Synthesis of Methyl-4,6-Dihydroxy-2-Oxo-1-Phenyl-5-Aryl Azo Pyridine-3-Carboxylate and Their Derivatives, Part-II: New Disperse Dyes

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Summary: The reaction of methyl-4, 6-dihydroxy-2-oxo-1-phenyl pyridine-3-carboxylate (**3**) with different diazotized substituted aromatic amines (**2**) yielded compound, methyl-4, 6-dihydroxy-2-oxo-1-phenyl-5-aryl azo pyridine-3-carboxylate (**4**) showing visible light absorption between λ max 590-605 nm, characteristic of azo dyes. Aqueous solution of (**4**) having a non ionic dispersing agent and a dye carrier at pH 5-6 and temperature of 135°C and 75°C when applied to polyester and acetate fiber furnished orange to yellow color.

Introduction

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is usually used as an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber. Archaeological evidence shows that, particularly in India and the Middle East, dyeing has been carried out for over 5000 years. William Henry Perkin discovered the first man made organic dye, mauveine, in 1856. Many thousands of dyes have since been prepared and because of vastly improved properties imparted upon the dyed materials quickly replaced the traditional natural dyes.

The development of disperses dyes led to an upsurge. In new dye chemistry resulting in novel intermediates for the synthesis of disperse dyes used for dyeing polyester fiber. Disperse dye originally developed for the dyeing of cellulose acetate. They are substantially water insoluble. They can also be used to dye nylon, triacetate and acrylic fibers. The most important heterocycles are five or six member's rings and to a lesser extent oxygen is the most frequently encountered heteroatom. Only nitrogen containing compounds as pyrazolones, indoles, pyridines, thiazoles, thiophene are used as diazo components [1]. Pyridines itself has little importance as dye intermediate. Its 2,6-dihydroxy derivatives have achieved prominence in recent years as coupling component for azo disperse dyes particularly in yellow shade [2].

In our previous work [3] new disperse dyes, from substituted pyridines, most of the dyes posses antioxidant activity depending upon chromophoric and auxochrome groups are shown in Table-1 [3].

Results and Discussion

Pyridine based new disperse dyes were synthesized from mono substituted aryl amines as diazo component [3], disubstituted aryl amines are taken as the diazo component (chromophoric group). Coloring of power and shades are also studied by application on polyester fiber. Visible light absorption spectra are also studied. The synthetic route of these dyes is shown in scheme 1.

Color and Spectral Properties of Dyes

The visible absorptions are recorded in 95% methanol. All dyes (**4a-4j**), which have been synthesized, are yellow orange to yellow with absorption maxima between 595 to 605 nm. As we know the electromagnetic spectrum lying between about 400 and 750 nm [4-6] is the visible region. Light having wavelength near 400 nm is violet, while that having wavelength near 750 nm is red. Therefore all dyes appeared orange yellow to yellow. The values of the logarithm of molar extinction coefficient (log ε) of the dyes are in the range of 4.02-4.81, indicating their very good absorption intensity. The R"-group in compounds (**4a-4j**) have the substituent which are nitro, chloro, amino, acetyl

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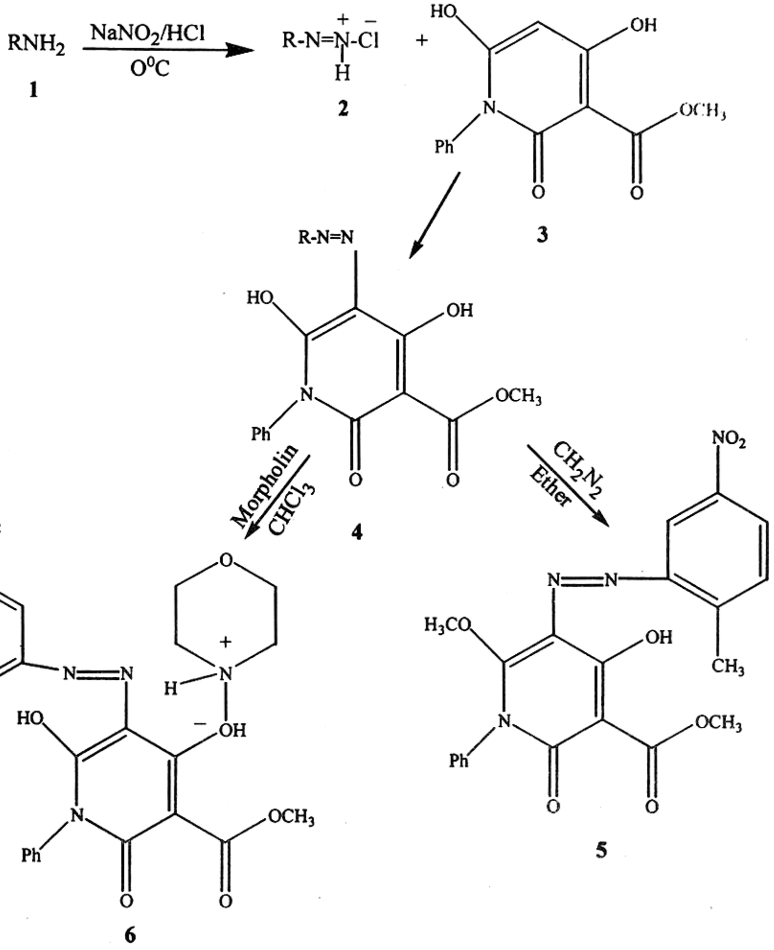

4a R = 5-Nitro-*o*-tolyl
4b R = 3-Nitro-*p*-tolyl
4c R = 2, 5-Dichloro phenyl
4d R = 3, 4-Dichloro phenyl
4e R = 2, 4-Dichloro phenyl
4f R = 2, 3-Dichloro phenyl
4g R = 4-Chloro-2-nitro phenyl
4h R = 2, 4-Dinitro phenyl
4i R = 4-Aminoacetyl phenyl
4j R = 4-Chloro-*o*-anisyl

Scheme 1

Table-1: Antioxidant Activity of Methyl-4, 6-Dihydroxy-2-Oxo-5-Aryl Azo Pyridine-3-Carboxylate 4

Compound	Dye sample, R (Aryl azo substituent)	Conc. mc	AA%
4a	5-Nitro-*o*-tolyl azo pyridine-3-carboxylate	200	33.56
4b	3-Nitro-*p*-tolyl azo pyridine-3-carboxylate	200	15.24
4c	2, 5-Dichloro phenyl azo pyridine -3- carboxylate	500	10.84
4d	3, 4-Dichloro phenyl azo pyridine-3-carboxylate	500	08.98
4e	2, 4-Dichloro phenyl azo pyridine-3-carboxilate	500	04.29
4f	2, 3-Dichloro phenyl azo pyridine-3-carboxylate	500	06.00
4g	4-Chloro-2-nitro phenyl azo pyridine-3-carboxylate	500	45.27
4h	2, 4-Dinitro phenyle azo pyridine-3-carboxylate	300	35.76

Table-2: Color Fastness Properties of Dyes on Acetate Fabric.

Compd	Color hue on acetate fabric at 75^{0}C	Light Fastness	Washing Fastness	Sublimation Fastness	Rubbing Fastness		Perspiration	
					Dry	Wet	Acid	Alkali
4c	Very light yellow with both (1% and 2%)	5	5	4	4	3	3	5
4d	Light yellow with both (1% and 2% dye)	5	5	4	4	3	3	5
4e	Light yellow (1% dye) Bright yellow (2% dye)	5	5	4	4	3	3	5
4f	Off white (1% dye) Light yellow (2% dye)	5	5	4	4	3	3	5
4g	Light yellow (1% dye)] Yellow (2% dye)	5	5	4	4	3	3	5
4h	Very light yellow (1% dye) Light yellow (2% dye)	5	5	4	4	3	3	5

Table-3: Color Fastness Properties of Dyes on Polyester Fabric

Compound	Color hue on polyester fabric at 130^{0}C	Light Fastness	Washing Fastness	Sublimation Fastness	Rubbing Fastness		Perspiration	
					Dry	Wet	Acid	Alkali
4c	Light yellow (1% dye) dark yellow (2% dye) with brightness	5	5	4	4	3	3	5
4d	Light yellow (1% dye) Dull	5	5	4	4	3	3	5
4e	Light yellow (1% dye) Light yellow (2% dye)	5	5	4	4	3	3	5
4f	Off white (1% dye) Very light yellow (2% dye)	5	5	4	4	3	3	5
4g	Off white (1% dye) Very light yellow (2% dye)	5	5	4	4	3	3	5
4h	Off white with both (1% dye and 2% dyes)	5	5	4	4	3	3	5

and methoxy, as these groups have electron-donating and electron-withdrawing properties and are situated in the phenyl ring in a suitable position affect the absorption characteristics of the dyes. There is a bathochromic shift (red shift) in the dye system.

Infrared spectra

The IR spectra of dyes **4a** to **4j** showed characteristic bands around 3400 (-OH stretching), 3100-2950 cm^{-1} these are due to aromatic stretching of the phenyl ring. A characteristic band at 1640-1550 cm^{-1} confirmed the presences of azo group (-N=N-) and amide moiety. A very strong band appeared at 1700 cm^{-1} is due to the C=O group.

Experimental

Melting points were taken on Gallenkamp melting point apparatus and are uncorrected. The IR spectra were measured on Jasco-A-30 spectrometer. Visible light spectra were determined in 95% methanol on spectromiczo Baush & Lomb. The ^{1}H-NMR were recorded in CDCl$_3$ at 500-MHz on brucker AM-300 spectrophotometer. Mass spectra were determined using finningan varian MAT-112 photometer. Microanalyses were carried out in microanalytical laboratory of PCSIR Complex, Lahore, Pakistan. Synthesis of methyl-4,6-diydroxy-2-oxo-1-phenyl-5-(5-nitro-*o*-tolyl) azo pyridine-3-carboxylate **4a**, was carried out according to method of Butt *et al.*, [7].

The compound **3**, 2.61 g (0.01 mol) was taken in 5% sodium hydroxide solution (100 ml) and temperature was kept at 0°C. Diazonium chloride solution **2** was prepared by taking 5-nitro-*o*-toluidine (1.52 g, 0.01 mol) in 5*N* HCl (5 ml), to this solution sodium nitrite (0.69 g, 0.01 mol) in 10 ml H$_2$O was added at 0-5°C, excess of sodium nitrite was checked by starch iodide paper.

To the coupling solution **3**, diazo solution was added drop wise at 0-5°C and pH of the solution was adjusted at 7-8 by addition of sodium acetate. The mixture was stirred for I h at 0-5°C. Yellow colored solid was separated out. The solid filtered and washed with water than dried, yield 75%.

Methyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(5-nitro-o-tolyl) azo pyridine-3-carboxylate (4a)

Crystallized from methanol: chloroform mixture 1:1; m.p. 256°C (d); Visible light absorption spectra at λ_{max} 595 nm (log ε = 4.28); IR (Jasco/cm^{-1}) :ν_{max} 3480 (OH), 1700 (C=O), 1640 (N=N), 1560 and 1480 (aromatic); ^{1}H-NMR ($CDCl_3$+D_2O): δH 2.44 (3H, s, CH_3), 3.96 (3H, s, OCH_3), 4.70 (2H, br.s, 2 OH), 7.18 (2H, d, *J* 7.0, 1.5), 7.43 (2H, td, *J* 7.0, 1.5), 7.46 (1H, dd, *J* 2.6, 1.5), 8.06 (1H, d, *J* 6.5, 1.5), 8.18 (1H, d, *J*8.5, 3.2). HREIMS *m/z* (rel. int.) = 424.1708 [M$^+$, $C_{20}H_{16}N_4O_7$ requires 424.3731, 20%] 365 (84), 409 (73), 378 (81), 347 (100), 288 (47), 260 (100). (Anal. calcd. for $C_{20}H_{16}N_4O_7$: C, 56.61; H, 3.80; N, 13.20%. Found: C, 56.40; H, 3.55; N, 13.02%).

Methyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(3-nitro-p-tolyl) azo pyridine-3-carboxylate (4b)

The compound **3** (2.61 g, 0.01 mol) was taken in 5% NaOH solution (100 ml), and kept at 0°C. 3-nitro-*p*-toluidine (1.52 g, 0.01 mol) was taken in 5*N* HCl solution (5 ml). Cooled to 0°C, sodium nitrite (0.69 g, 0.01 mol) was taken in 10 ml H_2O and cooled to 0°C. To the 3-nitro-*p*-toluidine solution in HCl at 0-5°C sodium nitrite solution was added. Cooled to 0-5°C, excess of $NaNO_2$ was checked by starch iodide paper. The diazo solution was added to coupling solution at 0°C drops wise with cooling and stirring. Yellow colored compound was separated. The reaction mixture stirred for 1 h. pH of the reaction mixture was adjusted at 7-8 by adding sodium acetate. Yellow colored solid was filtered, washed with water, dried and weighed, yield 70%.

Crystallize from methanol: chloroform mixture (1:1); m.p. 258°C (d). Visible light absorption spectra λ_{max} 605 (log ε = 4.30); IR (Jasco/cm^{-1}): ν_{max} 3600 (OH), 3010 (C=C), 1700 (C=O), 1630 (N=N), 1560 (N=O), 1520 (aromatic), 1441(C-N); ^{1}H-NMR ($CDCl_3$+D_2O): δH 2.44 (3H, s, CH_3), 2.44 (3H, s, OCH_3), 4.68 (2H, br.s, 2OH), 7.20 (2H, dd, *J* 7.0, 2.0), 7.37 (1H, d, $J_{5',6'}$ 8.5), 7.47 (1H, td, *J* 7.0, 2.0), 7.50 (2H, td, *J* 7.0, 1.5), 7.98 (1H, dd, $J_{6',5'}$ 8.5, $J_{6',2'}$ 2.0), 8.71 (1H, d, $J_{2',6'}$ 2.0); HREIMS m/z (rel. int.) = 424.1698 [M$^+$, $C_{20}H_{16}N_4O_7$ requires 424.3731, 73%] 409 (68), 378 (85), 365 (100), 347 (100), 288 (41), 260 (100), 164 (89), 136 (36), 77 (58). (Anal. calcd. for $C_{20}H_{16}N_4O_7$; C, 56.61; H, 3.80; N, 13.20%. Found: C, 56.36; H, 3.60; N, 13.01%).

Methyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(2,5 dichlorophenyl) azo pyridine-3-carboxylate (4c)

Compound **3** (2.61 g, 0.01 ml) was taken in 5% sodium hydroxide solution (100 ml), cooled to 0°C. 2, 5-dichloroaniline (1.62g, 0.01 ml) was taken in 5ml, 5*N* HCl. $NaNO_2$ (0.69g, 0.01 ml) in 10 ml water was added drop wise and solution cooled to 0-5°C. After addition the solution was tested by starch iodide paper for excess of $NaNO_2$. This clear diazotized solution was added drop wise to coupling solution and stirred magnetically for 1h. Yellow colored solid was separated out; filtered, washed with water and dried, yield 60%. Crystallized from MeOH: $CHCl_3$ (1:1); m.p. 188°C (d). Visible light absorption spectra λ_{max} 595 (log ε = 4.67). IR (Jasco/cm^{-1}): ν_{max} 3400 (OH), 3100 (C=C), 1700 (C=O), 1640 (C=O, amide), 1569 (N=N), 1515 (aromatic), 1260 (C-O), 1090 (aryl chloride). ^{1}H-NMR (CD_3OD) δ H: 3.30 (3H, s, OCH_3), 4.80 (2H, br.s, 2 OH), 7.22 (2H, dd, *J* 8.7), 7.44 (2H, d, *J* 8.7), 7.48 (2H, d, *J* 7.3), 7.50 (1H, d, *J* 8.7), 8.03 (1H, d, *J* 2.0); HREIMS *m/z* (rel. int.) = 437.2846 [M$^+$+4, $C_{19}H_{13}N_3O_5Cl_2$ requries 437.2644, 2%], 435.2908 [M$^+$+2, $C_{19}H_{13}N_3O_5Cl_2$ requries 435.2674, 5%], 433.4680 [M$^+$, $C_{19}H_{13}N_3O_5Cl_2$ requires 433.2704, 7%] 401 (39), 375 (5), 340 (5), 288 (10), 256 (49), 240 (18), 225 (26), 212 (8), 161 (48), 146 (9), 127 (41), 77 (100). (Anal. calcd. for $C_{19}H_{13}N_3O_5Cl_2$: C, 52.55; H, 3.02; N, 9.68%. Found: C, 52.30; H, 3.20; N, 9.46%).

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

Compound **3** (2.61 g, 0.01 mol) was taken in 5% sodium hydroxide solution (100 ml), cooled to 0°C. 3,4-dichloroaniline (1.62 g, 0.01 mol) was taken in 5*N* HCl (5ml), cooled to 0°C. Sodium nitrite (0.69 g 0.01 mol) was taken in 10 ml H_2O, and added to cooled 3,4-dichloroaniline in HCl, after addition starch iodide solution was tested for excess of sodium nitrite. Cooled to 0-5°C, this clear solution was added to the coupling solution with stirring at 0-5°C, pH of the solution was adjusted at 7-8 by the addition of sodium acetate. The solution was stirred for 1 h at 0-5°C. Yellow colored solid separated, filtered, washed with water and dried. Yield 62%, crystallized from methanol: chloroform (1:1); m.p. 210°C (d). Visible light absorption spectra λ_{max} 605 (log ε = 4.67). IR (Jasco/cm^{-1}): ν_{max} 3400 (OH), 3100 (C=C), 2990 (C-H), 1700 (C=O), 1590 (N=N), 1520 and 1460 (aromatic), 1098 (aryl chloride); ^{1}H-NMR (CD_3OD) δH: 3.29 (3H, s, OCH_3), 4.83 (2H, br.s, 2 OH), 7.22 (2H, d, *J* 7.2), 7.43 (2H, d, *J* 7.2), 7.48 (1H, d, *J* 7.2), 7.51 (1H, dd, $J_{6',5'}$ 8.8, $J_{6',2'}$ 2.3), 7.57 (1H ,d, $J_{5',6'}$ 8.8), 7.85 (1H, d, $J_{2',6'}$ 2.3); HREIMS *m/z* (rel. int.) =437.1987 [M$^+$+4, $C_{19}H_{13}N_3O_5Cl_2$ requries 437.2644, 3%], 435.2189 [M$^+$+2, $C_{19}H_{13}N_3O_5Cl_2$ requries

435.2674, 6.5%], 433.3023 [M$^+$, $C_{19}H_{13}N_3O_5Cl_2$ requires 433.2704, 10%] 401 (41), 375 (8), 340 (4), 288 (12). 256 (45), 240 (19), 225 (30), 212 (7), 161 (56), 146 (15), 127 (44), 77 (100). (Anal. calcd. for $C_{19}H_{13}N_3O_5Cl_2$: C, 52.55; H, 3.02; N, 9.68%. Found: C, 52. 25; H, 3.15; N, 9.50%).

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

Compound **3** (2.61g, 0.01 mol) was taken in 5% NaOH solution (100 ml), the solution was cooled to 0°C. 2, 4-dichloroaniline (1.62 g, 0.01 mol) was taken in 10 ml H_2O and added to the amine solution at 0-5°C. Excess of sodium nitrite was checked by starch iodide paper. To the coupling solution diazo solution was added drop wise at 0-5°C stirring continued for 1h, pH of the solution was kept at 7-8 by the addition of sodium acetate. Yellow colored solid was separated out, stirring continued for 1h at 0-5°C. Solid filtered, washed with water, dried, yield, 65%. It was crystallized from methanol: chloroform (1:1); m.p. 225°C (d). Visible light absorption spectra λ_{max} 600 (log ε = 481); IR (Jasco/cm^{-1}): ν_{max} 3400 (OH), 3100 (C=O), 1090 (aryl chloride); ^{1}H-NMR (CD_3OD + $CDCl_3$) δH: 3.30 (3H, s, OCH_3), 4.81 (2H, br. s, 2 OH), 7.22 (2H, d, J 9.0), 7.44 (2H, d, J 9.0), 7.48 (1H ,d, $J_{5',6'}$ 11.0), 7.49 (1H, d, J 9.0), 7.54 (1H, d, $J_{3',5'}$ 2.7), 7.99 (1H, d, $J_{6',5'}$ 11.0); HREIMS *m/z* (rel. int.) = 437.2108 [M$^+$+4, $C_{19}H_{13}N_3O_5Cl_2$ requries 437.2644, 2.8%], 435.1994 [M$^+$+2, $C_{19}H_{13}N_3O_5Cl_2$ requries 435.2674, 7%], 433.2085 [M$^+$, $C_{19}H_{13}N_3O_5Cl_2$ requires 433.2704, 10%] 401 (39), 375 (6), 340 (8), 288 (15), 256 (51), 240 (14), 225 (24), 212 (10), 161 (56), 146 (7), 127 (44), 77 (100). (Anal. calcd. for $C_{19}H_{13}N_3O_5Cl_2$: C, 52.55; H, 3.02; N, 9.68%. Found: C, 52. 30; H, 3.00; N, 9.50%).

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

The compound **3** (2.61 g, 0.01 mol) was taken in 5% NaOH solution (100 ml). The solution was cooled to 0°C. 2,3-dichloroaniline (1.62g, 0.01 mol) was taken in 5*N* HCl (5 ml), the solution was cooled to 0°C. Sodium nitrite (0.69 g, 0.01 mol) was taken in 10 ml H_2O. The sodium nitrite solution was added to amine solution, the temperature was kept at 0-5°C. The diazo solution was added with stirring at 0-5°C to coupling solution. Stirring continued for 1 h, yellow colored solid was separated out, filtered, washed with water and dried. Yield 58%, crystallized from MeOH: $CHCl_3$ (1:1); m.p. 222°C (d). Visible light absorption spectra λ_{max} 600 (log ε = 4.23); IR (Jasco/cm^{-1}): ν_{max} 3400 (OH), 3100 (C=C), 2990 (C-H), 1710 (C=O), 1640 (C=O, amide), 1580 (N=N), 1520 and 1440 (aromatic), 1090 (aryl chloride); ^{1}H-NMR (CD_3OD+$CDCl_3$) δH: 3.30 (3H, s, OCH_3), 4.80 (2H, br. s, 2 OH), 7.23 (2H, dd, J 9.0), 7.41 (1H, dd, $J_{4',5'}$ 6.7, $J_{4',6'}$ 1.7), 7.44 (2H, d, J 9.0), 7.45 (1H, d, $J_{6',5'}$ 5.2 , $J_{6',4'}$ 1.7), 7.49 (1H, d, J 9.0, 1.9), 7.98 (1H, dd, $J_{5',4'}$ 6.7, $J_{5',6'}$ 5.2); HREIMS *m/z* (rel. int.) = 437.2185 [M$^+$+4, $C_{19}H_{13}N_3O_5Cl_2$ requries 437.2644, 5%], 435.2241 [M$^+$+2, $C_{19}H_{13}N_3O_5Cl_2$ requries 435.2674, 9%], 433.4267 [M$^+$, $C_{19}H_{13}N_3O_5Cl_2$ requires 433.2704, 15%] 401 (44), 375 (6), 340 (10), 288 (13), 256 (48), 240 (18), 225 (29), 212 (11), 161 (56), 146 (9), 127 (46), 77 (100). (Anal. calcd. for $C_{19}H_{13}N_3O_5Cl_2$: C, 52.55; H, 3.02; N, 9.68%. Found: C, 52.30; H, 3.10; N, 9.40%).

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

The compound **3** (2.61 g, 0.01 mol) was taken in 5% NaOH solution (100 ml) and was cooled to 0°C. 4-chloro-2-nitroaniline (1.72 g, 0.01 mol) was taken in 5*N* HCl solution (5ml) and cooled to 0°C. Sodium nitrite (0.69 g, 0.01 mol) in 10 ml H_2O was taken and added to the amine solution at 0-5°C. Excess of sodium nitrite was checked with starch iodide paper. The diazo solution was added to coupling solution at 0-5°C with continuous stirring. Stirring continued for 1h. Yellow colored solid was separated out, filtered and washed with water and dried. Yield 60%, crystallized from MeOH: $CHCl_3$ (1:1); m.p. 212°C (d); Visible light absorption spectra λ_{max} 605 (log ε =4.09); IR (Jasco/cm^{-1}): ν_{max} 3410 (OH), 3100 (C=C), 2980 (C-H), 1700 (C=O), 1640 (C=O, amide), 1580 (N=N), 1500 (N=O); ^{1}H-NMR (CD_3OD) δH: 3.29 (3H, s, OCH_3), 4.84 (2H, br. s, 2 OH), 7.18 (2H, d, J 9.0), 7.44 (2H, d, J 9.0), 7.49 (1H, d, J 9.0), 7.95 (1H, dd, $J_{5',6'}$ 8.6, $J_{5',3'}$ 2.1), 8.27 (1H, d, $J_{3',5'}$ 2.1), 8.36 (1H, d, $J_{6',5'}$ 8.6); HREIMS *m/z* (rel. int.) = 446.3101 [M$^+$+2, $C_{19}H_{13}N_4O_7Cl$ requires 446.3040, 4%], 444.3072 [M$^+$, $C_{19}H_{13}N_4O_7Cl$ requires 444.3070, 11%] 409 (5), 398 (8), 385 (32), 367 (80), 287.5 (41), 259 (33), 77 (100). (Anal. calcd. for $C_{19}H_{13}N_4O_7Cl$: C, 51.31; H, 2.95; N, 12.60%. Found: C, 51.15; H, 2.87; N, 12.45%).

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

The compound **3** (2.61 g, 0.01 mol) was taken in 5% NaOH (100 ml) and cooled to 0°C. 2, 4-dinitroaniline (1.83 g, 0.01 mol) was taken in 5*N* HCl

(5 ml) and cooled to 0°C. Sodium nitrite (0.69 g, 0.01 mol) in 10 ml H_2O was added to the cold amine solution at 0-5°C. Excess of sodium nitrite was tested by starch iodide paper. To the coupling solution, diazo solution was added at 0-5°C with stirring, pH of the solution was adjusted at 7-8 by the addition of sodium acetate. Yellow colored solid was separated out, filtered, washed with water and dried, yield 56%, recrystallized from MeOH :$CHCl_3$ (1:1); m.p. 218°C (d); Visible light absorption spectra λ_{max} 600 (log ε = 4.09); IR (Jasco/cm^{-1}): ν_{max} 3478 (OH), 3110 (C=C), 1705 (C=O), 1640 (C=O, amide), 1580 (N=N), 1480 (N=O), 1340 (C-O); ^{1}H-NMR ($CDCl_3$ + CD_3OD) δH: 3.28 (3H, s, OCH_3), 4.83 (2H, br. s, 2 OH), 7.18 (2H, d, *J* 8.2), 7.66 (2H, d, *J* 8.2), 7.79 (1H, d, *J* 8.2), 7.95 (1H, d, $J_{6',5'}$ 8.6), 8.28 (1H, dd, $J_{5',6'}$ 8.6, $J_{5',3'}$ 2.0), 8.34 (1H, d, $J_{3',5'}$ 2.0); HREIMS *m/z* (rel. int.) = 455.4568 [M^+, $C_{19}H_{13}N_5O_9$ requires 455.3436, 10%] 438 (5), 424 (14), 409 (70), 396 (41), 378 (80), 363 (35), 288 (9), 260 (78), 183 (8), 195 (10), 167 (20), 77 (100). (Anal. calcd. for $C_{19}H_{13}N_5O_9$: C, 50.12; H, 2.88; N, 15.38%. Found: C, 50.05; H, 2.82; N, 15.01%.

Methyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(4-amino acetyl phenyl) azo pyridine-3-carboxylate (4i)

The compound **3** (2.61 g, 0.01 mol) was taken in 5% NaOH solution (100 ml). 4-amino acetanilide (1.50 g. 0.01 mol) was taken in 5*N* HCl solution (5 ml) and cooled to 0°C. Sodium nitrite (0.69 g, 0.01 mol) in 10 ml H_2O was added to amino-acetanilide solution at 0-5°C, excess of sodium nitrite was checked by starch iodide paper. To the coupling solution, diazotized solution was added drop wise with stirring at 0-5°C; pH was adjusted by sodium acetate to 7-8. Stirring continued for 1h. Yellow colored compound was separated out, filtered, washed with water, dried and weighed. Yield 65%, recrystallized from MeOH: $CHCl_3$ (1:1); m.p.258°C (d); Visible light absorption spectra at λ_{max} 600 (log ε = 4.09); IR (Jasco/cm^{-1}): ν_{max} 3410 (OH, NH), 3105 (C=O), 1700 (C=O), 1640 (C=O, amide), 1570 (N=N), 1100 (C-N); ^{1}H-NMR (CD_3OD) δH: 3.29 (3H, s, $COCH_3$), 3.30 (3H, s, OCH_3), 4.79 (2H, br. s, 2 OH), 7.21 (2H, d, *J* 8.8), 7.44 (2H, d, *J* 8.8), 7.47 (1H, d, *J* 8.8), 7.47 (2H, d, $J_{6',5'}$ 9.9, $J_{5',6'}$ 9.9), 7.58 (2H, d, $J_{3',2'}$ 9.9, $J_{2',3'}$ 9.9); HREIMS *m/z* (rel. int.) = 422.4156 [M^+, $C_{21}H_{18}N_4O_6$ requires 422.4008, 12%] 407 (5), 391 (9), 379 (12), 364 (51), 363 (14), 345 (22), 288 (71), 260 (63), 162 (15) , 134 (19) , 77 (100), 58 (6). (Anal. calcd. for $C_{21}H_{18}N_4O_6$: C, 59.71; H, 4.29; N, 13.26%. Found: C, 59.65; H, 4.05; N, 13.10%).

Methyl-4,6-dihydroxy-2-oxo-1-phenyl-5-(4-chloro-o-anisyl) azo pyridine-3-carboxylate (4j)

The compound **3** (2.61 g, 0.01 mol) was taken in 5% NaOH solution (100 ml), cooled to 0°C. 4-chloro-*o*-anisidine (1.59 g, 0.01 mol) was taken in 5*N*-HCl (5 ml), cooled to 0°C. Sodium nitrite (0.69 g 0.01 mol) was taken in 10 ml H_2O. Sodium nitrite solution was added to amine solution at 0-5°C. Excess of sodium nitrite was checked by starch iodide paper. Diazotized solution was added to the coupling solution with stirring and temperature was kept at 0-5°C, pH of the reaction mixture was kept at 7-8 by adding sodium acetate and was stirred for 1h. Yellow colored solid was separated out, filtered, washed with water and dried. Yield 60%, crystallized from MeOH: $CHCl_3$ (1:1); m.p. 256°C (d); Visible light absorption spectra λ_{max} 590 (log ε = 4.02); IR (Jasco/cm^{-1}): ν_{max} 3470 (OH), 3110 (C=C), 1700 (C=O), 1653 (C=O, amide), 1580 (N=N), 1109 (aryl chloride); ^{1}H-NMR (CD_3OD) δH: 3.28 (3H, s, OCH_3), 3.30 (3H, s, OCH_3), 4.83 (2H, br. s, 2 OH), 6.75 (1H, dd, $J_{5',6'}$ 8.5, $J_{5',3'}$ 2.1), 6.78 (1H, d, $J_{3',5'}$ 2.1), 7.05 (1H, d, $J_{6',5'}$ 8.5), 7.21 (2H, d, *J* 8.0), 7.45 (2H, d, *J* 8.0), 7.48 (1H, d, *J* 8.0); HREIMS m/z (rel. int.) = 431.3105 [M^++2, $C_{20}H_{16}N_3O_6Cl$ requires 431.3329, 8%] 429.3498 [M^+, $C_{20}H_{16}N_3O_6Cl$ requires 429.3359, 23%] 413 (10), 399 (18), 393 (5), 370 (30), 352 (71), 288 (59), 260 (44), 169.5(49), 141.5 (33), 77 (100). (Anal. calcd. for $C_{20}H_{16}N_3O_6Cl$: C, 55.89; H, 3.75; N, 9.77%. Found: C, 55.65; H, 3.55; N, 9.51%).

General Procedure for the Methylation of Compound 4

Compound (**4a**) 2.12 g, 0.01 mol was dissolved in 100 ml chloroform, the temperature of the solution was kept at 0°C. A freshly prepared solution of diazomethane in ether was added till the yellow color of ether was persistent. The reaction mixture was kept overnight at 0°C. Ether was removed under vacuum and the solid obtained was triturated with ether, filtered. Solid was separated out (1.5g). Crystallized from methanol: chloroform (1:1) gave compound **5**; m.p. 245°C (d), (Scheme 1). (Anal. calcd. for $C_{21}H_{18}N_4O_7$, C, 57.53; H, 4.14; N, 12.78%. Found: C, 57.50; H, 4.10; N, 12.70%).

Morpholine Salt of 4, Compound 6

To the compound **4a**, (2.12 g, 0.05 mol) morpholine in 50 ml chloroform was added. The mixture was refluxed under anhydrous condition for

30 min and solvent was removed under vacuum. Crystalline solid was obtained by addition of dry ether, filtered and gave solid (2.0 g). Crystallized from methanol yielded compound (**6**); m.p. 185°C (d). (Anal. calcd. for $C_{24}H_{25}N_5O_8$, C, 56.33; H, 4.92; N, 13.74%. Found: C, 56.37; H, 4.72; N, 13.80%).

Method of Application of Disperse Dyes (4a-4j) on Polyester Fiber

1% dye solution was prepared in 100 ml water containing 0.6 to 1g non ionic dispersing agent, 0.6 to 1 g dye carrier was added and pH of the solution was adjusted at 5-6 by dilute acetic acid. 5 g polyester fabric was added to this solution and temperature of the dye bath was raised to 130°C, kept the fabric in bath for 1h. Fabric was washed with cold water, then with 1% soap solution at 95°C. Finally the fabric was again washed with cold water and dried at 60°C.

Dyeing Properties of Dyes

The dyes **4c** to **4h** were applied at 1% and 2% on polyester fabrics at 130°C and on acetate fabrics at 75°C. Their dyeing properties are given in Table-2 and 3. These dyes give light yellow to bright yellow hues with brighter and deeper shades and excellent levelness on the fabrics. The dyeing showed very good washing, rubbing perspiration and sublimation fastness properties. The degree of levelness and brightness were excellent after washing indicated high quality penetration and excellent affinity of these dyes to the fabric.

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