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Microwave-Assisted Synthesis of Arylazoaminopyrazoles as Disperse Dyes for Textile Printing

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Abstract. The synthesis of heterocyclic azo-dyes via conventional heating and microwave (MW) heating was investigated. From a sequence of reactions starting from cyanoacetic acid, 4-arylazo-2*H*-pyrazol-3-ylamines and 4-arylazo-2-phenyl-2*H*-pyrazol-3-ylamines were obtained. The structures these compounds were obtained by inspection of spectroscopic and analytical techniques including ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analysis. The fastness properties and UV/Vis absorption spectroscopic data of these disperse dyes in printing polyester fabrics were investigated.

Introduction

Pyrazoles are significant intermediates that can be applied in photography,[1,2] agrochemicals,[3] dyes,[4–7] and biologically and pharmacologically complexes.[8–10] Aminopyrazoles belong to an important group of materials used for the development of a variety of functional derivatives essentially for the synthesis of fused heterocyclic molecular structures.[11–18] Fused pyrazoles have a broad range of attractive properties such as analgesic, antidiabetic, antimicrobial, antipyretics, and antiinflammatory.[13–19] Furthermore, fused pyrazoles can function as sedative-hypnotic medications and non-nucleoside HIV-1 reverse transcriptase inhibitors.[20,21] Azo-based disperse dyes can be synthesized from a variety of heterocyclic intermediates to afford heteroaromatic azo disperse dyes with good tinctorial strength and brighter coloration properties than those derived from aromatic azo components.[22,23]

Aminoarylazopyrazoles are already marketed disperse dyes as well as dyes in modern dye diffusion thermal transfer (D2T2) printing technology because of their promising properties.[24–26] However, all commercially available dyes have an alkyl or aryl substituent at the pyrazole carbon atom C-3.[12–19] As the substituent does not contribute to the color, the removal of this substituent is expected to produce tinctorially stronger dyes, which may have better properties as printing dyes especially that ones used in printing techniques, with which the dye only penetrates few angstroms into the fabric.[24,26]

Protecting human health and environment but maintaining commercial availability is a scientific challenge. Industrial chemistry adapts the concept of green chemistry to confront the modern environmental requirements. The emerging area of green chemistry implements the art of chemistry to minimize hazards while achieving the industrial targets. This could be achieved by exploring substitutional reaction conditions to perform the chemical transformation with minimized by-products and reduce the need for organic solvents. Microwave energy is an attractive alternative of conventional heating as a tool in modern organic chemistry, in order to maintain more green chemistry.[11,22,27]

Microwave is a controllable penetrating radiation that has been employed to accelerate chemical reactions due to the discriminatory absorption of microwave energy by polar molecules.[22] Microwave processing of materials is a relatively novel technique able to enhance their physical properties, processing, ecological impact, and cost effective due to time and energy savings.[11,27,28]

Herein, the synthesis of a series of 3-unsubstituted pyrazole-based azo-dyes and their potential application as disperse dyes for printing polyester fabrics is reported. As microwave heating replaces conventional heating, the outcomes of conventional and microwave heating are investigated. The fastness properties, color strength, and UV/Vis spectroscopic data of the presented dyes were also evaluated.

Results and Discussion

Synthesis of the Intermediates and Dyestuffs

The molecular structures of synthesized compounds were confirmed by a range of spectroscopic methods including ^{1}H- and ^{13}C NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analysis. *Elnagdi* et al.[14,29,30] reported that

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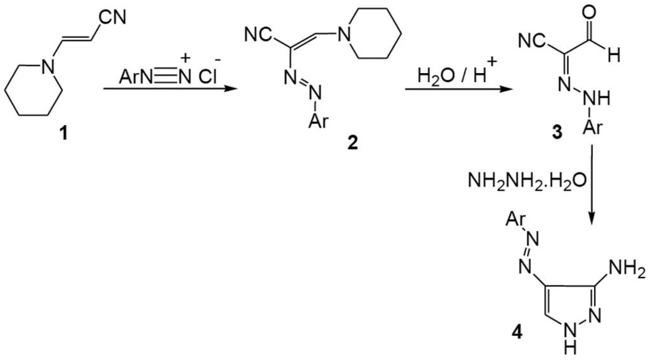
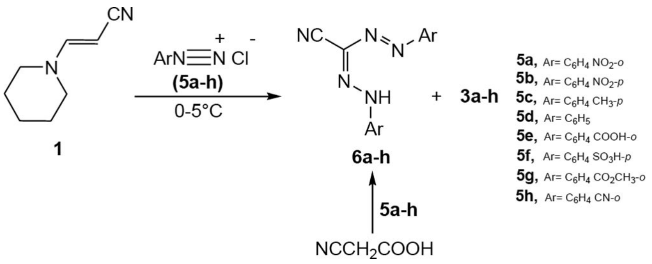
the reaction of enaminonitrile**1** with aromatic diazonium salts afforded arylhydrazones **3** via intermediacy of enazo derivatives **2**. The arylhydrazones **3** were readily converted into arylazoaminopyrazoles **4** in good yields.

It was investigated if reactions in Scheme 1 can constitute a general synthetic approach to 4-arylazo-2*H*-pyrazol-3-ylamines. Thus, the enaminonitrile **1** coupled smoothly with a variety of aromatic diazonium salts **5a–h** to afford yellow to red solids of arylhydrazones **3a–h** in moderate to very good yields. However, in every case the product was contaminated with the corresponding formazans **6a–h**. These formazans have also been prepared from coupling the corresponding diazonium salts **5a–h** with cyanoacetic acid utilizing literature procedures as shown in Scheme 2.[31,32]

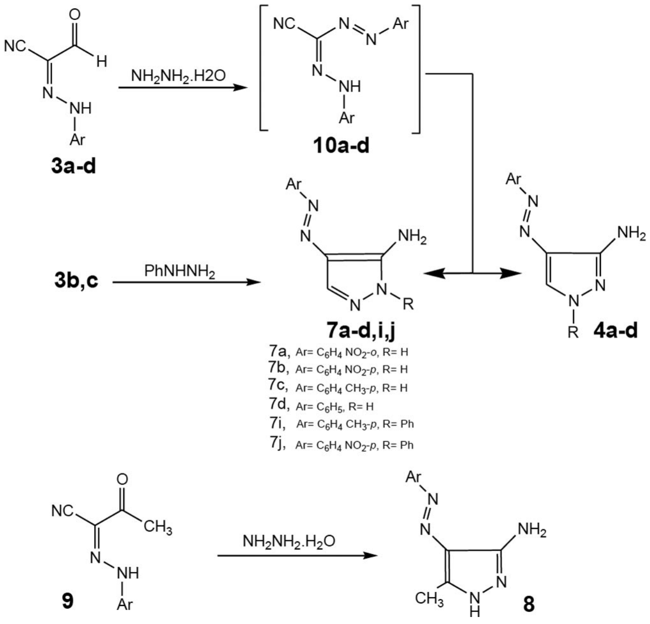


Scheme 1. Synthesis of arylazoaminopyrazoles **4** starting from enaminonitrile **1**.



Scheme 2. Formation of formazan derivatives.

Compounds **3a–d** reacted readily with hydrazine hydrate in refluxing ethanol to yield aminopyrazoles that may be formulated as **4a–d** or **7a–d**. The ^{1}H NMR spectra indicated that the chemical tautomeric structure **7** is the correct reaction product due to the presence of a pyrazole C–H singlet peak at δ ≈ 6 ppm. In the case of 5-substituted-3-aminopyrazoles **8**, the tautomeric form **4** is the preferred form as in these molecules, in contrast to ones with alkyl or aryl substituent at ring nitrogen, experience less steric strain.[12–19] In support of this view, compounds **3b** and **3c** reacted smoothly with phenylhydrazine to yield aminopyrazoles **7i** and **7j**. The UV/Vis absorption spectra of **7i** and **7j** were found very similar to those of **7a–d** and different than the UV/Vis absorption spectra of derivatives **8**; prepared by reaction of **9** with hydrazine hydrate as reported in the literature (Scheme 3).[13,31]



Scheme 3. Synthesis of aminopyrazole derivatives.

In contrast to marketed dyes of molecular structure **8**, dyes **7** show light brown to orange-red shades, whereas dyes **8** show yellow shades, which may be attributed to the presence of aryl or alkyl substituent at carbon C-3 of dye **8**, which restricts the conjugation with the amino group through a push-pull system,[23] and hence the amino group in **7** participate in the conjugation of that dyes as shown in Figure 1. Such observation would be an indication that **7** is the true structure form. This may supported by the similarity of the values of λ_{max} of dyes **7b** and **7c** and their analogues dyes **7i** and **7j** (Figure 1).

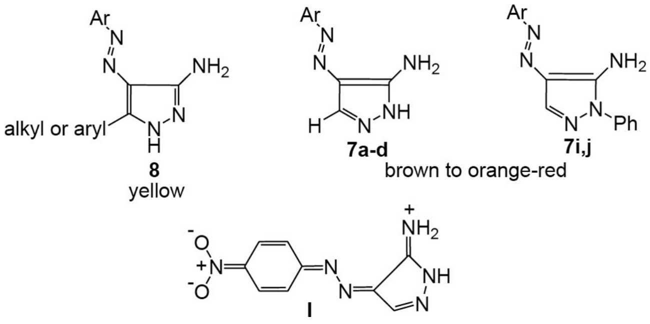
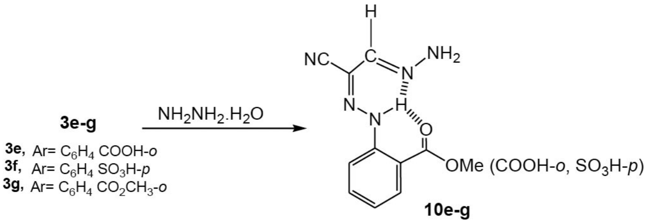


Figure 1. Structure effect of different aminopyrazole derivatives.

In contrast to the behavior of **3a–d,** compounds **3e–g** reacted with hydrazine hydrate to afford only the arylhydrazones **10e–g**, which could not be further cyclized. The effect of formation of a bifurcated hydrogen bond with hydrogen of NH as well as the methoxy carbonyl group is beyond stability of this intermediate despite deriving force for cyclization by resonance stabilization of a would-be formed aminopyrazole derivative (Scheme 4). The IR spectra of compound **10g** show a CN group sharp band at 2192 cm^{-1}.



Scheme 4. Formation of a bifurcated hydrogen bond.

The products **1**, **7a–d, 7i**, and **7j** were also obtained by microwave heating of reactants in DMF for 1–2 min and subsequent treatment with water. The same products were obtained with these conditions, better yields and lower time consuming have generally been established as indicated in Table 1.

Table 1. Yield and time comparison between conventional and MW heating.

Compound	Conventional heating		Microwave heating	
	Yield /%	Time /h	Yield /%	Time /min
1	67	2	79.6	1
7a	61.6	2–3	72.5	1
7b	63.1	2–3	71	1
7c	54.3	3	68.9	1
7d	52	2	67	1
7i	84	2	73	1
7j	54	2–3	76.8	1

UV/Vis Absorption Spectra and Color Strength

The color strength of the printed substrate for each dye, quantified as K/S, are listed in Table 2, together with the hues of the polyester samples and the absorption maxima of the presented dyes in DMF (Figure 2). Dyes **7b** and **7j** show a slight increase in color strength in accordance with electron-withdrawing groups (X = p-NO_2), whereas the opposite occurred with electron-donating groups (X = CH_3). Generally, dyes **7** show a slight decrease in color strength than other disperse dyes such as pyrazolopyrimidines, because of the higher molecular weight of the later ones.

Table 2. UV/Vis absorption spectra and color strength of the prepared dyes on polyester fabrics.

Dye no.	λ_{max} (DMF)	Color shade on polyester	K/S
7a	472	Brown	2.17
7b	489	Orange	3.72
7c	480	Yellow	1.84
7i	478	Yellow	2.91
7j	497	Orange-red	3.23

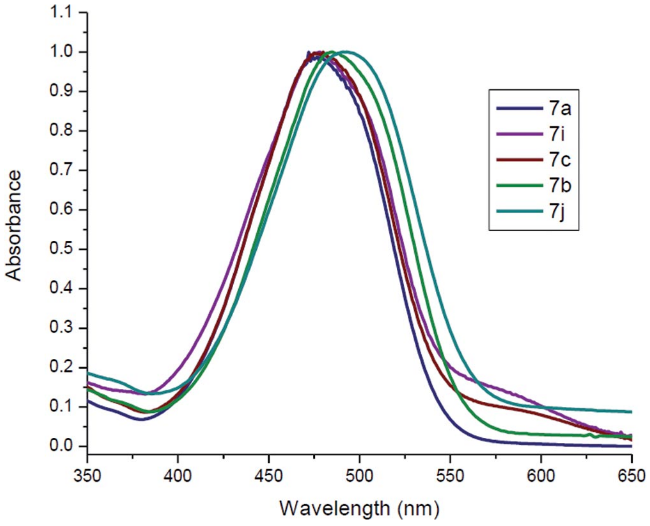


Figure 2. UV/Vis absorption spectra of the prepared dyes.

The hues of the printed fabrics were in agreement with the observed λ_{max} values of the produced dyestuffs in solution. The present dyes give light brown to orange-red shades. Dye **7a** is the most hypsochromic one, because of lower conjugation and the o-NO_2 substitution, which does not affect conjugation, whereas dye **7j** is the most bathochromic, because of their higher conjugation and the stronger electron-withdrawing substituent (p-NO_2). It is obvious that the existence of a nitro group *ortho* to the azo linkage does not seem to be harmful to the color shift.

Application of Dyes on Polyester Fabrics

The current discussion will explain the shifts of UV/Vis absorption maxima affected by the structure configuration of the 4-arylazo-2*H*-pyrazol-3-ylamine, 2-phenyl-4-arylazo-2*H*-pyrazol-3-ylamine derivatives. The intensity and shade of color together with the fastness properties of the printed polyester fabric are also evaluated.

Fastness Properties

In general, the fastness properties of the printed fabrics were satisfactory as shown in Table 3. The depth of color shade and dye molecular structure was observed to affect the fastness results.

Table 3. Fastness properties of the synthesized dyes on polyester fabrics.

Dye no.	Wash fastness[a)]		Perspiration fastness[a)]				Rubbing fastness		Light fastness
			Acidic		Basic				
	Alt.	St.	Alt.	St.	Alt.	St.	Dry	Wet	
7a	4–5	4–5	4–5	4–5	4	4–5	4–5	4–5	6–7
7b	3–4	4	4	4	4	4	4	4	3
7c	4–5	4–5	4–5	4–5	4–5	4–5	4	4	6–7
7i	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	5
7j	4	4	4	4	4	3–4	3–4	3–4	4

a) Alt. = alteration in color; St. = staining on cotton.

Washing Fastness

The rate of movement of the dyes out of polyester fibers during washing process depends on the molecular size of dye, nature of mechanical link formed between the dye and the fibers, and nature of charge located on the dye, which is affected by the electron donating or electron withdrawing nature of the substituents. The results of washing fastness properties for the printed polyester fabrics including alteration and stain on cotton were generally from poor to very good for both series. It was observed that high washing fastness results were obtained with electron-donating substituents indicating their higher substantivity to hydrophobic fabrics. On the other hand, a lower wash fastness results were obtained with electron-withdrawing ones and consequently having poor substantivity to hydrophobic fabrics.

Perspiration Fastness

The extent of dye removal from polyester fabric under the effect of perspiration solution is demonstrated in Table 3. The results show that the dye removal is mostly depends on the substituents on the dye. Thus, the dyes with electron-withdrawing groups indicate a lower stability to the perspiration solutions. Generally, the records represent perspiration fastness values from poor to very good with higher ratings for dyes with electron-donating groups.

Rubbing Fastness

A numerical evaluation for the removal of loosely adhered dye molecules from the surface of the polyester fabric can be accomplished by the color fastness to rubbing test. The obtained records demonstrate that the higher values of rubbing fastness are for dyes with the higher molecular weights. All dyes give, generally, good rubbing fastness results.

Light Fastness

The obtained dyes demonstrate light fastness values which varied from poor to very good depending on the dye molecular structure and depth of shade. Dyes **7a–c** had better fastness on polyester than the other colorants. Dyes **7a–c** had improved ratings on polyester than the other colorants **7i** and **7j** that could be attributed to their increased concentration in the fiber and the higher substantivity of 4-arylazo-2*H*-pyrazol-3-ylamine based dyes. In aminoazobenzene derivatives, an increase in the electron withdrawing effect of the diazo component leads to a decrease in the electron density on the amino nitrogen atom with photofading taking place due to singlet oxygen attack at this site.[22,23]

Generally, a similar photofading effect was observed with the present dyes containing the electron withdrawing *p*-nitro substituent. As mentioned before, the *o*-nitro group does not affect conjugation and hence this phenomenon does not affect dye **7a**.

Conclusions

A series of azo disperse dyes based on aminopyrazoles without substituents at carbon atom C-3 were synthesized via conventional heating. Microwave heating was employed to synthesize the same dyes to verify lower time and energy consumption. The produced dyes were printed on polyester fabrics to afford solid shades with satisfactory levelness and depth of shade. The observed shades are between yellow, orange, orange-red, and brown. The results of fastness properties the reported dyes demonstrated in most cases acceptable to very good fastness against light, rubbing, perspiration and washing on the polyester fabrics.

Experimental Section

Materials and Apparatus: All melting points are uncorrected and are expressed in °C. They were determined with a Stuart melting point apparatus. IR spectra were recorded in KBr with a FT-IR Nicolet 670 spectrometer. ^{1}H NMR spectra were recorded with a Varian GEMINI 200 MHz, using TMS as the internal standard, and chemical shifts are given in δ (ppm). The ^{13}C NMR spectra were obtained with a Joel-ex-400 MHz NMR spectrometer, the chemical shifts are expressed in δ (ppm) using TMS as the internal standard. Mass spectra were obtained with a Shimadzu GCMS-QP-1000 EX spectrometer in (70 ev) mode. UV/Vis absorption spectra and the maximum wavelength (λ_{max}) were recorded at room temperature with an UNICAM UV/Vis 300 instrument from dye solutions in DMF at a concentration of 1×10^{-4} mol·L^{-1}. Microanalysis for C, H and N were performed with a Perkin-Elmer 2400 III platina. The elemental analyses were performed at the Microanalytical Center, Cairo University. The fastness properties were determined at the National Research Centre, Dokki, Cairo, Egypt. The color strength was recorded with an UltraScan PRO Spectrophotometer (light source D65/10° observer). A Domestic 34L Microwave Stainless Steel oven (ME6124ST) was employed as a microwave source.

Dry solvents for syntheses and spectroscopic measurements (spectroscopic grade) were employed without further purification. Scoured and bleached 100 % polyester fabrics were supplied by El-Mahalla El-Kobra Company, El-Mahalla, Egypt. The fabrics were scoured in aqueous solution having a liquor ratio of 1:50 and containing 2 g·L^{-1} of non-ionic detergent solution (Hostapal; Clariant, Swiss) and 2 g·L^{-1} of sodium carbonate at 50 °C for 30 min to get rid of waxes and impurities, followed by rinsing in cold water, and finally dried at room temperature.

Printing Procedure: Dyes were grinded with a small mortar and pestle, and sieved by U.S.A. standard sieves (opening 0.0029 inches / 75 µm), Newark. A paste composed of synthetic thickener's stock paste (3.5 g ALCOPRINT DT-CS + 95 g water) and the grinded dye (1.5 g) was prepared by stirring the mixture very well. The printing paste was applied to the fabrics using the flat screen printing technique. Print fixation was done by thermofixation at 180–200 °C for 2–3 min in an automatic thermostatic oven (Wemer Mathis Co., Switzerland). The thermofixation process also was done at different periods and temperatures to determine the optimum conditions of fixation. Washing off process operated by cold water rinsing with soap at 40 °C using 1 g·L^{-1} Ciba "ERIOPON" OS. Reduction clear performed at 50 °C using 1–2 g·L^{-1} hydrosulfite, 1–2 g·L^{-1} caustic soda and 1 g·L^{-1} Ciba "ERIOPON" OS. The printed fabric was rinsed at 50 °C with cold water and finally dried.

Assessment of Color Fastness: Fastness to washing, perspiration, and light was tested according to the reported methods.

Color Strength Measurement: The color strength of the printed samples expressed as K/S was evaluated by high reflectance technique. The color strength expressed as K/S was assessed by applying the Kobelka Munk equation $[K/S = (1–R)^2/2R–(1–R_0)^2/2R_O]$, where K is the absorption coefficient; S is the scattering coefficient; and (R, R_O) are decimal fractions of the reflectance of the printed and unprinted fabric, respectively.

Colorfastness to Rubbing: The colorfastness to crocking was determined according to the AATCC test method (ISO 105-X12:1987 test method).[33] In this test the color transferred from the surface of the colored fabric to other surface by rubbing. A colored test specimen fastened to the base of a crockmeter was rubbed on a white crock test cloth under controlled conditions.

Dry Rubbing Test: The test specimen was placed on the base of the crockmeter, Atlas Crockmeter. A white testing cloth was mounted. The covered finger was lowered onto the test specimen and caused to slide back and forth 20 times by making ten complete turns at a rate of one turn per s. The white test sample was removed for evaluation using the Grey Scale for staining.

Wet Rubbing Test: The white test sample was thoroughly wetted out in water to a 65 % pick up. The procedure was run as before, the white test samples were then air-dried before evaluation.

Colorfastness to Washing: The color fastness to washing was determined according to the AATCC test method (ISO105-C02:1989method) [34] using Launder-Ometer. The specimens (5 × 10 cm) were sewed between two similar pieces of bleached cotton fabric. The composite specimen was immersed into an aqueous solution containing soap ($5\ g{\cdot}L^{-1}$) and sodium carbonate ($2\ g{\cdot}L^{-1}$) at a liquor ratio of 50:1. The bath was thermostatically adjusted to 45 °C. The test was run for 30 min at 42 r.p.m. The samples were removed, rinsed twice with occasional stirring or hand squeezing, and dried. The washing fastness was assessed using the Grey Scale reference for color change.

Colorfastness to Perspiration: Two artificial perspiration solutions (acidic and alkaline) were prepared according to the test method (ISO 105-E04:1989).[35]

Alkaline Solution: L-Histidine monohydrochloride monohydrate ($0.25\ g{\cdot}L^{-1}$), sodium chloride ($10\ g{\cdot}L^{-1}$), and sodium dihydrogen phosphate ($1\ g{\cdot}L^{-1}$) were dissolved in distilled water (1 L). Finally, the pH was adjusted to 8 by sodium hydroxide solution (0.1 N).

Acidic Solution: L-Histidine monohydrochloride monohydrate ($0.25\ g{\cdot}L^{-1}$), sodium chloride ($10\ g{\cdot}L^{-1}$), and sodium dihydrogen phosphate ($1\ g{\cdot}L^{-1}$) were dissolved in distilled water (1 L). Finally the pH was adjusted to 4.3 by acetic solution (10 %). The colored specimen 5 × 4 cm was sewed between two pieces of uncolored specimens to form composite specimen. The composite sample was immersed for 15–30 min in each solution with occasional agitation and squeezing to insure complete wetting. The test specimen was placed between two glass plates under a force of about 4–5 kg. The plates containing the composite specimen were then held vertical in the oven at 37 °C ± 2 for 4 h. The effect on the color of the test specimen was expressed and defined by reference to Grey Scale for color change.

Colorfastness to Light: Colorfastness to light was determined according to AATCC test method (ISO 105-B02:1988).[36] The evaluation was established using the blue scale as reference of color change. For light fastness testing, a FADE-OMETER, 18-F equipped with a UV lamp was employed, and light exposures were conducted for 35 h.

Syntheses of Intermediates

Synthesis of 3-Piperidin-1-yl-acrylonitrile (1):[14,29] A mixture of cyanoacetic acid (0.05 mol), triethyl orthoformate (0.05 mol), and piperidine (0.5 mL) was heated to reflux for 2 h, allowed to cool to room temperature, and poured into cold water. The reaction mixture was treated with sodium carbonate solution (1 molar, 50 mL), extracted with dichloromethane (100 mL), and the extract was left overnight to dry. The solvent was evaporated in vacuo. The compound was obtained as buff crystals. Yield: 67 %; mp. 60 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 2220 (CN) cm^{-1}. **MS**: *m/z* 137 (M^+). **^1H NMR** ($[D_6]DMSO$): δ = 1.43–1.56 (m, 6 H, piperidinyl-H), 3.12–3.30 (4 H, piperidinyl-H), 4.06 (d, 1 H, *J* = 14 Hz, vinyl-H), 7.13 (d, 1 H, *J* = 14 Hz vinyl-H). $C_8H_{12}N_2$ (136.20): calcd. C 70.55; H 8.88; N 20.57 %; found: C 70.52; H 8.80; N 21.2 %.

General Procedure for the Synthesis of 2-(Substituted-phenylhydrazono)-3-oxo-propionitrile 3a–g: An aryldiazonium salt (0.01 mol) solution was prepared by adding sodium nitrite solution (0.7 g in 10 mL H_2O) to a chilled solution of arylamine hydrochloride (0.01 mol of arylamine in 5 mL conc. HCl) with stirring. The resulting aryldiazonium solution was added to a cold solution of 3-piperidinoacrylonitrile (**1**) in acetic acid (50 mL) containing sodium acetate. The reaction mixture was stirred for 1 h. The solid product so formed was collected by filtration and crystallized from ethanol.

Synthesis of 2-(*N′*-[1-Cyano-2-oxo-ethylidene]-hydrazino)-benzoic Acid (3e): The compound was obtained as orange crystals (36 %), mp. 152 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3422 (OH), 3013 (NH), 2211 (CN), 1689 (CO, CHO), 1657 (CO, COOH) cm^{-1}. **MS**: *m/z* 217 (M^+). **^1H NMR** ($[D_6]DMSO$): δ = 2.5 (s, 1 H,OH), 7.2–8.00 (m, 4 H,Ar–H), 9.5 (s, 1 H,CHO), 13.3 (s, 1 H,NH). $C_{10}H_7N_3O_3$ (217.19): calcd. C 55.30; H 3.25; N 19.35 %; found: C 55.31; H 3.24; N 19.36 %.

Synthesis of 2-(*N′*-[1-Cyano-2-oxo-ethylidene]-hydrazino)-benzoic Acid Methyl Ester (3g): This compound was obtained as yellow crystals (82 %), mp. 138 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3132 (NH), 2209 (CN), 1692 (CO) cm^{-1}. **MS**: *m/z* 231 (M^+). **^1H NMR** ($[D_6]DMSO$) (there are extra protons indicating the presence of more than one isomer; signals for the most predominant isomer are underlined): δ = 3.9, 4.1 (s, 3 H, CH_3), 7.5–8.25 (m, 4 H, Ar-H), 9.1, 9.7 (s, 1 H, CHO), 13.2 (s, 1 H, NH hydrazone).**^{13}C NMR** ($[D_6]DMSO$): (there are extra carbons indicating the presence of more than one isomer; signals for the carbons of the predominant isomer are underlined): δ = 53.0 (CH_3), 108.9, 114.7, 115.8 (CH aromatic), 116.35, 118.5 (CN), 124.7, 126.0, 131.3, 134.96, 134.97 (CH aromatic), 142.6 (CH vinyl), 167.8, 167.9 (CO-OMe), 182.6, 184.7 (CHO). $C_{11}H_9N_3O_3$ (231.21): calcd. C 57.14; H, 3.92; N, 18.17 %; found: C 57.25; H, 3.82; N, 18.10 %.

Synthesis of 2-[(2-Nitro-phenyl)-hydrazono]-3-oxo-propionitrile (3a): The compound was obtained as yellow crystals (70 %), mp. 144 °C. **MS**: *m/z* 218 (M^+). $C_9H_6N_4O_3$ (218.17): C, 49.55; H, 2.77; N, 25.68 %; found: C 49.57; H, 2.76; N, 25.69 %.

Synthesis of 2-[(4-Nitro-phenyl)-hydrazono]-3-oxo-propionitrile (3b): The compound was obtained as red crystals (62 %), mp. 179 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3446 (NH), 2207 (CN), 1658 (CO) cm^{-1}. **MS**: *m/z* 218 (M^+). $C_9H_6N_4O_3$ (218.17): calcd. C 49.55; H, 2.77; N, 25.68 %; found: C 49.54; H, 2.75; N, 25.66 %.

Synthesis of 3-Oxo-2-(*p*-tolyl-hydrazono)propionitrile (3c): The compound was obtained as yellow crystals (54 %), mp. 178 °C. **IR**

(KBr): $\tilde{\nu}_{max}$ = 3170 (NH), 2958 (CH aliphatic), 2224 (CN), 1704 (CO) cm^{-1}. **MS**: *m*/*z* 187 (M$^+$). $C_{10}H_9N_3O$ (187.20): calcd. C 64.16; H, 4.85; N, 22.45 %; found: C 64.19; H, 4.86; N, 22.48 %.

Synthesis of 3-Oxo-2-(phenyl-hydrazono)propionitrile (3d): The compound was obtained as yellow crystals (58 %), mp. 172 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3415 (NH), 2204 (CN), 1661 (CO) cm^{-1}. **MS**: *m*/*z* 173 (M$^+$). $C_9H_7N_3O$ (173.18): calcd. C 62.42; H, 4.07; N, 24.26 %; found: C 62.48; H, 4.00; N, 24.24 %.

Synthesis of 4-(*N′*-[1-Cyano-2-oxo-ethylidene]-hydrazino)-benzenesulfonic Acid (3f): A mixture of sulfanilic acid dihydrate (10.5 g, 0.05 mol), anhydrous sodium carbonate (2.65 g, 0.025 mol), and water (100 mL) are warmed to obtain a clear solution. The mixture was cooled till 15 °C under tap water and sodium nitrite (3.7 g, 0.059 mol in 10 mL water) was added. The resulting solution was poured slowly with stirring into a mixture of conc. HCl (10.5 mL) and crushed ice (60 g). The resulting *p*-sulphonatephenyldiazonium chloride solution was added to a cold solution of 3-piperidinoacrylonitrile **1** (6.8 g, 0.05 mol) in ethanol (200 mL) containing sodium acetate. The mixture was stirred, and left in a cold place overnight. The solid product was collected by filtration and crystallized from ethanol. The compound was obtained as orange crystals (83 %), mp. 252 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3515 (OH), 3447 (NH), 2222 (CN), 1687 (SO_2), 1652 (CO) cm^{-1}. **MS**: *m*/*z* 235 (M$^+$). **^{1}H NMR** ([D$_6$]DMSO): δ = 3.36 (OH), 7.49–7.68 (m, 8 H, Ar–H), 9.5 (s, 1 H, CHO), 12.8 (s, 1 H, NH).**^{13}C NMR** ([D$_6$]DMSO): δ = 110.3 (CH aromatic), 114.58 (CN), 115.86,126.94,141.95 (CH aromatic), 145.10 (C vinyl), 196.65 (CHO). $C_9H_7N_3O_4S$ (253.24): calcd. C 42.69; H, 2.79; N, 16.59; S, 12.66 %; found: C 42.61; H, 2.77; N, 16.65; S, 12.70 %.

Synthesis of (2-Cyanophenylhydrazono)-(2-cyanophenylazo)-acetonitrile (6h): Sodium nitrite (1.5 g in 10 mL H_2O) was added to a cold solution of 2-cyanophenylamine hydrochloride (0.02 mol amine in 10 mL concentrated HCl) with stirring. The resulting 2-cyanophenyldiazonium chloride solution was added to a cold solution of 3-piperidinoacrylonitrile **1** (0.01 mol) in ethanol (50 mL) containing sodium acetate. The mixture was stirred and the solid product was collected by filtration and crystallized from ethanol to give red crystals (70 %), mp. 190 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3448 (NH), 2220 (CN) cm^{-1}. **MS**: (EI, 70 ev): *m*/*z* (%) = 299 (M$^+$). **^{1}H NMR** ([D$_6$]DMSO): δ = 7.52–7.92 (m, 8 H, Ar-H), 12.22 (s, 1 H, NH).**^{13}C NMR** ([D$_6$]DMSO): δ = 98.27, 101.81, 104.34, 109.18, 111.84 (CH aromatic), 114, 115, 116.67 (3 CN), 120, 64, 128, 129.23, 134.1, 134.3 (CH aromatic), 147.69 (C vinyl), 150.2 (CH aromatic). $C_{16}H_9N_7$ (299.28): calcd. C 64.21; H, 3.03; N, 32.76 %; found: C 64.0; H, 3.04; N, 32.75.

Syntheses of Dyestuffs

General Procedure for the Synthesis of 4-(Arylazo)-2H-pyrazol-3-ylamine (7a–d): A mixture of **3** (0.01 mol) and hydrazine hydrate (0.01 mol) in ethanol (25 mL) was heated to reflux for 2 h and poured into H_2O. The solid, so formed was collected by filtration and then crystallized.

Synthesis of 4-(2-Nitro-phenylazo)-2H-pyrazol-3-ylamine (7a): This dye was obtained as brown crystals from ethanol (62 %), mp. 184 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3451 (NH), 3336, 3175 (NH_2) cm^{-1}. **MS**: *m*/*z* 232 (M$^+$). **^{1}H NMR** ([D$_6$]DMSO): δ = 5.57 (s, 1 H, pyrazol-H), 7.36–7.87 (m, 4 H, Ar-H), 7.92–7.97 (s, 2 H, NH_2), 8.17 (s, 1 H, NH). $C_9H_8N_6O_2$ (232.20): calcd. C 46.55; H, 3.47; N, 36.19 %; found: C 46.51; H, 3.49; N, 36.23.

Synthesis of 4-(4-Nitro-phenylazo)-2H-pyrazol-3-ylamine (7b): This dye was obtained as red crystals from ethanol/H_2O (63 %), mp. 215 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3392 (NH), 3323,3190 (NH_2) cm^{-1}. **MS**: *m*/*z* 232 (M$^+$). **^{1}H NMR** ([D$_6$]DMSO): δ = 6.60 (s, 1 H, pyrazol-H), 7.30 (s, 2 H, NH_2, NH), 7.8–8.4 (m, 4 H, Ar-H). $C_9H_8N_6O_2$ (232.20): calcd. C 46.55; H, 3.47; N, 36.19 %; found: C 46.58; H, 3.48; N, 36.21.

Synthesis of 4-*p*-Tolylazo-2H-pyrazol-3-ylamine (7c): This dye was obtained as orange crystals from ethanol (54 %), mp. 198 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3362 (NH), 2922 (CH aromatic), 2854 (CH aliphatic) cm^{-1}. **MS**: *m*/*z* 201 (M$^+$). $C_{10}H_{11}N_5$ (201.23): calcd. C 59.69; H, 5.51; N, 34.80 %; found: C 59.71; H, 5.50; N, 34.79.

Synthesis of 4-Phenylazo-2H-pyrazol-3-ylamine (7d): This dye was obtained as reddish-brown crystals from ethanol (52 %), mp. 196 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3424 (NH), 2925 (CH aromatic) cm^{-1}. **MS**: *m*/*z* 187 (M$^+$). **^{1}H NMR** ([D$_6$]DMSO): δ = 6.71 (s, 1 H, pyrazol-H), 7.35–7.49 (m, 5 H, Ar-H), 7.67, 7.70 (s, 2 H, NH_2), 7.82, 7.89 (s, 1 H, NH). $C_9H_9N_5$ (187.21): calcd. C 57.74; H, 4.85; N, 37.41 %; found: C 57.76; H, 4.84; N, 37.43.

Synthesis of 2-(*N′*-[1-Cyano-2-hydrazono-ethylidene]-hydrazino)-benzoic Acid Methyl Ester (10g): A mixture of **3** (0.01 mol) and hydrazine hydrate (0.01 mol) in ethanol (25 mL) was heated to reflux for 2 h and poured into H_2O. The solid, so formed, was collected by filtration and crystallized from ethanol to give brown crystals (66 %), mp. 129 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3432 (NH), 2947 (CH aromatic), 2866 (CH aliphatic), 2192 (CN), 1700 (CO) cm^{-1}. **MS**: *m*/*z* 245 (M$^+$). **^{1}H NMR** ([D$_6$]DMSO): δ = 3.8 (s, 3 H, aliphatic-H), 7.14–8.16 (m, 4 H, Ar-H), 8.69 (s, 1 H, NH_2), 12.74 (s, 1 H, NH). $C_{11}H_{11}N_5O_2$ (245.24): calcd. C 53.87; H, 4.52; N, 28.56 %; found: C 53.89; H, 4.51; N, 28.55.

General Procedure for the Synthesis of *N*-phenyl-4-(arylazo)-pyrazol-3-ylamine 7i and 7j: Phenyl hydrazine (1.1 g, 0.01 mol) was added to a solution of **3** (0.01 mol) in ethanol (30 mL). The reaction mixture was heated to reflux for 2 h, and cooled to room temperature. The separated solid was filtered, washed with water, dried and recrystallized from ethanol.

Synthesis of 2-Phenyl-4-*p*-tolylazo-2H-pyrazol-3-ylamine (7i): This dye was obtained as orange crystals (84 %), mp. 164 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3387, 3262 (NH_2), 2920 (CH aromatic), 2858 (CH aliphatic) cm^{-1}. **MS**: *m*/*z* 277 (M$^+$). **^{1}H NMR** ([D$_6$]DMSO): δ = 3.3 (s, 3 H, aliphatic-H), 7.15 (s, 1 H, pyrazol-H), 7.25–7.66 (m, 9 H, Ar-H), 8.02 (s, 2 H, NH_2). $C_{16}H_{15}N_5$ (277.33): calcd. C 69.30; H, 5.45; N, 25.25 %; found: C 69.33; H, 5.44; N, 25.26.

Synthesis of 4-(4-Nitro-phenylazo)-2-phenyl-2H-pyrazol-3-ylamine (7j): This dye was obtained as red crystals (54 %), mp. 182 °C. **IR** (KBr): $\tilde{\nu}_{max}$ = 3390 (NH_2) cm^{-1}. **MS**: *m*/*z* 308 (M$^+$). **^{1}H NMR** ([D$_6$]DMSO): δ = 6.9 (s, 1 H, pyrazol-H), 7.36–7.98 (m, 9 H, Ar-H), 8.34, 8.29 (s, 2 H, NH_2). $C_{15}H_{12}N_6O_2$ (308.30): calcd. C 58.44; H, 3.92; N, 27.26 %; found: C 58.45; H, 3.92; N, 27.27 %.

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References

[1] P. Ovejero, E. Asensio, J. V. Heras, J. A. Campo, M. Cano, M. R. Torres, C. Núñez, C. Lodeiro, *Dalton Trans.* **2013**, *42*, 2107–2120.
[2] S. Radfar, M. B. Gholivand, K. Bahrami, *J. Electroanal. Chem.* **2016**, *760*, 1–5.

[3] F. Giornal, S. Pazenok, L. Rodefeld, N. Lui, J. P. Vors, F. R. Leroux, *J. Fluorine Chem.* **2013**, *152*, 2–11.
[4] Ç. Karabacak, T. Tilki, B. Ö. Tuncer, M. Cengiz, *Res. Chem. Intermediates* **2015**, *41*, 1985–1999.
[5] J. O. Otutu, E. M. Efurhievwe, *J. Appl. Sci.* **2013**, *13*, 924–928.
[6] H. F. Rizk, S. A. Ibrahim, M. A. El-Borai, *Dyes Pigm.* **2015**, *112*, 86–92.
[7] Ç. K. Atay, Y. Kara, M. Gökalp, I. Kara, T. Tilki, F. Karci, *J. Mol. Liq.* **2016**, *215*, 647–655.
[8] L. G. Yu, T. F. Ni, W. Gao, Y. He, Y. Y. Wang, H. W. Cui, C. G. Yang, W. W. Qiu, *Eur. J. Med. Chem.* **2015**, *90*, 10–20.
[9] Y. R. Li, C. Li, J. C. Liu, M. Guo, T. Y. Zhang, L. P. Sun, C. J. Zheng, H. R. Piao, *Bioorg. Med. Chem. Lett.* **2015**, *25*, 5052–5057.
[10] N. C. Desai, K. M. Rajpara, V. V. Joshi, *Bioorg. Med. Chem. Lett.* **2013**, *23*, 2714–2717.
[11] J. Quiroga, J. Portilla, R. Abonía, B. Insuasty, M. Nogueras, J. Cobo, *Tetrahedron Lett.* **2008**, *49*, 6254–6256.
[12] P. C. Tsai, J. Wang, *Dyes Pigm.* **2007**, *74*, 578–584.
[13] A. M. Al-Etaibi, N. A. Al-Awadi, N. M. A. El-Apasery, M. R. Ibrahim, *Molecules* **2011**, *16*, 5182–5193.
[14] N. R. Mohamed, M. M. T. El-Saidi, Y. M. Ali, M. H. Elnagdi, *Bioorg. Med. Chem.* **2007**, *15*, 6227–6235.
[15] A. Z. Sayed, M. S. Aboul-Fetouh, H. S. Nassar, *J. Mol. Struct.* **2012**, *1010*, 146–151.
[16] M. H. Elnagdi, E. M. Kandeel, E. M. Zayed, Z. E. S. Kandil, *J. Prakt. Chem.* **1978**, *320*, 533–538.
[17] F. Karcı, E. Bakan, *J. Mol. Liq.* **2015**, *206*, 309–315.
[18] A. A. Estrada, B. K. Chan, C. Baker-Glenn, A. Beresford, D. J. Burdick, M. Chambers, H. Chen, S. L. Dominguez, J. Dotson, J. Drummond, M. Flagella, *J. Med. Chem.* **2014**, *57*, 921–936.
[19] F. Karcı, N. Şener, M. Yamaç, İ. Şener, A. Demirçalı, *Dyes Pigm.* **2009**, *80*, 47–52.
[20] U. P. Singh, H. R. Bhat, A. Verma, M. K. Kumawat, R. Kaur, S. K. Gupta, R. K. Singh, *RSC Adv.* **2013**, *3*, 17335–17348.
[21] E. Cichero, E. P. Fossa, *J. Mol. Model.* **2012**, *18*, 1573–1582.
[22] A. M. Al-Etaibi, M. A. El-Apasery, M. R. Ibrahim, N. A. Al-Awadi, *Molecules* **2012**, *17*, 13891–13909.
[23] A. Mohammadi, B. Khalili, M. Tahavor, *Spectrochim. Acta Part A* **2015**, *150*, 799–805.
[24] R. Bradbury, *Dyes for Dye Diffusion Thermal Transfer (D2T2) Printing*, in *Modern Colorants: Synthesis and Structure*, Springer, Dordrecht, **1995**, pp. 154–176.
[25] P. Gregory, *Thermography*, in: *High-Technology Applications of Organic Colorants*, Springer, New York, **1991**, pp. 123–173.
[26] Y. Fujie, H. Mikoshiba, K. Omura, R. Shinohara, *Ink sheet for heat-sensitive transfer recording material, heat-sensitive transfer recording method, ink cartridge and azo dye*, U.S. Patent 7,947,625, Fujifilm Corporation, Tokyo, Japan, **2011**.
[27] K. M. Al-Zaydi, L. M. Nhari, R. M. Borik, M. H. Elnagdi, *Green Chem. Lett. Rev.* **2010**, *3*, 93–99.
[28] K. Haggag, N. S. Elshemy, W. Niazy, *Res. J. Text. Apparel* **2014**, *18*, 80–88.
[29] L. Rene, J. Poncet, G. Auzou, *Synthesis* **1986**, 419–420.
[30] S. O. Abdallah, N. H. Metwally, H. F. Anwar, M. H. Elnagdi, *J. Heterocycl. Chem.* **2005**, *42*, 781–786.
[31] S. A. S. Ghozlan, I. A. Abdelhamid, H. Gaber, M. H. Elnagdi, *J. Chem. Res.* **2004**, 789–793.
[32] A. A. Abbas, A. H. Elwahy, *Arkivoc* **2009**, *10*, 65–70.
[33] ISO 105-X12:1987 Textiles: Tests for color fastness. Part X12: Color fastness to rubbing (Basel: ISO, **1987**).
[34] ISO 105-C02:1989 Textiles: Tests for color fastness. Part C02: Color fastness to washing: Test 2 (Basel: ISO, **1989**).
[35] ISO 105-E04:1989 Textiles: Tests for color fastness. Part E04: Color fastness to perspiration (Basel: ISO, **1989**).
[36] ISO 105-B02:1988 Textiles: Tests for color fastness. Part B02: Color fastness to artificial light: Xenon arc fading lamp test (Basel: ISO, **1988**).

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