



# Facile synthesis of novel disperse azo dyes with aromatic hydroxyl group

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## ABSTRACT

A series of novel disperse azo dyes containing aromatic hydroxyl group were synthesized by a novel and simple synthetic strategy, in which, the stable solid diazonium salts of weakly basic amines were used to couple with aromatic hydroxyl compounds in alkaline aqueous solution. The experimental procedure was simple and had a high reaction rate and excellent yields. The structures of the dyes were confirmed by HRMS, FT-IR, <sup>1</sup>H NMR, and elemental analysis. Then, the synthesized azo dyes were used for dyeing polyester fabric and gave favorable color fastness that was comparable with that of commercial dyes.

## 1. Introduction

Azo dyes are used widely for dyeing textiles [1–3] and involved in nearly all dye categories, such as direct, reactive, and disperse dyes [4–6]. The molecule of azo dye contains one or more D–π–A systems, which can produce diverse colors by changing the electron-donating (D) or electron-accepting (A) functional groups [7,8].

Azo dyes produced from weakly basic amines are widely adopted as disperse dyes to dye synthetic fiber [9,10]. Such dyes have more than one strong electron withdrawing groups in their structures, which can provide dark shades and enhance color fastness. Traditionally, weakly basic amines are diazotized in concentrated sulfuric acid, and the subsequent coupling process can proceed only under acidic conditions [11–13]. Obtaining the structure that contains all the segments of weakly basic amines and aromatic hydroxyl compounds is difficult because the coupling reaction must be performed in alkaline aqueous solution.

Azo dyes with aromatic hydroxyl group are constantly used in the textile industry as water-soluble dyes, such as acid or reactive dyes for dyeing protein or cellulosic fibers [14–16], and they are widely adopted as colorant in foodstuffs, cosmetics, and drugs, or organic pigment for ink-jet printing, painting, and so on [17–20]. The syntheses of these dyes need to be conducted under alkaline conditions and the diazo components are primary amines with strong basicity as their diazotization can proceed in diluted hydrochloric acid [21–24]. Nevertheless, there is rare azo dyes with aromatic hydroxyl group in disperse dyes. The diazo components used for the preparation of disperse azo dyes are always weakly basic amines and their diazotizations are processed in concentrated sulfuric acid. It is difficult for the diazonium salts to react with aromatic hydroxyl compounds in alkaline aqueous solution as

large amounts of waste inorganic salt and strong heat of neutralization and dilution will be produced [25,26].

In our recent research, stable solid diazonium salts of weakly basic amines were obtained in organic solvent using 1,5-naphthalenedi-sulfonic acid as stabilizer, and they were separated from the acidic diazotization solution [27]. In this work, these diazonium salts were reacted conveniently with coupling components containing aromatic hydroxyl group to synthesize novel disperse azo dyes giving excellent yields. The generation of large amounts of inorganic salt and strong heat, as in the traditional method, was prevented. The dyeing properties of these dyes on the polyester fabric were satisfactory so that they are suitable for dyeing as industrial disperse dyes.

## 2. Experimental

### 2.1. General information

1-phenyl-3-methyl-2-pyrazolin-5-one and 2-naphthol were bought from Sinopharm Group Co., Ltd. Dispersing agent NNO (a mixture of salts of multicore condensate aromatic sulfonic acids) was bought from Zhejiang Jihua Group Co. Ltd. C. I. Disperse Yellow 163 (Y163) and C. I. Disperse Orange 30 (O30) were purchased from Zhejiang Longsheng Group Co., Ltd.

The purity of dyes was determined through standard curve obtained in ethyl acetate using an Agilent 8453 Spectroscopy System. HRMS were obtained by a LTQ Orbitrap XL™ instrument. Elemental analyses were recorded on a Vario EL III Analyzer. <sup>1</sup>H NMR spectra were obtained by a Bruker Avance III spectrometer with TMS as the internal standard. FT-IR spectra were measured on a Nicolet 6700 spectrometer with KBr pellets.

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## 2.2. Typical preparation of disperse azo dyes

The diazonium salts were prepared as stable solids in organic solvent using published method [27]. Typical coupling process is described as follows:

5 mmol 2-naphthol were dissolved in 50 ml water using 10 wt % sodium hydroxide solution adjusting pH to 10–11. The temperature was cooled to 0 °C–5 °C using ice-water bath. 5 mmol 2,4-dinitrobenzene diazonium salt prepared freshly were slowly added in for about 1 h with vigorously stirring and the pH was maintained in 10–11 using 10 wt % sodium hydroxide solution. Color reaction with H-acid was used to confirm the reaction endpoint. The dye was filtered, washed and dried by oven at 70 °C to afford the product.

## 2.3. Characterization of the dyes

Compound 4a:  $C_{16}H_{12}N_6O_5$ : HRMS,  $m/z$ : calcd for [M-H]<sup>-</sup>, 367.0796; found, 367.0787. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 14.56 (s, 1H), 8.96 (s, 1H), 8.63 (d,  $J = 9.4$  Hz, 1H), 8.36 (d,  $J = 9.2$  Hz, 1H), 7.91 (d,  $J = 7.9$  Hz, 2H), 7.56–7.46 (m, 2H), 7.29 (d,  $J = 6.3$  Hz, 1H), 2.39 (s, 3H). FT-IR (KBr,  $cm^{-1}$ ): 3423, 3105, 2924, 1673, 1614, 1601, 1575, 1523, 1492, 1421, 1374, 1344, 1324, 1313, 1270, 1208, 1153, 1139, 1125, 1002. Anal. Calcd: C, 52.18; H, 3.28; N, 22.82%. Found: C, 52.03; H, 3.01; N, 22.43%.

Compound 4b:  $C_{17}H_{12}N_6O_3$ : HRMS,  $m/z$ : calcd for [M-H]<sup>-</sup>, 347.0898; found, 347.0887. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 13.60 (s, 1H), 8.84 (d,  $J = 2.5$  Hz, 1H), 8.56 (d,  $J = 8.5$  Hz, 1H), 8.05 (d,  $J = 9.3$  Hz, 1H), 7.90 (d,  $J = 8.2$  Hz, 2H), 7.50 (t,  $J = 7.8$  Hz, 2H), 7.28 (t,  $J = 7.5$  Hz, 1H), 2.36 (s, 3H). FT-IR (KBr,  $cm^{-1}$ ): 3418, 3086, 2923, 2228, 1667, 1615, 1570, 1537, 1519, 1494, 1459, 1338, 1278, 1248, 1219, 1181, 1147, 1077, 1046. Anal. Calcd: C, 58.62; H, 3.47; N, 24.13%. Found: C, 58.81; H, 3.06; N, 24.07%.

Compound 4c:  $C_{16}H_{11}Cl_2N_5O_3$ : HRMS,  $m/z$ : calcd for [M-H]<sup>-</sup>, 390.0166; found, 390.0155. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 8.46 (s, 2H), 7.90 (d,  $J = 8.1$  Hz, 2H), 7.57–7.41 (m, 2H), 7.27 (s, 1H), 2.28 (s, 3H). FT-IR (KBr,  $cm^{-1}$ ): 3420, 3089, 2972, 2923, 1664, 1595, 1558, 1526, 1504, 1442, 1389, 1374, 1333, 1311, 1252, 1192, 1144, 1078, 1049, 1010. Anal. Calcd: C, 49.00; H, 2.83; N, 17.86%. Found: C, 48.88; H, 2.57; N, 17.67%.

Compound 4d:  $C_{16}H_{11}Br_2N_5O_3$ : HRMS,  $m/z$ : calcd for [M-H]<sup>-</sup>, 479.9135; found, 479.9119. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 8.60 (s, 2H), 7.90 (d,  $J = 8.1$  Hz, 2H), 7.49 (t,  $J = 7.9$  Hz, 2H), 7.26 (t,  $J = 7.4$  Hz, 1H), 2.30 (s, 3H). FT-IR (KBr,  $cm^{-1}$ ): 3420, 3082, 2922, 1663, 1586, 1556, 1517, 1431, 1373, 1331, 1306, 1248, 1189, 1147, 1130, 1077, 1048, 1007. Anal. Calcd: C, 39.94; H, 2.30; N, 14.56%. Found: C, 39.97; H, 1.95; N, 14.54%.

Compound 4e:  $C_{16}H_{12}ClN_5O_3$ : HRMS,  $m/z$ : calcd for [M-H]<sup>-</sup>, 356.0556; found, 356.0548. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 13.59 (s, 1H), 8.51 (d,  $J = 2.5$  Hz, 1H), 8.34 (dd,  $J = 9.1, 2.5$  Hz, 1H), 8.02 (d,  $J = 9.1$  Hz, 1H), 7.90 (d,  $J = 8.1$  Hz, 2H), 7.49 (t,  $J = 7.8$  Hz, 2H), 7.27 (t,  $J = 7.4$  Hz, 1H), 2.36 (s, 3H). FT-IR (KBr,  $cm^{-1}$ ): 3421, 3096, 2972, 1668, 1595, 1568, 1525, 1502, 1460, 1437, 1372, 1336, 1272, 1239, 1216, 1179, 1151, 1116, 1048, 1000. Anal. Calcd: C, 53.72; H, 3.38; N, 19.58%. Found: C, 53.51; H, 3.00; N, 19.34%.

Compound 4f:  $C_{16}H_{10}N_4O_5$ : HRMS,  $m/z$ : calcd for [M-H]<sup>-</sup>, 337.0578; found, 337.0571. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 16.35 (s, 1H), 8.97 (d,  $J = 2.7$  Hz, 1H), 8.69 (d,  $J = 9.3$  Hz, 1H), 8.59 (d,  $J = 9.8$  Hz, 1H), 8.47 (d,  $J = 7.8$  Hz, 1H), 7.97 (d,  $J = 9.8$  Hz, 1H), 7.73 (d,  $J = 7.7$  Hz, 1H), 7.65 (t,  $J = 7.7$  Hz, 1H), 7.61–7.55 (m, 1H), 6.68 (d,  $J = 9.8$  Hz, 1H). FT-IR (KBr,  $cm^{-1}$ ): 3442, 3111, 1611, 1589, 1528, 1494, 1481, 1448, 1401, 1341, 1259, 1181, 1132, 1094. Anal. Calcd: C, 56.81; H, 2.98; N, 16.56%. Found: C, 56.30; H, 2.43; N, 16.36%.

Compound 4g:  $C_{17}H_{10}N_4O_3$ : HRMS,  $m/z$ : calcd for [M-H]<sup>-</sup>, 317.0680; found, 317.0670. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 16.06 (s, 1H), 8.85 (s, 1H), 8.54 (d,  $J = 8.9$  Hz, 1H), 8.49 (d,  $J = 4.8$  Hz, 1H), 8.34 (d,  $J = 9.3$  Hz, 1H), 8.00 (d,  $J = 9.7$  Hz, 1H), 7.75

(d,  $J = 7.6$  Hz, 1H), 7.64 (t,  $J = 7.6$  Hz, 1H), 7.56 (t,  $J = 7.6$  Hz, 1H), 6.75 (d,  $J = 9.7$  Hz, 1H). FT-IR (KBr,  $cm^{-1}$ ): 3421, 3091, 2229, 1613, 1578, 1509, 1452, 1400, 1342, 1259, 1228, 1194, 1160, 1135, 1095, 1076. Anal. Calcd: C, 64.15; H, 3.17; N, 17.60%. Found: C, 63.65; H, 2.73; N, 17.67%.

Compound 4h:  $C_{16}H_9Cl_2N_3O_3$ : HRMS,  $m/z$ : calcd for [M-H]<sup>-</sup>, 359.9948; found, 359.9935. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 15.66 (s, 1H), 8.50 (s, 2H), 8.35 (d,  $J = 8.1$  Hz, 1H), 8.04 (d,  $J = 9.6$  Hz, 1H), 7.79 (d,  $J = 7.7$  Hz, 1H), 7.64 (t,  $J = 7.6$  Hz, 1H), 7.53 (t,  $J = 7.4$  Hz, 1H), 6.83 (d,  $J = 9.6$  Hz, 1H). FT-IR (KBr,  $cm^{-1}$ ): 3421, 3098, 1624, 1576, 1503, 1451, 1404, 1373, 1331, 1254, 1233, 1206, 1156, 1137, 1096, 1067. Anal. Calcd: C, 53.06; H, 2.50; N, 11.60%. Found: C, 53.11; H, 2.26; N, 11.54%.

Compound 4i:  $C_{16}H_9Br_2N_3O_3$ : HRMS,  $m/z$ : calcd for [M-H]<sup>-</sup>, 449.8917; found, 449.8903. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 15.25 (s, 1H), 8.64 (s, 2H), 8.48 (d,  $J = 8.1$  Hz, 1H), 8.07 (d,  $J = 9.5$  Hz, 1H), 7.82 (d,  $J = 7.7$  Hz, 1H), 7.64 (t,  $J = 7.7$  Hz, 1H), 7.54 (t,  $J = 6.9$  Hz, 1H), 6.92 (d,  $J = 9.5$  Hz, 1H). FT-IR (KBr,  $cm^{-1}$ ): 3419, 3090, 1624, 1572, 1510, 1450, 1401, 1366, 1329, 1235, 1205, 1154, 1130, 1093, 1057. Anal. Calcd: C, 42.60; H, 2.01; N, 9.32%. Found: C, 42.71; H, 1.70; N, 9.48%.

Compound 4j:  $C_{16}H_{10}ClN_3O_3$ : HRMS,  $m/z$ : calcd for [M-H]<sup>-</sup>, 326.0338; found, 326.0326. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 16.07 (s, 1H), 8.51 (s, 1H), 8.48 (d,  $J = 8.1$  Hz, 1H), 8.35 (d,  $J = 3.2$  Hz, 2H), 8.00 (d,  $J = 9.9$  Hz, 1H), 7.75 (d,  $J = 7.7$  Hz, 1H), 7.64 (t,  $J = 7.7$  Hz, 1H), 7.59–7.50 (m, 1H), 6.73 (d,  $J = 9.7$  Hz, 1H). FT-IR (KBr,  $cm^{-1}$ ): 3420, 3099, 1623, 1574, 1587, 1555, 1509, 1452, 1403, 1338, 1261, 1231, 1201, 1158, 1132, 1094, 1041. Anal. Calcd: C, 58.64; H, 3.08; N, 12.82%. Found: C, 58.66; H, 2.69; N, 12.81%.

## 2.4. Post-treatment of dyestuff

0.5 g dye, 0.5 g dispersing agent NNO, 20 ml water and 95.0 g zirconia bead of 2.0 mm diameter were successively added in a 100 ml glass grinding tube which installed with a glass grinding rod and a mechanical agitator. The mixture was stirred for 1 h at room temperature with a rotate speed of 350 r/min and then filtrated through a 200 mesh sieve. The suspension solution was dried through a rotary evaporation at 60 °C, so the commercialized dye was obtained.

## 2.5. Dyeing for polyester fabric

Dyeing of polyester fabric was conducted using high temperature high pressure method according to reference [7] in a rotary infrared laboratory dyeing machine (XW-HWR-30-12, Jingjiang Xinwang Dyeing & finishing Machinery factory, China). The fabric to liquor ratio was all 1:100 and the amount of dye used was different according to K/S. Take dye 4f as an example, the concentration of dye was 3% owf (on weight of fabric) and the typical dyeing process is described as follows:

0.02 g commercialized dye of 4f was dissolved to 100 ml in a volumetric flask with water and the pH was adjusted to 5–6 using 10% acetic acid solution. This dye liquor was poured into a 200 ml stainless steel dyeing cylinder and then 1.0 g polyester fabric was also put in. The dye bath temperature was raised from room temperature to 130 °C at a rate of 3 °C/min, maintained at 130 °C for 60 min, and then naturally cooled to 60 °C as depicted in Fig. 1. The dyed fabrics were rinsed with water and then reduction cleared using an aqueous solution of 1.4 g/L sodium hydroxide and 2.0 g/L sodium hydrosulfite at a fabric to liquor ratio of 1:80 at 70 °C for 15 min. The treated fabrics were rinsed to neutral with water and dried at ambient temperature.

## 2.6. Color measurement

The K/S, L\*, a\*, and b\* values of the dyed fabrics were obtained from an UltraScan XE spectrophotometer (Hunter Associates Laboratory, Inc., USA) equipped with Universal Software V4.10 using

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