



PYRIDAZINE AND ITS RELATED COMPOUNDS. PART 37.¹

SYNTHESIS AND APPLICATION OF SOME HETEROARYLAZO DISPERSE DYES DERIVED FROM PYRAZOLO[3,4-*c*]- PYRIDAZINE

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Keywords: 3-diazo-4,5-diphenyl-3*H*-pyrazolo[3,4-*c*]pyridazine; active methylenes; color fastness.

3-Diazopyrazolo[3,4-*c*]pyridazine was synthesized and its transformations were investigated. With reactive methylene compound the corresponding hydrazones were formed. The prepared azo disperse dyes were applied to polyester fabric, and their spectral and color fastness properties measured.

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Introduction

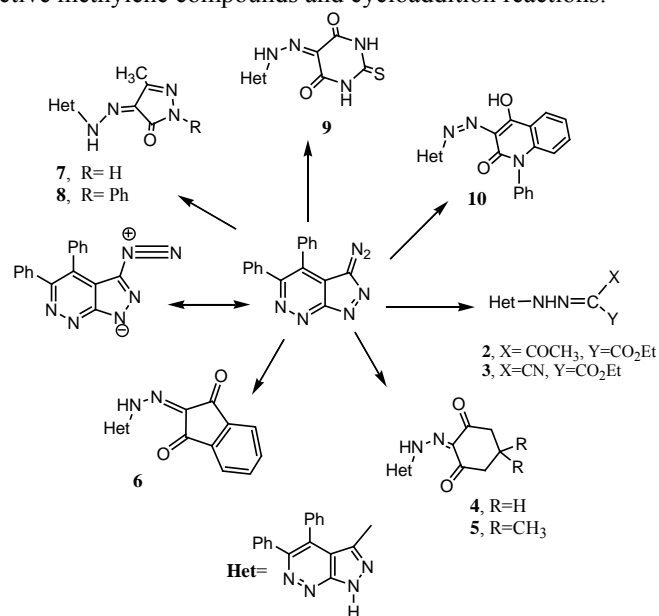
Azo compounds have for a great many years occupied a dominant position in the field of colouring matters due to their versatility. A large volume of publications and patents have appeared describing their synthesis and dyeing properties.^{2,3} Among these, azodyes using heterocyclic amines have become important as they give brighter and stronger results than those based on aniline-based diazo compounds.^{4,5}

The pyrazole 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.⁴ 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.⁶ Recently, our researches have been devoted to the synthesis of condensed tricyclic systems of potential biological activity with a pyrazole ring as the central nucleus.⁷⁻⁹ As a continuation of these studies we report here the synthesis of some 3-(4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)hydrazono derivatives and an evaluation of their properties on polyester fibers.

Results and Discussion

Our synthesis began with the preparation of 3-diazo-4,5-diphenyl-3*H*-pyrazolo[3,4-*c*]pyridazine **1** following the literature procedure by the diazotization of 3-amino-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine with sodium nitrite in glacial acetic acid at room temperature.¹⁰

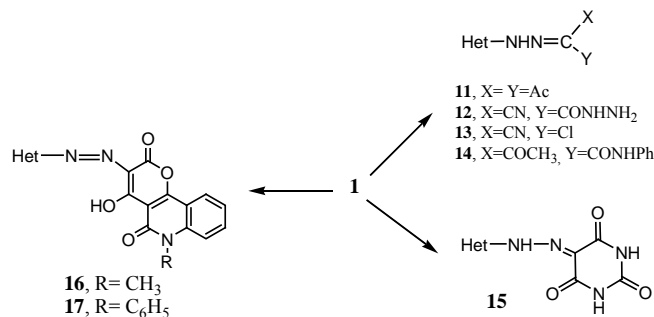
We reported the synthesis of 3-(4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)hydrazono derivatives **2-10** based on coupling reaction of 3-diazo-4,5-diphenyl-3*H*-pyrazolo[3,4-*c*]pyridazine **1** with active methylene compounds such as ethyl 3-oxobutanoate, ethyl 2-cyanoacetate, cyclohexane-1,3-dione, 5,5-dimethylcyclohexane-1,3-dione, 1*H*-indene-1,3(2*H*)-dione, 3-methyl-1*H*-pyrazol-5(4*H*)-one, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, 2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione, and 4-hydroxy-1-phenylquinolin-2(1*H*)-one.^{10,11} In continuation of this work, we report here the results of our further investigation on the reaction of compound **1** with further active methylene compounds and cycloaddition reactions.



Scheme 1. Reactions of 3-diazo-4,5-diphenyl-3*H*-pyrazolo[3,4-*c*]pyridazine

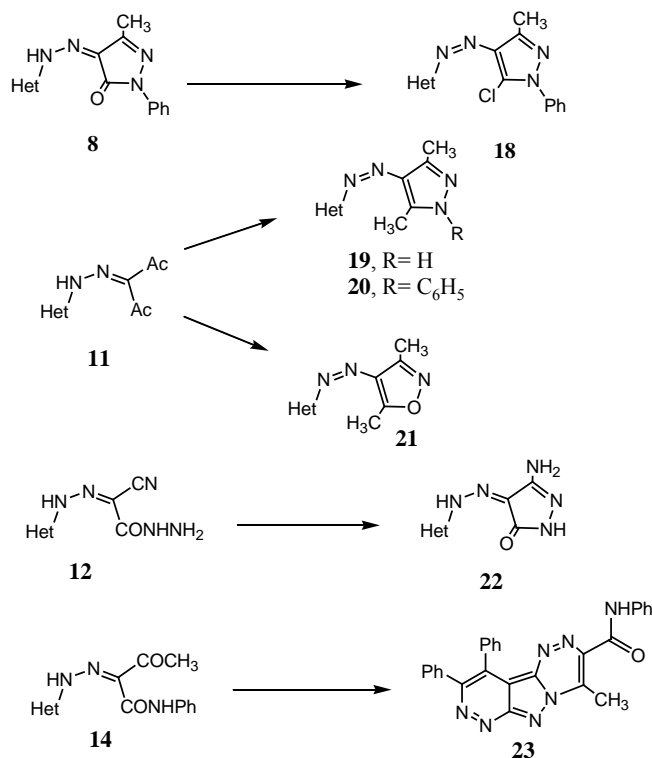
The reaction of **1** with pentane-2,4-dione, 2-cyanoacetohydrazide, 2-chloroacetonitrile, 3-oxo-*N*-phenylbutanamide, 4-hydroxy-6-methyl-2*H*-pyrano[3,2-*c*]quinoline-2,5(6*H*)-dione, 4-hydroxy-6-phenyl-2*H*-pyrano[3,2-*c*]quinoline-2,5(6*H*)-dione, and pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione formed easily the corresponding

hydrazone compounds **11-17**. For all compounds of this type several tautomeric forms can be written. For example compounds of the types **11**, **12**, and **13** can be regarded as azo compounds or as hydrazones, and the carbonyl part can be written in the keto or enolized form. The end of the reaction was judged by the disappearance of the diazo compound according to TLC analysis. The reaction time varied from a few minutes to several hours. The reaction products were isolated in high yield and gave satisfactory elemental analysis. The spectroscopic properties of the products were in excellent agreement with the proposed structures.



Scheme 2. Reaction routes to form hydrazone compounds

With view of studying some of the reaction of the hydrazones **8**, **11**, **12** and **14** that were allowed to react with some reagents. Treatment of compound **8** with phosphoryl chloride at refluxing temperature gave the corresponding chloro derivative **18**. Hydrazone **11** undergoes a smooth reaction with hydrazine hydrate and with phenyl hydrazine produced pyrazole derivative **19** and **20**, also reacts with hydroxyl amine hydrochloride in refluxing absolute ethanol in the presence of anhydrous potassium carbonate gave the isoxazole derivative **21**.



Scheme 3. Transformation of hydrazones

Similarly carbohydrazone hydrazone **12** was reacted with hydrazine hydrate producing aminopyrazolone derivative **22**. Compound **22** also was obtained by condensing hydrazone **3** with hydrazine hydrate.

The hydrazone **14** was also readily cyclized in ethanol at 78 °C to give the 4-methyl-N,9,10-triphenylpyridazino [3',4':3,4]pyrazolo[5,1-c][1,2,4]triazine-3-carboxamide derivative **23**. The assignment of the cyclic compound involves the intramolecular nucleophilic attack of pyrazole ring 2-nitrogen to the ketonic carbonyl with elimination of water molecule.

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 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 (ΔL^* , ΔC^* , ΔH^* and ΔE^*).

The results are measured using CIE-LAB techniques and given in Tables 2-6, where ΔL^* is the lightness difference, ΔC^* the chroma difference, ΔH^* the hue and ΔE^* the total color difference. A negative sign of ΔL^* 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 ΔC^* 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 ΔH^* 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 **2-22** vary from 5.97 to 50.48. The introduction of different couplers in dyes **2-22** varies the strength of K/S values (Table 1).

Table 1. Optical measurements, *K/S* and color coordinates, of dyes **2-22** on polyester fibers at sun light wavelength (D65/10), tungsten wavelength (A/10) and fluorescent wave length (F11/10).

Coordinates	<i>L</i> *	<i>a</i> *	<i>b</i> *	<i>C</i> *	<i>H</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>x</i>	<i>y</i>	<i>K/S</i>
Compound 2											
D65/10	74.46	5.43	14.67	15.65	69.68	46.87	47.42	37.84	0.3547	0.3589	20.98
A/10	76.03	8.93	16.34	18.62	61.34	59.33	49.94	12.69	0.4865	0.4095	
F11/10	75.29	5.91	16.72	17.74	70.54	52.94	48.75	22.83	0.4252	0.3915	
Compound 3											
D65/10	86.12	-4.30	60.87	61.02	94.04	62.80	68.22	20.51	0.4145	0.4502	37.85
A/10	88.58	5.52	59.93	60.18	84.74	84.48	73.29	7.68	0.5106	0.4430	
F11/10	87.86	-1.19	65.65	65.66	91.03	73.96	71.78	11.97	0.4690	0.4551	
Compound 4											
D65/10	71.15	3.10	40.27	40.39	85.60	41.21	42.40	17.85	0.4061	0.4179	50.84
A/10	73.63	10.95	40.54	41.99	74.88	55.75	46.13	6.52	0.5143	0.4255	
F11/10	72.61	4.71	45.82	46.06	84.14	48.03	44.57	10.03	0.4679	0.4343	
Compound 5											
D65/10	84.99	-0.46	29.21	29.21	90.89	62.36	65.98	40.82	0.3686	0.3900	13.08
A/10	86.67	6.08	29.35	29.97	78.29	80.28	69.34	14.17	0.4902	0.4233	
F11/10	86.01	1.32	32.55	32.58	87.68	71.27	68.00	24.14	0.4361	0.4161	
Compound 6											
D65/10	84.92	1.44	40.38	40.40	87.96	63.06	65.86	32.01	0.3919	0.4092	13.39
A/10	87.31	8.17	42.07	42.85	79.01	82.91	70.64	11.08	0.5036	0.4291	
F11/10	86.63	2.39	44.39	44.46	86.92	73.11	69.26	19.10	0.4528	0.4289	
Compound 7											
D65/10	87.87	-2.00	20.81	20.91	95.50	67.15	71.79	53.18	0.3495	0.3737	5.63
A/10	88.96	3.59	20.81	21.11	80.22	84.31	74.08	18.08	0.4778	0.4198	
F11/10	88.47	-0.50	23.16	23.16	91.24	75.62	73.05	31.72	0.4192	0.4050	
Compound 8											
D65/10	87.58	0.16	27.46	27.46	89.67	67.57	71.19	46.30	0.3651	0.3847	7.61
A/10	89.25	6.05	27.99	28.63	77.80	86.39	74.70	15.91	0.4881	0.4220	
F11/10	88.66	1.46	31.06	31.09	87.31	77.04	73.46	27.35	0.4332	0.4130	
Compound 9											
D65/10	82.61	5.53	51.58	51.86	84.08	60.47	61.43	22.29	0.4194	0.4261	23.71
A/10	85.81	12.20	54.00	55.36	77.27	81.59	67.61	7.90	0.5193	0.4304	
F11/10	84.89	5.69	57.21	57.50	84.32	71.05	65.80	13.05	0.4740	0.4389	
Compound 10											
D65/10	87.47	4.90	26.25	26.70	79.42	69.53	70.97	47.26	0.3703	0.3780	6.21
A/10	89.61	8.86	28.88	30.21	72.95	88.87	75.47	15.82	0.4933	0.4189	
F11/10	88.96	4.78	29.27	29.65	80.72	79.41	74.09	28.63	0.4360	0.4068	
Compound 11											
D65/10	85.49	-2.02	37.77	37.82	93.07	62.62	66.98	34.66	0.3812	0.4077	17.91
A/10	87.39	5.45	38.02	38.41	81.85	81.61	70.80	12.13	0.4960	0.4303	
F11/10	86.71	0.3	41.05	41.05	89.58	72.25	69.42	20.65	0.4451	0.4277	
Compound 12											
D65/10	80.86	7.08	23.08	24.14	72.94	58.05	58.21	24.29	0.3715	0.3726	12.28
A/10	83.08	10.80	25.95	28.11	67.40	74.64	62.31	13.38	0.4965	0.4145	
F11/10	82.34	6.53	25.96	26.77	75.88	66.26	60.94	39.99	0.4374	0.4023	

Contg. Table 1.

Coordinates	L*	a*	b*	C*	h	X	Y	Z	x	y	K/S
Compound 13											
D65/10	88.17	4.67	13.96	14.72	71.51	70.82	72.42	60.97	0.3468	0.3546	9.32
A/10	89.62	7.38	15.68	17.33	64.79	88.04	75.48	20.28	0.4790	0.4107	
F11/10	89.04	4.85	15.73	16.46	72.87	79.63	74.25	37.09	0.4170	0.3888	
Compound 14											
D65/10	89.28	-5.04	36.27	36.62	97.91	68.54	74.75	41.10	0.3717	0.40054	16.28
A/10	90.79	3.28	34.96	35.12	84.64	88.58	78.02	14.60	0.4889	0.4306	
F11/10	90.28	-2.07	40.39	40.44	92.94	78.80	76.90	23.91	0.4387	0.4282	
Compound 15											
D65/10	88.49	-0.87	27.84	27.85	91.78	68.89	73.08	47.40	0.3638	0.3859	8.6
A/10	90.07	5.02	28.02	28.74	79.85	87.79	76.45	16.34	0.4862	0.4233	
F11/10	89.60	0.28	31.78	31.78	89.50	78.51	75.45	27.84	0.4318	0.4150	
Compound 16											
D65/10	87.26	4.93	27.65	28.08	79.89	69.12	70.53	45.63	0.3731	0.3807	9.02
A/10	89.47	9.18	30.29	31.65	73.13	88.70	75.16	15.32	0.4950	0.4195	
F11/10	88.74	5.14	30.71	31.14	80.50	79.11	73.62	27.61	0.4386	0.4082	
Compound 17											
D65/10	82.84	8.28	25.78	27.08	72.20	62.14	61.87	40.59	0.3775	0.3759	18.58
A/10	85.33	12.14	29.04	31.47	67.32	80.44	66.66	13.60	0.5005	0.4148	
F11/10	84.42	7.99	28.85	29.93	74.53	71.18	64.87	24.63	0.4430	0.4037	
Compound 18											
D65/10	82.58	5.40	33.62	34.05	80.87	60.43	61.37	34.00	0.3879	0.3939	18.57
A/10	85.11	10.75	35.87	37.44	73.32	79.18	66.22	11.68	0.5041	0.4216	
F11/10	84.34	5.32	37.68	38.05	81.97	69.74	64.73	20.32	0.4505	0.4182	
Compound 19											
D65/10	89.18	-0.38	28.21	28.21	90.76	70.51	74.55	48.18	0.3649	0.3858	9.63
A/10	90.84	5.08	29.01	29.45	80.07	89.74	78.13	16.45	0.4869	0.4239	
F11/10	90.44	0.44	31.22	31.22	89.18	80.47	77.25	28.97	0.4310	0.4138	
Compound 20											
D65/10	86.81	2.44	33.40	33.49	85.82	67.11	69.63	39.95	0.3798	0.3941	14.35
A/10	89.02	7.83	35.09	35.96	77.42	86.84	74.22	13.69	0.4970	0.4247	
F11/10	88.51	2.38	37.27	37.35	86.34	77.17	73.13	23.94	0.4429	0.4197	
Compound 21											
D65/10	88.29	-6.81	49.71	50.18	97.80	65.82	72.68	29.54	0.3917	0.4325	21.64
A/10	90.15	2.87	47.93	48.02	86.58	86.77	76.62	10.85	0.4980	0.4398	
F11/10	89.64	-3.50	55.10	55.21	93.63	76.65	75.53	16.81	0.4536	0.4469	
Compound 22											
D65/10	85.15	4.20	17.18	17.69	76.27	64.70	66.30	52.13	0.3533	0.3621	5.97
A/10	86.74	7.76	19.03	20.55	67.82	81.34	69.47	17.39	0.4836	0.4130	
F11/10	86.11	4.27	19.24	19.70	77.49	72.92	68.21	31.62	0.4221	0.3948	

Assessment of color fastness

Most influences that can affect fastness are light, washing, heat, perspiration, crabbing and atmospheric pollution. Conditions of such tests are chosen to correspond closely to treatments employed in manufactu-

re and ordinary use conditions.¹² Results are given after usual matching of tested samples against standard reference (the grey scale).¹² The results revealed that these dyes have good fastness properties (Table 7).

Table 2. Color differences between dyes (**4**, **5**, **6**, **9**, **13**, **15**) using **14** as a standard on polyester fibers at sun light wavelength (D65/10), tungsten wavelength (A/10) and fluorescent wavelength (F11/10).

	Reference dye 14				Batch is
	ΔE^*	ΔL^*	ΔC^*	ΔH^*	
Compound 4					
D65/10	7.722	-5.674	2.119	-4.790	Darker less green yellow
A/10	7.601	-5.346	3.258	-4.311	Darker redder yellow
F11/10	7.237	-5.503	2.805	-3.770	Darker less green yellow
Compound 5					
D65/10	4.710	-1.497	-3.486	-2.791	Darker less green less yellow
A/10	4.109	-1.436	-2.527	-2.905	Darker redder less yellow
F11/10	4.504	-1.492	-3.558	-2.322	Darker less green less yellow
Compound 6					
D65/10	5.271	-1.422	1.940	-4.690	Darker less green yellow
A/10	4.921	-1.103	3.780	-2.951	Darker redder yellow
F11/10	3.784	-1.159	1.937	-3.037	Darker less green yellow
Compound 9					
D65/10	10.473	-2.439	6.764	-7.614	Darker less green less yellow
A/10	10.537	-1.826	9.234	-4.736	Darker redder yellow
F11/10	9.096	-1.976	7.190	-5.209	Darker less green yellow
Compound 13					
D65/10	11.937	-0.431	-9.995	-6.512	Darker less green less yellow
A/10	10.553	-0.489	-8.445	-6.309	Darker redder less yellow
F11/10	11.838	-0.503	-10.416	-5.602	Darker less green less yellow
Compound 15					
D65/10	4.614	-0.273	-3.866	-2.505	Darker less green less yellow
A/10	3.695	-0.243	-2.958	-2.200	Darker redder less yellow
F11/10	3.961	-0.227	-3.638	-1.551	Darker less green less yellow

Table 3. Color differences between dyes (**12**, **22**) using **3** as a standard on polyester fibers at sun light wavelength (D65/10), tungsten wavelength (A/10) and fluorescent wavelength (F11/10).

	Reference dye 3				Batch is
	ΔE^*	ΔL^*	ΔC^*	ΔH^*	
Compound 12					
D65/10	15.963	-2.174	-12.993	-9.014	Darker less green less yellow
A/10	14.425	-2.227	-11.343	-8.630	Darker redder less yellow
F11/10	15.323	-2.254	-13.343	-7.189	Darker less green less yellow
Compound 22					
D65/10	16.404	0.203	-15.481	-5.421	Darker less green less yellow
A/10	15.749	-0.161	-14.388	-6.401	Darker redder less yellow
F11/10	16.641	-0.115	-15.909	-4.882	Darker less green less yellow

Table 4. Color differences between dyes (**19**, **20**, **21**) using **11** as a standard on polyester fibers at sun light wavelength (D65/10), tungsten wavelength (A/10) and fluorescent wavelength (F11/10).

	Reference dye 11				Batch is
	ΔE^*	ΔL^*	ΔC^*	ΔH^*	
Compound 19					
D65/10	5.277	1.067	-4.804	-1.903	Lighter less green less yellow
A/10	4.678	1.006	-4.243	-1.694	Lighter redder less yellow
F11/10	4.876	1.098	-4.670	-0.873	Lighter less green less yellow
Compound 20					
D65/10	4.915	0.150	-2.397	-4.288	Lighter less green less yellow
A/10	3.541	0.298	-1.311	-3.276	Lighter redder less yellow
F11/10	3.203	0.335	-2.019	-2.464	Lighter less green less yellow
Compound 21					
D65/10	6.053	0.922	5.560	2.207	Lighter greener yellow
A/10	5.165	0.918	4.397	2.550	Lighter less red yellow
F11/10	6.613	0.978	6.172	2.162	Lighter greener yellow

Table 5. Color differences between dyes (**7**, **8**, **18**) using **2** as a standard on polyester fibers at sun light wavelength (D65/10), tungsten wavelength (A/10) and fluorescent wavelength (F11/10).

	Reference dye 2				Batch is
	ΔE^*	ΔL^*	ΔC^*	ΔH^*	
Compound 7					
D65/10	13.563	5.188	3.628	11.995	Lighter less red yellow
A/10	11.393	4.971	1.641	10.119	Lighter less red yellow
F11/10	11.821	5.083	3.587	10.052	Lighter less red yellow
Compound 8					
D65/10	14.328	4.941	8.181	10.675	Lighter less red yellow
A/10	13.191	4.952	6.462	10.379	Lighter less red yellow
F11/10	13.846	5.022	8.752	9.481	Lighter less red yellow
Compound 9					
D65/10	13.963	3.137	11.956	6.495	Lighter red yellow
A/10	14.499	3.469	11.308	8.384	Lighter red yellow
F11/10	14.545	3.464	12.389	6.787	Lighter less red yellow

Table 6. Color differences between dyes (**10**, **17**) using **16** as a standard on polyester fibers at sun light wavelength (D65/10), tungsten wavelength (A/10) and fluorescent wavelength (F11/10).

	Reference dye 16				Batch is
	ΔE^*	ΔL^*	ΔC^*	ΔH^*	
Compound 10					
D65/10	2.054	0.561	-0.926	1.745	Lighter redder less yellow
A/10	1.864	0.449	-1.205	1.349	Lighter redder less yellow
F11/10	1.909	0.514	-0.939	1.581	Lighter redder less yellow
Compound 17					
D65/10	3.192	-1.431	-0.810	-2.735	Darker redder less yellow
A/10	3.023	-1.367	-0.543	-2.641	Darker redder less yellow
F11/10	2.911	-1.426	-0.891	-2.376	Darker redder less yellow

Table 7. Fastness properties of compounds 2-22

Dyes	Fiber	Washing fastness			Crabbing fastness			Perspiration fastness, basic			Light fastness, 40 h
		Alt.	S. W	S. F	Alt.	S. W	S. F	Alt.	S. W	S. F	
2	Polyester	3	4	4	3	4	4	3	4	4	3
3	Polyester	4	4	4	4	4	4	4	4	4	1
4	Polyester	3-4	4	4	3-4	4	4	3-4	4	4	4
5	Polyester	4	4	4	4	4	4	4	4	4	2
6	Polyester	3-4	4	4	3-4	4	4	3	4	4	3
7	Polyester	3-4	4	4	3-4	4	4	3-4	4	4	4
8	Polyester	4	4	4	3-4	4	4	3-4	4	4	4
9	Polyester	3-4	4	4	3-4	4	4	3-4	4	4	1-2
10	Polyester	4	4	4	3-4	4	4	4	4	4	1
11	Polyester	4	4	4	4	4	4	4	4	4	3
12	Polyester	3	4	4	3	4	4	3	4	4	3-4
13	Polyester	3	4	4	3	4	4	3	4	4	2-3
14	Polyester	3-4	4	4	4	4	4	4	4	4	3
15	Polyester	4	4	4	3-4	4	4	3-4	4	4	2-3
16	Polyester	3-4	4	4	3-4	4	4	3-4	4	4	3
17	Polyester	3	4	4	3	4	4	3	4	4	3
18	Polyester	4	4	4	4	4	4	4	4	4	4
19	Polyester	4	4	4	4	4	4	4	4	4	4
20	Polyester	4	4	4	4	4	4	4	4	4	4
21	Polyester	3-4	4	4	3-4	4	4	3-4	4	4	3-4
22	Polyester	3	4	4	3-4	4	4	3-4	4	4	4

Alt = Alteration, S.W = Staining on wool, S.F = Staining on polyester..

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. ¹H-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 GC-MS–qp1000 EX Shimadzu spectrometer. Elemental analysis (C, H, N) were carried out at the Micro-Analytical Center of Cairo University, Giza, Egypt.

The dyeing assessment fastness tests, and color measurements were carried out at Misr Company for Spinning and Weaving, El-Mahala El-Kobra, Egypt.

General procedure for the preparation of coupling products from 3-diazo-4,5-diphenylpyrazolo[3,4-*c*]pyridazine 1 and active methylene compounds.

A solution of compound 1 (0.6 g, 2.0 mmol) in ethanol (30 mL) was treated with the corresponding active methylene compounds (2.0 mmol). The reaction mixture was stirred at room temperature for such time. The colored azo-dye precipitated was filtered, dried, and recrystallized from ethanol. In this manner the following compounds were prepared.

3-((4,5-Diphenyl-1H-pyrazolo[3,4-*c*]pyridazin-3-yl)diazenyl)-pentane-2,4-dione 11.

Prepared from pentane-2, 4-dione, and reaction time: 45 minutes, yellow crystals in 73 % yield, m.p. 250-252 °C. IR: 3500, 3300 (NH), 3060 (CH_{arom}), 2925 (CH_{aliph}), 1700 (C=O), 1630 (C=N), 1510 (C=C) cm⁻¹. ¹H-NMR (DMSO-*d*₆): δ = 7.9-7.2 (m, 10H, 2Ph) and 2.9 (s, 6H, 2CH₃). Anal. Calcd for C₂₂H₁₈N₆O₂: C, 66.32; H, 4.55; N, 21.10, Found: C, 66.20; H, 4.40; N, 20.90.

2-Cyano-2-((4,5-diphenyl-1H-pyrazolo[3,4-*c*]pyridazin-3-yl)diazenyl) acetohydrazide. 12

Prepared from 2-cyanoacetohydrazide, reaction time: 6 hours, reddish brown crystals in 69 % yield, m.p.: 180-182 °C. IR: 3345, 3197 (NH₂ & NH), 3030(CH_{arom}), 2928 (CH_{aliph}), 2259 (CN), 1687(C=O) cm⁻¹; MS: m/z 397 [M⁺, 1.35%]. Anal. Calcd for C₂₀H₁₅N₉O: C, 60.45; H, 3.80; N, 31.72. Found: C, 59.35; H, 3.78; N, 30.12.

(4,5-Diphenyl-1H-pyrazolo[3,4-*c*]pyridazin-3-yl) carbonocyanidohydrazonic chloride. 13

Prepared from 2-chloroacetonitrile, reaction time: 2 hours, brown crystals in 67 % yield, m.p.: 208-210 °C. IR: 3165(NH), 3105(CH_{arom}), 2900 (CH_{aliph}), 2130 (CN), 1651(C=N), cm⁻¹; MS: m/z 373.3 [M⁺, 10.75%], 374.5 [M⁺+1, 10.19%], 337.1 [M⁺-Cl, 9.65%] 273.2 [M⁺-N=N-CH(CN)Cl]. Anal. Calcd for C₁₉H₁₂ClN₇: C, 61.05; H, 3.24; N, 26.23. Found: C, 61.03; H, 3.19; N, 26.25.

5-(4,5-Diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine-3-yl)hydrazono-3-oxo-N-phenylbutanamide 14.

Prepared from 3-oxo-N-phenylbutanamide, reaction time: 2 hours, yellow crystals in 65 % yield, m.p. 279-281°C. IR: 3400 (NH), 1690 (C=O), 1650 (C=O amide), 1530 cm⁻¹; Anal. Calcd for C₂₇H₂₁N₇O₂: C, 68.20; H, 4.45; N, 20.62. Found: C, 68.30; H, 4.30; N, 20.70.

5-(2-(4,5-Diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)hydrazono)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione. 15

Prepared from pyrimidine-2,4,6(1*H*, 3*H*, 5*H*)-trione, the reaction time: 3.5 hours yellow crystals 90 % yield. m.p.: 310-312 °C. IR: 3168 (NH), 1713, 1674 (C=O), 1534 (C=N) cm⁻¹. MS: m/z 426.4 [M⁺, 8.97%], 427.4 [M+ 1, 3.18], 456 [M-Cl, 22.45]. Anal. Calcd for C₂₁H₁₄N₈O₃: C, 59.15; H, 3.31; N, 26.28. Found: C, 59.10; H, 3.26; N, 26.14.

3-((4,5-Diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)diazonyl)-4-hydroxy-6-methyl-2*H*-pyrano[3,2-*c*]quinoline-2,5(6*H*)-dione. 16

Prepared from, 4-hydroxy-6-methyl-2*H*-pyrano[3,2-*c*]quinoline-2,5(6*H*)-dione, the reaction time: 2 hours, orange crystals in 50 % yield, m.p.: 285-287 °C; IR: 3436 (NH and OH), 3078 (CH_{aromatic}), 2975 (CH_{aliphatic}), and 1645 (C=O) ester and 1606 (C=O) amide, cm⁻¹; MS: m/z 542.3 [M⁺, 0.31%]. Anal. Calcd for C₃₀H₁₉N₇O₄: C, 66.54; H, 3.54; N, 18.11. Found: C, 66.46; H, 3.50; N, 18.10.

3-((4,5-Diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)diazonyl)-4-hydroxy-6-phenyl-2*H*-pyrano[3,2-*c*]quinoline-2,5(6*H*)-dione. 17

Prepared from, 4-hydroxy-6-phenyl-2*H*-pyrano[3,2-*c*]quinoline-2,5(6*H*)-dione, the reaction time: 4 hours, orange crystals in 81 % yield, m.p.: 280-282 °C; IR: 3419 cm⁻¹ (-OH), 3146 (-NH), 3060 (CH_{aromatic}), 2789 (CH_{aliphatic}) 1647 (C=O) ester, 1608 cm⁻¹ (C=O) amide ring carbonyl, cm⁻¹; MS: m/z 604.40 [M⁺, 2.55 %]. Anal. Calcd for C₃₅H₂₁N₇O₄: C, 69.65; H, 3.51; N, 16.24. Found: C, 69.58; H, 3.48; N, 16.20.

3-((5-Chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl) diazenyl)-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine 18.

A mixture of 4-((4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)diazonyl)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one **8** (0.5g, 1.05 mmol) and phosphorylchloride (25 mL) was refluxed for 3h. The reaction mixture was cooled to room temperature and poured into crushed ice, the solid product was filtered, dried and recrystallized from ethanol. Brown crystals in 77 % yield, m.p.: 250-252 °C; IR: 3317 (NH), 3050 (CH_{arom}), 2968 (CH_{aliph}), 1591 (C=N) cm⁻¹. MS: m/z 491 [M⁺, 22.35 %], 492 [M+ 1, 17.53], 456 [M-Cl, 22.45]. Anal. Calcd for C₂₇H₁₉ClN₈: C, 66.05; H, 3.90; N, 22.28. Found: C, 65.86; H, 3.84; N, 22.42.

3-((3,5-Dimethyl-1*H*-pyrazol-4-yl)diazonyl)-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine 19.

To a solution of 3-((4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)diazonyl)pentane-2,4-dione **11** (0.8 g, 2.0 mmol) in acetic acid (20 mL), hydrazin hydrate (85 %, 1.0 mL) was added. The reaction mixture was refluxed for 3 h. The yellow solid product was filtered and recrystallized from methanol, yellow crystals in 81 % yield. m.p.: 281-282 °C; IR: 3170 (NH), 3068 (CH_{arom}), 2928 (CH_{aliph}) 1625 (C=N), 1590 (PhN) and 1535 (C=C) cm⁻¹, ¹H-NMR (DMSO-*d*₆) δ= 7.9-7.2 (m, 10H, 2Ph) and 2.9 (s, 6H, 2CH₃). Anal. Calcd for C₂₂H₁₈N₈: C, 66.99; H, 4.60; N, 28.4. Found: C, 66.80; H, 4.50; N, 28.30.

3-((3,5-Dimethyl-1-phenyl-1*H*-pyrazol-4-yl)diazonyl)-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine. 20

A mixture of 3-((4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)diazonyl)pentane-2,4-dione **11** (0.8 g, 2.0 mmol) and phenyl hydrazine (0.22 g, 2.0 mmol) in acetic acid (20 mL) was refluxed for 5 h. The cooled reaction mixture was poured into water (100 mL). The solid product obtained was filtered, and recrystallized from ethyl acetate, yellow crystals in 84 % yield, m.p.: 272-273 °C; IR: 3170 (NH), 3088 (CH_{arom}), 2918 (CH_{aliph}) 1625 (C=N), 1590 (PhN) and 1535 (C=C) cm⁻¹; ¹H NMR(DMSO-*d*₆): δ= 14.9 (br s, 1H, NH), 7.7 (s, 5H, phN) 7.4-6.8 (m, 10H, 2Ph) and 2.3 (s, 3H, CH₃), 1.9 (s, 3H, CH₃). Anal. Calcd for C₂₈H₂₂N₈: C, 71.74; H, 4.71; N, 23.8. Found: C, 71.30; H, 4.60; N, 23.70.

4-((4,5-Diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)diazonyl)-3,5-dimethylisoxazole 21.

A mixture of 3-((4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)diazonyl)pentane-2,4-dione **11** (0.8 g, 2.0 mmol) and hydroxylamine hydrochloride (0.14 g, 2.0 mmol) in pyridine (15 mL) was refluxed for 10 h. The reaction mixture was poured onto water (100 mL). The solid product obtained was filtered, and recrystallized from ethanol. Yellow crystals in 73 % yield, m.p.: 214-215 °C; IR: 3210 (NH), 3060 (CH_{arom}), 2948 (CH_{aliph}), 1630 (C=N), 1590 (PhN) and 1520 (C=C) cm⁻¹. ¹H NMR (DMSO-*d*₆): δ = 11.8 (s, 1H, NH), 7.6-6.8 (m, 10H, 2Ph) 2.1 (s, 3H, CH₃), 1.9 (s, 3H, CH₃). Anal. Calcd for C₂₂H₁₇N₇O: C, 66.82; H, 4.33; N, 24.80. Found: C, 66.70; H, 4.20; N, 24.70.

3-Amino-4-((4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)diazonyl)-1*H*-pyrazol-5(4*H*)-one 22.

To a solution of ethyl 2-cyano-2-(2-(4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazin-3-yl)hydrazono)acetate **3** (0.82 g, 2.0 mmol) in ethanol (50 mL), hydrazine hydrate (85 %, 1.0 mL) was added. The reaction mixture was refluxed for 3 h. Upon cooling the precipitated product was filtered and recrystallized from ethanol. Deep red crystals in 81 % yield, m.p.: >300 °C; IR: 3355, 3280, 3210, 3140 (NH₂ & NH), 1680 (C=O), 1620 (C=N) and 1570 (C=C) cm⁻¹;

^1H NMR (DMSO- d_6): δ = 7.8-7.2 (m, 10H, 2Ph) and 3.4 (br s, 2H, NH_2). Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{N}_9\text{O}$: C, 60.44; H, 3.80; N, 31.72. Found: C, 60.30; H, 3.70; N, 31.60.

4-Methyl-N,9,10-triphenyl pyridazino [3',4':3,4] pyrazolo[5,1-c][1,2,4]triazine-3-carboxamide **23**.

Compound **14** (0.8 g) was heated in ethanol (20 mL) for 30 minutes, after concentration, the solid crystals was filtered. Greenish yellow in 58% yield. M.p.: 279-281 °C; IR: 3342 (NH), 1689 cm^{-1} (amide C=O). Ms: m/z 457.15 [M^+ , 100%], 458.15 [$\text{M}+1$, 32.67], 442.10 [$\text{M}-\text{CH}_3$, 5.68], 337.05 [$\text{M}-\text{CONHPh}$, 24.57] 100%. Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{N}_7\text{O}$: C, 70.88; H, 4.19; N, 21.43. Found: C, 70.68; H, 4.16; N, 21.14.

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^{-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 Bayer)

The dye bath (1:20 liquor ratio), containing 5 g 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, then the dyed material was rinsed and soaped with 2 % nonionic detergent to improve wet fastness.

Assessment of color fastness (Table 7)

Fastness to washing, perspiration, light, and crabbing was tested according to the reported methods.

Fastness to washing

A specimen of dyed polyester fabric was stitched between two pieces of undyed samples (one from wool and the other one from the same fibre under test "polyester"), 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 Crabbing

A composite specimen was made by sewing a piece of dyed fabric between two equal weight pieces of undyed samples (one from wool and the other one from the same fiber under test "polyester"). The composite specimen was boiled at 100 °C in water for 2 minutes.

Fastness to perspiration (basic):

The AATCC standard test method 15-1960 was used. For each dyed sample two composite specimens were prepared by stitching a piece of dyed sample between two undyed samples (one from wool and the other one from the same fiber under test "polyester"). Each one of the two composite specimens were immersed in alkaline solution for 30 minutes with occasional agitation and squeezing to ensure complete wetting, then squeezed to about 200-300 % regain and put between the plastic plates of the perspiration tester in such a way that the specimens should be in a vertical position when placed in the oven. The loaded sample was kept in an oven at 38 °C for 6-8 hours, after which the sample was dried by conventional means. Change in color of the dyed samples and staining of the undyed ones were assessed using "International Geometric Grey Scale" (1-5).

The alkaline solution (pH= 8-8.5) contained sodium chloride (10 g l^{-1}), ammonium carbonate (4 g l^{-1}), disodium orthophosphate (1 g l^{-1}) and histidine monohydrochloride (0.25 g l^{-1}).

Fastness to Light

Dyed sample and standard Blue Scale samples were exposed to the sun light for 40 h. After exposure, the sample and standard were allowed to lie in the dark at room temperature for about 2h in order to cool off and regain normal moisture from air.

Light fastness of the dyed sample was given by comparison the change in color with relative "International Geometric Grey Scale" (1-5): 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent.

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 Tables 2-6.

Conclusions

A set of **21** disperse dyes **2-22** were synthesized by reaction of 3-diazo-4,5-diphenyl-3H-pyrazolo[3,4-c]-pyridazine **2** with active methylene compounds and their derivatives. All of them were investigated for their dyeing characteristics on polyester. The dyed fabrics exhibit moderate to good (3-4) washing, crabbing, and perspiration fastness properties (Table 7). The remarkable degree of levelness and brightness after washing is indicative of good penetration and excellent affinity of these dyes for fabric due to accumulation of polar groups. This in combination with the ease of preparation makes them particularly valuable.

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