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Synthesis and application of direct black dyes containing 4,4'-diaminodiphenyl sulfonamide☆

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Abstract

4, 4'-Diaminodiphenyl sulfonamide and black dyes based on this intermediate were synthesised. When mixtures of the black dyes were used to dye silk, the blackness at 5% shade depth was C. I. Direct of Black 38. Their exhaustion and fastness to light and washing was better than that of C. I. Direct Black 38. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 4, 4'-Diaminodiphenyl sulfonamide; Intermediate; Direct black dyes; Sysnthesis; Dye application

1. Introduction

It is well known that benzidine-based dye manufacture is prohibited due to the carcinogenicity of the precursor. Thus, extensive research has been conducted to find alternative dyes. All previous research work can be divided into two groups: one involves the use of benzidine homologs that are less toxic than benzidine and the second involves the use of diamino compounds that are not homologs of benzidine. The latter has received greater attention because the benzidine structure is avoided entirely. It has been reported [1–4] that 4, 4'-diaminodiphenyl sulfonamide (Scheme 1) could be substituted for benzidine in the synthesis-direct black dyes.

Although direct dyes are normally used on cotton, they can also be used to dye silk, especially in green and black shades. The properties of azo dyes containing 4, 4'-diaminodiphenyl sulfonamide (DADPSA) are very good when used on silk. Consequently, this paper deals with the synthesis of DADPSA, direct black dyes based on DADPSA, and the application of the new dyes to silk.

2. Experimental

2.1. Synthesis of DADPSA

2.1.1. Synthesis of p-acetamidobenzenesulfonyl chloride

2.1.1.1. Procedure. Chlorosulphonic acid 293g (2.49 mol) was added to a 500 ml three-necked flask equipped with a stirrer, thermometer and a reflux condenser connected to a HCl trap. The reagent was cooled to 5°C in an ice bath, and acetanilide 68.26g, (0.5 mol) was added slowly, while stirring at 5°C. The mixture was heated to 60°C

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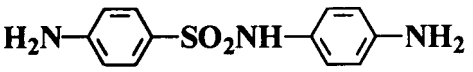


Scheme 1.

and kept for 2 h. As a test for reaction progress, Sodium hydroxide (1 ml 20%) was added to a small amount of reaction mixture in a test tube. The tube was heated, and cooled to room temperature. If no precipitate appeared, the reaction was deemed complete. After 1000g ice was added with stirring, the precipitate was collected by filtration, washed with cold water until neutral, dried and stored under vacuum. The reaction afforded 90g (77%) of acetamidobenzenesulfonyl chloride as a white powder M.p. 148-149°C (lit. 149°C [5]).

2.1.2. Synthesis of 4, 4'-diacetamido diphenyl sulfonamide

2.1.2.1. Procedure. Acetone (200ml) was added to p-aminoacetanilide (50g, 0.33 mol) in a round bottomed flask. After dissolution, p-acetamidobenzenesulfonyl chloride (85g, 0.36 mol) dissolved in acetone (150ml) was added to the former mixture. Pyridine (10ml) was added after 1 h and 2 h, respectively. Reaction progress was assessed after 5 h. When the reaction was complete, acetone was decanted and water (200ml) was added with stirring and beating. The product mixture was filtered, washed and dried. Yield of 4,4'-diacetamido diphenyl sulfonamide was 104.5g (96.7%). The compound was recrystallized from benzene, and evaluated by element analysis as PE2400 II.

Testing of reaction progress was conducted by hydrolysing a small amount of the reaction mixture with hot Sodium hydroxide (2 ml, 20%). After cooling, the solution was spotted on chromatographic paper and developed in an eluent containing butanol: pyridine: and ammonia (1:1:1). The Rf of 4,4'-diacetamidodiphenyl sulfonamide was 0.89.

2.1.3. Synthesis of DADPSA

2.1.3.1. Procedure. The product from the previous step was added to water (200ml). 150 ml 20% (w) Sodium hydroxide (150 ml, 20%) was slowly added with stirring. The mixture was refluxed for 2 h and cooled. The precipitate was collected by filtration to give DADPSA 75 g (89.2%). Recrystallization from alcohol and water gave M.p. 136.6–137.5°C (lit. 138–139°C[6]).

2.2. Synthesis of dye D_1

Diazotization of DADPSA: DADPSA (6.8 g, 0.02 mol) was dissolved in HCl (15 ml, 36% w) and water (30 ml) was added. At 0–5°C, nitrite (30%) was added dropwise until it was in excess. The reaction was stirred cold for 30 min and excess nitrous acid was decomposed with urea.

The first coupling: Al pH 4.5 (55 ml, 10% w H-acid) was added dropwise to the solution of diazotized DADPSA prepared above. The addition required about 30 minutes, and the reaction was stirred for 6 h at 8–10°C and pH 2. After the reaction was complete, the mixture was filtered and the cake was washed with water of pH = 3, to remove residual DADPSA.

Diazotization of aniline: Hydrochloric acid (5 ml, 36% w) and ice water (80 ml) were added to aniline (1.6 g) and the mixture was cooled to 0–5°C. Sodium nitrite (30% w) was added with stirring until it was in excess. When diazotization was complete, the excess nitrous acid was decomposed by using urea.

The second coupling: The diazo salt of aniline was added to a viscious solution of the product from the first coupling and saturated sodium carbonate was added to adjust the pH to 7–8. The reaction stirred for 2 h at 5–10°C, and was examined by a paper chromatography. Using butanol: pyridine: conc. ammonia (1:1:1). When the monoazo dyes (Rf = 0.57) was fully converted to product (Rf = 0.43), the pH of the solution was adjusted to 4 by adding hydrochloric acid. The product of the second coupling was salted out, filtered and the cake was mixed thoroughly with 200 ml ice water.

The third coupling: A solution of water (20 ml) m-phenylendiamine (1.8 g) and conc. HCl (1 ml) was added to the product of the second coupling and the reaction was stirred for 2 h at 10–15°C and pH 3–4. When disazo dyes (Rf = 0.43) disappeared, the pH of the solution containing product (Rf = 0.29) was adjusted to 6.5–7 using sodium carbonate. Sodium chloride was added to precipitate the product out, and filtered cake was dried below 80°C to give 21 g D_1.

2.3. Synthesis of dye D_2

The process differed from synthesis of dye D_1 only in the third coupling step. β-Naphthol was used and the pH of the reaction was 8–9.

2.4. Dyeing silk

Depth of shade: W% (according to weight of fibre)
Anhydrous Sodium Sulfate: 50–60 g/l
Bath ratio: 1:50

Dyeing method: Silk fabric (?g) was immerged into water (?ml) 30°C. After 5 min, 1/3 of total anhydrous sodium sulfate was added to the dyebath and kept for 15 min. The dyebath was heated to 60°C in 15 min and then another 1/3 of total salt was added and kept for 15 min. The dyebath was heated to 85°C in 30 min and the left salt was added. Then, the dyebath was heated to 90°C and kept for 60 min.

Aftertreatment: The dyed fabric was removed from the dyebath, rinsed using 50°C water and treated with Fixative solution which consisted of acetic acid (2g/l, 30%) and 100g/l Fixative Y (dicyandiaminde-formaldehyde resin, Shanghai auxiliary agents factory) for 30 min at 30°C, bath ratio 1:20. The fabric was rinsed using 50°C water and dried in room temperature.

3. Results and discussion

3.1. Synthesis of DADPSA

In the synthesis of p-acetamidobenzenesulfonyl chloride, chlorosulfonation employed excess chlorosulphonic acid with the molar ration of 1:5. The reaction rate was relatively fast and the yield was 77%. Optimum reaction temperature was 60°C, as lower temperature led to a slow reaction rate and an increase in the ortho isomer. High temperature led to decomposition of chlorosulphonic acid and p-acetamidobenzenesulfonyl chloride. p-Acetamidobenzenesulfonyl chloride is not stable, so it cannot be kept for a long time even in vacuo.

Reaction of p-acetamidobenzenesulfonyl chloride and p-aminoacetanilide was carried out in acetone, a medium that enhanced the separation of product and starting materials. The element analysis data supported the structure (Table 1).

The hydrolysis of 4, 4'-diaminodiphenyl sulfonamide was accomplished in hot sodium hydroxide solution. Amino value (6.036×19^{-3} mol/g) was determined by diazotization of DADPSA using 0.1004N sodium nitride solution.

The infrared absorption spectogram of DADPSA (Fig. 1) contains peaks at 1160 cm^{-1} and 1320 cm^{-1} which indicate the existence of SO_2NH group, a peak at 3300 cm^{-1} which indicates the presence of NH_2, a peak at 1285 cm^{-1} which indicates the stretching vibration of a peak at 840 cm^{-1} which indicates p-substitution. The element analysis data also supports the structure (Table 1).

3.2. Synthesis of azo dyes containing DADPSA

Using DADPSA and H-acid, three direct black dyes were synthesised, the structures and λ_{max} of which are shown in Table 2.

Since there are multiple steps in the synthesis of D_1–D_3, it is very important to control the reactions carefully to avoid forming impurity dyes and dull colors. The synthesis of dye D_1 is representative of the chemistry employed.

Table 1
The element analysis of intermediates

Intermediates	Element amount							
	C		H		N		S	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
4,4′-Diaceteamido diphenyl sulfonamide	55.01	55.32	4.89	4.93	12.13	12.10	9.19	9.23
4,4 ′-Diamino diphenyl sulfonamide (DADPSA)	54.42	54.73	4.95	4.98	16.03	15.96	12.14	12.18

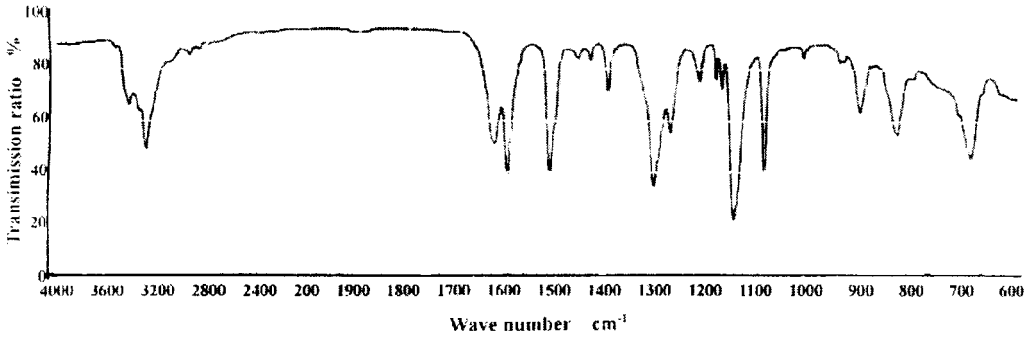
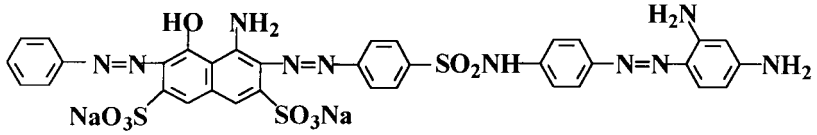
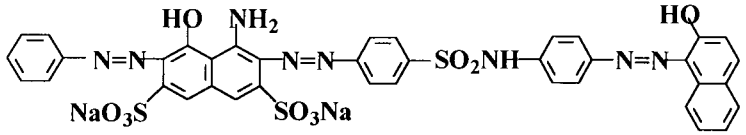


Fig. 1. IR of DADPSA.

Table 2
Structures and λ_{max} of DADPSA-based dyes

No.	Structures	λ_{max} (nm)
D_1		600∼610
D_2		485–490, 600
D_3		610

In the diazotization of DADPSA, the amount of acid used was more than 5.0 mole per mole DADPSA, in order to protect the product. A slight excess of sodium nitride was used for complete diazotization. The amount of the diazo salt of DADPSA was calculated from the amount of sodium nitride consumed, and was used to determine the quantity of couplers employed in subsequent steps.

In the coupling step involving H-acid, if pH value was too high, coupling *ortho* hydroxyl group also occurred. To decrease impurities acidified H-acid was added to a solution of the diazo salt fast initially, then slowly. The first coupling occurred *ortho* to the amino group of H-acid, and required 8–10°C and pH 2.

In the diazotization of aniline the amount of acid used was 3 mole per mole aniline and the temperature was 0–5°C. Use of pH 7–8 gave coupling *ortho* to the hydroxyl group of H-acid. To increase the purity of the final product, the solution from the second coupling was acidified (pH = 4) and the product was salted out and filtered. The cake was used in the final step.

The coupling between the product of the second coupling and m-phenylenediamine was relatively easy. The reaction conditions for D1 and D3 were 10–15°C and pH 3–4 and for D2 pH 7-8 was used. The reaction time was about 2 h. The progress of the reaction was monitored by paper chromatography.

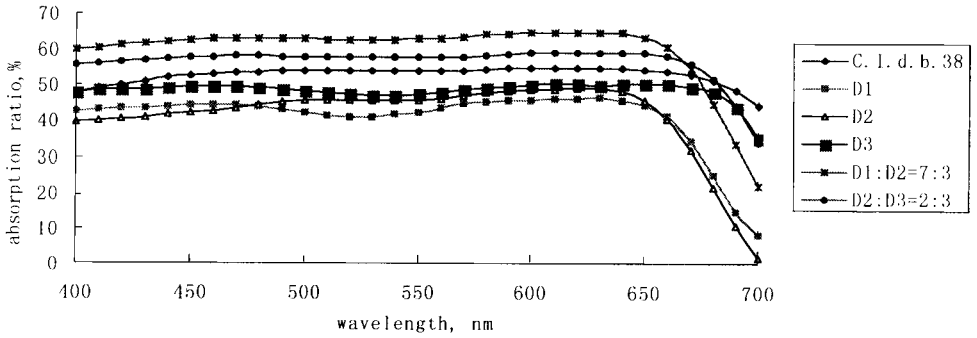


Fig. 2. Absorption spectra of dyed silk (5% ?).

Table 3
The fastness properties of dyes on silk

Dyes	Washing fastness			Light (normal) silk
	Alteration	Staining		
		Silk	Cotton	
D1:D2 = 7:3	4	3∼4	3	5∼6
D2:D3 = 2:3	4	3	4	5∼6
C.I. Direct Black 38	4	2∼3	2	5

The coupling ability of diazobenzene derivatives with electron-acceptors is greater than that of diazo compounds with electron-donors. For example, the relative couple rates for p-$N_2^+C_6H_4SO_3^-$(I), $X^-N_2^+C_6H_5$(II) and p-$X^-N_2^+C_6H_4OCH_3$(III) is 13:1:0.1[7]. Therefore, only p-$N_2^+C_6H_4SO_2^-$ R^1 takes part in the first coupling. The product of the first reaction between H-acid and bis-diazo salt of DADPSA is only the monoazo compound formed by coupling *ortho* to the amino group of H-acid. The coupling product is precipitate before the second coupling. Redissolving the product at pH 8 produces the corresponding hydroxyazo compound $R^2HNC_6H_4N=N\text{-}OH$, which cannot couple. In the third coupling, the pH was adjusted to 3–4 and $R^2HNC_6H_4N=N\text{-}OH$ [8] changed back into $R^2HNC_6H_4N=N^+X^-$. Coupling to m-phenylenediamine was then achieved.

3.3. Dyeing silks with azo dyes containing sulfonamide as link group

The synthesised dyes were applied at shade depths of 1 and 5% and the absorption spectra of dyed silk were recorded. Comparing the absorption spectra of D_1, D_2, D_3, and C.I. direct black 38, the spectrum of D_3 is found to be better than D_1 and D_2, and similar to C.I. Direct Black 38 in the 650–700nm region (Fig. 2).

Individually, neither of the new dyes gave a pure black at 5% shade depth. The colour of D_2 was a little red while that of D_1 and D_3 was a little green. In addition, exhaustion of single dyes was not as good as mixtures. Thus, mixed dyeing if D_1, D_2 and D_3 were used to give good blackness and high % exhaustion. According to test methods GB 3921-83 and GB 413-78, the fastness properties of dyed silk after applying mixtures are shown in Table 3.

Colour fastness of the synthesized dyes to soap washing and light was better than that of C.I. Direct Black 38.

4. Conclusion

(1). 4, 4-diaminodiphenyl sulfonamide was synthesized and the overall yield for the three steps was 66.4%.

(2). Three direct black dyes were synthesized from 4, 4-diaminodiphenyl sulfonamide, when mixtures of three dyes were applied to silk, blackness was similar to that of C.I. Direct Black 38 and the % exhaustion are better than C.I. Direct Black 38 when the shade depth was 5%. Fastness properties of mixture of the synthesized direct black dyes were better than C.I. Direct Black 38.

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