

Synthesis and Spectral Properties of Symmetrical and Asymmetrical 3-Cyano-1,5-diarylformazan Dyestuffs for Dyeing Polyester Fabrics

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IN THIS study, we report on a general synthetic approach to both symmetrical and asymmetrical 3-cyano-1,5-diarylformazan dyes. The reaction of enamionitrile with aromatic diazonium salts in slightly acidic medium affords arylhydrazonals as stable intermediate that are readily converted into asymmetrical formazans *via* second azo-coupling in a weak alkaline medium. Symmetrical formazan dyestuffs are synthesized directly *via* double azo-coupling of the key intermediate 3-piperidinylacrylonitrile with the corresponding diazonium salts in weak alkaline medium using sodium acetate as a weak base. The structures of the prepared dyestuffs and intermediates are demonstrated by elemental analysis (C, H, N), ¹H and ¹³C NMR, FTIR and GC-MS spectroscopic techniques. The prepared formazan disperse colorants are applied to dye polyester fabric to give satisfactory fastness properties to wash, perspiration, rubbing and light.

Keywords: Cyanoenamine, Hydrazone, Formazan, Azo-coupling, Dyeing, Polyester.

Introduction

Formazan dyes are characterized by the basic structure $[-N=N-C(R)=N-NH-]$ which is strongly related to the structure of azo dyes since they contain an azo functional group [1]. Formazans are a class of colored materials due to their $\pi-\pi^*$ transitions. There are a variety of formazans have been prepared and their structural, tautomerism and photochromism features have been studied [2]. As a result of their good fastness characteristics and intensity of color strength, formazan compounds can be employed as analytical reagents for the spectroscopic recognition of a variety of metal ions [3]. Cyclic formazans are lithium-specific colorimetric indicators which are valuable for quantitative recognition of lithium ions in biofluids such as blood [4]. Open bicyclic formazan colorants are utilized in inks for inkjet digital printing [5]. Recently, crown-based formazan dyes have been largely investigated due to their attractive ligand structures which can be employed as specific ion electrodes [6]. Many studies on the synthesis of formazans metal complexes have been explored [7, 8]. Mixtures of the nickel-coordinated tridentate formazan ligands are proved to afford good light fastness to optical

recording elements and layers [9]. Formazans can produce the parallel tetrazolium salt upon oxidation, while the tetrazolium compound can be reduced back to their formazan derivative [10, 11]. Water-soluble and colorless tetrazolium salts can be biologically and easily reduced to colored formazan dyes that cannot be dissolved in water. Therefore, tetrazolium salts have been used as biosensors in biochemistry, cytochemistry and histochemistry. They can function to sense biological oxidation-reduction processes in blood serum, live biological cells and tissues, lumps and microorganisms. Tetrazolium salts are known as markers of vitality, screening anti-cancer drugs, studying the activity of tumor cells, and recognition of sperm viability [12-14]. Tetrazolium salts can also be employed in the quick determination of microbial capacity in industrial wastewater and recognition of dehydrogenase enzyme in sludge. Transformation of tetrazolium salts into metallizable formazans are also employed as photoreagents in photographic development processes [15-18].

Many formazans are well suitable as dyes for textiles due to their high color strength and good

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DOI: 10.21608/ejchem.2017.1479.1103

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fastness properties. They can be simply mixed with yellow, orange, and red azo dyes to afford inexpensive alternatives to blue anthraquinone dyes for trichromatic dyeing systems [19]. There are three different methods to prepare formazans were reported in the literature [18]. The first synthetic approach is the condensation of phenylhydrazine with aromatic and aliphatic compounds containing aldehyde functional group followed by azo-coupling of the produced hydrazone. However, this is a low yield method and the product is hard to be purified. The second technique uses phase transfer approach, but necessitates particular and costly solvents such as crown ethers. The third one involves the azo-coupling of hydrazones in an alkaline medium which is the most common approach to afford formazans. However, some compounds containing active methyl group can produce only symmetrical formazans upon double azo-coupling with strong diazonium salts [20, 21]. Herein, we report on the preparation and characterization of some novel formazan disperse dyes *via* azo-coupling of different diazonium compounds with 3-piperidinylacrylonitrile and arylhydrazones to afford both of symmetrical and asymmetrical formazans respectively. Their structures and spectral behavior is demonstrated using ^1H - and ^{13}C -NMR, IR, elemental analysis, and GC-MS spectroscopic technique. The formazan dyes are applied on polyester garments to afford satisfactory color strength and fastness properties.

Experimental

All melting points are uncorrected and are expressed in $^{\circ}\text{C}$. They were determined on a Stuart melting point apparatus. IR spectra of the formazans synthesized in this study were recorded in KBr on a FT-IR Nicolet 670 spectrometer and ^1H NMR spectra were recorded on 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 on 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 from a Shimadzu GCMS-QP-1000 EX spectrometer in (70 eV) mode. Microanalysis for C, H and N were performed on a Perkin-Elmer 2400 III platina. The color strength was recorded using an UltraScan PRO Spectrophotometer (light source D65/10 $^{\circ}$ observer). Unless otherwise noted, all chemicals were supplied by Sigma Aldrich and used without further purification. Compounds 1, 2b, 2d, 4a,

4b are known in the literature [22-25]. Scoured and bleached 100% polyester fabrics (149 g/m 2) 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 60 $^{\circ}\text{C}$ for 30 minutes to get rid of waxes and impurities, followed by rinsing in cold water, and finally dried at room temperature.

Synthetic approaches

3-piperidin-1-yl-acrylonitrile (cyanoenamine 1)

A mixture of cyanoacetic acid (0.05 mol), triethyl orthoformate (0.05 mol) and piperidine (0.5 mL) was heated under reflux for 2 hours, allowed to cool to room temperature, then poured into cold water. The reaction mixture was treated with 1 molar sodium carbonate solution (50 mL), extracted with dichloromethane (100 mL), and then left to dry overnight in sodium sulfate. The mixture is filtered and solvent was evaporated under vacuum. This compound was obtained as buff crystals (yield 67%). mp: 60 $^{\circ}\text{C}$. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2220 (CN). MS: m/z 137 (M^+). ^1H NMR (DMSO- d_6): δ 1.43-1.56 (m, 6H, 3CH $_2$), 3.12-3.30 (m, 4H, 2NCH $_2$), 4.06 (d, 1H, $J = 14$ Hz, vinyl-H), 7.13 (d, 1H, $J = 14$ Hz vinyl-H). Anal: calcd for C $_8$ H $_{12}$ N $_2$ (136.19): C, 70.55; H, 8.88; N, 20.57. Found: C, 70.52; H, 8.80; N, 21.20

General procedure for the synthesis of symmetrical formazan dyes (2a-d)

An aryldiazonium salt (0.02 mol) solution was prepared by adding sodium nitrite solution (0.7 g in 10 mL H $_2$ O) to a chilled solution of arylamine hydrochloride (0.02 mol of arylamine in 5 mL conc. HCl) with stirring. The resulting aryldiazonium salt solution was then added dropwise to a cold solution (0-5 $^{\circ}\text{C}$) of 3-piperidinoacrylonitrile 1 (0.01 mol) in ethanol (5 mL) and in presence of sodium acetate (8 g). The reaction mixture was stirred for one additional hour. The solid product so formed was collected by filtration and crystallized from ethanol.

3-cyano-1,5-diphenylformazan (2a)

This compound was obtained as red crystals (yield 81%), mp. 116 $^{\circ}\text{C}$. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3326 (NH), 3032 (CH aromatic), 2221 (CN Nitrile), 1593 (C=N hydrazone), 1531 (-N=N-). MS: m/z 249 (M^+). ^1H NMR (DMSO- d_6): δ 7.31-7.68 (m, 10H, Ar-H), 12.19 (s, 1H, NH). ^{13}C NMR (DMSO- d_6): δ 111.09, 114.60, 115.28, 115.91,

117.98, 121.51, 127.29, 127.83, 135.82, 136.83, 146.22, 149.87; Anal: calcd for $C_{14}H_{11}N_5$ (249.27): C, 67.46; H, 4.45; N, 28.10; Found: C, 67.39; H, 4.53; N, 28.23

3-cyano-1,5-bis(4-methylphenyl)formazan (2b)

This compound was obtained as red crystals (yield 87%), mp. 132°C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3324 (NH), 3040 (CH aromatic), 2920 (CH aliphatic), 2224 (CN Nitrile), 1590 (C=N hydrazone), 1535 (-N=N-). MS: m/z 278 (M^+). ^1H NMR (DMSO- d_6): δ 2.41 (s, 6H, 2CH₃), 7.12-6.92 (m, 8H, Ar-H), 12.18 (s, 1H, NH). Anal: calcd for $C_{16}H_{15}N_5$ (277.32): C, 69.29; H, 5.45; N, 25.25; Found: C, 69.38; H, 5.41; N, 25.17

3-cyano-1,5-bis(4-benzenesulfonic acid)formazan (2c)

This compound was obtained as red crystals (yield 59%), mp. 252°C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3455 (OH), 3348 (NH), 3037 (CH aromatic), 2202 (CN Nitrile), 1620 (C=N hydrazone), 1586 (-N=N-), 1450 (S=O Sulfonic Hydrated). MS: m/z 427 (M^+ +18). ^1H NMR (DMSO- d_6): δ 3.41 (s, 2H, 2OH), 7.52-7.69 (m, 8H, Ar-H), 12.82 (s, 1H, NH). ^{13}C NMR (DMSO- d_6): δ 108.54, 110.40, 111.61, 114.53, 115.78, 115.82, 126.94, 129.06, 141.27, 145.14, 147.09, 151.26; Anal: calcd for $C_{14}H_{11}N_5O_6S_2$ (409.40): C, 41.07; H, 2.71; N, 17.11; S, 15.66; Found: C, 41.12; H, 2.68; N, 17.02; S, 15.78

3-cyano-1,5-bis(2-cyanophenyl)formazan (2d)

This compound was obtained as red crystals (yield 73%), mp. 190°C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3328 (NH), 2220 (CN) 3048 (CH aromatic), 2225 (CN Nitrile), 1588 (C=N hydrazone), 1557 (-N=N-). MS: m/z 299 (M^+). ^1H NMR (DMSO- d_6): δ 7.52-7.92 (m, 8H, Ar-H), 12.22 (s, 1H, NH). ^{13}C NMR (DMSO- d_6): δ 98.27, 101.81, 104.34, 109.18, 111.84, 114.00, 115.00, 116.67, 120.64, 128.00, 129.23, 134.10, 134.30, 147.69, 150.20; Anal: calcd for $C_{16}H_9N_7$ (299.29): C, 64.21; H, 3.03; N, 32.76; Found: C, 64.18; H, 3.09; N, 32.70

General procedure for the synthesis of arylhydrazonals (4a-b)

An aryldiazonium salt (0.01 mol) solution was prepared by adding sodium nitrite solution (0.7 g in 10 mL H₂O) 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 (0.01 mol) in acetic acid (25 mL) and in presence of sodium acetate (5 g). The reaction mixture was stirred for one additional hour. The solid product so formed was collected by filtration and crystallized from ethanol.

3-oxo-2-(p-tolyl-hydrazono)propionitrile (4a)

The compound was obtained as yellow crystals (yield 54%), mp. 178°C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3170 (NH), 2958 (CH aliphatic), 2224 (CN), 1704 (CO). 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

3-oxo-2-(phenyl-hydrazono)propionitrile (4b)

The compound was obtained as yellow crystals (yield 58%), mp. 172°C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3415 (NH), 2204 (CN), 1661 (CO). 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

General procedure for the synthesis of asymmetrical formazan dyes (6a-b)

To a stirred solution of hydrazonal 4 (0.02 mol) at 0-5°C in ethanol (10 ml) and in presence of sodium acetate (13 g); a diazonium chloride salt (0.02 mol) [prepared from the corresponding arylamine (0.02 mol) and the appropriate quantities of concentrated hydrochloric acid and sodium nitrite] was added dropwise. After addition of the diazonium salt, the reaction mixture was then stirred at room temperature for two additional hours. The precipitated product, separated upon dilution with cold water (30 ml), was filtered off, washed with water several times, dried, and re-crystallized to give the corresponding formazan.

3-cyano(phenyl)-5-p-tolylformazan (6a)

The compound was obtained as a red solid (yield 72%) from the aniline diazonium salt and 4a, mp. 186°C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3321 (NH), 3042 (CH aromatic), 2936 (CH aliphatic), 2225 (CN Nitrile), 1543 (C=N hydrazone), 1510 (-N=N-). MS m/z 263 (M^+). ^1H NMR (DMSO- d_6): δ 2.48 (s, 3H, CH₃), 7.32-7.08 (m, 8H, Ar-H), 12.38 (s, 1H, NH). ^{13}C NMR (DMSO- d_6): δ 26.81, 108.00, 109.74, 111.26, 113.35, 115.13, 115.39, 118.02, 122.57, 127.35, 128.81, 135.04, 136.48, 147.28, 150.33; Anal: calcd for $C_{15}H_{13}N_5$ (263.30): C, 68.42; H, 4.98; N, 26.60; found: C, 68.43; H, 5.07; N, 26.68

3-cyano(4-nitrophenyl)-5-phenylformazan (6b)

The compound was obtained as a red powder (yield 64%) from the 4-nitroaniline diazonium salt and 4b, mp. 167°C. IR (KBr) ν_{\max} /cm⁻¹: 3331 (NH), 3054 (CH aromatic), 2228 (CN Nitrile), 1588 (C=N hydrazone), 1518 (-N=N-). MS *m/z* 294 (M⁺). ¹H NMR (DMSO-d₆): δ 8.09-7.64 (m, 9H, Ar-H), 12.86 (s, 1H, NH). ¹³C NMR (DMSO-d₆): δ 109.00, 110.74, 112.06, 113.36, 115.08, 116.84, 118.24, 123.51, 127.72, 129.93, 136.38, 138.90, 147.68, 151.21; Anal: calcd for C₁₄H₁₀N₆O₂ (294.27): C, 57.14; H, 3.43; N, 28.56; found: C, 57.08; H, 3.49; N, 28.67

Dyeing procedure

The dyeing process is applied to the polyester fabric using the high temperature dyeing method. A dispersion of the dyestuff is performed by dissolving the appropriate quantity of dye (2% shade) in 1 mL DMF and then added dropwise with stirring to the dye-bath (liquor ratio 50:1) containing sodium lignin sulfonate as dispersing agent. The ratio of dispersing agent to the dye is 1:1. The pH of the dye-bath is adjusted to 4.85 using aqueous acetic acid and the wetted-out polyester fabrics are added. The dyeing process is achieved by increasing the dye-bath temperature to 130°C for 180 minutes under pressure in an infra-red dyeing machine. After dyeing, the fabrics are thoroughly washed and subjected to surface reduction clearing ((2 g NaOH + 2 g sodium hydrosulphite)/L, and soaped with 2% nonionic detergent to improve washing fastness). The samples are heated in this solution for 45 minutes at 80°C. Rinse well in cold water and neutralize with 1 g/L acetic acid for 5 minutes at 40°C, the dyed samples are removed, rinsed in tap water and allowed to dry at ambient temperature [26]. The color strength of the dyed samples expressed as K/S is evaluated by high reflectance technique [27].

Color fastness measurements

Fastness to wash, rubbing, perspiration and light is tested according to standard dyeing ISO methods [28-31]. The light fastness property of the dyed material is assessed according to the international blue scale (1-8), while the wash fastness is assessed according to the international grey scale (1-5), with scales 8 and 5, respectively, ranked the best, while 1 is the most inferior.

Results and Discussion

Chemistry of formazan dyes

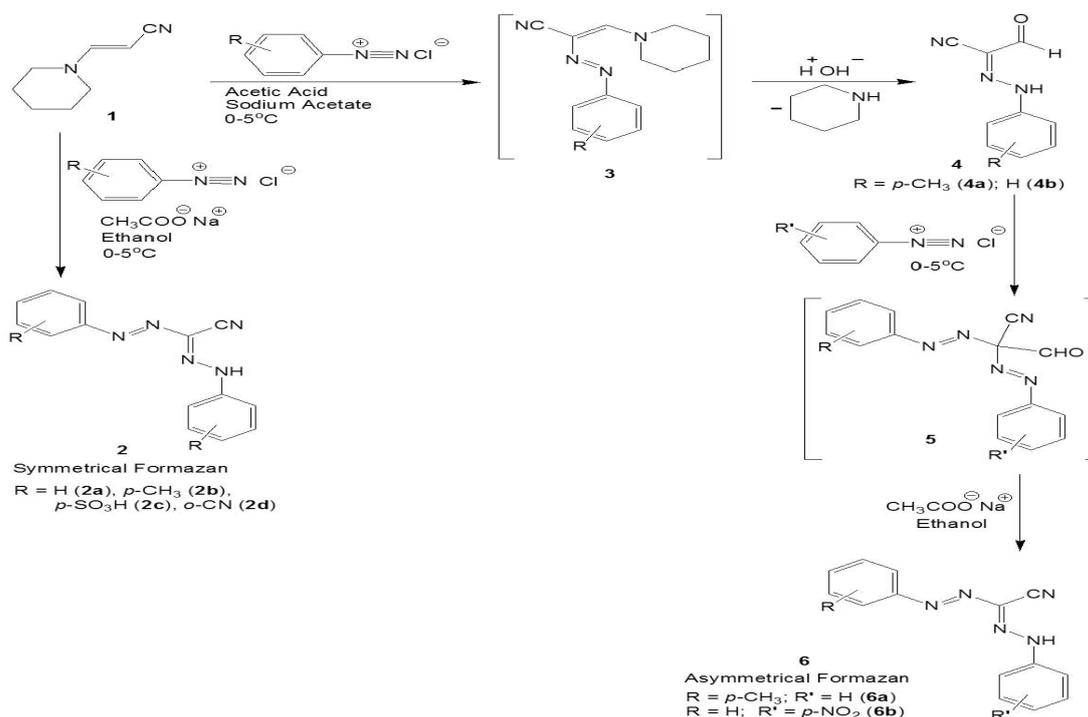
Recently Elnagdi et. al. [22, 32] reported that the reaction of enamionitrile 1 with aromatic diazonium salts affords arylhydrazones 4 *via* intermediacy of azoenaminonitrile 3. The arylhydrazones 4 are readily converted into asymmetrical formazans 6 in good to excellent yields. It occurred to us of value to see if chemical reaction in Scheme 1 can comprise a common route to both symmetrical and asymmetrical 3-cyano-1,5-diarylformazan dyes. Compound 1 is prepared by heating diethylamine, triethylorthoformate and cyanoacetic acid under reflux for two hours, following a reported procedure [22]. Thus the enamionitrile 1 is coupled efficiently with one equivalent of aromatic diazotized amines in presence of sodium acetate and acetic acid to yield the corresponding arylhydrazonals 4 in good yields. Further reaction of the produced arylhydrazonals 4 with different aromatic diazotized amines in presence of ethanolic sodium acetate as a weak base affords asymmetrical formazans 6. Furthermore, the enamionitrile 1 reacts *via* double azo-coupling with two equivalents of aromatic diazotized amines in presence of sodium acetate to afford the corresponding symmetrical formazan dyes 2 in medium to very good yields. The rationale for the preference of this synthetic approach is that the starting enamionitrile 1 is easy to prepare and it possesses the benefit to produce both symmetrical and asymmetrical target formazans. In addition, the stable intermediate arylhydrazonal can only be isolated in slightly acidic medium due to acid hydrolysis of the azoenaminonitrile 3 which can be converted to asymmetrical formazans only in slightly alkaline medium. The proposed mechanism for the development of substituted formazan dyes is shown in Scheme 1. The structures of the produced formazan dyes are demonstrated by elemental analysis (C, H, N), ¹H and ¹³C NMR, GC-MS, and FTIR spectroscopy.

The azo-coupling of enamionitrile 1 with aromatic diazonium salts affords the product of coupling (arylazenaminonitrile) and hydrolysis of the piperidine moiety. The arylhydrazonoaldehyde derivatives 4 seem to be useful candidates for further chemical transformations. Thus, it further coupled with aryldiazonium chloride salt, yielding the bisazo compound 6 *via* the intermediacy of 5.

The C-2 location of arylhydrazone 4 is highly nucleophilic and, as a result, these arylhydrazones convert easily into formazans 6 *via* azo-coupling with aromatic diazonium salts. Coupling occurs at hydrazone carbon atom and formed bisazo as the hydrazones undergoes azo-coupling normally followed by Japp-Klingemann cleavage of the aldehyde functional group. The proposed mechanism for the formation asymmetrical formazan dyes are shown in Scheme 2.

Dyeing performance

The produced formazan dyes can be considered as disperse dyes able to dye hydrophobic polyester fibers because they can be recognized as water-insoluble and non-ionic small molecules. They are applied to dye polyester fibers at 130°C and 2% shade utilizing the high temperature pressure dyeing technique [26]. All of synthesized dyestuffs 2a-d and 6a-b display very good color strength, quantified as K/S, due to the good

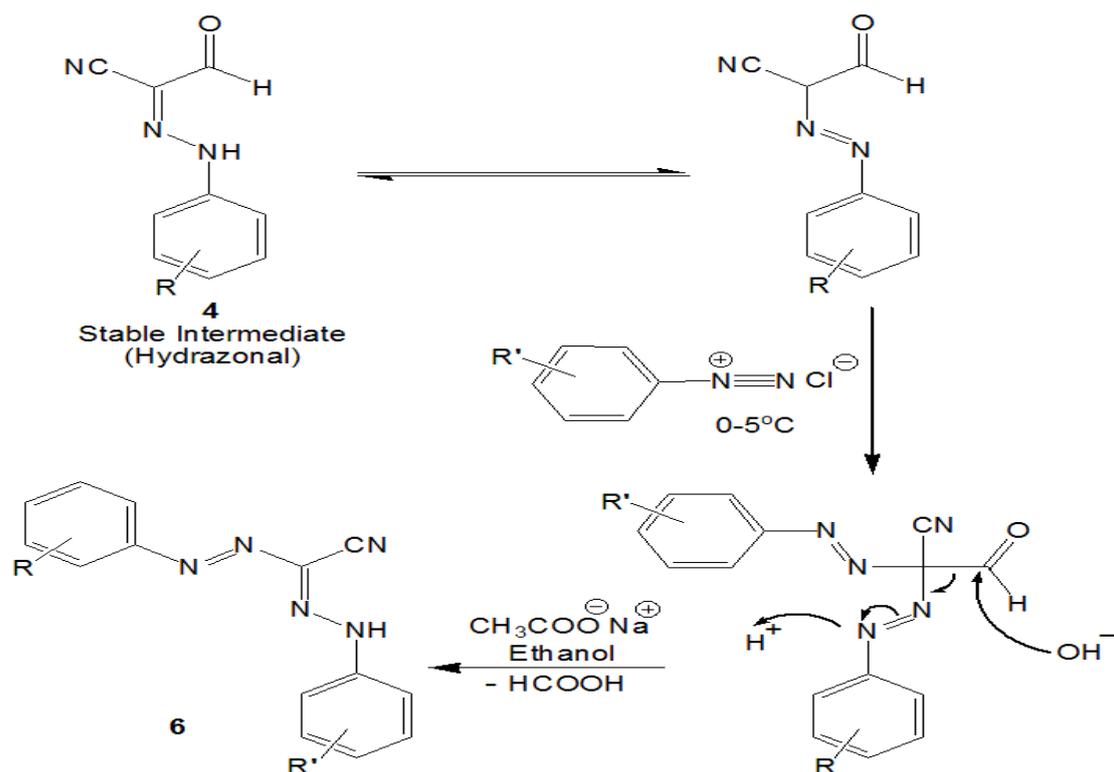


Scheme 1. Synthesis of symmetrical and asymmetrical formazans.

TABLE 1. Color strength and fastness properties of the produced formazan dyestuffs on polyester garments.

Dye No.	λ_{\max} (nm)	K/S	Shade	Wash		Perspiration				Rubbing		Light
				Alt.	St.	Acidic		Basic		Dry	Wet	
						Alt.	St.	Alt.	St.			
2a	468	12.47	Orange	4	4-5	4-5	4	4-5	4	3-4	4	5-6
2b	461	9.38	Orange	4-5	4	4	4	4	4-5	4	4	6-7
2c	473	4.69	Orange	4	3-4	4-5	4-5	4	4-5	4	3-4	6
2d	479	6.09	Orange-red	3-4	3-4	3	3	3-4	3-4	3-4	3-4	5-6
6a	483	3.29	Orange	4	4	4	4	4-5	4	4	4	6-7
6b	497	8.65	Red	4	3-4	4-5	4-5	4	4	4	3-4	6

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



Scheme 2. Proposed mechanism for the formation asymmetrical formazan dyes.

penetration of dye molecules into the bulk of the polyester fibers and excellent affinity of such dyes to polyester fabrics. The color shade varies from orange, orange-red, to red. The dyes on polyester fibers demonstrated acceptable fastness to wash, light, perspiration and rubbing tests (Table 1).

Conclusion

In conclusion, we could show that a series of symmetrical and asymmetrical formazan disperse dyestuffs have been synthesized. The produced dyestuffs are applied successfully on polyester fabrics employing the high temperature pressure dyeing technique to give solid shades with acceptable constancy and deepness. The developed shades occur between orange and red. The fastness properties of the produced formazan dyes demonstrate mostly very good color fastness against light, rubbing, perspiration and washing on the polyester garments.

Acknowledgement

Technical support from Textile Research Division, National Research Centre, Cairo, Egypt; is gratefully acknowledged.

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التحضير والخصائص الطيفية لأصباغ ٣-سيانو-١،٥-ثنائي اريل فورمازان المتماثلة والغير متماثلة لصباغة أقمشة البوليستر

توفيق خطاب وكريمة حجاج

قسم الصباغة والطباعة والمواد الوسيطة - شعبة بحوث الصناعات النسيجية - المركز القومي للبحوث - الدقي - القاهرة - مصر.

يهدف هذا البحث الي دراسة طريقة جديدة لتحضير صبغات 3-سيانو-1،5-ثنائي اريل فورمازان المتماثلة والغير متماثلة. يتفاعل مركب الاينامينو نيتريل مع املاح الديازونيوم الاروماتية في وسط حمضي ضعيف لانتاج مركبات الاريل هيدرازونال المستقرة والتي يمكن تحويلها بسهولة الي أصباغ الفورمازان الغير متماثلة من خلال تفاعل الازو للمرة الثانية ولكن هذه المرة في وسط قلوي ضعيف. يتم تحضير أصباغ الفورمازان المتماثلة مباشرة عن طريق تفاعل الازو المزدوج من مركب 3-بييريدينيل اكريلونيتريل مع أملاح الديازونيوم المناظرة في وسط قلوي ضعيف باستخدام خلات الصوديوم كقلوي ضعيف. وتم اثبات هياكل الأصباغ والمواد الوسيطة التي تم تحضيرها من خلال التحليل العنصري (كربون، هيدروجين، نيتروجين)، الرنين النووي المغناطيسي لنظائر الكربون والهيدروجين، الأشعة تحت الحمراء وتحليل الكتلة الطيفي. تم تطبيق ملونات الفورمازان المنتجة لصبغ اقمشة البوليستر لتعطي خصائص ثبات جيدة للغسيل، العرق، الاحتكاك والضوء.