

# Synthesis, Characterization and Dyeing Assessment of Novel Bisazo-Acid Dyes Derived from 2-hydroxy-4-Methoxybenzophenone-5-sulphonic acid

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**Abstract**— New bisazo-acid dyes were synthesised by the coupling of diazonium salt solution of different aromatic diamines with from 2-hydroxy-4-Methoxybenzophenone-5-sulphonic acid. The resulting bisazo-acid dyes were characterized by spectral techniques, i.e., elemental analysis, IR, <sup>1</sup>H-NMR and UV– visible spectroscopy. The dyeing performance of all the bisazo-acid dyes was evaluated on wool and silk fabrics. Dyeing of wool and silk fabrics resulted in dark blue to red shades with very good depth and levelness. The dyed fabrics showed excellent to very good light, washing, perspiration, sublimation and rubbing fastness.

**Index Terms**— Bisazo-acid dyes, UV-absorber, Light fastness, Washing Fastness, Rubbing Fastness, Perspiration fastness, Wool and Silk Fabrics.

## 1 INTRODUCTION

Traditionally, bisazo-acid dyes are the most important class of commercial dyes, occupying more than half of the dye chemistry, which contain phenols as intermediates<sup>1-7</sup>. If they contain sodium salts of a sulphonic acid group in addition to a phenolic group, they are referred as an acid azo dye. All such dyes having phenolic and sulphonic acid moieties, contain hydroxyl (–OH) and sulphonic (–SO<sub>3</sub>H) groups as auxochromic groups. Such an auxochromic (–OH) and chromophoric (C=O) groups-containing compound, i.e., 2-hydroxy-4-Methoxybenzophenone-5-sulphonic acid, has shown wide applications as a polymer additive. It is also known for its excellent UV absorbing capacity<sup>8,9</sup>, as it prevents the photo-degradability of most vinyl polymers<sup>10-13</sup>.

The bisazo-acid dyes formation based on this compound has not been developed except in a few patents<sup>14-16</sup>. Considering the above-mentioned importance of 2-hydroxy-4-Methoxybenzophenone-5-sulphonic acid, it was planned to explore the field of acid azo dyes based on this compound, which may yield dyes with good hue properties. Hence, in continuation of earlier work,<sup>17, 18</sup> the present communication comprises the synthesis, characterization and dyeing assessment of novel bisazo-acid dyes based on 2-hydroxy-4-Methoxybenzophenone-5-sulphonic acid. The proposed synthetic route is shown in Scheme 1.

## 2. Experimental

### 2.1 Materials and methods

All the employed chemicals were of analytical reagent grade. The aromatic amines shown in Table I was used for dia-

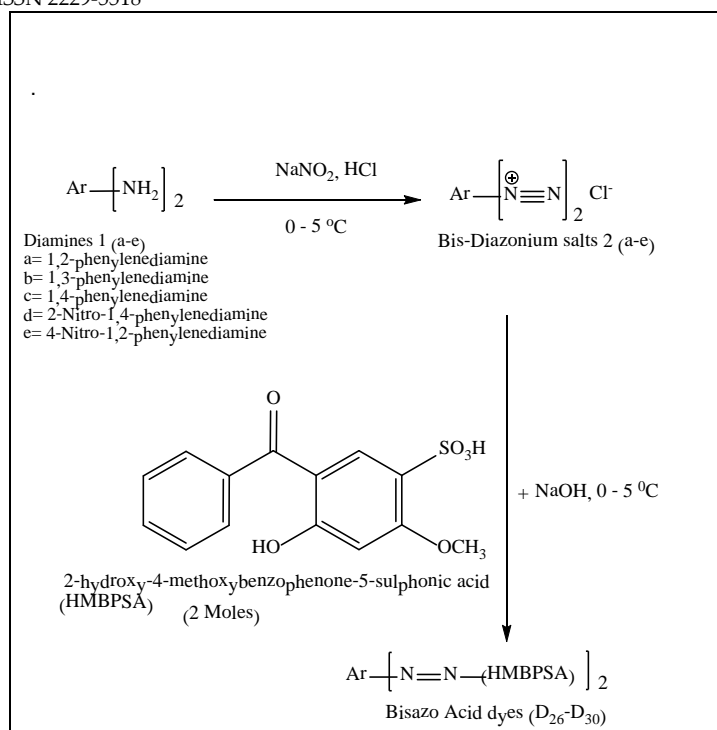
zotization. Wool and silk fabrics were gifted by Color Tax (Pvt) Ltd., Surat, India. Melting points were determined by the open capillary method and are given uncorrected. The UV–visible absorption spectra were measured on a Carl Zeiss UV/Vis Specord spectrometer, and the elemental analysis was realized using a Perkin Elmer CHNS/O Analyzer 2400 Series II. The infrared spectra were recorded in KBr pellets on a Perkin-Elmer Spectrum GX FT-IR model. The <sup>1</sup>H-NMR spectra were recorded on Hitachi R-1500 (400 MHz) in DMSO-*d*<sub>6</sub> solvent and thin layer chromatography (TLC) was run on aluminium sheets pre-coated with silica gel 60 F254 (Merck, Germany) using a methanol–water–acetic acid (12:3:7) solvent system. The colour spots were visualized by a UV cabinet. A HTHP dyeing machine (model LL) was used for dyeing.

### 2.2. Synthesis of acid mono azo dyes and dying

#### 2.2.1. Diazotization

Diazotization of various aromatic diamines (shown in Table I) was performed by a reported method<sup>19, 20</sup>.

Accordingly, each of the aromatic diamines (3.19 g, 0.010 mol) was mixed with HCl (35 mL, 40 %) in a mortar, transferred to a 3-neck round bottom flask, and additional HCl (40 mL, 40 %) was added. To the resultant suspension, crushed ice (25 g) and NaNO<sub>2</sub> (5 mL, 8M) were added. Diazotization was realized over 0.5 h at 0–5 °C under continuous stirring. The complete synthetic route is shown in Scheme 1 and the structures of the various aromatic amines and the corresponding bisazo acid dyes are shown in Table I.



Scheme 1. Synthesis of bisazo acid dyes ( $D_{26}$ - $D_{30}$ ) based on UV absorbing Material.

## 2.2.2. Coupling procedure

The coupling of above mentioned diazotized aromatic diamines (as shown in Table I) was performed by a method reported in the literature<sup>19, 20</sup>. The general procedure followed is given below: 2-hydroxy-4-Methoxybenzophenone-5-sulphonic acid, (8.60 g, 0.040 mol) was dissolved in aqueous sodium hydroxide (150 mL, 0.30 M) solution. The clear solution was cooled in an ice-salt bath and the bis diazonium salt solution of an aromatic diamine was added drop wise over a period of 30 min under vigorous stirring. The pH was maintained between 2.0 to 3.0 by the simultaneous addition of 10 % w/v sodium carbonate solution. Stirring was continued for 2 h, allowing the temperature to rise to ambient. The dye was then filtered off and dissolved in distilled water. Then the bisazo-acid dyes was obtained by the evaporation procedure and subsequently dried at room temperature. The dyes were designated as bisazo-acid dyes ( $D_{26}$ - $D_{30}$ ).

## 2.2.3. Dyeing method for acid bisazo-acid dyes

Wool and silk fabrics are conveniently dyed in the laboratory at 90–130 °C and at a high pressure (166–207 kPa). A model glycerine-bath, high-temperature beaker and HTHP (model LL) dyeing machine were used. For this purpose, a paste of finely powdered bisazo-acid dyes (0.060 g) was prepared with a dispersing agent dodamol (0.090 g), wetting agent Tween-80 (0.0060 g) and water (2.0 mL) in a ball mill. Water (10 mL) was added to this paste under stirring and the pH was adjusted to 2.0–4.0 using acetic acid. This dye suspension

TABLE I: Structure of the aromatic diamines and their corresponding Bisazo acid dyes.

Dyes No.	Aromatic diamines 1(a-e)	Bisazo Acid dye structure ( $D_{26}$ - $D_{30}$ )
$D_{26}$	1,2-phenylene diamine	
$D_{27}$	1,3-phenylene diamine	
$D_{28}$	1,4-phenylene diamine	
$D_{29}$	2-Nitro-1,4-phenylene diamine	
$D_{30}$	4-Nitro-1,2-phenylene diamine	

(100 mL) was added to a beaker provided with a lid and a screw cap. A wetted pattern of wool or silk fabric was rolled into the beaker and the lid was placed on the beaker 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 glycerine-bath and the temperature was raised to 90 °C at a rate of 2 °C/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 cold water and dried at room temperature.

### 2.3. Determination of the percentage exhaustion and fixation

The percentage exhaustion and fixation of the dyed fabrics were determined according to the reported methods<sup>[21-23]</sup>.

### 2.4. Fastness property

All the fastness properties of the synthesized bisazo-acid dyes were assessed, *i.e.*, the light, sublimation and perspiration fastnesses according to the British standard: 1006-1978, the wash fastness according to the Indian standard: IS: 765-1979 and the rubbing fastness using a Crock meter (Atlas) AATCC-1961.

## 3. Results and discussion

### 3.1. Physical properties of dyes

All the bisazo-acid dyes obtained upon recrystallization from acetone were crystalline powders ranging in colour from darkblue to red. The purity of the dyes was checked by TLC using methanol-water-acetic acid (12:3:7) solvent system. A single spot was observed for each dye.

### 3.2. Analytical and spectral data of the dyes

#### 3.2.1. 3,3'-(1E,1'Z)-1,2-phenylenebis(diazene-2,1-diyl)bis(5-benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid)(D<sub>26</sub>).

This compound was obtained as dark blue, Yield: 68%; m.p.: 148–152 °C; Rf. value: 0.79. Anal.Calcd. for C<sub>34</sub>H<sub>26</sub>N<sub>4</sub>O<sub>12</sub>S<sub>2</sub> (FW 746.72): C, 54.69; H, 3.51; N, 7.50; O, 25.71; S, 8.59%. Found: C, 54.62; H, 3.46; N, 7.48; O, 25.61; S, 8.53%. IR (KBr, cm<sup>-1</sup>): 3463 (–OH), 3072 (=CH, aromatic), 1628 (C=O, diaryl), 1521 (N=N), 1481 (C=C, aromatic), 1333 (C–N), 1101 (C–O), 1030, 650 (for sulphonic acid), 732, 584, 481 (for substituted benzene). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 3. 83 (6H, t, –CH<sub>3</sub>), 5.35 (2H, s, Ar–OH), 7.31–8.72 (16H, m, Ar–H), 8.0 to 8.2 (2H, s, –SO<sub>3</sub>H).

#### 3.2.2. 3,3'-(1E,1'Z)-1,3-phenylenebis(diazene-2,1-diyl)bis(5-benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid) (D<sub>27</sub>).

This compound was obtained as light blue, Yield: 70%; m.p.: 137–142 °C; Rf. value: 0.67. Anal.Calcd. for C<sub>34</sub>H<sub>26</sub>N<sub>4</sub>O<sub>12</sub>S<sub>2</sub> (FW 746.72): C, 54.69; H, 3.51; N, 7.50; O, 25.71; S, 8.59%.

Found: C, 54.56; H, 3.36; N, 7.41; O, 25.56; S, 8.43%. IR (KBr, cm<sup>-1</sup>): 3450 (–OH), 3082 (=CH, aromatic), 1624 (C=O, diaryl), 1522 (N=N), 1490 (C=C, aromatic), 1345 (C–N), 1101 (C–O), 1032, 653 (for sulphonic acid), 744, 564, 478 (for substituted benzene). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 3. 83 (6H, t, –CH<sub>3</sub>), 5.35 (2H, s, Ar–OH), 7.31–8.72 (16H, m, Ar–H), 8.0 to 8.2 (2H, s, –SO<sub>3</sub>H).

#### 3.2.3. 3,3'-(1'Z)-1,4-phenylenebis(diazene-2,1-diyl)bis(5-benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid) (D<sub>28</sub>).

This compound was obtained as dark blue, Yield: 78%; m.p.: 161–164 °C; Rf. value: 0.73. Anal.Calcd. for C<sub>34</sub>H<sub>26</sub>N<sub>4</sub>O<sub>12</sub>S<sub>2</sub> (FW 746.72): C, 54.69; H, 3.51; N, 7.50; O, 25.71; S, 8.59%. Found: C, 54.60; H, 3.44; N, 7.46; O, 25.59; S, 8.51%. IR (KBr, cm<sup>-1</sup>): 3481 (–OH), 3070 (=CH, aromatic), 1632 (C=O, diaryl), 1483 (C=C, aromatic), 1337 (C–N), 1103 (C–O), 1029, 650 (for sulphonic acid), 737, 562, 472 (for substituted benzene). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 3. 83 (6H, t, –CH<sub>3</sub>), 5.35 (2H, s, Ar–OH), 7.31–8.72 (16H, m, Ar–H), 8.0 to 8.2 (2H, s, –SO<sub>3</sub>H).

#### 3.2.4. 3,3'-(1'Z)-(2-nitro-1,4-phenylene)bis(diazene-2,1-diyl)bis(5-benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid) (D<sub>29</sub>).

This compound was obtained as reddish yellow, Yield: 72 %; m.p.: 148–150°C; Rf. value: 0.76. Anal.Calcd. for C<sub>34</sub>H<sub>25</sub>N<sub>5</sub>O<sub>14</sub>S<sub>2</sub> (FW 791.72): C, 51.58; H, 3.18; N, 8.85; O, 28.29; S, 8.10%. Found: C, 51.52; H, 3.14; N, 8.81; O, 23.29; S, 8.08%. IR (KBr, cm<sup>-1</sup>): 3633 (–OH), 3080 (=CH, aromatic), 1652 (C=O, diaryl), 1532 (N=N), 1473 (C=C, aromatic), 1338 (C–N), 1104 (C–O), 1032, 653 (for sulphonic acid), 782, 741, 583, 485 (for substituted benzene). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 3. 83 (6H, t, –CH<sub>3</sub>), 5.35 (2H, s, Ar–OH), 7.31–8.72 (15H, m, Ar–H), 8.0 to 8.2 (2H, s, –SO<sub>3</sub>H).

#### 3.2.5. 3,3'-(1E,1'Z)-(4-nitro-1,2-phenylene)bis(diazene-2,1-diyl)bis(5-benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid)(D<sub>30</sub>).

This compound was obtained as red, Yield: 75 %; m.p.: 158–160°C; Rf. value: 0.66. Anal.Calcd. for C<sub>34</sub>H<sub>25</sub>N<sub>5</sub>O<sub>14</sub>S<sub>2</sub> (FW 791.72): C, 51.58; H, 3.18; N, 8.85; O, 28.29; S, 8.10%. Found: C, 51.54; H, 3.16; N, 8.80; O, 28.21; S, 8.07%. IR (KBr, cm<sup>-1</sup>): 3580 (–OH, phenolic), 3070 (=CH, aromatic), 1621 (C=O, diaryl), 1531 (N=N), 1482 (C=C, aromatic), 1463 (C–N), 1338 (C–O), 1034, 650 (for sulphonic acid), 1103, 732, 574, 473 (for substituted benzene). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 3. 83 (6H, t, –CH<sub>3</sub>), 5.35 (2H, s, Ar–OH), 7.31–8.72 (15H, m, Ar–H), 8.0 to 8.2 (2H, s, –SO<sub>3</sub>H).

The results of elemental analyses of each bisazo-acid dyes were consistent with the predicted structure, as shown in Table I. The number of azo group was almost 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 comprised the important features of aromatic, azo, hydroxyl, keto, sulphonic acid and carboxylic acid groups.

The <sup>1</sup>H-NMR spectra of all the bisazo-acid dyes compounds based on 2-hydroxy-4-Methoxybenzophenone-5-sulphonic acid, shows important signals at their respective positions, confirming the structures of various bisazo-acid dyes, as shown in Table I. Two of the –OH protons in the all the dyes resonated as a singlet between 5.35 δ, also the –OCH<sub>3</sub> proton gave a triplet at 3.83 δ. The singlet of the –SO<sub>3</sub>H proton resonated between 8.0 to 8.2 δ in some of the bisazo-acid dyes.

TABLE II Absorption maxima in DMF(λ<sub>max</sub>), intensities (log ε), exhaustion (E) and fixation (F) of bisazo-acid dyes on wool and silk fabrics.

Dyes No.	Absorption maxima λ <sub>max</sub> /nm in DMF	Log ε	Disperse dyeing on Polyester	
			%E	%F
D <sub>26</sub>	482	4.8	72	90
D <sub>27</sub>	458	4.2	66	73
D <sub>28</sub>	434	4.2	77	88
D <sub>29</sub>	480	4.7	72	78
D <sub>30</sub>	476	4.7	68	73

The visible absorption spectroscopic properties of the bisazo-acid dyes were recorded in DMF. The absorption maximum (λ<sub>max</sub>) of all the bisazo-acid dyes falls in the range 434–482 nm in DMF and the values are given in Table II. The values of the logarithm of molar extinction coefficient (log ε) of all the dyes were in the range of 4.2–4.8, consistent with their high absorption intensity. Moreover, the presence of electron donating or electron attracting groups did not bring about any marked increase or decrease in λ<sub>max</sub> in the visible region and

TABLE III. Results of bisazo-acid dyes and their various fastness properties on wool fabrics.

Dyes No.	Color shades on wool	Light fastness	Washing fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
D <sub>26</sub>	Pinkish blue	5	5	5	4	4	3	3
D <sub>27</sub>	Pinkish blue	5	5	5	4	4	3	3
D <sub>28</sub>	Reddish brown	5	4	5	4	4	3	4
D <sub>29</sub>	Yellowish pink	5	4	5	4	4	3	3
D <sub>30</sub>	Chocolate brown	4	4	4	4	4	4	3

log ε remained nearly constant.

However, an electron attracting substituent, such as –SO<sub>3</sub>H, in the structure of the dyes increases the polarizability

and will results in bathochromic shifts

TABLE IV Results of bisazo-acid dyes and their various fastness properties on silk fabrics.

Dyes No.	Color shades on wool	Light fastness	Washing fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
D <sub>26</sub>	Pinkish blue	5	5	5	4	4	3	3
D <sub>27</sub>	Pinkish blue	5	5	5	4	4	3	3
D <sub>28</sub>	Reddish brown	5	4	5	4	4	3	4
D <sub>29</sub>	Yellowish pink	5	4	5	4	4	3	3
D <sub>30</sub>	Chocolate brown	4	4	4	4	4	4	3

This leads to a decrease in the energy between the highest occupied molecular orbital and lowest unoccupied molecular orbital and thus the π → π\* electronic transition occurs with a lower frequency photon, resulting in a bathochromic shift of the visible absorption band.

### 3.3. Dyeing properties of dyes

The bisazo-acid dyes were applied at a 2 % depth on wool and silk fabrics<sup>24-26</sup>. Their dyeing properties are shown in Tables III-IV. These dyes gave a wide range of colours varying from dark blue to red shades with good levelness, brightness and depth on the fabrics. 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 dyeing showed excellent fastness to light, with a very good to excellent washing, perspiration, rubbing and sublimation fastnesses.

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

## 4. Conclusions

All newly synthesized bisazo-acid dyes exhibited very good to excellent fastness to light, sublimation, and perspiration and rubbing. The remarkable degree of levelness after dyeing indicates good penetration into, and affinity of these dyes for the fabric matrix. They give deep and bright hues with levelling dyeing. The nature of the substituent in the coupling component has little influence on the UV-visible absorption and shade of the dyeing.

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