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Pyridazine derivatives and its related compounds. Part 31. Synthesis of some disperse dyes derived from 3-amino-1*H*-pyrzolo[3,4-*c*]pyridazine and their color assessment on polyester fabrics

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ABSTRACT

The 6-methyl-3, 4-diphenyl-7-(2-phenylhydrazono) pyrimido [1', 2':1, 5] pyrazolo [3,4-*c*] pyridazin-8(*7H*)-one and 3,4-diphenyl-7-(phenyldiazenyl)pyrimido[1',2':1,5]pyrazolo[3,4-*c*]pyridazine-6,8-diamine derivatives were applied to polyester fiber as disperse dyes. They were found to exhibit varying in hue from orange-yellow to orange-red, their absorption spectral characteristics, fastness properties and colour assessment are also reported.

1. Introduction

Azo disperse dyes derived from heterocyclic ring systems have many advantages, such as color deepening effect as an intrinsic property of heterocyclic ring and resulting in good sublimation fastness of dyes fibers [1]. For instance, amino-subtituted pyrazole, thiazole, thiophene compounds afforded very electronegative diazo components and, consequently, provide a pronounced benzenenoid compounds [2]. We have previously reported the synthesis of novel heterocyclic systems such as 3-substituted azo-3*H*-pyrazolo[3,4-*c*]pyridazines [3], 4-[(4-arylazo-3,5-dimethylpyrazol-1-yl)carbonyl]-3,6-diphenyl pyridazine-3(2*H*)-one (Part 30) [4], 3-(4-arylazo-3,5-disubstituted pyrazol-1-yl)-4,5,6-triphenylpyridazines [5] and 5-amino-6-[[4-arylazo-3,5-dimethylpyrazol-1-yl]-carbonyl]-3,4-diphenylthieno[2,3-c]pyridazines [6] and their application to polyester fibers as disperse dyes, which gave encouraging results.

In continuation of our studies, we report here the synthesis of 6-methyl-3,4-diphenyl-7-(2-phenylhydrazono)pyrimido [1', 2':1,5]pyrazolo[3,4-*c*]pyridazin-8(*7H*)-one and 3,4-diphenyl-7-(phenyldiazenyl)pyrimido[1',2':1,5]pyrazolo[3,4-*c*]pyridazine-6,8-diamine derivatives use as disperse dyes for polyester. The absorption spectral characteristics, fastness properties and color assessment of the dyes are also discussed.

2. Experimental

2.1. Instrumentation

All melting points were measured using a Büchi 510 melting point apparatus and are reported uncorrected. IR spectra were recorded on a Bruker Vector 22 Germany spectrometer (KBr). The ^{1}H NMR spectra were obtained on Varian Gemini 200MHz spectrometer, and chemical shifts are expressed in δ ppm using TMS as an internal standard. Mass spectra were obtained at 70eV using a GCMS-QP1000EX Shimadzu spectrometer. Electronic spectra were recorded on UV-visible recording Shimadzu spectrophotometer from dye solution in DMF at a concentration of 1×10^{-5}mole/L.

2.2. Synthesis

The synthesis of 3-amino-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **2** (Scheme 1) [7], and azobenzene compounds

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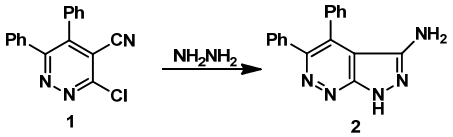
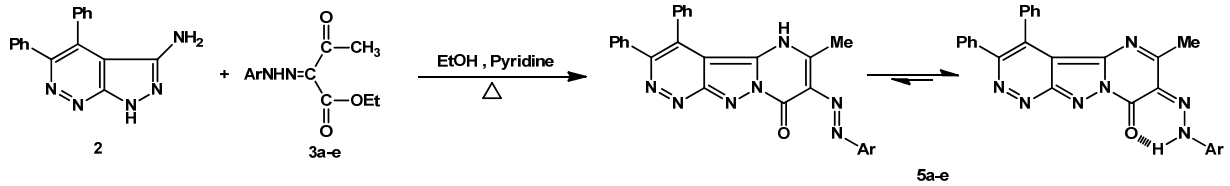
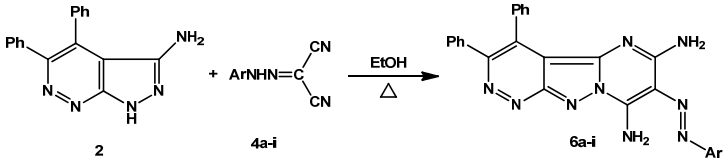


Scheme 1



a, Ar = Ph; b, Ar = 4-MeC$_6$H$_4$; c, Ar = 4-MeOC$_6$H$_4$; d, Ar = 2-ClC$_6$H$_4$; e, Ar = 4-NO$_2$C$_6$H$_4$

Scheme 2



a, Ar = Ph; b, Ar = 4-MeC$_6$H$_4$; c, Ar = 4-MeOC$_6$H$_4$; d, Ar = 2-ClC$_6$H$_4$; e, Ar = 4-NO$_2$C$_6$H$_4$; f, Ar = 2-MeC$_6$H$_4$; g, Ar = 3-MeC$_6$H$_4$; h, Ar = 2-MeOC$_6$H$_4$; i, Ar = 3-ClC$_6$H$_4$

Scheme 3

3a-e and **4a-i** [8], were conducted according to known procedures. Spectral data for compounds **3a-e** and **4a-i** were described in the previous parts (Scheme 2 and 3) [9,10].

2.2.1.General procedure for the synthesis of 6-methyl-3,4-diphenyl-7-(2-phenylhydrazono)pyrimido [1',2':1,5] pyrazolo[3,4-c]pyridazin-8(7H)-one (5a-e)

To a solution of 3-amino-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **2** (1.0 g, 3.48 mmoles) in a mixture of ethanol and pyridine 20 mL (3:1, *v*:*v*), ethyl azobenzeneacetoacetate derivatives **3a-e** (3.48 mmoles) were added, the reaction mixture was refluxed for specific reaction time. The solvent was reduced to its half and left at room temperature for 48 h. The separated solid was filtered off, washed with ethanol (80%), dried and recrystallized from ethanol (Scheme 2) .

6-Methyl-3,4-diphenyl-7-(2-phenylhydrazono)pyrimido [1',2':1,5]pyrazolo[3,4-c]pyridazin-8(7H)-one (**5a**): Prepared from ethyl phenylazoacetoacetate **3a**. Reaction time: 8 h. Color: Yellow crystals. Yield: 69%. M.p.: 232-233 °C. FT-IR (KBr, ν, cm^{-1}): 3446, 3176 (NH), 3073(CH$_{arom.}$), 2918 (CH$_{aliph.}$), 1671 (C=O), 1600 (C=N), 1546(C=C). UV/Vis (DMF, λ_{max}, nm, (log ε)): 267.4 (4.1). Anal. calcd. for $C_{27}H_{19}N_7O$: C, 70.88; H, 4.19; N, 21.43. Found: C, 70.70; H, 4.00; N, 21.40%.

6-Methyl-3,4-diphenyl-7-(2-(p-tolyl)hydrazono)pyrimido [1', 2':1,5]pyrazolo[3,4-c]pyridazin-8(7H)-one (**5b**): Prepared from ethyl 4-methylphenylazoacetoacetate **3b**. Reaction time: 10 h. Color: Yellow crystals. Yield: 73%. M.p.: 234-235 °C. FT-IR (KBr, ν, cm^{-1}): 3454, 3157 (NH), 3077 (CH$_{arom.}$), 2915, 2860 (CH$_{aliph.}$), 1671 (C=O), 1557 (C=C). UV/Vis (DMF, λ_{max}, nm, (log ε)): 266.5 (4.3). Anal. calcd. for $C_{28}H_{21}N_7O$: C, 71.32; H, 4.49; N, 20.79. Found: C, 71.20; H, 4.30; N, 20.75%.

7-(2-(4-Methoxyphenyl)hydrazono)-6-methyl-3, 4-diphenyl pyrimido[1',2':1,5]pyrazolo[3,4-c]pyridazin-8(7H)-one (**5c**): Prepared from ethyl 4-methoxyphenylazoacetoacetate **3c**. Reaction time: 7 h. Color: Yellow crystals. Yield: 83%. M.p.: 248-249 °C. FT-IR (KBr, ν, cm^{-1}): 3441 (NH), 3056 (CH$_{arom.}$), 2923 (CH$_{aliph.}$), 2838 (OCH$_3$), 1597 (C=N), 1539 (C=C). MS (EI, *m/z* (%)): 488 (M$^+$+1, 3.88), 487 (M$^+$, 7.70), 353 (0.55), 108 (100). UV/Vis (DMF, λ_{max}, nm, (log ε)): 275.7 (4.0). Anal. calcd. for $C_{28}H_{21}N_7O_2$: C, 68.98; H, 4.34; N, 20.11. Found: C, 68.80; H, 4.20; N, 20.10%.

7-(2-(2-Chlorophenyl)hydrazono)-6-methyl-3, 4-diphenylpyrimido[1',2':1,5]pyrazolo[3,4-c]pyridazin-8(7H)-one (**5d**): Prepared from ethyl 2-chlorophenylazoacetoacetate **3d**. Reaction time: 7 h. Color: Yellow crystals. Yield: 78%. M.p.: 245-246 °C. FT-IR (KBr, ν, cm^{-1}): 3188 (NH), 3032 (CH$_{arom.}$), 2924 (CH$_{aliph.}$), 1666 (C=O), 1546 (C=C), 756 (Cl-C). MS (EI, *m/z* (%)):494 (M$^+$+2, 0.57), 492(M$^+$, 0.42), 383 (2.89), 339 (10.58). UV/Vis (DMF, λ_{max}, nm, (log ε)): 265.2 (4.0). Anal. calcd. for $C_{27}H_{18}ClN_7O$: C, 65.92; H, 3.69; N, 19.93. Found: C, 65.90; H, 3.50; N, 19.90%.

6-Methyl-7-(2-(4-nitrophenyl)hydrazono)-3, 4-diphenylpyrimido[1',2':1,5]pyrazolo[3,4-c]pyridazin-8(7H)-one (**5e**): Prepared from ethyl 4-nitrophenylazoacetoacetate **3e**. Reaction time: 6 h. Color: Yellow crystals. Yield: 79.6%. M.p.: 242-243 °C. FT-IR (KBr, ν, cm^{-1}): 3421, 3188 (NH), 3082 (CH$_{arom.}$), 2931 (CH$_{aliph.}$), 1719 (C=O), 1611 (C=N), 1554 (C=C), 1517, 1338 (NO$_2$). MS (EI, *m/z* (%)): 501 (M$^+$-1, 14.7), 500 (M$^+$-2, 50.5), 123 (100). UV/Vis (DMF, λ_{max}, nm, (log ε)): 265 (4.2). Anal. calcd. for $C_{27}H_{18}N_8O_3$: C, 64.54; H, 3.61; N, 22.30. Found: C, 64.30; H, 3.40; N, 20.30%.

2.2.2. General procedure for the synthesis of 3,4-diphenyl-7-(phenyldiazenyl)pyrimido[1',2':1,5]pyrazolo[3,4-c] pyridazine-6,8-diamine (6a-i)

To a solution of 3-amino-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **2** (1.0 g, 3.48 mmoles) in a mixture of ethanol and pyridine 30 mL (3:1, *v*:*v*), azobenzene malononitrile derivatives **4a-i** (3.48 mmoles) was added, the reaction mixture was refluxed for specific time. The solvent was reduced and left at room temperature. The separated solid was filtered off, washed

with ethanol (80%), dried and recrystallized from ethanol (Scheme 3).

3,4-Diphenyl-7-(phenyldiazenyl)pyrimido[1',2':1,5] pyrazolo [3,4-c]pyridazine-6,8-diamine (**6a**): Prepared from phenylazo malononitrile **4a**. Reaction time: 18 h. Color: Yellow crystals. Yield: 62.5%. M.p.: 281-282 °C. FT-IR (KBr, ν, cm^{-1}):3444, 3378, 3324, 3151 (NH_2 groups), 3059 ($CH_{arom.}$), 2911 ($CH_{aliph.}$), 1613 (C=N), 1565 (C=C). UV/Vis (DMF, λ_{max}, nm, (log ε)):269.9(4.4). Anal. calcd. for $C_{26}H_{19}N_9$: C, 68.26; H, 4.19; N, 27.55. Found: C, 68.10; H, 4.00; N, 27.60%.

3,4-Diphenyl-7-(p-tolyldiazenyl)pyrimido[1',2':1,5] pyrazolo [3,4-c]pyridazine-6,8-diamine (**6b**): Prepared from 4-methyl phenylazomalononitrile **4b**. Reaction time: 24 h. Color: Yellow crystals. Yield: 61%. M.p.: > 300 °C. FT-IR (KBr, ν, cm^{-1}):3467, 3399, 3275, 3128 (NH_2 groups), 2919, 2854 ($CH_{aliph.}$), 1609(C=N). MS (EI, *m/z* (%)):472 (M^+, 0.63), 119 (2.62), 91 (5.51). UV/Vis (DMF, λ_{max}, nm, (log ε)): 265.4 (4.6). Anal. calcd. for $C_{27}H_{21}N_9$: C, 68.78; H, 4.49; N, 26.74. Found: C, 68.60; H, 4.30; N, 26.80%.

7-((4-Methoxyphenyl)diazenyl)-3,4-diphenylpyrimido [1',2': 1,5]pyrazolo[3,4-c]pyridazine-6,8-diamine (**6c**): Prepared from 4-methoxyphenylazomalononitrile **4c**. Reaction time: 24 h. Color: brown crystals. Yield: 70%. M.p.: 298-299 °C. FT-IR (KBr, ν, cm^{-1}):3455, 3407, 3262, 3122 (NH_2 groups), 2938 ($CH_{aliph.}$), 2834 (OCH_3), 1598 (C=N), 1545 (C=C). UV/Vis (DMF, λ_{max}, nm, (log ε)): 265.8 (4.1). Anal. calcd. for $C_{27}H_{21}N_9O$ (487.52): C, 66.52; H, 4.34; N, 25.86. Found: C, 66.40; H, 4.20; N, 25.80%.

7-((2-Chlorophenyl)diazenyl)-3,4-diphenylpyrimido[1',2':1,5] pyrazolo[3,4-c]pyridazine-6,8-diamine (**6d**): Prepared from 2-chlorophenylazomalononitrile **4d**. Reaction time: 14 h. Color: yellow crystals. Yield: 81.4%. M.p.: > 300 °C. FT-IR (KBr, ν, cm^{-1}):3466, 3389, 3270, 3139 (NH_2 groups), 3069 ($CH_{arom.}$), 2938 (CH_{aliph}), 1610 (C=N), 1544 (C=C), 751 (C-Cl). MS (EI, *m/z* (%)):494.4 (M^+ + 2, 0.2), 440 (100), 414 (2.32), 380 (1.05), 337 (0.19), 352 (0.77). Anal. calcd. for $C_{26}H_{18}ClN_9$ (491.94): C, 63.48; H, 3.69; N, 25.63. Found: C, 63.30; H, 3.50; N, 25.60%.

7-((4-Nitrophenyl)diazenyl)-3,4-diphenylpyrimido[1',2':1, 5] pyrazolo[3,4-c]pyridazine-6,8-diamine (**6e**): Prepared from 4-nitrophenylazomalononitrile **4e**. Reaction time: 24 h. Color: Red crystals. Yield: 68.2%. M.p.: > 300 °C. FT-IR (KBr, ν, cm^{-1}): 3450, 3338, 3273 (NH_2 groups), 1609 (C=N), 1579 (C=C), 1508, 1318 (NO_2). MS (EI, *m/z* (%)):503 (M^+, 25.45), 381 (3.44), 353 (6.06), 77 (100). UV/Vis (DMF, λ_{max}, nm, (log ε)): 266 (4.5). Anal. calcd. For $C_{26}H_{18}N_{10}O_2$: C, 62.15; H, 3.61; N, 27.87. Found: C, 62.00; H, 3.50; N, 27.80%.

3,4-Diphenyl-7-(o-tolyldiazenyl)pyrimido[1',2':1, 5]pyrazolo [3,4-c]pyridazine-6,8-diamine (**6f**): Prepared from 2-methyl phenylazomalononitrile **4f**. Reaction time: 24 h. Color: Yellow crystals. Yield: 67%. M.p.: 288-289 °C. FT-IR (KBr, ν, cm^{-1}): 3435, 3395, 3268, 3135 (NH_2 groups), 2915 ($CH_{aliph.}$), 1604 (C=N), 1517 (C=C). UV/Vis (DMF, λ_{max}, nm, (log ε)): 266.1 (4.1). Anal. calcd. for $C_{27}H_{21}N_9$: C, 68.78; H, 4.49; N, 26.74. Found: C, 68.60; H, 4.30; N, 26.65%.

3,4-Diphenyl-7-(m-tolyldiazenyl)pyrimido[1',2':1, 5]pyrazolo [3,4-c]pyridazine-6,8-diamine (**6g**): Prepared from 3-methyl phenylazomalononitrile **4g**. Reaction time: 24 h. Color: Yellow crystals. Yield: 61%. M.p.: 283-284 °C. FT-IR (KBr, ν, cm^{-1}): 3408, 3375, 3264, 3116 (NH_2 groups), 2918, 2853 ($CH_{aliph.}$), 1602 (C=N). MS (EI, *m/z* (%)): 396 (0.14), 382 (0.23), 354 (0.57), 319 (0.24), 91 (100). Anal. calcd. for $C_{27}H_{21}N_9$: C, 68.78; H, 4.49; N, 26.74. Found: C, 68.70; H, 4.50; N, 26.70%.

7-((2-Methoxyphenyl)diazenyl)-3,4-diphenylpyrimido [1', 2': 1,5]pyrazolo[3,4-c]pyridazine-6,8-diamine (**6h**): Prepared from 2-methoxyphenylazomalononitrile **4h**. Reaction time: 24 h. Color: Orange crystals. Yield: 74.5%. M.p.: 291-292 °C. FT-IR (KBr, ν, cm^{-1}): 3445, 3389, 3276, 3151 (NH_2 groups), 2912 ($CH_{aliph.}$), 2816 (OCH_3), 1612 (C=N), 1538 (C=C). UV/Vis (DMF, λ_{max}, nm, (log ε)): 269.6 (4.3). Anal. calcd. For $C_{27}H_{21}N_9O$: C, 66.52; H, 4.34; N, 25.86. Found: C, 66.30; H, 4.10; N, 25.75%.

7-((3-Chlorophenyl)diazenyl)-3,4-diphenylpyrimido[1',2':1,5] pyrazolo[3,4-c]pyridazine-6,8-diamine (**6i**): Prepared from 3-chlorophenylazomalononitrile **4i**. Reaction time: 18 h. Color: Yellow crystals. Yield: 64%. M.p.: >300 °C. FT-IR (KBr, ν, cm^{-1}): 3433, 3333, 3269, 3161 (NH_2 groups), 3057 ($CH_{arom.}$), 2914 ($CH_{aliph.}$), 1612 (C=N), 1561 (C=C), 763 (C-Cl). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm):7.34 -7.16 (m, 14H, Ph), 3.34 (s, 4H, $2NH_2$). UV/Vis (DMF, λ_{max}, nm, (log ε)): 266 (4.5). Anal. calcd. for $C_{26}H_{18}ClN_9$: C, 63.48; H, 3.69; N, 25.63. Found: C, 63.30; H, 5.60; N, 25.55%.

2.3. High temperature dyeing method (HT)

2.3.1. Materials

Scoured and bleached polyester 100% (150 130 g/m^2, 70/2 denier) was obtained from Misr Company for Spinning and Weaving El-Mahala El-Kobra, Egypt. The fabric was treated before dyeing with a solution containing non-ionic detergent (Sera Wash M-RK, 5 g/L) and sodium carbonate (2 g/L) in a ratio of 50:1 at 60 °C for 30 min, and then thoroughly washed with water and air dried at room temperature.

2.3.2. Dyeing

The dye baths were prepared from the dye (2% weight of fabric) to a final liquor of 50:1 (*w*:*w*). The pH value of the bath was adjusted to 4.5-5.0 with acetic acid (10%) in the presence of a 1:1 ratio of the dispersing agent (Sera Gal P-LP). The temperature was raised to 130 °C at the rate of 7 °C/min, and dyeing continued for 60 min. After dyeing, the fabrics were thoroughly washed and then subjected to a surface reduction cleaning [(2 g NaOH + 2 g sodium hydrosulphite)/L]. The samples were heated in this solution for 30 min at 85 °C and then thoroughly washed and air-dried. The dyeing was performed at 2% shade by high-temperature techniques and gave generally deep and bright intense hues, ranging from yellow to orange-yellow.

2.4. Color measurements and analyses

2.4.1. Color measurement

The colorimetric parameters of the dyed polyester fabrics were determined on areflectance spectrophotometer (Table 1). The color yields of the dyed samples were determined by using the light reflectance technique performed on UV/VIS Spectrophotometer. The colorstrengths, expressed as K/S values, were determined by applying the Kubelka-Mink Equation (1).

$$K/S = [(1 - R)^2 / 2R] - [(1 - R_o)^2 / 2R_o] \quad (1)$$

where R = Decimal fraction of the reflectance of the dyed fabric; R_o= Decimal fraction of the reflectance of the undyed fabric; K = Absorption coefficient; S = Scattering coefficient.

2.4.2. Fastness tests

2.4.2.1. Fastness to washing

After washing using 5 g/L of the nonionic detergent Hostapal CV and 2 g/L of sodium carbonate at 80 °C for 15 min, the dyed fabrics were tested by using ISO standard methods [11]. A specimen of dyed polyester fabric was stitched between two pieces of undyed cotton and wool fabrics, all of equal length, and then washed at 95 °C for 30 min. The staining on two pieces of undyed cotton and wool fabrics, all of equal length, and then washed at 95 °C for 30 min. The staining on the undyed adjacent fabrics was assessed according to the International Geometric gray scale: 1-poor, 2-fair, 3-moderate, 4-good, 5- excellent.

Table 1. Optical measurements of the synthesized monoazo disperse dyes **5a-e** and **6a-i** on the polyester fabrics†.

Dyes	a^*	b^*	C^*	h^*	L^*	ΔE^*	ΔL^*	ΔC^*	ΔH^*	K/S
5a	10.36	71.88	72.62	81.80	71.03	00.000	00.000	00.000	00.000	19.0
5b	19.20	82.38	84.59	76.88	66.16	14.570	-4.869	11.972	-6.727	24.5
5c	15.52	85.85	87.24	79.75	70.22	14.914	-0.806	14.618	-2.842	21.0
5d	17.03	83.62	85.08	81.35	84.91	15.380	-13.885	12.252	-4.422	21.5
5e	31.32	68.33	75.13	65.44	59.30	24.200	-11.730	2.508	-21.018	23.0
6a	20.87	78.52	81.25	75.12	20.87	00.000	00.000	00.000	00.000	16.0
6b	19.03	55.02	50.64	70.09	19.03	18.241	5.898	-16.608	-8.889	24.0
6c	11.55	58.16	61.25	39.89	37.55	60.783	32.801	-29.995	-40.784	19.5
6d	35.14	57.51	67.04	58.57	35.14	29.597	-15.191	-13.849	-21.294	21.9
6e	34.78	29.45	54.43	42.75	44.78	61.785	-30.323	-26.821	-37.278	22.0
6f	19.10	45.16	49.04	67.08	19.10	33.674	4.888	-32.214	-8.852	25.0
6g	12.90	62.11	63.44	78.27	12.90	8.418	2.539	16.810	6.948	23.5
6h	40.07	33.22	52.05	39.66	40.07	59.098	-32.735	-29.195	-39.607	21.0
6i	15.48	86.27	87.65	79.83	15.48	9.888	2.948	6.404	6.933	24.0

† a^*, red/green axis; b^*, yellow/blue axis; C^*, color brightness; h^*, hue value; L^*, lightness of the color; ΔE^*, total color difference; ΔL^*, lightness difference; ΔC^*, color difference; ΔH^*, hue difference; K/S = Amount of dye absorbed on the surface of the fabrics.

Table 2. Fastness properties of monoazo disperse dyes **5a-e** and **6a-i** on polyester fabrics.

Dyes	Washing	Acidic perspiration	Rubbing		Sublimation at 180 °C	Light (40 h)
			Dry	Wet		
5a	4	3-4	4	4	4	6-7
5b	4	3-4	4	4	3-4	6-7
5c	4	3-4	4	4	4	6-7
5d	4	3-4	4	4	3-4	6-7
5e	4	3-4	4	4	4	6-7
6a	4	4	4	4	4	5
6b	4	4	3-4	3-4	4	4-5
6c	4	4	4	4	4-5	5-6
6d	4	3-4	4	4	4	5-6
6e	4-5	4-5	4	4	4	6
6f	4	3-4	3-4	4	4	5
6g	4-5	3-4	4	4	4	6
6h	4	4-5	4	4	4	5
6i	4-5	3-4	3-4	4	4-5	4-5

2.4.2.2. Fastness to perspiration

The samples were prepared by stitching a piece of dyed polyester fabric between two pieces of cotton and wool fabrics, all of equal length, and then immersed in the acid or alkaline solution for 30 min. The staining on the undyed adjacent fabrics was assessed according tothe following gray scale: 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent. The acid solution (pH =4.5) contains sodium chloride (10 g/L), sodium dihydrogen orthophosphate (1 g/L) and histidine monohydrochloride (0.25 g/L). The alkaline solution (pH = 8.7) contains sodium chloride (10 g/L), disodium orthophosphate (1 g/L) and histidine monohydrochloride (0.25 g/L).

2.4.2.3. 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%, dark glass UV filter system) for 40 h. The changes in color were assessed according to the International Geometric blue scale: 1-poor, 3-moderate, 4-good, 6-very good, 8-excellent.

2.4.2.4. Fastness to sublimation

This test was made according to the ISO/R, 105/IV-1968 pt. 2. The dyed sample was sandwiched between two undyed samples (one from cotton and the other from the same fiber under test) and then placed in iron tester (Yasuda no. 138) at 180 °C for 30 seconds. Change in color of the-dyed samples and staining of the-undyed ones were assessed using International Geometric Grey Scale (1-5; 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent).

2.4.2.5. Fastness to rubbing

Two pieces of the dyed fabric (one dried and the other completely wetted with distilled water) were placed alternatively on the base of the Crockmeter, so that it rested flat on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloths were allowed to slide on the tested fabric back and forth twenty times by making ten complete turns of the crank according to the international standard procedures. The same procedures were applied to the wetted sample. The staining on the white testing cloth was assessed according to the International Geometric grey scale.

3. Results and discussion

3-Amino-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **2**, was prepared in 85% yield, as yellow crystalline (M.p. 244-245 °C) according to the reported procedures [7] by refluxing 3-chloro-5,6-diphenylpyridazine-4-carbonitrile **1** with hydrazine hydrate for 3 hours, (Scheme 1).

Compound **2**, when reacted with ethyl azobenzene acetoacetate derivatives **3a-e** in a mixture of ethanol and pyridine at refluxing temperature yielded 7-arylazo-6-methyl-3,4-diphenylpyrimido[1`,2`:1,5]pyrazole[3, 4-*c*]pyridazin-8(5*H*)-one derivatives **5a-e** (Scheme 2).

Compound **2**, when reacted with the azobenzene malononitrile derivatives **4a-I** in ethanol at refluxing temperature yielded 6,8-diamino-7-arylazo-3,4-diphenyl pyrimido [1`,2`:1,5]pyrazolo[3,4-*c*]pyridazine **6a-i** (Scheme 3).

The 3-[4-(arylazo)-3,5-disubstituted-pyrazol-1-yl]-4,5-di phenyl-1*H*-pyraz-olo[3,4-*c*]pyridazines **5a-e** and **6a-I** were synthesized to assess their dyeing properties on polyester fabrics. The dyeing was performed at 2% shade by high-temperature techniques and gave generally deep and bright intense hues, ranging from yellow to orange-yellow.

The values of K/S of compounds **5a-e** and **6a-i** vary from 16 to 25. The introduction of different groups in dyes **5a-e** and **6a-i** increases the strength of K/S values and deepens the color compared with the parent dyes **5a** and **6a**, respectively (Table 1). The values of K/S for the dyes **5a-c**,**e** derived from ethyl azobenzene acetoacetate derivatives **3a-c**,**e** with 3-amino pyrazolopyridazine **2** were greater than the corresponding

dyes **6a**-**c**, **e** derived from azobenzene malononitrile derivatives **4a**-**c**, **e** with the same 3-aminopyrazolopyridazine **2** on dyed polyester fibers. The color hues of the dyes **5a**-**e** and**6a**-**i** on polyester fabrics are shifted towards the reddish and yellowish directions on the red-green and yellow-blue axes, respectively.

Most influences that can affect fastness are light, washing, heat, perspiration, and atmospheric pollution. Conditions of such tests are chosen to correspond closely to treatments employed in manufacture and ordinary use conditions [11]. Results are given after usual matching of tested samples against standard reference (the grey scale) [11-13]. The results revealed that these dyes have good-excellent fastness properties (Table 2).

4. Conclusions

A set of 14 disperse dyes **5a**-**e** and **6a**-**i** were synthesized by reaction of3-amino-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **2** with ethyl arylazo acetoacetate and arylazo malononitrile derivatives. All of them were investigated for their dyeing characteristics on polyester. The dyed fabrics exhibit very good to excellent (4-5) washing, perspiration, rubbing and sublimation fastness properties. The remarkable degree of levelness and brightness after washings is indicative of good penetration and the excellent affinity of these dyes for the fabric due to the accumulation of polar groups. This in combination with the ease of preparation makes them particularly valuable.

References

[1]. Abdel Galil, F. M.; Khalifa, F. A.; Abdin, T. S. *Dyes Pigments* **1990**, *12*, 49-56.
[2]. Rajagopal, R.; Seshadri, S. *Dyes Pigments* **1990**, *13*, 93-105.
[3]. Deeb, A.; Shaqra, S.; Abo El-Fotoh, T.; Dief, S. *Eur. Chem. Bull*. **2014**, *3(7)*, 627-636.
[4]. Deeb, A.; El-Hossami, M.; Awad A. *Eur. Chem. Bull*. **2014**, *3(8)*, 745-751.
[5]. Deeb, A.; Yassine, F.; Aouf, N.; Shehta, W. *Int. J. Chem Tech Res*. **2014**, *6(1)*, 719-729.
[6]. Deeb, A.; Yassine, F.; Aouf, N.; Shehta, W. *Eur. Chem. Bull*. **2014**, *3(1)*, 18-23.
[7]. Deeb, A.; Bayoumy, B.; Essawy, A.; Fikry, R. *Heterocycles* **1991**, *32*, 895-900.
[8]. Deeb, A.; Bayoumy, B.; Essawy, A.; Fikry, R. *Heterocycles* **1991**, *32*, 901-907.
[9]. Deeb, A.; Yassin, F.; Ouf, N.; Shehta, W. *Chem. Heterocycl. Compd.* **2010**, *46*, 212-222.
[10]. Shawali, A. S.; Abdel Galil, F. M. *Tetrahedron* **1971**, *27*, 4305-4316.
[11]. Chrysler, L. P. Methods of Test for Color Fastness of Textiles and Leather, 7th ed., British Standards Institution, London, Bradford, 1990, pp. 89-94.
[12]. Al-Etaibi, A.; El-Apasery, M. A.; Al-Awadi, N. *Eur. J. Chem*. **2013**, *4(3)*, 240-244.
[13]. Al-Qalaf, F.; Almohammad, K.; El-Apasery, M. A.; Mohmoud, H. *Eur. J. Chem*. **2013**, *4(3)*, 211-215.