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PYRIDAZINE DERIVATIVES AND RELATED COMPOUNDS. 23*. SYNTHESIS OF 3-SUBSTITUTED PYRAZOLO[3,4-*c*]PYRIDAZINES AND THEIR APPLICATION AS DISPERSE DYES

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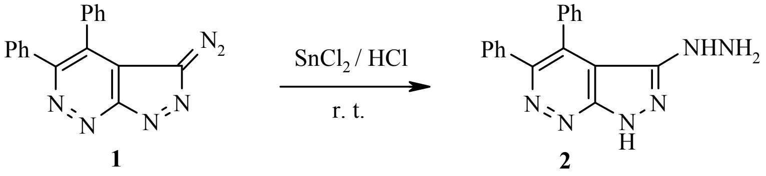
Acetylacetone and malononitrile were coupled with diazotized arylamines to give arylazoacetylacetones and arylazomalononitriles. When refluxed with 3-hydrazino-4,5-diphenyl-1H-pyrazolo-[3,4-c]pyridazine in the presence of ethanol/HCl, they yielded the corresponding 3-[4-(arylazo)-3,5-dimethylpyrazol-1-yl]- and 3-[3,5-diamino-4-(arylazo)pyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazine dyes. The dyes were applied to polyester and polyamide fabrics, and their spectral and fastness properties were measured.

Keywords: 3-hydrazino-1H-pyrazolo[3,4-*c*]pyridazine, monoazo dyes, color fastness.

Derivatives of the pyrazolopyridazine ring systems are known to possess potent biological and pharmacological properties [2-4]. On the other hand, some pyrazole derivatives are very important compounds due to their biological and pharmacological activities [5]. They are also used as a key starting material for the synthesis of commercial aryl/hetarylazopyrazole dyes [6]. All these properties aroused our interest in the synthesis of new heterocyclic compounds, including the pyrazolo[3,4-*c*]pyridazine moiety, which is a continuation of our previous work [7-12]. The present investigation deals with the synthesis of some 3-[4-(arylazo)-3,5-dimethylpyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazine and 3-[3,5-diamino-4-(arylazo)-pyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazine dyes from 3-hydrazino-4,5-diphenyl-1H-pyrazolo-[3,4-*c*]pyridazine and evaluation of their properties on polyester and polyamide fabrics.



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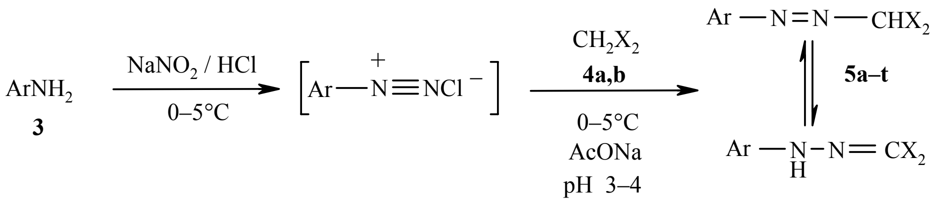
3-Hydrazino-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazine **2** [13] was prepared in 96% yield as yellow crystals (mp 168°C) by reduction of 3-diazo-4,5-diphenylpyrazolo[3,4-*c*]pyridazine **1** with stannous chloride/HCl at room temperature.



4 a X = COMe, **b** X = CN; **5 a,k** Ar = Ph, **b,l** Ar =2-MeOC_6H_4, **c,m** Ar = 4-MeOC_6H_4, **d,n** Ar = 2-ClC_6H_4, **e,o** Ar = 3-ClC_6H_4, **f,p** Ar = 2-MeC_6H_4, **g,q** Ar = 3-MeC_6H_4, **h,r** Ar = 4-MeC_6H_4, **i,s** Ar = 4-$O_2N$$C_6H_4$, **j,t** Ar = 2-naphthyl; **a-j** X = COMe, **k-t** X = CN

TABLE 1. Characteristics of Arylazoacetylacetone and Arylazomalononitrile Derivatives **5a-t**

Compound	Empirical formula	Found, % / Calculated, %			mp*, °C	Yield, %
		C	H	N		
5a	$C_{11}H_{12}N_2O_2$	64.50 64.69	5.80 5.92	13.80 13.72	88–89	85
5b	$C_{12}H_{14}N_2O_3$	61.50 61.53	5.90 6.02	12.10 11.96	117-119	90
5c	$C_{12}H_{14}N_2O_3$	61.50 61.53	6.10 6.02	11.90 11.96	99-100	91
5d	$C_{11}H_{11}ClN_2O_2$	55.20 55.36	4.60 4.65	11.60 11.74	117-118	89
5e	$C_{11}H_{11}ClN_2O_2$	55.30 55.36	4.70 4.65	11.70 11.74	92-94	90
5f	$C_{12}H_{14}N_2O_2$	65.90 66.04	6.40 6.47	12.70 12.84	118-119	87
5g	$C_{12}H_{14}N_2O_2$	66.10 66.04	6.40 6.47	12.80 12.84	80-81	88
5h	$C_{12}H_{14}N_2O_2$	66.10 66.04	6.60 6.47	12.60 12.84	94-96	88
5i	$C_{11}H_{11}N_3O_4$	53.10 53.01	4.40 4.45	16.70 16.86	208-209	92
5j	$C_{15}H_{14}N_2O_2$	70.70 70.85	5.40 5.55	11.10 11.02	223-25	86
5k	$C_9H_6N_4$	63.40 63.52	3.40 3.55	33.00 32.92	144-145	78
5l	$C_{10}H_8N_4O$	60.10 60.00	4.00 4.03	28.10 27.99	112-114	81
5m	$C_{10}H_8N_4O$	59.90 60.00	4.10 4.03	28.00 27.99	142-143	82
5n	$C_9H_5ClN_4$	52.70 52.83	2.40 2.46	27.50 27.38	100-102	84
5o	$C_9H_5ClN_4$	52.90 52.83	2.50 2.46	27.40 27.38	169-171	85
5p	$C_{10}H_8N_4$	65.10 65.21	4.40 4.38	30.30 30.42	99-100	80
5q	$C_{10}H_8N_4$	65.20 65.21	4.30 4.38	30.50 30.42	151-153	79
5r	$C_{10}H_8N_4$	65.30 65.21	4.50 4.38	30.40 30.42	171-172	80
5s	$C_9H_5N_5O_2$	50.10 50.24	2.30 2.34	32.60 32.55	224-226	85
5t	$C_{13}H_8N_4$	80.00 70.90	3.60 3.66	25.30 25.44	188-189	83

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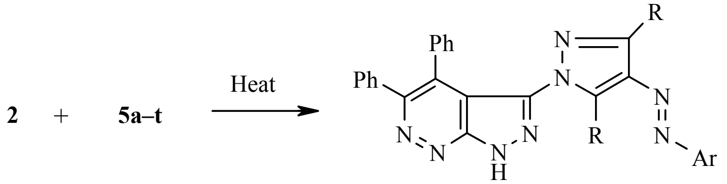
* Recrystallization solvent: chloroform.

Diazotized arylamines **3** were coupled with active methylene compounds such as acetylacetone **4a** and malononitrile **4b** in sodium acetate buffered solution to give azobenzeneacetylacetone and azobenzenemalononitrile derivatives **5a-j** and **5k-t** in good yield, respectively. Spectral data [14] for such compounds indicate them to have a hydrazone configuration [15]. The characteristics of compounds **5a-t** are shown in Table 1.



6a–t

6 a,k Ar = Ph, **b,l** Ar =2-MeOC$_6$H$_4$, **c,m** Ar = 4-MeOC$_6$H$_4$, **d,n** Ar = 2-ClC$_6$H$_4$, **e,o** Ar = 3-ClC$_6$H$_4$, **f,p** Ar = 2-MeC$_6$H$_4$, **g,q** Ar = 3-MeC$_6$H$_4$, **h,r** Ar = 4-MeC$_6$H$_4$, **i,s** Ar = 4-O$_2$NC$_6$H$_4$, **j,t** Ar = 2-naphthyl; **a-j** R = Me, **k–t** R = NH$_2$

TABLE 2. Characteristics of Compounds **6a-t**

Dye	Empirical formula	Found, % / Calculated, %			mp*, °C	Yield, %
		C	H	N		
6a	$C_{28}H_{22}N_8$	71.30 71.47	4.80 4.71	23.70 23.81	>300	85
6b	$C_{29}H_{24}N_8O$	69.60 69.59	4.80 4.83	22.30 22.39	211-212	94
6c	$C_{29}H_{24}N_8O$	69.70 69.59	4.70 4.83	22.40 22.39	219-221	93
6d	$C_{28}H_{21}ClN_8$	66.70 66.60	4.10 4.19	22.10 22.19	174-175	78
6e	$C_{28}H_{21}ClN_8$	66.40 66.60	4.20 4.19	22.30 22.19	291-293	95
6f	$C_{29}H_{24}N_8$	71.90 71.88	5.10 4.99	23.00 23.12	299-300	90
6g	$C_{29}H_{24}N_8$	71.80 71.88	4.90 4.99	23.20 23.12	212-213	75
6h	$C_{29}H_{24}N_8$	71.70 71.88	5.20 4.99	23.10 23.12	>300	94
6i	$C_{28}H_{21}N_9O_2$	65.20 65.23	4.00 4.11	24.50 24.45	>300	95
6j	$C_{32}H_{24}N_8$	73.70 73.83	4.60 4.65	21.60 21.52	193-195	77
6k	$C_{26}H_{20}N_{10}$	66.00 66.09	4.20 4.27	29.90 29.64	260-262	72
6l	$C_{27}H_{22}N_{10}O$	64.40 64.53	4.30 4.41	27.90 27.87	>300	80
6m	$C_{27}H_{22}N_{10}O$	64.50 64.53	4.50 4.41	27.70 27.87	149-151	92
6n	$C_{26}H_{19}ClN_{10}$	61.50 61.60	3.90 3.78	27.60 27.63	245-246	80
6o	$C_{27}H_{22}ClN_{10}$	61.50 61.60	3.70 3.78	27.70 27.63	240-242	93
6p	$C_{27}H_{22}N_{10}$	66.50 66.65	4.50 4.56	28.90 28.79	150–151	75
6q	$C_{27}H_{22}N_{10}$	66.60 66.65	4.60 4.56	28.60 28.79	>300	75
6r	$C_{27}H_{22}N_{10}$	66.60 66.65	4.70 4.56	28.70 28.79	179-181	76
6s	$C_{26}H_{19}N_{11}O_2$	60.30 60.34	3.60 3.70	29.80 29.77	214-215	83
6t	$C_{30}H_{22}N_{10}$	68.90 68.95	4.10 4.24	26.90 26.80	165-167	72

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* Recrystallization solvent: DMF.

TABLE 3. Spectral Characteristics of Compounds **6a-t**

Compound	IR (KBr), ν, cm^{-1}	^{1}H NMR, δ, ppm*	MS, *m/e* M$^+$
6a	3155, 3061, 2970	2.18 (3H, s, CH$_3$); 2.27 (3H, s, CH$_3$); 6.99-7.76 (15H, m, H Ar), 15.19 (1H, br. s, NH)	470.2
6b	3162, 3066, 2972, 2856		500.24
6c	3171, 3070, 2973, 2850		500.2
6d	3182, 3071, 2960		504.2
6e	3216, 3066, 2970	2.18 (3H, s, CH$_3$); 2.28 (3H, s, CH$_3$); 7.0-7.7 (14H, m, H Ar); 15.2 (1H, br. s, NH)	504.1
6f	3200, 3060, 2970		484.21
6g	3184, 3060, 2960		484.23
6h	3190, 3065, 2965		484.2
6i	3212, 3081, 2974, 1525, 1342		515.15
6j	3156, 3063, 2972		520.2
6k	3400, 3300, 3160, 3060	5.4 (4H, br. s, 2NH$_2$); 6.98-7.5 (15H, m, H Ar); 13.22 (1H, br. s, NH)	470.2
6l	3425, 3380, 3182, 3061, 2857		502.3
6m	3365, 3334, 3158, 3060, 2854	3.78 (3H, s, CH$_3$); 5.5 (4H, br. s, 2NH$_2$); 6.94-7.67 (14H, m, H Ar); 14.9 (1H, br. s, NH)	502.2
6n	3350, 3304, 3182, 3060		506.24
6o	3361, 3310, 3180, 3062		506.17
6p	3380, 3328, 3170, 3062, 2987		486.5
6q	3372, 3324, 3181, 3060, 2987		486.9
6r	3385, 3325, 3162, 3062, 2986		486.7
6s	3476, 3360, 3190, 1524, 1340		517.2
6t	3394, 3324, 3150, 3058		522.3

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* The ^{1}H NMR spectra were obtained in DMSO-d$_6$ (compounds **6a,e,m**) and CDCl$_3$ (compound **6k**).

Compound **2** when reacted with azobenzeneacetylacetone derivatives **5a-j** in ethanol/HCl yields 3-[4-(arylazo)-3,5-dimethylpyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazine dyes **6a-j**. The reaction proceeds in two stages, *viz*. the initially formed hydroxypyrazoline subsequently loses water by an acid-catalyzed reaction [16, 17]. Compound **2**, when reacted with azobenzenemalononitrile derivatives **5k-t** in a similar manner, gives 3-[3,5-diamino-4-(arylazo)pyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazines **6k-t**. The characteristics and spectral data of compounds **6a-t** are shown in Tables 2 and 3.

The absorption maxima of dyes **6a-t** were recorded in DMF and are shown in Table 4. The absorption maxima of dyes **6a-j** varied from 343 to 372 nm, and those of dyes **6k-t** from 352 to 400 nm. It was observed in general that dyes **6k-t** derived from azobenzenemalononitrile derivatives **5k-t** were bathochromic when compared with analogous dyes **6aj** derived from azobenzeneacetylacetone derivatives **5a-j**. This bathochromic shift is attributed to the stronger electron release of the amino group with respect to the methyl group in positions 3 and 5 of the pyrazole ring, thus enhancing electron delocalization in the dye molecule [18].

Dyeing of polyamide and polyester fabrics and dyeing properties [19]. 3-[4-(Arylazo)-3,5-dimethylpyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazines **6a-j** and 3-[3,5-diamino-4-(arylazo)pyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazines **6k-t** were synthesized to assess their dyeing properties on polyamide and 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.

TABLE 4. Absorption Spectra and Dyeing Properties of 3-[4-(Arylazo)-3,5-disubstituted pyrazol-1-yl]-4,5-diphenyl-1H–pyrazolo[3,4-*c*]pyridazine Derivatives **6a–t***

Com-pound	Absorption λ_{max} in DMF	Log ε	Washing fastness						Rubbing fastness				Perspiration fastness					
			Polyamide			Polyester			Polyamide		Polyester		Polyamide			Polyester		
			Alt.	S.W.	S.C.	Alt.	S.W.	S.C.	Dry	Wet	Dry	Wet	Alt.	S.W.	S.C.	Alt.	S.W.	S.C.
6a	343	4.60	4–5	4	4	4–5	4–5	4	4	4	4	4	4	4	4	4	3–4	4
6b	338	4.41	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4	4	4–5	4	4–5	4–5	4	4
6c	355	4.01	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4	4	4–5	4	4–5	4–5	4	4–5
6d			4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4	4	4–5	4	4–5	4–5	4	4
6e	345	4.65	4–5	4–5	4–5	4–5	4	4–5	4–5	4	4	4	4–5	4	4	4–5	4	4
6f			4–5	4–5	4–5	4–5	4	4	4	4	4	3–4	4–5	4	4	4–5	4	4
6g	345	4.34	4–5	4	4	4	4	4	4	3–4	4	3–4	4	3–4	3–4	4	3–4	4
6h	344	4.41	4–5	4	4–5	4–5	4	4	4	4	4	3–4	4–5	4	4	4	3–4	4
6i	372	4.53	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5	4–5	4–5	4–5	4	4–5
6j	358	4.27	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5	4–5	4–5	4–5	4	4
6k	362	4.36	4–5	4–5	4–5	4–5	4–5	4	4	4	4	4	4–5	4	4–5	4–5	4	4
6l			4–5	4–5	4–5	4–5	4–5	4–5	4	4	4	4	4–5	4–5	4–5	4–5	4	4
6m	372	4.65	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5	4	4–5	3–4	4	4–5	4	4
6n	362	4.95	4–5	4–5	4–5	4–5	4	4–5	4–5	4	4	4	4–5	4	4	4–5	4	4
6o	362	4.53	4–5	4–5	4–5	4–5	4	4–5	4–5	4	4	4	4–5	4	4	4–5	4	4
6p	362	4.37	4–5	4–5	4–5	4–5	4–5	4	4–5	4	4	4	4–5	4	4	4–5	4	4
6q			4–5	4–5	4	4	4–5	4	4	3–4	4	3–4	4–5	3–4	4	4	3–4	4
6r			4–5	4–5	4–5	4–5	4–5	4	4–5	4	4	4	4–5	4	4	4–5	4	4
6s	400	4.35	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5	4	4–5	4–5	4–5	4–5	4	4–5
6t	350	4.77	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5	4	4–5	4	4	4–5	4	4

TABLE 4 (continued)

Compound	Sublimation fastness															Light (40 h)	
	Polyamide						Polyester										
	160°C			180°C			160°C			180°C			210°C			Poly-amide	Poly-ester
	Alt.	S.C.	S.N.	Alt.	S.C.	S.N.	Alt.	S.C.	S.P.	Alt.	S.C.	S.P.	Alt.	S.C.	S.P.		
6a	4	4	4	4	4	4	4	4	4	4	4	4	3–4	3	3–4	4	4
6b	4–5	4–5	4–5	4–5	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4	4	5–6	5–6
6c	4–5	4–5	4–5	4–5	4	4–5	4–5	4–5	4–5	4–5	4	4–5	4	4	4	5–6	5–6
6d	4–5	4	4–5	4	3–4	4	4–5	4–5	4–5	4–5	4	4–5	4	4	4	5	5
6e	4–5	4	4–5	4	3–4	4	4–5	4–5	4–5	4–5	4	4–5	4	4	4	5	5
6f	4	4	4	4	3–4	4	4	4	4	4	3–4	4	3–4	3–4	4	4–5	4–5
6g	4	4	4	4	3–4	4	4	4	4	4	4	4	3–4	3–4	4	4–5	5
6h	4	4	4	4	3–4	4	4	4	4	4	3–4	4	3–4	3–4	4	4–5	5
6i	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5	4	4	4	6–7	6–7
6j	4–5	4	4–5	4–5	4	4	4–5	4–5	4–5	4–5	4	4	4	3–4	4	6	6
6k	4–5	4	4–5	4–5	3–4	4	4–5	4	4–5	4–5	4	4–5	4	3–4	3–4	4–5	5
6l	4–5	4	4–5	4–5	3–4	4	4–5	4	4–5	4–5	4	4–5	4	3	4	6–7	6
6m	4–5	4	4–5	4–5	4	4	4–5	4	4–5	4–5	4	4–5	4	3–4	4	6–7	6
6n	4–5	4–5	4–5	4–5	4	4–5	4–5	4	4	4–5	4	4	4	3–4	3–4	6	5–6
6o	4–5	4–5	4–5	4–5	4	4–5	4–5	4	4	4–5	4	4	4	3–4	3–4	6	5–6
6p	4–5	4	4–5	4	3–4	4	4–5	4	4–5	4–5	4	4	4	3–4	4	5–6	5–6
6q	4–5	4	4–5	4	3–4	4	4–5	4	4–5	4	3–4	4	4	3–4	4	5	5–6
6r	4–5	4	4–5	4	3–4	4	4–5	4	4–5	4–5	4	4	4	3–4	4	5–6	5–6
6s	4–5	4–5	4–5	4–5	4	4	4	4–5	4–5	4–5	4	4–5	4	4	4	7	7
6t	4–5	4–5	4–5	4–5	4	4	4–5	4–5	4–5	4–5	4	4	4	3–4	3–4	6	5–6

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* Alt. – alteration, S.C. – staining on cotton, S.N. – staining on polyamide, S.P. – staining on polyester, S.W. – staining on wool.

Versatility is the first technical property of the present dyes to be emphasized. Satisfactory color yields, as 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 an excellent coloration uniformity of polyamide and polyester without the use of a retarding agent. Relevant fastness data for the dyes are given in Table 4, which reveals the following:

a) Excellent behavior is shown in fastness to washing at 50°C and to perspiration on dyed polyamide and polyester fabrics.

b) Most of the dyes have a good to excellent rubbing fastness (4–5) (dry and wet); only a few of these dyes have a good to moderate rubbing fastness (wet) and this may be attributed to inadequate diffusion of the dye molecules into the fabrics.

c) Most of the dyes show a good sublimation fastness.

d) The light fastness of 3-[4-(arylazo)-3,5-dimethylpyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazines **6a-j** and 3-[3,5-diamino-4-(arylazo)pyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazines **6k-t** on polyamide and polyester is significantly affected by the nature of the substituent in the arylazo component. In this study the inclusion of the electron-withdrawing nitro group improves the light fastness. In most cases, the best light fastness was obtained by dyes containing a nitro group in the arylazo component (e.g., dyes **6i** and **6s**).

The intensity of color for the dyes applied on polyamide and polyester fabrics expressed as K/S values is given in Table 5. The following generalizations can be drawn.

The intensity of color for all dyes, expressed as K/S values, applied on nylon is greater than on polyester fabrics.

a) The K/S values of dyes **6k-t** derived from azobenzenemalononitrile derivatives **5k-t** are greater than those of dyes **6a-j** derived from azobenzeneacetylacetone derivatives **5a-j**. This bathochromic shift is attributed to the stronger electron release of the amino group with respect to the methyl group in positions 3 and 5 of the pyrazole ring, thus enhancing electron delocalization in the dye molecule and consequently increases the vibration energy of the dye molecule, which in turn increases the color strength (K/S) values of the dyed fabrics and directs the color towards reddish and yellowish directions on the red-green and yellow-blue axis, respectively.

The color of the dyed fabric was assessed by tristimulus colorimetry. The results are listed in Table 6.

TABLE 5. K/S* Value of Dyes **6a-t** on Polyamide and Polyester Fabrics at λ_{max} 420 nm

Dye	K/S		Dye	K/S	
	Polyamide	Polyester		Polyamide	Polyester
6a	19.0	7.0	**6k**	20.0	6.1
6b	17.5	5.0	**6l**	17.3	5.0
6c	18.0	7.2	**6m**	19.2	4.8
6d	18.5	9.5	**6n**	20.0	12.5
6e	18.0	11.2	**6o**	20.5	5.0
6f	18.0	3.4	**6p**	19.0	8.0
6g	18.2	11.0	**6q**	21.5	5.2
6h	16.0	5.3	**6r**	18.5	7.5
6i	17.5	5.0	**6s**	19.9	3.0
6j	19.5	12.8	**6t**	15.0	2.2

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* K/S – color strength.

TABLE 6. Color Coordinates of Dyes **6a-t** on Polyamide Fabrics at Sunlight Wavelength (D65/10), Tungsten Wavelength (A/10), and Fluorescent Wavelength (F11/10)

Dye	D65/10					A/10					F11/10				
	L*	a*	b*	C*	H	L*	a*	b*	C*	H	L*	a*	b*	C*	H
6a	72.25	5.64	41.98	42.36	82.35	75.09	11.74	43.93	45.47	75.04	74.30	5.36	46.94	47.24	83.48
6b	78.97	1.38	38.95	38.97	87.97	81.26	8.39	39.54	40.42	78.01	80.63	8.39	43.62	43.69	86.97
6c	76.85	4.62	39.88	40.15	83.39	79.53	11.12	41.39	42.86	74.96	78.68	5.17	44.61	44.91	83.39
6d	74.82	4.12	36.31	36.54	83.53	77.29	10.26	37.74	39.11	74.80	76.49	4.27	40.63	40.85	84.00
6e	78.27	6.71	52.99	53.41	82.78	81.63	13.39	55.02	56.63	76.32	80.77	6.11	59.14	59.45	84.10
6f	82.30	1.55	38.40	38.43	87.69	84.60	8.37	39.14	40.03	77.93	83.94	2.59	42.82	42.90	86.53
6g	76.81	7.10	54.49	54.95	82.57	80.26	13.47	56.66	58.24	76.63	79.59	5.45	61.13	61.38	84.90
6h	79.06	6.89	42.49	43.05	80.78	82.11	11.74	45.54	47.03	75.55	81.80	4.19	48.07	48.25	85.02
6i	68.73	8.08	51.58	52.21	81.09	72.12	13.72	54.17	55.88	75.79	71.23	5.75	57.43	57.72	84.28
6j	75.42	1.84	57.01	57.04	88.15	78.32	10.70	55.90	56.91	79.16	77.30	3.69	65.09	65.19	86.76
6k	72.13	5.93	50.15	50.50	83.26	75.26	13.48	50.68	52.45	75.11	74.25	6.37	57.77	58.12	83.71
6l	75.11	3.76	52.77	52.90	85.92	78.10	11.57	53.07	54.31	77.70	77.24	4.45	59.76	59.93	85.75
6m	67.64	12.55	56.79	58.16	77.54	71.62	19.09	59.04	62.05	72.08	70.10	12.57	64.16	65.38	87.92
6n	67.57	7.23	58.07	58.52	82.91	70.99	15.95	58.25	60.40	74.69	69.68	8.86	65.39	65.99	82.29
6o	67.41	8.47	51.59	52.29	80.68	70.80	16.45	52.39	54.91	72.57	69.48	9.71	59.24	60.03	80.69
6p	72.22	5.06	53.25	53.49	84.57	75.33	13.33	53.41	55.05	75.99	74.29	6.29	60.05	60.98	84.08
6q	68.44	9.39	46.46	47.40	78.57	71.80	16.93	46.46	50.68	70.49	70.51	10.28	54.05	55.02	79.23
6r	71.90	9.07	49.87	50.68	79.69	75.36	15.88	51.56	53.95	72.88	74.19	9.10	57.02	57.74	80.93
6s	57.75	37.63	66.67	76.56	60.56	64.65	37.58	77.81	86.41	64.22	61.49	33.65	72.91	80.30	65.23
6t	78.47	7.16	38.35	39.01	79.43	81.38	11.73	41.13	42.77	74.08	80.94	4.77	43.35	43.61	83.72

It was observed that

a) the color hues of dyes **6a-t** on dyed polyamide and polyester fabrics are shifted towards the reddish and yellowish directions on the red-green and yellow-blue axes, respectively;

b) dyes 3-[4-(arylazo)-3,5-dimethylpyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazines **6a-j** are lighter than the corresponding 3-[3,5-diamino-4-(arylazo)pyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazines **6k-t** according to the color lightness values (L*);

c) 3-[3,5-diamino-4-(arylazo)pyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazines **6k-t** are brighter than the corresponding 3-[4-(arylazo)-3,5-dimethylpyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazines **6a-j** according to the color brightness values (C*).

We have come to the following conclusions. A set of 20 disperse dyes **6a-t** was synthesized by the reaction of 3-hydrazino-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazine **2** with arylazoacetylacetone and arylazo-malononitrile derivatives. All of them were investigated for their dyeing characteristics on polyamide and polyester. The electronic absorption spectra cover a λ_{max} range of 343-400 nm at uniformly high absorption intensity and give bright intense hues from yellow to orange-yellow on polyamide and polyester fabrics due to the variations in polarity. The changes in color coordinates between dyes **6a-t** (Table 6) are remarkable in view of minor variations of the absorption maxima in solution. The dyed fabrics exhibit a very good to excellent (4-5) washing, perspiration, rubbing, and sublimation fastness properties (Table 4). The remarkable degree of levelness and brightness after washings is indicative of a good penetration and excellent affinity of these dyes for the fabric due to the accumulation of polar groups. In combination with the ease of preparation, this makes them particularly valuable.

EXPERIMENTAL

All melting points are uncorrected and are in °C. IR spectra were recorded on a Bruker Vector 22 Germany spectrometer (KBr). The ^{1}H NMR spectra were obtained on a Varian Gemini 200 MHz spectrometer using TMS as an internal standard. Electron impact mass spectra were obtained at 70 eV using a GCMS-qp1000 EX Shimadzu spectrometer. Electronic spectra were recorded on UV-Visible Recording Shimadzu spectrophotometer from the dye solution in DMF at a concentration of $1 \cdot 10^{-5}$ mol/l.

Azobenzeneacetylacetone derivatives 5a-j (General Method). The appropriate arylamine **3** (0.01 mol) was dissolved in aqueous hydrochloric acid (8 ml, 1:1) and cooled to 0-5°C, prior to the addition of a cold solution of sodium nitrite (0.7 g in 3 ml water), while maintaining the temperature at 0-5°C. A diazonium salt solution was then added dropwise to a cooled and stirred mixture of acetylacetone **4a** (1.0 g, 0.01 mol) and sodium acetate (2.0 g, dissolved in 10 ml of 50% aqueous ethanol). Stirring was continued for 1.5 h and the resulting crystals collected, washed with water, and recrystallized from chloroform.

Azobenzenemalononitrile derivatives 5k-t (General Method). The above procedure was repeated, except that acetylacetone **4a** was replaced by malononitrile **4b**.

3-[4-(Arylazo)-3,5-dimethylpyrazol-1-yl]-4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazines 6a-j (General Method). A mixture of 3-hydrazino-4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazine **2** (0.6 g, 2 mmol) and arylazoacetylacetone **5a-j** (2 mmol) was refluxed in ethanol (50 ml) with a few drops of hydrochloric acid for 10 h. The reaction mixture was cooled to room temperature and the separated solid was filtered off, washed with water, dried, and recrystallized from DMF.

3-[3,5-Diamino-4-(arylazo)pyrazol-1-yl]-4,5diphenyl-1H-pyrazolo[3,4-c]pyridazines 6k-t. The above procedure was repeated, except that arylazoacetylacetone was replaced by arylazomalononitrile **5k-t**.

Dyeing and fastness determinations.

Dyeing procedure. The fabric was dyed with 2.0% dye (calculated by weight of the fabric) and 1 g/l Viscavine as a dispersing agent, kept at a liquor ratio of 30:1. The process was started at 40°C (for polyamide fabric) and 60°C (for polyester fabric) raised at a rate of 2°C/min to 98°C (for polyamide fabric) and 130°C (for polyester fabric) and maintained there for 60 min. After cooling, the fabric was taken out and washed in a solution containing 5 g/l detergent at 60°C for 15 min. Finally, the washed fabric samples were rinsed with water and dried at ambient conditions.

Color fastness tests. The results are collected in Table 5.

(i) Fastness to washing.

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

(ii) Fastness to perspiration.

The samples were prepared by stitching a piece of dyed fabric between two pieces of undyed wool and cotton fabric, all of equal length, and then immersed into the acid solution for 30 min. The change in color of the dyed fabric and staining on the undyed adjacent fabric were assessed according to the following grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent. The acid solution (pH 3.5) contained sodium chloride (10 g/l^{-1}), lactic acid (1 g/l^{-1}), disodium orthophosphate (1 g/l^{-1}), and histidine monohydrochloride (0.25 g/l^{-1}).

(iii) Fastness to rubbing.

The dyed fabric was placed on the base of the Crockmeter, so that it rested flat on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was 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 procedure. For the wet rubbing test, the testing squares were thoroughly immersed into distilled water. The rest of the procedure was the same as in the dry test. The staining on the white testing cloth was assessed according to the grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent.

(iv) Fastness to sublimation.

Sublimation fastness was measured with an iron tester (Yasuda No. 138). The samples were prepared by stitching a piece of dyed fabric between two pieces of undyed fabric, one of which was cotton and the other similar to the fabric under test, all of equal length, and then treated at 160 and 180°C in case of testing polyamide and 160, 180, and 210°C in case of testing polyester each for 1 min. Any staining on the undyed adjacent fabric or change in color of the dyed fabric was assessed according to the following grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent.

(v) Fastness to light.

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

Color assessment. Table 6 reports the color parameters of the dyed fabric assessed by tristimulus colorimetry. The color parameters of the dyed fabric were determined on a spectral multichannel photodetector (model MCPD-110A), equipped with D65, tungsten, and fluorescent sources. The color of the dyed fabric was assessed in terms of tristimulus colorimetry. The values of the chromaticity coordinates and luminance factor and the positions of colors in the CIELAB color solid are reported.

REFERENCES

1. A. Deeb, E. Mourad, and D. Elenany, *Phosphorous*, *Sulfur, Silicon*, **185**, 222 (2010).
2. J. Witherington, V. Bordas, D. Haigh, D. M. B. Hickey, R. J. Ife, A. D Rawlings, B. P. Slingsby, D. G. Smith, and R. W. Ward, *Bioorg. Med. Chem. Lett.*, **13,** 1581 (2003).

3. P. Beswick, S. Bingham, C. Bountra, T. Brown, K. Browning, L Campbell, I. Chessell, N. Clayton, S. Collins, J. Corfield, S. Guntrip, C. Haslam, P. Lambeth, F. Lucas, N. Mathews, G. Murkit, A. Naylor, N. Pegg, E. Pickup, H. Player, H. Price, A. Stevens, S. Stratton, and J. Wiseman, *Bioorg. Med. Chem. Lett*., **14**, 5445 (2004).
4. M. F. Brana, M. Cacho, M. L Garcia, E. P. Mayoral, B. Lopez, A. Ramos, N. Acero, F. Llinares, O. Lozach, L. Meijer, and B. de Pascual-Teresa, *J. Med. Chem*., **48**, 6843 (2005).
5. S. Scheibye, A. A. El-Barbary, S. O. Lawesson, H. Fritz, and G. Rihs, *Tetrahedron*, **38**, 3753 (1982).
6. Y. W. Ho, *Dyes Pigments*, **64,** 2223 (2005).
7. A. Deeb, F. El-Mariah, and M. Hosny, *Bioorg. Med. Chem. Lett*., **14**, 5013 (2004).
8. M. Amer, M. F. Zayed, and A. Deeb, *J. Chem. Res*., 643 (2005).
9. F. El-Mariah, M. Hosny, and A. Deeb*, Phosphorus*, *Sulfur*, *Silicon*, **18**, 809 (2006).
10. A. Deeb and M. Kotb, *Heterocycles*, **63**, 1143 (2004).
11. A. Deeb, B. Bayoumy, A. Hataba, and R. Fikry, *Heterocycles*, **32**, 901 (1991).
12. A. Deeb, B. Bayoumy, and R. Fikry, *Heterocycles*, **32**, 895 (1991).
13. A. Deeb, M. Hassaneen, and M. Kotb, *Heteroatom Chem.*, **16**, 278 (2005).
14. S. Shawali and F. A. Abdel Galil, *Tetrahedron*, **27**, 4305 (1971).
15. D. D. Agarwal and J. V. Agarwal, *J. Indian Chem. Soc*., **68**, 360 (1991).
16. A. I. Rutavichyus, S. P.Valyulene, and V. V. Mozolis, *J. Org. Chem. USSR*, 1083 (1987).
17. S. P. Singh Kumar, *Heterocycles*, **31**, 855 (1990).
18. R. M. Ilverstein, G. C Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th Edition (1981), p. 309.
19. *Standard Methods for the Determination of the Color Fastness of Textiles and Leather*, 5th Edn., Amendment No. 1, Society of Dyers and Colorists, Bradford, UK, 1978.