

NEW AZO DISPERSE DYES CONTAINING CYCLOHEXANONE RING FOR DYEING POLYESTER AND NYLON FABRICS

Hatem E. Gaffer¹, Mohamed A. E. Khalifa², Shaima F. El-Bially¹, Mohamed A. Metwally^{3*}

¹Textile Research Division, National Research Center, Dokki, Cairo, Egypt

²Higher Institute of Engineering and Technology, New Damietta, Egypt

³Faculty of Science, Mansoura University, Mansoura, Egypt

*mamegs@mans.edu.eg

Condensation of 2,4-diacarboethoxy-5-hydroxy-3-(4-methoxyphenyl)-5-methyl cyclohexanone (**1**) with equimolar amounts of hydrazine hydrate and phenyl hydrazine afforded the corresponding 2*H*-indazole-5-carboxylates **2a** and **2b**, respectively. Coupling of **2** with diazotized aromatic amines furnished the corresponding azo compounds **3a-n**. When compound **1** was subjected to the Japp-Klingemann reaction in alkaline medium with diazotized aromatic amines furnished the corresponding hydrazones **4a-g**. The treatment of **4a-g** with phenyl hydrazine in acetic acid allows the isolation of arylhydrazono derivatives **5a-g**. The structures of the dyes were established using analytical and spectral data. Evaluation of the technical properties and color assessment of the dyes were done.

Key words: Japp-Klingemann reaction; phenyl hydrazine; indazole; cyclohexane

НОВИ АЗО-ДИСПЕРЗНИ БОИ ШТО СОДРЖАТ ЦИКЛОХЕКСАНОНСКИ ПРСТЕН ЗА БОЕЊЕ НА ПОЛИЕСТЕРСКИ И НАЈЛОНСКИ ПРОИЗВОДИ

Кондензацијата на 2,4-дикарбоетокси-5-хидрокси-3-(4-метоксифенил)-5-метилциклохексанон (**1**) со еквимоларно количество на хидразинхидрат и фенилхидразин е можна преку 2*H*-индазол-5-карбоксилати **2a** и **2b**. Спрегањето на **2** со диазотираните ароматични амини доведува до соодветните азо-соединенија **3a-n**. Кога соединението **1** беше подложено на Јап-Клингеманова реакција во алкална средина со диазотираните ароматични амини, ги даде соодветните хидразони **4a-g**. Третирањето на **4a-g** со фенилхидразин во оцетна киселина овозможува изолирање на арилхидразоно-дериватите **5a-g**. Структурите на боите се толкувани преку користење на аналитички и спектроскопски податоци. Извршено е оценување на техничките својства и испитување на боите кај овие соединенија.

Клучни зборови: Јап-Клингеманова реакција; фенилхидразин; индазол; циклохексан

1. INTRODUCTION

Intensive research efforts have been made for the past four decades in the area of disperse dyes that have been used for the coloration of hydrophobic fabrics [1–3]. β -Keto esters have attracted the attention as a key intermediate for the synthesis of different types of heterocyclic moieties [4–6]. In this work, the interest was focused on exploring the synthetic potentialities of cyclic β -keto esters

utilizing 2,4-diacarboethoxy-5-hydroxy-3-(4-methoxy phenyl)-5-methyl cyclohexanone (**1**), which was reported to have various biological activities [7] and their application as disperse dyes on polyester and nylon fabrics where the synthesized dyes gave excellent uniformity of coloration and satisfactory fastness properties against washing, perspiration, sublimation and light according to the international grey scale.

2. EXPERIMENTAL

1. General remarks

All melting points (uncorrected) are in degrees centigrade and were determined on the Gallenkamp electric melting point apparatus. Elemental analyses were carried out at the microanalytical unit, Faculty of Science, University of Mansoura. IR spectra were recorded (KBr) on a Mattson 5000 FTIR spectrometer. ^1H NMR spectra were measured on a Bruker WP 300 in CDCl_3 or DMSO as a solvent, using the TMS as an internal standard. Elemental analyses were carried out by the Micro analysis unit – Cairo University. The substrates used for dyeing 100% polyester fabrics and nylon(6,6) were kindly provided by the Misr Beida Dyers company, Alexandria, Egypt, a product of Misr for synthetic fibers company, Kafr El-Dawar, Egypt. All applications and fastness properties of the dyes were studied at the National Research Center, Cairo, Egypt. The color parameters of the dyed fabrics were determined on a Gretag Macbeth

CE 7000a spectrophotometer in the National Research Center, Cairo, Egypt. Compounds **1–3** were prepared according to the literature procedures [7] and were found to be identical with the reported ones.

2. Preparation of dyes (**3a-n**)

Aryl diazonium chlorides were prepared by the addition of a cold sodium nitrite solution (0.69 g in 15 ml H_2O) to a stirred cold suspension of amines (0.01 mol) in concentrated HCl (6 ml). The resulting diazonium chlorides were added dropwise to a stirred cold solutions of **2** (0.01 mol) in ethanol (20 ml) in the presence of sodium acetate (0.02 mol). The mixture was stirred for 2 h and the solids obtained were filtered, washed with water followed by cold ethanol and then dried. The products were recrystallized from ethanol to give the corresponding dyes **3a-n**. Elemental analyses, m.p. yield% and I.R spectral data of **3a-n** are listed in Table 1.

Table 1

Characterization data of compounds **3a-n**

Cpd.	Yield (%)	m.p. ($^{\circ}\text{C}$)	Mol. formula (Mol. Wt.)	Elemental analysis : found (calcd.)			IR bands (cm^{-1})			
				C	H	v(OH)	v(NH)	v(C=O)	v(N=N)	
3a	82	>300	$\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_5$ (450.49)	63.84 (63.99)	5.53 (5.82)	3510	3292	1720	1540	
3b	73	>300	$\text{C}_{25}\text{H}_{28}\text{N}_4\text{O}_5$ (464.51)	64.34 (64.64)	5.84 (6.08)	3481	3296	1710	1539	
3c	87	>300	$\text{C}_{24}\text{H}_{25}\text{N}_5\text{O}_7$ (495.48)	58.43 (58.18)	5.18 (5.09)	3510	3322	1706	1530	
3d	82	>300	$\text{C}_{25}\text{H}_{28}\text{N}_4\text{O}_6$ (480.51)	62.22 (62.49)	5.45 (5.87)	3500	3322	1703	1535	
3e	77	>300	$\text{C}_{24}\text{H}_{25}\text{N}_4\text{O}_5\text{Br}$ (529.38)	54.23 (54.45)	4.57 (4.76)	3508	3280	1707	1531	
3f	79	>300	$\text{C}_{24}\text{H}_{25}\text{N}_5\text{O}_7$ (495.48)	58.43 (58.18)	5.17 (5.09)	3508	3283	1709	1535	
3g	83	>300	$\text{C}_{24}\text{H}_{25}\text{N}_5\text{O}_7$ (495.48)	58.23 (58.18)	5.11 (5.09)	3492	3283	1709	1535	
3h	55	130	$\text{C}_{30}\text{H}_{30}\text{N}_4\text{O}_4$ (510.58)	70.74 (70.57)	6.01 (5.92)	3506	3224	1713	1542	
3i	74	170	$\text{C}_{31}\text{H}_{32}\text{N}_4\text{O}_4$ (524.61)	70.81 (70.97)	6.38 (6.15)	3487	3389	1713	1531	
3j	65	190	$\text{C}_{30}\text{H}_{29}\text{N}_5\text{O}_6$ (555.58)	64.06 (64.85)	5.37 (5.26)	3497	3338	1718	1529	
3k	57	180	$\text{C}_{31}\text{H}_{31}\text{N}_4\text{O}_5$ (540.61)	68.53 (68.87)	5.45 (5.97)	3512	3343	1721	1538	
3l	50	166	$\text{C}_{30}\text{H}_{29}\text{N}_4\text{O}_4\text{Br}$ (589.48)	61.15 (61.13)	5.14 (4.96)	3488	3337	1728	1534	
3m	62	150	$\text{C}_{30}\text{H}_{29}\text{N}_5\text{O}_6$ (555.58)	65.03 (64.85)	5.24 (5.26)	3513	3325	1722	1533	
3n	64	160	$\text{C}_{30}\text{H}_{29}\text{N}_5\text{O}_6$ (555.58)	64.47 (64.85)	5.22 (5.26)	3510	3338	1729	1538	

^1H NMR (DMSO) (**3a**): $\delta = 1.1$ (t, 3H, CH_3), 1.2 (s, 3H, CH_3), 2.8 (d, 2H), 3.4 (s, 3H, OCH_3), 4.1 (q, 2H, CH_2), 4.2 (d, 1H), 4.4 (s, 1H, OH), 6.8–7.4 (m, 9H, Ar-H), 10.4 (s, 1H, NH),

^1H NMR (DMSO) (**3d**): $\delta = 1.1$ (t, 3H, CH_3), 1.4 (s, 3H, CH_3), 2.8 (d, 2H), 3.4, 3.7 (2s, 6H, 2OCH_3), 4.2 (d, 1H), 4.3 (q, 2H, CH_2), 4.4 (d, 1H), 4.7 (s, 1H, OH), 7.2–7.8 (m, 8H, Ar-H), 10.9 (s, 1H, NH),

^1H NMR (DMSO) (**3f**): $\delta = 1.1$ (t, 3H, CH_3), 1.2 (s, 3H, CH_3), 2.3 (d, 1H), 2.8 (d, 2H), 3.4 (s, 3H, OCH_3), 4.1 (q, 2H, CH_2), 4.2 (d, 1H), 4.4 (d, 1H), 4.7 (s, 1H, OH), 7.0–7.7 (m, 8H, Ar-H), 10.7 (s, 1H, NH),

^1H NMR (DMSO) of (**3h**): $\delta = 1.1$ (t, 3H, CH_3), $\delta = 1.2$ (s, 3H, CH_3), $\delta = 2.3$ (d, 1H), 2.8 (d, 2H, $\text{C}_7\text{-H}_2$), 3.4 (s, 3H, OCH_3), 4.1 (q, 2H, CH_2), $\delta = 4.2$ (d, 1H), $\delta = 4.4$ (d, 1H), 4.5 (s, 1H, OH) and $\delta = 6.8$ –7.7 (m, 14H, Ar-H),

^1H NMR (DMSO) of (**3i**): $\delta = 1.1$ (t, 3H, CH_3), 1.2 (s, 3H, CH_3), 2.4 (s, 3H), 2.8 (d, 2H), 3.4 (s, 3H, OCH_3), 4.1 (q, 2H, CH_2), 4.2 (d, 1H), 4.3 (d, 1H), 4.7 (s, 1H, OH), 6.8–7.4 (m, 13H, Ar-H),

^1H NMR (DMSO) of (**3k**): $\delta = 1.1$ (t, 3H, CH_3), 1.4 (s, 3H), 2.8 (d, 2H), 3.4, 3.8 (2s, 6H, 2OCH_3), 4.1 (d, 1H), 4.2 (d, 1H), 4.3 (q, 2H), 4.5 (s, 1H, OH), 7.2–7.8 (m, 12H, Ar-H).

3. Preparation of dyes **4a-g**

To a cold stirred solution of **1** (0.01 mol) in 25 ml ethanolic KOH (40 g in 100 ml ethanol), a cold aqueous solution of aryl diazonium chloride (0.01 mol) was added dropwise with stirring for

2 h. The reaction mixture was filtered, washed with water followed by cold ethanol, recrystallized from ethanol and then dried. Elemental analyses, m.p. yield% and I.R spectral data of **4a-g** are listed in Table 2.

Table 2

Characterization data of compounds **4a-g**

Cpd.	Yield (%)	m.p. (°C)	Mol. formula (Mol. Wt.)	Elemental analysis : found (calcd.)		IR bands (cm ⁻¹)			
				C	H	ν(OH)	ν(CO) _{ester}	ν(C=O) _{ketone}	ν(N=N)
4a	79	123	C ₂₃ H ₂₆ N ₂ O ₅ (410.46)	67.23 (67.30)	6.23 (6.38)	3467	1710	1665	1553
4b	72	132	C ₂₄ H ₂₈ N ₂ O ₅ (424.49)	67.63 (67.91)	6.33 (6.65)	3480	1703	1682	1580
4c	71	110	C ₂₃ H ₂₅ N ₃ O ₇ (455.46)	60.43 (60.65)	5.52 (5.53)	3490	1710	1669	1569
4d	69	135	C ₂₄ H ₂₈ N ₂ O ₆ (440.49)	65.31 (65.44)	6.23 (6.41)	3500	1709	1664	1583
4e	72	160	C ₂₃ H ₂₅ N ₂ O ₅ Br (489.36)	56.45 (56.45)	4.98 (5.15)	3460	1699	1670	1550
4f	75	120	C ₂₃ H ₂₅ N ₃ O ₇ (455.46)	60.85 (60.65)	5.98 (5.53)	3476	1695	1666	1550
4g	80	95	C ₂₃ H ₂₅ N ₃ O ₇ (455.46)	63.52 (63.15)	5.53 (5.30)	3466	1700	1674	1556

¹H NMR (DMSO) for (**4b**): δ = 1.2 (s, 3H, CH₃), 1.4 (t, 3H, CH₃), 2.1 (s, 2H), 2.3 (s, 3H, p-CH₃-C₆H₄), 3.8 (s, 3H, OCH₃), 4.1 (q, 2H, CH₂), 4.2 (d, 1H), 4.3 (t, 1H), 4.5 (s, 1H, OH), 6.6–7.1 (m, 8H, Ar-H),

¹H NMR (DMSO) for (**4c**): δ = 1.2 (s, 3H, CH₃), 1.4 (t, 3H, CH₃), 2.1 (s, 2H), 3.8 (s, 3H, OCH₃), 4.1 (d, 1H, C4-CH), 4.2 (t, 1H), 4.3 (q, 2H, CH₂), 4.5 (s, 1H, OH) and 6.6–7.1 (m, 8H, Ar-H),

¹H NMR (DMSO) for (**4d**): δ = 1.2 (s, 3H, CH₃), 1.4 (t, 3H, CH₃), 2.1 (s, 2H), 3.6, 3.8 (2s, 6H, 2OCH₃), 4.1 (d, 1H), 4.2 (t, 1H), 4.3 (q, 2H, CH₂), 4.5 (s, 1H, OH) and 6.6–7.1 (m, 8H, Ar-H).

4) Condensation of **4a-g** with phenyl hydrazine:
Formation of arylhydrazono-3-ethylcarboxylate-4-hydroxy-2-(4-methoxyphenyl)-4-methyl-6-(phenylhydrazono)cyclohexane derivatives **5a-g**

A mixture of **4a-g** (0.01 mol) and phenyl hydrazine (0.01 mol) in acetic acid (10 ml) was

heated under reflux for 4 hours, and then allowed to cool and then poured into cooled water. The solid products were collected by filtration, washed with cold ethanol and recrystallized from ethanol to give pure **5a-g**. Elemental analyses, m.p. yield% and I.R spectra of **5a-g** are listed in Table 3.

Table 3

Characterization data of compounds **5a-g**

Cpd.	Yield (%)	m.p. (°C)	Mol. formula (Mol. Wt.)	Elemental analysis : found (calcd.)		IR bands (cm ⁻¹)		
				C	H	ν(NH)	ν(CO) _{ester}	ν(N=N)
5a	72	120	C ₂₉ H ₃₀ N ₄ O ₃ (482.57)	72.64 (72.18)	6.88 (6.27)	3318	1710	1555
5b	82	>300	C ₃₀ H ₃₂ N ₄ O ₃ (496.60)	72.39 (72.56)	4.68 (6.49)	3290	1703	1581
5c	69	170	C ₂₉ H ₂₉ N ₅ O ₅ (527.57)	66.64 (66.02)	5.88 (5.54)	3318	1710	1569
5d	78	104	C ₃₀ H ₃₂ N ₄ O ₄ (512.60)	70.85 (70.29)	6.29 (6.29)	3327	1709	1587
5e	86	90	C ₂₉ H ₂₉ N ₄ O ₃ Br (561.47)	62.64 (62.04)	5.25 (5.21)	3294	1699	1577
5f	82	120	C ₂₉ H ₂₉ N ₅ O ₅ (527.57)	66.38 (66.02)	5.43 (5.54)	3281	1695	1576
5g	86	140	C ₂₉ H ₂₉ N ₅ O ₅ (527.57)	66.01 (66.02)	4.14 (5.54)	3292	1700	1569

¹H NMR (CDCl₃) for (**5a**): δ = 1.2 (s, 3H, CH₃), 1.4 (t, 3H, CH₃), 2.3 (s, 2H, CH₂), 2.7 (d, 1H), 3.2 (d, 1H), 3.5 (t, 1H), 3.8 (s, 3H, OCH₃), 4.1 (q, 2H, CH₂), 4.2 (d, 1H), 4.3 (t, 1H), 4.7 (s, 1H, OH), 7–7.6 (m, 12H, Ar-H), 9.9, 10.4 (s, 2H, 2NH),

¹H NMR (CDCl₃) for (**5b**): δ = 1.1 (s, 3H, CH₃), 1.4 (t, 3H, CH₃), 2.2 (s, 2H, CH₂), 2.3 (s, 3H, CH₃), 2.8 (d, 1H), 3.2 (d, 1H), 3.5 (t, 1H), 3.8 (s, 3H, OCH₃), 4.1 (q, 2H, CH₂), 4.2 (d, 1H), δ = 4.3 (t, 1H), 4.5 (s, 1H, OH) and 6.8–7.2 (m, 12H, Ar-H), 9.8, 10.9 (s, 2H, 2NH),

¹H NMR (CDCl₃) for (**5d**): δ = 1.1 (s, 3H, CH₃), 1.4 (t, 3H, CH₃), 2.2 (s, 2H), 2.5 (s, 3H, CH₃), 2.8 (d, 1H), 3.2 (d, 1H), 3.4, 3.8 (s, 6H, 2OCH₃), 4.1 (q, 2H, CH₂), 4.2 (d, 1H), 4.4 (t, 1H), 4.5 (s, 1H, OH) and 6.8–7.5 (m, 12H, Ar-H), 10, 10.4 (s, 2H, 2NH),

¹H NMR (CDCl₃) for (**5f**): δ = 1.1 (s, 3H, CH₃), 1.4 (t, 3H, CH₃), 2.4 (s, 2H), 2.6 (d, 1H), 3.2 (d, 1H), 3.4 (t, 1H), 3.7 (s, 3H, OCH₃), 4.1 (q, 2H, CH₂), 4.2 (d, 1H), 4.3 (t, 1H), 4.4 (s, 1H, OH) and 6.7–7.8 (m, 12H, Ar-H), 9.8, 10.6 (s, 2H, 2NH).

5. Dyeing and fastness determinations

Preparation of dye dispersion: The required amount of the dye (2% shade) was dissolved in acetone and added dropwise with stirring to a solution of Setamol WS, 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.

5.1) Dyeing of polyester fabrics

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

5.2) Dyeing of nylon fabrics

The dyebath was normally set with a nonionic dispersing agent (Uniperol EL., BASF; 1 g/l) with ammonium hydroxide (0.5 g/l, 1:50 material to liquor) at pH 8.5 and (2% dye owf). The fabric was entered at 40 °C, the temperature was raised to 90 °C within 45 min and then maintained at this temperature for 60 min. The sample was picked up, followed by washing with water, reduction-clearing to remove surface dye, rinsing and finally air dried.

5.3) Color fastness tests (Tables 4–7)

(i) Fastness to washing: A specimen of dyed polyester fabrics 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; where 1 = poor, 2 = fair, 3 = moderate, 4 = good, 5 = excellent.

(ii) 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), disodium orthophosphate anhydrous (1 g/l)

and histidine mono-hydrochloride (0.25 g/l). The alkaline solution contained sodium chloride (10 g/l), ammonium carbonate (4 g/l), disodium orthophosphate anhydrous (1 g/l) and histidine mono-hydrochloride (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. The composite specimen was immersed in the perspiration solution for 30 minutes with occasional agitation and squeezing to insure complete wetting, then squeezed to about 200–300 % regain, 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 hours, after which fabrics were dried by conventional means. The change in color of the dyed material and staining on the undyed adjacent fabrics was assessed according to the international Grey scale.

(iii) Fastness to rubbing: The dyed polyester fabric was placed on the base of crockmeter, so that it rested flat on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was mounted over the end of the finger which protects downward on the wetted specimen sliding back and forth twenty times by making ten 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.

(iv) 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 seconds. After conditioning the sample for 16 hours, the change in color of the dyed sample and the staining of white ones were assessed according to the Grey scale.

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

Table 4

Fastness properties of the synthesized dyes 3 on polyester fabrics

Dye	Washing	Perspiration		Rubbing		Sublimation fastness		Light (40 h)
		Acid	Alkali	Dry	Wet	Staining at 180 °C	Staining at 210 °C	
3a	4	4-5	4-5	2-3	4	4	3	5
3b	4-5	4-5	4-5	2-3	3-4	3	3	4
3c	4	4-5	4-5	2-3	3-4	3-4	4	4
3d	4-5	4-5	4-5	4-5	4-5	3-4	4	5-6
3e	4-5	4-5	4-5	4	4-5	4	4	5-6
3f	4-5	4-5	4-5	2	2-3	3	2-3	4
3g	4-5	4-5	4-5	3	3-4	2-3	2-3	4
3h	4-5	4-5	4-5	3	4	3	2-3	4-5
3i	4-5	4-5	4-5	3	4	3-4	3	4
3j	4-5	4-5	4-5	3-4	3	3-4	3-4	4
3k	4-5	4-5	4-5	2	2	3	3	6
3l	4-5	4-5	4	2	2	4	3-4	4
3m	4-5	4	4-5	2	2	2-3	2-3	4
3n	4-5	4-5	4-5	2	2	3	3-4	3

Table 5

Fastness properties of the synthesized dyes 4 and 5 on polyester fabrics

Dye	Washing	Perspiration		Rubbing		Sublimation fastness		Light (40 h)
		Acid	Alkali	Dry	Wet	Staining at 180 °C	Staining at 210 °C	
4a	3-4	4	4	4	3-4	3	2-3	6
4b	4-5	4-5	4-5	4-5	4-5	3	2-3	4
4c	4-5	4	4-5	3	3	4	4	4
4d	4-5	4-5	4-5	3-4	4-5	4	4	6
4e	4	4	4	4	4	3	3	7
4f	4-5	4	4-5	2-3	4	4	3	6
4g	4-5	4-5	4-5	2-3	3	3-4	2-3	6
5a	4	4-5	4-5	2	3	4	2-3	5
5b	4-5	4-5	4-5	4	4	4	4	6
5c	4-5	4	4-5	4	3-4	4	4	4-5
5d	4-5	4-5	4-5	3	4	4	2-3	5
5e	4-5	4-5	4-5	2	3	4	3	5-6
5f	4-5	4-5	4-5	3	4	4	3-4	5
5g	4	4-5	4-5	2	2-3	4	3	4

Table 6

Fastness properties of the synthesized dyes 3 on nylon fabrics

Dye	Washing	Perspiration		Rubbing		Light (40 h)
		Acid	Alkali	Dry	Wet	
3a	4	4-5	4-5	4	4	7
3b	4-5	4-5	4-5	4-5	4-5	7
3c	4-5	4	4-5	4	4-5	7
3d	4-5	4	4-5	4	4	6-7
3e	4-5	4	4-5	4-5	4-5	7
3f	4	4	4-5	4-5	4-5	6
3g	4	4-5	4-5	3-4	3-4	6-7
3h	4-5	4-5	4	4-5	4	7
3i	4-5	4-5	4-5	4-5	4	6
3j	4-5	4-5	4-5	4-5	4	6
3k	4-5	4-5	4-5	4-5	4	7
3l	4-5	4-5	4-5	4-5	4	6-7
3m	4-5	4-5	4-5	4-5	4	6-7
3n	4	4-5	4-5	4-5	3-4	7

Table 7

Fastness properties of the synthesized dyes 4 and 5 on nylon fabrics

Dye	Washing	Perspiration		Rubbing		Light (40 h)
		Acid	Alkali	Dry	Wet	
4a	4-5	4-5	4-5	4	3-4	6
4b	4-5	4-5	4-5	4-5	4-5	7
4c	4-5	4	4-5	4	3	5-6
4d	4-5	4-5	4-5	3-4	4-5	7
4e	4-5	4	4	4-5	4	6-7
4f	4-5	4	4-5	2-3	4	6
4g	4-5	4-5	4-5	2-3	3	6-7
5°	4	4-5	4-5	2	3	4-5
5b	4-5	4-5	4-5	4	4	5
5c	4-5	4	4-5	4	3-4	5
5d	4-5	4-5	4-5	3	4	6
5e	4-5	4-5	4-5	2-3	3	7
5f	4-5	4-5	4-5	3	4	4-5
5g	4	4-5	4-5	3	2-3	4

5.4) Color assessment

The color parameters of the dyed fabrics were determined on a GretagMacbeth CE 7000a spectrophotometer. The values of the chromaticity coordinates, luminance factor and the positions of colors in the CIELab color solid are reported in Tables 8–11.

Table 8

Optical measurements of dyes 3 on polyester fabrics

Dye	K/S	L*	a*	b*	C*	H
3a	3.55	78.88	-1.27	38.59	38.61	87.82
3b	2.52	85.11	-0.89	13.76	16.38	86.22
3c	3.53	86.64	-2.19	7.07	7.401	86.96
3d	1.80	82.58	0.28	14.17	14.17	83.79
3e	2.37	75.48	6.71	31.74	32.44	82.16
3f	2.71	80.28	2.41	15.24	15.43	81.75
3g	2.76	71.14	12.70	28.01	30.75	77.50
3h	2.86	75.43	2.72	30.23	30.35	81.3
3i	1.38	81.66	-1.05	21.31	21.34	84.40
3j	1.49	78.99	1.02	23.50	23.52	82.42
3k	1.18	79.39	2.63	18.37	18.56	81.49
3l	1.41	77.22	3.27	25.49	25.69	81.38
3m	1.68	81.26	-1.77	23.87	23.94	84.71
3n	1.73	80.36	-0.60	22.85	22.86	83.55

Table 9

Optical measurements of dyes 4 and 5 on polyester fabrics

Dye	K/S	L*	a*	b*	C*	H
4a	7.35	68.30	6.97	44.64	45.18	81.89
4b	0.38	81.07	3.34	20.41	20.68	80.71
4c	13.56	40.99	35.32	41.81	54.73	49.81
4d	1.43	74.23	9.13	37.20	38.31	76.21
4e	0.33	89.36	-1.78	3.14	3.61	85.84
4f	11.17	79.93	2.77	16.75	16.97	81.71
4g	1.25	72.91	34.11	47.57	58.54	76.13
5a	3.95	65.51	5.37	30.77	31.24	72.58
5b	3.04	80.93	-1.55	14.02	14.11	82.15
5c	3.45	72.85	3.39	29.50	29.69	78.67
5d	3.69	77.18	1.52	21.97	22.02	80.26
5e	3.77	82.52	-0.18	16.19	16.19	84.09
5f	3.80	78.58	1.84	26.06	26.12	82.81
5g	2.25	74.23	2.08	21.34	21.44	77.27

Table 10

Optical measurements of dyes 3 on nylon fabrics

Dye	K/S	L*	a*	b*	C*	H
3a	2.48	67.51	12.18	43.38	45.06	78.31
3b	1.62	81.20	-0.48	18.97	18.98	83.39
3c	0.17	84.17	-3.21	17.17	17.47	100.59
3d	1.82	80.87	-0.39	20.37	20.37	83.39
3e	2.31	72.07	80.55	47.54	48.19	80.55
3f	2.11	78.33	-1.03	30.79	30.81	84.17
3g	1.98	78.27	3.23	22.54	22.77	81.51
3h	3.68	77.79	-0.66	29.46	29.47	83.18
3i	3.7	75.07	0.86	30.19	30.20	80.92
3j	2.77	79.35	-1.3	25.57	25.60	83.38
3k	4.02	67.26	8.53	23.12	24.64	71.64
3l	2.53	80.28	-1.27	21.53	21.57	83.12
3m	4.18	78.67	-1.28	28.50	28.53	83.69
3n	5.65	77.32	1.71	33.85	33.89	84.42

Table 11

Optical measurements of dyes 4 and 5 on nylon fabrics

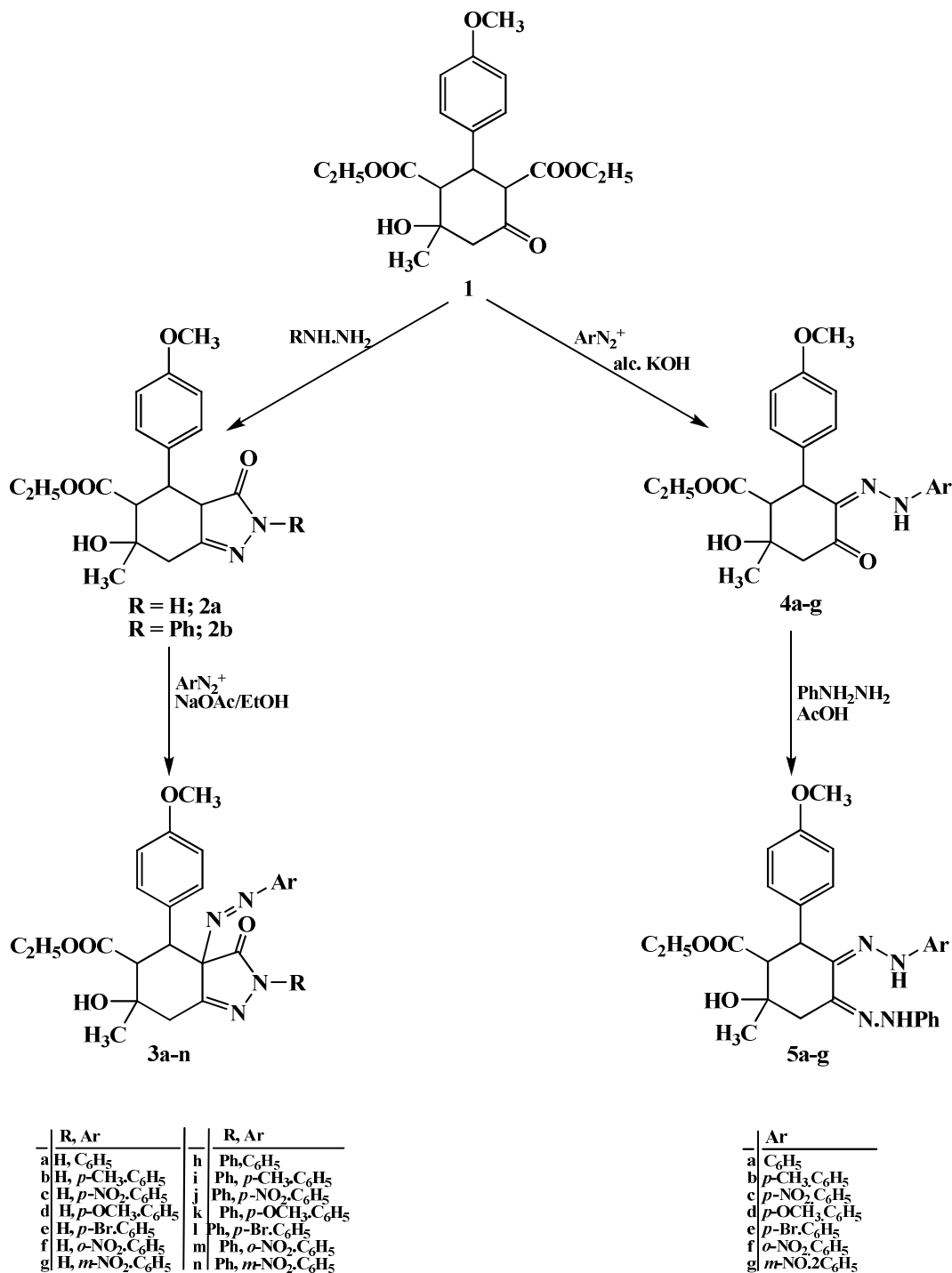
Dye	K/S	L*	a*	b*	C*	H
4a	4.93	72.92	8.5	65.45	65.99	82.59
4b	1.38	82.8	-3.4	14.84	15.22	84.19
4c	4.06	61.09	14.65	44.07	46.44	71.61
4d	2.54	78.45	-1.5	34.16	34.19	85.58
4e	0.11	84.67	-2.88	13.92	14.21	1.67
4f	2.38	77.97	-0.5	32.28	32.28	89.78
4g	3.06	75.25	1.45	39.28	39.30	82.7
5a	1.17	81.61	-0.55	11.54	11.55	82.42
5b	3.37	80.53	-1.71	20.33	20.40	83.07
5c	4.76	78.25	-0.53	34.74	34.74	85.62
5d	2.22	79.10	-1.87	32.04	32.09	85.36
5e	2.92	80.27	-4.00	28.11	28.39	85.14
5f	2.62	80.67	-3.50	29.69	29.89	86.03
5g	2.65	78.69	-1.65	31.74	31.78	84.87

3, RESULTS AND DISCUSSION

Structure elucidation of prepared dyes

Condensation of cyclic β -keto ester (**1**) with equimolar amount of hydrazine hydrate in ethanol and phenylhydrazine in acetic acid afforded the

corresponding ethyl-6-hydroxy-4-(4-methoxyphenyl)-6-methyl-3-oxo-3,3a,4,5,6,7-hexahydro-2H-indazole-5-carboxylate (**2a**) [7] and ethyl-6-hydroxy-4-(4-methoxyphenyl)-6-methyl-3-oxo-2-phenyl-3,3a,4,5,6,7-hexahydro-2H-indazole-5-carboxylate (**2b**), respectively (Scheme 1).



Scheme 1

Coupling of **2a** and or **2b** with different diazotized aromatic amines, afforded the corresponding new azo compounds ethyl 3a-(2-aryldiazenyl)-3,3a,4,5,6,7-hexahydro-6-hydroxy-4-(4-methyl-3-oxo-2H-indazole-5-carboxylates **3a-n** (Scheme 1). The structure of these compounds was assigned from their elemental analyses and spectral data. The IR spectra showed bands at 3439–3510 cm^{-1} (OH), 3292–3190 cm^{-1} (NH_2 , NH), 1702–1728 cm^{-1} (CO amide), 1505–1511 cm^{-1} (C=C aromatic ring).

Further extension to the formation of dye compounds was achieved when 2,4-diacarboethoxy-5-hydroxy-3-(4-methoxyphenyl)-5-methyl cyclohexanone (**1**) was subjected to the Japp-Klingemann reaction in alkaline medium with diazotized aromatic amines namely (aniline, *o*-, *m*-, *p*-nitroanilines, *p*-toulidine and *p*-bromoaniline) to produce the corresponding hydrazones **4a-g** (Scheme 1). The IR spectra of **4a-g** showed absorption bands at 1550–1590, 1620–1630, 1695–1710 and 3460–3500 cm^{-1} corresponding to N=N, C=N, α - β unsaturated CO-cyclohexanone, CO-ester) and OH groups, respectively.

Treatment of **4a-g** with phenyl hydrazine in acetic acid produced 1-arylhydrazono-3-ethylcarboxylate-4-hydroxy-2-(4-methoxyphenyl)-4-methyl-6-(phenylhydrazono) cyclohexanes **5a-g** (Scheme 1). Their structures were confirmed by elemental analytical and spectral data. The IR spectra exhibited bands at 1505–1509 cm^{-1} (C=C in the aromatic ring), 1713–1721 cm^{-1} (CO ester), 3190–3294 (NH), and 3418–3502 cm^{-1} (OH).

Absorption spectral characteristics

The visible absorption data for the synthesized dyes were measured in chloroform and are recorded in Table 12. The absorption maxima of the synthesized dyes ranged from 331 to 502 nm. Within the series of azo dyes investigated, the relation between the shift observed in the absorption maxima, and polar characteristics of substituent, may be summarized as follows:

1) The introduction of an electron donating group in the para-position of the arylhydrazono moiety gave a bathochromic shift relative to the unsubstituted compound (e.g. compounds **4** and **5c,d**).

2) The introduction of a nitro group gave a better exhaustion and noticeable depth of color on dye (e.g. compound **4c**).

3) The bathochromic shift accompanying the substituents in the diazo component was in the following order $\text{H} \rightarrow \text{CH}_3 \rightarrow \text{OCH}_3 \rightarrow \text{Br} \rightarrow \text{NO}_2$

Table 12

Electronic absorption spectra of dyes 3–5

	Absorption λ_{max} nm			Absorption λ_{max} nm	
	3	4	5	3	
a	386	395	381	h	392
b	423	331	383	i	372
c	346	502	371	j	422
d	424	394	267	k	442
e	447	384	381	l	357
f	353	411	334	m	400
g	385	352	419	n	381

Fastness properties of the dyed polyester fabrics

The synthesized disperse dyes (**3–5**) under investigation were applied to polyester fabrics at 2 % shade by high-temperature pressure technique (130 °C) and gave generally deep and bright hues, ranging from yellow to brown. The dyes on polyester fabrics were evaluated in terms of their fastness properties. The dyes gave excellent uniformity of coloration on polyester fabrics and the overall fastness properties of the dyes are shown in Tables 4 and 5.

a) *Fastness to washing.* The results obtained showed that dyed fabrics have good fastness to washing according to the international geometric Grey scale [8, 9]. The rather good fastness properties to washing may be due to:

1) The absence of solubilizing groups, which renders solubility, and wash ability of the dye-out of the fabrics.

2) The size of the dye molecule is considered relatively big.

3) The good intrafiber diffusion of the dye molecules inside the fabrics.

b) *Fastness to perspiration (acid and alkaline).* The AATCC standard test method 15-1960 was used where, the prepared dyes showed satisfactory fastness to acid and alkaline perspiration ranging 4–5.

c) *Fastness to rubbing*. The rubbing fastness test was carried out using a Crockmeter of Atlas electronic type as per the AATCC 8-1961 standard methods of testing. Fastness to rubbing (wet and dry) is a boarder line ranging 2–4 and this may be attributed to inadequate diffusion of the dye molecule into the fabrics.

d) *Fastness to sublimation*. The sublimation resistance of disperse dyestuffs is determined mainly by its molecular size [10]. Consequently, the majority of these dyes were found to have good sublimation fastness 3–4 according to the international Geometric Grey Scale.

e) The light fastness of synthesized dyes **3–5** on polyester is affected significantly by the nature of the substituents in the diazo component. In this study, the inclusion of the electron-withdrawing (nitro or bromo) group improves the light fastness, (e.g. **4e**). This is in agreement with the notion that the azo compounds appended with electron-withdrawing substituents on the diazo components are less prone to photofading [11]. Generally, the prepared dyes showed satisfactory fastness to light ranging 4–6 according to the international Geometric Grey Scale.

The color of the synthesized dyes on *polyester fabrics* was evaluated using the CIELAB system in terms of L*, a* and b*. The dyes have bright and good affinity to polyester fabrics and the results are listed in Tables 8 and 9.

Dyes **3**: The K/S values through the dyes **3** range from 0.45 to 3.55 where the introduction of bromine (*p*) and nitro (*m*) in the phenylhydrazono group (e.g. dyes **3e** and **3g**) increases the color strength on polyester fabrics. The color hue of most of these dyes on polyester fabrics is shifted to the greenish direction on the red-green axis as indicated from the negative value of a*.

Dyes **4** and **5**: The K/S values in this group of the synthesized dyes vary from 0.33 to 13.56 (Table 5). The color hue of the dye **4**, **5b** and **5e** (substituted by bromo and methyl in the phenylhydrazono group) on polyester fabrics is shifted to the

greenish direction on the red-green axis as indicated from the negative value of a*.

The application of the dyes **3–5** on *nylon fabrics* has shown that such dyes have bright colors and good affinity to nylon fabrics. These results are listed in Tables 10 and 11.

Dyes **3**: The K/S values through the dyes **3** (Table 10) range from 0.17 to 5.65 where the introduction of the nitro group in the phenylhydrazono group (e.g. dyes **3m,n**) increases the color strength on nylon fabrics. On the other hand, the introduction of phenyl group associated to indazole moiety (e.g. compounds **3h** and **3n**) increases the color strength on nylon fabrics. The color hue of most of these dyes on nylon fabrics is shifted to the greenish direction on the red-green axis as indicated from the negative value of a*.

Dyes **4** and **5**: The K/S values in this group of the synthesized dyes vary from 0.11 to 4.93 (Table 11). The color hue of these series on nylon fabrics is shifted to the greenish direction on the red-green axis as indicated from the negative value of a*.

REFERENCES

- [1] E. Heinz, H. Guenter, and S. Guenther. *Ger. Offen.* 2908357 (1981). C. A. 94 (1981) 4944z.
- [2] L. Kiaus, *Ger. Offen*, DE 3609343 (1986). C. A. **108** (1988) 23326y.
- [3] D. F. Francesco, C. Roberto, V. Roberto, M. Angelo, and T. Federico, *Ger. Offen* 2949302 (1978). C.A. 93 (1980) 133825q.
- [4] S. A. Raw and A. T. Turner. *Tetrahedron Lett.*, **50**, 696–699 (2009).
- [5] D. Li, K. Schröder, B. Bitterlich, M. K. Tse, and M. Beller. *Tetrahedron Lett.*, **49**, 5976–5979 (2008).
- [6] T. Boisse, P. Gautret, B. Rigo, L. Goossens, J. -P. Hé-nichart, and L. Gavara. *Tetrahedron*, **64**, 7266–7272 (2008).
- [7] B. Lal and A. P. Bhaduri. *Indian J. Chem.*, **15**, 359–363 (1977).
- [8] W. Beckmann. *Candian Textile J*, 83–69 (1966).
- [9] P. Senner and A. Rezk. *Melliand Textilber*, 50–64 (1969).
- [10] R. Kern, *Candian Textile J*, 80–52 (1963).
- [11] P. F. Gordon, P. Gregory. *Organic Chemistry in Color*, Springer, Berlin (1983) 289.