# 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

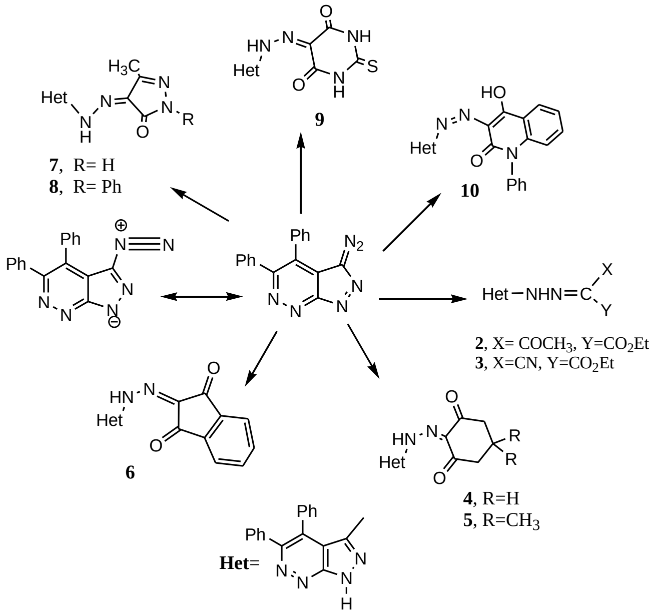
Azo compounds have for a great many years occupied a dominant position in the field of colouring matters due to their versatility. A large volume of publications and patents have appeared describing their synthesis and dyeing properties.[2,3] Among these, azodyes using heterocyclic amines have become 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

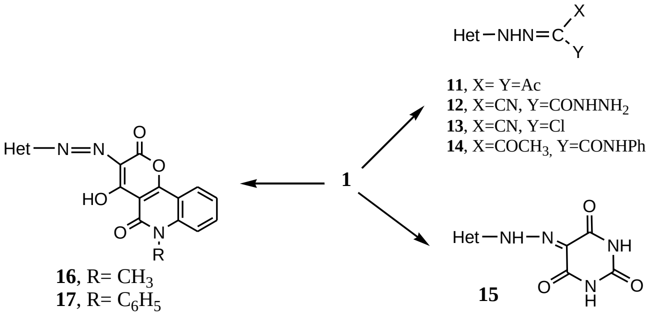
Our synthesis began with the preparation of 3-diazo-4,5-diphenyl-3*H*-pyrazolo[3,4-*c*]pyridazine **1** following the literature procedure by the diazotization of 3-amino-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine with sodium nitrite in glacial acetic acid at room temperature.[10]

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-dimethylcyclo-hexane-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.



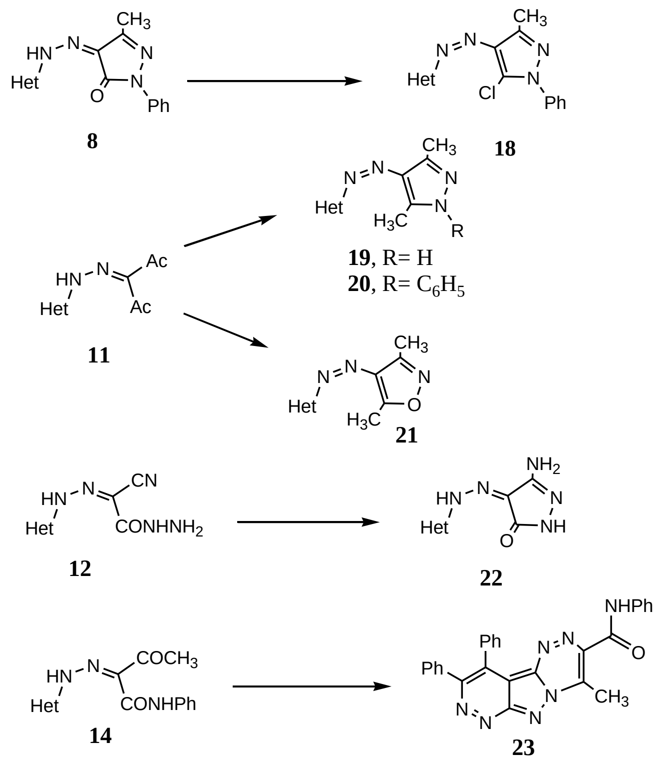

**Scheme 1.** Reactions of 3-diazo-4,5-diphenyl-3H-pyrazolo[3,4-c]pyridazine

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 carbohydrazide 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 elemination 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*:

$$\frac{K}{S}=\frac{\left(1-R\right)^2}{2R} \qquad (1)$$

In this equation *R* is used as a ratio, e.g., 32 % reflectance as 0.32. The *K/S* value at λ max was taken as a measure of color depth. On the other hand, the psychometric coordinates (*L**, *a**, *b**) for each dyed sample were obtained to illustrate the color hues, where *L** is the lightness, ranging from 0 to 100 ( 0 for black and 100 for white ); *a** is the red-green axis, (+) for red, zero for grey, and (-) for green; and *b** is the yellow-blue axis, (+) for yellow, zero for gray, and (-) for blue.

The parent dyestuff in each group is taken as the standard in color difference calculation (Δ*L**, Δ*C**, Δ*H** and Δ*E**).

The results are measured using CIE-LAB techniques and given in Tables 2-6, where Δ*L** is the lightness difference, Δ*C** the chroma difference, Δ*H** the hue and Δ*E** the total color difference. A negative sign of Δ*L** indicates that the dyed fiber becomes darker than the standard, but a positive sign indicates that the dyed fiber becomes lighter than the standard. A negative sign of Δ*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 Δ*H**indicates that the color directed to red color, while a positive sign indicates that the color directed to yellowish. The values of *K/S* of **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 | *L** | *a** | *b** | *C** | *H* | *X* | *Y* | *Z* | *x* | *y* | *K/S* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **Compound 2** | | | | | | |
| D65/10 | 74.46 | 5.43 | 14.67 | 15.65 | 69.68 | 46.87 | 47.42 | 37.84 | 0.3547 | 0.3589 | |
| A/10 | 76.03 | 8.93 | 16.34 | 18.62 | 61.34 | 59.33 | 49.94 | 12.69 | 0.4865 | 0.4095 | *20.98* |
| 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 | |
| A/10 | 88.58 | 5.52 | 59.93 | 60.18 | 84.74 | 84.48 | 73.29 | 7.68 | 0.5106 | 0.4430 | *37.85* |
| 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 | |
| A/10 | 73.63 | 10.95 | 40.54 | 41.99 | 74.88 | 55.75 | 46.13 | 6.52 | 0.5143 | 0.4255 | *50.84* |
| 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 | |
| A/10 | 87.31 | 8.17 | 42.07 | 42.85 | 79.01 | 82.91 | 70.64 | 11.08 | 0.5036 | 0.4291 | *13.39* |
| 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 | |
| A/10 | 88.96 | 3.59 | 20.81 | 21.11 | 80.22 | 84.31 | 74.08 | 18.08 | 0.4778 | 0.4198 | *5.63* |
| 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 | |
| A/10 | 89.25 | 6.05 | 27.99 | 28.63 | 77.80 | 86.39 | 74.70 | 15.91 | 0.4881 | 0.4220 | *7.61* |
| 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 | |
| A/10 | 85.81 | 12.20 | 54.00 | 55.36 | 77.27 | 81.59 | 67.61 | 7.90 | 0.5193 | 0.4304 | *23.71* |
| 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 | |
| A/10 | 89.61 | 8.86 | 28.88 | 30.21 | 72.95 | 88.87 | 75.47 | 15.82 | 0.4933 | 0.4189 | *6.21* |
| 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 | |
| A/10 | 87.39 | 5.45 | 38.02 | 38.41 | 81.85 | 81.61 | 70.80 | 12.13 | 0.4960 | 0.4303 | *17.91* |
| 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 | |
| A/10 | 83.08 | 10.80 | 25.95 | 28.11 | 67.40 | 74.64 | 62.31 | 13.38 | 0.4965 | 0.4145 | *12.28* |
| 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 | |
| A/10 | 89.62 | 7.38 | 15.68 | 17.33 | 64.79 | 88.04 | 75.48 | 20.28 | 0.4790 | 0.4107 | *9.32* |
| 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 | |
| A/10 | 90.79 | 3.28 | 34.96 | 35.12 | 84.64 | 88.58 | 78.02 | 14.60 | 0.4889 | 0.4306 | *16.28* |
| 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 | |
| A/10 | 90.07 | 5.02 | 28.02 | 28.74 | 79.85 | 87.79 | 76.45 | 16.34 | 0.4862 | 0.4233 | *8.6* |
| 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 | |
| A/10 | 89.47 | 9.18 | 30.29 | 31.65 | 73.13 | 88.70 | 75.16 | 15.32 | 0.4950 | 0.4195 | *9.02* |
| 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 | |
| A/10 | 85.33 | 12.14 | 29.04 | 31.47 | 67.32 | 80.44 | 66.66 | 13.60 | 0.5005 | 0.4148 | *18.58* |
| 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 | |
| A/10 | 85.11 | 10.75 | 35.87 | 37.44 | 73.32 | 79.18 | 66.22 | 11.68 | 0.5041 | 0.4216 | *18.57* |
| 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 | |
| A/10 | 90.84 | 5.08 | 29.01 | 29.45 | 80.07 | 89.74 | 78.13 | 16.45 | 0.4869 | 0.4239 | *9.63* |
| 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 | |
| A/10 | 89.02 | 7.83 | 35.09 | 35.96 | 77.42 | 86.84 | 74.22 | 13.69 | 0.4970 | 0.4247 | *14.35* |
| 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 | |
| A/10 | 90.15 | 2.87 | 47.93 | 48.02 | 86.58 | 86.77 | 76.62 | 10.85 | 0.4980 | 0.4398 | 21.64 |
| 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 | |
| A/10 | 86.74 | 7.76 | 19.03 | 20.55 | 67.82 | 81.34 | 69.47 | 17.39 | 0.4836 | 0.4130 | 5.97 |
| 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 manufacture 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 | | | | |
|---|---|---|---|---|---|
| | *ΔE** | *ΔL** | *ΔC** | *ΔH** | *Batch is* |
| **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 | | | | |
|---|---|---|---|---|---|
| | *ΔE** | *ΔL** | *ΔC** | *ΔH** | *Batch is* |
| **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** | | | | |
|---|---|---|---|---|---|
| | ***ΔE**** | ***ΔL**** | ***ΔC**** | ***ΔH**** | ***Batch is*** |
| **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** | | | | |
|---|---|---|---|---|---|
| | ***ΔE**** | ***ΔL**** | ***ΔC**** | ***ΔH**** | ***Batch is*** |
| **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** | | | | |
|---|---|---|---|---|---|
| | ***ΔE**** | ***ΔL**** | ***ΔC**** | ***ΔH**** | ***Batch is*** |
| **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 |


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**Table 7. F**astness 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. $^1$H-NMR spectra were recorded on Varian Gemini 200 MHz spectrometer using the indicated solvents and tetramethylsilane (TMS) as an internal reference. Electron impact mass spectra were obtained at 70 eV using a 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-1*H*-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$^{-1}$. $^1$H-NMR (DMSO-$d_6$): δ = 7.9-7.2 (m, 10H, 2Ph) and 2.9 (s, 6H, $2CH_3$). Anal. Calcd for $C_{22}H_{18}N_6O_2$: 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-1*H*-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 ($NH_2$ &NH), 3030($CH_{arom}$), 2928 ($CH_{aliph}$), 2259 (CN), 1687(C=O) cm$^{-1}$ ; MS: m/z 397 [ $M^+$, 1.35%]. Anal. Calcd for $C_{20}H_{15}N_9O$: C, 60.45; H, 3.80; N, 31.72. Found: C, 59.35; H, 3.78; N, 30.12.

**(4,5-Diphenyl-1*H*-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 $C_{19}H_{12}ClN_7$: C, 61.05; H, 3.24; N, 26.23. Found: C, 61.03; H, 3.19; N, 26.25.

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

Prepared from 3-oxo-N-phenylbutanamide, reaction time: 2 hours, yellow crystals in 65 % yield, m.p. 279-281ºC. IR: 3400 (NH), 1690 (C=O), 1650 (C=O amide), 1530 $cm^{-1}$; Anal. Calcd for $C_{27}H_{21}N_7O_2$: 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*, 3H, 5H)-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 $C_{21}H_{14}N_8O_3$: 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)diazenyl)-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 $C_{30}H_{19}N_7O_4$: 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)diazenyl)-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 $C_{35}H_{21}N_7O_4$: 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)diazenyl)-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 cruched 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 $C_{27}H_{19}ClN_8$ : 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)diazenyl)-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)diazenyl)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) $cm^{-1}$, $^1$H-NMR (DMSO-$d_6$) $\delta$= 7.9-7.2 (m, 10H, 2Ph) and 2.9 (s, 6H, $2CH_3$). Anal. Calcd for $C_{22}H_{18}N_8$: 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)diazenyl)-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)diazenyl)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) $cm^{-1}$; $^1$H NMR(DMSO-$d_6$): $\delta$= 14.9 (br s, 1H, NH), 7.7 (s, 5H, phN) 7.4-6.8 (m, 10H, 2Ph) and 2.3 (s, 3H, $CH_3$), 1.9 (s, 3H, $CH_3$). Anal. Calcd for $C_{28}H_{22}N_8$ : 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)diazenyl)-3,5-dimethylisoxazole 21.**

A mixture of 3-((4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]-pyridazin-3-yl)diazenyl)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 in73 % yield, m.p.: 214-215 °C; IR: 3210 (NH), 3060 ($CH_{arom}$), 2948 ($CH_{aliph}$), 1630 (C=N), 1590 (PhN) and 1520 (C=C) $cm^{-1}$. $^1$H NMR (DMSO-$d_6$): $\delta$ =11.8 (s, 1H, NH), 7.6-6.8 (m, 10H, 2Ph) 2.1 (s, 3H, $CH_3$), 1.9 (s, 3H, $CH_3$). Anal. Calcd for $C_{22}H_{17}N_7O$: 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)-diazenyl)-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 ($NH_2$ &NH), 1680 (C=O), 1620 (C=N) and 1570 (C=C) $cm^{-1}$;

$^1$H NMR (DMSO-$d_6$): δ = 7.8-7.2 (m, 10H, 2Ph) and 3.4 (br s, 2H, $NH_2$). Anal. Calcd for $C_{20}H_{15}N_9O$: 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[M+ 1, 32.67], 442.10 [M-$CH_3$, 5.68], 337.05[M-CONHPh, 24.57] 100%. Anal. Calcd for $C_{27}H_{19}N_7O$: 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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