

Synthesis and application of new mordent and disperse azo dyes based on 2,4-dihydroxybenzophenone

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Abstract: Novel mordent and disperse azo dyes were prepared by the coupling of various diazo solutions of aromatic amines with 2,4-dihydroxybenzophenone. The resultant dyes were characterized by elemental analyses as well as IR and NMR spectral studies. The UV-visible spectral data have also been discussed in terms of structural property relationship. The dyeing assessment of all the dyes was evaluated on wool and polyester textile fibers. The dyeing of chrome treated (*i.e.*, chrome mordented) wool and polyesters was also monitored. The results show that a better hue was obtained on mordented fibers. The results of the anti-bacterial properties of the chrome dyes revealed that the toxicity of these dyes against bacteria is fairly good.

Keywords: disperse dye, mordent dye, UV absorber, dyeing, antimicrobial activity.

INTRODUCTION

In the field of azo dyes, phenols and naphthols play major roles for most of the commercial dyes.^{1–6} Most of the dyes are marketed in the form of azo disperse, azo-vat, azo-acid dyes, *etc.* All have the naphthols moiety bearing hydroxyl group(s) as an auxochrome group. One such compound is 2,4-dihydroxybenzophenone, bearing two hydroxy (as auxochrome) groups and a keto (chromophore) group. This compound has wide applications as a polymer additive.^{7,8} It is an excellent UV absorber, which prevents the photodegradation of most vinyl polymers.^{9–11} Azo dye formation based on this simple compound is an area which has not been developed, except in a few patents.^{12–15} The formation of dyes based on this compound may yield dyes with good hue properties. Hence, it was thought to be of interest to explore the field of azo dyes based on 2,4-dihydroxybenzophenone. The present communication comprises studies of azo dyes based on 2,4-dihydroxybenzophenone.

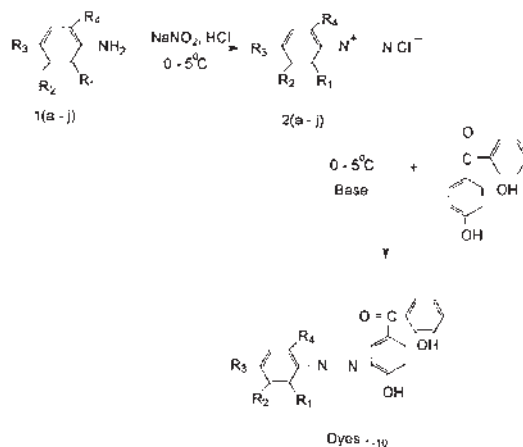
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EXPERIMENTAL

All the employed chemicals were of commercial grade and were further purified by crystallization. Melting points were determined by the open capillary method and are uncorrected. The visible absorption spectra were measured in dimethylformamide (DMF) on a Carl Zeiss UV/VIS Specord spectrometer; elemental analyses were carried out on Perkin-Elmer CHNS/O Analyzer 2400, Series II instrument; NMR spectra were recorded on a Hitachi R-1500 instrument. TLC (Thin layer chromatography) was run on a pretreated silica gel aluminum sheet using the methanol–water–acetic acid (12:3:7) solvent system. A spot color was visualized in a UV chamber. The equipment used for dyeing was a HTHP (High Temperature High Pressure) dyeing machine (model-LL).

Preparation of the azo disperse dyes

Diazotization. Diazotization of various aromatic amines (**1a-j**) was carried out by a method reported in the literature (Scheme 1).¹⁶



Dyes no	R ₁	R ₂	R ₃	R ₄	Amines 1(a-j)
D ₁	NO ₂	H	H	H	2-Nitroaniline
D ₂	H	H	NO ₂	H	4-Nitroaniline
D ₃	H	NO ₂	H	H	3-Nitroaniline
D ₄	Cl	H	NO ₂	Cl	2,6-Dichloro-4-nitroaniline
D ₅	CH ₃	H	CH ₃	H	2,4-Dimethylaniline
D ₆	H	Cl	H	H	3-Chloroaniline
D ₇	H	H	Cl	H	4-Chloroaniline
D ₈	H	H	OH	H	4-Hydroxyaniline
D ₉	H	H	CH ₃	H	4-Methylaniline
D ₁₀	CH ₃	H	H	H	2-Methylaniline

Scheme 1. Synthesis of 2,4-dihydroxybenzophenone based dyes (**D₁₋₁₀**).

Coupling procedure. The coupling of the above-mentioned diazotized aromatic amines was carried out in a similar manner. The general procedure adopted is given below.

2,4-Dihydroxybenzophenone (2.64×10^{-3} kg, 0.02 mol) was dissolved in 1.6×10^{-5} m³ sodium hydroxide (0.02 M) solution. The clear solution was cooled in an ice-bath and the diazonium solu-

tion of amine was added dropwise over 30 min with vigorous stirring. The pH was maintained between 7.5 and 8 by the simultaneous addition of 10 % w/v sodium carbonate solution. Stirring was continued for a further 2 h, whereby the temperature was allowed to rise to ambient. The dye was then filtered off, washed with warm water and with cold water until it was acid free and then dried at 50 °C in an oven. The dyes were reprecipitated from DMF and designated as dye **D₁₋₁₀**.

The purity of the dyes was checked by TLC using the solvent system methanol–water–acetic acid (12:3:7). The melting points of the purified dyes were measured in an open capillary tube. The melting points are uncorrected. The visible absorption spectroscopic properties of the dyes were recorded in DMF solution.

Disperse dyeing method

The dyeing of polyester fiber in the laboratory is convenient at 363.15–408.15 K and at high pressure (165.6 kPa – 207 kPa). A model glycerin-bath high-temperature beaker and HTHP-LL dyeing machine was used. For this purpose, a paste of finely powdered dye (5×10^{-5} kg) was prepared with the dispersing agent dodamol (9×10^{-5} kg), the wetting agent Tween-80 (5×10^{-6} kg) and water (1×10^{-6} m³) in a ball mill. To this paste, water (9.9×10^{-5} m³) was added under stirring and the pH was adjusted to 4.5–5 using acetic acid. The dye suspension (1×10^{-4} m³) was added to a beaker provided with a lid and a screw cap. Before closing the lid and lightening the metal cap over the beaker a wetted pattern of polyester was rolled into the beaker and then the lid was closed and the metal cap tightened. The beaker was then placed vertically on the rotatory carrier inside the tank and the clamp plate was firmly tightened. The rotatory carrier was then allowed to rotate in the glycerin-bath and the temperature was raised to 363.15 K at a rate of 2 K/min. The dyeing was continued for 1 h under pressure. After cooling for 1 h, the beaker was removed from the bath and washed with distilled water. The dyed pattern was thoroughly washed with hot water at 323.15 K and then with cold water and dried at room temperature.

Mordent dyeing method

The dye pattern of wool obtained as mentioned above was treated with potassium dichromate solution equal to half of the weight of the dye and again rolled into the beaker. The beaker was once more placed vertically on the rotatory carrier inside the tank and the dyeing was continued for 1 h under pressure. After cooling for 1 h the beaker was removed from the bath and washed with distilled water. The dyed pattern was thoroughly washed with warm water, then with cold water and air dried at room temperature.

Fastness property

The fastness to light, sublimation and perspiration of the dye pattern was assessed according to British standard 1006-1978 and the wash fastness test according to Indian standard (IS) 765–1979. The rubbing fastness was tested using a Crock meter (Atlas) AATCC-1961.

Determination of the percentage exhaustion and fixation

The percentages were determined according to a known method.¹⁷

RESULTS AND DISCUSSION

Physical properties of dyes

All the dyes were obtained as amorphous powders ranging in color from yellow to reddish brown. The TLC results showed that only a single spot was observed for each dye.

Characteristic data of dyes

1-[2,4-Dihydroxy-5-(2-nitrophenylazo)phenyl]-1-phenylmethanone (**D₁**). Yield: 78 %, m.p.: 232–233 °C, R_f value: 0.84. Calculated for C₁₉H₁₃O₅N₃: m.wt.: 363;

C, 62.80 %; H, 3.58 %; N, 11.57 %. Found: C, 62.50 %; H, 3.38 %; N, 11.31 %. IR cm^{-1} : 3460 (–OH), 3077 (=CH, aromatic), 1630 (C=O, diaryl), 1525 (N=N), 1484 (C=C, aromatic), 1338 (C–N), 1123 (C–O), 737, 586, 480. $^1\text{H-NMR}$: δ/ppm 7.2–7.4 (Ar-H, *m*), 5.8 (Ar-OH, *s*).

1-[2,4-Dihydroxy-5-(4-nitrophenylazo)phenyl]-1-phenylmethanone (**D**₂). Yield: 79 %, m.p.: 215–216 °C, R_f value: 0.87. Calculated for $\text{C}_{19}\text{H}_{13}\text{O}_5\text{N}_3$: m.wt.: 363; C, 62.80 %; H, 3.58 %; N, 11.57 %. Found: C, 62.40 %; H, 3.28 %; N, 11.29 %. IR cm^{-1} : 3453 (–OH), 3087 (=CH, aromatic), 1628 (C=O, diaryl), 1528 (N=N), 1490 (C=C, aromatic), 1348 (C–N), 1100 (C–O), 740, 568, 479. $^1\text{H-NMR}$: δ/ppm 7.2–7.3 (Ar-H, *m*), 6.0 (Ar-OH, *s*).

1-[2,4-Dihydroxy-5-(3-nitrophenylazo)phenyl]-1-phenylmethanone (**D**₃). Yield: 79 %, m.p.: 215–216 °C, R_f value: 0.79. Calculated for $\text{C}_{19}\text{H}_{13}\text{O}_5\text{N}_3$: m.wt.: 363; C, 62.80 %; H, 3.58 %; N, 11.57 %. Found: C, 62.44 %; H, 3.28 %, N, 11.32 %. IR cm^{-1} : 3480 (–OH), 3072 (=CH, aromatic), 1631 (C=O, diaryl), 1540 (N=N), 1480 (C=C, aromatic), 1339 (C–N), 1104 (C–O), 738, 560, 470. $^1\text{H-NMR}$: δ/ppm 7.2–7.4 (Ar-H, *m*), 5.8 (Ar-OH, *s*).

1-[5-(2,6-Dichloro-4-nitrophenylazo)-2,4-dihydroxyphenyl]-1-phenylmethanone (**D**₄) Yield: 77 %, m.p.: 258–259 °C, R_f value: 0.82. Calculated for $\text{C}_{19}\text{H}_{11}\text{O}_5\text{N}_2\text{Cl}_2$: m.wt.: 418; C, 54.54 %; H, 2.63 %; N, 6.69 %. Found: C, 54.14 %; H, 2.33 %; N, 6.32 %. IR cm^{-1} : 3636 (–OH), 3080 (=CH, aromatic), 1658 (C=O, diaryl), 1531 (N=N), 1478 (C=C, aromatic), 1343 (C–N, C–O), 780, 741, 584, 489. $^1\text{H-NMR}$: δ/ppm 7.2–7.3 (Ar-H, *m*), 6.18 (Ar-OH, *s*).

1-[5-(2,4-Dimethylphenylazo)-2,4-dihydroxyphenyl]-1-phenylmethanone (**D**₅). Yield: 83 %, m.p.: 205–206 °C, R_f value: 0.88, Calculated for $\text{C}_{21}\text{H}_{18}\text{O}_3\text{N}_2$: m.wt.: 346; C, 72.83 %; H, 5.2 %; N, 8.09 %. Found: C, 72.40 %; H, 4.89 %; N, 7.82 %. IR cm^{-1} : 3573 (–OH), 3075 (=CH, aromatic), 1620 (C=O, diaryl), 1534 (N=N), 1484 (C=C, aromatic), 1463 (C–N), 1343 (C–O), 1100, 736, 570, 469. $^1\text{H-NMR}$: δ/ppm 7.2–7.3 (Ar-H, *m*), 6.0 (Ar-OH, *s*), 1.94 (–CH₃, *s*).

1-[5-(3-Chlorophenylazo)-2,4-dihydroxyphenyl]-1-phenylmethanone (**D**₆). Yield: 87 %, m.p.: 165–166 °C, R_f value: 0.92. Calculated for $\text{C}_{19}\text{H}_{13}\text{O}_3\text{N}_2$: m.wt.: 317; C, 71.92 %; H, 4.10 %; N, 8.83 %. Found: C, 71.53 %; H, 3.79 %; N, 8.46 %. IR cm^{-1} : 3430 (–OH); 3066 (=CH, aromatic), 1630 (C=O, diaryl), 1584 (N=N), 1482 (C=C, aromatic), 1350 (C–N), 1104 (C–O), 786, 740, 586, 489. $^1\text{H-NMR}$: δ/ppm 7.2–7.5 (Ar-H, *m*), 5.9 (Ar-OH, *s*).

1-[5-(4-Chlorophenylazo)-2,4-dihydroxyphenyl]-1-phenylmethanone (**D**₇). Yield: 89 %, m.p.: 115–116 °C, R_f value: 0.86 Calculated for $\text{C}_{19}\text{H}_{13}\text{O}_3\text{N}_2$: m.wt.: 317; C, 71.92 %; H, 4.10 %; N, 8.83 %. Found: C, 71.61 %; H, 3.87 %; N, 8.49 %. IR cm^{-1} : 3591 (–OH), 3060 (=CH, aromatic), 1629 (C=O, diaryl), 1532 (N=N), 1470 (C=C, aromatic), 1323 (C–N), 1104 (C–O), 780, 737, 581, 470. $^1\text{H-NMR}$: δ/ppm 7.1–7.4 (Ar-H, *m*), 6.0 (Ar-OH, *s*).

1-[2,4-Dihydroxy-5-(4-hydroxyphenylazo)phenyl]-1-phenylmethanone (**D₈**). Yield: 84 %, m.p.: 137–138 °C, R_f value: 0.78. Calculated for $C_{19}H_{14}O_4N_2$: m.wt.: 334; C, 68.26 %; H, 4.19 %; N, 8.38 %. Found: C, 67.98 %; H, 3.87 %; N, 8.08 %. IR cm^{-1} : 3580 (–OH), 3056 (=CH, aromatic), 1635 (C=O, diaryl), 1523 (N=N), 1475 (C=C, aromatic), 1327 (C–N), 1101 (C–O), 742, 578, 470. 1H -NMR: δ/ppm 7.2–7.4 (Ar-H, *m*), 5.8 (Ar-OH, *s*).

1-[2,4-Dihydroxy-5-(4-methylphenylazo)phenyl]-1-phenylmethanone (**D₉**). Yield: 80 %, m.p.: 104–105 °C, R_f value: 0.87. Calculated for $C_{20}H_{16}O_3N_2$: m.wt.: 332; C, 72.28 %, H, 4.81 %; N, 8.43 %. Found, C, 72.0 %, H, 4.46 %; N, 8.13 %. IR cm^{-1} : 3630 (–OH), 3024 (=CH, aromatic), 1626 (C=O, diaryl), 1527 (N=N), 1468 (C=C, aromatic), 1446 (–CH₃), 1351 (C–N), 1111 (C–O), 744, 580, 473. 1H -NMR: δ/ppm 7.4 (Ar-H, *m*), 5.9 (Ar-OH, *s*), 1.99 (–CH₃, *s*).

1-[2,4-Dihydroxy-5-(2-methylphenylazo)phenyl]-1-phenylmethanone (**D₁₀**). Yield: 79 %, m.p.: 116–117 °C, R_f value: 0.81. Calculated for $C_{20}H_{16}O_3N_2$: m.wt.: 332; C, 72.28 %; H, 4.81 %; N, 8.43 %. Found: C, 71.90 %; H, 4.43 %; N, 8.08 %. IR cm^{-1} : 3503 (–OH), 3053 (=CH, aromatic), 1630 (C=O, diaryl), 1535 (N=N), 1478 (C=C, aromatic), 1450 (CH₃), 1320 (C–N), 1109 (C–O), 747, 579, 468. 1H -NMR: δ/ppm 7.2–7.3 (Ar-H, *m*), 5.7 (Ar-OH, *s*), 1.98 (–CH₃, *s*).

The results of the elemental analyses of each dye are consistent with the predicted structure, as shown in Scheme 1.

The number of azo groups is one for each dye. The nitrogen content and number of azo group for each dye are co-related with each other. The IR spectrum of each dye exhibited the important features (shown above) of aromatic, azo, hydroxyl and keto groups. The NMR spectra also showed the important signals at their expected positions for all the diazo compounds based on the well known structure of 2,4-dihydroxybenzophenone and reactive site for azo coupling. The structures of the azo dyes shown in Scheme 1 were thus confirmed.

The absorption maxima (λ_{max}) in the visible spectra of all the dyes recorded in DMF fall in the range 410–455 nm, as shown in Table I. The value of the logarithm of the molar extinction coefficient ($\log \epsilon$) of all the dyes were in the range 4.12 – 4.31, which is consistent with their high absorption intensity.

TABLE I. Absorption maxima (λ_{max}), intensities ($\log \epsilon$), exhaustion (E) and fixation (F) of disperse / mordent dyes on polyester / wool

Dye no.	Absorption maxima λ_{max}/nm in DMF	$\log \epsilon$	Mordent dyeing on wool		Disperse dyeing on polyester	
			% E	% F	% E	% F
D₁	430	4.26	80	93	71	90
D₂	427	4.18	74	91	76	87
D₃	431	4.24	78	93	80	92
D₄	455	4.18	81	96	75	84

TABLE I. Continued

Dye no.	Absorption maxima λ_{\max} /nm in DMF	$\log \epsilon$	Mordent dyeing on wool		Disperse dyeing on polyester	
			% E	% F	%E	%F
D₅	436	4.26	78	92	75	89
D₆	440	4.31	74	91	72	91
D₇	442	4.30	86	92	75	90
D₈	410	4.12	80	92	71	83
D₉	432	4.28	77	91	72	90
D₁₀	424	4.19	73	90	78	91

Moreover, the presence of electron donating or electron attracting groups did not bring about any marked increase or decrease in λ_{\max} in the visible region and $\log \epsilon$ remained nearly constant. However, electron-attracting substituents, such as $-\text{Cl}$ and $-\text{NO}_2$ in the substituent group of the coupler, increased the polarizability. This leads to a decrease in the energy between the highest occupied molecular orbital and lowest unoccupied molecular orbital and, thus, the $\pi \rightarrow \pi^*$ electronic transition occurs with lower frequency photons, resulting in a bathochromic shift of the visible absorption band.

Dyeing properties of the dyes

The mordent and dispersed dyes were applied at 2 % depth on wool and polyester fabric, respectively. The results of the exhaustion of the dye bath and the fixation of the dyed fabric are given in Table I. Their dyeing properties are given in Tables II and III. These dyes gave a wide range of colors, varying from yellowish brown to reddish brown shades, with a good levelness, brightness and depth on the fabric. The variation in the shades of the dye fabric results from both the nature and position of the substituent present on the diazotized compound. The light fastness values of the dyes are more consistent (as shown in Table III). The dyeing showed an excellent fastness to light, with very good to excellent fastness to washing, perspiration and sublimation but showed poor rubbing fastness.

TABLE II. Results of disperse dyeing and various fastness properties of the dyes on polyester

Dye no.	Color shades on polyester	Light fastness	Washing fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
D₁	Brick red	5	5	5	5	5	3	3
D₂	Yellowish red	5	4	4	5	5	3.4	3.4
D₃	Yellowish red	5	5	5	5	5	3	3
D₄	Brick red	4.5	5	4.5	5	5	3.4	4
D₅	Light orange	5	4	4.5	5	5	3.4	3

TABLE II. Continued

Dye no.	Color shades on polyester	Light fastness	Washing fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
D₆	Light maroon	4.5	5	5	5	5	4	3.4
D₇	Light orange	4	4.5	4.5	5	5	3.4	3.4
D₈	Light brown	4	3	4	4	4	3	3
D₉	Reddish brown	5	5	5	5	5	3.4	3
D₁₀	Reddish brown	5	5	5.4	5	5	3.4	3

TABLE III. Results of mordent dyeing and various fastness properties of dyes on wool

Dye no.	Color shades on wool	Light fastness	Wash fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
D₁	Brick red	5	5	5	5	5	4	4
D₂	Dark red	5	4	4	5	5	4	4
D₃	Dark red	5	5	5	5	5	5	5
D₄	Brick red	5	5	4	5	5	4	4
D₅	Dark orange	5	4	5	5	5	4	4
D₆	Dark maroon	5	5	5	5	5	5	4.5
D₇	Deep orange	5	4	5	5	5	4	4
D₈	Dark brown	5	5	4	4	4	5	4.5
D₉	Reddish brown	5	5	5	5	5	5	5
D₁₀	Reddish brown	5	5	4	5	5	5	4

TABLE IV. Antibacterial activity of chrome dyes (**D₁**-**D₁₀**)

Dyes no.	Organisms			
	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Salmonella typhi</i>	<i>Bacillus subtilis</i>
D₁	+	+	+	+
D₂	+	+	+	+
D₃	+	+	+	+
D₄	++	+++	++	+++
D₅	++	++	+	+++
D₆	+	+	-	++
D₇	+	+	+	+
D₈	+	+	+	+
D₉	+	+	+	+
D₁₀	+	+	+	+

(Diameter of inhibition zone in mm; concentration 100 µg/mL); (-) = inactive (12 mm and less). (+) = weakly active (13–16 mm). (++) = moderately active (17–20 mm); (+++) = highly active (21 mm and above).

A remarkable degree of levelness after washing was observed. This may be attributed to the good penetration into and affinity of the dye for the fiber structure.

The most prominent feature of these dyes is that the dye pattern treated with a Cr(III) salt solution afforded excellent shining shades of the dyes. This might be due to chrome complex formation on the fiber.

The antibacterial activity of the chrome complexes of the dyes was monitored against 4 strains (Table IV). The results showed that these dyes inhibit bacterial growth by about 70%. The dye pattern of chrome treated dye may be affordable for the human body. A study of the pigmentation of vinyl polymers, *e.g.* poly(methyl methacrylate) by these dyes is in progress.

CONCLUSION

The synthesized dyes have good fastness to light, sublimation and perspiration properties but exhibit poor rubbing fastness. The nature of the substituent in the coupling components has little influence on the visible absorption and the shade of the dyeing. It was found that mordent dyes have better shades than disperse dyes.

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ИЗВОД

СИНТЕЗА И ПРИМЕНА НОВИХ МОРДАНТНИХ И ДИСПЕРЗНИХ АЗО БОЈА ЗАСНОВАНИХ НА 2,4-ДИХИДРОКСИБЕНЗОФЕНОНУ

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Нове мордантне и дисперзне азо боје добијене су купловањем различитих диазо раствора ароматичних амина са 2,4-дихидроксибензофеноном. Добијене боје окарактерисане су елементалном анализом, као и IR и NMR спектроскопијом. Корелисани су и подаци добијени UV-видљивом спектроскопијом са структурним својствима. Процена могућности обојавања за све боје проверена је на вуненим и полиестерским текстилним влакнима. Праћена је такође могућност обојавања вуне и полиестера третираних хромним мордантом. Резултати показују бољу обојеност на влакнима третираним мордантом. Резултати испитивања антибактеријских својстава хромних боја показали су да је токсичност ових боја за бактерије сасвим добра.

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