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Structure–properties relationships investigation on the azo dyes derived from benzene sulfonamide intermediates

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Abstract

Several diaminobenzene and aminobenzene intermediates based on sulfonamide and azo dyes derived therefrom were synthesized and characterized by FTIR, MS and ^{1}H NMR. These azo dyes have been used to dye cotton and wool fibre, further their spectroscopic data and application properties were estimated. Especially, it was found that the properties of these derived azo dyes are affected by the sulfonamide substituted bridged groups between the two benzene rings of the corresponding intermediates. In addition, the crystallographic structure of a new type of 1,4-bis-(4-amino-benzenesulfonyl)-piperazine intermediate was determined by X-ray diffraction, which reveals that its molecular configuration is non-planar.

Keywords: Benzene sulfonamide; Azo dye; X-ray diffraction; Dyeing properties

1. Introduction

Since it was well known that benzidine is a carcinogenic and mutagenic compound [1–7], it has become important to replace the dyestuffs and corresponding intermediates based on benzidine or its homologues. Thus, many researches [8–17] have been conducted to find their replacements. One important method involves the use of arylamine compounds introduced as bridged groups between the two benzene rings of benzidine. In this regard, benzene sulfonamide compounds have been proved to be non-carcinogenic, as the use of intermediates based on them in the synthesis of azo dyes is well established, and the resultant dyes exhibit improved dyeing properties [18–27]. It has been reported that 4-amino-*N*-(4-aminophenyl) benzene sulfonamide (Fig. 1, **a**) [28–33] and 1,2-bis-sulfanilylamino-ethane (Fig. 1, **b**) [34] were substituted for benzidine to synthesize azo dyes. However, on account of ionization of the hydrogen linked to nitrogen atom in the sulfonamide bridged group between the two benzene rings of these sulfonamide intermediates, in the presence of alkali such azo dyes based on the intermediates (Fig. 1, **a**, **b**; Fig. 12, **g**, **h**) above will not be stable under alkaline conditions. This fact stimulated us to search for an efficient route to synthesize new improved benzene sulfonamide intermediates. In this paper, we report the synthesis of some diaminobenzene and aminobenzene sulfonamide intermediates (Fig. 1, **c**, **d**) and their derived azo dyes under mild conditions. The properties of azo dyes containing new sulfonamide bridged groups were studied, compared to that based on 1,2-bis-sulfanilylamino-ethane (Fig. 1, **b**). Furthermore, the structure of a new type of diaminobenzene sulfonamide intermediate – 1,4-bis-(4-amino-benzenesulfonyl)-piperazine (Fig. 1, **d**) was determined by X-ray diffraction analysis.

2. Experimental

2.1. General

p-Acetamidobenzene sulfonyl chloride (ASC) was a commercial product (≥99%); other chemicals and solvents were of analytical grade and commercially available.

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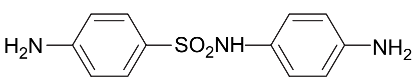
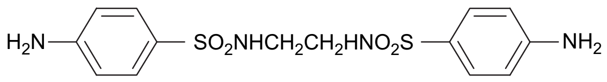
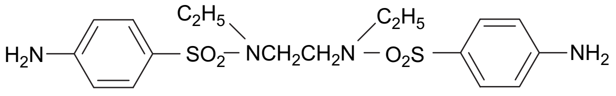


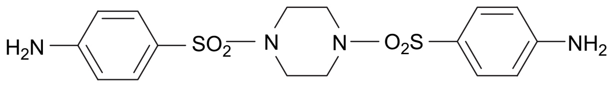
4-amino-N-(4-aminophenyl) benzene sulfonamide **(a)**



1,2-bis-sulfanilylamino-ethane **(b)**



4,4'-diamino-N,N'-diethyl-bisbenzenesulfonyl ethylenediamine **(c)**



1,4-bis-(4-amino-benzenesulfonyl)-piperazine **(d)**

Fig. 1. Chemical structures of diaminobenzene sulfonamide intermediates.

The elemental analyses were performed on an Elementar vario EL III analyzer. The IR spectra were recorded on a Nicolet 5SXC FT-IR spectrometer using pressed KBr. The mass spectra were determined by a Micromass GCT (70 eV) mass spectroscope. The intermediate samples were dissolved in $CDCl_3$ or DMSO-d_6 and placed in NMR tubes, and their NMR spectra were determined by an Avance 500 (Bruker) NMR spectrometer (TMS, 500 Hz). The UV spectra were determined by a Cary 100 UV spectrophotometer. The monocrystal structures were determined by X-ray crystallography method with a Bruker Smart APEX-CCD diffractometer. The *K*/*S* values of fibres were obtained using a Datacolor SF 600X reflection spectrometer, the washing fastness was tested by an SW-12A Fabric Color fastness apparatus, and the rubbing fastness was tested by a YG(B) 410D Full atomic Fabric Rubbing fastness instrument.

2.2. Synthesis

2.2.1. Synthesis of intermediates

2.2.1.1. Synthesis of 1,2-bis-sulfanilylamino-ethane (Fig. 1, ***b****) [35].* Aqueous solution of ASC (0.0505 mol, 11.8 g) and ethanediamine (0.025 mol, 1.5 g) were stirred at 30 °C for 1 h, then heated to 70 °C for 3 h; meanwhile sodium carbonate liquor was added to keep the reactant alkalescent. The termination of the condensation reaction was determined by TLC. The condensation compound was hydrolyzed by 10% NaOH aqueous solution. After the hydrolysis liquor was cooled to room temperature, 10% hydrochloric acid aqueous solution was added to adjust the hydrolysate neutral, and the product was suspended. Recrystallization from deionized water gave a pale powder; yield of product: 84%. FTIR (KBr, cm^{-1}): 3439.89, 3360.28 (NH_2); 3283.36 (NH); 2935.13, 2888.48 (CH_2); 1310.52, 1148.12 (SO_2). MS *m*/*z* (relative intensity): 65.0 (22.12), 92.1 (39.62), 108.1 (27.87), 140.0 (19.46), 156.0 (100.00), 185.1 (27.73), 370.1 (5.49). ^1H NMR (DMSO-d_6) δ (ppm): 2.63 (s, 4H, $NHCH_2$), 6.59 (d, 4H, $J = 3.51$ Hz, NH_2–*Ph*–*H*), 7.33 (d, 4H, $J = 3.43$ Hz, Ph–H). Anal. Calcd. for $C_{14}H_{18}N_4O_4S_2$ (%): C, 45.39; H, 4.90; N, 15.12. Found (%): C, 45.47; H, 4.91; N, 15.09.

2.2.1.2. Synthesis of 4,4′-diamino-N,N′-diethyl-bisbenzenesulfonyl ethylenediamine (Fig. 1, ***c****).* ASC (0.0505 mol, 11.8 g) and *N*,*N*′-diethlylethanediamine (0.025 mol, 2.9 g) dissolved in 50 mL acetone were stirred at room temperature for 2 h, then heated at 50 °C for 2 h, triethylamine was added to keep the reactant alkalescent. TLC revealed the condensation process. To hydrolyze the condensation compound it was refluxed in 10% NaOH aqueous solution. The hydrolysate was insoluble in alkali liquor, so it was needless to add hydrochloric acid to deposit it. The precipitate was collected and recrystallized with ethanol. Finally the white powder obtained was collected; yield of product: 91%. FTIR (KBr, cm^{-1}): 3435.68, 3385.21 (NH_2); 2929.61, 2867.74 (CH_2); 2971.09, 1462.62 (CH_3); 1305.93, 1147.59 (SO_2). MS *m*/*z* (relative intensity): 92.1 (18.39), 108.0 (11.29), 156.0 (100.00), 213.1 (61.78), 270.1 (22.53). ^1H NMR (DMSO-d_6) δ (ppm): 1.00 (t, 6H, $J = 3.48$, 3.50 Hz, CH_2CH_3), 3.05 (m, 8H, CH_2NCH_2), 6.0 (s, 4H, NH_2), 6.60 (d, 4H, $J = 4.20$ Hz, NH_2–*Ph*–*H*), 7.38 (d, 4H, $J = 4.20$ Hz, Ph–H). Anal. Calcd. for $C_{18}H_{26}N_4O_4S_2$ (%): C, 50.68; H, 6.14; N, 13.13. Found (%): C, 50.85; H, 6.12; N, 12.98.

2.2.1.3. Synthesis of 1,4-bis-(4-amino-benzenesulfonyl)-piperazine (Fig. 1, ***d****).* A similar procedure as given in Section 2.2.1.2 was carried out to give a white powder; yield of product: 93%. FTIR (KBr, cm^{-1}): 3385.57, 3474.38 (NH_2); 2909.22, 2888.48 (CH_2); 1319.74, 1155.74 (SO_2). MS *m*/*z* (relative intensity): 65.0 (11.26), 92.1 (30.07), 108.1 (16.69), 156.0 (100.00), 240.1 (55.92), 396.1 (2.44). ^1H NMR (DMSO-d_6) δ (ppm): 2.83 (s, NCH_2, 8H), 6.63 (d, 4H, $J = 4.36$ Hz, NH_2–*Ph*–*H*), 7.29 (d, 4H, $J = 4.36$ Hz, Ph–H). Anal. Calcd. for $C_{16}H_{20}N_4O_4S_2$ (%): C, 48.47; H, 5.08; N, 14.13. Found (%): C, 48.51; H, 5.06; N, 14.14.

2.2.1.4. Synthesis of 1-sulfanilyl-piperidine (Fig. 13, ***e****).* A similar procedure as given in Section 2.2.1.2 was carried out to give a white powder; yield of product: 86%. FTIR (KBr, cm^{-1}): 3435.82, 3361.33 (NH_2); 2949.46, 2835.34 (CH_2); 1307.91, 1153.20 (SO_2). MS *m*/*z* (relative intensity): 65.0 (11.26), 84.1 (100.00), 92.0 (42.94), 93.0 (48.01), 108.0 (38.23), 140.0 (13.80), 156.0 (71.50), 157.0 (21.34), 239.1 (18.65), 240.1 (76.01), 241.1 (8.44), 242.1 (3.63). ^1H NMR (DMSO-d_6) δ (ppm): 1.41 (m, 2H, piperidine ring-4), 1.63 (m, 4H, piperidine ring-3), 2.94 (t, 4H, $J = 2.71$, 2.76 Hz, piperidine ring-2), 4.10 (s, 2H, NH_2), 6.70 (d, 2H, $J = 4.34$ Hz, NH_2–*Ph*–*H*), 7.54 (d, 2H, $J = 4.34$ Hz, Ph–H). Anal. Calcd. for $C_{11}H_{16}N_2SO_2$ (%): C, 54.98; H, 6.71; N, 11.66. Found (%): C, 55.04; H, 6.66; N, 11.43.

2.2.1.5. Synthesis of 4-sulfanilyl-morpholin (Fig. 13, ***f****).* A similar procedure as given in Section 2.2.1.2 was carried out to give a pale powder; yield of product: 89%. FTIR (KBr, cm^{-1}): 3474.38, 3385.57 (NH_2); 2984.15, 2846.01 (CH_2); 1312.39, 1152.32 (SO_2); 1107.66 (C–O–C). MS *m*/*z* (relative intensity): 56.0 (40.26), 65.0 (11.80), 86.1 (100), 92.0 (18.48), 107.1 (8.91), 108.0 (11.46), 156.0 (27.93), 242.1 (40.26), 243.1 (4.26), 244.1 (1.93). ^1H NMR (DMSO-d_6) δ (ppm): 2.97 (t, 4H, $J = 2.35$, 2.32 Hz, CH_2 N), 3.74 (t, 4H, $J = 2.37$ Hz, CH_2O), 4.15 (s, 2H, NH_2), 6.71 (d, 2H, $J = 4.34$ Hz, NH_2–*Ph*–*H*), 7.53 (d, 2H, $J = 4.33$ Hz, Ph–H). Anal. Calcd. for $C_{10}H_{14}N_2SO_3$ (%): C, 49.57; H, 5.82; N, 11.56. Found (%): C, 49.64; H, 5.77; N, 11.46.

2.2.1.6. Synthesis of sulfanilic acid ethylamide (Fig. 13, ***g****).* A similar procedure as given in Section 2.2.1.1 was carried out to give a flavescent crystal; yield of product: 82%. FTIR (KBr, cm^{-1}): 3376.58 (NH_2); 2927.61, 2890.13 (CH_2); 2974.62 (CH_3); 1300.00, 1152.32 (SO_2). MS *m*/*z* (relative intensity): 65.0 (80.20), 92.0 (100.00), 93.1 (43.31), 108.0 (69.67), 156.0 (64.19), 200.1 (13.84), 201.1 (1.29). ^1H NMR (DMSO-d_6) δ (ppm): 1.10 (t, 3H, $J = 3.58$, 3.59 Hz, CH_3), 2.98 (m, 2H, CH_2), 4.14 (s, 2H, NH_2), 6.69 (d, 2H, $J = 4.21$ Hz, NH_2–*Ph*–*H*), 7.64 (d, 2H, $J = 4.20$ Hz, Ph–H). Anal. Calcd. for $C_8H_{12}N_2O_2S$ (%): C, 47.98; H, 6.04; N, 13.99. Found (%): C, 47.89; H, 6.06; N, 13.86.

2.2.1.7. Synthesis of sulfanilic acid-(2-hydroxy-ethylamide) (Fig. 13, ***h****).* A similar procedure as given in Section 2.2.1.1 was carried out to give white crystal; yield of product: 78%. FTIR (KBr, cm^{-1}): 3386.11 (OH); 3205.79 (NH_2); 2927.51, 2854.65 (CH_2); 1320.74, 1132.52 (SO_2); 1059.45 (ν_{C-O} of primary alcohol); MS *m*/*z* (relative intensity): 65.0 (30.37), 92.1 (47.98), 93.1 (8.33), 108.0 (30.49), 156.0 (100.00), 216.1(17.66). ^1H NMR (DMSO-d_6) δ (ppm): 3.08 (t, 2H, $J = 2.48$, 2.49 Hz, NH*CH_2*), 3.70 (t, 2H, $J = 2.49$, 2.56 Hz, *CH_2*OH), 4.13 (s, 2H, NH_2), 6.70 (d, 2H, $J = 4.34$ Hz, NH_2–*Ph*–*H*), 7.65 (d, 2H, $J = 4.33$ Hz, Ph–H). Anal. Calcd. for $C_8H_{12}N_2O_3S$ (%): C, 44.43; H, 5.59; N, 12.95. Found (%): C, 44.56; H, 6.02; N, 12.92.

2.2.2. Synthesis of azo dyes

Three bisazo dyes and three trisazo dyes were synthesized, and their structures are shown in Fig. 2.

The bisazo dyes were synthesized by the three diaminobenzene sulfonamide intermediates and 1-naphthylamine-4-sulfonic acid as coupling component, the process is as follows.

Diazotization: 0.01 mol dye intermediate was added to 6 mL hydrochloric acid and 30 mL water, then stirred under ultrasound condition and heated until it dissolved completely, which was then cooled in an ice-bath. Cold $NaNO_2$ (0.021 mol) was added to the intermediate, and the mixture was stirred in the ice-bath for 30 min. When diazotization was complete, the excess nitrous acid was decomposed by aminosulfonic acid.

Coupling: 0.02 mol 1-amino-4-naphthalenesulfonic acid was dissolved in 30 mL water and pH was adjusted to 5–7. The diazo liquid was added dropwise into it, and the pH was kept at 5–7 during the process. Then the reactants were stirred at 0–5 °C for 3 h, after that the pH was adjusted to 7, and the mixture continuously stirred for 1 h.

Purification: after the coupling process was accomplished, the product was filtered, washed with deionized water, and then dried. The dried dye was dissolved in DMF and filtered. The filter cake was washed with DMF, then a large amount of ethyl ether was added into the filtrate, and the precipitate was obtained immediately. After frozen for 15 min, the precipitate was filtered, the filter cake obtained was treated by the same method as above for two more times. The final precipitate was washed with ethyl ether and dried at 50 °C, the product was detected by elemental analysis and testified pure.

The trisazo dyes were synthesized according to the literature method [32]. Since there are multiple steps in the

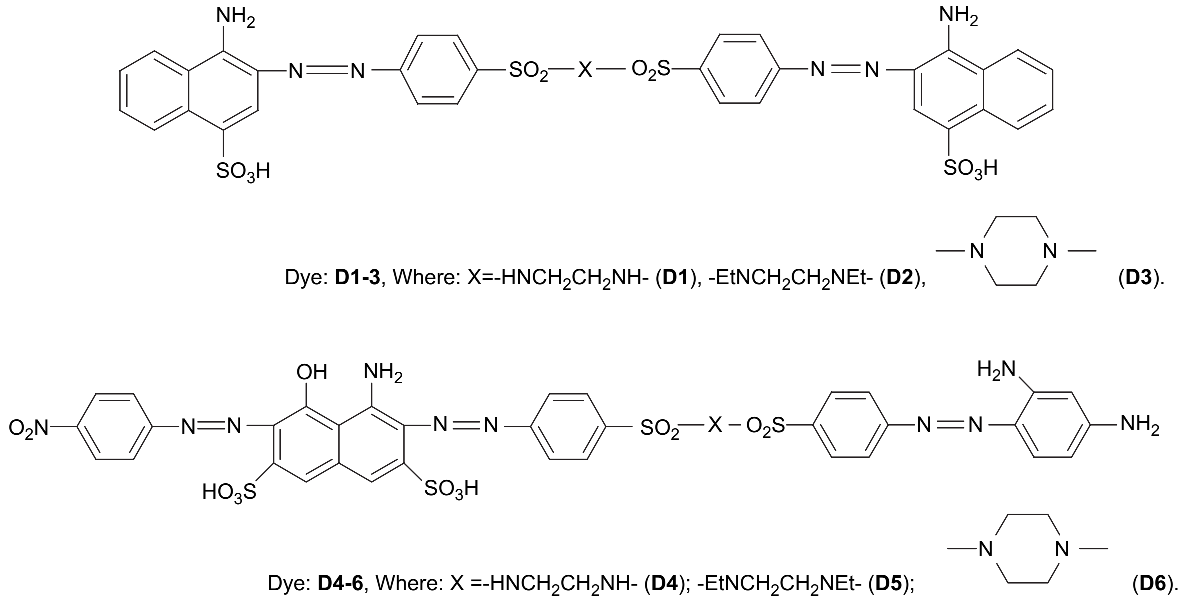


Fig. 2. The bisazo and trisazo dyes based on the diaminobenzene sulfonamide intermediates.

Table 1
Selected bond angles (°) of 1,4-bis-(4-amino-benzenesulfonyl)-piperazine (Fig. 1, **d**)

Angles	(°)	Angles	(°)
O(2)−S(1)−O(1)	117.4(5)	N(1)−S(1)−C(3)	108.4(4)
O(2)−S(1)−N(1)	105.8(4)	C(2)−N(1)−C(1)	110.9(8)
O(1)−S(1)−N(1)	107.9(4)	C(2)−N(1)−S(1)	115.8(6)
O(2)−S(1)−C(3)	108.8(5)	C(1)−N(1)−S(1)	116.0(6)
O(1)−S(1)−C(3)	108.2(4)		

synthesis of the trisazo dyes and the steps are similar, the synthesis of dye **D4** is representative of the chemistry employed. The primary procedure is as follows.

Diazotization of 4,4′-diamino-N,N′-diethyl-bisbenzenesulfonyl ethylenediamine: the process was same as the diazotization in the synthesis of corresponding bisazo dyes.

The first coupling: H-acid (0.01 mol, 3.19 g, 10%w/w) was dissolved by NaOH aqueous solution, then acidulated to pH = 5.5−6, and was added dropwise to the solution of diazotized 4,4′-diamino-diphenylsulfonyl ethylenediamine prepared above. The addition required about 1 h, and the reaction mixture was stirred for 4 h at 10−12 °C and $\text{pH} < 3.0$. After the reaction was complete, the mixture was filtered and the cake was washed with ice-water of $\text{pH} < 3$ to remove residual 4,4′-diamino-diphenylsulfonyl ethylenediamine.

Diazotization of paranitroanilinum: paranitroanilinum (0.01 mol, 1.38 g) was added with 2 mL hydrochloric acid and 10 mL water, heated and stirred for a while to ensure that the paranitroanilinum was dissolved. After that the mixture was cooled to 0−5 °C, sodium nitrite (30%w/w) was added with stirring until it was in excess. When diazotization was complete, the excess nitrous acid was decomposed using aminosulfonic acid.

The second coupling: the diazo salt of paranitroanilinum was added to the product from the first coupling and saturated sodium carbonate was added to adjust the pH to 6−7, and was examined by paper chromatography. The developing agent used is butanol:water:DMF (11:11:13), the termination was noted by the complete disappearance of the monoazo dyes. The product of the second coupling was filtered until the filtrate became bluish violet.

The third coupling: a solution of water (20 mL), *m*-phenylendiamine (0.01 mol, 1.14 g) and hydrochloric acid (1 mL) was added to the product of the second coupling and the reaction mixture was stirred for 2 h at 10−12 °C and pH 3−4. When bisazo dyes disappeared, the pH of the solution containing the product was adjusted to 6−7 using sodium carbonate. Sodium chloride (15%w/w) was added to precipitate the product out, and the filtered cake was dried at 50 °C to give 7.9 g of **D4**. The purification processes of trisazo dyes are similar to the bisazo dyes.

*2.3. Preparation of the single crystal of the intermediate and its determination on an X-ray diffractometer (Fig. 1, **d**)*

2.3.1. Crystallization

Crude 1,4-bis-(4-amino-benzenesulfonyl)-piperazine (0.1 g) was dissolved in DMSO (3 mL), methanol was added dropwise carefully to the upper surface of the solution; 3 days later some turbid substance appeared in the interface of DMSO and methanol, the monocrystals would grow along it; after 6−8 days transparent single crystals were obtained and suitable crystals were selected for X-ray analysis.

2.3.2. Crystal data for 1,4-bis-(4-amino-benzenesulfonyl)-piperazine

$C_{16}H_{20}N_4O_4S_2$; FW = 396.48; monoclinic system, $P2_1/c$ space group, $a = 7.109(2)$ Å, $b = 6.5406(18)$ Å, $c = 18.926(5)$

Table 2
Least-squares planes and deviations from them of 1,4-bis-(4-amino-benzenesulfonyl)-piperazine (Fig. 1, **d**)

	Least-squares plane no. 1 (piperazidine ring)	Least-squares plane no. 2 (left aromatic ring)	Least-squares plane no. 3 (right aromatic ring)
	$-4.4810(0.0373)x + 3.1745(0.0356)y + 13.0541(0.1215)z = 4.2866(0.0756)$	$6.2837(0.0139)x - 2.5764(0.0257)y + 2.3278(0.0716)z = 1.6646(0.0190)$	$6.2837(0.0139)x - 2.5764(0.0257)y + 2.3278(0.0716)z = 6.9469(0.0480)$
Deviation (nm)	C1 0.0000 (0.0000)	C3 −0.0203 (0.0066)	C3A 0.0203 (0.0066)
	C2 0.0000 (0.0000)	C4 0.0139 (0.0073)	C4A −0.0139 (0.0073)
	C1A 0.0000 (0.0000)	C5 0.0100 (0.0074)	C5A −0.0100 (0.0074)
	C2A 0.0000 (0.0000)	C6 −0.0276 (0.0070)	C6A 0.0276 (0.0070)
	N1 0.6797 (0.0137)	C7 0.0216 (0.0072)	C7A −0.0216 (0.0072)
	N1A −0.6797 (0.0137)	C8 0.0023 (0.0069)	C8A −0.0023 (0.0069)
Rms deviation of fitted atoms	0.0000	0.0180	0.0180
	$0.1621(0.0673)x - 0.1040(0.0554)y + 18.6623(0.0320)z = 8.8014(0.0108)$		
Deviation (nm)	N1 0.0000 (0.0000)		
	C1 0.0000 (0.0000)		
	C2 0.0000 (0.0000)		
Rms deviation of fitted atoms	0.0000		
Angle to plane	54.30° (0.67)	73.84° (0.58)	0.00° (0.50)

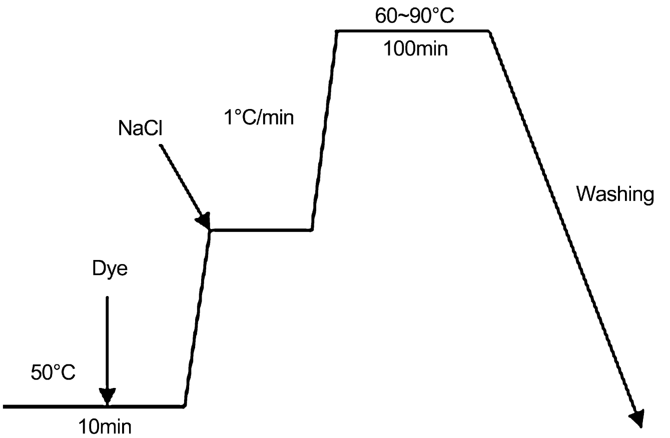


Fig. 3. The dyeing craft curve.

Å; $\alpha = 90°$, $\beta = 98.218(5)°$, $\gamma = 90°$; $V = 870.9(4)$ Å^3; $D_c = 1.512$ Mg/m^3, $Z = 2$.

2.3.3. Crystal structure determination

The single crystal with dimensions of $0.295 \times 0.192 \times 0.061$ mm was mounted on a Bruker Smart APEX-CCD diffractometer with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 293(2) K using an $\omega{-}2\theta$ scan mode in the range of $2.17° < \theta < 25.5°$. A total of 4294 reflections were collected, of which 1603 were unique ($R_{\mathrm{int}} = 0.0694$) and 1362 were observed with $I > 2\sigma(I)$. The final R indices $[I > 2\sigma(I)]$: $R1 = 0.0644$ and $wR2 = 0.1872$, R indices (all data): $R1 = 0.0681$ and $wR2 = 0.1889$, $w = 1/[\sigma^2(F_o^2) + (0.1374P)^2 + 12.80P]$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$. The goodness of fit on F^2 is 1.138. The maximum and minimum peaks in the final Fourier map are 1.545 and −0.545 e/Å^3. Detailed crystal structure data are listed in Tables 1 and 2. The perspective view of the crystal structure and packing diagram are shown in Figs. 5 and 6.

2.4. Dyeing

These trisazo dyes have been applied to cotton fabric and wool by a dyeing process, and the dyeing properties of the dyes were tested.

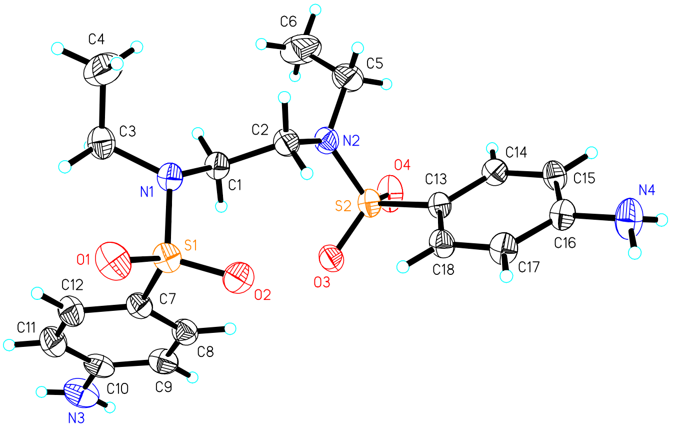


Fig. 4. Structure of 4,4′-diamino-*N*,*N*′-diethyl-bisbenzenesulfonyl ethylenediamine (Fig. 1, **c**).

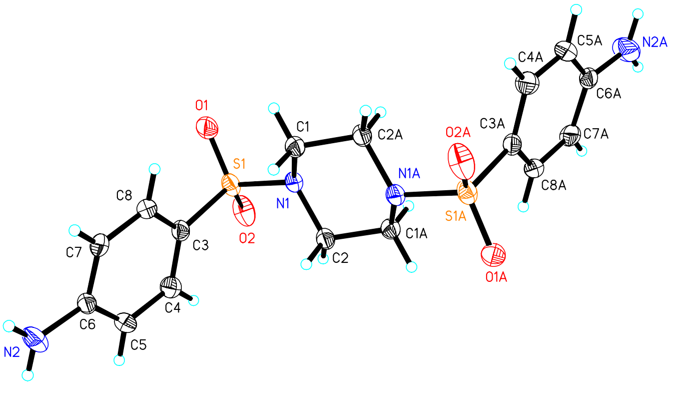


Fig. 5. Structure of 1,4-bis-(4-amino-benzenesulfonyl)-piperazine (Fig. 1, **d**).

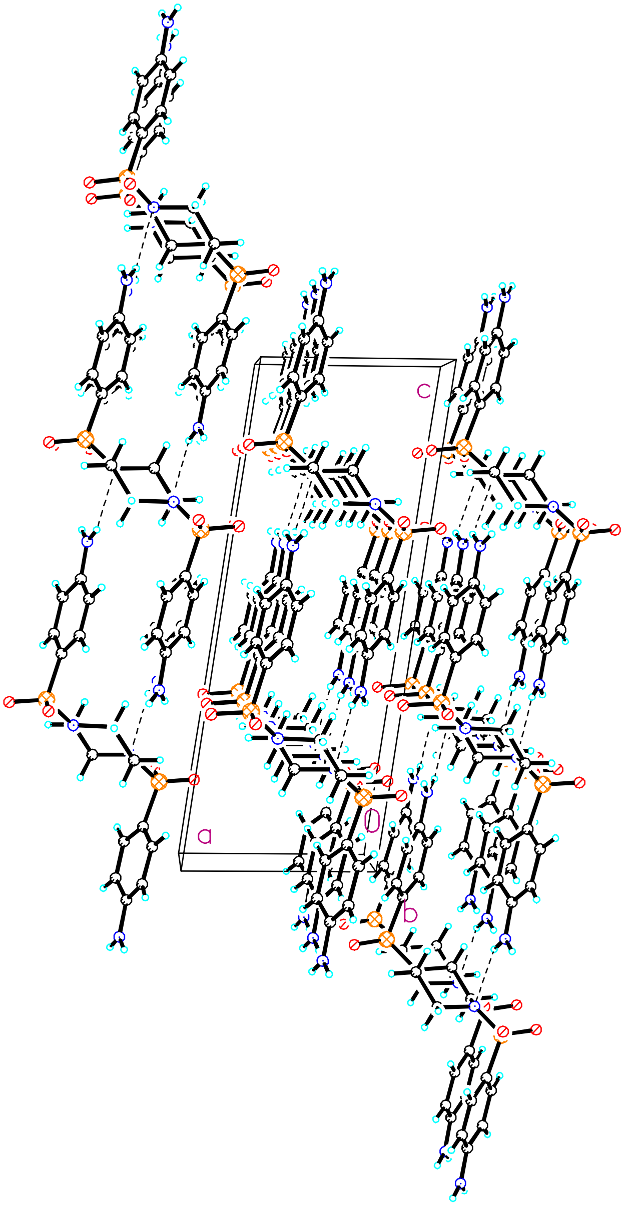


Fig. 6. Packing diagram of 1,4-bis-(4-amino-benzenesulfonyl)-piperazine (Fig. 1, **d**).

Dyeing prescription: dyes: 4% (owf), NaCl: 20 g/L, bath ratio: 1:60. The craft curves are shown in Fig. 3.

The dye exhaustion was calculated from the formula: $\%E = (1 - A_1/A_0) \times 100$ where A_1 = the absorbance of dye solution after dyeing and A_0 = the absorbance of the dye solution before dyeing.

The results are given in Table 5.

3. Results and discussion

3.1. Single crystal structure analysis

3.1.1. Structure of 4,4′-diamino-N,N′-diethyl-bisbenzenesulfonyl ethylenediamine (Fig. 1, *c*)

In our preceding work, we have reported the crystallization method and the crystal data of this intermediate in detail in [40]. It was found that the dihedral angle between benzene plane no. 1 (C7–C12) and benzene plane no. 2 (C13–C18) of the sulfonamide intermediate is 113.49°, which is to be twisted to 66.51°, so that the two benzene rings are not coplanar (Fig. 4).

3.1.2. Structure of 1,4-bis-(4-amino-benzenesulfonyl)-piperazine (Fig. 1, *d*)

The bond angle of O(1)–S(1)–O(2) in this crystal is increased to 117.4° (Table 1) due to the repulsion of the lone pair of electrons; while angles O(1)–S(1)–N(1) and O(2)–S(1)–N(1) have to be pressed and narrowed down to 107.9° and 105.8°, respectively. The angles O(1)–S(1)–C(3) and O(2)–S(1)–C(3) are kept 108.2° and 108.8°, respectively, close to a normal sp^3 bond angle.

Note that the deviation of N1 and N1A is 0.6797 and −0.6797 nm, respectively, and the deviation of C1, C2, C1A and C2A are all 0.0000 nm (Table 2). So we can imagine that C1, C2, C1A, C2A are coplanar which can also be seen from Fig. 5. But N1 and N1A deflect to the opposite direction, so it should be in the "chair conformation". Table 2 shows that the plane no. 2 (C3–C4) is twisted to 73.84° relative to plane no. 2 (C3A–C4A), and the plane no. 1 (C1–N1–C2) is to be twisted to 54.30°, and accordingly, the plane (C1A–N1A–C2A) is to be twisted to −54.30°. The phenyl rings of the two sulfonamide groups are positioned like two lids [36] over the piperazidine ring (Fig. 6).

3.2. Spectrophotometric properties of azo dyes based on intermediates (Fig. 1, *b*, *c* and *d*)

A group of disazo red dyes and trisazo black dyes have been obtained, respectively. The UV spectrophotometric properties of these bisazo dyes were measured by solvent effect and pH effect. Measurements were performed with a UV Spectrophotometer Cary 100. The results are given in Table 3 and shown in Figs. 7–12. Dyes **D1–3** display one major absorption band, in contrast, **D4–6** display two peaks in accordance with the fact that two individual monoazo dyes located on both the sides of the trisazo dyes produce a mixed color.

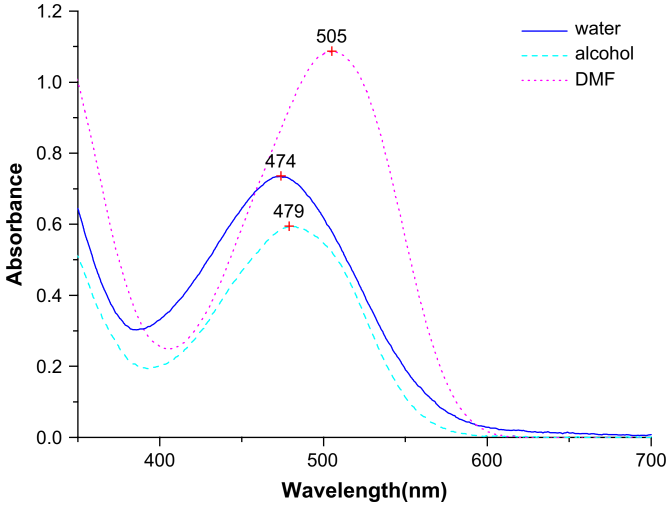


Fig. 7. Absorption spectra of dye **D1** in different solvents: (—) water, (- - -) alcohol, and (···) DMF; concentration of dye: 5×10^{-5} mol/dm^3.

It can be found in Figs. 7–9 that the λ_{max} of the dyes **D1–3** in different solvents are substantially in the order, **D2**, **D3** > **D1**. The result is expected since **D2** and **D3** contain electron-donating groups on the nitrogen atom of sulfonamide bridged groups, so that the λ_{max} of dyes **D2** and **D3** showed slight bathochromic shift relative to dye **D1**.

Overall, dye **D3** had higher tinctorial strength, and was not easily aggregated in solvents because the two benzene rings on both the sides of piperazidine sulfonamide bridge group of the corresponding intermediate (Fig. 1, **d**) are to be twisted to 73.84°. Furthermore, the molecular configuration of dye **D3** shows the weakest linearity. Likewise, the dihedral angle between the two benzene rings in the intermediate (Fig. 1, **c**) is 113.49°. Not only the two benzene rings are not coplanar, but also the bridged group distorts sharply (66.51°). It was observed that dye **D2** gave the highest tinctorial strength in

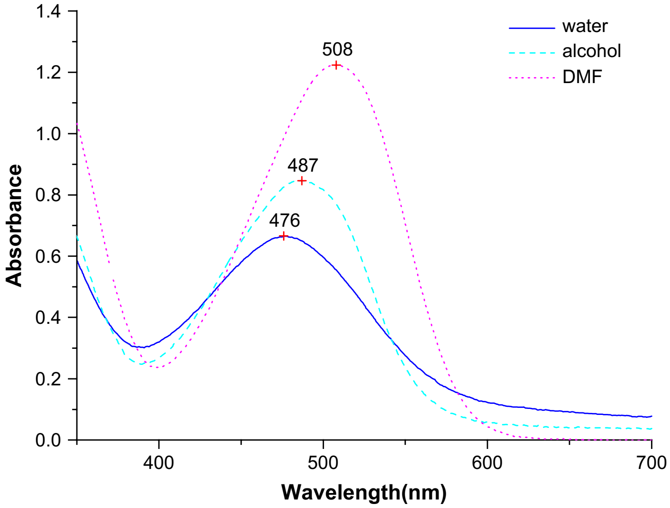


Fig. 8. Absorption spectra of dye **D2** in different solvents: (—) water, (- - -) alcohol, and (···) DMF; concentration of dye: 5×10^{-5} mol/dm^3.

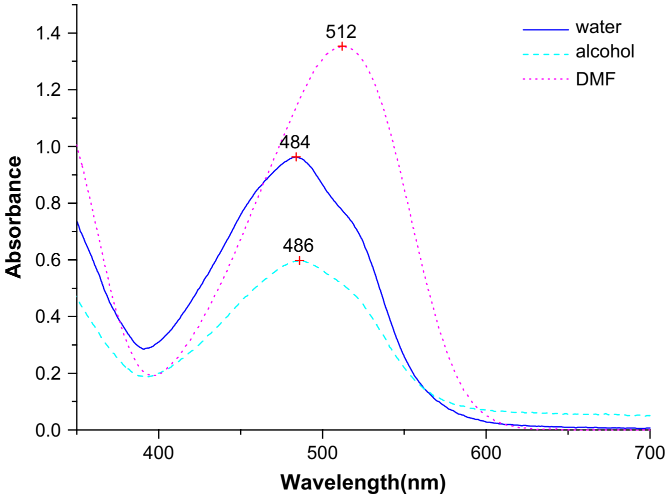


Fig. 9. Absorption spectra of dye **D3** in different solvents: (–) water, (- - -) alcohol, and (···) DMF; concentration of dye: 5×10^{-5} mol/dm^3.

alcohol. Dyes based on all the three intermediates show significant large bathochromic shifts in the strong polar solvent (DMF).

The effect of pH upon absorption spectra of dye was measured by a UV spectrophotometer carried out in water at pH = 7, 1–2, 12–13, respectively. All the three examined disazo dyes presented one main visible absorption band in the case of pH = 7 and their corresponding colors were orange to red. Dye **D1** showed an obvious hypsochromic effect from neutral to alkaline condition, its λ_{max} being 474 and 447 nm, respectively, ($\Delta\lambda_{max} = 27$ nm). The alkaline effect of dye **D2** resulted in a bathochromic shift of absorption band ($\Delta\lambda_{max} = 16$ nm), while λ_{max} of dye **D3** is changed by only 4 nm in a bathochromic way. The results represented that dye **D3** had the highest stability in alkaline condition; meanwhile, dye **D1** displayed inferior stability. The plausible reason is that the sulfonamide groups (–SO_2NH–) are ionized at pH 12–13 and the spectrum is shifted in a hypsochromic way (Fig. 10). Whereas all the three bisazo dyes showed distinct UV spectrophotometric change effects under acidic conditions: the tinctorial strength of dye **D1** decreased apparently and its absorption spectra simultaneously split into two peaks at $\lambda_{max} = 423$ and 492 nm; the acidity effect caused a bathochromic shift of dye **D2** to λ_{max} 524 nm, and meanwhile its tinctorial strength decreased; similarly, it caused a bathochromic shift of dye **D3** to λ_{max} 539 nm. Contrary to **D1** and **D2**, the tinctorial strength of dye **D3** increased. In many investigations, these effects were considered to be caused by the change of equilibrium due to tautomerism between the azo and hydrazone configurations, the change of acid–base equilibrium, or the aggregation of the dyes in solution [37]. Especially, when hydrochloric acid was added into the dye solution to

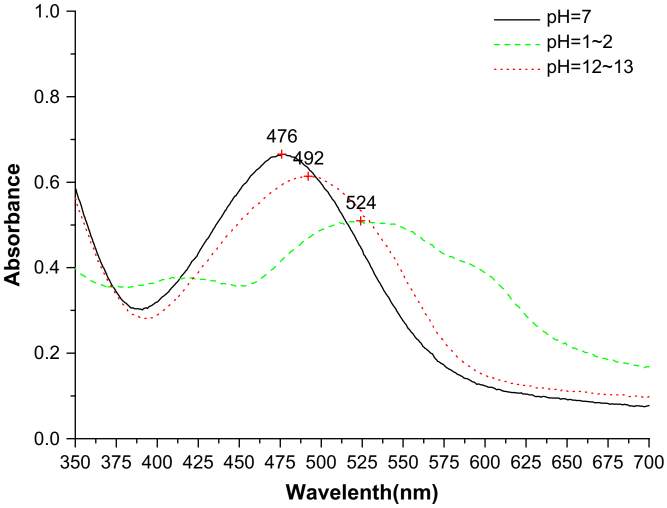


Fig. 11. Absorption spectra of dye **D2** in different pH conditions: (–) water, pH 7; (- - -) water, pH 1–2; (···) water, pH 12–13; concentration of dye: 5×10^{-5} mol/dm^3.

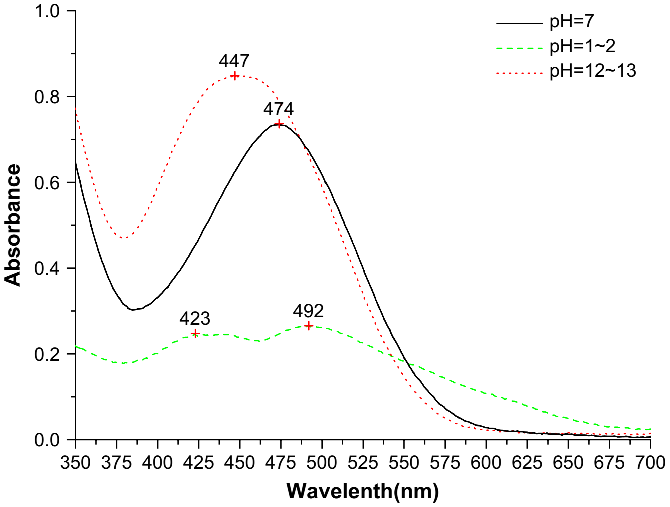


Fig. 10. Absorption spectra of dye **D1** in different pH conditions: (–) water, pH 7; (- - -) water, pH 1–2; (···) water, pH 12–13; concentration of dye: 5×10^{-5} mol/dm^3.

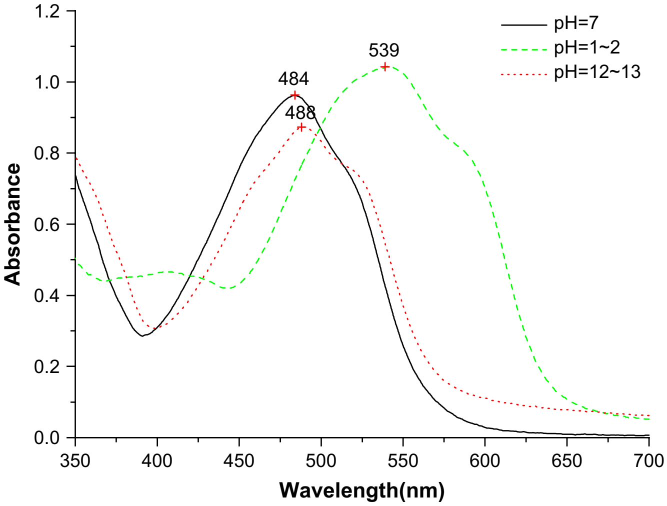


Fig. 12. Absorption spectra of dye **D3** in different pH conditions: (–) water, pH 7; (- - -) water, pH 1–2; (···) water, pH 12–13; concentration of dye: 5×10^{-5} mol/dm^3.

Table 3
Spectrophotometric properties and colors of azo dyes based on intermediates (Fig. 1, **b**,**c** and **d**)

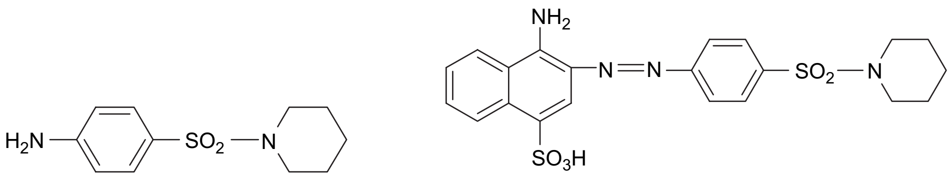
Dye	Molecular weight	Water			Alcohol			DMF		
		λ_{max} (nm)	ε_{max} ($dm^3 mol^{-1} cm^{-1}$)	Color	λ_{max} (nm)	ε_{max} ($dm^3 mol^{-1} cm^{-1}$)	Color	λ_{max} (nm)	ε_{max} ($dm^3 mol^{-1} cm^{-1}$)	Color
D1	838	474	14 720	Golden	477	11 900	Golden	505	21 740	Claret
D2	894	476	13 320	Orange red	487	16 920	Orange red	506	25 060	Brilliant red
D3	864	484	19 280	Blonde red	486	11 940	Blonde red	512	27 060	Scarlet
D4	968	461, 581	28 540	Red black	475	13 440	Red brownish	479, 584	51 260	Purple
D5	1024	478, 585	21 480	Navy blue	470, 591	15 300	Light blue	476, 597	53 680	Mazarine
D6	994	500, 670	31 720	Gray black	456, 591	14 560	Yellow blue	450, 592	56 940	Blue black

Concentration of dye: 5×10^{-5} mol/dm^3.

adjust the to pH 1–2, the configuration of dye was apt to form hydrazone tautomer and its λ_{max} would cause a bathochromic shift, moreover, along with the increase of hydrogen-ion concentration in dye solution, dye molecules get more likely aggregated with each other to form micellars. The phenomenon that was observed in our study is that flocculate appeared in the dye solutions when the pH decreased and bordeaux floc was precipitated in **D1** solutions, while mauve and pink homologue appeared in **D2** and **D3** solutions, respectively. It has been revealed that pH-induced color change of dye solution is known as halochromism, which is caused by protonation of the azo bond and by resonance interactions [38].

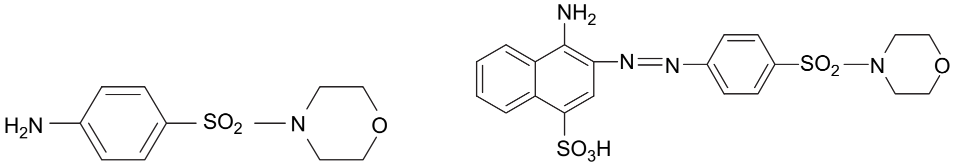
In order to investigate dye **D3** deeply, we have designed and synthesized another four monoazo dyes (Fig. 13, dyes **D7–10**), and their spectrophotometric properties were determined and compared with dyes **D1** and **D3**.

UV–visible spectra of the mono- and bis-azo dyes based on different sulfonamide intermediates were observed. On comparing λ_{max} of **D3**, **D7** and **D8** in Table 4, it is well known that their λ_{max} are very close and they exhibit a similar color.



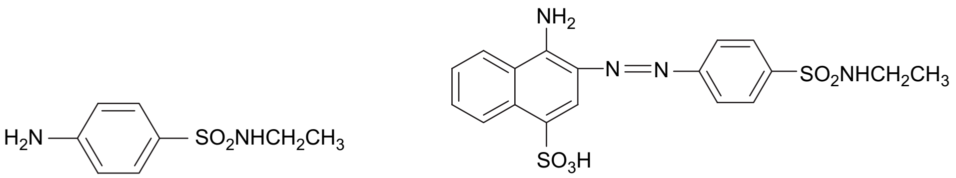
1-sulfanilyl-piperidine (**e**)

Dye: **D7**



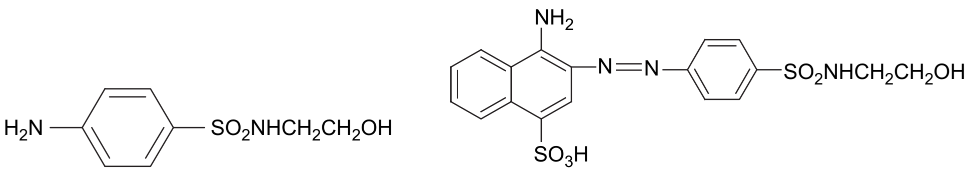
4-sulfanilyl-morpholin (**f**)

Dye: **D8**



sulfanilic acid ethylamide (**g**)

Dye: **D9**



sulfanilic acid-(2-hydroxy-ethylamide) (**h**)

Dye: **D10**

Fig. 13. Several aminobenzene sulfonamide intermediates and the derived monoazo dyes.

Table 4
Spectrophotometric properties of monoazo dyes **D7–10** in contrast with disazo dyes **D1** and **D3**

Dye	λ_{max} (nm)	Absorbance	ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)	Color	Dye	λ_{max} (nm)	Absorbance	ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)	Color
D3	484	0.964	19 280	Orange red	**D1**	474	0.736	14 720	Golden
D7	477	0.661	13 220	Orange	**D9**	478	0.665	13 300	Orange
D8	480	0.664	13 280	Orange	**D10**	473	0.649	12 980	Orange

Solvent: water, pH: 7, concentration: 5×10^{-5} mol/L.

Moreover, the absorption intensity of dye **D3** is nearly 1.5 times that of **D7** and **D8** because the color of dye **D3** could be matched by two similar individual monoazo dyes located on both the sides of the sulfonamide bridged group of the intermediate (Fig. 1, **d**), and the tinctorial strength of dye **D3** would increase obviously. However, compared with dyes **D1**, **D9** and **D10**, their λ_{max} are also similar, but the absorption intensity of **D1** is as much as **D9** and **D10**.

3.3. Dyeing and fastness properties

Dyes **D4**, **D5** and **D6** were applied to dye cotton and wool fibre, and the results are given in Table 5. It can be seen that the dye-uptake of the shades on cotton fibre are in the following order: **D4** > **D5** > **D6**, in contrast to the results of the dye-uptake on wool fibre. The better the coplanarity of the molecular configuration, higher is the exhaustion on the cellulosic fibre [37]. The linearity of **D4** is better than **D5** and **D6**, so it has high substantivity to cellulosic fibers. In dye **D5**, the configuration of the torsion of bridged group and the non-planarity of benzene rings lead to hindrance of electron atmosphere in the whole intermediate or dye molecule, so the color of the azo dyes can be matched intramolecularly, and the dye molecules will be more pliant [39]. In dye **D6**, the non-planar configuration leads to a lower substantivity on cotton fibre, but dye **D6** can be employed as an acid dye, and is soluble in water and would be used for dyeing wool, leather and polyamide fibres.

4. Conclusions

In conclusion, we have successfully developed and synthesized several diaminobenzene and aminobenzene intermediates based on benzene sulfonamide and a series of azo dyes derived therefrom, which have been used in dyeing application and are evaluated by UV–vis analysis. In addition, the crystal structures of the new intermediate (Fig. 1, **d**) were determined by X-ray diffraction, and the relationships between structure and properties of these intermediates and their corresponding azo dyes were investigated. The results show that the two benzene rings on both the sides of sulfonyl amide bridged group in diaminobenzene intermediates conjugated systems are twisted, so their configuration are not coplanar, further the non-coplanarity makes the derived azo dyes match colors intramolecularly. In particular, compared with the dyes prepared from other known diaminobenzene sulfonamide intermediate (Fig. 1, **a**, **b**), the dyes derived from the synthesized intermediates in our study (Fig. 1, **c**, **d**) have better resistance to aqueous alkali, meanwhile they may be classified as acid dyes and can be efficiently applied to the wool, leather and polyamide fibres by dyeing process.

Table 5
Dyeing and fastness properties of azo dyes **D4–6**

Dye	Exhaustion (%)		*K/S*		Washing fastness		Dry rubbing fastness	
	Cotton	Wool	Cotton	Wool	Cotton	Wool	Cotton	Wool
D4	81.83	83.81	10.842	11.112	4	3–4	4	5
D5	76.50	93.52	9.487	13.254	3–4	4	4	4
D6	63.39	97.32	7.571	14.378	3–4	4–5	4	5

Acknowledgements

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