

Synthesis of Some Azo Disperse Dyes from 1-Substituted 2-Hydroxy-6-pyridone Derivatives and Their Colour Assessment on Polyester Fabric

Kurenkaka Johnson Sakoma, Kasali Ademola Bello, Mohammed Kabir Yakubu

Department of Textile Science and Technology, Ahmadu Bello University, Zaria, Nigeria

Email: belloka2003@yahoo.com

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ABSTRACT

The synthesis of a series of 3-(p-substituted phenylazo)-6-pyridone dyes which is suitable for the dyeing of polyester fabrics, is described. Visible absorption spectra of the dyes were examined in various solvents and the compounds in solution exhibited hydrazone-common anion equilibrium. The electronic absorption spectra cover a λ_{\max} range of 404 - 464 nm in DMF at uniformly high absorption intensity between 5.33×10^4 - 8.55×10^4 l·mol⁻¹·cm⁻¹ and gave bright intense hues of yellow to orange on polyester fabrics. The colour parameters of the dyed fabrics were measured and the dyes have excellent exhaustion between 72% - 79% for polyester fabrics, more intense and of very good fastness properties on polyester fabrics. The remarkable degree of levelness and brightness after washing is indicative of good penetration and excellent affinity of these dyes for the polyester fabric.

Keywords: Pyridone; Disperse Dye; Exhaustion; Carrier; Polyester; Fastness

1. Introduction

Pyridone derivatives are relatively recent heterocyclic intermediates for the preparation of dyes. The azo pyridone dyes give bright hues and are therefore of investigative interest. In our previous investigations, we reported the use of pyridone as an active methylene compounds for the production of methine dyes [1-5]. In this paper some 3-(p-substituted phenylazo)-6-pyridone dyes were prepared by coupling the diazonium salts of p-substituted phenylamines with a 1-substituted 2-hydroxy-4-methyl-5-cyano-6-pyridone coupling components. The spectral characteristics of the dyes and also a colorimetric evaluation of the dyes on polyester fabrics were investigated in order to examine the influence of substituent on the colour of the prepared dyes.

2. Materials and Methods

2.1. General Information

All the chemicals used in the synthesis of the dyes and intermediates were of analytical grade and were used without purification. Melting points were determined by the open capillary method. The visible absorption spectra were measured using HEX10SY UV-visible spectrophotometer. IR spectra were recorded on a Nicolet FTIR-100 Thermoelectron spectrophotometer and the Mass spectra were determined on an Agilent 6890 Mass spectrometer.

2.2. Synthesis of 3-Cyano-4-methyl-6-hydroxyl-1-amino-2-pyridone (4a)

A mixture of ethyl acetoacetate (65.07 g, 0.5 mol), ethyl cyanoacetate (56.56 g, 0.5 mol), ethanol (50 ml) and ammonia (70 ml, 0.5 mol) was stirred and refluxed until the reaction was completed (about 7 - 8 h). During the reaction, the white product precipitated. The crude product was filtered, dried and recrystallised from ethanol to give white crystals (91%), m.p. 303.1 °C (*P*⁺ at *m/e* 150).

2.3. Synthesis of 3-Cyano-4-methyl-6-hydroxyl-1-methyl-2-pyridone (4b)

The pyridone (4b) was prepared in a manner similar to 4a, except methylamine was used instead of ammonia, and after completion of the reaction, the alcohol was removed by evaporation and the viscous residue poured slowly into ice-cold 10% aqueous hydrochloric acid (600 ml) to precipitate the product. The crude product was recrystallised from ethanol as white crystals (86%), m.p. 296.5 °C (*P*⁺ at *m/e* 164).

2.4. Synthesis of 3-Cyano-4-methyl-6-hydroxyl-1-ethyl-2-pyridone (4c)

Compound 4c was prepared in a similar manner to that described above for 4b, except ethylamine was used instead of methylamine, and was recrystallised from ethanol

as white crystals (90%), m.p 178°C (P⁺ at *m/e* 177).

2.5. Synthesis of 3-Phenylazo-2-hydroxy-4-methyl-5-cyano-6-pyridone (7a)

Aniline (9.3 ml, 0.1 mol) was dissolved in aqueous hydrochloric acid (26.7 ml, 0.3 mol), the solution was cooled with stirring to 0°C - 5°C and sodium nitrite (7.04 g, 0.102 mol) was added to it. The mixture was stirred for 40 - 45 min at 0°C - 5°C and excess nitrous acid was destroyed by the addition of urea. The clear diazonium salt solution was slowly poured into a solution of 2-hydroxy-4-methyl-5-cyano-6-pyridone (15 g, 0.1 mol) in water-acetone (1:1, 300 ml), keeping the pH at 3 - 4, and the liquor was stirred for 4 - 5 h at 0°C - 5°C. The yellow dye was filtered off, washed with water, dried and recrystallised from acetone to yield yellow crystals. Yield, melting point and appearance of the crystals are summarized in **Table 1**.

The other dyes 7b, 8 and 9 were prepared in a similar manner to that described for 7a. Absorption spectra, IR are summarized in **Table 1** and **Table 2**.

2.6. Dyeing and Fastness Properties Measurement

The dye baths were prepared from the dye (1.0% weight of fibre) with a dispersol-levelling agent (1 g·litre⁻¹) and 5% phenol as carrier to a final liquor of 30:1, w/w. The pH value of the bath was adjusted to 4 - 5 with acetic acid (10%). The polyester fabrics, previously wetted, were placed into the liquor at 25°C - 30°C. The temperature was raised to 100°C at the rate of 2°C/min, and dyeing continued for 60 min. After cooling, the dyed fabrics were reduction cleared in sodium hydroxide (6 g·litre⁻¹), soap (1 g·litre⁻¹) and hydrosulphite (2 g·litre⁻¹) at 75°C and then washed and dried. The percentage exhaustion was determined by the usual method [6], washfastness and lightfastness were determined by the standard procedure [7]. The results are summarized in **Table 4**.

3. Results and Discussion

3.1. Synthesis of Dyes and Intermediates

1-Substituted-2-hydroxy-4-methyl-5-cyano-6-pyridones (4a - 4c) were prepared from a mixture of ethyl cyanoacetate (1), ethyl acetoacetate (2) and amines (3a - 3c) in ethanol under reflux. The p-substituted anilines (5a - 5f) were diazotized using hydrochloric acid and sodium nitrite at 0°C - 5°C and the diazonium salts (6a - 6f) were coupled with pyridone compounds (4a - 4c) at pH 3 - 4 to give the 1-substituted 3-(p-substituted phenylazo)-6-pyridone dyes (7 - 9). The dyes were purified by recrystallisation from acetone and their purity examined by thin-layer chromatography. The structures of the pyridones were confirmed by mass spectrometry and IR while the structures of the dyes were confirmed by IR. The physical characteristics of the dyes are summarized in **Table 1**.

3.2. Infrared Spectra of the Dyes

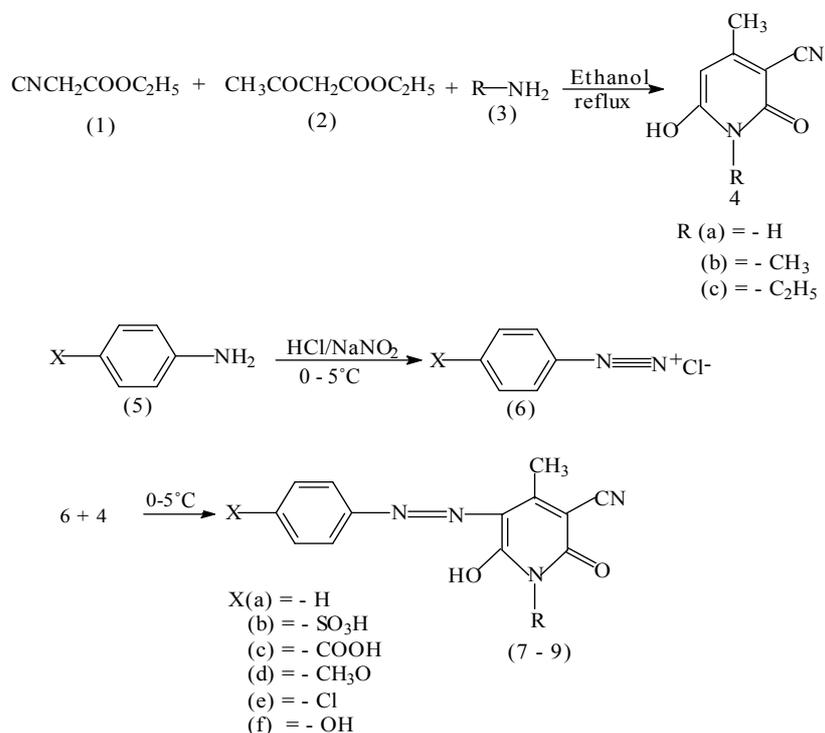
As can be seen from the infra-red spectra results in **Table 2**, all the dyes gave absorption peaks due to azo group, N=N stretching vibration at 1428 - 1376 cm⁻¹; aromatic C-H stretching vibration bands appeared in the region of 2953 - 2923 cm⁻¹; aromatic C-H bending vibration bands appeared in the region of 892 - 721 cm⁻¹; C≡N stretching vibration bands appeared in the region of 2260 - 2220 cm⁻¹; C=C stretching vibration band appeared in the region of 1675 - 1600 cm⁻¹; C=O stretching vibration bands appeared in the region of 1850 - 1550 cm⁻¹; C-H stretching vibration bands appeared in the region of 1292 - 757 cm⁻¹, N-H stretching vibration bands appeared in the region of 3443 - 2953 cm⁻¹; N-H bending vibration bands appeared in the region of 1631 - 1513 cm⁻¹; O-H stretching vibration bands appeared in the region of 3520 - 3139 cm⁻¹; OH bending vibration bands appeared in the region of 1498 - 1457 cm⁻¹; C-Cl stretching vibration appeared in

Table 1. Physical characteristics of the dyes.

Dye No	Molar Mass	M. Pt °C	Wt of Dye (g)	% Yield	Colour of Crystals
7a	255	200-203	1.12	60.83	Yellow
7b	335	198-201	2.27	74.62	Deep yellow
7d	285	158-161	1.71	62.33	Orange
7e	289	218-221	1.79	64.68	Light yellow
7f	271	207-210	2.01	75.57	Orange
8a	270	199-201	0.79	42.03	Yellow
8b	359	158-160	2.83	90.46	Deep yellow
8c	314	158-160	1.49	74.03	Light yellow
8d	300	143-145	2.34	82.54	Orange
8e	304	172-173	1.86	65.05	Light yellow
8f	286	178-180	0.99	35.88	Orange
9a	284	116-117	0.87	45.54	Yellow
9b	364	159-161	1.96	60.84	Deep yellow
9c	328	195-198	1.68	82.07	Light yellow
9d	314	119-120	2.79	95.71	Orange
9f	300	157-160	1.35	47.76	Orange
9e	318	160-162	1.50	50.75	Light yellow

Table 2. Infra-red spectra for the dyes.

Function group	Azo N=N	Aromatic C-H	Atomic C-H	C \equiv N	C=C	C=O	Aliphatic C-H	C-H	N-H	COOH	C-Cl	C-SO ₃ H	O-H	O-H
Type of vibration	Stretching vibration	Stretching vibration	Bending	Stretching	Stretching	Stretching	Bending	Stretching	Stretching	Stretching	Stretching	Stretching	Stretching	Bending
DYE NO.	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7a	1377	2923	723	2220	1663	1631	2853	757	3127	-	-	-	3378	1465
7b	1377	2923	888	2224	1603	1690	2853	1275	-	-	-	1222	3432	1457
7c	1428	2923	853	2231	1670	1582	2853	1292	3443	3210	2359	-	3520	1465
7d	1399	2924	892	2222	1649	1603	2853	1246	3139	-	-	-	3139	1460
7e	1383	2923	825	2223	1672	1635	2852	825	-	-	2358	-	3390	1465
8a	1376	2924	766	2231	1643	1588	2853	1276	-	-	2362	-	3410	1459
8b	1377	2953	721	2231	1645	1590	2853	1277	-	-	-	1223	-	1465
8c	1378	2924	852	2231	1617	1721	2853	1229	3214	3210	-	-	-	1458
8d	1377	2954	819	2220	1628	1576	2853	1257	-	-	-	-	-	1462
8e	1377	2925	721	2231	1635	1676	2853	1272	-	-	2231	-	-	1464
8f	1402	2954	819	2221	1631	1675	2853	1219	2953	-	-	-	-	1498
9a	1377	2924	878	2223	1672	1629	2853	1277	-	-	-	-	-	1462
9b	1376	2923	824	2224	1671	1628	2853	1281	-	-	-	1223	-	1465
9c	1376	2923	824	2224	1642	1635	2853	1281	-	3210	-	-	-	1465
9d	1377	2923	834	2222	1628	1630	2853	1249	-	-	-	-	-	1459
9e	1378	2923	877	2229	1675	1635	2853	1276	-	-	2361	-	3420	1464
9f	1376	2924	721	2223	1654	1624	2853	1272	2954	-	-	-	-	1462



Scheme 1. Synthetic route for intermediates and dyes.

the region 2363 - 2231 cm^{-1} ; COOH and C-SO₃H stretching vibration bands appeared at the peak of 3210 cm^{-1} and 1222 cm^{-1} respectively.

The dyes may exist in two tautomeric forms, namely the azohydroxypyridone form **A** and the diketohydrazone form **B**. The deprotonation of the two tautomers leads to a common anion **C**, as shown in Scheme 2.

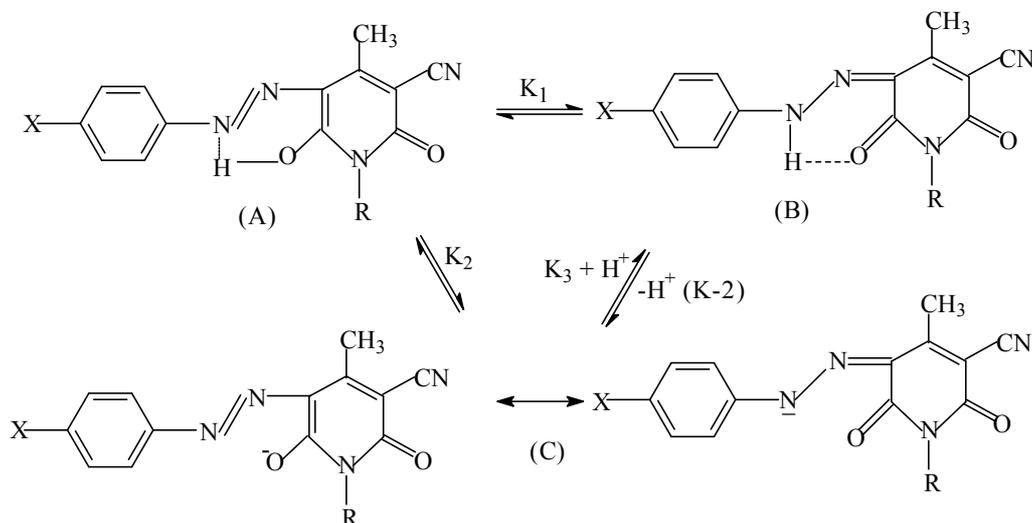
The infrared spectra of all the compounds (in **KBr**) showed two intense carbonyl bands at 1700 and 1600 cm^{-1} ; intensities of the two bands were very similar, and the latter band is related to intramolecularly hydrogen-bonded carbonyl. It was therefore assigned to the diketohydrazone form **B**. In the infrared spectra of the compounds in **CHCl₃**, two carbonyl bands were also observed, with the 1600 cm^{-1} band having lower intensity. This suggests that the dyes exist in the hydrazone form in the solid state and predominantly in the hydrazone form in **CHCl₃**. These conclusions are in accord with those of Ertan [8] and Cheng [9].

3.3. Visible Absorption Spectra of the Dyes

Visible absorption maxima of the dyes in various solvents are given in **Table 3**. The visible absorption spectra of the dyes were found to exhibit a strong solvent dependence which did not show a regular variation with the dielectric constants of the solvent. It was observed that in DMF, ethanol and ethanol plus a drop of HCl the absorption spectra of the dyes did not change significantly. λ_{max} of the dyes shifted considerably in acetone for example

dye 7a, λ_{max} is 404.0 nm in DMF and 467.0 nm in acetone. The absorption maxima of most of the dyes also showed bathochromic shifts when a small amount of HCl was added to dye solutions in ethanol. A typical example is 7d with λ_{max} of 400.00 nm in ethanol and 459.50 when a drop of HCl was added to the solution in ethanol.

Dye 7a was obtained by diazotising aniline and coupling to 3-cyano-4-methyl-6-hydroxy-2-pyridone and absorbed at 467.0 nm in acetone and when sulphonic acid group was introduced into para-position of the diazo component (aniline) the resulting dye 7b absorbed at 460.0 nm in the same solvent and thus the dye 7b was hypsochromic by 7 nm when compared with dye 7a. Replacement of the sulphonic acid group in dye 7b by carboxylic group gave dye 7c which absorbed at 468.0 nm and showed a bathochromic shift of 8 nm and 1 nm respectively when compared with dye 7b and 7a. Substitution of methoxy group into the para-position of aniline gave dye 7d with maximum absorption wavelength of 445.0 nm in the same solvent. This is highly hypsochromic when compared with all the other dyes in this series. This may be due to the fact that methoxy group is an electron donating group compared with all the other substituents that are electron withdrawing groups. Replacement of the methoxy group by chlorine gave dye 7e with λ_{max} of 480.0 nm in acetone and this is bathochromic when compared with dyes 7a - 7d with enhanced extinction coefficient. Dye 7f was obtained by replacing the chlorine group in dye 7e by the hydroxyl group with λ_{max} of 502.0 nm in the same solvent. When methyl group was



Scheme 2. Hydrazone-common anion equilibrium.

Table 3. The UV Spectroscopic properties of dyes.

Dye No.	ϵ_{\max} in acetone $\times 10^4$ $\text{lmol}^{-1}\text{cm}^{-1}$	Acetone λ_{\max} (nm)	Dimethylformamide λ_{\max} (nm)	Ethanol λ_{\max} (nm) a	ethanol + HCl λ_{\max} (nm) b	Change in λ_{\max} (nm) (b-a)
7a	5.57	467.0	404.00	433.50	433.00	-0.5
7b	5.33	460.0	439.50	460.00	400.00	-60.0
7c	5.50	468.0	414.00	431.00	434.50	+3.5
7d	4.98	445.0	447.50	400.00	459.50	+59.50
7e	6.65	480.0	412.50	459.00	436.00	-23.0
7f	6.64	502.0	434.50	458.50	462.50	+4.0
8a	6.52	472.0	412.50	429.50	434.50	+5.0
8b	6.13	479.0	420.00	436.50	433.00	-3.5
8c	6.07	473.0	428.50	438.50	433.50	-5.0
8d	6.16	536.0	453.00	423.50	430.50	+7.0
8e	6.76	472.0	412.50	432.00	462.00	+30.0
8f	5.56	531.0	464.00	458.50	457.50	-1.0
9a	6.93	452.0	410.00	454.50	432.50	-22.0
9b	8.55	470.0	418.00	458.00	415.50	-42.5
9c	7.90	499.0	433.50	438.00	432.50	-5.5
9d	7.85	510.0	414.00	434.00	444.00	+10.0
9e	7.24	480.0	417.50	438.00	476.00	+38.0
9f	7.11	493.0	460.00	438.00	458.00	+20.0

introduced into the coupling component to produce 3-cyano-4-methyl-6-hydroxyl-1-methyl-2-pyridone (4b) and then coupled to aniline and substituted anilines, this gave dyes in series 8. The introduction of the various substituent groups gave slight changes in the visible absorption wavelength. With the exception of dyes 8d and 8f which absorbed at 536 nm and 531 nm that are highly bathochromic when compared with all the dyes in series 7 and 8.

When the alkyl chain length was increased by replacing the methyl group by ethyl group to give 3-cyano-4-methyl-6-hydroxyl-1-ethyl-2-pyridone 4c and then coupled to aniline and substituted anilines, this gave dyes in series 9. From the results summarized in **Table 3**, the

introduction of different substituent into the coupling component did not show any specific pattern in the visible absorption spectra. Similarly, the introduction of different substituent into the diazo component did not follow a specific pattern.

The effects of solvent polarity on the visible absorption spectra were also studied and from the results summarized in **Table 3**, there is no specific pattern in the results. For example, dye 7a absorbed at 467.0 nm in acetone and gave λ_{\max} of 404.0 nm in DMF which is hypsochromic by 63 nm. Most of the dyes showed negative solvatochromism when the solvent was changed to more polar solvents. Similarly, the effects of few drops

of HCl on ethanolic solution of the dyes showed positive and negative halochromism as can be seen in the results summarized in **Table 3**. This means that the dyes can be used as indicator in acid-base titration. The extinction coefficients of the dyes are very high, ranging from 4.98×10^4 - 7.90×10^4 $\text{lmol}^{-1}\text{cm}^{-1}$ which are very good for textile application.

3.4. Dyeing and Fastness Properties

The dyes were applied to polyester fabric using carrier dyeing method and the wash fastness property was examined using I.S.O. 3 procedure. The results of the wash fastness rating are summarized in **Table 4**. The dyes gave very good levelness and fibre penetration on polyester. The exhaustion was good ranging from 73% - 79% and the wash fastness rating is very good with rating of 4 and 5 in most cases. The staining of the adjacent white fabric is also limited with rating of 4 - 5 indicating slight staining in most cases. The excellent wash fastness obtained on polyester is due to the crystalline structure of the polyester which disallowed the migration of dye out of the fabric when this has entered the fabric. The light fastness of the dyes is similarly studied and the results are summarized in **Table 4**. From these results the light fastness are good with rating of 5 in all cases. This is also good for commercial applications.

4. Conclusion

The synthesise of azo-disperse dyes based on pyridone as coupling component was undertaken. The relative mo-

lecular mass of 3-cyano-4-methyl-6-hydroxyl-1-methyl-2-pyridone and 3-cyano-4-methyl-6-hydroxyl-1-ethyl-2-pyridone were confirmed using mass spectrophotometer. Generally, the exhaustion of the dyes was very good on polyester fabric with excellent wash and light fastness properties. These dyes, however, are noteworthy in their excellent affinity and intensity of colour. Other outstanding characteristics of these dyes are that they give deep and bright hues with level dyeings. The bright hue might be attributed to the greater planarity of the pyridone ring, because of the lower steric interaction of a five membered ring. The remarkable degree of levelness and brightness after washing is indicative of good penetration and the excellent exhaustion of these dyes for the polyester fabric due to the accumulation of polar groups.

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Table 4. % Exhaustion and fastness properties of the dyes.

Dye No	% Exhaustion	Wash Fastness Rating		Light Fastness Rating
		Change in Shade	Staining of White	
7a	74	5	4-5	5
7b	77	4	4-5	5
7d	76	4	4	5
7e	77	5	4-5	5
7f	72	4	4-5	5
8a	75	5	4-5	5
8b	79	4	4-5	5
8c	76	4	5	5
8d	73	4	4	5
8e	75	4	5	5
8f	75	4	4-5	5
9a	75	5	4	5
9b	75	4	4-5	5
9c	78	4	4-5	5
9d	74	5	4	5
9e	74	5	5	5
9f	74	4	4-5	5