrations (μg/cm^3) were tested to detect the minimum inhibitory concentration (MIC) by the serial dilution method [19,20]. Most of the prepared compounds **2**–**8** were tested for their antifungal activity using *Aspergillus ochraceus* Wilhelm (AUCC-230) in Glucose-Czapek's agar medium [21] was used for the fungi.

3. Results and discussion

3.1. Dyestuffs synthesis

The coupling of 4-acetamidophenyldiazonium chloride with malononitrile produced 2-(4-acetamidophenylazo)malononitrile (**2**). The mass spectrum of **2** was compatible with molecular formula $C_{11}H_9N_5O$ (M^+ 227) and the base peak was observed at *m*/*e* 107 (100%). On the other hand, compound **2** was reacted with different nucleophilic reagent afforded different compounds. Thus, 2-(4-acetamidophenylazo)malononitrile (**2**) and hydrazine hydrate was refluxed in ethanol to afford the corresponding arylazo derivative **3**; as shown in Scheme 1. The mass spectrum of **3** was compatible with molecular formula $C_{11}H_{13}N_7O$ (M^+ 259; base beak 100%). The structure of **3** was established on the basis of elemental analysis and spectral data.

Reaction of **3** with ethyl α-cyanocinnamate derivatives yielded **4a**–**c**. Similarly, arylidene malononitrile, compound **3** reacted with α-cyanocinnamonitrile derivatives afforded the corresponding

Table 1
Some dyeing properties for dyes 2–8 on polyester at 130 °C.

Dye	Dye take-up (%)	Washing	Perspiration		Rubbing		Sublimation fastness		Light
			Acid	Alkali	Dry	Wet	Staining at 180 °C	Staining at 210 °C	(40 h)
2	78	4	4	4	4	4	4	3	4
3	79	4	4	4	4	4	4	3	4
4a	83	4–5	4–5	4–5	4	4	4	4	6
4b	85	4–5	4–5	4–5	4	4	4	4	6
4c	85	4–5	4–5	4–5	4	4	4	4	6
5a	82	4–5	4–5	4–5	4	4	4	4	6
5b	85	4–5	4–5	4–5	4	4	4	4	6
5c	87	4–5	4–5	4–5	4	4	4	4	6
5d	86	4–5	4–5	4–5	4	4	4	4	6
6	83	4	4	4	4	4	4	3	5
7a	86	4–5	4–5	4–5	4	4	4	4	6
7b	86	4–5	4–5	4–5	4	4	4	4	6
7c	83	4–5	4–5	4–5	4	4	4	4	6
8	82	4–5	4–5	4–5	4	4	4	4	6

pyrazolo[1,5-*a*]pyrimidine derivatives **5a**–**d**. The interaction of compound **3** with 2-cyano-3-ethoxy-acrylic acid ethyl ester by refluxing in EtOH/Et_3N *via* EtOH elimination afforded compound **6**.

The behavior of **3** towards α,β-unsaturated ketones has also been investigated. Thus, compound **3** reacted with chalcones in absolute EtOH containing a catalytic amount of piperidine, under reflux, to yield the corresponding pyrazolo[1,5-*a*]pyrimidine derivatives (**7a**–**c**) in acceptable yield.

On the other hand, compound **3** on condensation with ethyl acetoacetate in glacial acetic acid afforded the ketone **8**; Scheme 2. The mass spectrum of compound **8** was compatible with molecular formula $C_{15}H_{15}N_7O_2$ (M^+ 325; base beak 100%). The structures of all compounds were established on the basis of elemental analysis and spectral data.

The structures of synthesized compounds **2**–**8** were confirmed by various spectroscopy techniques including IR, ^{1}H NMR, mass and accurate mass data. The IR spectra of **2**–**8** are characterized by the presence of absorption bands within the $\bar{\nu} = 3395—3545\ cm^{-1}$ corresponding to the stretching vibrations of the NH and NH_2 groups. The bands within $\bar{\nu} = 2211—2225\ cm^{-1}$ are due to the stretching vibration of the CN group. The absorption bands at the $\bar{\nu} = 1605—1677\ cm^{-1}$ are due to the stretching vibration of the C=O group. The absorption bands at the $\bar{\nu} = 1411—1417\ cm^{-1}$ are due to the symmetric stretching vibrations of the azo group. The ^{1}H NMR spectra showed a characteristic NH signal in the $\bar{\nu} = 9.90—12.80$, pyrimidine NH at 6.51 and NH_2 at 5.90–6.82 ppm. The structure of dyes **2**–**8** were confirmed further by mass and accurate mass data. The electron impact mass spectra indicated mass spectra indicated the presence of molecular ion peaks in all cases.

3.2. Dyeing properties of dyes

The functionalized azopyrazolo[1,5-*a*]pyrimidine disperse dyes **2**–**8** were applied to polyester fabrics at 2% shade by high-temperature pressure (130 °C) and gave generally deep and bright hues, ranging from yellow, orange to reddish-violet.

The visible absorption spectra of synthesized dyes **2**–**8** were measured in ethanol at 1.98×10^{-5} M and their molar extinction coefficients ($\log\varepsilon$) were determined. The uptake of disperse dyes by fabrics takes place by the progressive adsorption of the small concentration of dye in solution, which is always present in an aqueous dispersion. The dye uptake of the dyed polyester is given in Table 1; it can be seen that high exhaustion levels ranging from 78 to 87 were obtained; Fig. 1.

The dyes **2**–**8** were investigated for their dyeing characteristics on polyester and they showed good light, washing, heat and acid perspiration fastness. The remarkable brightness of these dyes

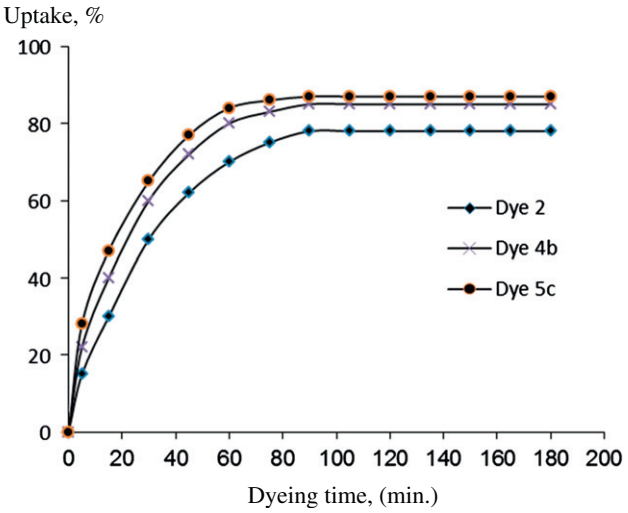


Fig. 1. Uptake of some dyes **2**, **4b**, **5c** on polyester fiber at 2% (omf) and 130 °C.

after washing are indicative of their good penetrations and excellent fabric affinities due to their accumulation of polar groups; Table 1.

Light fastness of some dyestuffs **2**–**8** from compound **1** are listed in Table 1. The light fastness results are good and acceptable ranging "4–6" and showing little or no fading of light shades. The variations in the substituent atom, and/or groups in the coupling component have only very limited effect on fastness properties, especially to light. Washing fastness assessment of obtained colors on polyester fibers has shown rather good levels (4–5). The sublimation fastness of dyes **2**–**8** were in the range of 3–4, thus showed good sublimation fastness properties on polyester fibers.

3.3. Evaluation of biological activity for synthesized dyestuffs

Some of the synthesized compounds **2**–**8** were evaluated for their antimicrobial activities against some bacteria such as: *S. aureus*, *S. marcesens* and also against some fungi such as *A. ochraceus* Wilhelm, Table 2).

3.3.1. Antibacterial activity

The toxicity of these compounds mainly arises due to its undesirable coordination with the metallo-enzymes and metalloproteins for organisms, therefore, makes inhibition for growth

Table 2
Antibacterial and antifungal activity of compounds **2**–**8** and inhibition zones.

Compd. No.	Gram-positive *Staphylococcus aureus*		Gram-negative *Serratia marcesens*		Fungi *Aspergillus ochraceus*	
	Zone	MIC	Zone	MIC	Zone	MIC
2	++	155	++	150	++	115
3	++	155	++	175	++	115
4a	+++	110	+++	150	++	175
4b	+++	130	+++	150	++	150
4c	++	120	++	140	++	150
5a	+++	175	+++	115	+++	160
5b	+++	150	+++	120	+++	140
5c	++	125	++	150	++	125
5d	++	120	++	150	++	120
6	+++	120	++	175	+++	125
7a	++	125	++	150	++	150
7b	+++	120	+++	175	+++	150
7c	+++	120	+++	150	+++	150
8	++	125	++	150	++	160
Control*	++++	25	++++	25	+++	30

+: Less active (0.2–1 cm); ++: moderate active (1–2.4 cm); +++: highly active (2.5–3.5 cm); ++++: extremely active (more than 3.5 cm).
* Ampicillin (25 μg) and mycostatine (30 μg) were used as control for bacteria and fungi, respectively: manufactured by Bristol-Myers Squibb, Giza, Egypt.

and killing for microorganisms by the penetration into the cell membrane, followed by destruction of cell membranes and leakage of cell inclusion body. The results depicted in Table 2) reveal that compounds **4a**, **4b**, **5a**, **5b**, **7b** and **7c** exhibited relatively high activities against the reference Ampicillin. It is worth mentioning that the incorporation of chloro, bromo and floro group onto the pyrazolopyrimdine moiety caused significant activity.

In general, the tested compounds exhibit moderate to strong activities (inhibition zones ranged from 24 to 35 mm) in comparison to Ampicillin (25 μg) as control ranged from 35 to 40 mm. It appears that all synthesized compounds showed that considerable activity against all tested microorganisms, hence it might be broad spectra; Table 2.

3.3.2. Antifungal activity

The results indicated that most of the tested compounds exhibit moderate to weak actives (inhibition zones ranged from 10 to 24 mm in comparison to Mycostatine (30 μg) as control ranged from 25 to 35 mm, Table 2.

It appears that all synthesized compounds showed those considerable activities against all tested microorganisms, hence they might be considered broad spectra or dyeing of clothes. This study finds some times importance in dyeing of garments which direct contact with human skin in some places were bacteria and fungi may be present.

4. Conclusions

In this work, a series of azopyrazolo[1,5-*a*]pyrimidine dyes have been synthesized. The characterization and the absorption ability of 14 novel disperse dyes **2**–**8** were studied. The synthesized dyes were applied successfully using high temperature dyeing to obtain solid shades on polyester fibers with satisfactory levelness of dyeing and depth of shade, with observed shades of yellow, orange, brown and reddish-violet. The results of fastness properties showed in most cases acceptable to good fastness to light and washing fastness on the polyester fibers and also significant antimicrobial activity. The latter property may be beneficial to the wearer of a garment dyed with such compounds.

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