Synthesis of Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5- arylazopyridine-3-carboxylate, Part (IV): New Disperse Dyes

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Summary: The reaction of ethyl-4,6-dihydroxy-2-oxo-1-phenyl pyridine-3-carboxylate (**3**) with different diazotized substituted aromatic amine (**2**) yielded compound ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-arylazopyridine-3-carboxylate (**4**) showing visible light absorption between λ_{max} 550-600 nm which shows the characteristic of azo dyes. Aqueous solution of (**4**) with non-ionic dispersing agent a dye carrier at pH 5-6 at the temperature 130 °C when applied to polyester fiber formed yellow to orange color.

Introduction

Disperse dyes are non-ionic dyes relatively insoluble in water at room temperature and have only limited solubility at higher temperatures [1]. They do, however, possess substantivity for hydrophobic fibers such as nylon and polyester, in which they are quite soluble. As their name implies, these dyes are present in the dye bath as a fine aqueous suspension in the presence of the dispersing agent. The water dissolves a small amount of the dye in monomolecular form. The hydrophobic fibers then absorb the dye from the solution. Since these dyes are non-ionic organic compounds of relatively low molecular weight, may sublime on heating and dyeing by absorption of the dye vapors is also possible [2].

Disperse dyes are much more soluble in the fiber than in water so deep dyeing is possible. The majority of disperse dyes are low molecular weight, non-ionic mono-azo and anthraquinone derivatives. Light and washing fastness of disperse dyes on synthetic and acetate fibers are usually moderate to good. The washing fastness on nylon, however, is only fair, particularly for deep shades [3].

Yellow disperse dyes are known from a wide range of chemical classes but azo dyes derived from heterocyclic coupling components have gained importance in recent years. The mono-azo subclass dominates throughout the disperse dye range and there are no metal-complex disperse dyes for consideration have favored the introduction of new hydrophobic fibers, although they do exist as a subgroup of 'acid dyes, for wool. Anthraquinone derivatives have traditionally dominated the bright red to bright green series but here again cost mono-azo dyes, often with heterocyclic amines as diazo components, for the dyeing of polyester fibres [4]. Browns and blacks on polyester and acetate fibers have always been provided entirely by azo disperse dyes [5].

Result and Discussion

Color and Spectral Properties of Disperse Dyes

Color is a visual perception associated with the various wavelengths in the visible portion of the electromagnetic spectrum. In other words it is a physical phenomenon of light. Electromagnetic spectrum visible to man is the range of wavelength between 400 and 700 nm. Light with a wavelength of 700 nm is perceived as red and light of 400 nm wavelength is perceived as violet [6].

The visible absorption is recorded in 95% methanol. All dyes that have been synthesized are yellow to orange with maximum absorption between 550 to 600 nm. The values of the logarithm of molar extinction coefficient (log ε) of the dyes are in the range of 4.1-4.6, indicating their very good absorption intensity.

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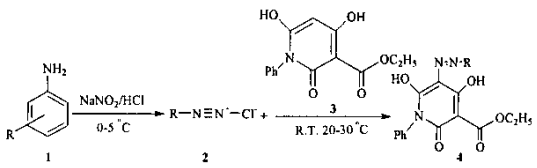
Infra-red radiation being of lower energy lies at longer wavelengths (greater than 700 nm) than visible light. IR spectra of solid samples were obtained by grinding 1 mg of sample with 200 mg of anhydrous potassium bromide and pressing the resulting powder into a thin KBr disc. The manual hydraulic press was used to press the powder with a maximum pressure of 15 tons.

Pyridine based new disperse dyes were synthesized from mono and di substituted aryl amines are taken as the diazo component (chromophoric group) [1a]. Coloring of power and shades of these dyes are studied by application on polyester fiber. The synthetic route of these dyes is shown in Scheme 1.



R = H
R = 4-Nitro
R = 5-Nitro, 2-Methyl
R = 4-Methyl
R = 2-Nitro
R = 2-CH_3
R = 2-Chloro, 4-Nitro
R = 4-Methoxy
R = 2-Nitro, 4-Chloro

Scheme 1

Experimental

Melting points were taken on Gallen-Kamp melting point apparatus and are uncorrected. The IR spectra were measured on a JASCO A-30 spectrometer and visible light spectra were determined in methanol 95 % on spectromiczo Baush & Lomb. The ^{1}HNMR were recorded in DMSO at 300 MHz on Brucker AM-300 ASPECT 300 spectrophotometer. Mass spectrum was determined using a Finningan Varian MAT 112 spectrophotometer. The compound 3 was synthesized according to method of Butt *et. al.*, 1991 [1d].

Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(phenyl) azo pyridine-3-carboxylate (4a)

The compound **3**, 0.69 g (2.5 mmol) was taken in ethanol (30 mL) and 1 % NaOH solution (10 mL) and water (100 mL) was added, the solution was stirred magnetically to obtain a clear solution.

Diazonium chloride solution **2** was prepared by taking aniline (0.25 mL; 2.5 mmol) in concentrated HCl (25 mL), solid was dissolved in cold water (100 mL). Solid $NaNO_2$ (0.2 g; 2.5 mmol) was dissolved in H_2O (10 mL) was added to amine hydrochloride solution at 0-5 °C. Clear diazo solution was added to coupling solution slowly, pH of the solution was adjusted by drop wise addition of sodium acetate 1 % and HCl 0.5 % solution. Dye precipitated at pH 5-6 which were kept for 1-2 h, yellow color dye was filtered, washed with water and dried at 60-80 °C under vacuum to afford 87 % yield. Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(phenyl) azo pyridine-3-carboxylate (**4a**) was crystallized from MeOH: CH_2Cl_2 (1:1) m. p. 218 °C visible light absorption spectra λ_{max} 592.8 nm (log ε = 4.2); IR: ν_{max} 3622 (OH), 1562 (N=N), 1696 (C=O, ester) and 1648 (C=O, lactone) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.25 (3H, t, J = 7.1 Hz), 4.26 (2H, q, J = 7.1 Hz), 7.25 (3H, m), 7.44 (5H, m), 7.77 (2H, d, J = 7.9 Hz), 14.3 (2H, br. s, 2OH); EI MS *m/z* (%): 379 (46, M$^+$), 333 (100), 304 (9), 256 (71), 91 (44), 77 (71); HREI MS Calcd for $C_{20}H_{17}N_3O_5$: C, 63.32; H, 4.52; N, 11.08; Found: C, 63.23; H, 4.20; N, 11.28.

Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(4-nitrophenyl) azo pyridine-3-carboxylate (4b)

The compound **3**, 0.69 g (2.5 mmol) was taken in ethanol (30 mL) and 1 % NaOH solution (10 mL) and water (100 mL) was added, the solution was stirred magnetically to obtain a clear solution. Diazonium chloride solution **2** was prepared by taking 4-nitrophenyl aniline (0.35 g; 2.5 mmol) in concentrated HCl (25 mL), solid was dissolved in cold water (100 mL). Solid $NaNO_2$ (0.2 g; 2.5 mmol) was dissolved in H_2O (10 mL) was added to amine hydrochloride solution at 0-5 °C. Clear diazo solution was added to coupling solution slowly, pH of the solution was adjusted by drop wise addition of sodium acetate 1 % and HCl 0.5 % solution. Dye precipitated at pH 5-6 which were kept for 1-2, yellow color dye was filtered, washed with water and dried at 60-80 °C under vacuum to afford 83 % yield. Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(4-nitrophenyl) azo pyridine-3-carboxylate (**4b**) was crystallized from MeOH: CH_2Cl_2 1:1, m. p. 228 °C visible light absorption spectra λ_{max} 593.2 nm (log ε = 4.2); IR (cm^{-1}): ν_{max} 3646 (OH), 1579 (N=N), 1705 (C=O,

ester) and 1647 (C=O, lact); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.25 (t, J = 7.1 Hz, 3H), 4.26 (q, J = 7.1 Hz, 2H), 7.29 (dd, J = 1.1, 9 Hz, 2H), 7.47 (3H, m,), 8.02 (d, J = 9.20 Hz, 2H), 8.26 (d, J = 9.20 Hz, 2H,), 14.15 (br s, 2OH, 2H,); EI MS *m/z* (%): 424 (13.2, M^+), 396 (4), 378 (100), 362 (3), 352 (14), 286 (5), 256 (67), 119 (21), 93 (20), 77 (23); HREI MS Calcd for $C_{20}H_{16}N_4O_7$: C, 56.61; H, 3.80; N, 13.20; Found: C, 56.21; H, 3.18; N, 13.30.

Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(5-nitro-2-methylphenyl) azo pyridine-3-carboxylate (4c)

The compound **3**, 0.69 g (2.5 mmol) was taken in ethanol (30 mL) and 1 % NaOH solution (10 mL) and water (100 mL) was added, the solution was stirred magnetically to obtain a clear solution. Diazonium chloride solution **2** was prepared by taking 5-nitro-methylphenyl aniline (0.38 g; 2.5 mmol) in concentrated HCl (25 mL), solid was dissolved in cold water (100 mL). Solid $NaNO_2$ (0.2 g; 2.5 mmol) was dissolved in H_2O (10 mL) was added to amine hydrochloride solution at 0-5 °C. Clear diazo solution was added to coupling solution slowly, pH of the solution was adjusted by drop wise addition of sodium acetate 1 % and HCl 0.5 % solution. Dye precipitated at pH 5-6 which were kept for 1-2 h, yellow color dye was filtered, washed with water and dried at 60-80 °C under vacuum yield 84 %. Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(5-nitro-methylphenyl) azo pyridine-3-carboxylate (**4c**) crystallized from MeOH: CH_2Cl_2 1:1, m. p. 254 °C visible light absorption spectra λ_{max} 600 nm (log ε = 4.4); IR (cm^{-1}): ν_{max} 3629 (OH), 1566 (N=N), 1688 (C=O, ester) and 1636 (C=O, lact); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.26 (t, J = 7.1 Hz, 3H), 2.37 (3H, s, CH_3) 4.27 (q, J = 7.1 Hz, 2H), 7.29 (d, J = 6.7 Hz, 2H), 7.42 (t, J = 6.7 Hz, 1H), 7.46 (1H, m), 7.49 (t, J = 6.7 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.95 (dd, J = 8.4, 2.3 Hz, 1H), 8.98 (d, J = 2.3 Hz, 1H), 14.4 (br s, 2OH, 2H); EI MS *m/z* (%): 438 (19, M^+), 392 (76), 366 (84), 287 (6), 256 (30), 228 (10), 178 (32), 152 (30), 119 (77), 104 (46), 93 (100), 77 (73); HREI MS Calcd for $C_{21}H_{18}N_4O_7$: C, 57.53; H, 4.14; N, 12.78. Found: C, 57.23; H, 4.20; N, 12.28.

Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(4-methylphenyl) azo pyridine-3-carboxylate (4d)

The compound **3** (0.69 g, 2.5 mmol) was taken in ethanol (30 mL) and 1 % NaOH solution (10 mL) and water (100 mL) was added, the solution was stirred magnetically to obtain a clear solution. Diazonium chloride solution **2** was prepared by taking 4-methylphenyl aniline (0.27 g; 2.5 mmol) in concentrated HCl (25 mL), solid was dissolved in cold water (100 mL). Solid $NaNO_2$ (0.2 g; 2.5 mmol) was dissolved in H_2O (10 mL) was added to amine hydrochloride solution at 0-5 °C. Clear diazo solution was added to coupling solution slowly, pH of the solution was adjusted by drop wise addition of sodium acetate 1 % and HCl 0.5 % solution. Dye precipitated at pH 5-6 which were kept for 1-2 h, yellow color dye was filtered, washed with water and dried at 60-80 °C under vacuum yield 84 %. Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(4-methylphenyl) azo pyridine-3-carboxylate (**4d**) crystallized from MeOH: CH_2Cl_2 1:1 m. p. 212 °C visible light absorption spectra λ_{max} 593 nm (log ε = 4.1); IR (cm^{-1}): ν_{max} 3640 (OH), 1567 (N=N), 1693 (C=O, ester) and 1626 (C=O, lact); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.25 (t, J = 7.1 Hz, 3H), 2.30 (s, 3H), 4.26 (q, J = 7.1 Hz, 2H), 7.26 (dd, J = 8.4, 3.0, 1.2 Hz, 4H), 7.39 (m, 2H), 7.46 (d, J = 7.5 Hz, 2H), 7.6 (d, J = 8.4 Hz, 2H), 14.0 (br s, 2OH, 2H); EI MS *m/z* (%): 393 (57, M^+), 347 (100), 321 (14), 256 (48), 132 (21), 119 (28), 91 (87), 77 (39); HREI MS Calcd for $C_{21}H_{19}N_3O_5$: C, 64.12; H, 4.87; N, 10.68; Found: C, 64.23; H, 4.97; N, 10.68.

Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(2-nitro phenyl) azo pyridine-3-carboxylate (4e)

The compound **3** (0.69 g, 2.5 mmol) was taken in ethanol (30 mL) and 1 % NaOH solution (10 mL) and water (100 mL) was added, the solution was stirred magnetically to obtain a clear solution. Diazonium chloride solution **2** was prepared by taking 2-nitro phenyl aniline (0.35 g; 2.5 mmol) in concentrated HCl (25 mL), solid was dissolved in cold water (100 mL). Solid $NaNO_2$ (0.2 g; 2.5 mmol) was dissolved in H_2O (10 mL) was added to amine hydrochloride solution at 0-5 °C. Clear diazo solution was added to coupling solution slowly, pH of the solution was adjusted by drop wise addition of sodium acetate 1 % and HCl 0.5 % solution. Dye precipitated at pH 5-6 which were kept for 1-2 h, yellow color dye was filtered, washed with water and dried at 60-80 °C under vacuum yield 78 %. Ethyl-4, 6-dihydroxy-2-oxo-1-phenyl-5-(2-nitro phenyl) azo pyridine-3-carboxylate (**4e**) crystallized from MeOH: CH_2Cl_2 1:1 m. p. 265 °C visible light absorption spectra λ_{max} 593.6 nm (log ε = 4.6); IR (cm^{-1}): ν_{max} 3649 (OH), 1579 (N=N), 1703 (C=O, ester) and

1646 (C=O, lact); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.25 (t, J = 7.1 Hz, 3H), 4.27 (2H, q, J = 7.1 Hz), 7.28 (d, J = 6.6 Hz, 2H), 7.44 (3H, m), 7.37 (t, J = 8.5 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.88 (t, J = 7.5 Hz, 2H), 8.25 (d, J = 8.5 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 15.30 (br s, 2OH, 2H); EI MS *m/z* (%): 424 (10, M^+), 378 (100), 352 (18), 286 (5), 256 (89), 119 (22), 77 (21), 91 (14); HREI MS Calcd for $C_{20}H_{16}N_4O_7$: C, 56.61; H, 3.80; N, 13.20. Found: C, 56.11; H, 3.08; N, 13.40.

Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(2-methylphenyl) azo pyridine-3-carboxylate (4f)

The compound **3** (0.69 g, 2.5 mmol) was taken in ethanol (30 mL) and 1 % NaOH solution (10 mL) and water (100 mL) was added, the solution was stirred magnetically to obtain a clear solution. Diazonium chloride solution **2** was prepared by taking 2-methylphenyl aniline (0.26 mL; 2.5 mmol) in concentrated HCl (25 mL), solid was dissolved in cold water (100 mL). Solid $NaNO_2$ (0.2 g; 2.5 mmol) was dissolved in H_2O (10 mL) was added to amine hydrochloride solution at 0-5 °C. Clear diazo solution was added to coupling solution slowly, pH of the solution was adjusted by drop wise addition of sodium acetate 1 % and HCl 0.5 % solution. Dye precipitated at pH 5-6 which were kept for 1-2 h, yellow color dye was filtered, washed with water and dried at 60-80 °C under vacuum yield 84 %. Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(2-methylphenyl) azo pyridine-3-carboxylate (**4f**) crystallized from MeOH: CH_2Cl_2 1:1 m. p. 244 °C visible light absorption spectra λ_{max} 595 nm (log ε = 4.1); IR (cm^{-1}): ν_{max} 3625 (OH), 1568 (N=N), 1686 (C=O, ester) and 1630 (C=O, lact); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.25 (t, J = 7.1 Hz, 3H), 3.15 (s, CH_3, 3H), 4.27 (q, J = 7.1 Hz, 2H), 7.15 (t, J = 7.9 Hz, 1H), 7.27 (d, J = 6.6 Hz, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.46 (3H, m), 8.08 (d, J = 7.9 Hz, 1H,), 14.6 (br s, 2OH, 2H); EI MS *m/z* (%): 393 (23, M^+), 347 (36), 256 (7), 132 (36), 91 (100), 77 (86); HREI MS Calcd for $C_{21}H_{19}N_3O_5$: C, 64.12; H, 4.87; N, 10.68 %. Found: C, 64.23; H, 4.97; N, 10.68 %.

Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(2-chloro-4-nitro phenyl) azo pyridine-3-carboxylate (4g)

The compound **3** (0.69 g, 2.5 mmol) was taken in ethanol (30 mL) and 1 % NaOH solution (10 mL) and water (100 mL) was added, the solution was stirred magnetically to obtain a clear solution. Diazonium chloride solution **2** was prepared by taking 2-chloro-4-nitro phenyl aniline (0.43 g; 2.5 mmol) in concentrated HCl (25 mL), solid was dissolved in cold water (100 mL). Solid $NaNO_2$ (0.2 g; 2.5 mmol) was dissolved in H_2O (10 mL) was added to amine hydrochloride solution at 0-5 °C. Clear diazo solution was added to coupling solution slowly, pH of the solution was adjusted by drop wise addition of sodium acetate 1 % and HCl 0.5 % solution. Dye precipitated at pH 5-6 which were kept for 1-2 h, yellow color dye was filtered, washed with water and dried 60-80 °C under vacuum 81 %. Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(2-chloro-4-nitro phenyl) azo pyridine-3-carboxylate (4 g) crystallized from MeOH: CH_2Cl_2 1:1 m. p. 258 °C visible light absorption spectra λ_{max} 594 nm (log ε = 4.2); IR (cm^{-1}): ν_{max} 3597 (OH), 1578 (N=N), 1706 (C=O, ester) and 1646 (C=O, lact); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.25 (t, J = 7.1 Hz, 3H), 4.27 (q, J = 7.1 Hz, 2H), 7.29 (d, J = 6.5 Hz, 2H), 7.46 (m, 3H), 8.37 (dd, J = 9.4, 2.4 Hz, 1H), 8.46 (d, J = 2.4 Hz, 1H), 8.5 (d, J = 9.4 Hz, 1H), 14.5 (br s, 2 OH, 2H); EI MS *m/z* (%): 458 (7, M^+), 412 (23), 302 (4), 256 (38), 119 (57), 77 (100), HREI MS Calcd for $C_{20}H_{15}N_4O_7Cl$: C, 52.36; H, 3.30; N, 12.21 %. Found: C, 52.56; H, 3.60; N, 12.61 %.

Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(4-methoxy-phenyl) azo pyridine-3-carboxylate (4h)

The compound **3** (0.69 g, 2.5 mmol) was taken in ethanol (30 mL) and 1 % NaOH solution (10 mL) and water (100 mL) was added, the solution was stirred magnetically to obtain a clear solution. Diazonium chloride solution **2** was prepared by taking 4-methoxyphenyl aniline (0.307 g; 2.5 mmol) in concentrated HCl (25 mL), solid was dissolved in cold water (100 mL). Solid $NaNO_2$ (0.2 g; 2.5 mmol) was dissolved in H_2O (10 mL) was added to amine hydrochloride solution at 0-5 °C. Clear diazo solution was added to coupling solution slowly, pH of the solution was adjusted by drop wise addition of sodium acetate 1 % and HCl 0.5 % solution. Dye precipitated at pH 5-6 which were kept for 1-2 h, yellow color dye was filtered, washed with water and dried at 60-80 °C under vacuum 79 %. Ethyl-4, 6-dihydroxy-2-oxo-1-phenyl-5-(4-methoxyphenyl) azo pyridine-3-carboxylate (**4h**) crystallized from MeOH: CH_2Cl_2 1:1 m. p. 211 °C visible light absorption spectra λ_{max} 598 nm (log ε = 4.5); IR (cm^{-1}): ν_{max} 3449 (OH), 1559 (-N=N-), 1690 (C=O, ester) and 1628 (C=O, lact); ^{1}H NMR (300 MHz, DMSO-d_6): δ

Table-1: Color Fastness Properties of Dyes on Polyester Fabric.

Compound	Color hue on polyester fabric at 130 °C (1% shade)	Light Fastness	Washing Fastness	Sublimation Fastness	Rubbing Fastness		Perspiration Fastness	
					Dry	Wet	Acid	Alkaline
4a	Yellow	3-0	3-0	4-5	4-5	3-4	4-5	4-5
4b	Light Yellow	3-4	3-4	5-0	3-4	3-4	4-5	4-5
4c	Yellow	3-4	2-3	5-0	4-0	3-0	4-5	4-5
4d	Yellow	3-0	4-0	5-0	3-4	3-4	4-0	4-0
4e	Yellow	3-0	3-0	5-0	4-5	4-0	4-0	4-5
4f	Yellow	3-0	4-0	5-0	4-0	4-0	4-5	4-5
4g	Yellow	4-0	3-0	5-0	3-0	2-3	4-5	4-0
4h	Orange	3-0	3-0	5-0	4-5	3-4	4-5	4-5
4i	Light Yellow	4-0	3-0	5-0	4-0	3-4	4-5	4-0

= 1.25 (t, J = 7.1 Hz, 3H), 3.7 (s, OCH_3,3H), 4.27 (q, J = 7.1 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H), 7.27 (d, J = 6.9 Hz, 2H), 7.49 (m, 3H), 7.76 (d, J = 9.0 Hz, 2H), 14.53 (br s, 2 OH, 2H); EI MS *m/z* (%): 409, (9, M^+), 363 (73), 256 (2), 175 (3), 122 (100), 107 (33), 77 (33); HREI MS Calcd for $C_{21}H_{19}N_3O_6$: C, 61.61; H, 4.68; N, 10.26 %. Found: C, 61.66; H, 4.48; N, 10.56%.

Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5- (4-chloro-2-nitro phenyl) azo pyridine-3-carboxylate (4i)

The compound **3** (0.69 g, 2.5 mmol) was taken in ethanol (30 mL) and 1 % NaOH solution (10 mL) and water (100 mL) was added, the solution was stirred magnetically to obtain a clear solution. Diazonium chloride solution **2** was prepared by taking 4-cholro-2-nitro aniline (0.43 g; 2.5 mmol) in concentrated HCl (25 mL), solid was dissolved in cold water (100 mL). Solid $NaNO_2$ (0.2 g; 2.5 mmol) was dissolved in H_2O (10 mL) was added to amine hydrochloride solution at 0-5 °C. Clear diazo solution was added to coupling solution slowly, pH of the solution was adjusted by drop wise addition of sodium acetate 1 % and HCl 0.5 % solution. Dye precipitated at pH 5-6 which were kept for 1-2 h, yellow color dye was filtered, washed with water and at 60-80 °C under vacuum 76 %. Ethyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(4-chloro-2-nitro phenyl) azo pyridine-3-carboxylate (**4i**) crystallized from MeOH: CH_2Cl_2 1:1, m. p. 273 °C visible light absorption spectra λ_{max} 600 nm (log ε = 4.2); IR (cm^{-1}): ν_{max} 3448 (OH), 1590 (N=N), 1713 (C=O, ester) and 1647 (C=O, lact); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.25 (t, J = 7.4 Hz, 3H), 4.27 (q, J = 7.1 Hz, 2H), 7.29 (d, J = 6.0 Hz, 2H), 7.46 (m, 3H), 8.00 (dd, J = 9.2, 2.4, Hz, 1H), 8.27 (d, J = 2.4 Hz, 1H), 8.78 (d, J = 9.2 Hz, 1H), 15.28 (br s, 2 OH, 2H); EI MS m/z (%): 458 (11, M^+), 85 (100), 77 (76), 119 (51), 172 (15), 256 (50), 302 (12), 412 (24); HREI MS Calcd for $C_{20}H_{15}N_4O_7Cl$: C, 52.36; H, 3.30; N, 12.21 %. Found: C, 52.56; H, 3.60; N, 12.61 %.

Method of Application of Disperse Dyes (4a-4i) on Polyester Fabric

Dye solution was prepared (1 %), 1 % dye solution (5 mL), water (95 mL), non-ionic dispersing agent (0.6 to 1 g), dye carrier (0.6 to 1 g) were added and pH of the solution was adjusted at 5-6 by adding dilute acetic acid. Polyester fabric (5 g) was added to this solution and temperature of the dye bath was raised to 130 °C, kept the fabric in bath for 45 min. Fabric was washed with cold water, and then with soap solution (1 %) at 95 °C. Finally the fabric was again washed with cold water and dried at 60 °C.

Dyeing Properties of Dyes

The dyes **4a-4i** was applied on polyester fabric. These dyes give light yellow to orange hues with brighter and deeper shades and excellent levelness on the fabric. The dyeing showed very good washing, light, rubbing, sublimation and perspiration fastness properties, which indicated high quality penetration and excellent affinity of these dyes to the fabric. Dyeing properties of these disperse dyes are given in Table-1.

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