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Pyridazine and its related compounds: Part 33. Synthesis of some disperse dyes derived from 3-hydrazinyl-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine and their color assessment on polyester fabric

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ABSTRACT

Active methylene compound such as ethyl acetoacetate was coupled with diazotized arylamines to give ethyl arylazoacetoacetates. When the obtained compounds refluxed with 3-hydrazinyl-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine in the presence of ethanol yielded 1-(4,5-Diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)-3-methyl-4-(2-phenylhydrazono)-1*H*-pyrazol-5(4*H*)-one derivatives. The dyes were applied to polyester fabric, and their absorption spectral characteristics, fastness properties and color assessment measured.

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1. Introduction

Derivatives of the pyrazolopyridazine ring systems are known to possess potent biological and pharmacological properties [1]. On the other hand, some pyrazole derivatives are very important class of heterocycles due to their biological and pharmacological activities [2,3]. Also, they are used as key starting material for the synthesis of commercial aryl/hetarylazopyrazole dyes [4]. All these properties aroused our interest in synthesis new heterocyclic compounds including the pyrazolo[3,4-*c*]pyridazine moiety which is a continuation of our previous work [5-9].

The present investigation deals with the synthesis of some 1-(4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)-3-methyl-4-(2-phenylhydrazono)-1*H*-pyrazol-5(4*H*)-one derivatives, **6a**-**i**, and an evaluation of their properties on polyester fabric.

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 200 MHz spectrometer, and chemical shifts are expressed in δ ppm using TMS as an internal standard. Mass spectra were obtained at 70 eV 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-hydrazinyl-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine (**2**) [8], and azobenzene compounds (**5a**-**i**) [9], were conducted according to known procedures (Scheme 1). Spectral data for compounds **5a**-**i** were described in the previous parts [9-10].

2.2.1. Ethyl 3-(2-(4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazin-3-yl)hydrazono)butanoate (3)

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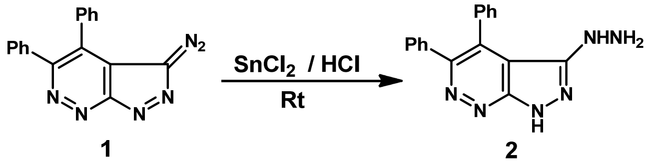
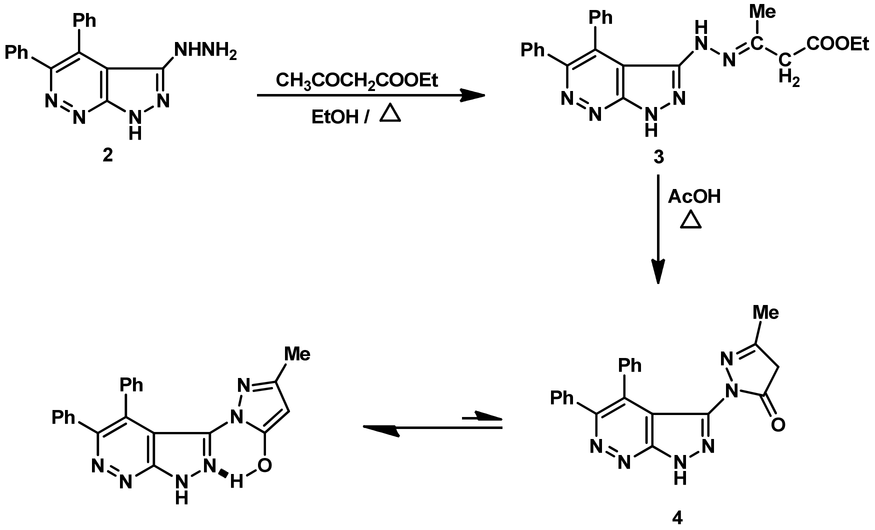


Scheme 1



Scheme 2

A mixture of compound **2** (1.0 g, 3.3 mmol) and ethyl acetoacetate (0.4 g, 3.1 mmol) was refluxed in absolute ethanol (20 mL) for 4 h. The solvent was then evaporated under vacuum and the residue was treated with diethyl ether. The solid product was filtered off and recrystallized from ethanol. Prepared from 3-hydrazinyl-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine (**2**) (Scheme 2). Reaction time: 4 h. Color: Yellow crystals. Yield: 56.2%. M.p.: 252-253 °C. Anal. calcd. for $C_{23}H_{22}N_6O_2$: C, 66.65; H, 5.35; N, 20.28. Found: C, 66.40; H, 5.10; N, 19.95%.

2.2.2. 1-(4,5-Diphenyl-1H-pyrazolo[3,4-c]pyridazin-3-yl)-3-methyl-1H-pyrazol-5(4H)-one (4)

Compound **3** (0.4 g, 0.97 mmol) was heated under reflux in glacial acetic acid (10 mL) for 10 h. The cooled reaction mixture was poured into cold water (100 mL). The white precipitation was filtered off, washed with water and recrystallized from ethanol to give 0.3 g of compound **4** (Scheme 2). Prepared from ethyl 3-(2-(4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)hydrazono)butanoate (**3**). Reaction time: 10 h. Color: Yellow crystals. Yield: 84.38%. M.p.: 210-212°C. FT-IR (KBr, ν, cm^{-1}): 3138 (NH), 3059 ($CH_{arom.}$), 2923, 2854 ($CH_{aliph.}$), 1674 (C=O), 1572 (C=N), 1464, 1422, 1395, 1134 (Aromatic sys.). MS (EI, *m/z* (%)): 368 (M^+, 12.15), 367 (M^+-1, 8.76), 353 (4.92), 285 (8.95), 271 (7.01). Anal. calcd. for $C_{21}H_{16}N_6O$: C, 68.47; H, 4.38; N, 22.81. Found: C, 68.30; H, 4.10; N, 22.65%.

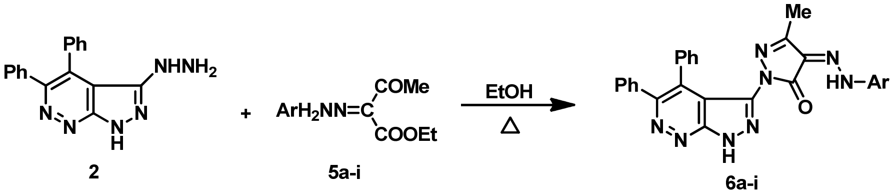
2.2.3. General procedure for the synthesis of 1-(4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazin-3-yl)-3-methyl-4-(2-phenylhydrazono)-1H-pyrazol-5(4H)-one (6a-i)

A mixture of 3-hydrazinyl-4,5-diphenyl-1*H*-pyrazolo[3,4-c]pyridazine (**2**) (0.75 g, 2.5 mmol) and the ethyl azobenzene acetoacetate (**5a**-**i**) (2.5 mmol) was refluxed in ethanol (30 mL). The reaction mixture was cooled to room temperature and the separated solid was filtered off, washed with ethanol (10 mL), dried and recrystallized from ethanol (Scheme 3).

1-(4, 5-Diphenyl-1H-pyrazolo[3, 4-c]pyridazin-3-yl)-3-methyl-4-(2-phenylhydrazono)-1H-pyrazol-5(4H)-one (**6a**): Prepared from ethylphenylazoacetoacetate (**5a**). Reaction time: 10 h. Color: Yellow crystals. Yield: 86%. M.p.: 273-274 °C. FT-IR (KBr, ν, cm^{-1}): 3425, 3139 (NH), 3058 ($CH_{arom.}$), 2922 ($CH_{aliph.}$), 1652 (C=O), 1583 (C=N). MS (EI, *m/z* (%)): 473.15 (M^++1, 13.73), 472.15 (M^+, 43.96), 395.15 (7.08), 242.05 (3.23). UV/Vis (DMF, λ_{max}, nm, (log ε)): 266 (4.3). Anal. calcd. for $C_{27}H_{20}N_8O$: C, 68.63; H, 4.27; N, 23.72. Found: C, 68.50; H, 4.10; N, 23.55%.

1-(4, 5-Diphenyl-1H-pyrazolo[3, 4-c]pyridazin-3-yl)-3-methyl-4-(2-(o-tolyl)hydrazono)-1H-pyrazol-5(4H)-one (**6b**): Prepared from ethyl 2-methylphenylazoacetoacetate (**5b**). Reaction time: 12 h. Color: Yellow crystals. Yield: 75%. M.p.: 272-273 °C. FT-IR (KBr, ν, cm^{-1}): 3443, 3163 (NH), 3062 ($CH_{arom.}$), 2989, 2886 ($CH_{aliph.}$), 1669 (C=O), 1577 (C=N), 1551 (C=C). UV/Vis (DMF, λ_{max}, nm, (log ε)): 271 (3.96). Anal. calcd. for $C_{28}H_{22}N_8O$: C, 69.12; H, 4.56; N, 23.03. Found: C, 69.10; H, 4.40; N, 22.85%.

1-(4, 5-Diphenyl-1H-pyrazolo[3, 4-c]pyridazin-3-yl)-3-methyl-4-(2-(m-tolyl)hydrazono)-1H-pyrazol-5(4H)-one (**6c**): Prepared from ethyl 3-methylphenylazoacetoacetate (**5c**). Reaction time: 11 h. Color: Yellow crystals. Yield: 66%. M.p.: 269-270 °C. FT-IR (KBr, ν, cm^{-1}): 3444, 3164 (NH), 3062 ($CH_{arom.}$), 2922, 2886 ($CH_{aliph.}$), 1669 (C=O), 1550 (C=C), 1575 (C=N).



Scheme 3

^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 15.13 (s, 1H, NH-Pyr.), 7.14-7.15 (m, 14H, Ar-H), 7.00 (s, 1H, NH-hydrazide), 3.32 (s, 3H, CH_3-Pyr.), 2.31 (s, 3H, CH_3-Toluene). Anal. calcd. for $C_{28}H_{22}N_8O$: C, 69.12; H, 4.56; N, 23.03. Found: C, 69.00; H, 4.40; N, 22.90%.

1-(4, 5-Diphenyl-1H-pyrazolo[3, 4-c]pyridazin-3-yl)-3-methyl-4-(2-(p-tolyl)hydrazono)-1H-pyrazol-5(4H)-one (**6d**): Prepared from ethyl 4-methylphenylazoacetoacetate (**5d**). Reaction time: 10 h. Color: Yellow crystals. Yield: 66%. M.p.: 276-277 °C. FT-IR (KBr, ν, cm^{-1}): 3422, 3173 (NH), 2917 ($CH_{aliph.}$), 1661 (C=O), 1577 (C=N), 1542 (C=C). MS (EI, *m/z* (%)): 487 (M^++1, 70.3), 486 (M^+, 66.5), 471 (0.7), 395 (11.9), 368 (1.7), 335 (0.8), 90 (100). UV/Vis (DMF, λ_{max}, nm, (log ε)): 270.5 (3.8). Anal. calcd. for $C_{28}H_{22}N_8O$: C, 69.12; H, 4.56; N, 23.03. Found: C, 69.10; H, 4.40; N, 22.80%.

1-(4, 5-Diphenyl-1H-pyrazolo[3, 4-c]pyridazin-3-yl)-4-(2-(2-methoxyphenyl) hydrazono)-3-methyl-1H-pyrazol-5 (4H)-one (**6e**): Prepared from ethyl 2-methoxyphenylazoacetoacetate (**5e**). Reaction time: 11 h. Color: Yellow crystals. Yield: 72%. M.p.: 273-274 °C. FT-IR (KBr, ν, cm^{-1}): 3423, 3322 (NH), 3059 ($CH_{arom.}$), 2922 ($CH_{aliph.}$), 2850 (OCH_3), 1658 (C=O), 1583 (C=N), 1540 (C=C). Anal. calcd. for $C_{28}H_{22}N_8O$: C, 66.92; H, 4.41; N, 22.30. Found: C, 66.80; H, 4.30; N, 22.15%.

1-(4, 5-Diphenyl-1H-pyrazolo[3, 4-c]pyridazin-3-yl)-4-(2-(4-methoxyphenyl) hydrazono)-3-methyl-1H-pyrazol-5 (4H)-one (**6f**): Prepared from ethyl 4-methoxyphenylazoacetoacetate (**5f**). Reaction time: 9 h. Color: Yellow crystals. Yield: 80%. M.p.: 272-273 °C. FT-IR (KBr, ν, cm^{-1}): 3313 (NH), 3061 (CH_{arom}), 2921 ($CH_{aliph.}$), 2849 (OCH_3), 1658 (C=O), 1591 (C=N), 1539 (C=C). MS (EI, *m/z* (%)): 504 (M^++2, 7.7), 503 (M^++1, 52.5), 502 (M^+, 93.2), 395 (27.3), 367 (13.1), 271 (10.4), 77 (100). UV/Vis (DMF, λ_{max}, nm, (log ε)): 260 (3.8). Anal. calcd. for $C_{28}H_{22}N_8O_2$: C, 66.92; H, 4.41; N, 22.30. Found: C, 66.80; H, 4.30; 22.25%.

4-(2-(2-Chlorophenyl)hydrazono)-1-(4, 5-diphenyl-1H-pyrazolo[3,4-c]pyridazin-3-yl)-3-methyl-1H-pyrazol-5(4H)-one (**6g**): Prepared from ethyl 2-chlorophenylazoacetoacetate (**5g**). Reaction time: 10 h. Color: Yellow crystals. Yield: 71%. M.p.: 297-298 °C. FT-IR (KBr, ν, cm^{-1}): 3449, 3164 (NH), 3064 ($CH_{arom.}$), 2924 ($CH_{aliph.}$), 1676 (C=O), 1597 (C=N), 1551 (C=C), 755 (C-Cl). MS (EI, *m/z* (%)): 509 (M^++2, 31.9), 508 (M^++1, 27.4), 507 (M^+, 89), 395 (16.3), 271 (9.2), 472 (24.8), 368 (5.2). UV/Vis (DMF, λ_{max}, nm, (log ε)): 267.3 (3.9). Anal. calcd. for $C_{27}H_{19}ClN_8O$: C, 63.97; H, 3.78; N, 22.10. Found: C, 63.80; H, 3.60; N, 21.80%.

4-(2-(3-Chlorophenyl)hydrazono)-1-(4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazin-3-yl)-3-methyl-1H-pyrazol-5(4H)-one (**6h**): Prepared from ethyl 3-chlorophenylazoacetoacetate (**5h**). Reaction time: 10 h. Color: Yellow crystals. Yield: 87%. M.p.: 279-280 °C. FT-IR (KBr, ν, cm^{-1}): 3419, 3243 (NH), 3058 ($CH_{arom.}$), 2922 ($CH_{aliph.}$), 1679 (C=O), 1597 (C=N), 1544 (C=C), 768 (C-Cl). MS (EI, *m/z* (%)): 509 (M^++2, 31.9), 508 (M^++1, 27.4), 507 (M^+, 89), 395 (16.3), 271 (9.2), 472 (24.8), 368 (5.2). UV/Vis (DMF, λ_{max}, nm, (log ε)): 267.3 (3.9). Anal. calcd. for $C_{27}H_{19}ClN_8O$: C, 63.97; H, 3.78; N, 22.10. Found: C, 63.80; H, 3.60; N; N, 21.85%.

1-(4, 5-Diphenyl-1H-pyrazolo[3, 4-c]pyridazin-3-yl)-3-methyl-4-(2-(4-nitrophenyl)hydrazono)-1H-pyrazol-5(4H)-one (**6i**): Prepared from ethyl 4-nitrophenylazoacetoacetate (**5i**). Reaction time: 8 h. Color: Yellow crystals. Yield: 94%. M.p.: > 300 °C. FT-IR (KBr, ν, cm^{-1}): 3279 (NH), 3056 ($CH_{arom.}$), 2921 ($CH_{aliph.}$), 1688 (C=O), 1602 (C=N), 1559 (C=C), 1506, 1338 (NO_2). MS (EI, *m/z* (%)): 518.15 (M^++1, 8.24), 517.15 (M^+, 25.45), 367 (4.17), 270.95 (5.35), 121.95 (9.41). UV/Vis (DMF, λ_{max}, nm, (log ε)): 265.3 (4.3). Anal. calcd. for $C_{27}H_{19}N_9O_3$: C, 62.66; H, 3.70; N, 24.36. Found: C, 62.50; H, 3.60; N, 24.15%.

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

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

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

Table 1. Fastness properties, K/S values and color shades of dyes **6a-i** on polyester fibers *.

Dyes	Washing fastness			Perspiration fastness						Rubbing fastness		Sublimation fastness 180 ° C			Light fastness (40 h)	K/S	Color shades
				Alkaline			Acidic										
	Alt	SF	SW	Alt	SF	SW	Alt	SF	SW	Dry	Wet	Alt	SF	SW			
6a	4-5	4-5	4-5	4	4	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5-6	2.9	Yellow
6b	4-5	4-5	4-5	4-5	4	4	4	4	4	4	4	4-5	4-5	4-5	6	3.1	Pale yellow
6c	4	4	4	4	4	4	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	6	6.5	Reddish yellow
6d	4-5	4-5	4-5	4	4	3-4	4	4	4	4	4	4-5	4-5	4-5	5-6	3.5	Yellow
6e	4-5	4-5	4-5	4	4	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5-6	3.2	Orange
6f	4	4	4	4	4	3-4	4	4	4	4	4	4	4	4	4-5	3.2	Orange
6g	4-5	4-5	4-5	4	4	4	3-4	3-4	3-4	4	4	4	4	4	4-5	3.2	Orange
6h	4-5	4-5	4	4	4	4	4	4	4	4-5	4-5	4-5	4-5	4	5-6	3.7	Yellow
6i	4-5	4-5	4-5	4	4	4	4	3-4	3-4	4	4	4	4	4	4-5	10.2	Orange yellow

* Alt = Alteration; SF = Staining on the same fiber (Poly ester); SC = Staining on cotton; SW= Staining on wool.

After washing using 5 g/L of the non-ionic 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.

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 to the 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 monohydro chloride (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 Xeno test 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-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 Crock meter, 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-Hydrazinyl-4, 5-diphenyl-1*H*-pyrazolo[3, 4-*c*]pyridazine (**2**) [8] was prepared in 96% yield as yellow crystals (M.p.: 168 °C) by reduction of 3-diazo-4,5-diphenylpyrazolo[3, 4-*c*] pyridazine (**1**) with $SnCl_2$/HCl at room temperature (Scheme 1).

Condensation of compound **2** with ethyl acetoacetate in refluxing ethanol gave ethyl 3-(2-(4,5-diphenyl-1*H*-pyrazolo [3,4-*c*]pyridazin-3-yl)hydrazono)butanoate (**3**), which when heated in glacial acetic acid, undergoes cyclodehydration to give 2-(4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)-5-methyl-1*H*-pyrazol-3(2*H*)-one (**4**) (Scheme 2).

The structure of hydrazono derivative **3** and pyrazolone derivative **4** are supported by their analytical and spectral data. The infrared spectrum of compound **3** revealed the presence of (NH) group at 3416 and 3133, ($CH_{arom.}$) at 3058, ($CH_{aliph.}$) at 2920 and 2853, (C=O, ester) at 1703, (C=N) at 1585 cm^{-1}. The mass spectrum could be accounted as follows: the molecular ion-1 at *m/z* 413 underwent the following fragmentation. It could be lose CH_3 to give the ion at *m/z* 398, which in turn gives rise to the ion at *m/z* 353 by loss OEt, which in turn gives rise to the ion at *m/z* 271 by loss $NHN{=}CCH_2CO$.

Compound **4** exist in two tautomeric forms due to its *keto-enol* tautomerism. The spectral data proved that it existed in *enol* form due to intra-molecular chelation by H-bond. This phenomenon is confirmed by infrared spectra. The infrared spectrum revealed the presence of NH, OH (enolic) at 3439 cm^{-1} and carbon-nitrogen double bond at 1620 cm^{-1}. The mass spectrum could be accounted as follows: the molecular ion at *m/z* 368 underwent the following fragmentation. It could be lose CH_3 to give the ion at *m/z* 353, which in turn gives rise to the ion at *m/z* 285 by loss $N{=}C{-}CH_2{-}C({=}O)$, which in turn gives rise to the ion at *m/z* 271 by loss N atom.

In a similar way compound **2**, when reacted with the ethyl azobeneneacetoacetate derivatives **5a-i** [10] in ethanol yielded the 1-(4, 5-Diphenyl-1*H*-pyrazolo[3, 4-*c*]pyridazin-3-yl)-3-methyl-4-(2-phenylhydrazono)-1*H*-pyrazol-5(4*H*)-one (**6a-i**) (Scheme 3).

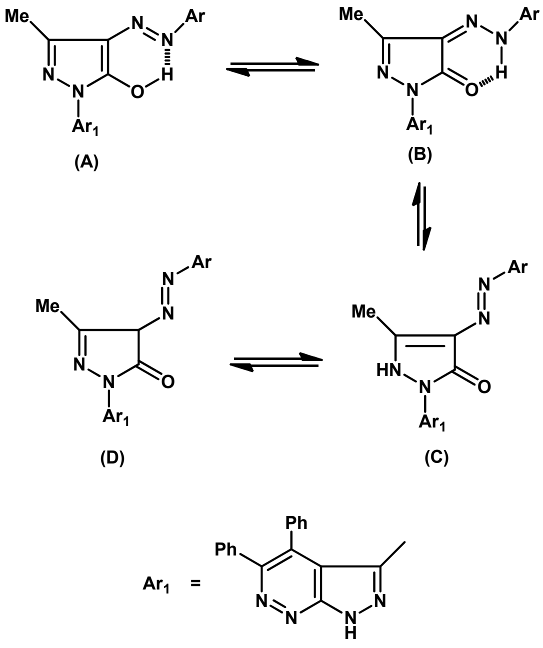
The dyes **6a-i** may exist in four possible tautomeric forms, namely two *azo-keto* forms (**D**) and (**C**), the *azo-enol* form (**A**) and the hydrazone-*keto* form (**B**) as shown in (Scheme 4). The spectral data generally lead to the conclusion that the tautomeric equilibrium of the arylazopyrazolone dyes is in favor of the hydrazone form (**B**) in the solid state [12].

The spectral data proved that the 4-arylhydrazo pyrazolones (**B**) are the existing structure of the synthesized dyes due to their stabilization by intramolecular hydrogen bonding.

Table 2. Optical measurements of the synthesized monoazo disperse dyes **6a**-**i** on the polyester fabrics †.

Dyes	a^*	b^*	C^*	h^*	L^*	ΔE^*	ΔL^*	ΔC^*	ΔH^*	Batch is
6a	-3.32	57.56	57.66	93.30	87.72	00.00	00.00	00.00	00.00	-
6b	11.46	46.17	47.57	76.06	81.77	19.592	-5.956	-10.087	-15.705	Darker less green less yellow
6c	21.36	49.52	53.93	66.67	77.39	27.937	-10.335	-3.728	-25.686	Darker less green less yellow
6d	-4.36	62.52	62.67	93.99	85.69	5.453	-2.035	5.008	0.717	Darker greener yellow
6e	22.45	71.62	75.06	75.60	75.88	31.655	-11.848	17.397	-23.643	Darker less green yellow
6f	09.32	66.37	67.03	82.01	83.17	16.067	-4.553	9.365	-12.235	Darker less green yellow
6g	-1.77	41.86	41.90	92.42	88.57	15.803	0.843	-15.762	-0.756	Lighter less green less yellow
6h	-5.46	57.02	57.28	95.47	88.89	2.490	1.162	-0.380	2.169	Lighter greener less yellow
6i	09.26	68.30	68.92	82.28	81.40	17.707	-6.325	11.262	-12.113	Darker less green yellow

† 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.



Scheme 4

The structures of compounds were confirmed on the basis of spectroscopic data (IR, Mass, and ^{1}H NMR spectra) and elemental analysis as described in the experimental part.

The 1-(4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)-3-methyl-4-(2-phenylhydrazono)-1*H*-pyrazol-5(4*H*)-one (**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.

Versatility is the first technical property of the present dyes to be emphasized. Satisfactory color yields, compared with commercial dyes applied under similar conditions, were obtained at 2% depth, and excellent leveling and exhaustion of dye liquors were also achieved. Furthermore, the dyes gave excellent uniformity of coloration of polyester without the use of retarding agent. Relevant fastness data for the dyes are given in Table 1 from which the following were noticed:

1) Excellent behavior is shown in the fastness to washing at 50 °C on dyed polyester fabrics.
2) Most of the dyes have a good to excellent rubbing fastness (4-5).
3) The dyed polyester fibers have good to excellent fastness to perspiration.
4) All of the dyes showed good to excellent sublimation fastness.
5) Fastness to light was good to very good.

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 [11,13,14].

The intensity of color for the dyes applied on polyester fabrics expressed as K/S values given in Table 1. The color of the dyed fabric was assessed by tristimulus colorimetry. The results are listed in the Table 2. The color hues of the dyes **6a**-**i** polyester fabrics are shifted towards the reddish and yellowish directions on the red-green and yellow-blue axes, respectively. The color lightness values (L^*) of the prepared dyes are almost above 50 (Table 2), this means lightness of color on different fibers.

4. Conclusion

A set of nine disperse dyes **6a**-**i** were synthesized by reaction of 3-hydrazinyl-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*] pyridazine (**2**) with ethyl arylazoacetoacetates derivatives. All of them were investigated for their dyeing characteristics on polyester. The dyed fabrics exhibit 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.

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