

## Pyridazine and its related compounds: Part 26.<sup>[1]</sup> Synthesis and Application of some Monoazo disperse dyes derived from 3-hydrazinopyridazine

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**Abstract:** 3-Hydrazine-4,5,6-triphenylpyridazine was used as key intermediate for synthesis of 3-(4-aryloxy-3,5-disubstituted pyrazol-1-yl)-4,5,6-triphenylpyridazines. Some of the dyes produced were applied to polyester as disperse dyes, and their color, and fastness properties were evaluated.

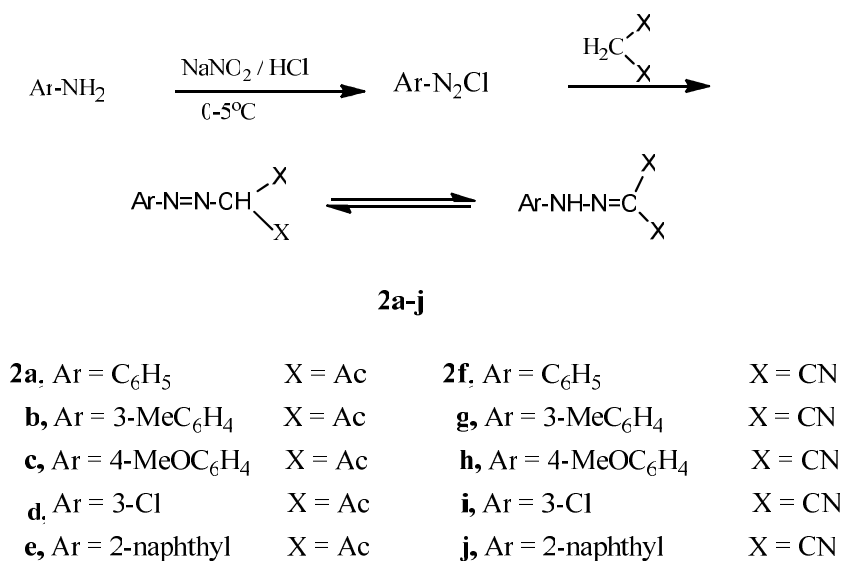
**Keywords:** 3-(Pyrazol-1-yl)pyridazine. Azodispersed dyes, Polyester fabrics. Color measurements. Fastness properties.

### Introduction

Derivatives of the pyridazine ring systems are known to possess potent biological and pharmacological properties.<sup>[2-4]</sup> On the other hand some pyrazole derivatives are very important class of heterocycles due to their biological and pharmacological activities.<sup>[5]</sup> Also, they are used as key starting material for the synthesis of commercial aryl/hetarylazopyrazole dyes.<sup>[6]</sup> All these properties aroused our interest in synthesizing new heterocyclic compounds including the pyridazine moiety which is a continuation of our previous work.<sup>[7,8]</sup> The present investigation deals with the synthesis of some 3-[4-aryloxy-3,5-disubstituted pyrazol-1-yl]-4,5,6-triphenylpyridazine and 4-aryloxy-3-methyl-1-(4,5,6-triphenylpyridazin-3-yl)-1*H*-pyrazol-5-ol dyes from 3-hydrazino-4,5,6-triphenylpyridazine and an evaluation of their properties on polyester fabric.

### Results and Discussion

Coupling of active methyl compounds such as acetylacetone and malononitrile with various aryldiazonium chlorides in sodium acetate buffered solution afforded the corresponding azobenzene acetylacetone and azobenzenemalononitrile derivatives **2a-e** and **2f-g** in good yield, respectively (Scheme 1). Spectral data for such compounds indicate them to have a hydrazone configuration,<sup>[9]</sup> characterisation and spectral data for compounds **2a-j** were described in the previous part.<sup>[10]</sup>

**Scheme 1**

3-Hydrazino-4,5,6-triphenylpyridazine **1**,<sup>[11]</sup> when reacted with azobenzeneacetylacetone derivatives **2a-e** in absolute ethanol at refluxing temperature yielded 3-[4-arylo-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine derivatives **3a-e** (Scheme 2). The reaction proceeds in two stages, viz., the initially formed hydroxylpyrazoline subsequently loses water. Compound **1** when reacted with azobenzene malononitrile derivatives **2f-j** in a similar manner gave 3-[4-arylo-3,5-diaminopyrazol-1-yl]-4,5,6-triphenylpyridazine derivatives **3f-j**. Characterisation and spectral data of compounds **3a-j** are shown in the Experimental part.

When 3-[4-(3-chlorophenyl)azo-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine **3d** reduced with Zn/AcOH in ethanol gave a product. The product was proven to be 3-[4-amino-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine **4**.

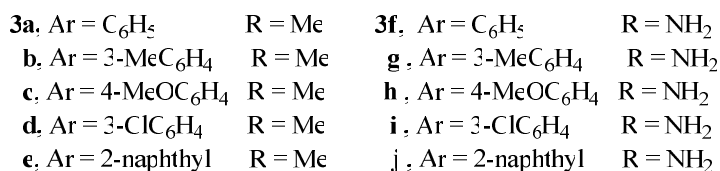
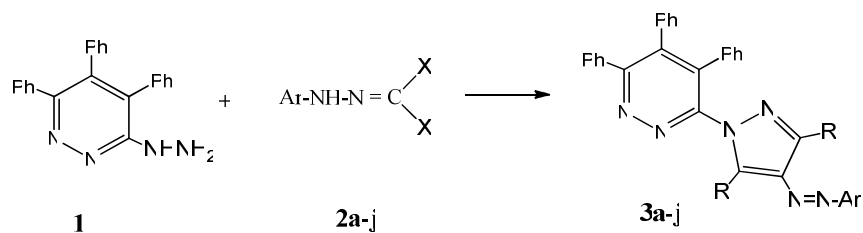
The assignment of structure of **4** was based on analytical and spectral data. The IR spectrum showed the presence of NH<sub>2</sub> group at (3390, 3264) and CH<sub>arom.</sub> at 3057 cm<sup>-1</sup>. Additional evidence for the structure of 4-amino derivative **4** was provided by its diazotization and coupling. The 3-[4-amino-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine **4** was diazotized with hydrochloric acid and sodium nitrite to afford the diazonium salt **5**. This, when coupled with β-naphthol in presence of sodium acetate yielded the 3-[4-(2-hydroxy-1-naphthyl)azo-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine **6** (Scheme 3).

Structure of compound **6** was established on the basis of analytical and spectral data. The IR spectrum revealed no absorption band due to NH<sub>2</sub> group instead broad bonded OH group absorption at 3396 cm<sup>-1</sup> and –N=N– group at 1534 cm<sup>-1</sup> were shown.

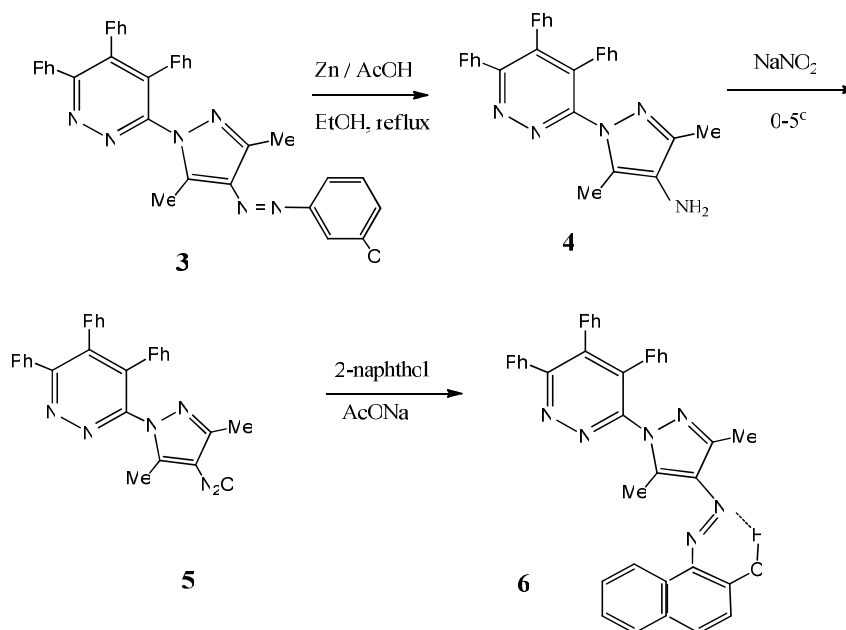
On the other hand, condensation of 3-hydrazino derivative **1** with ethyl acetoacetate in boiling ethanol led to the formation of ethyl 3-butoate-(4,5,6-triphenylpyridazin-3-yl)hydrazone **7** (Scheme 4). However when heated with ethyl acetoacetate at 150-160°C, the product isolated was 3-methyl-1-(4,5,6-triphenylpyridazin-3-yl)-1H-pyrazol-5-ol **8**.<sup>[12]</sup>

Compound **8** exist in two tautomeric forms due to its keto-enol tautomerism. The spectral data proved that it existed in enol form due to intramolecular chelation by H-bonded. This phenomenon is confirmed by <sup>1</sup>H-NMR and IR absorption spectra.

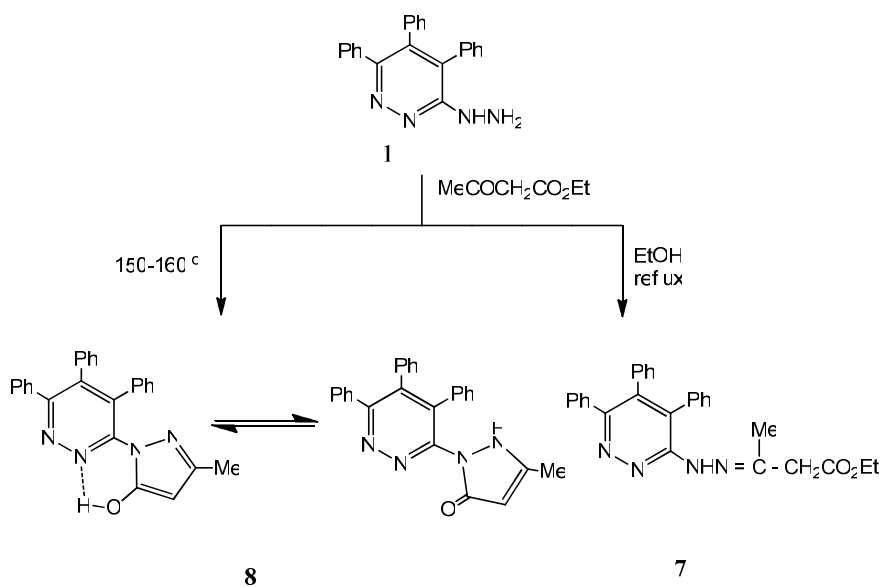
4-Arylo of 3-methyl-1-(4,5,6-triphenylpyridazin-3-yl)-1H-pyrazol-5-ol **9** was prepared by coupling of the pyrazolinone with a freshly prepared solution of aryl diazonium salt in an ice bath, namely, aniline, *p*-anisidine and *p*-nitroaniline in the presence of sodium acetate (Scheme 5).



Scheme 2



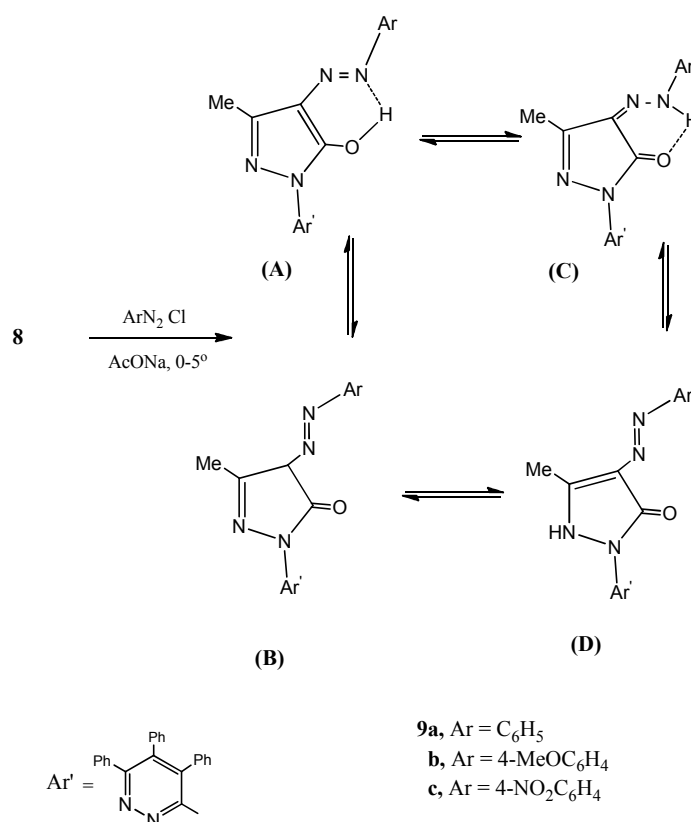
Scheme 3



Scheme 4

The dyes **9a-c** may exist in four possible tautomeric forms, namely two azo-keto forms (**B**) and (**D**), the azo-enol form (**A**) and the hydrazone-keto form (**C**), as shown in (Scheme 5). The spectral data generally lead to the conclusion that the tautomeric equilibrium of the arylazopyrazolone dyes is in favor of the hydrazone form (**C**) in the solid state.<sup>[13]</sup> Characterisation and spectral data of compounds **9a-c** are shown in the experimental part.

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



Scheme 5

### Dyeing of polyester fabrics and dyeing properties

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 are 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  $S$ :

$$K/S = (1-R)^2 / 2R. \quad (1)$$

In this equation  $R$  is used as a ratio, e.g., 32% reflectance as 0.32. The  $K/S$  value at  $\lambda_{\text{max}}$  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 ( $\Delta L^*$ ,  $\Delta C^*$ ,  $\Delta H^*$ , and  $\Delta E^*$ ). The results are measured using CIE-LAB techniques and given in Table 1, Where  $\Delta L^*$  is the lightness difference,  $\Delta C^*$  the chroma difference,  $\Delta H^*$  the hue difference, and  $\Delta E^*$  the total color difference. A negative sign of  $\Delta L^*$  indicates that the dyed fiber becomes darker than the standard, but a positive sign indicates that the dyed fiber becomes lighter than the standard. A negative sign of  $\Delta C^*$  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  $\Delta H^*$  indicates that the color directed to red color, while a positive sign indicates that the color directed to yellowish.

**Table 1** Optical measurements of compounds **3a-j**

Dye	R%	$a^*$	$b^*$	$L^*$	$C^*$	$H^*$	$\Delta L^*$	$\Delta C^*$	$\Delta H^*$	$\Delta E^*$	K/S
<b>3a</b>	7.12	2.07	11.56	89.33	11.74	79.85	-	-	-	-	5.9
<b>3b</b>	4.88	1.53	16.85	87.51	16.92	84.81	1.30	-5.8	1.58	6.19	7.4
<b>3c</b>	2.95	-1.4	16.33	90.83	16.40	95.10	0.35	6.63	1.76	6.87	7.5
<b>3d</b>	2.08	0.69	14.58	87.84	14.59	87.28	1.72	-7.75	1.45	8.07	7.6
<b>3e</b>	4.77	2.53	14.91	86.10	15.12	80.38	-0.09	-9.23	-0.63	9.25	7.2
<b>3f</b>	2.60	11.54	70.71	69.58	71.65	80.73	-	-	-	-	20.5
<b>3g</b>	6.10	13.54	70.22	67.34	71.51	79.09	5.15	-12.4	1.86	13.64	21.0
<b>3h</b>	5.30	14.94	61.52	69.07	63.31	76.35	4.71	-4.88	-2.69	7.29	15.5
<b>3i</b>	3.88	-2.67	66.84	84.07	66.89	92.29	13.84	-0.46	14.99	20.41	17.5
<b>3j</b>	2.85	9.07	49.87	71.90	50.68	70.69	-0.54	2.65	-0.89	2.84	14.5

R reflectance;  $a^*$  red-green axis;  $b^*$  yellow-blue axis;  $L^*$  lightness;  $C^*$  chroma;  $H^*$  hue;  $\Delta L^*$  lightness difference;  $\Delta C^*$  chroma difference;  $\Delta H^*$  hue difference;  $\Delta E^*$  total color difference

The values of K/S of **3a-j** vary from 5.9 to 21.0. The introduction of amino, methyl, methoxy, chloro, and naphthyl group in dyes varies the strength of K/S values and deepens the color compared with the parent dyes **3a** and **3f** (Table 1).

The replacement of the methyl by an amino group in the pyrazole moiety increase the value of K/S, indicating that the dyes **3f-j** show higher affinity towards dyeing of polyester fabrics than **3a-e**. Dyes **3c,j** with positive  $\Delta C^*$  values are brighter than the parent dyes **3a** and **3f**, while the other dyes are duller than the parent dyes. Dyes **3b-d,h,i** with positive  $\Delta L^*$  are darker than the parent. The positive value of  $a^*$  and  $b^*$  indicates that all groups shift the color hues of the dye to reddish direction on the red-green axis and to the yellowish direction in the yellow-blue axis, respectively.

### Assessment of color fastness

Most influences that can affect fastness are light, washing, heat, perspiration, and atmospheric pollution. Condition of such tests are chosen to correspond closely to treatments employed in manufacture and ordinary use condition [14]. The results revealed that those dyes have good fastness properties (Table 2).

## Conclusions

In this work, we have synthesized two series of monoazo dyes **3a-j** and **9a-c** derived from 3-hydrazino-4,5,6-triphenylpyridazine. Dyes **3a-j** were investigated for their dyeing characteristic on polyester. They give bright intense hues from yellow to orange-yellow on polyester fabric, due to the variations in polarity. The dyed fabrics exhibit good to excellent (4-5) washing, perspiration and good (4) rubbing and sublimation 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.

**Table 2** Fastness properties of compounds **3a-j**

Dye	Washing , 75 °C	Rubbing		Sublimation		Acid perspiration	Light, 40 h
		Dry	Wet	180 °C	210°C		
<b>3a</b>	4	3-4	3-4	3-4	3	3-4	4
<b>3b</b>	4-5	4	4	4	3-4	4	5-6
<b>3c</b>	4-5	4	3-4	4	3-4	4	5
<b>3d</b>	4-5	4	3-4	3-4	3	4	6
<b>3e</b>	4	4	3-4	3-4	3-4	4	4-5
<b>3f</b>	4	4	3-4	3-4	3	4	4-5
<b>3g</b>	4-5	4	4	4	3-4	4	4
<b>3h</b>	4	4	3-4	3-4	3	4	5
<b>3i</b>	4-5	4	4	3-4	3	4	5
<b>3j</b>	4-5	4	3-4	4	3	3-4	4

## 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 F<sub>254</sub> precoated aluminum sheets. Infrared spectra were recorded on FTIR 5300 Spectrometer and Perking Elmer Spectrum RXIFT-IR System, using the potassium bromide wafer technique. <sup>1</sup>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 3-hydrazino-4,5,6-triphenylpyridazine<sup>[11]</sup>, arylazoacetylacetone, and arylazomalono nitrile **2a-j**<sup>[9]</sup> were conducted according to known procedures.

### *Synthesis of 3-[4-(arylozo)-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenyl-pyridazines 3a-e: general procedure:*

A mixture of 3-hydrazino-4,5,6-triphenylpyridazine **1** (1 g, 3 mmoles) and the arylazoacetylacetone **2a-e** (3 mmoles) was refluxed in ethanol (50 cm<sup>3</sup>) for 10 h. The reaction mixture was cooled to room temperature and the separated solid was filtered, washed with water, dried, and recrystallized from dimethylformamide.

#### *3-[4-(Phenylazo)-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine (3a, C<sub>33</sub>H<sub>26</sub>N<sub>6</sub>)*

Yellow crystals in (66 %) yield, M.P.: 199-201 °C; IR (KBr):  $\nu$  = 3,062 (CH<sub>arom.</sub>), 2,920 (CH<sub>aliph.</sub>), 1,632 (C=N), 1,600 (C=C), 1,506 (N=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.3 (s, 3H, 3-CH<sub>3</sub>), 2.7 (s, 3H, 5-CH<sub>3</sub>),

7.4-7.5 (m, 15H, 3Ph), 7.7-7.8 (m, 5H, Ar-H) ppm; MS:  $m/z = 506$  ( $M^+$ , 100%), 401 ( $M - N=NPh$ , 11%), 307 ( $M - \text{substituted pyrazole}$ , 8%).

*3-[4-(3-MethylPhenylazo)-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine (3b, C<sub>34</sub>H<sub>28</sub>N<sub>6</sub>)*

Yellow crystals in (51.3 %) yield, M.P.: 169-171 °C; IR (KBr):  $\nu = 3,050$  ( $CH_{\text{arom.}}$ ), 2,922 ( $CH_{\text{aliph.}}$ ), 1,606 ( $C=N$ ), 1,564( $C=C$ ), 1,509 ( $N=N$ )  $cm^{-1}$ ;  $^1H$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 2.34$  (s, 3H, 3- $CH_3$ ), 2.77 (s, 3H, 5- $CH_3$ ), 2.8 (s, 3H,  $m-CH_3$ ), 7.31-7.52 (m, 15H, 3Ph), 7.7-7.85 (m, 4H, Ar-H) ppm; MS :  $m/z = 520.3$  ( $M^+$ , 15%).

*3-[4-(4-MethoxyPhenylazo)-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine (3c, C<sub>34</sub>H<sub>28</sub>N<sub>6</sub>O)*

Orange-Yellow crystals in (74.5 %) yield, M.P.: 179-180 °C; IR (KBr):  $\nu = 3,056$  ( $CH_{\text{arom.}}$ ), 2,926 ( $CH_{\text{aliph.}}$ ), 2,850 ( $OCH_3$ ), 1,630 ( $C=N$ ), 1,605( $C=C$ ), 1,534 ( $N=N$ )  $cm^{-1}$ ;  $^1H$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 2.34$  (s, 3H, 3- $CH_3$ ), 2.70 (s, 3H, 5- $CH_3$ ), 3.84 (s, 3H,  $OCH_3$ ), 7.05-7.77 (m, 4H, Ar-H), 7.41-7.79 (m, 15H, 3Ph) ppm; MS :  $m/z = 536.2$  ( $M^+$ , 27%).

*3-[4-(3-ChloroPhenylazo)-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine (3d, C<sub>33</sub>H<sub>25</sub>ClN<sub>6</sub>)*

Yellow crystals in (68 %) yield, M.P.: 178-180 °C; IR (KBr):  $\nu = 3,060$  ( $CH_{\text{arom.}}$ ), 2,926 ( $CH_{\text{aliph.}}$ ), 1,650 ( $C=N$ ), 1,562( $C=C$ ), 1,530 ( $N=N$ )  $cm^{-1}$ ;  $^1H$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 2.34$  (s, 3H, 3- $CH_3$ ), 2.77 (s, 3H, 5- $CH_3$ ), 7.21-7.54 (m, 4H, Ar-H), 7.41-7.79 (m, 15H, 3Ph) ppm; MS :  $m/z = 541$  ( $M^+$ , 22%).

*3-[4-(2-Naphthylazo)-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine (3e, C<sub>37</sub>H<sub>28</sub>N<sub>6</sub>)*

Orange crystals in (60 %) yield, M.P.: 231-232 °C; IR (KBr):  $\nu = 3,052$  ( $CH_{\text{arom.}}$ ), 2,924 ( $CH_{\text{aliph.}}$ ), 1,654 ( $C=N$ ), 1,562( $C=C$ ), 1,539 ( $N=N$ )  $cm^{-1}$ ;  $^1H$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 2.48$  (s, 3H, 3- $CH_3$ ), 2.62 (s, 3H, 5- $CH_3$ ), 7.05-8.28 (m, 22H, 3Ph and Ar-H) ppm; MS :  $m/z = 556.3$  ( $M^+$ , 22%).

*Synthesis of 3-[4-(aryloazo)-3,5-diaminopyrazol-1-yl]-4,5,6-triphenyl-pyridazines 3f-j:*

The above procedure was repeated, except that arylazoacetone was replaced by arylazomalononitrile **2f-j**.

*3-[4-(Phenylazo)-3,5-diaminopyrazol-1-yl]-4,5,6-triphenyl-pyridazines 3f (C<sub>31</sub>H<sub>24</sub>N<sub>8</sub>)*

Yellow crystals in (72 %) yield, M.P.: 213-215 °C; IR (KBr):  $\nu = 3,424$  and 3,345 ( $NH_2$ ), 3,054 ( $CH_{\text{arom.}}$ ), 1,606 ( $C=N$ ), 1,550( $C=C$ ), 1,533 ( $N=N$ )  $cm^{-1}$ ;  $^1H$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 5.8$  (b, s, 4H, 2 $NH_2$ ), 7.32-7.6 (m, 5H, Ar-H), 7.69-7.81 (m, 15H, 3Ph) ppm ; MS :  $m/z = 508.2$  ( $M^+$ , 2%).

*3-[4-(3-Methylphenylazo)-3,5-diaminopyrazol-1-yl]-4,5,6-triphenyl-pyridazines 3g (C<sub>32</sub>H<sub>26</sub>N<sub>8</sub>)*

Yellow crystals in (57.3 %) yield, M.P.: 175-177 °C; IR (KBr):  $\nu = 3,434$  and 3,357 ( $NH_2$ ), 3,050 ( $CH_{\text{arom.}}$ ), 1,616 ( $C=N$ ), 1,546( $C=C$ ), 1,536 ( $N=N$ )  $cm^{-1}$ ;  $^1H$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 2.34$  (s, 3H,  $m-CH_3$ ), 5.7 (b, s, 4H, 2 $NH_2$ ), 7.32-7.6 (m, 4H, Ar-H), 7.69-7.81 (m, 15H, 3Ph) ppm; MS :  $m/z = 522.2$  ( $M^+$ , 15%).

*3-[4-(4-Methoxyphenylazo)-3,5-diaminopyrazol-1-yl]-4,5,6-triphenyl-pyridazines 3h (C<sub>32</sub>H<sub>26</sub>N<sub>8</sub>O)*

Orange-yellow crystals in (80.2 %) yield, M.P.: 233-235 °C; IR (KBr):  $\nu = 3,434$  and 3,357 ( $NH_2$ ), 3,058 ( $CH_{\text{arom.}}$ ), 2,850 ( $OCH_3$ ), 1,614 ( $C=N$ ), 1,564( $C=C$ ), 1,539 ( $N=N$ )  $cm^{-1}$ ;  $^1H$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 3.79$  (s, 3H,  $OCH_3$ ), 6.99-7.2 (m, 4H, Ar-H), 5.8 (b, s, 4H, 2 $NH_2$ ), 7.7.41-7.79 (m, 15H, 3Ph) ppm; MS :  $m/z = 538.2$  ( $M^+$ , 12%).

*3-[4-(3-Chlorophenylazo)-3,5-diaminopyrazol-1-yl]-4,5,6-triphenyl-pyridazines 3i (C<sub>31</sub>H<sub>23</sub>ClN<sub>8</sub>)*

Orange-yellow crystals in (73.6 %) yield, M.P.: 140-141 °C; IR (KBr):  $\nu = 3,425$  and 3,370 ( $NH_2$ ), 3,060 ( $CH_{\text{arom.}}$ ), 1,608 ( $C=N$ ), 1,560( $C=C$ ), 1,535 ( $N=N$ )  $cm^{-1}$ ;  $^1H$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 5.6$  (b, s, 4H, 2 $NH_2$ ), 7.21-7.54 (m, 4H, Ar-H), 7.55-7.79 (m, 15H, 3Ph) ppm; MS:  $m/z = 545$  ( $M^+ + 2$ , 27%), 544 ( $M + 1$ , 34%), 543 ( $M$ , 76%), 401 [( $M + 2$ ) -  $N=NC_6H_4Cl$ , 3%], 307 ( $M - \text{substituted pyrazole}$ , 4%).

*3-[4-(2-Naphthylazo)-3,5-diaminopyrazol-1-yl]-4,5,6-triphenyl-pyridazines 3j (C<sub>35</sub>H<sub>26</sub>N<sub>8</sub>)*

Orange-yellow crystals in (71.4 %) yield, M.P.: 190-191 °C; IR (KBr):  $\nu = 3,450$  and  $3,406$  (NH<sub>2</sub>),  $3,050$  (CH<sub>arom.</sub>),  $1,614$  (C=N),  $1,575$  (C=C),  $1,550$  (N=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 5.6-5.8$  (b, s, 4H, 2NH<sub>2</sub>),  $7.44-7.79$ (m, 15H, 3Ph),  $7.45-8.08$  (m, 7H, Ar-H) ppm; MS :  $m/z = 558.2$  (M<sup>+</sup>, 12%).

#### **Reduction of 3-[4-(3-chlorophenyl)azo-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine 3d:**

To a solution of 3-[4-(3-chlorophenylazo)-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine **3d** (1.1 g, 20 mmoles) in ethanol-acetic acid (20 cm<sup>3</sup>, 1:1), zinc dust (0.5g) was added in portions with stirring. The reaction mixture was refluxed for 2 h, t.l.c. showed the reduction to be completed. Thereafter, the reaction mixture was filtered on hot and the solvent was evaporated under reduced pressure. After the addition of H<sub>2</sub>O (50 cm<sup>3</sup>), the solid product was filtered and recrystallized from ethanol to give 3-[4-amino-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenyl-pyridazine **4**.

Yield: 0.45 g (53.6%); m.p.:156°C; IR (KBr):  $\nu = 3,390-3,264$  (NH<sub>2</sub>),  $3,057$  (CH<sub>arom.</sub>),  $2,925$  (CH<sub>aliph.</sub>),  $1,659$  (C=N),  $1,595$  (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 2.77$  (s, 6H, 2CH<sub>3</sub>),  $6.27$  (s, 2H, NH<sub>2</sub>),  $7.52-7.79$ (m, 15H, 3Ph) ppm; MS :  $m/z = 417.2$  (M<sup>+</sup>,30%).

#### **Diazotization of 3-[4-amino-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenyl-pyridazine 4 and coupling with $\beta$ -naphthol: formation of 3-[4-(2-hydroxy-1-naphthyl)azo-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine 6:**

3-[4-Amino-3,5-dimethylpyrazol-1-yl]-4,5,6-triphenylpyridazine **4** (0.42 g, 1 mmole) was dissolved in warm conc. hydrochloric acid (10 cm<sup>3</sup>) and water (3 cm<sup>3</sup>) and the solution was then cooled to 0-5°C with stirring. Sodium nitrite (0.14 g, 2 mmoles) in water (2 cm<sup>3</sup>) was gradually added to this solution over 15 min. at 0-5°C with stirring. The reaction mixture was then stirred for 1 h while maintaining 0-5°C. Excess nitrous acid was destroyed by the addition of urea, and the solution was filtered to obtain a clear diazonium salt solution **8**.

$\beta$ -Naphthol (0.14g, 1 mmole) and sodium acetate (2g) were dissolved in ethanol-water (10 ml, 1:1) and the solution cooled to 0-5°C. To the cooled solution, the diazonium salt **8** was added slowly so that the temperature did not rise above 5°C. The mixture was then stirred for 2 h at 0-5°C, filtered, and the press cake washed with water, dried, and recrystallized from ethanol as mauve precipitate.

Yield: 0.4 g (70%); m.p.: 114-115°C; IR (KBr) :  $\nu = 3,396$  (OH, H-bonded),  $3,053$  (CH<sub>arom.</sub>),  $2,920$  (CH<sub>aliph.</sub>),  $1,600$  (C=C),  $1,534$  (N=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 2.34$  (s, 3H, 2-CH<sub>3</sub>),  $2.76$  (s, 3H, 5-CH<sub>3</sub>),  $5.35$  (w,s 1H, OH),  $7.41-7.79$  (m, 15H, 3Ph),  $8.0-8.22$  (m, 6H, Ar-H) ppm; MS:  $m/z = 572.3$  (M<sup>+</sup>, 1.2%).

#### **Ethyl 3-butanoate-(4,5,6-triphenylpyridazin-3-yl)hydrazone (7, C<sub>28</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>)**

A mixture of 3-hydrazino-4,5,6-triphenylpyridazine **1** (1.0 g, 3.0 mmoles) and ethyl acetoacetate (0.39 g, 3.0 mmoles) was refluxed in ethanol (30 cm<sup>3</sup>) for 2 h. the solvent was then evaporated invacue and the residue was triturated with diethyl ether. The solid product was filtered, dried and recrystallized from ethanol.

Yield: 1.0 g (75%); m.p.: 175-176°C; IR (KBr) :  $\nu = 3,355$  (NH<sub>2</sub>),  $3,053$  (CH<sub>arom.</sub>),  $2,920$  (CH<sub>aliph.</sub>),  $1,730$  (C=O),  $1,600$  (C=C),  $1,534$  (N=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 1.20$  (s, 3H, CH<sub>2</sub>CH<sub>3</sub>),  $1.60$  (s, 3H, CH<sub>3</sub>),  $4.13$  (q, CH<sub>2</sub>CH<sub>3</sub>),  $6.80-7.40$  (m, 16H, 3Ph, and NH).

#### **3-Methyl-1-(4,5,6-triphenylpyridazin-3-yl)-1H-pyrazol-5-ol (8, C<sub>26</sub>H<sub>20</sub>N<sub>4</sub>O)**

This compound was prepared by heating compound **1** (1.69 g, 5.0 mmoles) with ethyl acetoacetate (5.0 g) for 10 minutes in an oil bath t 150-160°C, The cooled reaction mixture was triturated with diethyl ether (20 cm<sup>3</sup>) and the solid product was filtered, dried and recrystallized from methanol.

Yield: 1.7 g (84%); m.p.: 152-153°C; IR (KBr) :  $\nu = 3,439$  (NH, OH enoic),  $3,053$  (CH<sub>arom.</sub>),  $2,920$  (CH<sub>aliph.</sub>),  $1,620$  (C=N),  $1,510$  (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 1.8$  (s, 3H, CH<sub>3</sub>),  $3.30$  (br s, 1H, OH),  $6.80-7.40$  (m, 16H, 3Ph, 4-H).



***Diazocoupling of the pyrazolone derivative 8 with aryl diazonium salts: formation of 4-arylozo-3-methyl-1-(4,5,6-triphenylpyridazin-3-yl)-1H-pyrazol-5-ol derivatives 9a-c: general procedure:***

The desired aromatic amines, namely aniline, *p*-anisidine and 4-nitroaniline (3.0 mmoles) was dissolved in concentrated hydrochloric acid (2 cm<sup>3</sup>), diluted with water (4 cm<sup>3</sup>) and cooled at 0-5°C in an ice bath. An aqueous cold solution of sodium nitrite (3 mmoles in 4 cm<sup>3</sup> water) was added to the prepared aromatic amine hydrochloride to give the diazonium chloride solution. The latter solution was added drop-wise with stirring for 30 min. in an ice bath to a cold suspension of 3-methyl-1-(4,5,6-triphenylpyridazin-3-yl)-1H-pyrazol-5-ol **8** (0.81g, 2 mmoles) in ethanol-water (40 cm<sup>3</sup>; 1:1) containing sodium acetate (0.4g). After complete addition, the colored precipitated dyes were filtered, washed with water (3 x 25 cm<sup>3</sup>) and dried. The solid products **9a-c** are crystallized from ethanol.

***4-Phenylazo-3-methyl-1-(4,5,6-triphenylpyridazin-3-yl)-1H-pyrazol-5-ol (9a, C<sub>32</sub>H<sub>24</sub>N<sub>6</sub>O)***

Red crystals in (68.6 %) yield, M.P.: 195-196 °C; IR (KBr):  $\nu = 3,423$  (NH), 3,050 (CH<sub>arom.</sub>), 2,925 (CH<sub>aliph.</sub>), 1,650 (C=O), 1,635 (C=N), 1,240 (exocyclic C=N); cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 2.31$  (s, 3H, 3-CH<sub>3</sub>), 6.81-7.35(m, 6H, Ar-H, and NH), 7.41-7.79 (m, 15H, 3Ph) ppm.

***4-(4-Methoxyphenylazo-3-methyl-1-(4,5,6-triphenylpyridazin-3-yl)-1H-pyrazol-5-ol (9b, C<sub>33</sub>H<sub>26</sub>N<sub>6</sub>O<sub>2</sub>)***

Red crystals in (65%) yield, M.P.: 226-228 °C; IR (KBr):  $\nu = 3,424$  (NH), 3,059 (CH<sub>arom.</sub>), 2,934(CH<sub>aliph.</sub>), 2,845 (OCH<sub>3</sub>), 1,631 (C=O, and C=N), 1,240 (exocyclic C=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 2.33$  (s, 3H, 3-CH<sub>3</sub>), 3.83 (s, 3H, OCH<sub>3</sub>), 7.05-7.53 (m, 5H, Ar-H, and NH), 7.42-7.78 (m, 15H, 3Ph) ppm.

***4-(4-Nitrophenylazo-3-methyl-1-(4,5,6-triphenylpyridazin-3-yl)-1H-pyrazol-5-ol (9c, C<sub>32</sub>H<sub>23</sub>N<sub>7</sub>O<sub>3</sub>)***

Red crystals in (72%) yield, M.P.: 185-187 °C; IR (KBr):  $\nu = 3,433$  (NH), 3,056 (CH<sub>arom.</sub>), 2,926(CH<sub>aliph.</sub>), 1,685 (C=O), 1,505 and 1,333 (NO<sub>2</sub>), 1,245 (exocyclic C=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 2.31$  (s, 3H, 3-CH<sub>3</sub>), 7.20-7.53 (m, 5H, Ar-H, and NH), 7.42-7.78 (m, 15H, 3Ph) ppm.

***Dyeing procedures******Preparation of dye dispersion***

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<sup>3</sup>), 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 5 g/dm<sup>3</sup> 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, 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.

***Fastness to washing***

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

### ***Fastness to perspiration***

The samples were prepared by stitching pieces of dyed polyester fabric between two pieces of undyed cotton fabric, all of equal diameter, and then immersing in the acid medium for 30 min. The staining on the undyed adjacent fabric was assessed according to the following grey scale: 1-poor, 2-fair, 3-moderate, 4-good, and 5-excellent. The acid solution (pH 3.5) contained sodium chloride 10 g/dm<sup>3</sup>, lactic acid I g/dm<sup>3</sup>, disodium ortho-phosphate 1 g/dm<sup>3</sup>, and histidine monohydrochloride 0.25 g/dm<sup>3</sup>.

### ***Fastness to rubbing***

The dyed polyester fabric was placed on the base of crockmeter (Atlas electronic type), so that it rested flat on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was allowed to slide on the tested fabric back and forth 20 times by making ten complete turns of the crank. For wet rubbing test, the testing square was thoroughly wet in distilled water. The rest of the procedure was the same as the dry test. The staining on the white testing cloth was assessed according to grey scale: 1-poor, 2-fair, 3-moderate, 4-good, and 5-excellent.

### ***Fastness to sublimation***

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

### ***Fastness to light***

Light fastness was determined by exposing the dyed polyester on a Xenotest 150 [Original Hanau, chamber temperature 25-30°C, black panel temperature 60 °C, relative humidity 50-60%, and dark glass (UV) filter system] for 40 h. The changes in color were assessed according to the following blue scale. 1-poor, 3-moderate, 5-good. and 8-very good.

### ***Color assessment***

Table 1 reports the color parameters of the dyed fabrics assessed by tristimulus colorimetry. 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.

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