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New azodisperse dyes with 4-hydroxymethyl-2-pyrazolin-5-one ring for dyeing polyester fabrics, Part 5

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Abstract

4-Hydroxymethyl-2-pyrazolin-5-one was used for the preparation of new 4-arylazo-4-hydroxymethyl-2-pyrazolin-5-one and the 4,4′-bisazo (*o*-, *m*- and *p*-phenylene) derivatives. Assessments of their dyeing performance on polyester fabrics are considered.

Keywords: Pyrazolin-5-one; Diazonium salts; Azo coupling; Disperse dyes; Polyester fabric; Fastness properties

1. Introduction

The 4-arylazopyrazolones were used as dyes for approximately all kinds of fibers, whether natural or synthetic [4]. A number of 4-arylazo-2-pyrazolin-5-ones have been reported in the literature due to the application of most of them as dyes of commercial value [5]. Continuing earlier studies designed to prepare new azodisperse dyes for dyeing polyester fabrics [1,2], 4-hydroxymethyl-2-pyrazolin-5-one was used for the preparation of new 4-arylazo-4-hydroxymethyl-2-pyrazolin-5-one and the 4,4′-bisazo (*o*-, *m*- and *p*-phenylene) derivatives.

2. Experimental

Microanalysis of the elements: Carbon and hydrogen were determined at Microanalytical Laboratories, Faculty of Science, Mansoura and Cairo Universities. All melting points are in degree centigrade and are uncorrected. Infrared spectra were recorded on a Pye Unicam SP 2000 spectrophotometer using potassium bromide wafer technique. 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.

2.1. Preparation of 4-arylazo-1,3-diphenyl-4-hydroxymethyl-2-pyrazolin-5-ones and bisazo derivatives ($\mathbf{A_{1-19}}$)

To a cold ethanolic solution of 1,3-diphenyl-4-hydroxymethyl-2-pyrazolin-5-one (**1**) (0.01 mol) containing sodium acetate (3.8 g), an aqueous solution from the corresponding diazonium salt (0.01 mol) was added dropwise with stirring. The obtained products were filtered off, washed with water, dried and recrystallised from ethanol [6]. The results are given in Table 1.

2.2. Preparation of acetylated derivative (**2**)

A mixture of 1,3-diphenyl-4-hydroxymethyl-2-pyrazolin-5-one (**1**) (0.02 mol) in 15 ml acetyl chloride was refluxed for

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Table 1
Characterization data of compounds $\mathbf{A_{1-19}}$

Dye	R (colour)	Melting point (°C)	Yield (%)	IR γ (cm^{-1})	Molecular formula	Molecular weight	Elemental analyses: Calc. (found)		
							C	H	N
$\mathbf{A_1}$	H (orange)	166	80	1550, 1590, 1660, 3425	$C_{22}H_{18}N_4O_2$	370.39	71.33 (71.4)	4.89 (4.8)	15.13 (15.1)
$\mathbf{A_2}$	*o*-Me (orange)	168	75	1550, 1590, 1650, 3500	$C_{23}H_{20}N_4O_2$	384.42	71.85 (71.71)	5.24 (5.39)	14.57 (14.63)
$\mathbf{A_3}$	*p*-Me (Y. orange)	181	83	1550, 1590, 1650, 3425	$C_{23}H_{20}N_4O_2$	384.42	71.85 (71.79)	5.24 (5.21)	14.57 (14.66)
$\mathbf{A_4}$	*m*-Me (red)	169	84	1550, 1590, 1650, 3500	$C_{23}H_{20}N_4O_2$	384.42	71.85 (71.71)	5.24 (5.23)	14.57 (14.64)
$\mathbf{A_5}$	*2,5*-Me (brown)	197	72	1540, 1580, 1650, 3425	$C_{24}H_{22}N_4O_2$	398.45	72.34 (72.50)	5.65 (5.52)	14.06 (14.1)
$\mathbf{A_6}$	*p*-Ome (brown)	157	67	1550, 1590, 1680, 3425	$C_{23}H_{20}N_4O_3$	400.42	68.98 (68.88)	5.03 (5.10)	13.99 (13.89)
$\mathbf{A_7}$	*m*-Ome (green)	160	70	1500, 1590, 1700, 3400	$C_{23}H_{20}N_4O_3$	400.42	68.98 (69.1)	5.03 (5.09)	13.99 (13.92)
$\mathbf{A_8}$	*o*-Cl (brown)	135	76	1500, 1590, 1650, 3500	$C_{22}H_{17}N_4O_2Cl$	404.84	65.26 (65.20)	4.23 (4.10)	13.83 (13.99)
$\mathbf{A_9}$	*p*-Cl (Y. brown)	142	80	1500, 1590, 1650, 3450	$C_{22}H_{17}N_4O_2Cl$	404.84	65.26 (65.25)	4.23 (4.3)	13.83 (13.92)
$\mathbf{A_{10}}$	*m*-Cl (brown)	148	81	1500, 1590, 1650, 3450	$C_{22}H_{17}N_4O_2Cl$	404.84	65.26 (65.28)	4.23 (4.21)	13.83 (13.80)
$\mathbf{A_{11}}$	*o*-NO_2 (Orange)	154	66	1500, 1600, 1650, 3450	$C_{22}H_{17}N_5O_4$	415.4	63.60 (62.99)	4.12 (4.20)	16.86 (16.90)
$\mathbf{A_{12}}$	*p*-NO_2 (red brown)	232	78	1500, 1590, 1640, 3425	$C_{22}H_{17}N_5O_4$	415.4	63.60 (63.80)	4.12 (4.20)	16.86 (16.87)
$\mathbf{A_{13}}$	*m*-NO_2 (red brown)	174	80	1500, 1600, 1650, 3450	$C_{22}H_{17}N_5O_4$	415.4	63.60 (63.70)	4.12 (4.30)	16.86 (16.89)
$\mathbf{A_{14}}$	*p*-OH (brown)	199	82	1490, 1600, 1680, 3400	$C_{22}H_{18}N_4O_3$	386.39	68.38 (68.60)	4.69 (4.71)	14.50 (14.52)
$\mathbf{A_{15}}$	*p*-COOH (brown)	192	80	1495, 1600, 1700, 3450	$C_{25}H_{22}N_4O_4$	442.46	67.85 (67.39)	5.01 (5.10)	12.66 (13.62)
$\mathbf{A_{16}}$	− (brown)	>255	86	1540, 1590, 1640, 3420	$C_{38}H_{30}N_8O_4$	662.69	68.90 (68.70)	4.60 (4.40)	16.90 (16.89)
$\mathbf{A_{17}}$	− (dark brown)	>255	84	1550, 1590, 1640, 3420	$C_{38}H_{30}N_8O_4$	662.69	68.90 (68.82)	4.60 (4.57)	16.90 (16.80)
$\mathbf{A_{18}}$	H (brown)	158	84	1500, 1600, 1700, 3420	$C_{44}H_{34}N_8O_4$	738.78	71.52 (71.47)	4.63 (4.59)	15.16 (15.10)
$\mathbf{A_{19}}$	Me (brown)	154	79	1500, 1600, 1710, 3425	$C_{46}H_{38}N_8O_4$	766.83	72.04 (72.02)	4.90 (4.85)	14.60 (14.57)

4–6 h. The reaction mixture was left to cool and then poured into ice cold water. The solid product that separated was filtered off, washed with water, dried and crystallised from ethanol to give yellow crystals of **2** (yield 70%, m.p. 204 °C).

Elemental analysis of $C_{18}H_{15}N_2O_3$ (307.32): C 70.34 (found 70.51), H 4.91 (5.0), N 9.11 (9.3).

2.3. Preparation of acetylated derivatives $\boldsymbol{B_{1-19}}$

A mixture of $\mathbf{A_{1-19}}$ (0.02 mol) in 15 ml acetyl chloride was refluxed for 4–6 h. The reaction mixture was left to cool and then poured into ice cold water. The solid products that separated were filtered off, washed with water, dried and crystallised from ethanol. The results are given in Table 2.

2.4. Coupling of **2** with aromatic diazonium salts: preparation of $\boldsymbol{B_{1-19}}$

To a cold ethanolic solution of **2** (0.01 mol) containing sodium acetate (3.8 g), an aqueous solution from the corresponding diazonium salt (0.01 mol) was added dropwise with stirring. The obtained products were filtered off, washed with water, dried and recrystallised from ethanol. The results are given in Table 2.

Table 2
Characterization data of compounds $\mathbf{B_{1-19}}$

Dye	R (colour)	Melting point (°C)	Yield (%)	IR γ (cm^{-1})	Molecular formula	Molecular weight	Elemental analyses: Calc. (found)		
							C	H	N
$\mathbf{B_1}$	H (red)	163	80	1550, 1630, 1650, 1590	$C_{24}H_{20}N_4O_3$	412.43	69.9 (69.87)	4.9 (4.89)	13.58 (13.57)
$\mathbf{B_2}$	*o*-Me (orange)	159	63	1590, 1340, 1710, 1650	$C_{25}H_{22}N_4O_3$	426.46	70.4 (70.29)	5.2 (5.19)	13.13 (13.1)
$\mathbf{B_3}$	*p*-Me (orange)	178	82	1340, 1590, 1650, 1710	$C_{25}H_{22}N_4O_3$	426.46	70.4 (70.04)	5.2 (5.2)	13.13 (13.1)
$\mathbf{B_4}$	*m*-Me (brown)	163	82	1340, 1590, 1650, 1710	$C_{25}H_{22}N_4O_3$	426.46	70.4 (70.35)	5.2 (5.09)	13.13 (13.32)
$\mathbf{B_5}$	*2,5*-Me (brown)	194	70	1365, 1500, 1550, 1650	$C_{26}H_{24}N_4O_3$	440.48	70.89 (70.8)	5.49 (5.5)	12.72 (12.7)
$\mathbf{B_6}$	*p*-Ome (red)	138	68	1340, 1550, 1590, 1710	$C_{25}H_{22}N_4O_2$	442.45	67.86 (67.82)	5.01 (5.0)	12.66 (12.63)
$\mathbf{B_7}$	*m*-Ome (G. brown)	126	71	1360, 1500, 1590, 1700	$C_{25}H_{22}N_4O_2$	442.45	67.88 (67.82)	5.01 (5.05)	12.66 (12.6)
$\mathbf{B_8}$	*o*-Cl (R. brown)	113	61	1340, 1550, 1590, 1650	$C_{24}H_{19}N_4O_3Cl$	446.87	64.5 (64.7)	4.28 (4.4)	12.53 (12.7)
$\mathbf{B_9}$	*p*-Cl (Y. brown)	183	77	1340, 1550, 1590, 1650	$C_{24}H_{19}N_4O_3Cl$	446.87	64.5 (64.69)	4.28 (4.39)	12.53 (12.61)
$\mathbf{B_{10}}$	*m*-Cl (brown)	156	80	1340, 1550, 1590, 1650	$C_{24}H_{19}N_4O_3Cl$	446.87	64.53 (64.7)	4.28 (4.27)	12.53 (12.53)
$\mathbf{B_{11}}$	*o*-NO_2 (R. brown)	169	65	1360, 1500, 1590, 1650	$C_{24}H_{19}N_5O_5$	457.43	63.01 (63.0)	4.20 (4.20)	15.3 (15.280)
$\mathbf{B_{12}}$	*p*-NO_2 (R. brown)	186	79	1360, 1500, 1590, 1650	$C_{24}H_{19}N_5O_5$	457.43	63.01 (63.0)	4.20 (4.20)	15.3 (15.280)
$\mathbf{B_{13}}$	*m*-NO_2 (Y. brown)	109	81	1360, 1500, 1590, 1650	$C_{24}H_{19}N_5O_5$	457.43	63.01 (63.0)	4.20 (4.20)	15.3 (15.280)
$\mathbf{B_{14}}$	*p*-OH (orange)	180	82	1360, 1500, 1590, 1650	$C_{24}H_{20}N_4O_3$	428.43	67.3 (67.28)	4.7 (4.7)	13.07 (13.1)
$\mathbf{B_{15}}$	*p*-COOH (brown)	182	81	1360, 1500, 1600, 1700	$C_{27}H_{24}N_4O_5$	484.49	66.9 (66.89)	4.99 (5.0)	11.6 (11.6)
$\mathbf{B_{16}}$	− (brown)	>255	82	1360, 1500, 1590, 1650	$C_{42}H_{34}N_8O_6$	746.76	65.90 (65.89)	4.60 (4.40)	15.0 (15.0)
$\mathbf{B_{17}}$	− (dark brown)	>255	81	1320, 1500, 1590, 1650	$C_{42}H_{34}N_8O_6$	746.76	65.90 (65.78)	4.60 (4.57)	15.0 (14.31)
$\mathbf{B_{18}}$	H (brown)	143	82	1340, 1500, 1600, 1660	$C_{48}H_{38}N_8O_6$	822.86	70.05 (70.3)	4.63 (4.59)	13.6 (13.49)
$\mathbf{B_{19}}$	Me (Y. brown)	209	80	1370, 1500, 1650, 1710	$C_{50}H_{42}N_8O_6$	882.91	68.0 (68.3)	4.90 (4.85)	12.60 (12.66)

2.5. Dyeing and fastness determinations

2.5.1. Dyeing of polyester fabrics

Preparation of fabrics: Polyester fabrics were prepared by treating the polyester/cotton blend (65/35%) product of Kafr El-Dawar Spinning & Weaving Co. according to the standard methods of AATCC with sulfuric acid (50%) at 75 °C for 20 min to remove cotton fibers and to get the 100% polyester fabric.

Preparation of dye dispersion: The required amount of the dye (2% shade) was dissolved in DMF and added dropwise with stirring to a solution of Setamol WS (0.5−1.5), an anionic dispersing agent of BASF (sodium salt of a condensation product of naphthalene sulfonic acid and formaldehyde). The dye was precipitated in a fine dispersion ready for use in dyeing after evaporation of the solvent by warming.

Dyeing procedure: The dye bath (1:20, good to dye liquor ratio) containing 2−4 g/l Remol HT-ET (carrier of Hoechst), 4% ammonium sulfate and acetic acid at pH = 5.5 was brought to 60 °C. The fabric was entered at this degree and run for 15 min. Two percent dye in the fine dispersion was added, temperature was raised to the boiling point within 45 min, dyeing was continued at the boiling point for about 90 min, then dyed fibers were rinsed and soaped with 2% nonionic detergent and ammonia (pH = 8.5) at 50 °C for 30 min to improve washing fastness.

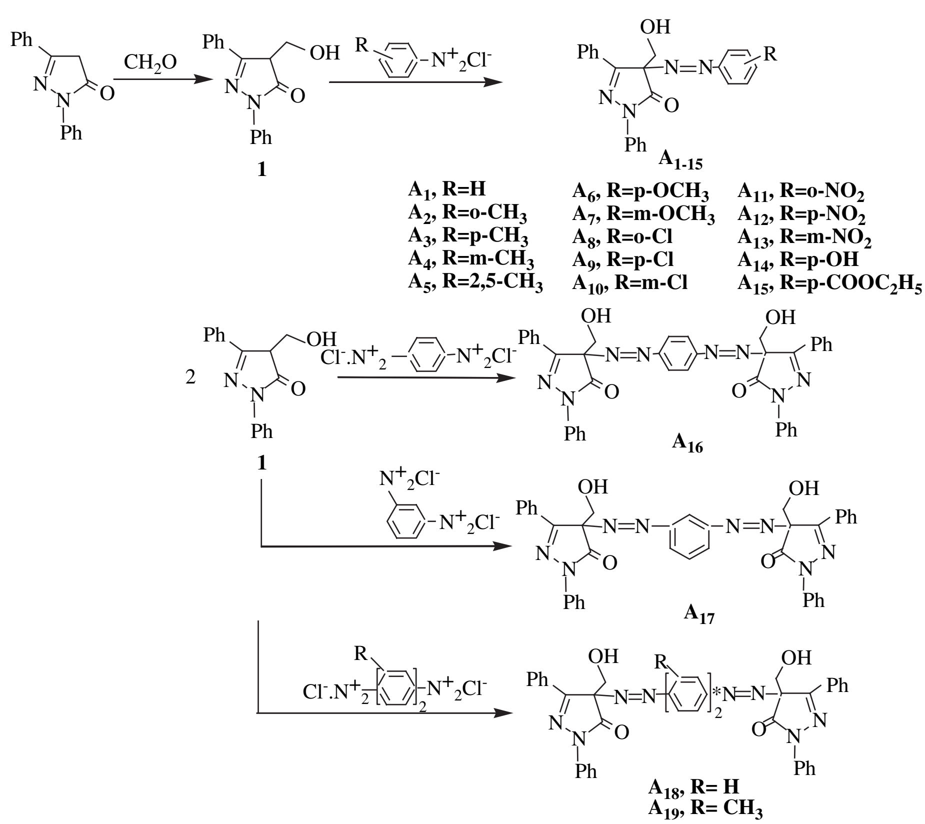
2.5.2. Fastness to washing

A specimen of dyed polyester fabric was stitched between two pieces of undyed cotton and polyester fabrics (10 cm × 4 cm), all approximately of equal weight and then washed at 50 °C. The staining on the white adjacent fabrics was assessed according to the International Grey scale [7] where 1 = poor, 2 = fair, 3 = moderate, 4 = good, and 5 = excellent.

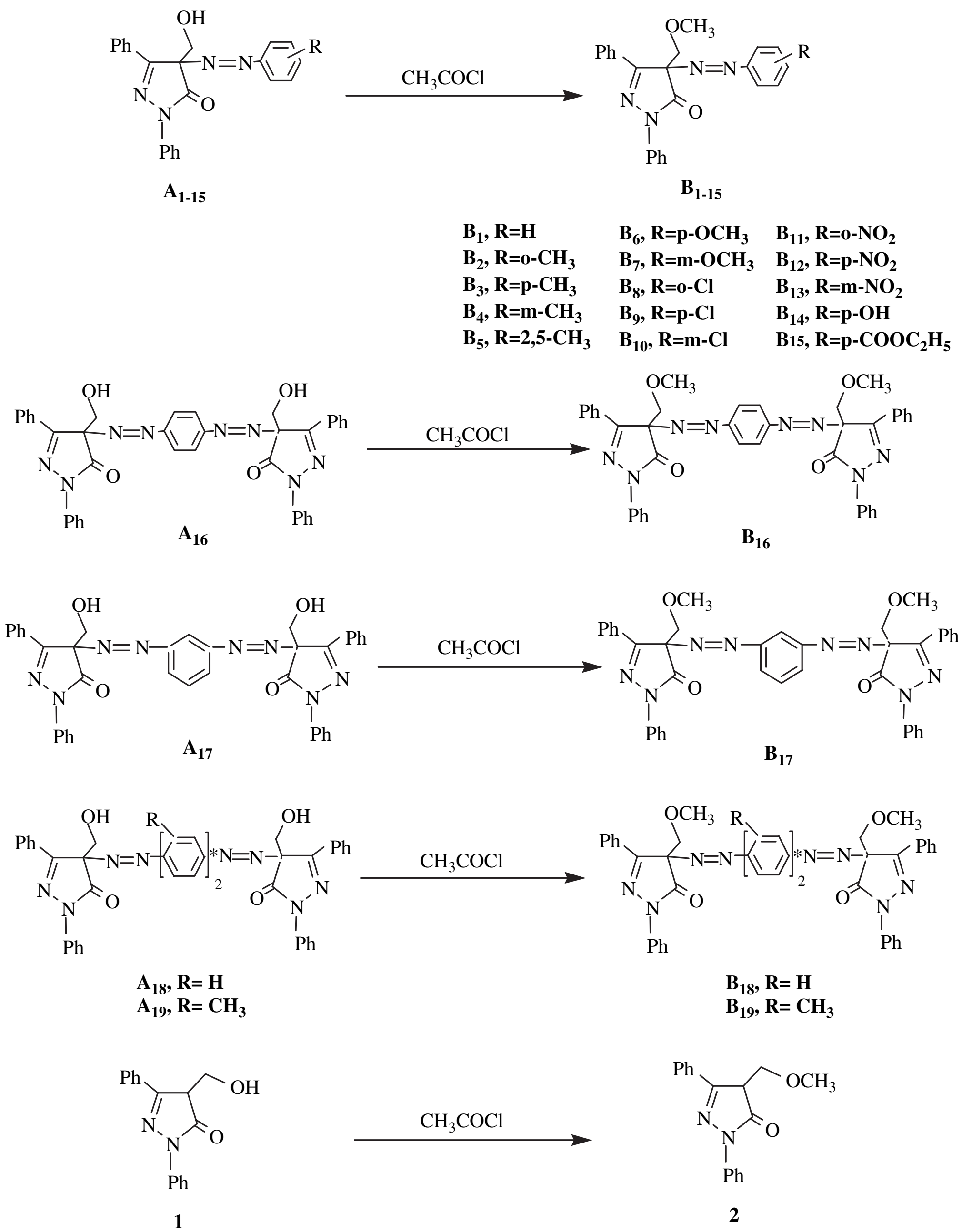
2.5.3. Fastness to acid and alkaline perspiration

The AATCC standard test method 15 (1960) was used. The acid solution (pH = 3.5) contained sodium chloride (10 g/l), lactic acid U.S.P. 85% (1 g/l), anhydrous disodium orthophosphate (1 g/l) and histidine monohydrochloride (0.25 g/l). The alkaline solution contained sodium chloride (10 g/l), ammonium carbonate (4 g/l), anhydrous disodium orthophosphate (1 g/l) and histidine monohydrochloride (0.25 g/l).

A composite specimen was made from the dyed sample as a layer between undyed cotton and polyester fabrics as the same weight as the dyed sample, composite specimen was immersed in the perspiration solution for 30 min with occasional agitation and squeezing to insure complete wetting, then stitched between the plastic in such a way that the fabric will be in a vertical position when placed in the oven. The loaded sample was kept in an oven at 37 °C for 6−8 h, after which fabrics were dried by conventional means. The change in the colour of the dyed material and staining on the undyed



Scheme 1.



Scheme 2.

adjacent fabrics were assessed according to the International Grey scale [7].

2.5.4. Fastness to rubbing

The dyed polyester fabric was placed on the base of a crockmeter, so that it rested flat on the abrasive cloth with its long dimension in the direction of rubbing. For dry rubbing test, a square of white testing cloth was mounted over the end of the finger which projects downward on the dry specimen sliding back and forth 20 times by making 10 complete turns of the crank at the rate of one turn per second. For wet rubbing test, the testing squares were thoroughly wet in distilled water and squeezed between filter papers through hand wringer under standard conditions. The rest of the procedure is the same as the dry crocking test. The staining on the white cloth was assessed according to the International Grey scale [7].

2.5.5. Fastness to sublimation

The fastness to sublimation was assessed according to ISO/R 10S/IV − Part 2. The dyed polyester fabric was stitched between two pieces of white polyester and cotton fabrics, all of equal length. The samples were treated at 185 and 210 °C for 30 s. After conditioning the sample for 16 h, the change in colour of the dyed sample and the staining of white ones were assessed according to the Grey scale [7].

2.5.6. Fastness to light

The tested samples and standard blue scales were exposed to the ''Weather-o-meter'' (Atlas Electric Devices Co., USA) [7]. The exposure of both tested sample and standard was discontinued at one of the times indicated in AATCC standard, 5, 10, 20, 40, 80, 160, 320 and 640 h, at which the standard showed just appreciable fading. In the present work the dyed fabrics were exposed to light for 160 h, after which the fabrics were allowed to lie in the dark at room temperature for about 2 h in order to cool-off and regain normal moisture from air. The samples were viewed in the daylight fluorescent lamp. The changes in colour were assessed according to the following scale rating standard of AATCC: 1 = poor, 3 = moderate, 5 = good, and 8 = very good.

The fastness properties of the dyes are given in Tables 5 and 6.

3. Results and discussion

3.1. Dyestuff synthesis

Some active aldehydes such as formaldehyde [8] do not eliminate water from 1,3-diphenyl-2-pyrazolin-5-one but form 4-hydroxymethyl-2-pyrazolin-5-one (**1**). Assignment of the product **1** was based on elemental analysis, IR, and ^{1}H NMR spectral data.

Compound **1** was treated with different aromatic diazonium salts to obtain a new series of 4-arylazo-1,3-4-hydroxymethyl-2-pyrazolin-5-ones ($\mathbf{A_{1-15}}$).

Bisazo derivatives $\mathbf{A_{16-19}}$ can be prepared by coupling of tetrazotized *m*- and *p*-phenylenediamine and benzidines with two molecules of **1**. Assignment of the products $\mathbf{A_{1-19}}$ was based on elemental analysis, IR, and ^{1}H-NMR spectral data (Scheme 1).

As a further extension for the above reaction, bis acetyl derivatives can be prepared upon treatment of $\mathbf{A_{1-19}}$ with acetyl chloride to obtain products $\mathbf{B_{1-19}}$. Products $\mathbf{B_{1-19}}$ were confirmed by their correct elemental analysis, IR, and ^{1}H-NMR spectral data (Scheme 2).

In connection with the above successful reaction it seemed of interest to react 1,3-diphenyl-4-hydroxymethyl-2-pyrazolin-5-one (**1**) with acetyl chloride to yield the acetyl derivative **2**.

The formation of **2** found its support from the correct elemental analysis, IR, ^{1}H NMR spectral data and coupling with monoarylazo and tetrazotized *m*- and *p*-phenylenediamine to form $\mathbf{B_{1-19}}$ (Scheme 2).

3.2. Analysis of dyeing performance from aqueous dispersions

This work describes the application of the synthesized compounds as new disperse dyes for dyeing polyester fabrics where a range of bright colour shades have been obtained, as the visual colour shades varied from yellow, golden yellow, orange, and reddish brown to brown. These compounds are classified into two groups according to their chemical structures as **A** and **B**. The differentiation of the number of chromophoric groups and substituents seems to effect noticeably the hue and colour shades. The leveling in all dyes is satisfactory. The performance is further examined by means of the following techniques.

3.2.1. Colour fastness tests

It can be noticed from the results shown in Tables 5 and 6 that the fastness to washing, perspiration, sublimation, rubbing and light is rather satisfactory according to the international scales (AATCC). Dyes $\mathbf{A_{8-13,15}}$ and $\mathbf{B_{8-13}}$ have remarkable colour fastness to light. This may be due to the presence of groups resistant to oxidation of photodegradation such as Cl, NO_2 and OH.

3.2.2. Colour difference measurements

The aim of this work was to assess the dyeing behavior of the prepared new dyes when applied to polyester fabrics. Thus, the

Table 3
Optical measurements of dyes $\mathbf{A_{1-19}}$

Dye	Visual colour	*K/S*	*L*	*a*	*b*	*c*	*H*	Δ*L*	Δ*a*	Δ*b*	Δ*c*	Δ*H*	Δ*E*
$\mathbf{A_1}$	Yellow	2.83	85.4	1.69	50.2	50.2	87.7	–	–	–	–	–	–
$\mathbf{A_2}$	G. yellow	4.12	76.3	19	76.2	78.6	75.9	−9.1	17.3	26.1	28.4	−11.8	32.6
$\mathbf{A_3}$	G. yellow	4.96	74.2	12.2	70.2	71.3	80.2	−11.3	10.5	20.1	21.1	−7.5	25.3
$\mathbf{A_4}$	Yellow	2.56	81.8	6.41	60.1	60.4	83.9	3.59	4.72	9.85	10.2	−3.8	11.5
$\mathbf{A_5}$	Y. brown	4.56	72.6	19.4	51.9	55.4	69.5	−12.9	17.8	1.74	5.2	−18.2	21.9
$\mathbf{A_6}$	Y. brown	5.59	69.7	13.9	54.7	56.4	75.5	−15.7	12.2	4.5	6.2	−12	20.4
$\mathbf{A_7}$	R. brown	11.9	75.4	11.2	44.2	45.5	75.8	−10.1	9.46	−6	−4.7	−11.9	15.1
$\mathbf{A_8}$	Yellow	4.86	80.8	10.7	58.6	59.6	79.6	−4.61	9.03	8.42	9.4	−3.1	13.2
$\mathbf{A_9}$	Yellow	5.86	79.9	9.49	64.6	65.2	81.6	−5.5	7.8	14.3	15	−6.1	17.3
$\mathbf{A_{10}}$	Yellow	5.06	78.9	11.6	59.6	60.7	79	−6.51	9.88	9.41	10.5	−9.7	15.1
$\mathbf{A_{11}}$	G. yellow	6.54	74.6	11.5	40.5	42.1	74.1	−10.8	9.81	−9.67	−8.1	−13.6	17.5
$\mathbf{A_{12}}$	G. yellow	5.81	88.1	−1.97	36.4	36.5	86.9	2.86	3.66	−13.8	−13.7	−0.8	14.4
$\mathbf{A_{13}}$	Brown	5.9	68.6	6.5	39.8	40.3	80.7	−16.8	4.81	−10.4	−9	−7	20.3
$\mathbf{A_{14}}$	Brown	2.67	81.9	2.61	37.4	37.4	86	−3.45	0.92	−12.8	−12.8	−1.7	13.3
$\mathbf{A_{15}}$	Yellow	2.45	86.7	−3.56	46.4	46.5	85.6	1.32	5.25	−3.8	−3.7	−2.1	6.6
$\mathbf{A_{16}}$	Orange	9.56	65.1	28.5	44.7	52.9	57.5	−20.4	26.8	−5.49	2.79	−30.2	34.1
$\mathbf{A_{17}}$	Brown	6.1	76.4	12.6	35.7	37.9	70.5	−9.04	10.9	−14.5	−12.3	−17.2	20.3
$\mathbf{A_{18}}$	Orange	7.47	82.5	4.5	41.8	42	83.9	−2.92	2.81	−8.37	−8.2	−3.8	8.8
$\mathbf{A_{19}}$	Orange	6.91	69.6	19.7	59	62.2	71.6	−15.9	17.9	−8.84	12	−16.1	25.5

Table 4
Optical measurements of dyes $\mathbf{B_{1-19}}$

Dye	Visual colour	*K*/*S*	*L*	*a*	*b*	*c*	*H*	Δ*L*	Δ*a*	Δ*b*	Δ*c*	Δ*H*	Δ*E*
$\mathbf{B_1}$	Yellow	2.45	85.9	−0.05	46.4	46.4	89.9	–	–	–	–	–	–
$\mathbf{B_2}$	G. yellow	3.2	73.7	17.9	7.1	73.2	75.8	−12.2	17.9	24.6	26.8	−14.1	32.8
$\mathbf{B_3}$	Yellow	2.41	84.8	−1.26	62.0	62	88.8	−1.06	−1.21	15.6	15.6	−1.1	15.7
$\mathbf{B_4}$	Yellow	1.63	4.8	2.5	37.2	37.3	86.2	6.2	−2.8	17.6	17	11.3	18.9
$\mathbf{B_5}$	Yellow	3.15	79.9	8.2	51.2	51.9	80.9	2.1	2.9	31.6	31.6	6	31.8
$\mathbf{B_6}$	Yellow	2.46	87.2	1.1	63.2	63.2	89	1.27	1.15	16.8	16.8	−0.9	16.9
$\mathbf{B_7}$	Brown	5.98	69.2	8.97	29.9	31.2	73.3	−16.7	9.02	−17	−15	−16.6	25.1
$\mathbf{B_8}$	Yellow	2.42	69.3	15.2	38.7	41.8	68.6	−8.5	9.9	19.1	21.3	−6.3	23.1
$\mathbf{B_9}$	Yellow	5.1	81.1	6.73	67.1	67.4	84.3	−4.81	6.78	20.6	21	−5.6	22.2
$\mathbf{B_{10}}$	Yellow	4.9	84.7	0.19	52.8	52.8	89.8	−1.16	0.24	6.39	6.4	−0.1	6.5
$\mathbf{B_{11}}$	Yellow	3.42	86.3	1.54	41.6	41.6	87.8	0.38	1.59	−4.8	−4.8	−2.1	5.1
$\mathbf{B_{12}}$	Yellow	2.16	87.14	−0.04	41.9	41.9	89.8	1.24	0.01	−4.4	−4.4	−0.1	4.7
$\mathbf{B_{13}}$	Yellow	1.33	88.3	−3.21	35.9	36.1	84.9	2.4	−3.16	−10	−10	−5	11.1
$\mathbf{B_{14}}$	Yellow	2.09	84.6	7.59	48.8	49.4	81.2	−1.35	7.64	2.4	2.99	−8.74	8.1
$\mathbf{B_{15}}$	Yellow	2.17	85.3	2.17	11.8	12	79.6	−0.57	2.22	−35	−34	−10.3	34.6
$\mathbf{B_{16}}$	R. yellow	8.15	67.7	15.6	40.4	43.3	68.9	−18.2	15.7	−6	−3.1	−21	24.7
$\mathbf{B_{17}}$	Yellow	5.76	83.4	1.5	33.4	33.4	87.4	−2.5	1.55	−13	−13	−2.5	13.3
$\mathbf{B_{18}}$	Yellow	2.7	78.9	7.7	41.9	42.6	79.6	−6.95	7.74	−4.53	−3.8	−10.3	11.3
$\mathbf{B_{19}}$	Y. orange	4.87	72.6	19.4	15.9	25.1	39.1	−13.3	19.5	−30.5	−21.3	50.6	38

dyes under investigation were used for dyeing polyester fabrics at 2% on mass of fabric (o.m.f.) shade by carrier technique (100 °C). Colour measurements are assessed quantitatively according to the CIE colour system using continuous scanning spectrocolourmeter (ACS-600 colour control system) for reflectance colour measurements in the visible spectrum (390–700 nm), hue angle (*H*), chromaticity difference (Δ*C*) and colour buildup (*K*/*S*) where *L*, *a*, *b*, *c*, *H* and *K*/*S* values are calculated and given in Tables 3 and 4, which show the possibility to assess quantitatively colour shade. From these values, the colour difference calculations and the depth of the dyed samples are obtained related to the parent dyestuff as standard and correlated with the chemical structure of the dyes.

3.2.2.1. Group **A**. The values of *K*/*S* in this group vary from 2.45 to 11.97. The introduction of the methoxy and nitro groups in dyes $\mathbf{A_{6-7}}$ and $\mathbf{A_{11-13}}$ deepens the colour compared with the parent dye $\mathbf{A_1}$ as indicated from the values of *K*/*S* from 5 to 12 for the former and $K/S = 2.83$ for the latter (parent).

Brightness or dullness of colour for each dye on polyester fabric is measured by comparing chromaticity difference *C*

Table 5
Fastness properties of dyes $\mathbf{A_{1-19}}$ on polyester fabrics

Dye	Washing (staining)	Perspiration		Rubbing		Sublimation				Light (80 h)
		Acidic	Alkaline	Dry	Wet	Cotton		Polyester		
						180 °C	210 °C	180 °C	210 °C	
$\mathbf{A_1}$	4–5	4–5	4–5	4	4	4	4	4	4	3
$\mathbf{A_2}$	4	4–5	4–5	4	3–4	4	3–4	3–4	3	2–3
$\mathbf{A_3}$	4–5	4–5	4–5	2–3	2–3	4	4	2–3	2–3	2–3
$\mathbf{A_4}$	4–5	4–5	4–5	4–5	4–5	4	4	4	4	3
$\mathbf{A_5}$	4–5	4–5	4–5	3–4	4	4	4	4	4	2–3
$\mathbf{A_6}$	4–5	4–5	4–5	4–5	4–5	4	4	2–3	3	3
$\mathbf{A_7}$	4–5	4–5	4–5	4–5	4–5	4	4	3–4	2–3	2–3
$\mathbf{A_8}$	4–5	4–5	4–5	4–	4–5	4	4	4	3–4	5
$\mathbf{A_9}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3	5
$\mathbf{A_{10}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3	5
$\mathbf{A_{11}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	4	4
$\mathbf{A_{12}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3	5
$\mathbf{A_{13}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3–4	4
$\mathbf{A_{14}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3–4	2–3
$\mathbf{A_{15}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3–4	5
$\mathbf{A_{16}}$	4–5	4–5	4–5	2–3	4	4	4	3	3	3
$\mathbf{A_{17}}$	4–5	4–5	4–5	4	4	4	4	4	4	2–3
$\mathbf{A_{18}}$	4–5	4–5	4–5	3	4	4	4	4	4	2–3
$\mathbf{A_{19}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3	2–3

Table 6
Fastness properties of dyes $\mathbf{B_{1-19}}$ on polyester fabrics

Dye	Washing	Perspiration		Rubbing		Sublimation				Light (80 h)
	(staining)	Acidic	Alkaline	Dry	Wet	Cotton		Polyester		
						180 °C	210 °C	180 °C	210 °C	
$\mathbf{B_1}$	4–5	4–5	4–5	4	4–5	4	4	3–4	3–4	3
$\mathbf{B_2}$	4	4–5	4–5	3	3–4	4	3–4	2–3	2	2–3
$\mathbf{B_3}$	4–5	4–5	4–5	3–4	3–4	4	4	4	2–3	3
$\mathbf{B_4}$	4–5	4	4	4–5	4–5	4	4	4	4	2–3
$\mathbf{B_5}$	4–5	4–5	4–5	4–5	4–5	4	4	4	4	3
$\mathbf{B_6}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3	3
$\mathbf{B_7}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3–4	3
$\mathbf{B_8}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3–4	3
$\mathbf{B_9}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3	5
$\mathbf{B_{10}}$	4–5	4–5	4–5	4–5	4–5	4–5	4	3	4–5	5
$\mathbf{B_{11}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	3	5
$\mathbf{B_{12}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	4	5
$\mathbf{B_{13}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	4	4
$\mathbf{B_{14}}$	4–5	4–5	4–5	4–5	4–5	4	4	4–5	4	2–3
$\mathbf{B_{15}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	4	4
$\mathbf{B_{16}}$	4–5	4–5	4–5	4–5	4–5	4	4	4	4	2–3
$\mathbf{B_{17}}$	4–5	4–5	4–5	4–5	4–5	4	4	4–5	4	3
$\mathbf{B_{18}}$	4–5	4–5	4–5	4–5	4	4	4	4	4	2–3
$\mathbf{B_{19}}$	4–5	4–5	4–5	4–5	4–5	4	4	3–4	3	2–3

(+ve means brightness and −ve means dullness). The results shown in Table 3 show that the increase in chroma, e.g., by 2.7–28.3 for the dye $\mathbf{A_2}$, means that these dyes are brighter than the parent dye $\mathbf{A_1}$.

On the other hand, the darkness or lightness of the dye on polyester fabric is measured by comparing the values of L (+ve means lightness while −ve means darkness). The $+L$ values given in Table 3 show that the introduction of methyl, nitro and carboethoxy groups in dyes $\mathbf{A_4}$, $\mathbf{A_{12}}$ and $\mathbf{A_{15}}$, respectively, makes each of these dyes lighter than the parent dye $\mathbf{A_1}$. On the other hand, the introduction of methoxy, hydroxyl and chlorine groups in dyes $\mathbf{A_{6,7}}$, $\mathbf{A_{14}}$ and $\mathbf{A_{8-10}}$, respectively, makes each of these dyes darker than the parent dye $\mathbf{A_1}$.

These results are in line with those previously reported by Műller [9] on the effect of substituent in the dye structure and hue.

*3.2.2.2. Group **B***. The chemical structure of dyes in this group deals with the effect of acetate group on the brightness or dullness and lightness or darkness of the dyed samples by comparing the values of C and L.

The data in Table 4 show a K/S range from 1.3 to 8.1 where the introduction of methoxy group and chlorine in dyes $\mathbf{B_7}$ and $\mathbf{B_9}$, respectively, deepens the colour compared with the parent dye $\mathbf{B_1}$ as indicated from the value of $K/S = 5.9$ and 5.1 for the former and $K/S = 2.45$ for the latter. While the increase in chroma, e.g., by 2.9–26.78 for dye $\mathbf{B_2}$, as indicated by the results in Table 4 means that these dyes are brighter than the parent dye $\mathbf{B_1}$.

On the other hand, the $+L$ values given in Table 4 show that the introduction of methyl, methoxy and nitro groups in dyes $\mathbf{B_5}$, $\mathbf{B_6}$ and $\mathbf{B_{11-13}}$, respectively, makes each of these dyes lighter than the parent, whereas the introduction of chlorine, hydroxide and carboethoxy groups in dyes $\mathbf{B_{8-10}}$, $\mathbf{B_{14}}$ and $\mathbf{B_{15}}$, respectively, makes each of these dyes darker than the parent dye $\mathbf{B_1}$.

4. Conclusion

A set of 38 disperse dyes $\mathbf{A_{1-19}}$ and $\mathbf{B_{1-19}}$ were synthesized by azo coupling. All of them were investigated for their dyeing characteristics on polyester fabrics. The electronic absorption spectra give bright hues from yellow to brown on polyester fabrics. The dyed fabrics exhibit very good to excellent washing, perspiration and sublimation fastness properties with little variation in the good to excellent rubbing fastness. The remarkable degree of levelness and brightness after washing is indicative of good penetration and the excellent affinity of these dyes for polyester fabric. This in combination with the ease of preparation makes them particularly valuable.

References

[1] Amer FA, Metwally AM, El-Zimaity M. J Appl Chem Biotechnol 1980;28:560.
[2] Metwally MA, Darwish YM, EL-Hussini MM, Amer FA. J Indian Chem Soc 1988;LXV:54.
[4] Ashoeffer (Etablissmmets, Buuchet and Cie) Fr1, 325, 692; May 1963.
[5] Wiely RH, Wiely P. Pyrazolone, pyrazildone and derivatives. New York: Interscience Publishers Inc.; 1964.
[6] Hayriye A, Adalet O. Fac Sci Univ Istanbul 1951;16A:76; Chem Abstr 1952;46:4533.
[7] SDL Atlas Ltd. P.O. Box 162, Crown Royal, Shawcross St., Stockport SK1 3JW.
[8] Amal H, Ozger A. Rev Fac Sci Univ Istanbul 1951;16A:71; Chem Abstr 1952;46:4534.
[9] Műller C. Recent developments in the chemistry of disperse dyes and their intermediate. Am Dyestuff Reporter March 1970;37–44.