American Journal of Chemistry 2013, 3(3): 59-67
DOI: 10.5923/j.chemistry.20130303.04

Synthesis, Spectroscopic Studies and Technical Evaluation of Novel Disazo Disperse Dyes Derived from 3-(2-hydroxyphenyl)-2-pyrazolin-5-ones for Dyeing Polyester Fabrics

Moaz M. Abdou[1,*], **Samir Bondock**[2], **El-Sayed I. El-Desouky**[2] , **M. A. Metwally**[2]

[1]Egyptian Petroleum Research Institute, Nasr city, P.O. 11727, Cairo, Egypt
[2]Department of Chemistry, Faculty of Science, Mansoura University, ET-35516, Egypt

---

Abstract In one of our projects, on disperse dye, we were interested in the synthesis, tautomeric structures and evaluation of pyrazolin-5-one azodyes with better dyeing properties. In this regard novel bisazo-pyrazolin-5-one dyes **3a-f** were synthesized via coupling of the select diazotizated *p*-nitroaniline with 4-arylhydrazono-3-(2`-hydroxyphenyl)-2-pyrazolin-5-ones **2a-f.** On further treatment of these products **3a-f** with acetic anhydride in the presence of *p*-toluenesulfonic acid furnished the corresponding diacetylpyrazolone derivatives **4a-f**. A combination of spectral evidence and acetylation reaction provided a coherent picture of compounds under scrutiny is best described as the azo-hydrazone tautomeric form ($\mathbf{A_{24}}$) as the *Z,E*-configuration. Finally, two series of the synthesized dyes **3a-f** and **4a-f** were applied as disperse dyes for dyeing polyester fabrics and their fastness properties were evaluated. Also, the position of color in CIELAB coordinates (L*, a*, b*, H*, C* and K/S) estimated and discussed.

Keywords Bisazo dye, Pyrazolin-5-ones, Azo-hydrazone Tautomerism, Acetylation, Disperse Dyes, Polyester Fabrics, Dyeing Characteristics

---

1. Introduction

Azo dyes are aversatile class of coloured organic dyes and receive a large amount of attention in the literature, as a consequence of their exciting biological properties and their applications in various fields, such as textiles, papers, leathers, additives, cosmetics and organic synthesis[1–5]. A typical example in this respect are those containing azopyrazolone moieties that deserve special attention due to their applications as disperses dyes[6-8], as well as their widely important applications in biological activities and in analytical chemistry[9-12]. These compounds are potentially tautomeric entities and much attempts[13-18] have subjected to their molecular structure. It has now been conclusively established that they almost exist as the hydrazono tautomer with intramolecular hydrogen bonding between the CO and NH groups.

On the other hand, among the known azo dyes, azophenolic compounds have an elegance role in dyes chemistry due to their auxochromic nature. These properties have made them useful in dyeing of almost all kind of fabrics, whether natural or synthetic. Also, the intriguing properties of these class of compounds in relation to its tautomeric behavior can be ascribed to the existence of azophenol or hydrazoquinone tautomer[19-25].

Therefore, we expect that, the obtained bisazo dyes of two of the above-mentioned azo dye together in a single entity possess interesting tautomeric structure and dyeing characteristics, mainly strong ability of these dyes on fabrics. We have previously reported the synthesis and elucidation of the tautomeric structures of mono and bis-azodyes containing 4-arylhydrazono-3-(2`-hydroxyphenyl)-2-pyrazolin-5-ones, which were able to dye polyester[26-28]. Based on these result, it was thought judicious to study the synthesis of novel bisazo compounds **3a-f** and **4a-f** in order to obtain information for an inclusive study of their tautomeric structure and exploring their application in dyeing polyester fabrics.

2. Experimental Section

2.1. Materials and Instrumentation

All reagents and solvents were used as obtained from the supplier or recrystallized/redistilled as necessary.

---

* Corresponding author:
moaz.chem@gmail.com (Moaz M. abdou)

2,3,4-Chromantrione-3-arylhydrazones **1a-f** were prepared by the process reported in the literature[29]. The various 4-arylhydrazono-3-(2`-hydroxyphenyl)-2-pyrazolin-5-ones **2a-f** were prepared as previously we described[26]. Elemental analyses were performed at the Micro analytical Center, Cairo University, using CHNS-932 (LECO) Vario Elemental Analyzers and the results were within the accepted range (±0.40) of the calculated values. The number of azo group in each disperse dye was determined by the reported process[30], indicating that there are two azo groups (–N,N–) present in the disperse dye molecule. IR spectra were recorded for KBr disc on a Mattson 5000 FTIR spectrometer. The Ultraviolet absorption spectra were recorded in the range 200-800 nm on shimadzu 700 spectrophotometer in spectroquality solvents (Fluka) using a concentration of 10^{-4} mol dm^{-3}. ^{1}H NMR spectra were measured on a Bruker WP 300 in DMSO as a solvent, using TMS as an internal standard, chemical shifts are expressed as δ/ppm, and *J* values are given in Hz. D_2O exchange was applied to confirm the assignment of the signals of OH, and NH protons. Purity of the compounds was assessed by TLC on aluminum silica gel 60 F_{254} (Merck) detected by UV light (254 nm). Scoured and bleached polyester 100% (150 130 g/m^2, 70/2 denier) was obtained from El-Shourbagy, Egypt. The fabric was further treated before dyeing with a solution containing 5 g/L nonionic detergent (Hostapal CV, Clariant-Egypt) and 2 g/L sodium carbonate at a liquor ratio 50:1 at 60°C for 30 min, thoroughly washed in water and air dried at room temperature. The dispersing agent Setamol WS was supplied by BASF (Germany). The dyeing assessment, fastness tests, and color measurements were carried out in Laboratories and Research sector in El-Nasr Company for Spinning and Weaving, El-Mahalla El-Kubra, Egypt. The colorimetric measurements (L*, a*, b*, C*, H* and K/S) were carried out using a Gretag Macbeth CE 7000A spectrophotometer (D65 illumination, 10^0 observer). Fastness to washing was carried out using the automatic launder Rotadyer (sponsored by the British Standard Institute-Society of Dyers and Colourists), fastness to perspiration was assessed according to the test sponsored by the (BSS), fastness to rubbing was carried out according to the standard method of testing (BSS) using Crockmeter of Electric Hungarian FD-17 type, fastness to sublimation was carried out using the Electric Japanese Thermotester T-10 type and fastness to light was carried out using the "Weather-o-meter" (Atlas Electric Devices Co. USA), AATCC standard test method.

2.2. Synthesis and Spectroscopic Characterization

2.2.1. General Procedure for the Synthesis of 4-arylhydrazono-3-(5`-(4-nitrophenylazo)-2`-hydroxyphenyl)-2-pyrazolin-5-ones **3a-f**

A mixture of *p*-nitroaniline (5 mmol), water (4 ml) and conc. HCl (2 ml) was heated with stirring until a clear solution was obtained. This solution was cooled to 0–5℃ and a solution of $NaNO_2$ (5 mmol, 0.35 g) in 3 ml H_2O was added dropwise while the temperature was maintained below 5℃. The resulting mixture was stirred for 30 min in an ice bath. Then, it has been added to a well-stirred solution of 4-arylhydrazono-3-(2`-hydroxyphenyl)-2-pyrazolin-5-ones **2a-f** (5 mmol) and sodium hydroxide (5 mmol, 0.2 g) in ethanol (20 ml). The reaction mixture was allowed to stir at (0–5°C) for 2 hrs, and then the solid was collected by filtration. The crude products thus obtained, were dried and recrystallized from the appropriate solvent to give the corresponding compounds **3a-f.**

2.2.1.1. 4-(2-Phenylhydrazono)-3-(5`-(4-nitrophenylazo)-2`-hydroxyphenyl)-2-pyrazolin-5-one **(3a)**

Yield: 70%; UV-Vis (λ_{max} in dioxane): 265, 362, 400, 440 nm. IR (KBr, ν_{max}/cm^{-1}): 3400 (OH), 33155, 3200 (NH), 3022, 2986 (CH, Ar.), 1658 (C=O, Pyrazolinone), 1612 (>C=N), 1545 (C=C-NH-N=), 1520, 1360, 1330 (NO_2 and $C_{arom.}$-N), 1464 (-N=N-), 1250 (C–O), ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 7.10-8.29 (m, 12H, Ar-H), 10.11 (s, 1H, OH, D_2O exch.), 12.22 (s, 1H, $NH_{(pyrazoline)}$, D_2O exch.), 14.13 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{21}H_{15}N_7O_4$ (429.12): C, 58.74; H, 3.52; N, 22.83. Found: C, 58.67; H, 3.62; N, 22.91.

2.2.1.2. 4-(4-Methylphenyl)hydrazono)-3-(5`-(4-nitrophenyl azo)-2`-hydroxyphenyl)-2-pyrazolin-5-one **(3b)**

Yield: 79%; UV-Vis (λ_{max} in dioxane): 268, 358, 409, 443 nm. IR (KBr, ν_{max}/cm^{-1}): 3412 (OH), 3250, 3190 (NH), 3041, 3021 (CH, Ar.), 2909 (CH, Aliph.), 1661 (C=O, Pyrazolinone), 1619 (>C=N), 1569 (C=C-NH-N=), 1518, 1362, 1340 (NO_2 and $C_{arom.}$-N), 1458 (-N=N-), 1255 (C–O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 2.49 (s, 3H, CH_3), 7.08-8.20 (m, 11H, Ar-H), 10.22 (s, 1H, OH, D_2O exch.), 12.30 (s, 1H, NH $_{(pyrazoline)}$, D_2O exch.), 14.21 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{22}H_{17}N_7O_4$ (443.13): C, 59.59; H, 3.86; N, 22.11. Found: C, 59.71; H, 3.99; N, 22.08.

2.2.1.3. 4-(4-Methoxyphenyl)hydrazono)-3-(5`-(4-nitrophen ylazo)-2`-hydroxyphenyl)-2-pyrazolin-5-one **(3c)**

Yield: 81%; UV-Vis (λ_{max} in dioxane): 276, 362, 412, 446 nm. IR (KBr, ν_{max}/cm^{-1}): 3396 (OH), 3240, 3188 (NH), 3048, 3022 (CH, Ar.), 2912 (CH, Aliph.), 1666 (C=O, Pyrazolinone), 1629 (>C=N), 1560 (C=C-NH-N=), 1526, 1364, 1322 (NO_2 and $C_{arom.}$-N), 1469 (-N=N-), 1262 (C–O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 3.23 (s, 3H, OCH_3), 7.19-8.17 (m, 11H, Ar-H), 10.27 (s, 1H, OH, D_2O exch.), 12.31 (s, 1H, NH $_{(pyrazoline)}$, D_2O exch.), 14.09 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{22}H_{17}N_7O_5$ (459.13): C, 57.52; H, 3.73; N, 21.34. Found: C, 57.69; H, 3.92; N, 21.43.

2.2.1.4. 4-(4-Chlorophenyl)hydrazono)-3-(5`-(4-nitrophenyl azo)-2`-hydroxyphenyl)-2-pyrazolin-5-one **(3d)**

Yield: 68%; UV-Vis (λ_{max} in dioxane): 266, 356, 401, 440 nm. IR (KBr, ν_{max}/cm^{-1}): 3436 (OH), 3261, 2193 (NH), 3054

(CH, Ar.), 1662 (C=O, Pyrazolinone), 1631 (>C=N), 1548 (C=C-NH-N=), 1527, 1369, 1341 (NO_2 and $C_{arom.}$-N), 1466 (-N=N-), 1276 (C–O), 770 (C–Cl). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 7.22-8.29 (m, 11H, Ar-H), 10.48 (s, 1H, OH, D_2O exch.), 12.24 (s, 1H, $NH_{(pyrazoline)}$, D_2O exch.), 14.40 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{21}H_{14}ClN_7O_4$ (463.08): C, 54.38; H, 3.04; N, 21.14. Found: C, 54.60; H, 3.21; N, 21.30.

2.2.1.5.4-(4-Bromophenyl)hydrazono)-3-(5`-(4-nitrophenylazo)-2`-hydroxyphenyl)-2-pyrazolin-5-one (**3e**)

Yield: 78%; UV-Vis (λ_{max} in dioxane): 274, 363, 422, 449 nm. IR (KBr, ν_{max}/cm^{-1}): 3500 (OH), 3251, 3188 (NH), 3044, 3010 (CH, Ar.), 1664 (C=O, Pyrazolinone), 1616 (>C=N), 1553 (C=C-NH-N=), 1509, 1375, 1348 (NO_2 and $C_{arom.}$-N), 1472 (-N=N-), 1259 (C–O), 580 (C–Br). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 7.30-8.21 (m, 11H, Ar-H), 10.34 (s, 1H, OH, D_2O exch.), 12.27 (s, 1H, $NH_{(pyrazoline)}$, D_2O exch.), 14.18 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{21}H_{14}BrN_7O_4$ (507.03): C, 49.62; H, 2.78; N, 19.29. Found: C, 49.86; H, 2.90; N, 19.41.

2.2.1.6. 4-(4-Nitrophenyl)hydrazono)-3-(5`-(4-nitrophenylazo)-2`-hydroxyphenyl)-2-pyrazolin-5-one (**3f**)

Yield: 83%; UV-Vis (λ_{max} in dioxane): 278, 359, 424, 453 nm. IR (KBr, ν_{max}/cm^{-1}): 3400 (OH), 3200 (NH), 3030, 2987 (CH, Ar.), 1664 (C=O, Pyrazolinone), 1634 (>C=N), 1555 (C=C-NH-N=), 1499, 1378, 1330 (NO_2 and $C_{arom.}$-N), 1458 (-N=N-), 1254 (C–O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 7.11-8.14 (m, 11H, Ar-H), 10.22 (s, 1H, OH, D_2O exch.), 12.40 (s, 1H, $NH_{(pyrazoline)}$, D_2O exch.), 14.36 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{21}H_{14}N_8O_6$ (474.1): C, 53.17; H, 2.97; N, 23.62. Found: C, 53.07; H, 3.12; N, 23.80.

2.2.2. General Procedure for the Synthesis of 4-arylhydrazono-3-(5`-(4-nitrophenylazo)-2`-acetoxyphenyl)-1-acetyl-2-pyrazolin-5-ones **4a-f**

A mixture of **3a-f** (5 mmol) and acetic anhydride (20 ml) in the presence of a catalytic amount of *p*-toluenesulfonic acid was stirred at 100℃ for 4-8.5 h. After removal of the solvent in vacuo, cold water was added to the residue. The resulting diacetylpyrazolone derivatives **4a-f** were filtered off and recrystallized from the appropriate solvent.

2.2.2.1.4-(Phenylhydrazono)-3-(5`-(4-nitrophenylazo)-2`-acetoxyphenyl)-1-acetyl-2-pyrazolin-5-one (**4a**)

Yield: 65%; IR (KBr, ν_{max}/cm^{-1}): 3190 (NH), 3033, 3010 (CH, Ar.), 1726 (C=O, ester), 1687 (C=O, *N*-acetyl), 1655 (C=O, Pyrazolinone), 1620 (>C=N), 1546 (C=C-NH-N=), 1527, 1365, 1339 (NO_2 and $C_{arom.}$-N), 1420 (-N=N-), 1266 (C–O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 2.99 (s, 3H, $NCOCH_3$), 3.35 (s, 3H, $OCOCH_3$), 7.21-8.04 (m, 12H, ArH), 13.89 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{25}H_{19}N_7O_6$ (513.14): C, 58.48; H, 3.73; N, 19.10. Found: C, 58.63; H, 3.88; N, 19.32.

2.2.2.2.4-(4-Methylphenyl)hydrazono)-3-(5`-(4-nitrophenylazo)-2`-acetoxyphenyl)-1-acetyl-2-pyrazolin-5-one (**4b**)

Yield: 79%; IR (KBr, ν_{max}/cm^{-1}): 3212 (NH), 3054 (CH, Ar.), 2931 (CH, Aliph.), 1732 (C=O, ester), 1690 (C=O, *N*-acetyl), 1662 (C=O, Pyrazolinone), 1623 (>C=N), 1539 (C=C-NH-N=), 1527, 1373, 1349 (NO_2 and $C_{arom.}$-N), 1426 (-N=N-), 1268 (C–O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 2.48 (s, 3H, CH_3), 3.02 (s, 3H, $NCOCH_3$), 3.37 (s, 3H, $OCOCH_3$), 7.24-8.11 (m, 11H, Ar-H), 14.23 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{26}H_{21}N_7O_6$ (527.16): C, 59.20; H, 4.01; N, 18.59. Found: C, 59.42; H, 4.20; N, 18.67.

2.2.2.3.4-(4-Methoxyphenyl)hydrazono)-3-(5`-(4-nitrophenylazo)-2`-acetoxyphenyl)-1-acetyl-2-pyrazolin-5-one (**4c**)

Yield: 73%; IR (KBr, ν_{max}/cm^{-1}): 3219 (NH), 3054, 3023(CH, Ar.), 2919 (CH, Aliph.), 1718 (C=O, ester), 1688 (C=O, *N*-acetyl), 1655 (C=O, Pyrazolinone), 1618 (>C=N), 1552 (C=C-NH-N=), 1519, 1370, 1346 (NO_2 and $C_{arom.}$-N), 1420 (-N=N-), 1259 (C–O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 2.99 (s, 3H, OCH_3), 3.25 (s, 3H, $NCOCH_3$), 3.45 (s, 3H, $OCOCH_3$), 7.29-8.09 (m, 11H, Ar-H), 14.37 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{26}H_{21}N_7O_7$ (543.15): C, 57.46; H, 3.89; N, 18.04. Found: C, 57.34; H, 4.08; N, 18.20.

2.2.2.4.4-(4-Chlorophenyl)hydrazono)-3-(5`-(4-nitrophenylazo)-2`-acetoxyphenyl)-1-acetyl-2-pyrazolin-5-one (**4d**)

Yield: 84%; IR (KBr, ν_{max}/cm^{-1}): 3253 (NH), 3046, 3011 (CH, Ar.), 1730 (C=O, ester), 1679 (C=O, *N*-acetyl), 1648 (C=O, Pyrazolinone), 1610 (>C=N), 1549 (C=C-NH-N=), 1526, 1373, 1342 (NO_2 and $C_{arom.}$-N), 1428 (-N=N-), 1259 (C–O), 771 (C–Cl). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 3.02 (s, 3H, $NCOCH_3$), 3.61 (s, 3H, $OCOCH_3$), 7.11-8.40 (m, 11H, Ar-H), 14.22 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{25}H_{18}ClN_7O_6$ (547.1): C, 54.80; H, 3.31; N, 17.89. Found: C, 54.98; H, 3.50; N, 17.77.

2.2.2.5.4-(4-Bromophenyl)hydrazono)-3-(5`-(4-nitrophenylazo)-2`-acetoxyphenyl)-1-acetyl-2-pyrazolin-5-one (**4e**)

Yield: 69%; IR (KBr, ν_{max}/cm^{-1}): 3233 (NH), 3034, 3002 (CH, Ar.), 1741 (C=O, ester), 1684 (C=O, *N*-acetyl), 1659 (C=O, Pyrazolinone), 1617 (>C=N), 1555 (C=C-NH-N=), 1514, 1361, 1336 (NO_2 and $C_{arom.}$-N), 1411 (-N=N-), 1266 (C–O), 578 (C–Br). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 3.03 (s, 3H, $NCOCH_3$), 3.38 (s, 3H, $OCOCH_3$), 7.13-8.37 (m, 11H, Ar-H), 14.12 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{25}H_{18}BrN_7O_6$ (591.05): C, 50.69; H, 3.06; N, 16.55. Found: C, 50.88; H, 3.25; N, 16.68.

2.2.2.6. 4-(4-Nitrophenyl)hydrazono)-3-(5`-(4-nitrophenylazo)-2`-acetoxyphenyl)-1-acetyl-2-pyrazolin-5-one **(4f)**

Yield: 60%; IR (KBr, ν_{max}/cm^{-1}): 3212 (NH), 3091, 3060 (CH, Ar.), 1734 (C=O, ester), 1687 (C=O, *N*-acetyl), 1662 (C=O, Pyrazolinone), 1622 (>C=N), 1551(C=C-NH-N=), 1519, 1374, 1339 (NO_2 and $C_{arom.}$-N), 1423 (-N=N-), 1272 (C–O). ^{1}HNMR (300 MHz, DMSO-d_6, δ/ppm): 3.22 (s, 3H, $NCOCH_3$), 3.50 (s, 3H, $OCOCH_3$), 7.13-8.30 (m, 11H, Ar-H), 14.31 (s, H, $NH_{(hydrazone)}$, D_2O exch.). Anal. Calcd. for $C_{25}H_{18}N_8O_8$ (558.12): C, 53.77; H, 3.25; N, 20.06. Found: C, 53.97; H, 3.14; N, 20.19.

2.3. Dyeing and Fastness Determinations

2.3.1. Preparation of Dye Dispersion

The required amount of the dye (2% shade) was dissolved in 1 ml acetone and then added dropwise with stirring to a solution of Setamol WS (sodium salt of a condensation product of naphthalene sulfonic acid and formaldehyde) as anionic dispersing agent of BASF. The dye was precipitated in a fine dispersion ready for use in dyeing after evaporation of the solvent by warming.

2.3.2. Dyeing of Polyester Fabrics

The dye bath (1:20, good to dye liquor ratio) in a sealed stainless steel dye pots of 250 ml capacity in "Galvanin-Marino VI-Italy" dyeing machine. Additional dispersing agent (0.5-1.0 g/l) was added and the pH of the bath adjusted to 5.5 using glacial acetic acid. Dyeing carried out by raising the dye bath temperature from 20to 130℃ at a rate of 3℃/min and holding at this temperature for 60 min before rapidly cooling to 50°C at 9.9°C/min. The dyed fabrics were then rinsed with cold water, reduction-cleared using sodium hydroxide (2 g/l) and sodium hydrosulphite (1 g/l) and soaped with 2% nonionic detergent and ammonia (pH 8.5) at 50°C for 30 min to improve washing fastness.

2.3.3. Color Fastness Tests

The color fastness of dyeing was evaluated using the standard method[31] and given in Table 1. The fastness to light, sublimation and perspiration was assessed in accordance with AATCC-15 (1985). The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC-88 (1988) and the wash fastness test in accordance with IS: 765-1979.

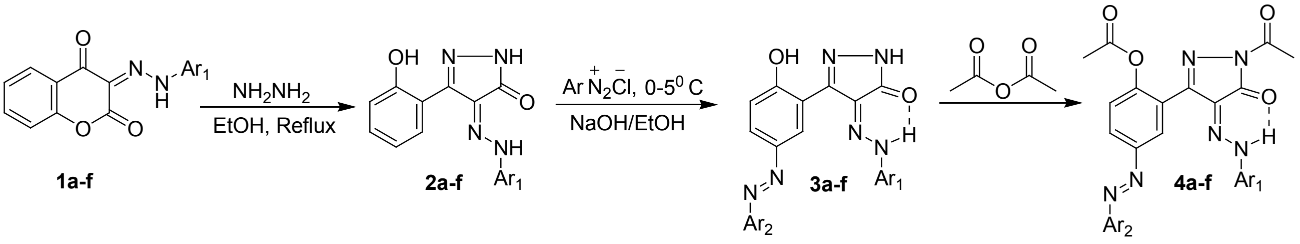
2.3.4. Color Assessment

The colorimetric parameters (Table 2) of the dyed polyester fabrics were determined on a reflectance spectrophotometer (GretagMacbeth CE 7000a), equipped with a D65/108 source and barium sulfate as standard blank, UV excluded ,specular component included and three repeated measurements average settings.

3. Results and Discussions

3.1. Synthesis and Tautomeric Structure

The basic synthetic route employed for the construction of the target compounds **4a-f** is outlined in Scheme 1. The 4-arylhydrazono-3-(2`-hydroxyphenyl)-2-pyrazolin-5-ones **2a-f** required for the construction of the target molecules were synthesized by reaction of 2,3,4-chromantrione-3-aryl hydrazones **1a-f** with hydrazine hydrate in boiling ethanol as we have recently reported[27]. Coupling of compounds **2a-f** in an alkaline solution at 0-5 ℃ with diazotized *p*-nitroaniline afforded the corresponding bis-arylazo derivatives **3a-f**. Treatment of these products, **3a-f,** with acetic anhydride in the presence of *p*-toluenesulfonic acid gave the corresponding diacetyl derivatives **4a-f** (Scheme 1).



Ar_1 : a) C_6H_5- b) 4-CH_3-C_6H_4- c) 4-$CH_3OC_6H_4$- d) 4-Cl-C_6H_4- e) 4-Br-C_6H_4- f) 4-NO_2-C_6H_4-
Ar_2 : 4-NO_2-C_6H_4-

Scheme 1. Synthesis of the studied compounds **3a-f** and **4a-f**

It is noteworthy to point out that several tautomeric structures may be postulated for bisazo dyes **3a-f**. The following are theoretically possible $\mathbf{A_{1-24}}$ owing to tautomeric displacement (Fig. 1). It is possible to disqualify the most of these structures by examining the spectral data and chemical properties of the compounds actually obtained.

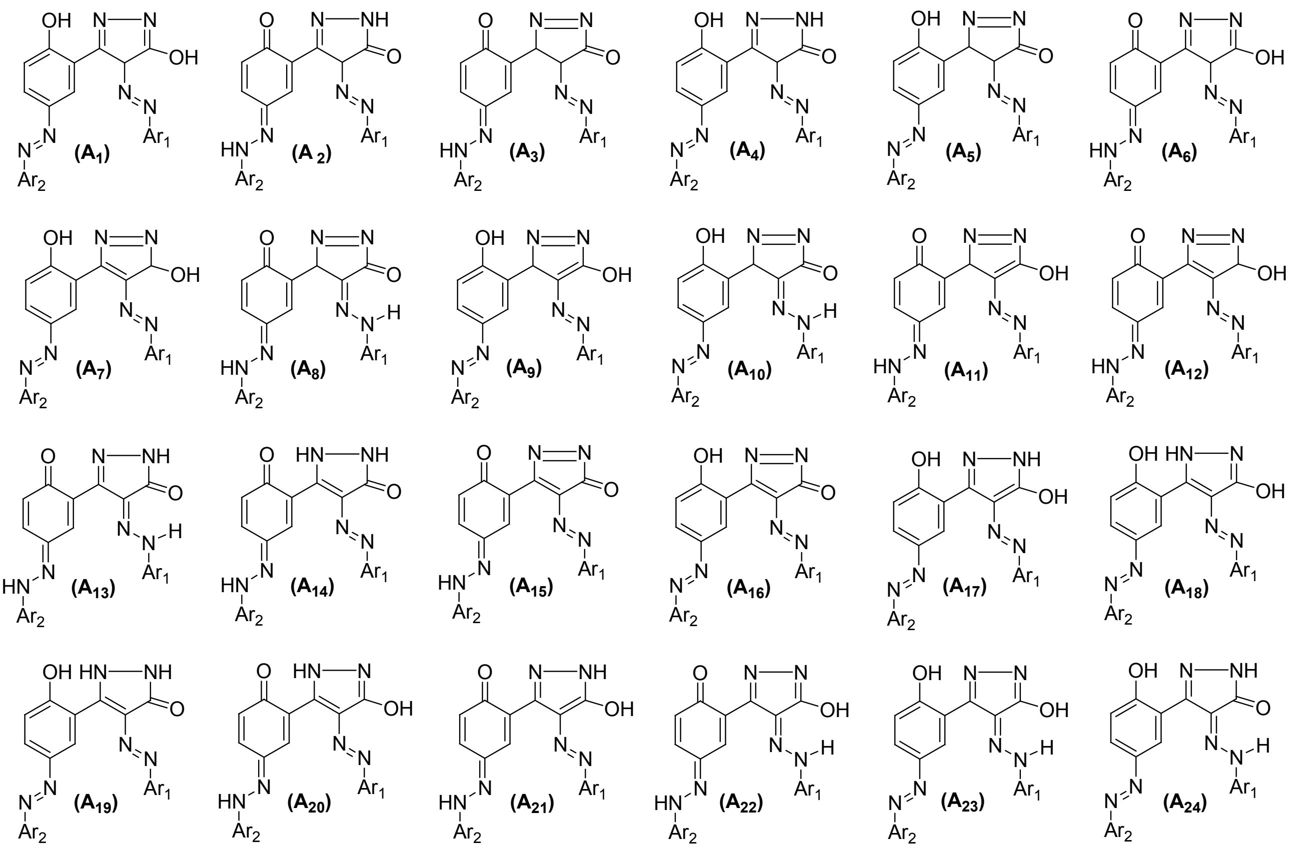


Figure 1. Possible tautomeric structures of compounds under scrutiny **3a-f**

In an attempt to shed light on the actual tautomeric structure(s) of these compounds **3a-f**, we studied their ^1H NMR spectra. The latter spectra revealed that absence of a proton at C-4 signal at about 6.4 ppm[32] excludes the possibility of the CH-azo structures A_{1-6}. The fact that the coupling products **3a-f** showed a set of three deuterium exchangeable protons confirming the presence of three different (N–H) groups and/or (O–H) groups (see the experimental part). On the basis of this fact, it is reasonable to rule out the possibility of structures A_{7-12} since these structures would not possess this property.

Moreover, the deconvolution of the electronic absorption spectral data of that compounds **3a-f** revealed that all investigated dyes showed in each case four absorption bands in the regions 265-278, 358-363, 400-424 and 430-450 nm. The first three absorption pattern were observed and these values are practically very close to those reported for the hydrazo chromophore of pyrazolin-5-one dyes[11] which also, is in agreement with that reported in our recent publications of the annulated similar mono and bis azodyes containing 4-arylhydrazono-3-(2`-hydroxyphenyl)-2-pyrazolin-5-ones[26-28]. Also, the possibility that compounds **3a-f** exist in hydrazo-quinone structure is ruled out because of these compounds showed no absorption between 475–510 nm[33]. Thus, the observation of bands at 440–453 nm is indicative of the azophenol form of compounds[25,34]. These compounds, therefore, prefers to stay exclusively in the azo-hydrazone tautomeric structure (A_{24}) and this evidence is in agreement with those values for 4-arylhydrazono-3-(5`-(4-nitrophenylazo)-2`-hydroxy phenyl)-1-phenyl-2-pyrazolin-5-ones[28].

Corroborative evidence that compounds **3a-f** exist in the tautomeric form (A_{24}) comes from the infrared spectra since the band at 1666-1658 cm^{-1} which is assigned to C=O stretching vibration[32] eliminates the tautomeric structures with no carbonyl group ($A_{1,7,9,17,18,23}$) from consideration. In addition, the structures ($A_{2,3,8,13,14,15}$) were discarded on the basis of this compounds exhibit absorption bands between 3500-3396 cm^{-1} region are attributed to the hydroxyl OH group[26-28]. Further evidence that this compounds gave a deep color with ferric chloride that prove the existence of enolic hydroxyl group[35]. Also, the weak bands assignable to the stretching vibration of azo linkages in compounds **3a-f** can be observed at the frequency range of 1474-1458 cm^{-1} as reported in the correlation data for N=N bonds[36]. In addition, the absorption maxima at 3200-3188 and 3315-3200 cm^{-1} which were assigned to NH (hydrazone) and NH (pyrazoline) stretching frequencies respectively [26-28]. The NH frequency assigned to the hydrazone NH at 3200-3188 cm^{-1} is low for an unbonded NH group since the hydrazone NH group is involved in intramolecular hydrogen bonding (tautomer A_{24})[27]. The prominent band occurs around 1550 cm^{-1}, on the basis of previous results[37], reasonably be ascribed to the benzene ring C=C skeletal vibration associated with the -NH-N= linkage. In the region

1634-1612 cm^{-1}, the hydrazone $\nu_{C=N}$ stretching vibration is also expected[38, 39]. The pyrazolinones investigated possess the hydrazono moiety; therefore, the stretching vibration of the $C_{arom.}$-N linkage show band around 1350 cm^{-1} in their spectra[40]. These results were compatible with a conclusion of such compounds **4a-f** exist as the structure (**A_{24}**).

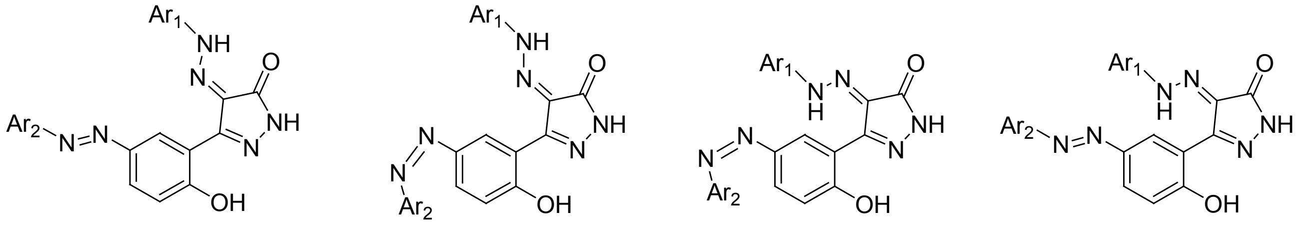
This rationalization is substantiated by that we have previously reported for structurally related compounds [26-28] and also this is rather confirmed from other investigations that were carried out to establish the tautomeric structures of arylazopyrazolone and arylazophenol using a variety of spectroscopic techniques. The spectral data generally led to the conclusion that the tautomeric equilibrium of the arylazopyrazolone dyes is in favor of hydrazone form[7] and the tautomeric equilibrium of arylazophenol dyes is in favour of azo form[19-25]. These suggest that these dyes are predominantly in azo-hydrazo form (**A_{24}**).

Next to, gain further insight into the structure of tautomerism of the azo-hydrazo form (**A_{24}**), we carried out the acetylation reaction of **3a-f**. Thus, treatment of **3a-f** with acetic anhydride in the presence of *p*-toluenesulfonic acid afforded the corresponding O- and *N*-diacetyl derivatives (compounds **4a-f**, scheme 1). ^{1}H NMR spectra of **4a-f** emphasis that one deuterium exchangeable proton confirming the presence of hydrazone NH proton, while signal characteristic for OH (phenolic) and NH (pyrazoline) protons are absent (see the experimental part). This is coincident with the outputs of reading their IR spectra revealed three carbonyl absorption bands in regions 1741-1718, 1690-1679 and 1662-1648 cm^{-1} characteristic for O-acetyl, *N*-acetyl and pyrazolone carbonyl groups, respectively. The conspicuous absence of absorption bands characteristic for OH (phenolic) and NH (pyrazoline) confirms the assumption for O- and *N*-acetylation reaction. Further evidence that diacetylation occurred was obtained by elemental analysis. Hence, these results arose the conclusion that compounds **3a-f** exist in the tautomeric form (**A_{24}**).

Additionally, it is noteworthy to cast some light on the configuration of the double bonds of $C=N_{(hydrazo\ pyrazolone)}$ and $N=N_{(azophenol)}$ for the most stable form (**A_{24}**) can lead to four possibilities: *ZE, ZZ, EE, EZ* isomers (Fig. 2). Here, the effect of intramolecular hydrogen bonding and steric factor can heavily tilt the equilibrium toward one of the isomers[41]. Thus, the last two isomers can be rationalized rejection on the basis of steric factor. In agreement of this conclusion, the Z-configuration of hydrazone are expected to be stabilized by intramolecular hydrogen bonding between the C=O and hydrazo NH group. This also based on analog of the our recently reported structure of 4-arylhydrazono-3-(2`-hydroxyphenyl)-2-pyrazolin-5-ones, whose *Z*-isomer has been confirmed by spectroscopic data and supported by theoretical calculation[26-28]. On the other hand, the preferential formation of *trans*-azophenol supports from the identity of the UV characteristics of them with those of *trans*-azobenzene (λ_{max}=445)[42]. This *trans* configuration can be evident from the diagnostic bands assignable to the stretching-vibration mode of N=N at 1474-1458 cm^{-1}[43]. The absence of tangible band associated with the bending mode at 927 cm^{-1} has also ruled out the existence of compounds in mixed conformers of *cis* and *trans*[43]. It is therefore realistic to conclude that such compounds **3a-f** prefer to stay exclusively in the azo-hydrazo structure (**A_{24}**) as the *Z,E*-configuration.

3.2. Dyeing and Fastness Properties

The development of disperse dyes "Dyes insoluble in water and applied from aqueous dispersion rather than from solution" was a revolutionary solution to the problem of coloration of synthetic fibers. The dyes were essentially insoluble in water and were prepared for application by being ground, in the presence of dispersing agents, to microscopically fine particles of the order of a few microns and, then, by pan drying the resultant suspension. The resulting readily dispersible solid could then dye the more hydrophobic acetate fiber by partitioning into the fiber from low dye bath concentrations. The synthesized disperse dyes under investigation **3a-f**, **4a-f** were applied to polyester fabric at 2% shade by high-temperature pressure technique (130℃). The dyes on polyester fabrics were evaluated in terms of their fastness properties as shown in Table 1.



Z,E (cis-trans) *Z,Z* (cis-cis) *E,Z* (trans-cis) *E,E* (trans-trans)

Figure 2. Possibilities configuration for the compounds **3a-f** as they exist in the tautomeric form (**A_{24}**)

Table 1. Fastness properties[a] of the synthesized dyes **3a-f, 4a-f** on polyester fabrics

Compound no.	Washing	Perspiration		Rubbing		Sublimation fastness		Light (80 h)
		Acid	Alkali	Dry	Wet	180^{o}C	210^{o}C	
3a	4-5	4	4	4	4-5	4	4	6
3b	5	3-4	4	3	4-5	4	3-4	6
3c	4	4	4	4	3-4	4-5	4	6
3d	4	4	4-5	3	4	5	4	6
3e	5	4	4	4	4	5	4-5	7
3f	4	4	4	4	3-4	5	4-5	7
4a	4	3-4	4	3-4	3-4	4	3-4	6-7
4b	4	4	3-4	3-4	3-4	4	4	6-7
4c	4	3-4	3-4	4	4-5	4	3-4	6
4d	4	4	4-5	3	3-4	4	4	7
4e	4	4	3-4	4	4	4	3-4	6-7
4f	3-4	4	4	3-4	3-4	4-5	4	7

[a] = light fastness, 1–8 scale; washing, perspiration, rubbing and sublimation fastness, 1–5 scale

3.2.1. Fastness to Washing

The dyed polyester fabrics have good fastness to washing according to the international Geometric Grey scale[44] and this may be attributed to inadequate diffusion of dye molecule into the fabrics.

3.2.2. Fastness to Perspiration: (Acid and Alkaline)

The majority of these dyes were found to have good perspiration fastness 3–4. Also, the acetylation of hydroxyl group reduced the fastness to perspiration properties.

3.2.3. Fastness to Rubbing

The test is designed to determine the amount of color transferred from the surface of colored fabrics to another surface by rubbing. Most of the dyes have a moderate (3) to good (4) rubbing fastness and this may be attributed to inadequate diffusion of dye molecule into the fabrics.

3.2.4. Fastness to Sublimation

Sublimation fastness properties of synthesized dyes expressed as color staining on the undyed polyester piece ranged from good to very good according to the international Geometric Grey Scale[44]. In most cases, the best sublimation fastness was obtained by unacetylated dyes.

3.2.5. Fastness to Light

It is significantly depended on nature of the substituents which change the electron density around hydrazo group. The high fastness to light may be attributed to electron accepting groups. This agrees with the notion that the azo compounds appended with electron-withdrawing substituents on the diazo components are less prone to photofading[45]. Generally, the prepared dyes showed satisfactory fastness to light ranging 6-7 according to the international Geometric Grey Scale[44].

3.3. Color Assessment

The color parameters (Table 2) of the dyed polyester fabrics were measured using a spectrophotometer (GretaMacbeth Color Eye 7000A, USA) under illuminant D65, with a 10^{o} standard observer. The assessment of color-dyed fabrics was made in terms of tristimulus colorimetry. The following CIELAB coordinates are measured, lightness (L*), chroma (C*), hue angle from 0^{o} to 360^{o} (h), (a*) value represents the degree of redness (positive) and greenness (negative) and (b*) represents the degree of yellowness (positive) and blueness (negative). The K/S value which has been employed as the dye uptake or color strength was calculated for each dyed specimen as well as for an undyed one at a maximum absorption wavelength of 360 nm from the reflectance values using the Kubelka-Munk equation[43] as follows;

$$K/S = (1-R)^2 / 2R,$$

where K is the coefficient of absorption; S is the coefficient of scattering; R is the reflectance value of the fabric at peak wavelength. The parent dyestuff in each group is taken as the standard in the color difference calculation (ΔL*, ΔC*, and ΔH*). The results were obtained using CIELAB techniques, and are given in Table 2, where ΔL* is the lightness difference, ΔC* is the chroma difference, and ΔH* is the hue difference. A negative sign of ΔL* indicates that the dyed fiber becomes darker than the standard, whereas 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, whereas a positive sign indicates that the dyed fiber becomes brighter than the standard. A negative sign of ΔH* indicates that the color shifted to a red color, while a positive sign indicates that the color shifted to yellowish. The results are shown in Table 2 tend to give the following conclusions:

i. K/S values in the dyes under investigation **3a-f, 4a-f** vary from 36.9 to 40.2, which all members of this groups increases strength of the K/S value of the polyester fabric compared with that of the parent **3a.** Dyes **4a-f** which contain the acetate moiety are characterized by higher K/S values compared with their analogues **3a-f**, indicating that the introduction of acetate moiety in dyes **4a-f** increases the color strength on polyester fabric.

Table 2. Colour values of dyes **4a-f** on polyester fabrics (light source D65/10º observer)

Compound no.	K/S	L*	a*	b*	C*	H*	Δa*	Δb*	ΔC*	ΔL*	ΔH*
3a	36.9	58.3	31.1	68.1	78.2	64.9	--	--	--	--	--
3b	37.4	60.9	28.1	69.5	80.8	68.8	-3.0	1.4	2.6	2.6	3.8
3c	38.2	59.1	37.5	74.6	84.9	63.6	6.4	6.5	6.7	0.8	-0.2
3d	38.0	66.5	20.1	66.5	72.1	73.8	-11.0	-1.6	-6.1	8.2	6.5
3e	37.7	60.2	29.4	70.9	77.2	67.8	-2.7	2.8	-1.0	1.9	3.0
3f	38.2	59.3	38.1	74.8	74.8	63.1	7.0	6.7	-3.4	1.0	-1.0
4a	37.2	68.1	20.5	80.8	72.8	75.1	-10.6	12.7	-5.4	9.8	11.9
4b	38.0	60.1	16.9	70.7	76.1	76.3	-14.2	2.6	-2.1	1.8	12.4
4c	39.0	61.3	22.7	74.2	78.3	71.6	-8.4	6.1	0.1	3.0	5.2
4d	40.2	72.2	24.6	73.8	76.2	78.6	-6.5	5.7	-2.0	13.9	14.0
4e	38.6	68.6	11.1	65.6	60.1	80.8	-20.0	-2.5	-18.1	10.3	16.9
4f	38.1	62.7	25.2	71.7	66.1	70.2	-5.9	3.6	-12.1	4.4	6.6

ii. The color hues of the dyes under investigation on polyester fabric are shifted to the yellowish direction on the yellow-blue axis according to the positive values of b*.

iii. The color hue of the most of the dyes on polyester fabric is shifted to the greenish direction on the red-green axis as indicated from the negative value of a*.

iv. In general, dyeing with the acetylated dyes **4a-f** were lighter (as shown by the higher L* values) and duller (as shown by the lower C* values) than the corresponding unacetylated dyes **3a-f**.

4. Conclusions

This article describes the synthesis of the hitherto unreported two series of novel bisazo disperse dyes **3a-f** and **4a-f** having different substituted groups. The influence of the dye structures on the spectroscopic and dyeing properties was investigated. The spectroscopic data of the compounds prepared **3a-f** and their acetylation reaction have provide the contention that such compounds prefers to exist exclusively in the azo-hydrazo structure (**A_{24}**) as the *Z,E* -configuration. Finally, the prepared dyestuffs were dyed on polyester fabrics and subsequently their dyeing properties, light, washing, perspiration, rubbing and sublimation fastnesses and color coordinates were determined. The outstanding characteristics of these properties were proved to be good. Finally, it is worth referring from these investigations, it may be concluded that dyestuffs **3a-f** and **4a-f** are reasonable bis azo disperse that may be endowed with important dyeing properties on polyester fabrics.

ACKNOWLEDGMENTS

Thanks are due to chemist. Afaf El tanahy, Head of processing sector, El-Nasr Company for Textile, Spinning and Weaving, El-Mahalla El-Kubra, Egypt. for dyeing assessment, fastness tests, and color measurements. Mr. Moaz M. Abdou is grateful for the support from Academy of Scientific Research and Technology Fund (ASRT, Egypt) for this research work.

REFERENCES

[1] Klaus, H. Industrial Dyes, Chemistry, Properties, Applications; Wiley-VCH: Weinheim; 2003; pp. 20–35.

[2] Catino, SC.; Farris, RE. In: Grayson M. (Ed.); Concise Encyclopedia of Chemical Technology; Wiley: New York; 1985; pp. 142–144.

[3] Zollinger, H. Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments, 3rd revised ed.; Wiley-VCH: Weinheim; 2003.

[4] El-Sonbati, AZ.; Belal, AAM.; El-Wakeel, SI.; Hussien, MA. Spectrochim Acta Part A: Mol Biomol Spectrosc., 2004, 60, 965–972.

[5] Herbst, W.; Hunger, K. Industrial Organic Pigments: Production, Properties, Applications 2nd; VCH: Weinheim, Germany, 1997.

[6] Metwally MA, Bondock S, El-Desouky SI, Abdou MM. A worthy insight into the dyeing applications of azo pyrazolyl dyes. Int. J. Modern Org. Chem., 2012, 1: 165-92.

[7] Metwally MA, Bondock S, El-Desouky SI, Abdou MM. Pyrazol-5-ones: tautomerism, synthesis and reactions. Int. J. Modern Org. Chem. 2012, 1: 19-54.

[8] Karci F, Ertan N. Hetarylazo disperse dyes derived from 3-methyl-1-(3′,5′-dipiperidino-s-triazinyl)-5-pyrazolone as coupling component. Dyes Pigm. 2002; 55: 99–108.

[9] Ozdemir A, Turan-Zitouni G, AsimKaplancikli Z, Revial G, Demirci F, Iscan G. Preparation of some pyrazoline derivatives and evaluation of their antifungal activities. J Enzyme Inhib Med Chem. 2010; 25: 565–71.

[10] Küçükgüzel SG, Rollas S. Synthesis, characterization of novel coupling products and 4-arylhydrazono-2-pyrazoline-5 -ones as potential antimycobacterial agents. Farmaco 2002; 57: 583–87.

[11] Küçükgüzel SG, Rollas S, Erdeniz H, Kiraz M, Cevdet Ekinci A, Vidin A. Synthesis, characterization and pharmacological properties of some 4-arylhydrazono-2-pyrazoline-5-one derivatives obtained from heterocyclic amines. Eur. J. Med.

Chem. 2000; 35 (7): 761−71.

[12] Takeo S, Ei-ichi Y, Yoshio O, Teruo A, Kazuo H. The photochemical transannular reaction of[2.2]metacyclophane. Bull. Chem. Soc. Jap. 1965; 38 (6): 1049–50.

[13] Minkin, VI, Garnovskii AD, Elguero J, Katritzky AR, Denisko OV. The tautomerism of heterocycles: Five-membered rings with two or more heteroatoms. Adv. Heterocycl. Chem., 2000, 76: 157−323.

[14] Whitaker A. CI. pigment Yellow 10, 4[(2`,5`Dichlorophenyl)hydrazono]-5-methyl-2-phenyl-3H-pyrazol-3-one. Acta crystallogr., 1988; C44: 1767−70.

[15] Whitaker A. CI. pigment Yellow 60, 4-(2-Chlorophenylhydr azono)-3-methyl-1-phenyl-5-pyrazolone. Acta crystallogr., 1988; C44: 1587−90.

[16] Connor JA, Kennedy RJ, Dawies HM, Hursthouse MB, Walker NPC. Structural studies of arylazo and arylimino compounds. 15N NMR and X-ray crystallographic studies of azo–hydrazo tautomerism. J. Chem. Soc., Perkin Trans., 1990; 2: 203−07.

[17] Whitaker A. Crystal structures of azo colorants derived from pyrazolone: a review. J. Soc. Dyers Colour 1995, 11, 66−72.

[18] Emeleus LC, Cupertino DC, Harris SG, Owens S, Parsons S, Swart RW, Tasker PA, White DJ. Diazopyrazolones as weak solvent extractants for copper from ammonia leach solutions. J. Chem. Soc., Dalton Trans., 2001, 2, 1239−45.

[19] Sawicki E. Physical properties of the aminoazobenzene dyes. VII. Absorption spectra of 4-aminoazobenzene dyes in ethanol. J. Org. Chem., 1957; 22 (8): 915–919.

[20] Sawicki E. Physical properties of the aminoazobenzene dyes. VIII. Absorption spectra in acid solution. J. Org. Chem., 1957; 22 (9), 1084–88.

[21] Lycka A, Machacek V. 13C and 15N-NMR studies of the azo-hydrazone tautomerism of some azo dyes.Dyes Pigm., 1986; 7(3), 171–85.

[22] Ueno K. Polyazobenzenes. III. infrared absorption spectra of some polyazobenzenes. J. Am. Chem. Soc., 1957; 79 (12), 3205–08.

[23] Burawoy A, Thompson AR. The effect of solvents on the tautomeric equilibria of 4-arylazo-1-naphthols and the ortho-effect. J. Chem. Soc., 1953: 1443–47.

[24] Hadzi D. Absorption spectra and structure of some solid hydroxyazo-compounds. J. Chem. Soc., 1956: 2143–50.

[25] Ospenson J. Some studies on azo dyes. II. Acta Chem.Scand., 1951, 5, 491.

[26] Metwally MA, Bondock S, El-Desouky SI, Abdou MM. Synthesis, tautomeric structure, dyeing characteristics, and antimicrobial activity of novel 4-(2-arylazophenyl)-3-(2-hyd roxyphenyl)-1-phenyl-2-pyrazolin-5-ones. J. Korean Chem. Soc., 2012, 56: 82-91.

[27] Metwally MA, Bondock S, El-Desouky SI, Abdou MM. A facile synthesis, tautomeric structure of novel 4-arylhydrazono-3-(2-hydroxyphenyl)-2-pyrazolin-5-ones and their application as disperse dyes. Color. Technol., issue 6, 2013 (in press).

[28] Metwally MA, Bondock S, El-Desouky SI, Abdou MM. Synthesis, structure investigation and dyeing assessment of novel bisazo disperse dyes derived from 3-(2-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-ones for dyeing polyester fabrics. J. Korean Chem. Soc., 2012, 56: 348-356.

[29] Metwally MA, Bondock S, El-Desouky SI, Abdou MM. Synthesis, structure elucidation and application of some new azo disperse dyes derived from 4-hydroxycoumarin for dyeing polyester fabrics, American Journal of Chemistry, 2012, 2: 347.

[30] Vogel, AI. Elementary Practical Chemistry. Part-III. Quantitative Organic Analysis, second ed. CBS Publishers. India, Delhi, 1987, pp. 754.

[31] Anonymous. Standard methods for the determination of the color fastness of textiles and leather.(5th ed.). England, Bradford: The Society of Dyers and Colorists; 1990, pp. 619–30.

[32] Yasuda H, Nidokawa H. The structure of 2-pyrazolin-5-one dyes. J. Org. Chem., 1966, 31: 1722–25.

[33] Oakes J, Gratton P.Kinetic investigations of azo dye oxidation in aqueous media. J. Chem. Soc., Perkin Trans. 1998; 2: 1857–64.

[34] Brode W, Herdle L. The relation between the absorption spectra and the chemical constitution of dyes. XIX. Mono and poly- azo dyes with a single auxochrome. J. Org. Chem. 1941; 6: 713–21.

[35] Geissman TA, Armen A. The rearrangement of 2-acetyl- and 2-benzoylcoumarone oxime p-toluenesulfonates. J. Am. Chem. Soc., 1955; 77: 1623–27.

[36] Bellamy LJ. Adv. Infrared group frequencies. Methuen, London; 1968, pp. 52.

[37] Russell PE. The reaction of diazomethane with 2-phenylazo-1,3-diketones. J. Am. Chem. Soc., 1953; 75: 5315–20.

[38] Randall HM, Fuson N, Fowler RG, Dangl JR. Infrared determination of organic compounds. New York: D.Van Nostrand, Co., Inc; 1949, pp. 222.

[39] Gagnon PE, Boivin JL, MacDonald BR. Yaffe L. Syntheses and absorption spectra of 2-substituted-3-hydroxy-5-pyrazoli nes: 4-n-hexyl-5-pyrazolines-4-C14. Can. J. Chem., 1954; 32: 823–38.

[40] Colthup NB. Spectra-structure correlations in the infrared region. J. Opt. Soc. Am. A. 1950; 40: 397–400.

[41] Millar 1T, Springall HD “Sidgwick’s organic chemistry of nitrogen,” Clarendon Press, Oxford, 1966, pp. 310.

[42] Chakravorty A, Ktlia KC. Hydrogen bonding and isomerism in arylazo oximes. J. Org. Chem., 1970, 35: 2231–34.

[43] Bellamy LJ, The infrared spectra of complex molecules, London: Chapman and Hall; 1975, pp. 303.

[44] SDL. Atlas Ltd. P.O. Box 162, Crown Royal, Shawcross St., Stockport SK1 3JW.

[45] Gordon PF, Gregory P. Organic chemistry in color, Berlin: Springer-Verlag; 1983, pp. 289.