



# PYRIDAZINE AND ITS RELATED COMPOUNDS. 25<sup>1</sup>

## SYNTHESIS OF NEW ARYLAZOPYRAZOLTHIENO[2,3-*c*]-PYRIDAZINE TYPE DISPERSION DYES

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Acetylacetone was coupled with diazotized aryl amines to give arylazoacetylacetones; these when refluxed with 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carbohydrazide in glacial acetic acid yielded the corresponding 5-amino-6-[[4-arylo-3,5-dimethylpyrazol-1-yl]-carbonyl]-3,4-diphenylthieno[2,3-*c*]pyridazine dyes. The dyes were applied to polyester fabric, and their spectral and fastness properties measured.

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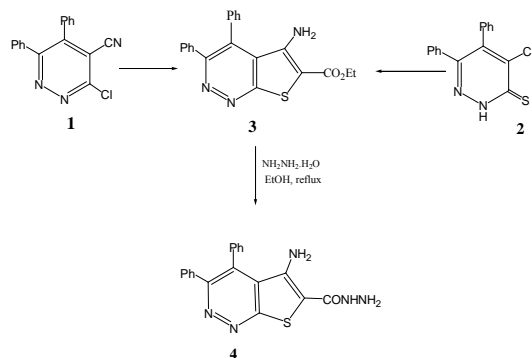
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### INTRODUCTION

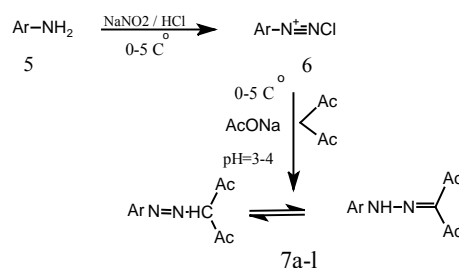
Interest in the design of azo dyes containing heterocyclic moieties stems from their high degree of brightness compared to azo dyes derived from anilines.<sup>2</sup> The thiophene derivatives based azo dyes are known as disperse dyes with excellent brightness of shade. This class of dyes was established as an alternative to more expensive anthraquinone dyes.<sup>3</sup> The heterocyclic nature of the thiophene ring has also allowed for excellent sublimation fastness on the dyed fibers.<sup>4</sup> Additionally, the sulfur atom plays a decisive role by acting as an efficient electron sink as explained by valence bond theory.<sup>5</sup> On the other hand heterocyclic annulated pyridazines continue to attract considerable attention which mainly arises from the large variety of interesting pharmacological activities observed with pyridazine derivatives.<sup>6</sup> Recently, our researches have been devoted to the synthesis of condensed tricyclic systems of potential biological activity with a thiophene ring as the central nucleus.<sup>7-9</sup> As a continuation of these studies we report here the synthesis of some 6-[[4-(arylo)-3,5-dimethylpyrazol-1-yl]carbonyl]thieno[2,3-*c*]pyridazine dyes from 5-amino-3,4-diphenyl-6-ethoxycarbonylthieno[2,3-*c*]pyridazine and an evolution of their properties on polyester fibers.

Our synthesis began with the preparation of ethyl 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carboxylate **3**, which was obtained from the reaction of 3-chloro-4-cyanopyridazine **1** or 4-cyanopyridazine-3-thione **2** with ethyl mercaptoacetate or ethyl chloro(bromo)acetate, respectively.<sup>10</sup> Compound **3** reacted with 85% excess of hydrazine hydrate in refluxing ethanol to give 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carbohydrazide **4**, (Scheme 1).

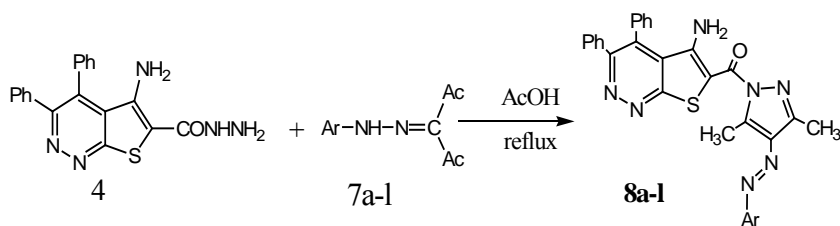


Scheme 1.

Arylamine derivatives **5** were diazotized using sodium nitrite in hydrochloric acid; the temperature was maintained below 5 °C in an ice bath. The diazotized products **6** were then coupled with active methylene compounds such as acetylacetone in sodium acetate buffered solution to give the azobenzeneacetylacetone derivatives **7** in good yields, respectively (Scheme 2). Spectral data<sup>11,12</sup> for such compounds indicate them to have a hydrazone configuration, characterization data for compounds **7a-l** were described in the previous part.<sup>13</sup>



Scheme 2.



**Scheme 3.** Compounds **7** and **8**: **a** (Ar=Ph); **b** (Ar=2-MeC<sub>6</sub>H<sub>4</sub>); **c** (Ar=3-MeC<sub>6</sub>H<sub>4</sub>); **d** (Ar=4-MeC<sub>6</sub>H<sub>4</sub>); **e** (Ar=2-MeOC<sub>6</sub>H<sub>4</sub>); **f** (Ar=4-MeOC<sub>6</sub>H<sub>4</sub>); **g** (Ar=2-ClC<sub>6</sub>H<sub>4</sub>); **h** (Ar=3-ClC<sub>6</sub>H<sub>4</sub>); **i** (Ar=3-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>); **j** (Ar=4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>); **k** (Ar=2-naphthyl); **l** (Ar=3-pyridyl)

Compound **4**, when reacted with the azobenzeneacetone derivatives **7a-l** in glacial acetic acid at refluxing temperature yielded the 5-amino-6-[[4-aryloxy-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine **8a-l** (Scheme 3). The reaction proceeds in two stages, viz., the initially formed hydroxypyrazoline subsequently loses water by an acid-catalysed reaction.<sup>14,15</sup>

## 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 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  $S$ :

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

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.

The values of  $K/S$  of **8a-l** vary from 3.0 to 13.7. The introduction of different groups in dyes **8a-l** increases the strength of  $K/S$  values and deepens the color compared with the parent dye **8a** (Table 1).

The replacement of the phenyl by tolyl, anisyl, chlorophenyl, nitrophenyl, naphthyl and pyridyl groups in the pyrazolo moiety decreases the value of  $K/S$ , indicating that the dye **8k** show higher affinity towards dyeing of polyester fabrics, than the other dyes. Dyes **8b-f** and **8h-l** with positive  $\Delta C^*$  values are brighter than the parent dye **8a** while the other dyes are duller than the parent dye. Dyes **8b-l** with negative  $\Delta L^*$  values are darker than the parent dye **8a**. 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. Conditions of such tests are chosen to correspond closely to treatments employed in manufacture and ordinary use conditions.<sup>16</sup> Results are given after usual matching of tested samples against standard reference (the grey scale).<sup>16</sup> 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 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. 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 Shimadzu spectrometer. Elemental analysis (C,H,N) were carried out at the micro-analytical Center of Cairo University, Giza, Egypt.

**Table 1** Optical measurements of compounds **8a-l**

Dye	R, %	a*	b*	L*	C*	H*	$\Delta L$	$\Delta C$	$\Delta H$	$\Delta E$	K/S
<b>8a</b>	5.63	6.35	28.3	53.73	28.84	1.25	-	-	-	-	10.5
<b>8b</b>	7.33	5.17	22.17	49.52	22.76	1.12	-8.22	7.64	-1.5	11.32	8.5
<b>8c</b>	8.00	4.08	27.98	51.47	28.28	1.22	-4.45	6.92	0.13	8.23	3.0
<b>8d</b>	5.28	4.68	27.04	50.37	27.44	1.19	-7.45	11.86	-0.85	14.04	11.8
<b>8e</b>	2.85	5.12	32.68	53.92	33.09	1.43	-4.26	24.32	-0.26	24.70	12.0
<b>8f</b>	3.88	2.14	33.75	54.40	33.82	0.88	-11.3	17.82	-1.90	21.18	7.20
<b>8g</b>	5.30	7.76	25.34	44.53	26.48	1.14	-14.0	-0.59	-2.78	14.29	13.7
<b>8h</b>	6.10	6.38	21.10	40.81	22.04	.095	-10.2	3.18	-2.83	11.06	6.2
<b>8i</b>	2.60	7.10	20.19	42.90	25.22	1.09	-12.9	3.58	-5.98	8.06	13.5
<b>8j</b>	4.77	8.42	33.46	45.98	34.50	1.49	-18.7	9.66	-6.98	22.17	13.2
<b>8k</b>	2.08	1.36	37.67	60.54	37.70	1.63	-10.7	19.34	-2.84	22.31	8.5
<b>8l</b>	2.95	7.01	31.00	51.01	29.81	1.29	-12.1	12.44	-3.8	10.91	12.5

**Table 2.** Fastness properties of compounds **8a-l**

Dye	Washing, 75 °C	Rubbing		Sublimation		Acid perspiration	Light, 40 h
		Dry	Wet	180 °C	210 °C		
<b>8a</b>	4	3-4	3	3-4	3	4	4
<b>8b</b>	4	4	4	3-4	3	4	5
<b>8c</b>	4	4	4	4	3-4	4	4
<b>8d</b>	4	3	3	3-4	3	4	4-5
<b>8e</b>	4	3-4	3-4	4	3-4	4	5
<b>8f</b>	3-4	3	4	4	3-4	4	5
<b>8g</b>	4	4	3-4	3-4	3	3-4	4
<b>8h</b>	4	3-4	3	3-4	3	4	4
<b>8i</b>	4	4	3-4	4	3-4	4	4-5
<b>8j</b>	4	4	4	3-4	3	4	6-7
<b>8k</b>	4-5	4	4	3-4	3-4	4	6
<b>8l</b>	4	4	3	4	3	4	5

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 **4**,<sup>9</sup> and arylazoacetylacetone **7**<sup>12</sup> were conducted according to known procedures.

#### Synthesis of 5-amino-6-[[4-arylo-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine, **8a-l**: General procedure

A mixture of 5-amino-3,4-diphenylthieno[2,3-c]pyridazine-6-carbohydrazide **4** (1.1 g, 3 mmol) and the arylazoacetylacetone derivatives **7a-l** (3 mmol) was refluxed in glacial acetic acid (25 cm<sup>3</sup>) with stirring for 10 h. The reaction mixture was cooled to room temperature and poured into water (100 cm<sup>3</sup>). The separated solid was filtered off, washed with water, dried and recrystallized from dimethylformamide.

#### 5-Amino-6-[[4-phenylazo-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (**8a**, C<sub>30</sub>H<sub>23</sub>N<sub>7</sub>OS)

Yellow crystals in 69.4% yield. M.p.: 140-142 °C; IR:  $\nu$  = 3,400, 3,316 (NH<sub>2</sub>), 3,060 (CH<sub>arom</sub>), 2,925 (CH<sub>aliph</sub>), 1,676 (CO), 1,512 (N=N) cm<sup>-1</sup>; MS:  $m/z$  = 529 [M<sup>+</sup>, 5.35%], 424 [M - Ph-N=N, 5.3%], [M - substituted pyrazole, 50%].

#### 5-Amino-6-[[4-(2-methylphenylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (**8b**, C<sub>31</sub>H<sub>25</sub>N<sub>7</sub>OS)

Deep yellow crystals in 88.2% yield. M.p. 131-133 °C; IR:  $\nu$  = 3,450, 3,370 (NH<sub>2</sub>), 3,056 (CH<sub>arom</sub>), 2,924 (CH<sub>aliph</sub>), 1,678 (CO), 1,623 (C=N), 1,502 (N=N) cm<sup>-1</sup>. MS:  $m/z$  = 544 [M<sup>+</sup> +1, 12.8%], 424 [M - N=NC<sub>6</sub>H<sub>5</sub>Me, 9.2%], 330 [M - substituted pyrazole, 5.7%].

**5-Amino-6-[[4-(3-methylphenylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (8c, C<sub>31</sub>H<sub>25</sub>N<sub>7</sub>OS)**

Yellow crystals in 59.6% yield. M.p.: 132-134 °C; IR:  $\nu$  = 3,360(NH<sub>2</sub>), 3,059 (CH<sub>arom</sub>), 2,924 (CH<sub>aliph</sub>), 1,678 (CO), 1,620 (C=N), 1,590 (C=C), 1,502 (N=N), cm<sup>-1</sup>.

**5-Amino-6-[[4-(4-methylphenylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (8d, C<sub>31</sub>H<sub>25</sub>N<sub>7</sub>OS)**

Yellow crystals in 66.2% yield. M.p.: 150-152 °C; IR:  $\nu$  = 3,400, 3,320(NH<sub>2</sub>), 3,060 (CH<sub>arom</sub>), 2,925 (CH<sub>aliph</sub>), 1,671 (CO), 1,623 (C=N), 1,590 (C=C), 1,502 (N=N), cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.33 (s, 3H, *p*-CH<sub>3</sub>), 2.36 (s, 3H, 3-CH<sub>3</sub>), 2.77 (s, 3H, 7-CH<sub>3</sub>), 6.28 (s, 2H, NH<sub>2</sub>), 6.89-7.25 (m, 4H, Phenylazo), 7.46-7.78 (m, 10H, 2Ph).

**5-Amino-6-[[4-(2-methoxyphenylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (8e, C<sub>31</sub>H<sub>25</sub>N<sub>7</sub>O<sub>2</sub>S)**

Yellow crystals in 71% yield. M.p.: 165-167 °C; IR:  $\nu$  = 3,450, 3,400(NH<sub>2</sub>), 3,057 (CH<sub>arom</sub>), 2,923 (CH<sub>aliph</sub>), 2,852 (OCH<sub>3</sub>), 1,668 (CO), 1,628 (C=N), 1,598 (C=C), 1,500 (N=N), cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.23 (s, 3H, 3-CH<sub>3</sub>), 2.33 (s, 3H, *p*-CH<sub>3</sub>), 2.77 (s, 3H, 7-CH<sub>3</sub>), 3.83 (s, 3H, *o*-OCH<sub>3</sub>), 6.27(s, 2H, NH<sub>2</sub>), 6.88-7.24 (m, 4H, Phenylazo), 7.45-7.79 (m, 10H, 2Ph).

**5-Amino-6-[[4-(4-methoxyphenylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (8f, C<sub>31</sub>H<sub>25</sub>N<sub>7</sub>O<sub>2</sub>S)**

Yellow crystals in 71.5% yield. M.p.: 150-152 °C; IR:  $\nu$  = 3,372, 3,337(NH<sub>2</sub>), 3,060 (CH<sub>arom</sub>), 2,924(CH<sub>aliph</sub>), 2,854 (OCH<sub>3</sub>), 1,670 (CO), 1,630 (C=N), 1,597 (C=C), 1,505 (N=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.22 (s, 3H, 3-CH<sub>3</sub>), 2.32 (s, 3H, *p*-CH<sub>3</sub>), 2.78 (s, 3H, 7-CH<sub>3</sub>), 3.84 (s, 3H, *p*-OCH<sub>3</sub>), 6.26(s, 2H, NH<sub>2</sub>), 6.89-7.23 (m, 4H, Phenylazo), 7.44-7.78 (m, 10H, 2Ph).

**5-Amino-6-[[4-(2-chlorophenylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (8g, C<sub>30</sub>H<sub>22</sub>ClN<sub>7</sub>OS)**

Red crystals in 89.7% yield. M.p.: 130-132 °C; IR:  $\nu$  = 3,420, 3,350 (NH<sub>2</sub>), 3,090 (CH<sub>arom</sub>), 2,925(CH<sub>aliph</sub>), 1,685 (CO), 1,637 (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>):  $\delta$  = 2.34 (s, 3H, 3-CH<sub>3</sub>), 2.77 (s, 3H, 7-CH<sub>3</sub>), 6.27(s, 2H, NH<sub>2</sub>), 7.27-7.49 (m, 4H, Phenylazo), 7.41-7.79 (m, 10H, 2Ph).

**5-Amino-6-[[4-(3-chlorophenylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (8h, C<sub>30</sub>H<sub>22</sub>ClN<sub>7</sub>OS)**

Red crystals in 76.9% yield. M.p.: 150-152 °C; IR:  $\nu$  = 3,385, 3,305(NH<sub>2</sub>), 3,059(CH<sub>arom</sub>), 2,921(CH<sub>aliph</sub>), 1,670

(CO), 1,634 (C=N), 1,591 (C=C), 1,507 (N=N), cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.35 (s, 3H, 3-CH<sub>3</sub>), 2.76 (s, 3H, 7-CH<sub>3</sub>), 6.26(s, 2H, NH<sub>2</sub>), 7.28-7.48 (m, 4H, Phenylazo), 7.42-7.78 (m, 10H, 2Ph). MS: *m/z* = 564 [M<sup>+</sup>, 4.2%], 463 [M - 1, 6.3%], 424 [M - N=NC<sub>6</sub>H<sub>5</sub>Cl, 2.2%], 330 [M - substituted pyrazole, 9%].

**5-Amino-6-[[4-(3-nitrophenylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (8i, C<sub>30</sub>H<sub>22</sub>N<sub>8</sub>O<sub>3</sub>S)**

Redich-brown crystals in 59.3% yield. M.p.: 159-161 °C; IR:  $\nu$  = 3,439, 3,360(NH<sub>2</sub>), 3,052(CH<sub>arom</sub>), 2,922CH<sub>aliph</sub>), 1,673(CO), 1,639 (C=N), 1,590 (C=C), 1,515, 1,333 (NO<sub>2</sub>), 1,500 (N=N), cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.34 (s, 3H, 3-CH<sub>3</sub>), 2.77 (s, 3H, 7-CH<sub>3</sub>), 6.27(s, 2H, NH<sub>2</sub>), 7.17-7.99 (m, 4H, Phenylazo), 7.41-7.79 (m, 10H, 2Ph). MS: *m/z* = 575 [M + 1, 0.09%], 424 [M - N=NC<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, 30.2%].

**5-Amino-6-[[4-(4-nitrophenylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (8j, C<sub>30</sub>H<sub>22</sub>N<sub>8</sub>O<sub>3</sub>S)**

Redich-brown crystals in 50.3% yield. M.p.: 156-157 °C; IR:  $\nu$  = 3,430, 3,364(NH<sub>2</sub>), 3,050(CH<sub>arom</sub>), 2,925CH<sub>aliph</sub>), 1,670 (CO), 1,634 (C=N), 1,591 (C=C), 1,516, 1,335 (NO<sub>2</sub>), 1,507 (N=N), cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.34 (s, 3H, 3-CH<sub>3</sub>), 2.77 (s, 3H, 7-CH<sub>3</sub>), 6.27(s, 2H, NH<sub>2</sub>), 7.18, 8.10 (d,2H; d,2H Phenylazo), 7.41-7.79 (m, 10H, 2Ph). MS: *m/z* = 575 [M + 1, 0.02%], 424 [M - N=NC<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, 33.2%].

**5-Amino-6-[[4-(2-naphthylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (8k, C<sub>34</sub>H<sub>25</sub>N<sub>7</sub>OS)**

Brown crystals in 81.2% yield. M.p.: 118-120 °C; IR:  $\nu$  = 3,425, 3,364(NH<sub>2</sub>), 3,058(CH<sub>arom</sub>), 2,924CH<sub>aliph</sub>), 1,673 (CO), 1,624 (C=N), 1,592 (C=C), 1,506(N=N), cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.35 (s, 3H, 3-CH<sub>3</sub>), 2.76 (s, 3H, 7-CH<sub>3</sub>), 6.26(s, 2H, NH<sub>2</sub>), 7.41-8.01 (m, 17H, naphthyl and 2Ph); MS: *m/z* = 580 [M + 1, 1%], 424 [M - N=NC<sub>10</sub>H<sub>7</sub>, 1%] and 330[M - substituted pyrazole, 10%].

**5-Amino-6-[[4-(3-pyridylazo)-3,5-dimethylpyrazol-1-yl]carbonyl]-3,4-diphenylthieno[2,3-c]pyridazine (8l, C<sub>29</sub>H<sub>22</sub>N<sub>8</sub>OS)**

Brown crystals in 47.6% yield. M.p.: 237-239°C; IR:  $\nu$  = 3,390, 3,3308(NH<sub>2</sub>), 3,058(CH<sub>arom</sub>), 2,921CH<sub>aliph</sub>), 1,677 (CO), 1,600 (C=N), 1,562 (C=C), 1,504 (N=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>), 2.77 (s, 3H, 7-CH<sub>3</sub>), 6.27(s, 2H, NH<sub>2</sub>), 7.34-8.45 (m, 14H, pyridyl and 2Ph); MS: *m/z* = 532 [M + 3.04, 1%], 424 [M - N=NC<sub>5</sub>H<sub>4</sub>N, 4.03%] and 330[M - substituted pyrazole, 10.8%].



## 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 Bayer)*

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 1 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.

## Conclusions

A set of 12 disperse dyes **8a-l** were synthesized by reaction of 5-amino-3,4-diphenylthieno[2,3-c]pyridazine-6-carbohydrazide **4** with arylazoacetylacetone derivatives. Most of them were investigated for their dyeing characteristics on polyester. They give bright intense hues from yellow to orange-yellow on polyester fabrics, due to the variations in polarity. The dyed fabrics exhibit good (4) washing, perspiration, rubbing and good to excellent (4-5) 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.

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