

Synthesis and Application of Azo Disperse Reactive Dyes derived from p-Aminobenzaldehyde

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ABSTRACT

Disperse reactive dyes were synthesized by diazotizing p-aminobenzaldehyde and coupling with different substituted pyridones and 2-naphthol. The dyeing performance of the dyes was assessed on polyester, nylon, cotton and wool fabrics. The dyes obtained gave various shades of yellow with good depth, brightness and leveling properties on the fabrics. The dyed fabric showed fairly good to very good light fastness and very good to excellent fastness to washing, hot pressing and rubbing. The dyebath exhaustion on the polyester, nylon, wool and cotton fabrics was found to be very good and fixation on wool was better than on cotton fabric.

Keywords: p-aminobenzaldehyde; pyridone; disperse-reactive dyes; exhaustion; fixation; polyester, nylon, wool.

I. INTRODUCTION

The development of disperse dyes for dyeing secondary cellulose acetate fibres in the early 1920s was a major technological breakthrough. The major use of this dye today is for the coloration of polyester, the most important group of synthetic fibres¹. Disperse dyes are used in aqueous dyebaths in the form of fine dispersions, because their solubility in water is very low, even at high dyeing temperatures². In the conventional disperse dyeing of polyester, dispersing agents are usually added to increase the dispersion stability and solubility of disperse dyes. However, after the dyeing process is finished, they are not adsorbed onto polyester and discharged as effluents with the residual dyeing liquor, which increases the COD and BOD values of the effluent³⁻⁴.

It is widely known that the presence of an aldehyde group in a dye molecule renders the dye capable of reacting with the free functional groups of the wool keratin, or with the hydroxyl group of the cellulose⁵⁻⁶. Azo dyes containing aldehyde group can thus be considered as reactive dyes⁷. In this paper, we report a series of azo dyes containing an aldehyde group which are capable of reacting with polyamide, cellulose, and wool giving good fixation and fastness properties.

II. EXPERIMENTAL

2.1 Materials and apparatus

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 using the Gallenkamp melting apparatus. The visible absorption spectra were measured using Jenway 6405 UV/Vis spectrophotometer, IR was measured

and recorded in KBr pellets using the FTIR-8400S Fourier Transform Infra-red Spectrometer, and GC-MS using the GCMS-QP2010 PLUS SHIMADZU Japan. The rubbing fastness test was carried out with a Crockmeter.

2.2 Synthesis of p-amino benzaldehyde

To 600ml of distilled water in a beaker was added 30g (0.125 mol.) of sodium sulphide monohydrate, 15g sulphur and 27g (0.67 mol.) sodium hydroxide. The mixture was heated on a steam bath for 15-20 minutes with occasional stirring and then poured into a round-bottomed flask containing hot solution of 50g (0.36 mol.) of p-nitrotoluene in 300ml of 95% ethanol. The mixture was refluxed for three hours under heat. The resulting clear but deep red solution was steam-distilled and stopped when the distillate was clear. The residue was rapidly chilled in an ice bath with occasional vigorous shaking and stirring to induce crystallization⁸.

2.3 Synthesis of pyridone derivatives

A mixture of (0.1 mole, 11.3g) ethylcyanoacetate, (28.2ml) and (0.3 mol, 10.5g) ethylamine (72ml) were stirred until a clear solution was obtained and (0.1 mol., 13.0g) ethylacetoacetate was added. The mixture was refluxed at 110°C for 9 hours. The solution was diluted with water (400ml) and acidified with hydrochloric acid to give a white solid. This was filtered and washed with water. The process was repeated by replacing ethylamine with butylamine and dedocylamine respectively to obtain other pyridone derivatives.

2.4 Diazotization of p-aminobenzaldehyde

P-Aminobenzaldehyde (2.42g, 0.02 mol) was added to a mixture of acetic acid (24ml) and water (6ml) and cooled with stirring in a ice bath. Sodium nitrite (1.5g, 0.021 mol) dissolved in water (10ml) was added in portion within thirty minutes and then concentrated hydrochloric acid (10ml) was added immediately. The mixture was left in the ice bath for 15 minutes and the excess nitrous acid destroyed by adding small amount of urea.

2.5 Coupling diazotized p-aminobenzaldehyde with Pyridone

A solution of the coupling component (0.02mole) was dissolved in 5mls of 2% stock solution of sodium hydroxide, 50g of crushed ice was added to the solution. The diazonium salt of p-aminobenzaldehyde was added in portion into the solution with constant stirring for over 30 minutes, the reaction was allowed to proceed for another one hour. The dye produced was filtered and dried in the oven at 50°C. The final product was recrystallized from ethanol.

2.6 Dyeing of Polyester

The dye baths of liquor ratio 50:1 were prepared by using 2% on weight of fabric from 1% stock solution of the dye with a dispersol-levelling agent (1 g⁻¹litre) and 5% phenol as carrier. 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, reduction clearing of the dyed fabrics was carried out in a solution of sodium hydroxide (2g/L) and dispersing agent (1.5 g/L) at 60°C for 30mins and then washed and dried. Percentage exhaustion was calculated to determine the dye absorption unto the fabric.

2.7 Dyeing of nylon

The Nylon fabric was dyed following the same procedure as in the dyeing of polyester but without using a carrier.

2.8 Dyeing of wool

1% stock solution of each dye was prepared; a dye bath of liquor ratio of 50:1 was used with 2% shade on weight of fabric (o.w.f). The dyeing was carried out at pH of 3-4, at 70°C for 1 hour after which the solution was made alkaline using sodium carbonate for fixation of the dyes into the fabric

2.9 Dyeing of cotton

1% stock solution of each dye was also prepared, a dye bath of liquor ratio of 50:1 was used with 2% shade on weight of fabric (o.w.f) at 70°C using 25g/L of salt and at pH 8 for 1 hour.

2.10 Determination of % Exhaustion and Fixation

Percentage exhaustion of the dyes was calculated by taking the optical density of the dyebath before dyeing and after the dyeing and from the values obtained the % exhaustion and fixations were calculated using the following formula:

$$\% \text{ Exhaustion} = \frac{OD_1 - OD_2}{OD_1} \times 100$$

where OD₁ = Optical density before dyeing

OD₂ = Optical density after dyeing

$$\% \text{ Fixation} = \frac{OD_1 - OD_2 - \Delta}{OD_1} \times 100$$

where Δ is the optical density of the dye striped from the dyed fabric

2.11 Fastness Tests

The washing fastness, light fastness, hot pressing and rubbing fastness tests were carried out on each dyed fabric. The wash fastness test was carried out using the ISO number 4 method, the light fastness test was carried out under natural day light and assessed using 8 blue wool standard, the hot pressing was carried out using ISO standard and the rubbing fastness test was carried out using crockmeter (Atlas) in ISO standard⁹.

III. RESULTS AND DISCUSSION

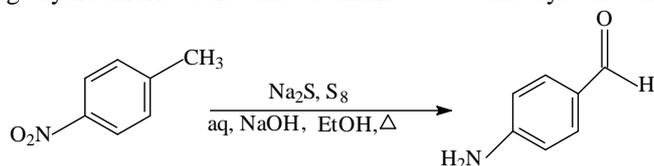
3.1 Synthesis of Intermediates and Dyes

P-Aminobenzaldehyde was synthesized by following the reaction steps in Scheme 1. In this Scheme, mixture of crystalline sodium sulphide monohydrate, flowers of sulfur and sodium hydroxide pellets in water was heated on a steam bath with occasional stirring and then poured into hot solution of p-nitrotoluene in 95% ethanol under reflux. The resulting solution was rapidly steam-distilled. The residue in the flask is diluted with

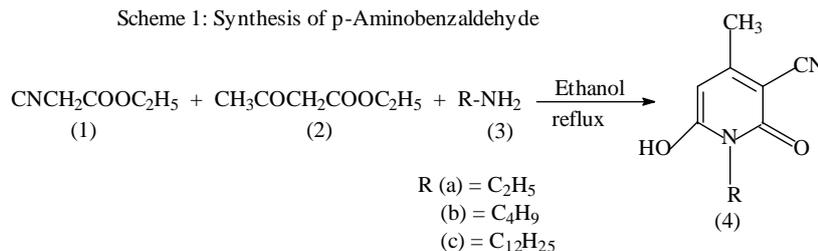
hot water and shilled in an ice bath with vigorous shaking to induce crystallization. Golden yellow crystals of p-aminobenzaldehyde are colleted by filtration.

1-Substituted-2-hydroxy-4-methyl-5-cyano-6-pyridones (4a-4c) were prepared from a mixture of ethylcyanoacetate (1), ethylacetoacetate (2) and amines (3a – 3c) in ethanol under reflux as shown in Scheme 2. p-Aminobenzaldehyde was diazotized using hydrochloric acid and sodium

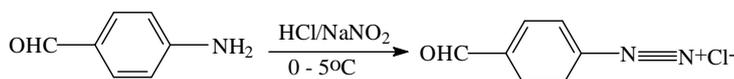
nitrite at 0° – 5°C and the diazonium salts coupled with pyridones (4a – 4c) at pH 3 – 4 to give the 1-substituted 3-(p-substituted phenylazo)-6-pyridone dyes (5a – 5) as shown in Schemes 3 and 4. Dye (5) was synthesized by coupling the diazonium salt with 2-naphthol. The structures of the pyridones were confirmed by mass spectrometry and IR while the structures of the dyes were confirmed by IR. The physical characteristics of the intermediates and dyes are summarized in Table 1.



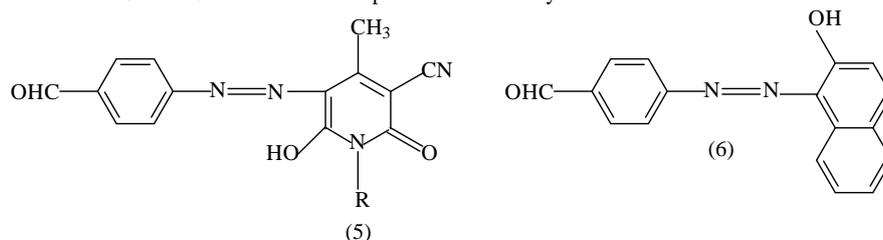
Scheme 1: Synthesis of p-Aminobenzaldehyde



Scheme 2: Synthesis of Pyridones



Scheme 3: Diazotization of p-Aminobenzaldehyde



Scheme 4: Synthesis of pyridone dyes (5a - 5c)

3.2 Physical Characteristics of the Intermediates and Dyes

The physical characteristics of the intermediates and dyes are summarized in Table

1. Table 1: Physical Characteristics of the Intermediates and Dyes

Intermediate and dye No	Molar mass g/mol	Melting point (°C)	Yield (%)	Colour of the crystal
(4a)	178	244-246	83	White
(4b)	206	136-138	75	White
(4c)	318	76-79	79	White
(5a)	310	274-275	70	Yellow
(5b)	338	200-202	86	Yellow
(5c)	450	118-129	60	Yellow
(6)	276	157-158	68	Reddish brown

3.3 Infrared Spectral of Intermediates and Dyes

The results obtained from the Infrared spectral analysis are shown in Table 2

Table 2: Infrared Spectra of the Intermediates and Dyes

Functional group	ArC-C	ArC-H	CN	C=C	C=O	ArN-H	OH	CHO	N=N
Type of vibration	Stretch	Bend	Stretch	Stretch	Stretch	Bend/stretch	Stretch	Stretch	Stretch
(4a)	1420	823	2201	1089	1622	-	3423	-	-
(4b)	1422	825	2199	1039	1575	-	3425	-	-
(4c)	1420	827	2200	1046	1601	-	3426	-	-
(5a)	1417	806	2225	1157	134	1516	3430	1422	1578
(5b)	1416	808	2223	1019	1634	1508	3448	1480	1577
(5c)	1416	799	2225	1021	1637	1514	3462	1500	1576
(6)	1421	872	-	1047	-	-	3469	1510	1522

From the results in Table 2, all the synthesized pyridone based coupling component gave absorption peaks due to aromatic C=C stretching vibration band at 1422-1420 cm^{-1} , aromatic C-H bending vibration band at 827-823 cm^{-1} , CN stretching vibration at 2201-2199 cm^{-1} , C=O stretching vibration at 1622-1575 cm^{-1} and OH stretching vibration at 3884-3433 cm^{-1} . As can also 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 1578-1421 cm^{-1} , aromatic C-C stretching vibration band at 1421-1416 cm^{-1} , aromatic C-H bending vibration

band at 872-799 cm^{-1} , CN stretching vibration at 2225-2223 cm^{-1} , C=C stretching vibration band at 1157-1019 cm^{-1} , C=O stretching vibration at 1637-1634 cm^{-1} , aromatic amine (NH) stretching vibration at 1516-1508 cm^{-1} and OH stretching vibration at 3469-3430 cm^{-1} .

3.4 Visible Absorption Spectra of the Dyes

The visible absorption spectra of the dyes are measured in different solvents and extinction coefficient calculated in DMF. The results obtained are summarized in Table 3.

Table 3: Visible Absorption Spectra of the Dyes

Dye No.	$\epsilon_{\text{max}} \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1}$ in DMF	Ethanol λ_{max}	Ethanol + HCl λ_{max}	DMF λ_{max}	Change in λ_{max}
(5a)	3.8	432	435	437.5	+3
(5b)	2.2	457	435	442	-22
(5c)	2.3	485	435	442	-50
(6)	3.0	420	486	486	+66

The visible absorption properties of the dyes were measured in ethanol, ethanol + HCl and DMF respectively, and the results are summarized in Table 3. From Table 3, it can be seen that the bathochromicity increases in the order of dyes (5c) > (5b) > (5a). This may be attributed to the longer alkyl chain length attached to the coupling component in dyes (5c), (5b), and (5a) which are coupled with pyridone derivatives. Hence, dye (5c) with 1-dedocy-2-hydroxyl-4-methyl-5-cyano-6-pyridone coupling component contains more alkyl chain length and thus has the maximum absorption wavelength of 485nm which is more bathochromic than dye (5b) with coupling component 1-butyl-2-hydroxyl-4-methyl-5-cyano-6-pyridone which absorbed at 457 and dye (5a) with 1-ethyl-2-hydroxyl-4-methyl-5-cyano-6-pyridone with 432nm in ethanol respectively. However dye (6) which was obtained by coupling with 2-naphthol, gave maximum absorption wavelength of 420 nm in the same solvent, which is hypsochromic when compared with dyes in series (5).

It can also be seen from results in Table 3 that two of the dyes, dyes (5b) and (5c) showed negative solvatochromism as the wavelength tends to

reduce with increasing polarity of the solvent. The maximum absorption wavelength values shifted to shorter wavelength when the solvent was changed from ethanol to DMF. This implies that the dye molecules have more polar ground state than the excited state and this will increase the energy difference between the ground and the excited states, thus leading to hypsochromic shift in the visible absorption region of the spectrum¹⁰. However, dyes (5a) and (6) showed positive solvatochromism. For example dye (5a) gave maximum absorption wavelength of 432nm in ethanol, and 437.5nm in DMF and similarly dye (6) gave maximum absorption wavelength of 420 nm in the same solvent and 486 nm in DMF, giving positive solvatochromism of 5.5 nm and 66 nm respectively. This means that dyes (5a) and (6) have more polar excited state than the ground state and a polar solvent can stabilize this more than the ground state.

The effect of few drops of acids on ethanol solution of the dyes was also observed and the result are also summarized in Table 3. From the results obtained it can be deduced that dyes (6) and (5a) have positive halochromism as they absorbed at 420nm

and 432nm, respectively in neutral solution of ethanol and absorbed maximally at 486nm and 435nm respectively in acidic solution of ethanol, indicating a bathochromic shift of +66 and +3, respectively. Dyes (5a) and (5b) showed negative halochromism absorbing at 457nm and 485nm in neutral solution of ethanol and 435nm in acidic solution of the ethanol having hypsochromic shift -22 nm and -50 nm, respectively. The shift may be attributed to the electron withdrawing strength of the substituent, if the electron withdrawing strength of the substituent is sufficiently high, zero or negative halochromism can be observed¹¹.

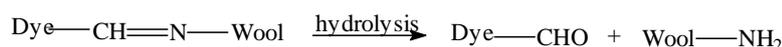
The molar extinction coefficient of the dyes was calculated using DMF as solvents. The results obtained are shown in Table 3, and from the results, it can be concluded that the dyes possess high molar extinction coefficient. The higher molar extinction coefficients value of the dyes implies the probability for more electronic transition, the fact that they transmit more light in comparison to others and therefore have narrow absorption bands with sharp peaks¹².

3.5 Dyeing and Fastness properties

The synthesized dyes were applied to polyester, nylon 6,6, wool and cotton fabrics and the

results are summarized in Table 4. The results in Table 4 indicate a higher percentage exhaustion on nylon 6,6 and polyester fabric as compared to wool and cotton. The dyes gave very good levelness and fibre penetration on all the fabrics used. The exhaustion was between 92% and 80% on polyester, between 88% and 80% on nylon 6,6, between 89% and 70% on wool and between 79% and 76% on cotton fabrics. The higher percentage exhaustion in polyester fabric may be attributed to the presence of dispersing agents which assist in the reduction of particle size of dyes, facilitated reverse change from powder to dispersion when the dye bath was prepared and maintaining dispersion during dyeing. The percentage fixation values were higher in wool compared to cotton. The dyes gave excellent to very good wash fastness, good to fair light fastness, excellent fastness to hot press on nylon 6,6 and polyester fabrics and excellent to good rubbing fastness.

Wool, nylon and cotton dyed with the synthesized dyes showed no loss of dye when treated with warm pyridine and also with DMF-H₂O (1:1) mixture. This confirmed the formation of covalent bond between the dye and the substrates. The dye fibre reaction leading to covalent bond and hydrolysis on wool is summarized as shown in Scheme 5¹³.



Scheme 5: Reaction leading to covalent fixation and hydrolysis of the dyes

Table 4: Percentage Exhaustion and Fixation of Dyes on Different substrates

Dye No.	% exhaustion on Polyester	% exhaustion on Nylon 6,6	Wool		Cotton	
			% exhaustion	% fixation	% exhaustion	% fixation
(5a)	80	80	70	82	78	58
(5b)	80	80	81	88	79	54
(5c)	88	81	89	98	77	59
(6)	92	88	72	80	76	60

Table 5: Wash Fastness Properties of the Dyes

Dye No.	Change in colour				Staining of adjacent fabric			
	Polyester	Nylon 6,6	Wool	Cotton	Polyester	Nylon 6,6	Wool	Cotton
(5a)	5	5	4-5	4-5	5	4-5	4-5	4-5
(5b)	5	5	4-5	4-5	5	5	4	4-5
(5c)	5	5	5	4-5	5	5	4	4-5
(6)	5	5	4	5	5	5	4	4-5

Table 6: Light Fastness Properties of the Dyes

Dye No.	Polyester	Nylon 6,6	Wool	Cotton
(5a)	7	7	5	5
(5b)	7	6	6	6
(5c)	7	7	5	5
(6)	7	7	5	4

Table 7: Rubbing Fastness Properties of the Dyes on Different Substrates

Dye No.	Polyester		Nylon		Wool		Cotton	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
(5a)	4-5	4-5	5	5	5	4-5	4	3-4
(5b)	4-5	4-5	5	5	5	5	4-5	4
(5c)	5	5	4-5	4-5	4-5	4	4-5	4
(6)	5	4-5	5	4-5	5	4-5	4	3-4

Table 8: Hot Pressing Fastness of the Dyes on the Substrates

Dye No.	Polyester			Nylon 6,6		
	Dry	Damp	Wet	Dry	Damp	Wet
(5a)	5	5	5	5	5	5
(5b)	5	5	5	5	5	5
(5c)	5	5	5	4	4-5	4-5
(6)	4	4	4	5	5	5

IV. CONCLUSION

The dyes produced from coupling with the alkyl-2-hydroxy-4-methyl-5-cyano-6-pyridone groups and 2-naphthol showed disperse-reactive property. These dyes gave mostly yellow and orange colours. The remarkable degree of levelness after washing indicates good penetration and affinity of these dyes for the fabrics. Exhaustion and fixation of these dyes were very good and indicate that the dyes have good affinity for the fabrics. The dyes showed excellent fastness to washing, rubbing and hot pressing. The light fastness is excellent on polyester and nylon and good on wool and cotton fabrics.

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