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ORIGINAL ARTICLE

Synthesis of some novel heterocyclic dyes derived from pyrazole derivatives

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Abstract Diazotized aryl amines were coupled with 3-substituted 5-amino pyrazoles to produce a series of novel 3-substituted 5-amino-4-arylazopyrazoles. Also, 3-substituted 5-amino-pyrazoles were diazotized and coupled with different phenols to give the corresponding novel 3-substituted 5-aryl azo pyrazoles. These dyes were characterized by elemental analysis and spectral data, applied to different types of fibres (wool, polyester and a blend of wool/polyester as disperse dyes) and their fastness properties were evaluated.

1. Introduction

It is well known that nitriles are widely used as intermediates in the synthesis of a large number of heterocycles. Amino pyrazoles can be readily obtained by the reaction of nitriles with hydrazine derivatives (Elnagdi et al., 1977; Elnagdi et al., 1979; Zvilichovsky and Mordechai, 1983; Kandeel et al., 1985). Pyazoles are an important class of compounds because of their biological and pharmacological activities (Karci, 2005; Junpei and Masayuki, 1991; Junji and Hiroyuki, 1991; Singh, 1990). Also, fused pyrazole moieties have a wide range of interesting properties such as anti-hyperglycemic analgesic, anti-inflammatory, anti-pyretic, anti-bacterial and sedative-hypnotic activities (Braulio et al., 1999).

Recently, some pyrazoles were reported to have non- nucleoside HIV-1 reverse transcriptase inhibitory activities (Karci and Karci, 2008; Kucukguzel et al., 2000) some azo pyrazole derivatives have various applications in the synthesis of dyes and complexes (Ertan, 2000; Khalil et al., 2005; Emandi et al., 1994; Tsai and Wang, 2005; Ho, 2005; Kandil et al., 2004; Abdel-latif, 2001). As part of continuing interest in heterocyclic chemistry, we have reported simple and convenient approaches for the synthesis of various pyrazoles (Naresh et al., 2005; Krishna et al., 1979; David et al., 1979; Simay and Takacs, 1980). We now report on the successful synthesis of some new 3-substituted 5-amino-4-arylazopyrazoles and 3-substituted 5-arylazopyrazoles and their applications as disperse dyes for wool, polyester and wool/polyester blend.

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2. Experimental

2.1. General

All melting points were uncorrected and in degree celsius. IR spectra were recorded on a Perkin–Elmer1430 spectrophotometer using KBr disk technique. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AC spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in DMSO, chemical shifts were expressed in δ ppm using TMS as an internal standard. Electron impact mass spectra (EI) were obtained using a Finnigan MAT 8222 spectrometer at 70 eV.

Microanalyses for C, H and N were performed on a Perkin–Elmer 240 elemental analyzer in Cairo University. Electronic spectra were recorded in DMF at a concentration of 1×10^{-5} using Shimadzu UV-3101 PC spectrophotometer. Progress of reactions was monitored by the of thin-layer chromatography (TLC) using benzene/ethylacetate (9:1) as eluent. Characterization data of products are shown in Tables 1 and 2.

2.2. Synthesis of 3-substituted 5-amino-4-arylazopyrazoles (2a–l)

A solution of sodium nitrite (12.7 mmol, 0.9 g) was gradually added to a cold (0 °C) solution of aromatic amines (13.7 mmol) in conc. HCl (4 ml). The diazonium salt obtained was added with continuous stirring to a cold (0 °C) of 5-aminopyrazoles **1a–c** (8.5 mmol) in ethanol (42 ml) containing sodium acetate (3.4 g). The reaction mixture was stirred at 0 °C for 2 h and the coloured solid formed was filtered, washed with water and crystallized from ethanol. The reaction is shown in Scheme 1.

2.2.1. 5-Amino-4-(p-methoxyphenylazo)-1,3-diphenyl-pyrazole (2$_a$)

M.p. 138–140 °C (82% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 3.8 (s, 3H, OCH$_3$), 7.1–7.8 (m, 14H, Ar–H), 8.2 (s, exch., 2H, NH$_2$); MS (EI): m/z (%) = 369 (M, 99), 326 (15), 234 (26), 128 (27), 105 (16), 77 (100), 51 (28). *Anal.* Calc. for $C_{22}H_{19}N_5O$: C, 71.6; H, 5.17; N, 18.97. Found: C, 71.32; H, 5.09; N, 18.57%.

2.2.2. 5-Amino-4-(p-chlorophenylazo)-1,3-diphenylpyrazole (2$_b$)

M.p. 180–182 °C (98% yield). ^{1}H NMR (DMSO-d6): δ/ppm = 7.5–8.0 (m, 14H, Ar–H), 8.2 (s, exch., 2H, NH$_2$); MS (EI): m/z (%) = 376(M + 3, 13), 373 (M, 39), 233 (19), 127 (35), 77 (100), 105 (46), 77 (93), 51 (34). *Anal.* Calc. for $C_{21}H_{16}N_5Cl$: C, 67.5; H, 4.31; N, 18.75; Cl, 9.48. Found: C, 67.45; H, 4.11; N, 18.35; Cl, 9.19%.

2.2.3. 5-Amino-4-(p-carboxyphenylazo)-1,3-diphenylpyrazole (2$_c$)

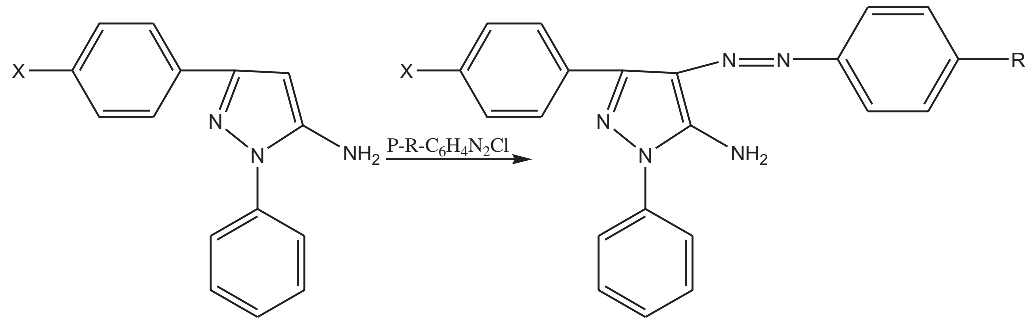
M.p. 280–283 °C (95% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 7.5–7.9 (m, 14H, Ar–H), 8.2 (s, exch., 2H, NH$_2$), 12.0 (s, exch., 1H, COOH). *Anal.* Calc. for $C_{22}H_{17}N_5O_2$: C, 68.98; H, 4.46; N, 18.28. Found: C, 68.65; H, 4.23; N, 18.11%.

Table 1 Characterization data compounds **2a**–**l**.

Cpd. no.	FT-IR (cm^{-1}, in KBr)					UV:λ_{max} (ε) (DMF)
	γNH$_2$	γarom.-H	γaliph.-H	γN=N	γC=O	
2a	3431	3050	2923	1499	–	386.5 (11.250)
2b	3435	3056	2925	1508	–	376.5 (15.850)
2c	3424	3054	2930	1502	1677	413 (11.240)
2d	3436	3050	2926	1496	–	411 (12.453)
2e	3430	3059	2920	1561	–	371.5 (7.505)
2f	3435	3056	2925	1503	–	363.5 (12.194)
2g	3442	3053	2929	1519	1675	396.5 (12.832)
2h	3428	3056	2923	1562	–	386 (9.621)
2i	3423	3052	2916	1566	–	374 (12.075)
2j	3436	3050	2926	1499	–	380 (11.417)
2k	3424	3052	2925	1499	1674	395 (9.256)
2l	3430	3050	2923	1563	–	385 (14.520)

Table 2 Characterization data compounds **3a**–**i**.

Cpd. no.	FT-IR (cm^{-1}, in KBr)					UV:λ_{max} (ε) (DMF)
	γOH	γarom.-H	γaliph.-H	γN=N	γC=O	
3a	3429	3059	2920	1519	–	483.82 (7.830)
3b	3425	3058	2922	1495	1773	488.1 (8.975)
3c	3426	3056	2925	1519	–	416.2 (6.290)
3d	3429	3050	2920	1505	–	437.2 (4.704)
3e	3422	3060	2921	1495	1767	485.25 (8.925)
3f	3424	3058	2923	1599	–	425 (18.192)
3g	3437	3056	2921	1502	–	473.5 (9.140)
3h	3460	3099	2934	1599	1794	515.48 (8.655)
3i	3426	3056	2925	1598	–	431.5 (7.430)



I$_{A\text{-}C}$

A: X = H
B: X = Cl
C: X = CH_3

2$_{a\text{-}l}$

a : X = H , R = OCH_3 **b**: X= H, R = Cl
c : X = H , R = COOH **d**: X= H, R = OH
e : X = Cl , R = OCH_3 **f**: X= Cl, R = Cl
g : X = Cl , R = COOH **h**: X= Cl, R = OH
i : X = CH_3 , R = OCH_3 **j**: X= CH_3, R = Cl
k : X = CH_3 , R = COOH **l**: X=CH_3, R = OH

Scheme 1 Synthesis of 3-substituted 5-amino-4-arylazopyrazoles.

2.2.4. 5-Amino-4-(p-hydroxyphenylazo)-1,3-diphenylpyrazole (2$_d$)

M.p. 150–153 °C (86% yield); MS (EI): m/z (%) = 358(M + 3,33), 355 (M, 100), 234 (36), 128 (31), 105 (8), 77 (72), 51 (45). *Anal.* Calc. for $C_{21}H_{17}N_5O_2$: C, 71.04; H, 4.81; N, 19.72. Found: C, 71.01; H, 4.58; N, 19.49%.

2.2.5. 5-Amino-4-(p-methoxyphenylazo)-3-(4-chlorophenyl)-1-phenyl-1H-pyrazol (2$_e$)

M.p. 185–187 °C (80% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 3.82 (s, 3H, OCH_3), 7.0–7.7 (m, 13H, Ar–H), 8.2 (s, exch., 2H, NH_2). *Anal.* Calc. for $C_{22}H_{18}N_5OCl$: C, 66.31; H, 4.54; N, 17.57; Cl, 8.78. Found: C, 66.19; H, 4.22; N, 17.39; Cl, 8.57%.

2.2.6. 5-Amino-4-(p-chlorophenylazo)-3-(4-chlorophenyl)-1-phenyl-1H-pyrazol (2$_f$)

M.p. 190–192 °C (90% yield); MS (EI): m/z (%) = 411(M + 3, 31), 408 (M, 96), 296 (42), 233 (17), 162 (38) 105 (12), 77 (100), 51 (39). *Anal.* Calc. for $C_{21}H_{15}N_5OCl_2$: C, 61.8; H, 3.69; N, 17.16; Cl, 17.37. Found: C, 61.56; H, 3.39; N, 17.06; Cl, 17.08%.

2.2.7. 5-Amino-4-(p-carboxyphenylazo)-3-(4-chlorophenyl)-1-phenyl-1H-pyrazol (2$_g$)

M.p. 300–301 °C (95% yield); ^{1}H NMR(DMSO): δ/ppm = 7.2–8 (m, 13Ar–H), 8.2 (s, 2H, NH_2), 13 (s, 1H, COOH). *Anal.* Calc. for $C_{22}H_{16}N_5OCl$: C, 63.28; H, 3.85; N, 16.77; Cl, 8.48. Found: C, 63.21; H, 3.55; N, 16.59; Cl, 8.25%.

2.2.8. 5-Amino-4-(p-hydroxyphenylazo)-3-(4-chlorophenyl)-1-phenyl-1H-pyrazol (2$_h$)

M.p. 175–177 °C (82% yield); ^{1}H NMR (DMSO): δ/ppm = 5.8 (s, exch., 1H, OH), 7.2-8.0 (m, 13H, Ar–H), 8.2 (s, exch., 2H, NH_2); ^{13}C NMR (DMSO-d6): δ/ppm = 92.6 (C_4), 142.8(C–Cl), 144.4 (C–NH_2), 161.2 (C_3), 172 (C–OH), 126.1, 128.0, 128.7, 129.1, 132, 132.9, 133.66, 134.5, 134.7, 134.8, 135.9, 136.1, 137.8, 139.3, 144.3 ($C_{aromatic}$). *Anal.* Calc. for $C_{21}H_{19}N_5OCl$: C, 64.75; H, 4.13; N, 17.98; Cl, 9.09. Found: C, 64.45; H, 4.03; N, 17.78; Cl, 8.99%.

2.2.9. 5-Amino-4-(p-methoxyphenylazo)-3-(p-tolyl)-1-phenyl-1H-pyrazol (2$_i$)

M.p. 170–171 °C (90% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 2.1(s, 3H, CH_3), 3.8(s, 3H, OCH_3), 7.2–7.9 (m, 13H, Ar–H), 8.2 (s, exch., 2H, NH_2). *Anal.* Calc. for $C_{23}H_{21}N_5O$: C, 72.12; H, 5.51; N, 18.28. Found: C, 72.08; H, 5.35; N, 18.19%.

2.2.10. 5-Amino-4-(p-chlorophenylazo)-3-(p-tolyl)-1-phenyl-1H-pyrazol (2$_j$)

M.p. 160–161 °C (95% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 2.47 (s, 3H, CH_3), 7.1–8.0 (m, 13H, Ar–H), 8.05 (s, exch., 2H, NH_2). *Anal.* Calc. for $C_{22}H_{81}N_5Cl$: C, 68.18; H, 4.67; N, 18.07; Cl, 9.14. Found: C, 68.12; H, 4.39; N, 17.99; Cl, 8.96%.

2.2.11. 5-Amino-4-(p-carboxyphenylazo)-3-(p-tolyl)-1-phenyl-1H-pyrazol (2$_k$)

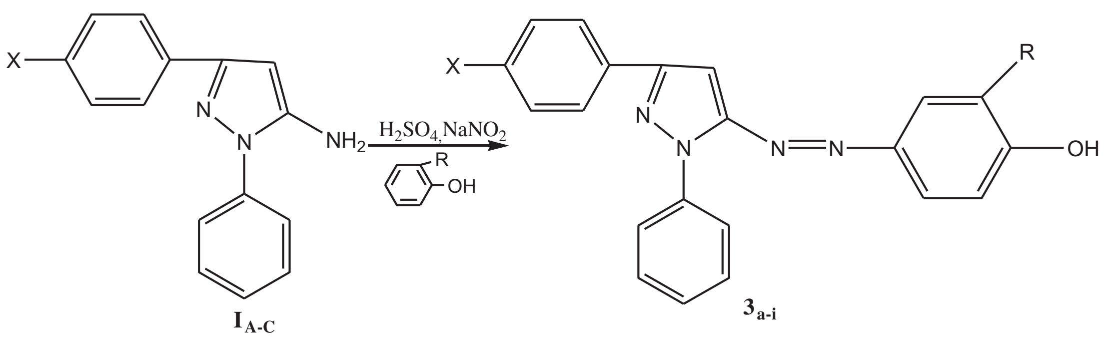
M.p. 300–303 °C (93% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 2.3 (s, 3H, CH_3), 7.1–8.0 (m, 13H, Ar–H), 8.1 (s, exch., 2H, NH_2); ^{13}C NMR (DMSO-d6): δ/ppm = 21.8 (CH_3), 121.7 (C_4), 149.6 (C–NH_2), 156.7 (C_3), 167.9 (COOH), 123.3, 123.6, 124.7, 125.8, 128.6, 129.9, 130.4, 131.4, 131.7, 137.3, 138.2, 139.0, 140.4. *Anal.* Calc. for $C_{23}H_{19}N_5O_2$: C, 69.57; H, 4.81; N, 17.64. Found: C, 69.29; H, 4.58; N, 17.45%.

2.2.12. 5-Amino-4-(p-hydroxyphenylazo)-3-(p-tolyl)-1-phenyl-1H-pyrazol (2$_l$)

M.p. 170–172 °C (91% yield); MS (EI): m/z (%) = 369 (M, 100), 248 (31), 142 (27), 105 (2), 77 (51), 51 (17). *Anal.* Calc. for $C_{22}H_{19}N_5O$: C, 71.6; H, 5.17; N, 18.97. Found: C, 71.34; H, 5.05; N, 18.69%.

2.3. Synthesis of 3-substituted 5-arylazo pyrazoles

Sodium nitrite (2.1 mmol) was added to cold (ice–acetone bath) conc. H_2SO_4 (21.2 ml) and the suspension obtained was stirred for 10–15 min at 20 °C. The mixture was cooled to 0–5 °C and a cold solution of pyrazole (2.1 mmol) was carefully added in



$I_{A\text{-}C}$

$3_{a\text{-}i}$

A: X = H
B: X = Cl
C: X = CH_3

a : X = H, R = NO_2
b: X = H, R = CHO
c : X = H, R = NH_2
d: X = Cl, R = NO_2
e : X = Cl, R = CHO
f: X = Cl, R = NH_2
g : X = CH_3, R = NO_2
h: X = CH_3, R = CHO
i : X = CH_3, R = NH_2

Scheme 2 Synthesis of 3-substituted 5-arylazopyrazoles.

portions. The mixture was stirred continuously at 0–5 °C for 2 h. Phenol (2.1 mmol) was dissolved in NaOH (2.1 mmol, 0.085 g) in water (8 ml) and the solution was added dropwise to the diazonium salt of pyrazole in which the temperature was kept at 0–5 °C and the pH of the mixture was kept at 10 (5 N NaOH was added when necessary). The mixture stirred continuously at room temperature for 1 h and the solid formed was filtered off, washed with water, dried, and crystallized from ethanol. The reaction is shown in Scheme 2.

2.3.1. 2-Nitro-4-(1′,3′-diphenyl pyrazole-5-ylazo) phenol (3_a)

M.p. 130–132 °C (70% yield); MS (EI): *m*/*z* (%) = 385 (M, 45), 357 (46), 235 (15), 105 (9), 77(100), 51 (58). *Anal.* Calc. for $C_{21}H_{15}N_5O_3$: C, 65.51; H, 3.92; N, 18.19. Found: C, 65.37; H, 3.69; N, 18.11%.

2.3.2. 2-Aldehydo-4-(1′,3′-diphenyl pyrazole-5-ylazo) phenol (3_b)

M.p. 100–102 °C (85% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 7.2 (s, 1H, CH), 7.3–8.1 (m, 13H, Ar–H), 9.1 (s, exch., 1H, OH), 10.2 (s, 1H, CHO). *Anal.* Calc. for $C_{22}H_{16}N_4O_2$: C, 71.79; H, 4.37; N, 15.78. Found: C, 71.49; H, 4.15; N, 15.54%.

2.3.3. 2-Amino-4-(1′,3′-diphenyl pyrazole-5-ylazo) phenol (3_c)

M.p. 158–160 °C (60% yield); MS (EI): *m*/*z* (%) = 355 (M, 45), 128 (26), 105 (18), 77(100), 51(47). *Anal.* Calc. for $C_{21}H_{17}N_5O$: C, 71.05; H, 4.82; N, 19.72. Found: C, 69.88; H, 4.59; N, 19.65%.

2.3.4. 2-nitro-4-(1′-phenyl-3′-(4-chlorophenyl) pyrazole-5-ylazo)phenol (3_d)

M.p. 160–162 °C (65% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 7 (s, 1H, CH), 7.3–8.1 (m, 12H, Ar–H), 8.2 (s, exch., 1H, OH). *Anal.* Calc. for $C_{21}H_{14}N_5O_3Cl$: C, 60.12; H, 3.36; N, 16.69; Cl, 3.98. Found: C, 59.87; H, 3.13; N, 16.39; Cl, 3.74%.

2.3.5. 2-Aldehydo-4-(1′-phenyl-3′-(4-chlorophenyl) pyrazole-5-ylazo)phenol (3_e)

M.p. 165–167 °C (80% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 6.9 (s, 1H, CH), 6.8–8.2 (m, 12H, Ar–H), 9.8 (s, exch., 1H, OH), 10.0 (s, 1H, CHO). *Anal.* Calc. for $C_{22}H_{15}N_4O_2Cl$: C, 65.64; H, 3.75; N, 13.92; Cl, 8.08. Found: C, 65.8; H, 3.95; N, 13.72; Cl, 7.88%.

2.3.6. 2-Amino-4-(1′-phenyl-3′-(4-chlorophenyl)pyrazole-5-ylazo)phenol (3_f)

M.p. 155–156 °C (55% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 6.9 (s, 1H, CH), 7.5–8.5 (m, 12H, Ar–H), 9.7 (s, exch., 1H, OH), 11.7 (s, exch., 2H, NH_2). *Anal.* Calc. for $C_{21}H_{16}N_5OCl$: C, 64.75; H, 4.13; N, 17.98; Cl, 9.09. Found: C, 64.45; H, 4.05; N, 17.75; Cl, 8.99%.

2.3.7. 2-Nitro-4-(1′-phenyl-3′-(p-tolyl)pyrazole-5-ylazo)phenol (3_g),

M.p. 140–143 °C (80% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 2.49 (s, 3H, CH_3), 7.15 (s, 1H, CH), 7.8–8.2 (m, 12H, Ar–H), 8.7 (s, exch., 1H, OH). *Anal.* Calc. for $C_{22}H_{17}N_5O_3$: C, 66.22; H, 4.28; N, 17.55. Found: C, 66.19; H, 4.15; N, 17.34%.

2.3.8. 2-Aldehydo-4-(1′-phenyl-3′-(p-tolyl)pyrazole-5-ylazo) phenol (3_h)

M.p. 130–132 °C (85% yield); ^{1}H NMR (DMSO-d6): δ/ppm = 2.4 (s, 3H, CH_3), 6.9 (s, 1H, CH), 8.0–8.8 (m, 12H, Ar–H), 9.7 (s, exch., 1H, OH), 11.3 (s, 1H, CHO). *Anal.* Calc. for $C_{23}H_{18}N_4O_2$: C, 72.85; H, 4.74; N, 14.66. Found: C, 72.59; H, 4.58; N, 14.49%.

2.3.9. 2-Amino-4-(1′-phenyl-3′-(p-tolyl)pyrazole-5-ylazo) phenol (3_i)

M.p. 170–171 °C (65% yield); MS (EI): *m*/*z* (%) = 370 ($M^+ + 1$, 100), 235(11), 122 (67), 105 (4), 77 (38), 51 (21). *Anal.* Calc. for $C_{22}H_{19}N_5O$: C, 71.60; H, 5.81; N, 18.97. Found: C, 71.39; H, 5.38; N, 18.73%.

3. Results and discussion

Reaction of phenyl hydrazine with ketonitrile derivatives in ethanol gave 5-amino-1,3-diphenyl pyrazole **1a** in 65% yield, 5-amino-3-(4-chlorophenyl-1-phenyl)pyrazole **1b** in 65% yield and 5-amino-3-(4-methylphenyl-1-phenyl)pyrazole **1c** in 70% yield (Naresh et al., 2005; Krishna et al., 1979; David et al., 1979; Simay and Takacs, 1980). 5-Amino pyrazoles were coupled in position 4 with a variety of aromatic diazonium salts in ethanol buffered with sodium acetate solution to produce the corresponding 3-substituted 5-amino-4-arylazopyrazole **2a–l** in good yields (Scheme 1), leaving a free amino group (Metwally et al., 2004) which supported by the clear band at 3423–3424 cm^{-1} in IR spectra.

The azo group (N=N) vibration frequencies of **2a–l** were found at 1496–1596 cm^{-1} (Table 1). ^1H NMR spectra of **2al** showed exchangeable signals within the 8.05–8.20 ppm region and were attributed to NH_2 groups adjacent to the azo group. Also, the diazotization of the amino group at position 5 of the pyrazole ring by the nitrosyl sulfuric acid method followed by coupling with different phenols (Scheme 2) in NaOH solution at pH 10 give rise to corresponding dyes **3a–I** (Scheme 2).

The IR spectra of compounds **3a-I** showed absorption bands within the region of 1495–1599 cm^{-1} and assigned to the azo (N=N) group. They also showed abroad absorption bands at 3422–3460 cm^{-1} for the OH group (Karci and Karci, 2008). IR spectra showed the absence of the frequency for NH_2 groups (Table 2). The ^1H NMR spectra of compounds **3a–I** showed singlet signals at 6.7–7.15 ppm for CH proton at position 4 of the pyrazole ring and also showed the absence of signal of NH_2 group. The spectral data for such compounds are recorded in Tables 1 and 2.

3.1. Electronic absorption spectra

The electronic spectra showed intense bands at λ_{max} ranging from 363.5–413 nm and λ_{max} ranging from 443–515.48 nm for dyes **2a–l** and **3a–I**, respectively. It was found that: (a) a clear bathchromic shift was obtained for the prepared dyes when the coupling component contained OCH_3, Cl, OH, and COOH in the *p*-position. The bath chromic shifts accompanying methoxy substituents result from hyper conjugation in which the σ-electrons of methoxy group are mobile enough to interact with the chromphoric group (Ho and Wang, 1995; Silverstein, 1981). (b) The bath chromic shifts accompanying the substituents in dyes component increased is in the following order OCH_3 > OH > Cl > COOH. (c) The bathchromic shifts of the COOH group are particularly large due to polarization effect (Kaaska and Sokolowska, 1987; Ho, 2005). (d) The bathchromic shifts causes by the azo group at position 5 are much greater than that causes by the azo group at position 4. (e) The bathchromic shifts accompanying the subsistent in the dyes **3a–I** increased in the following order NH_2 > NO_2 > CHO.

4. Dyeing and fastness determinations

4.1. Dyeing procedure

All applications and fastness properties of dye stuffs have been performed at Misr Spinning and Weaving Company, Central Q.C. Laboratories, Mehalla El-Kubra, Egypt.

4.1.1. Dyeing of polyester

The required amount of the dye (2% shade) was suspended in water and then added drop wise to a stirred solution of Dispersogen PI cc/I (dispersing agent of Hoechst). A sample of fibre was immersed in a bath of 50 °C for 5 min with a liquor ratio 1:20. 2 g/l Eganal RAP (levelling agent of Hoechst) and 4 g/l Hostatex LOET (carrier of Hoechst) was added to the bath with stirring for 10 min.

The pH was adjusted to 4–5 by the addition of acetic acid. The thoroughly dispersed dye solutions were added to the bath and the temperature was raised to 98 °C within 60 min. Total dyeing time was then being 90 min afterwards it was cooled to 60 °C and then subjected to washing, dyed samples rinsed and dried.

4.1.2. Dyeing of polyester/wool fibre (55/45)

The dyestuffs are pasted with small amount of warm water (1 g), then further dilution to 100 ml with warm water at 60–70 °C. Sample of 5 g of PES/wool blend was immersed in bath of 50 °C with a liquor 1:20 which adjusted with acetic acid to pH 4–5 and Levegal PT carrier from (Bayer) was added to the dye bath by 4 g/L at 50–60 °C. The sample was allowed to run for about 15 min, then the dyestuff was added to the liquor and the temperature was raised to 98 °C within 45 min. At 98 °C, dyeing was carried out for 60–90 min. Then the sample was taken, rinsed with cold water and divided into four pieces.

4.1.3. Dyeing of wool fibre

The dyestuffs were dissolved by pasting in small amount of hot water (1 g) at 70 °C. And dilute with hot water to 100 ml. Take 20 ml to the dye bath. A sample of 5 g of wool (100%) fibre was immersed in the dye bath at 60 °C with a liquor ratio 1:20 and adjusted by acetic acid to a pH 5 for 10 min. Then 50 g/L of anhydrous sodium sulfate (Na_2SO_4) was added. The temperature was raised to 90 °C during 45 min, with continuous stirring and the dyeing was continued at 90 °C for 1 h. The results are collected in the Tables 3–8.

4.1.3.1. Fastness to washing. The test assessed using the launder-o-metersponsored by the American Association of Textile Chemists and Colorists (**A.A.T.C.C.**). A test specimen (10 cm × 4 cm) of the dyed fibre is taken and a samples (5 cm × 4 cm) of the white cotton and polyester fibres were placed in the container of the washing machine, with the necessary amount of the soap solution (5 g/l) previously heated to 50 °C. The specimen was rinsed twice in cold water for 10 min. and squeezed, and then the composite specimen is opened out and dried in air. The colour alteration of the uncovered portion of the specimen and the staining of both undyed fabrics was assessed using the international Grey scale.

4.1.3.2. Fastness to perspiration. The test specimen (6 cm × 6 cm) is placed between 2 species of undyed fabrics (cotton and polyester) and sewed along one side to form the test specimen. Testing fabrics were immersed into the solution of pH 4 at room temperature for 30 min. The solution was poured off and the sample was placed between two plastic plates (7.5 cm × 6.5 cm) under a force of about 4.5 kg. The plates containing the composite samples are kept in an oven at 37 °C for 4 h. The specimen is then separated from the undyed samples. Colours alteration of dyed material and staining of the undyed samples were assessed using the international Grey scale.

4.1.3.3. Fastness to rubbing. Test assessment was made according to the Grey scale using Crokmeter of atlas electronic type.

Table 3 Fastness properties of dyes **2a–l** on polyester fabrics.

Dye	Colour	Washing		Perspiration		Rubbing		Sublimation		Light
		PES	Cotton	PES	Cotton	Dry	Wet	PES	Cotton	
2a	Golden-yellow	4–5	4–5	3–4	3–4	4	3–4	4	4	6
2b	Lemon-yellow	4–5	4–5	3–4	3–4	4	3–4	3–4	4–3	6
2c	Lemon-yellow	4–5	4–5	3–4	3–4	3–4	3–4	4	4	5–6
2d	Yellow-brown	4–5	4–5	3–4	3–4	3–4	3–4	4	4	5–6
2e	Golden yellow	4–5	4–5	4	4	4–5	4	4	4	6
2f	Lemon-yellow	4–5	4–5	3–4	3–4	4–3	3–4	3	4	6
2g	Lemon-yellow	4–5	4–5	4	4	4	3–4	3–4	4	6
2h	Buff	4–5	4–5	4	4	4	5	4	3–4	6
2i	Lemon-yellow	4–5	4–5	3–4	4	4	3–4	4	4	6
2j	Lemon-yellow	4–5	4–5	3–4	3–4	4–5	3–4	3–4	4	6
2k	Lemon-yellow	4–5	4–5	3–4	3–4	4	3–4	4	4	6
2l	Brown	4–5	4–5	3–4	3–4	4	3–4	4	3–4	5–6

Table 4 Fastness properties of dyes **2a–l** on wool fabrics.

Dye	Colour	Washing		Perspiration		Rubbing		Light
		PES	Cotton	PES	Cotton	Dry	Wet	
2a	Golden-yellow	4–5	4–5	3–4	3–4	4	3–4	6
2b	Lemon-yellow	4–5	4–5	4	3–4	4	3–4	6
2c	Golden-yellow	4–5	4–5	2–3	2–3	2–3	2–3	6
2d	Yellow-brown	4–5	4–5	3–4	3–4	3–4	3–4	6
2e	Golden-yellow	4–5	4–5	4	4	4–5	4	6
2f	Lemon-yellow	4–5	4–5	4	4	3–4	3–4	6
2g	Golden-yellow	4–5	4–5	4	4	3–4	3–4	6
2h	Buff	4–5	4–5	4	4	4–5	4	6
2i	Lemon-yellow	4–5	4–5	3–4	3–4	4	3–4	4–5
2j	Lemon-yellow	4–5	4–5	3–4	3–4	4	3–4	4–5
2k	Lemon-yellow	4–5	4–5	3–4	3–4	3–4	3–4	6
2l	Brown	4–5	4–5	3–4	3–4	4	4	4–5

Table 5 Fastness properties of dyes 2a-l on polyester/wool fabrics.

Dye	Colour	Washing		Perspiration		Rubbing		Sublimation		Light
		PES	Cotton	PES	Cotton	Dry	Wet	PES	Cotton	
2a	Lemon-yellow	4–5	4–5	3–4	4	2–3	3–4	4	4	6
2b	Lemon-yellow	4–5	4–5	3–4	4	3–4	3–4	4	4	6
2c	Golden-yellow	4	3–4	3–4	4	4	2–3	4	4	6
2d	Olive	4–5	4–5	3–4	4	3–4	3–4	4	4	6
2e	Yellow-brown	4–5	4–5	4	4	4	4	4	4	6
2f	Buff	4–5	4–5	4	4	4	4	4	4	5–6
2g	Brown	4–5	4–5	4	4	3	3	4	4	5–6
2h	Brown	4–5	4–5	4	4	3	4	4	4	6
2i	Lemon-yellow	4–5	4–5	4	4	2–3	3	4	4	6
2j	Lemon-yellow	4–5	4–5	3–4	3–4	2–3	3	4	4	6
2k	Lemon-yellow	4–5	4–5	4	4	2	3	4	4	6
2l	Olive	4–5	4–5	4	4	3	3–4	4	4	6

Dyed fabrics to be tested were placed on the base of the Crockmeter. A square of white testing cloth was mount over the end of the finger which protects downward on the specimen sliding back, and force to make ten complete turns of the crank at the rate of one turn per a second. For wet rubbing test, the testing squares were thoroughly wet in distilled water and squeezed between filter papers through hand wringer under standard conditions. The rest of the procedure is similar to that used in dry rubbing test.

4.1.3.4. Fastness to sublimation. A composite specimen (10 cm × 4 cm) of the dyed fiber contacted with undyed fiber (cotton and polyester) is rolled into a cylinder and placed in an oven at 180 °C for 1 min. The specimen is removed from

Table 6 Fastness properties of dyes **3a–i** on polyester fabrics.

Dye	Colour	Washing		Perspiration		Rubbing		Sublimation		Light
		PES	Cotton	PES	Cotton	Dry	Wet	PES	Cotton	
3a	Yellow-brown	4–5	4–5	3–4	3–4	4	3–4	4	4	6
3b	Lemon-yellow	4–5	4–5	3–4	4	4	3–4	4	4	6
3c	Yellow-brown	4–5	4–5	3–4	3–4	4	3–4	4	4	6
3d	Yellow-brown	4–5	4–5	3–4	3–4	4	3–4	4	4	6
3e	Yellow-brown	4–5	4–5	3–4	3–4	4	3–4	4	4	6
3f	Yellow-brown	4–5	4–5	3–4	3–4	3–4	3–4	3–4	3–4	6
3g	Yellow-brown	4–5	4–5	3–4	3–4	3–4	3–4	4	4	6
3h	Yellow-brown	4–5	4–5	4	4	4–3	3–4	4	4	6
3i	Yellow-brown	4–5	4–5	3–4	3–4	3–4	3–4	4	4	6

Table 7 Fastness properties of dyes **3a–i** on wool fabrics.

Dye	Colour	Washing		Perspiration		Rubbing		Light
		PES	Cotton	PES	Cotton	Dry	Wet	
3a	Yellow-brown	4–5	4–5	3–4	3–4	4	3–4	6
3b	Golden-yellow	4–5	4–5	3–4	4	4	3–4	6
3c	Yellow-brown	4–5	4–5	3–4	3–4	4	3–4	6
3d	Yellow-brown	4–5	4–5	4	4	2–3	2–3	6
3e	Yellow-brown	4–5	4–5	3–4	3–4	3–4	3–4	6
3f	Yellow-brown	4–5	4–5	4	4	2–3	2–3	6
3g	Yellow-brown	4–5	4–5	3–4	3–4	2–3	2–3	6
3h	Yellow-brown	4–5	4–5	3–4	3–4	3–4	3–4	6
3i	Yellow-brown	4–5	4–5	3–4	3–4	2–3	2–3	6

Table 8 Fastness properties of dyes **3a–i** on polyester/wool fabrics.

Dye	Colour	Washing		Perspiration		Rubbing		Sublimation		Light
		PES	Cotton	PES	Cotton	Dry	Wet	PES	Cotton	
3a	Yellow-brown	4–5	3–4	4	3–4	4	3–4	4	4	6
3b	Yellow-brown	4–5	4–5	3–4	4	3–4	3	4	4	6
3c	Yellow-brown	4–5	4–5	4	4	4	3–4	4	4	6
3d	Yellow-brown	4–5	4–5	3–4	3–4	4	3–4	4	4	6
3e	Brown	4–5	4–5	4	4	3	3	4	4	5–6
3f	Yellow-brown	4–5	4–5	4	4	4	4	4	4	5–6
3g	Yellow-brown	4–5	4–5	3–4	3–4	3–4	3–4	4	4	6
3h	Yellow-brown	4–5	4–5	4	4	3–4	3–4	4	4	6
3i	Golden-yellow	4–5	4–5	4	4	3–4	3–4	4	4	6

the tube and unrolled. The colour which sublimes on the undyed cloth is assessed with the standard Grey scale for staining.

4.1.3.5. Fastness to light. The specimen of the dyed textiles are exposed, in a well ventilated exposure chamber to light from a xenon arc, along with dyed wool standards. The air temperature in the chamber was maintained at 30 °C. The effective humidity was maintained at 45 + 5%. The variation of light intensity over the area covered by specimen and standards should not exceed 20%. The samples and standards were exposed simultaneously under the same conditions for the same time. The samples were viewed in the light from a day-light fluorescent lamp and given a degree in comparison with the relative to Blue scale (1–8) standards of A.A.T.C.C.

5. Conclusion

A set of 21 disperse dyes $\mathbf{2}_{a\text{–}l}$, $\mathbf{3}_{a\text{–}I}$, these dyes were synthesized by azo coupling. All of the dyes were investigated for their dyeing characteristics on polyester, wool and wool/polyester blend. The electronic absorption spectra cover λ_{max} a range of 363.5–413 for dyes 2 and λ_{max} range of 443–515 for dyes 3 at uniformly high absorption intensity and give bright intense hues from yellow to orange due to variation in polarity.

The dyed fabrics exhibit very good to excellent (4–5) washing, perspiration and sublimation fastness properties with a little variation in the moderate, good to excellent rubbing fastness dry and wet The light fastness of dyed fabrics exhibit very good to excellent (5–6) fastness properties.

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