

Trisazo Direct Black dyes based on nonmutagenic 3,3'-disubstituted benzidines

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Abstract

Using 3,3'-di-*n*-propoxybenzidine, 3,3'-di-*n*-butoxybenzidine and 3,3'-di-(β -hydroxyethoxy)-benzidine as diazo components, and 2,4-diamino-*n*-propoxybenzene, 2,4-diamino-*n*-butoxybenzene and 2,4-diaminophenyl- β -hydroxyethyl ether as coupling components, a series of new black trisazo dyes were prepared as homologues of C.I. Direct Black 38. Assessment of the resultant dyes indicated that their color and the dyeing properties were comparable or slightly better than the properties of C.I. Direct Black 38. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Nonmutagenic; Benzidine intermediates; Direct Black dyes; Synthesis; Dye application

1. Introduction

C.I. Direct Black 38 (**1**) was one of the most important commercial direct dyes during the first half of 20th century. It was characterized by an economical price, a beautiful black hue and ease of application. However, because it is produced from benzidine (**2**), a known human carcinogen, all industrialized nations have stopped producing it. Similarly, benzidine homologues such as **3** were used prior to their identification as cancer suspect agents [1]. The aforementioned observations have led dye chemists to search for another simple aryldiamine as a benzidine substitute.

In the search for nongenotoxic benzidine replacements, a number of approaches have been

developed [2]. Studies in this area have included the synthesis of diamines (**7**) that contain a bridging group between the two phenylene rings [3]. In all but one case, extended conjugation is disrupted, causing a distinct hypsochromic effect. Moreover, most of these diamines give dyes of lower affinity for cellulose than benzidine-based dyes, and their synthetic routes lead to appreciably higher costs. Consequently, these diamines are not suitable benzidine substitutes.

Similarly, heterocyclic diamines have been examined as potential benzidine substitutes. For example, 5,5'-diamino-2,2'-bipyridine and 4,5'-diamino-2,2'-phenylpyridine were used in the synthesis of C.I. Direct Black 38 analogues [4]. While the dyes were interesting from an academic viewpoint, it is clear that this approach is not technically feasible.

Non-carcinogenic alkyl and alkoxy benzidine analogues have been developed, taking advantage of results from a prior study, which showed that

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the mutagenicity of *meta*-phenylenediamine could be lowered or eliminated by incorporating bulky alkyl or alkoxy substituents *ortho* to an amino group in the parent structure [5]. Subsequently, diamines **4** and **5** were employed in the synthesis of nonmutagenic water-soluble disazo dyes such as **8** [6–8]. In closely related studies, nonmutagenic tetra-substituted benzidine analogues have been used in the synthesis of organic pigments [9,10].

In the present paper, we report the synthesis and evaluation of new black trisazo dyes (**9**) based on benzidine analogues **4–6**. Nonmutagenic substitutes for *meta*-phenylenediamine (cf. **11**) were also used in the syntheses.

2. Experimental

2.1. General

2-Nitrophenol and 2,4-dinitrochlorobenzene were obtained from Jilin Chemical Engineering Company, and were chemical grade reagents. The sample of C.I. Direct Black 38 was provided by Tianjin Dyestuff Plant, while the other chemicals were purchased from Tianjin Chemical Plant and were analytical grade reagents. Melting points were recorded on a WSR-1A apparatus and are uncorrected. NMR spectra and mass spectra were recorded on a TDEL FX90Q spectrometer and a Hewlett Packard HPLC/CE-ESI (APCI)-MS spectrometer, respectively. The reflectance spectra of dyed cotton were plotted using a Hunterlab UltraScan TMXE color measuring and matching system (standard mode: RSIN, areaview: large, portsize: 25.4 mm).

2.2. Synthesis of 2-nitroalkoxybenzenes

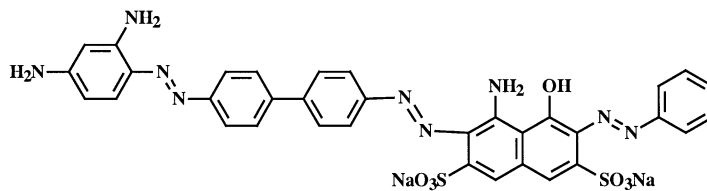
The methods employed were the same as reported previously [9]. For instance, in the synthesis of 2-nitro-*n*-propoxybenzene, 2-nitrophenol (16.6 g, 0.117 mol) was alkylated in acetone (200 ml) with *n*-bromopropane (21.6 g, 0.176 mol) in the presence of K_2CO_3 (16.2 g, 0.117 mol). The crude product was purified by vacuum distillation (b.p. 112 °C/3 mmHg) to give a clear, pale yellow liquid (18.6 g, 88% yield).

Similarly, 2-nitro-*n*-butoxybenzene was prepared using *n*-bromobutane. The pure product was obtained as a pale yellow liquid, b.p. 117 °C / 4 mmHg (19.4 g, 85% yield). 2-Nitro-(β -hydroxyethoxy)benzene was prepared from 2-chloroethanol to give a red liquid (15.8 g, 73.6% yield), which could be used without distillation.

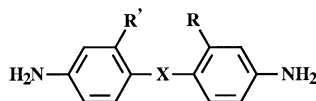
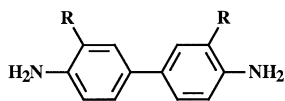
2.3. Synthesis of 3,3'-di-alkoxybenzidines

The procedure used was the same as reported previously [9]. For instance, a solution of 2-nitro-*n*-propoxybenzene (5.0 g, 0.028 mol) in ligroin (20 ml, b.p. 90–120 °C) was stirred at 25 °C, as zinc (4.0 g, 0.061 mol) was added. The mixture was heated to 70 °C and 0.3 ml 50% (w/w) NaOH (5.7 mmol) and 0.3 ml water were added slowly, causing a temperature rise to 86 °C. When the exotherm subsided, additional zinc (2 g, 0.030 mol) was added, followed by 10% (w/w) NaOH (1.1 mmol, 0.4 ml). The mixture was stirred until the organic layer turned colorless, water (10 ml) was added, and the mixture was stirred for another 5 min and filtered immediately. The organic layer was washed with 6% HCl (w/w) and added to a stirred solution of 20% (w/w) HCl (20 ml) at 5–10 °C over 30 min. After stirring for 4 h, the gray precipitate was collected, washed with 20% HCl, and dried at 40 °C, to give the benzidine dihydrochloride (2.7 g, 53.0% yield). The dihydrochloride was stirred with 25% ammonia to release the amine, which in turn was recrystallised twice from *para*-dimethylbenzene to provide pure **4**, m.p. 141–143 °C (lit. [9], 141–142 °C). MS (positive ion API-ES): 301 ($[M+H]^+$, base peak), 323 ($[M+Na]^+$). 1H -NMR (d_6 -DMSO), δ (ppm): 6.88 (2H, *s*), 6.58–6.78 (4H, *t*, $J=9.0$), 4.29 (4H, broad *s*), 3.92–4.06 (4H, *t*, $J=6.3$), 1.64–1.94 (4H, *s*extet, $J=6.8$), 0.98–1.15 (6H, *t*, $J=7.3$).

For the synthesis of 3,3'-di-*n*-butoxybenzidine (**5**) 2-*n*-butoxynitrobenzene (5.0 g, 0.026 mol) was used. The dihydrochloride was obtained as a pale white solid (58.0% yield). The free amine was recrystallised twice to provide pure **5**, m.p. 69–71 °C (lit. [9], 69–71 °C). MS (Positive ion API-ES): 329 ($[M+H]^+$, base peak), 351 ($[M+Na]^+$). 1H -NMR (d_6 -DMSO), δ (ppm): 6.90 (2H, *s*), 6.65–6.82 (4H, *t*, $J=7.8$), 2.8–5.5 (4H, broad *s*), 3.97–4.11 (4H, *t*,

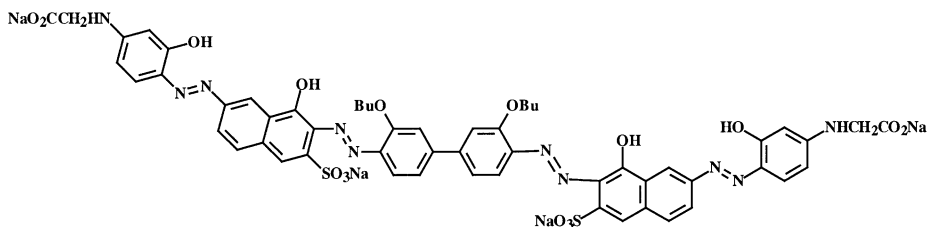


1. CI Direct Black 38

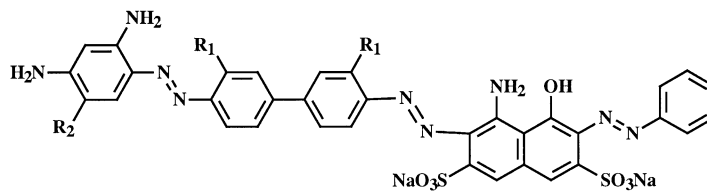


$\begin{array}{c} \text{R} \qquad \qquad \text{R} \\ \hline \text{2. H} \qquad \qquad \text{5. OBU} \\ \text{3. Me, OMe} \quad \text{6. OCH}_2\text{CH}_2\text{OH} \\ \text{4. OPr} \end{array}$

7
 (X = CONH, NHCONH, CH=CH,
 SO₂NH, NH)
 (R, R' = H, SO₃Na)

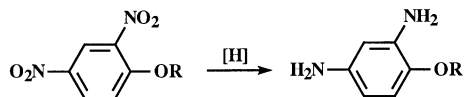


8



9

(R₁ = OPr, OBU, OC₂H₄OH; R₂ = H, OPr, OBU, OC₂H₄OH)



10

11

(a. R = Pr, b. R = Bu, c. R = CH₂CH₂OH)

$J=6.1$), 1.41–1.87 (8H, m , $J=5.9$), 1.00–1.41 (6H, t , $J=6.8$).

For the synthesis of 3,3'-bis-(β -hydroxyethoxy)benzidine (**6**) 2-nitro-(β -hydroxyethoxy)benzene (5.0 g, 0.027 mol) was employed. The dihydrochloride was obtained as a pale white solid (2.6 g, 51.0% yield) and the free amine had m.p. 200–202 °C. MS (positive ion API-ES): 305 ($[M+H]^+$, base peak), 327 ($[M+Na]^+$); IR (KBr): 3380 (ν -OH), 2880~2580 (ν -NH₃⁺), 1620, 1590, 1526, 1498 (ν -benzene), 1265, 1080, 1046 (ν -C-O-C), 854, 809 (ν -Ar-H); ¹³C-NMR, δ (ppm): 152.48, 142.07, 125.07, 120.76, 119.77, 112.19, 70.96 (–O–CH₂), 61.02 (–CH₂–OH).

2.4. Synthesis of 2,4-dinitro-1-alkoxybenzenes (**10**)

The method employed is illustrated for the synthesis of 2,4-dinitro-*n*-propoxybenzene (**10a**). A mixture of *n*-propanol (12.6 ml, 0.168 mol), 2,4-dinitrochlorobenzene (8.1 g, 0.04 mol), and anhydrous K₂CO₃ (9.4 g, 0.068 mol) was stirred under reflux for 8 h. The product was precipitated by adding water (20 ml), collected by filtration, and washed to neutrality with water. After drying, a pale yellow solid (8.7 g, 96.1% yield) was obtained having m.p. 34–35 °C (lit. [11], m.p. 34–35 °C).

Similarly, 2,4-dinitro-*n*-butoxybenzene (**10b**) was obtained as a red liquid (9.2 g, 95.8% yield) and 2,4-dinitro-(β -hydroxyethoxy)benzene (**10c**) was obtained as colorless needles (7.5 g, 82.2% yield), m.p. 109–110 °C (lit. [12], m.p. 109 °C).

2.5. Synthesis of hydrochloride salts of 2,4-diaminoalkoxybenzenes (**11**)

A mixture of 2,4-dinitro-1-alkoxybenzene (0.017 mol) and ethanol (20 ml) was added to a 200 ml autoclave and hydrogenated in the presence of 5% Pd/C (0.1 g) at 60 °C until hydrogen uptake ceased. The catalyst was removed and the filtrate was acidified using HCl gas. The solvent was removed (in the cases involving **11a** and **11b**) or the mixture was filtered (in the case involving **11c**) to give the products. Compound **11a** was obtained in 94.6% yield. MS (positive ion API-ES): m/z 167 ($[M+H]^+$, base peak), 125, 124. Compound **11b** was obtained in 95.8% yield. MS (positive ion

API-ES): m/z 181($[M+H]^+$, base peak), 125, 124. Compound **11c** was obtained in 90.2% yield. MS (positive ion API-ES): m/z 169 ($[M+H]^+$, base peak), 125, 124.

2.6. Dye synthesis

2.6.1. Step 1—tetrazotization

To individual solutions of diamines **4–6** (0.01 mol) in water (10 ml) containing HCl (0.06 mol) a solution of 30% NaNO₂ (w/w, 0.02 mol) was added dropwise at 0–5 °C. Each solution was stirred for 30 min and excess nitrous acid was decomposed by the addition of urea.

2.6.2. Step 2—first coupling

H-acid (4-amino-5-hydroxy-2,7-naphthalene disulfonic acid, 0.01 mol) was stirred with water (20 ml) and 10% Na₂CO₃ (w/w) was added to give pH 6. The resultant solution was added dropwise to each solution of tetrazonium compound at 10 °C and pH 2 over 3 h. After the addition, each solution was stirred for about 6 h, maintaining pH 2–2.5 by adding 10% Na₂CO₃.

2.6.3. Step 3—diazotization of aniline

NaNO₂ (0.01 mol) was added dropwise at 0–5 °C to a solution of aniline (0.01 mol) in water (10 ml) containing HCl (0.03 mol). The solution was stirred for 15 min and excess nitrous acid was decomposed by the addition of urea.

2.6.4. Step 4—second coupling

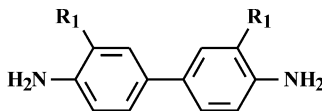
Diazotised aniline from step 3 was added to each solution from step 2 and 10% Na₂CO₃ (w/w) was added to adjust the pH to 8.5–9. The resultant solutions were stirred at 3–5 °C for 1 h to complete this reaction.

2.6.5. Step 5—the third coupling

The dihydrochloride of *meta*-phenylenediamine or 2,4-diamino-1-alkoxybenzenes **11** (0.01 mol) was dissolved individually in water (50 ml) and added to each solution from step 4. The resultant solutions were stirred for 3 h at pH 7.5–8 and 10 °C. The dyes were precipitated by adding 2–4% (w/v) NaCl and adjusting the pH to 6.5–7, giving overall trisazo dye yields of about 70%.

Table 1
Reaction conditions employed in the synthesis of diamines **2** and **4–6**

Diamine	R ₁	Solvent	Reaction temperature (°C)	Yield (%)
2	H	<i>o</i> -Dichlorobenzene	115–130	82.5
4	OPr	Ligroin	70–88	53.0
5	OBu	Ligroin	70–88	58.0
6	OC ₂ H ₄ OH	1,2-Dichloroethane	70–80	51.0



2.7. Dye application

The commercial sample of C.I. Direct Black 38 was used without further purification, while the new dyes were re-dissolved in water and salted out three times prior to their use. The dyeing of all fabrics was carried out in a Roaches 1002 dyeing machine, using 5% dye, 20% Na₂SO₄ and 2% Na₂CO₃ based on the fabric weight (owf). The dye liquor to fabric ratio was 40:1. The bath containing dye, Na₂SO₄ and Na₂CO₃ was heated from 25 to 90 °C over 30 min. Then, another 20% (owf) Na₂SO₄ was added to the dye liquor and dyeing was conducted at 90 °C for 30 min. The dyed fabrics were rinsed thoroughly with water and dried at room temperature. The degree of dye exhaustion (%Exh) was determined by colorimetry, measuring the dye concentration in the dyebath before (C₁) and after (C₂) dyeing and using Eq. (1):

$$\%Exh = (C_1 - C_2)/C_1 \times 100\% \quad (1)$$

2.8. Aftertreatment

The dyed fabric was treated with a solution containing HOAc (2g/l, 30%) and dicyandiamide-formaldehyde resin (fixative Y, 100 g/l) for 30 min at 50–60 °C, using a 30:1 liquor to fabric ratio. The fabric was rinsed with water and dried at room temperature.

2.9. Test methods

Fastness testing was conducted according to test methods GB/T3921–97 (method 1, for wash

fastness) and GB 8427–87 (for light fastness). The rating system used was 1 (poor) to 5 (excellent).

3. Results and discussion

3.1. Synthesis

3.1.1. Diamines

Benzidine homologues **4–6** were synthesized in two steps from the corresponding nitro compounds, namely alkaline reduction and benzidine rearrangement [9]. The optimum reduction conditions for each substituted nitrobenzene are shown in Table 1. Exceeding the reported temperatures led to the formation of alkoxyaniline by-products.

We also found that solvents played an important role in the synthesis of diamine **6**. When ligroin, alcohol, toluene or chlorobenzene was used, no diamine was obtained. 1,2-Dichloroethane was found to be the best solvent for the synthesis, probably due to the solubility of the intermediate hydrazo compound in this medium.

3.1.2. Dyes

The route employed in the synthesis of dyes was similar to that used in the synthesis of C.I. Direct Black 38. Since there are multiple steps in the synthesis (cf. Fig. 1), it was very important to carefully control the reaction conditions for each step to minimize the formation of by-products. For instance, at pH 2 and 9–11 °C, coupling occurred mainly *ortho* to the NH₂ group of H-acid when tetrazotised benzidine was used, with a minor amount of coupling *ortho* to the OH group

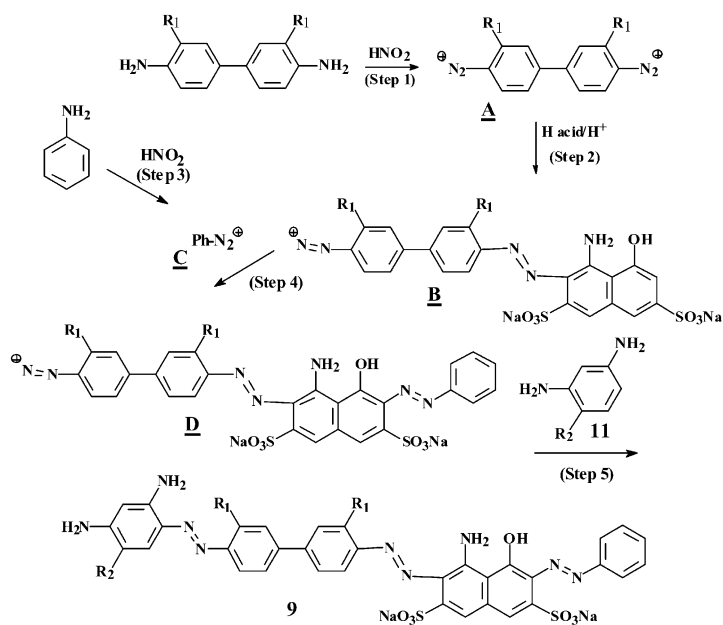


Fig. 1. Synthesis of trisazo dyes (9) used in this investigation.

observed. Although a lower pH value decreased the amount of by-product, it also decreased the coupling rate appreciably. The same reaction conditions were appropriate for coupling tetrazotised **6** to H-acid; however tetrazotised **4** and **5** required different conditions. In these cases, the coupling step was not complete after 2 days at pH 2. When the pH was raised to 3, the coupling step was complete in 8–12 h. The longer reaction time or a higher pH also gave trisazo dyes of somewhat lower purity than those synthesized from **2** and **6**.

In the second coupling step ($B + C \rightarrow D$), Na_2CO_3 was added quickly to avoid the formation of CO_2 . This addition should be completed within 40 min at 3–5 °C because the unreacted diazo group of the benzidine moiety (cf. B) is sensitive to alkaline solution. The third coupling step ($D \rightarrow 9$) was performed immediately after the second coupling was complete. Using 3,3'-alkoxybenzidines as substitutes for benzidine and *meta*-phenylenediamine or 1-alkoxy-2,4-diaminobenzenes as coupling components, 12 new black trisazo dyes (**9b–m**) were prepared as analogues of C.I. Direct Black 38.

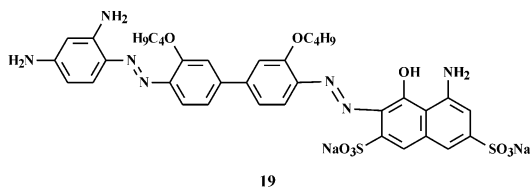
All of the trisazo dyes had a greenish-black component as the major product on silica gel TLC plates, using BuOH/MeOH/25% NH_4OH /pyridine

(4:1:3:2) as the eluent. The associated R_f values are shown in Table 2. We found that each dye contained small amounts of colored impurities that were difficult to remove completely.

IR spectra of C.I. Direct Black 38 and representative dyes synthesized from three 3,3'-substituted benzidines are shown in Fig. 2. The four spectra are quite similar, differing mainly by the presence of peaks at 2900–3000 cm^{-1} in the spectra of **9b**, **9f** and **9j**, which are due to the alkoxy groups.

A representative mass spectrum is shown in Fig. 3. In this example, the negative ion ESI mass spectrum of **9b** contains signals due to $[M-H]^-$ ($m/z = 852.5$), $[M-2H+Na]^-$ ($m/z = 874.5$), and $[M-2H]^{2-}$ ($m/z = 426.4$) ions. ESI-MS was also useful for establishing the course of the first coupling step in Fig. 1. For instance, the results in Fig. 4 show that the synthesis of **9f** can lead to the formation of by-product **19** when the pH gets above 3 in the first coupling step. The spectrum in Fig. 4 shows signals for **9f** at $[M-H]^-$ ($m/z = 880.7$), $[M-2H]^{2-}$ ($m/z = 440.3$), along with signals for **19** at $[M-H]^-$ ($m/z = 776.7$) and $[M-2H]^{2-}$ ($m/z = 388.1$). The formation of **19** arises from coupling of the tetrazonium compound *ortho* to the $-OH$ group in H-acid to give an intermediate

that does not couple with diazotised aniline. Therefore, the coupling step involving *meta*-phenylenediamine gave **19**, a dye with a redder hue than **9f**.

**19**

3.2. Dyeing and fastness properties

The exhaustion, visible absorption and fastness properties of dyes **9b–m** were examined and compared with data from C.I. Direct Black 38 (**9a**), the results of which are shown in Table 2. Comparing %Exh values for the dyes on cotton, it was

found that exhaustion decreased when bulky alkoxy groups were introduced into the benzidine moiety. For instance, when *meta*-phenylenediamine was used as the terminal coupler, the %Exh was 75.1, 59.6, 43.1 and 70.7% for C.I. Direct

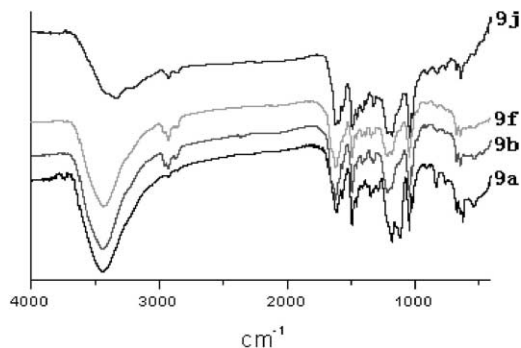
Fig. 2. IR spectra of dyes **9a**, **9b**, **9f** and **9j**.

Table 2
Key properties of dyes **9a–m**

Dye	R_1	R_2	R_f^a	λ_{\max}		%Exh	Wash fastness				Light fastness			
				λ_1	λ_2		Color change	Staining		Color change	Staining			
								I	III		II	I	II	I
9a^b	H	H	0.71	473	596	75.1	4–5	3	4–5	4	3	4–5	3	3
9b	OC ₃ H ₇	H	0.72	480	583	56.3	4–5	2	4–5	3–4	2–3	3–4	3	3–4
9c	OC ₃ H ₇	OC ₃ H ₇	0.73	475	555	41.9	4	2	4–5	2–3	3	3–4	2–3	3
9d	OC ₃ H ₇	OC ₄ H ₉	0.74	473	574	41.1	4–5	2	5	3	3	4	2–3	3
9e	OC ₃ H ₇	OC ₂ H ₄ OH	0.71	482	553	58.4	4–5	2	4–5	3	2–3	4	2–3	3
9f	OC ₄ H ₉	H	0.72	483	581	43.6	3–4	2–3	4–5	4	3	3–4	2–3	3
9g	OC ₄ H ₉	OC ₃ H ₇	0.74	485	550	37.0	3–4	3	4–5	2–3	2–3	3–4	2	3
9h	OC ₄ H ₉	OC ₄ H ₉	0.74	480	553	37.8	4–5	3	5	3–4	3	4–5	2	3
9i	OC ₄ H ₉	OC ₂ H ₄ OH	0.72	486	552	45.0	4–5	2–3	4–5	3	3	4–5	2–3	3
9j	OC ₂ H ₄ OH	H	0.69	–	588	70.7	4–5	3	5	3	2–3	4–5	3	3–4
9k	OC ₂ H ₄ OH	OC ₃ H ₇	0.70	480	569	58.5	4–5	2–3	5	4	2–3	4–5	3–4	3–4
9l	OC ₂ H ₄ OH	OC ₄ H ₉	0.70	472	569	59.3	4	2–3	5	3–4	2–3	4–5	3–4	3–4
9m	OC ₂ H ₄ OH	OC ₂ H ₄ OH	0.68	482	568	66.6	4–5	2	5	4	2–3	4–5	3–4	3

I. Cotton; II. silk; III. wool.

^a Broad spot centered here. Eluent = BuOH/MeOH/25%NH₄OH/pyridine (4:1:3:2).

^b CI Direct Black 38.

Black 38 (**9a**), **9b** ($R_1 = \text{OPr}$), **9f** ($R_1 = \text{OBu}$) and **9j** ($R_1 = {}^{\circ}\text{C}_2\text{H}_4\text{OH}$), respectively. We believe that these results can be attributed to decreased solubility of the dyes in water. It is also possible that

the bulky alkoxy groups have an adverse influence on substantivity due to enhanced hydrophobicity. This is evident from the %Exh value for **9j**, which was only 4.4% lower than the value for **9a**.

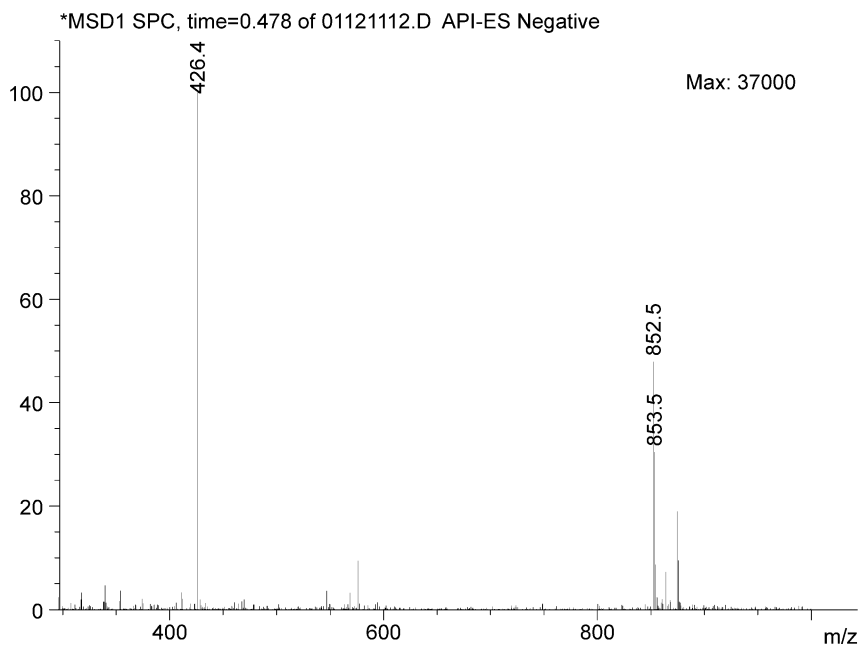


Fig. 3. Negative-ion ESI mass spectrum of dye **9b**.

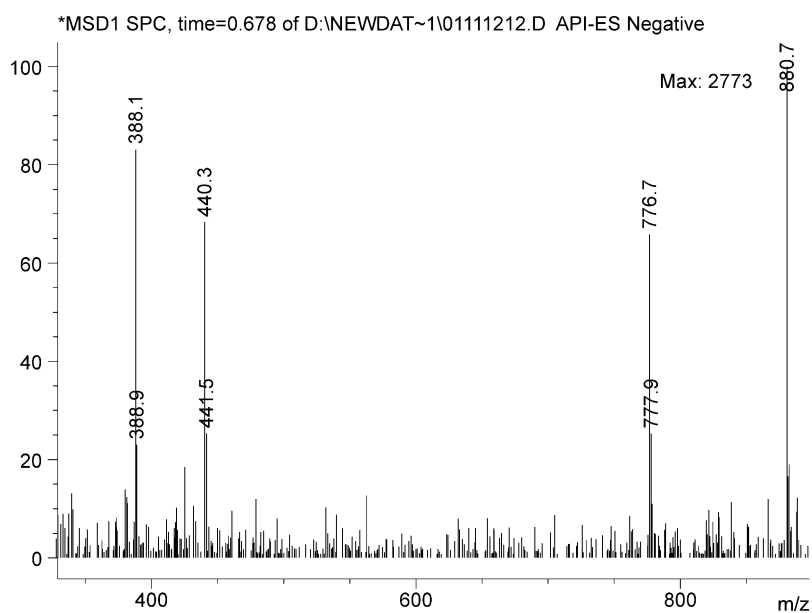


Fig. 4. Negative-ion ESI mass spectrum of dye **9f** containing by-product **19**.

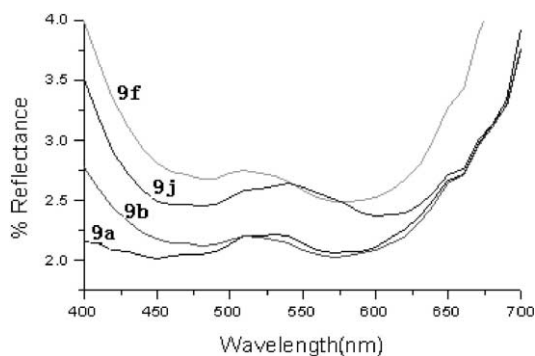


Fig. 5. Reflectance spectra for dyes **9a**, **9b**, **9f** and **9j**.

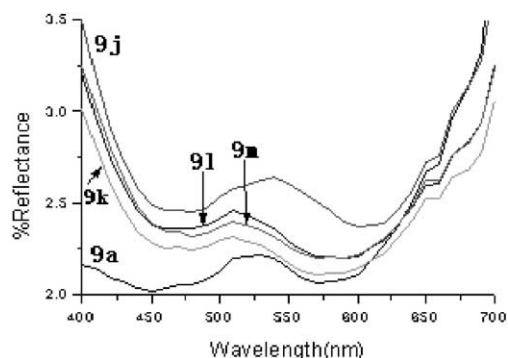


Fig. 6. Reflectance spectra for dyes **9j–m**.

The wash fastness values for the new dyes on cotton were similar to the results obtained for C.I. Direct Black 38 (cf. Table 2). In this regard, a rating of 4–5 for color change was generally observed, with dyes **9c**, **9f**, **9g** and **9l** identified as exceptions. On silk, wash fastness was generally lower, with only three dyes (**9f**, **9k** and **9m**) giving wash fastness comparable to **9a**. In this case, **9a** gave a rating of 4 for color change, while most of the other dyes gave a rating of 3 or 3–4. While all the dyes gave significant staining of cotton (rating = 2–3), there was little staining of wool and silk fabric.

The light fastness of the new dyes on silk was equal to or higher than **9a**. However, in the case of cotton, only those dyes derived from diamine **6** (cf. **9j–9m**) and **9b** were equal to or higher than **9a** in light fastness.

We also found that the color of **9b**, **9f** and **9j–9m** was similar to that of **9a**. A comparison of the

reflectance spectra for these dyes is shown in Figs. 5 and 6. Comparing the three dyes synthesized from alkoxy substituted benzidine (Fig. 5), it can be seen that the reflectance spectra of **9b** and **9j** are similar to that of **9a** in the 450–700 nm region, but that of **9f** is less similar. Similarly, the three dyes derived from 2,4-diamino-1-alkoxy benzene as a coupling component (cf. **9k–m**) gave reflectance spectra that were similar to that of **9a** in the 450–600 nm region, and better than **9a** in the 650–700 nm region (Fig. 6).

4. Conclusions

The results of this study indicate that certain trisazo dyes based on 3,3'-disubstituted benzidine are potential replacements for C.I. Direct Black 38. When these dyes were applied to cotton and silk at a 5% shade depth, the blackness level and fastness properties were similar to or better than the results obtained using the commercial black dye. It is also evident that the % exhaustion for the experimental dyes is generally lower than the value obtained using C.I. Direct Black 38. In this regard, 3,3'- β -hydroxyethoxy groups are better than the *n*-propoxy and *n*-butoxy groups in that they cause less reduction in % exhaustion.

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