# PYRIDAZINE AND ITS RELATED COMPOUNDS: PART 30.[1] SYNTHESIS AND APPLICATION OF SOME MONOAZO DISPERSE DYES DERIVED FROM PYRIDAZIN-3(2*H*)-ONE

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**Keywords:** 5,6-diphenyl-2,3-dihydro-3-oxopyridazine-4-carbohydrazide; disperse dyes; dyeing; fixation; fastness.

A series of monoazo disperse dyes based on 5,6-diphenyl-2,3-dihydro-3-oxopyridazine-4-carbohydrazide was prepared by reacting with azobenzeneacetylacetone, ethyl azobenzeneacetoacetate, and azobenzenemalononitrile derivatives. The dyeing performance of these dyes was assessed on polyester fabrics. The dyes were found to give yellow to brown color shades on dyeing with good depth levelness on fabrics. The dye bath exhaustion, fixation and fastness properties of the dye were also determined.

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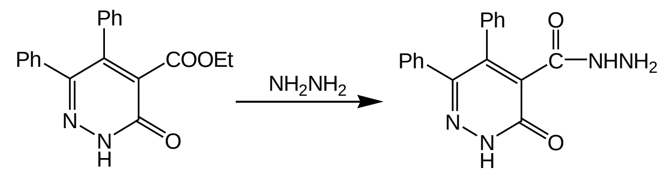
## Introduction

Many pyridazine ring systems are of considerable importance because of their biological and pharmacological properties.[2] On the other hand some pyrazole derivatives are very important class of heterocycles due to their biological and pharmacological activities.[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 synthesizing new heterocyclic compounds including the pyridazine and pyrazole moieties which is a continuation of our previous work.[5,6]

The present investigation deals with the synthesis of 4-[(4-arylazo-3,5-dimethylpyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one, 4-[(4-arylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one, and 4-[(4-arylazo-3,5-diaminopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one derivatives and an evaluation of their properties on polyester fabrics.

### Results and discussion

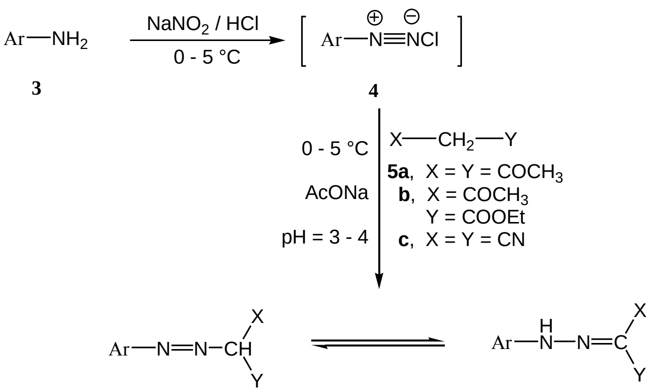
The starting material 5,6-diphenyl-2,3-dihydro-3-oxopyridazine-4-carbohydrazide **2** was prepared as reported[6] from 4-carbethoxy-5,6-diphenyl-3(2*H*)-pyridazinone **1** by refluxing with hydrazine hydrate in 1-butanol (Scheme 1).[7,8]




**1** **2**

**Scheme 1**

Arylamine derivatives **3** were diazotized using sodium nitrite in hydrochloric acid, the temperature was maintained below 5°C in an ice-bath. The diazotized products **4** were then coupled with active methylene compounds such as acetylacetone **5a**, ethyl acetoacetate **5b**, and malononitrile **5c** in sodium acetate buffered solution to give the azobenzeneacetylacetone **7a-h**, ethyl azobenzene-acetoacetate **7a-h**, and azobenzenemalononitrile **8a-h** derivatives in good yields (Scheme 2). Spectral data for such compounds indicate them to have a hydrazone configuration, characterization and spectral data for compounds **6a-h**, **7a-h**, and **8a-h** were described in the previous work.[9]



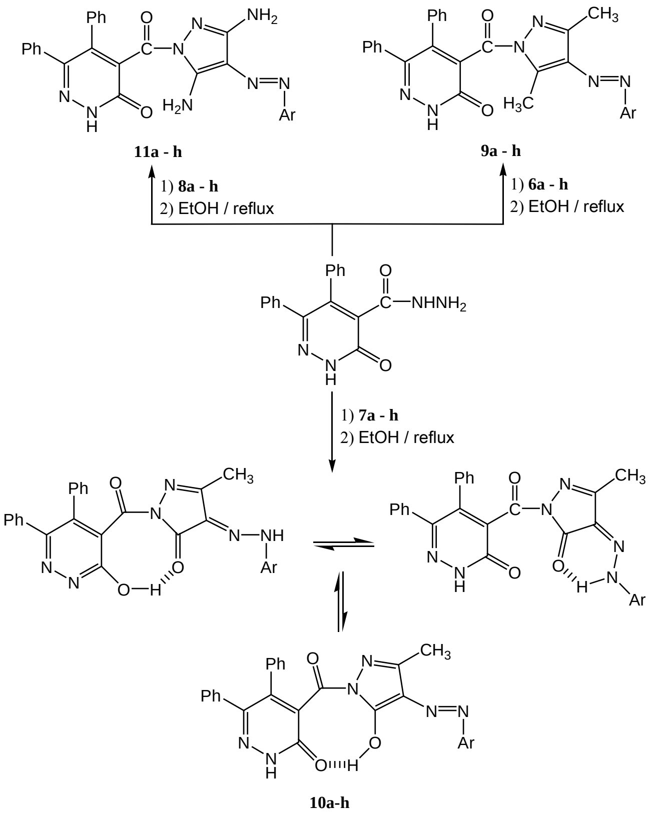

**6a - h, 7a-h** and **8a-h**

**Scheme 2.** Compounds **6,7** and **8**: **a** (Ar = Ph); **b** (Ar = 2-Me$C_6H_4$); **c** (Ar = 4-Me$C_6H_4$); **d** (Ar = 2-MeO$C_6H_4$); **e** (Ar = 4-MeO$C_6H_4$); **f** (Ar = 2-Cl$C_6H_4$); **g** (Ar = 3-Cl$C_6H_4$); **h** (Ar = 4-$NO_2C_6H_4$); **6a-h** (X,Y = $COCH_3$); **7a-h** (X=$COCH_3$, Y = COOEt); **8a-h** (X,Y= CN).

Compound **2** when reacted with azobenzeneacetylacetone derivatives **6a-h** in absolute ethanol at reflux temperature yielded 4-[(4-arylazo-3,5-dimethylpyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one derivatives **9a-h**. The reaction proceeds in two stages, viz, the initially formed hydroxypyrazoline subsequently loses water.[10] Compound **2**, when reacted with the ethyl azobenzeneacetoacetate derivatives **7a-h** in a similar manner yielded 4-[(4-arylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one derivatives **10a-h**.

In addition 3,5-diaminopyrazole derivatives **11a-h** were prepared by treatment of compound **2** with azobenzenemalononitrile **8a-h** in a similar manner gave the corresponding 4-[(4-arylazo-3,5-diaminopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one derivatives **11a-h**.

The structures of the prepared compounds were supported by their spectroscopic and elemental analysis and these data are shown in Experimental part.



**Scheme 3.** Compounds **9**, **10** and **11**: **a** (Ar=Ph); **b** (Ar=2-$MeC_6H_4$); **c** (Ar=4-$MeC_6H_4$); **d** (Ar=2-$MeOC_6H_4$); **e** (Ar=4-$MeOC_6H_4$); **f** (Ar=2-$ClC_6H_4$); **g** (Ar=3-$ClC_6H_4$); **h** (Ar=4-$NO_2C_6H_5$).

**Dyeing of polyester fabrics and dyeing properties**

**Color measurement**

The effect of the nature of different substituents on dyeing behavior, color hue, and depth was investigated. This investigation depends on some spectral data of the dyed materials. The most commonly used function *f*(R) is that developed theoretically by Kubelka and Munk. In their theory, the optical properties of a sample were described by two values: *K* is the measure of the light absorption, and *S* is a measure of the light scattering. On textiles, *K* is determined primarily by the dyestuffs and *S* only by the substrate. From the wavelength, Kubelka and Munk calculate Eq. (1) for the reflectance *R* of thick, opaque samples with the constants of *K* and *S*:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{1}$$

In this equation *R* is used as a ratio, e.g., 32 % reflectance as 0.32. The *K*/*S* value at λ max was taken as a measure of color depth.

On the other hand, the psychometric coordinates (*L**, *a**, *b**) for each dyed sample were obtained to illustrate the color hues, where *L** is the lightness, ranging from 0 to 100 (0 for black and 100 for white); *a** is the red-green axis, (+) for red, zero for grey, and (-) for green; and *b** is the yellow-blue axis, (+) for yellow, zero for gray, and (-) for blue.

The parent dyestuff in each group is taken as the standard in color difference calculation (Δ*L**, Δ*C**, Δ*H** and Δ*E**). The results are measured using CIE-LAB techniques and given in Table 1, Where Δ*L** is the lightness difference, Δ*C** the chroma difference, Δ*H** the hue difference and Δ*E** the total color difference. A negative sign of Δ*L** indicates that the dyed fiber becomes darker than the standard, but a positive sign indicates that the dyed fiber indicates that the dyed fiber becomes duller than the standard, but a positive sign indicates that the dyed fiber becomes brighter than the standard. A negative sign of Δ*H** indicates that the color directed to red color, while a positive sign indicates that the color directed to yellowish. The values of *K*/*S* of compounds **9, 10,** and **11** vary from 1.2 to 14. The introduction of different groups in dyes **9, 10,** and **11** increases the strength of *K*/*S* values and deepens the color compared with the corresponding parent dye **9a, 10a, 11a** (Table 1).

The values of K/S for 3,5-diaminopyrazol dyes **11** derived from azobenzenemalononitrile derivatives **8a-h** with acid hydrazide **2** were greater than the corresponding 3,5-dimethyl pyrazole dyes **9** derived from azobenzeneacetylacetone derivatives **6a-h** with the same acid hydrazide **2** on dyed polyester fibers except **11b** and **11f**. This bathochromic shift is attributed to the stronger electron-releasing of the amino group with respect to the methyl group at the 3-, 5-position of the pyrazole ring, thus enhancing electron delocalization in the dye molecule and consequently increases the vibrational energy of the dye molecule which in turn increases the color strength (K/S) values of the dyed fibers and directed the color toward reddish and yellowish directions on the red-green and yellow-blue axis respectively.

**Assessment of color fastness**

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

**Table 1.** Optical measurements of compounds **9ah**, **10a-h** and **11a-h**.

| K/S | $\Delta H^*$ | $\Delta C^*$ | $\Delta L^*$ | $\Delta E^*$ | $L^*$ | $h^*$ | $C^*$ | $b^*$ | $a^*$ | Dyes |
|---|---|---|---|---|---|---|---|---|---|---|
| 1.2 | 00.00 | 00.00 | 00.00 | 00.00 | 87.94 | 86.20 | 31.44 | 31.37 | 2.08 | 9a |
| 14 | -0.992 | -7.795 | 1.468 | 7.994 | 80.71 | 82.17 | 98.82 | 97.90 | 13.47 | 9b |
| 2 | -32.598 | 6.208 | -13.929 | 35.989 | 74.01 | 29.64 | 37.64 | 18.62 | 32.72 | 9c |
| 2 | -1.324 | 66.800 | -4.819 | 66.986 | 83.12 | 84.84 | 98.24 | 97.84 | 8.84 | 9d |
| 4 | 6.908 | 15.356 | 1.114 | 16.875 | 89.05 | 96.54 | 46.79 | 46.49 | -5.33 | 9e |
| 2.5 | -10.541 | 11.937 | -16.656 | 23.044 | 71.28 | 69.79 | 43.37 | 40.70 | 14.98 | 9f |
| 1.2 | 5.073 | 13.029 | 1.332 | 14.045 | 89.27 | 93.98 | 44.46 | 44.36 | -3.09 | 9g |
| 3.9 | -0.233 | 0.569 | 0.435 | 0.753 | 88.37 | 85.78 | 32.00 | 31.92 | 2.35 | 9h |
| 2.3 | 00.00 | 00.00 | 00.00 | 00.00 | 90.12 | 99.28 | 49.62 | 48.97 | -8.00 | 10a |
| 3.9 | -4.441 | -5.759 | -0.826 | 7.319 | 89.30 | 93.82 | 43.86 | 43.76 | -2.93 | 10b |
| 1.2 | -6.170 | -17.701 | -1.326 | 18.792 | 88.34 | 85.41 | 32.18 | 32.08 | 2.58 | 10c |
| 2.3 | -26.592 | -21.576 | -25.796 | 42.873 | 64.32 | 57.52 | 28.04 | 23.66 | 15.06 | 10d |
| 3.8 | -20.970 | 49.045 | -9.418 | 54.165 | 80.70 | 82.04 | 98.66 | 79.72 | 13.66 | 10e |
| 2.8 | -1.261 | 9.235 | -0.590 | 9.339 | 89.53 | 97.94 | 58.85 | 58.29 | -8.13 | 10f |
| 2.1 | -11.116 | -20.758 | -1.459 | 23.597 | 88.66 | 82.39 | 28.86 | 28.61 | 3.82 | 10g |
| 11.5 | -5.496 | 23.734 | -3.493 | 24.611 | 86.63 | 94.06 | 73.35 | 73.17 | -5.19 | 10h |
| 2.8 | 00.00 | 00.00 | 00.00 | 00.00 | 73.14 | 73.70 | 80.29 | 77.06 | 22.53 | 11a |
| 11 | -22.255 | -51.299 | -35.455 | 66.211 | 37.68 | 47.03 | 28.99 | 21.21 | 19.76 | 11b |
| 7.1 | -1.595 | -3.591 | 2.613 | 4.719 | 75.75 | 72.54 | 76.70 | 73.16 | 23.02 | 11c |
| 11.3 | -10.633 | -4.272 | -7.119 | 13.491 | 66.02 | 65.90 | 76.02 | 69.39 | 31.05 | 11d |
| 11.1 | -10.915 | -4.240 | -5.384 | 12.888 | 67.75 | 65.69 | 76.05 | 69.31 | 31.31 | 11e |
| 1.8 | -15.139 | -30.456 | 4.624 | 34.324 | 77.76 | 59.95 | 49.83 | 43.14 | 24.95 | 11f |
| 1.8 | 18.869 | -38.392 | 15.430 | 45.475 | 88.57 | 92.42 | 41.90 | 41.86 | -1.77 | 11g |
| 7.4 | -37.413 | -23.059 | -21.259 | 48.820 | 51.88 | 41.66 | 52.23 | 38.04 | 42.76 | 11h |

$a^*$, red/green axis**;** $b^*$, yellow/blue axis; $C^*$, color brightness; $h^*$, hue value; $L^*$, lightness of the color, $\Delta E^*$, total color difference, $\Delta L^*$, lightness difference, $\Delta C^*$, color difference, $\Delta H^*$, hue difference.

**Table 2.** Fastness properties of compounds **9ah**, **10a-h** and **11a-h**.

| Light (40 h) | Sublimation 180 º C | Rubbing | | Acidic Perspiration | Washing | Dyes |
|---|---|---|---|---|---|---|
| | | wet | dry | | | |
| 5-6 | 4 | 4 | 4 | 4 | 4 | **10e** |
| 5 | 4 | 4 | 3-4 | 3-4 | 4-5 | **10f** |
| 4-5 | 4 | 4 | 4 | 4 | 4 | **10g** |
| 4-5 | 4 | 4 | 4 | 4 | 4-5 | **10h** |
| 5-6 | 4 | 3-4 | 3-4 | 4 | 4 | **11a** |
| 4 | 4 | 3-4 | 3-4 | 4 | 4 | **11b** |
| 4-5 | 4 | 3-4 | 3-4 | 4 | 4 | **11c** |
| 5 | 4-5 | 4 | 3-4 | 4 | 4-5 | **11d** |
| 4-5 | 4-5 | 3-4 | 3-4 | 4-5 | 4 | **11e** |
| 5-6 | 4-5 | 4 | 3-4 | 4-5 | 4-5 | **11f** |
| 4 | 4 | 4 | 3-4 | 4 | 4 | **11g** |
| 5 | 4 | 3-4 | 3-4 | 4 | 4 | **11h** |
| 5-6 | 4 | 4 | 4 | 3-4 | 4-5 | **9a** |
| 4-5 | 4 | 4 | 4 | 4 | 4 | **9b** |
| 5-6 | 4 | 4 | 4 | 3-4 | 4 | **9c** |
| 6 | 4 | 3-4 | 4 | 4 | 4 | **9d** |
| 4-5 | 4 | 4 | 4 | 4 | 4--5 | **9e** |
| 4 | 4 | 4 | 3-4 | 4-5 | 4 | **9f** |
| 5-6 | 4 | 4 | 4 | 4 | 4 | **9g** |
| 4-5 | 4 | 4 | 3-4 | 4-5 | 4-5 | **9h** |
| 5-6 | 4 | 4 | 3-4 | 3-4 | 4-5 | **10a** |
| 5-6 | 4-5 | 4-5 | 4 | 4-5 | 4-5 | **10b** |
| 5-6 | 4 | 4 | 4 | 4 | 4-5 | **10c** |
| 5-6 | 4-5 | 4-5 | 4-5 | 4-5 | 4 | **10d** |

employed in manufacture and ordinary use conditions.[11] Results are given after usual matching of tested samples against standard reference (the grey scale).[11] The results revealed that these dyes have good fastness properties (Table 2).

## Experimental

All melting points were determined on a Gallenkamp electric melting point apparatus. Thin-layer chromatography (TLC) analysis was carried out on silica gel 60 F254 precoated aluminum sheets. Infrared spectra were recorded on FTIR 5300 Spectrometer and Perking Elmer Spectrum RXIFT-IR System, using the potassium bromide wafer technique. $^{1}$H-NMR spectra were recorded on Varian Gemini 200 MHz spectrometer using the indicated solvents and tetramethylsilane (TMS) as an internal reference. Electron impact mass spectra were obtained at 70 eV using a GCMS–qp1000 EX Shimadzo spectrometer. Elemental analysis (C, H, N) were carried out at the micro-analytical Center of Cairo University, Giza, Egypt.

The elemental analyses were found to agree favorably with the calculated values. The dyeing assessment fastness tests, and color measurements were carried out at Misr Company for Spinning and Weaving, El-Mahala El-Kobra, Egypt. The syntheses of carbohydrazide **2**,[6-8] and azobenzene compounds **6a-h**, **7a-h**, and **8a-h**[9] were conducted according to known procedures.

### Synthesis of 4-[(4-arylazo-3,5-dimethylpyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one 9, 10 and 11.

*General procedure*: A mixture of 5,6-diphenyl-2,3-dihydro-3-oxopyridazine-4-carbohydrazide **2** (0.50 g, 1.6 mmole) and the azobenzeneacetylacetone derivatives **6a-h** (1.6 mmole) was refluxed in ethanol (20 mL) for 6 hours. The reaction mixture was cooled to room temperature and the separated solid was filtered off, washed with diluted ethanol (10 mL), dried and recrystallized from ethanol.

### 4-[(4-Phenylazo-3,5-dimethylpyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (9a, $C_{28}H_{22}N_6O_2$).

Yellow crystals in 77 % yield; mp 282 – 283 °C; IR: 3445.1 and 3193.5 (NH), 3059.3 ($CH_{arom.}$), 2927.3 ($CH_{aliph.}$), 1734.1 and 1652 (C=O groups), 1583.2 (C=N) and 1495.4 (C=C) $cm^{-1}$; Ms (m/z): 476 [$M^+$ + 2, 5%], 475 [$M^+$ + 1, 16.6%], 474 [$M^+$, 11.3%], 397 [$M^+$ - $C_6H_5$, 13.4%], 275 [$M^+$ - substituted pyrazole ring, 31.9 %, ion A], 247 [ion A - CO, 6.9 %], 199 [$M^+$ - diphenyloxopyridazinone, 86.2 % ion B], 122 [ion B - $C_6H_5$, 100 %] and 77 [$(C_6H_5)^+$, 35.6 %]; $^{1}$H-NMR ($CDCl_3$): δ 12.09 (s, 1H, NH), δ 7.82 - 7.04 (m, 15H, aromatic protons), 2.84 (s, 3H, $CH_3$-5) and 2.46 (s, 3H, $CH_3$-3).

### 4-[(4-(2-Methyphenylazo)-3,5-dimethylpyrazol-1 yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (9b, $C_{29}H_{24}N_6O_2$).

Yellow, crystals in 75 % yield; mp 260 – 261 °C; IR: 3435.7, 3193.7 and 3134.3 (NH), 3058 ($CH_{arom.}$), 2923.1 ($CH_{aliph.}$), 1727.6 and 1646.4 (C=O groups), 1587.8 (C=N) and 1503 (C=C) $cm^{-1}$; $^{1}$H-NMR ($CDCl_3$): δ 11.5 (s, 1H, NH), 7.7 (d, 4H, aryl protons), 7.30 -7.00 (m, 10H, 2 ph), 2.82 (s, 3H, ortho $CH_3$), 2.40 (s, 6H, $CH_3$-3 and $CH_3$-5); UV (DMF): $\lambda_{max}$ (log ε); 266.1 (4.2).

### 4-[(4-(4-Methyphenylazo)-3,5-dimethylpyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (9c, $C_{29}H_{24}N_6O_2$).

Yellow crystals in 81 % yield; mp. 251 – 252 °C; IR: 3436.8, 3193.9 and 3134.6 (NH), 3058 ($CH_{arom.}$), 2922.4 ($CH_{aliph.}$), 1727.6 and 1646.4 (C=O groups), 1589.1 (C=N) and 1503.6 (C=C) $cm^{-1}$; Ms (m/z): 489 [$M^+$ + 1, 24.4%], 488 [$M^+$, 13.8%], 275 [$M^+$ - substituted pyrazole ring, 29.3%, ion A], 274 [ion A - H, 56.1], 213 [$M^+$ - substituted pyridazinone, 100 %, ion B], 122 [ion B - $MeC_6H_4$, 97.6 %], 91 [$(CH_2C_6H_5)^+$, 28.5 %] and 77 [$(C_6H_5)^+$, 47.2 %].

### 4-[(4-(2-Methoxyphenylazo)-3,5-dimethylpyrazol-1-yl)carbonyl]- 5,6-diphenylpyridazin-3(2*H*)-one (9d, $C_{29}H_{24}N_6O_3$).

Yellow crystals in 85 % yield; mp 249 - 250 °C; IR: 3450, 3297 and 3194.3 (NH), 3059.1 ($CH_{arom.}$), 2938.9 ($CH_{aliph.}$), 2874.9 ($OCH_3$), 1738.1 and 1648.4 (C=O groups), 1598.5 (C=N) and 1547 (C=C) $cm^{-1}$; UV (DMF): $\lambda_{max}$ (log ε); 266.2 (3.7).

### 4-[(4-(4-Methoxyphenylazo)-3,5-dimethylpyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (9e, $C_{29}H_{24}N_6O_3$).

Yellow crystals in 92 % yield; mp 265–266 °C; IR: 3432.4, 3307.4 and 3196.8 (NH), 3061.1 ($CH_{arom}$), 2927.4 ($CH_{aliph.}$), 2836.8 ($OCH_3$), 1727.6 and 1653 (C=O groups), 1600.8 (C=N) and 1501.6 (C=C) $cm^{-1}$; Ms (m/z): 506 [$M^+$ + 1, 22.1 %], 505 [$M^+$, 48.8 %], 476 [$M^+$ - OMe, 7.2 %], 275 [$M^+$ - substituted pyrazole ring, 47.8 %, ion A], 247 [ion A - CO, 7.2 %], 229 [$M^+$ - substituted pyridazinone, 73.7%, ion B], 123 [ion B - $MeOC_6H_4$, 100 %, ion C], 107 [$(CH_2OC_6H_4)^+$, 17 %], 95 [ion C – $N_2$, 30.7 %] and 77 [$(C_6H_5)^+$, 53.3 %].

### 4-[(4-(2-Chlorophenylazo)-3,5-dimethylpyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (9f, $C_{28}H_{21}ClN_6O_2$).

Yellow crystals in 90 % yield; mp 279 – 280 °C; IR: 3425.4, 3298 and 3195 (NH), 3060.8 ($CH_{arom.}$), 2927 ($CH_{aliph}$), 1723.4 and 1645.1 (C=O groups), 1586.9 (C=N), 1538.1 (C=C) and 758.4 (Cl-C) $cm^{-1}$; Ms (m/z): 509 [$M^+$, 4 %], 474 [$M^+$ - Cl, 24.9 %], 354 [$M^+$ - $2C_6H_5$, 11 %], 275 [$M^+$ - substituted pyrazole ring, 43.9%, ion A], 247 [ion A - CO, 13.3 %], 233 [$M^+$ - substituted pyridazinone, 50.9 %, ion B], 123 [ion B - $ClC_6H_5$, 100 %], 111 [$(ClC_6H_4)^+$, 62.4 %] and 77 [$(C_6H_5)^+$, 63 %].

### 4-[(4-(3-Chlorophenylazo)-3,5-dimethylpyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (9g, $C_{28}H_{21}ClN_6O_2$).

Yellow crystalsin 84 % yield; mp 271 – 272 °C; IR: 3426.7, 3299 and 3196 (NH), 3061.4 ($CH_{arom.}$), 2928.3 ($CH_{aliph.}$), 1724 and 1645.5 (C=O groups), 1587.4 (C=N), 1538.2 (C=C) and 758.2 (Cl-C) $cm^{-1}$; UV (DMF): $\lambda_{max}$ (log ε); 267.9 (5.2).

**4-[(4-(4-Nitrophenylazo)-3,5-dimethylpyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (9h, $C_{28}H_{21}N_7O_4$).**

Yellow crystals in 94 % yield; mp 264 - 265 °C; IR: 3443.2 and 3198.4 (NH), 3061.8 ($CH_{arom.}$), 2885.2 ($CH_{aliph.}$), 1732.5 and 1653.6 (C=O groups), 1578.1 (C=N) and 1525.7 and 1341.3 ($NO_2$ group) $cm^{-1}$; UV (DMF): $\lambda_{max}$ (log ε); 267.4 (3.7).

**Synthesis of 4-[(4-arylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one derivatives 10a-h.**

*General procedure*: A mixture of 5,6-diphenyl-2,3-dihydro-3-oxopyridazine-4-carbohydrazide **2** (0.50 g, 1.6 mmole) and the ethyl azobenzeneacetoacetate derivatives **7a-h** (1.6 mmole) was refluxed in ethanol (20 mL) for 6 hours. The reaction mixture was cooled to room temperature and the separated solid was filtered off, washed with diluted ethanol (10 mL), dried and recrystallized from ethanol.

**4-[(4-Phenylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (10a, $C_{27}H_{20}N_6O_3$).**

Yellow crystals in 77 % yield; mp 297 – 298 °C; IR: 3422.4, 3301.6 and 3173.2 (NH), 3057.1 ($CH_{arom.}$), 2930.1 ($CH_{aliph.}$), 1723.4, 1702.5 and 1657.7 (C=O groups), 1598.4 (C=N) and 1545.1 (C=C) $cm^{-1}$; Ms (m/z): 476 [$M^+$, 14.1 %], 371 [$M^+$ - $N=NC_6H_5$, 0.3 %, ion A], 275 [ion A - substituted pyrazolone, 100 %, ion B], 247 [ion B - CO, 3.8 %], 299 [$M^+$ - substituted pyridazinone, 0.9 %, ion C] and 201 [ion C - CO, 0.3 %]; UV (DMF): $\lambda_{max}$ (log ε); 266.7 (4.1).

**4-[(4-(2-Methylphenylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (10b, $C_{28}H_{22}N_6O_3$).**

Yellow crystals in 75 % yield; mp > 300 °C; IR: 3446.8, 3289.8 and 3179.7 (NH), 3061.6 ($CH_{arom.}$), 2922.7 and 2855.7 ($CH_{aliph.}$), 1713.4, 1690.7 and 1655.7 (C=O groups), 1599.6 (C=N) and 1542.1 (C=C) $cm^{-1}$; Ms (m/z): 490 [$M^+$, 75.4 %], 275 [$M^+$ - substituted pyrazolone, 100 %], 91 [$(CH_2C_6H_5)^+$, 17.9 %] and 77 [$(C_6H_5)^+$, 17.9 %].

**4-[(4-(4-Methylphenylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (10c, $C_{28}H_{22}N_6O_3$).**

Yellow crystals in 81 % yield; mp 283 – 284 °C; IR: 3396.7, 3291.2 and 3179.6 (NH), 3061.9 ($CH_{arom.}$), 2921 and 2856.3 ($CH_{aliph.}$), 1713.7, 1690.9 and 1655.6 (C=O groups), 1600.2 (C=N) and 1541.8 (C=C) $cm^{-1}$.

**4-[(4-(2-Methoxyphenylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (10d, $C_{28}H_{22}N_6O_4$).**

Yellow crystals in 75 % yield; mp 289 - 290 °C; IR: 3425.3 and 3291 (NH), 3067 ($CH_{arom.}$), 2923.7 ($CH_{aliph.}$), 2852.9 ($OCH_3$), 1708.6 and 1669.8 (C=O groups), 1604.3 (C=N) and 1541.2 (C=C) $cm^{-1}$; UV (DMF): $\lambda_{max}$ (log ε); 266.2 (3.5).

**4-[(4-(4-Methoxyphenylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (10e, $C_{28}H_{22}N_6O_4$).**

Yellow crystals in 78 % yield; mp 281 – 282 °C; IR: 3448.1 and 3193.3 (NH), 3061.3 ($CH_{arom.}$), 2872.2 ($OCH_3$), 1738.8 and 1648.6 (C=O groups), 1600.3 (C=N) and 1544.4 (C=C) $cm^{-1}$.

**4-[(4-(2-Chlorophenylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (10f, $C_{27}H_{19}ClN_6O_3$).**

Yellow crystals in 90 % yield; mp 271 – 272 °C; IR: 3416.3 and 3190.1 (NH), 3059.6 ($CH_{arom.}$), 1720, 1685.1 and 1655.4 (C=O groups), 1590.4 (C=N), 1548.8 (C=C) and 751.4 (Cl-C) $cm^{-1}$; MS (m/z): 511 [$M^+$, 30.3 %], 275 [$M^+$ - substituted pyrazolone ring, 100%], 111[$(ClC_6H_4)^+$, 6.4%] and 77 [$(C_6H_5)^+$, 17.5 %].

**4-[(4-(3-Chlorophenylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (10g, $C_{27}H_{19}ClN_6O_3$).**

Yellow crystals in 84 % yield; mp 274 – 276 °C; IR: 3420.8 and 3191.9 (NH), 3060.8 ($CH_{arom.}$), 1720.6, 1685.5 and 1656.3 (C=O groups), 1590.6 (C=N), 1549.7 (C=C) and 751.2 (Cl-C) $cm^{-1}$; UV (DMF): $\lambda_{max}$ (log ε); 266.2 (3.5).

**4-[(4-(4-Nitrophenylazo-4,5-dihydro-3-methyl-5-oxopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (10h, $C_{27}H_{19}N_7O_5$).**

Yellow crystals in 94 % yield; mp > 300 °C; IR: 3414.4 and 3262.3 (NH), 3064.7($CH_{arom.}$), 3027 ($CH_{aliph.}$), 1642.4, 1686 and 1712.3 (C=O groups), 1596.9 (C=N) and 1554 (C=C) 1506.4 and 1332.4 ($NO_2$) $cm^{-1}$; Ms (m/z): 398 [$M^+$ - $NO_2C_6H_4$, 20.2 %], 275 [$M^+$ - substituted pyrazolone ring, 4.9 %, ion A], 247 [ion A - CO, 3.7 %], 122 [$(NO_2C_6H_4)^+$, 8.2 %] and 77 [$(C_6H_5)^+$, 100 %]; UV (DMF): $\lambda_{max}$ (log ε); 265.3 (4.1).

**Synthesis of 4-[(4-arylazo-3,5-diaminopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one derivatives 11a-h.**

*General procedure*: A mixture of 5,6-diphenyl-2,3-dihydro-3-oxopyridazine-4-carbohydrazide **2** (0.50 g, 1.6 mmole) and azobenzenemalononitrile derivatives **8a-h**

(1.6 mmole) was refluxed in ethanol (20 mL) for 6 hours. The reaction mixture was cooled to room temperature and the separated solid was filtered off, washed with diluted ethanol (10 mL), dried and recrystallized from ethanol.

**4-[(4-Phenylazo-3,5-diaminopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (11a, $C_{26}H_{20}N_8O_2$).**

Yellow crystals in 76 % yield; mp > 300 °C; IR: 3488.8, 3404.1, 3371.6, 3259.1 and 3115.1(NH and $NH_2$), 1651.8 (C=O) and 1603.6 (C=N) $cm^{-1}$.

**4-[(4-(2-Methylphenylazo)-3,5-diaminopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (11b, $C_{27}H_{22}N_8O_2$).**

Yellow crystals in 82 % yield; mp>300 °C;IR: 3440.1 and 3225.3 (NH and $NH_2$), 2926.7 ($CH_{aliph.}$) and 1600.3 (C=N) $cm^{-1}$.

**4-[(4-(4-Methylphenylazo)-3,5-diaminopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (11c, $C_{27}H_{22}N_8O_2$).**

Yellow crystals in 75 % yield; mp >300 °C; IR: 3467.2, 3395.8, 3274.9 and 3127.4 (NH and $NH_2$), 2916.9 and 2855.4 ($CH_{aliph.}$) and 1609.2 (C=N) $cm^{-1}$.

**4-[(4-(2-Methoxyphenylazo)-3,5-diaminopyrazol-1-yl)carbo-nyl]-5,6-diphenylpyridazin-3(2*H*)-one (11d, $C_{27}H_{22}N_8O_3$).**

Yellow crystals in 91 % yield; mp >300 °C; IR: 3456.3, 3408.7, 3258.5 and 3118.8 (NH and $NH_2$), 2960 ($CH_{aliph.}$), 2833.2 ($OCH_3$) and 1597.7 (C=N) $cm^{-1}$; $^1$H-NMR (DMSO): δ 9.22 (s, 1H, NH), 7.98 - 6.82 (m, 14H, 3Ph), 3.8 (s, 2H, $NH_2$-3), 3.4 (s, 2H, $NH_2$-5) and 3.3 (s, 3H, $OCH_3$).

**4-[(4-(4-Methoxyphenylazo)-3,5-diaminopyrazol-1-yl)carbo-nyl]-5,6-diphenylpyridazin-3(2*H*)-one (11e, $C_{27}H_{22}N_8O_3$).**

Yellow crystals in 85 % yield; mp >300 °C; IR: 3456.7, 3410, 3259.4 and 3120.7 (NH and $NH_2$), 2960.6 ($CH_{aliph.}$), 2833.6 ($OCH_3$) and 1597.7 (C=N) $cm^{-1}$; Ms (m/z): 275 [$M^+$ - substituted pyrazole ring, 13.1 %], 230 [$M^+$ - substituted pyridazinone , 2.1 %, ion A], 135 [ion A – diaminopyrazole, 10.6 %] and 107 [$(CH_2OC_6H_4)^+$, 74.6 %].

**4-[(4-(2-Chlorophenylazo)-3,5-diaminopyrazol-1-yl)-carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (11f, $C_{26}H_{19}ClN_8O_2$).**

Yellow crystals in 79% yield; mp >300°C; IR: 3466.5, 3389.7, 3271.5 and 3141.3 (NH and $NH_2$), 2926.4 ($CH_{aliph.}$), 1610.6 (C=N) and 751.5 (Cl-C) $cm^{-1}$; Ms (m/z): 509 [$M^+$ - 2, 7.6%], 275 [$M^+$ - substituted pyrazole, 69.2%], 236 [$M^+$ - substituted pyridazinone, 21.1%, ion A], 139 [ion A - diaminopyrazole, 10.6%, ion B], 123 [ion A - $C_6H_4Cl$, 100%, ion C], 111[ion B - $N_2$, 61.6%] and 95 [ion C - $N_2$, 25%].

**4-[(4-(3-Chlorophenylazo)-3,5-diaminopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (11g, $C_{26}H_{19}ClN_8O_2$).**

Yellow crystals in 85% yield; mp 279 - 280°C; IR: 3370.7 and 3244.8 (NH and $NH_2$), 3050.6 ($CH_{arom.}$), 2925.7 ($CH_{aliph.}$), 1603.1 (C=N) and 766.4 (Cl-C) $cm^{-1}$; Ms (m/z): 236 [$M^+$ - substituted pyridazinone, 3.97%, ion A], 139 [ion A - diaminopyrazole, 6.53%, ion B], 123 [ion A - $C_6H_4Cl$, 9.96%, ion C], 111[ion B - $N_2$, 34.95%] and 95 [ion C - $N_2$, 11.10%].

**4-[(4-(4-Nitrophenylazo)-3,5-diaminopyrazol-1-yl)carbonyl]-5,6-diphenylpyridazin-3(2*H*)-one (11h, $C_{26}H_{19}N_9O_4$).**

Red crystals in 88% yield; mp >300 °C; IR: 3449.8 (NH and $NH_2$), 2924.7 ($CH_{aliph.}$), and 1609 (C=N) $cm^{-1}$; Ms (m/z): 275 [$M^+$ - substituted pyrazole ring, 11.2%], 122 [$(NO_2C_6H_4)^+$, 34.95%].

**Dyeing procedure**

The required amount of dye (2% shade) was dissolved in DMF 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.

**Dyeing of polyester at 130°C under pressure using Levegal PT (carrier of Buyer)**

The dye bath (1:20 liquor ratio), containing 5g/dm$^3$Levegal PT (Bayer) as carrier, 4% ammonium sulfate, 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, and then the dyed material was rinsed and soaped with 2% nonionic detergent to improve rubbing and wet fastness.

**Assessment of color fastness (Table 2)**

Fastness to washing, perspiration, light, and sublimation was tested according to the reported methods.[11]

**Color assessment**

Table 1 reports the color parameters of the dyed fabrics assessed by tristimuluscolorimetry. The color parameters of the dyed fabrics were determined using a SPECTRO multichannel photodetector (model MCPD1110A), equipped with a D65 source and barium sulfate as a standard blank. The values of the chromaticity coordinates, luminance factor, and the position of the color in the CIE-LAB color solid are reported.

**Conclusions**

A set of 24 disperse dyes **9, 10, and 11** were synthesized by reaction of 5,6-diphenyl-2,3-dihydro-3-oxopyridazine-4-carbohydrazide **2** with arylazoacetylacetone, ethyl arylazoacetoacetate and arylazomalononitrile derivatives.

All of them were investigated for their dyeing characteristics on polyester. They give bright intense hues from yellow to pale brown on polyester fabrics, due to the variations in polarity.The dyed fabrics exhibit very good to excellent (4-5) washing, perspiration, sublimation and good (4) rubbing fastness properties (Table 2). 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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Received: 25.05.2014.
Accepted: 30.06.2014.