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Synthesis and properties of disazo acid dyes

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Abstract

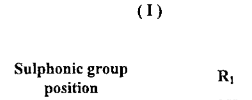
Disazo yellow, orange and red dyes have been synthesised, using amines not belonging to MAK III A1 and MAK III A2 groups, as middle components, and derivatives of N,N-dialkylaniline and phenol as final components. The dyes obtained were examined to assess their application and fastness properties, and spectroscopic measurements were used to determine structural properties of the dyes. It was found that the dyes exhausted completely on polyamide fibres from weakly acidic dyebaths and showed high colour fastness to light and water. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Acid dyes; Disazo acid dyes; Dyeing polyamide fibres

1. Introduction

Disazo acid dyes containing one sulphonic group have been widely used for dyeing polyamide fibres. These dyes can be prepared by coupling diazotised aromatic amines with couplers containing diazotizable amino groups (middle components) and the resultant azo dyes are then diazotised and coupled with final components. Suitable middle components are amines and dyes derived therefrom are *p*-cresidine (Acid Orange 156), *o*-anisidine (Acid Yellow 219), *o*-toluidine (Acid Yellow 159) and 1-naphthylamine (Acid Orange 116, Acid Red 299). As a result of toxicological testing performed using laboratory animals, *p*-cresidine, *o*-toluidine and *o*-anisidine have been found to be carcinogenic compounds (MAK III A2 group), while 1-naphthylamine containing strongly carcinogenic 2-naphthylamine (MAK III A1 group) as an impurity is a potential hazard both to dye manufacturers and users [1–2].

The system of conjugated azo bonds in diazo acid dyes affords increased colour efficiency when compared with the corresponding dyes. Consequently disazo acid dyes are still of interest [3–7]. The aim of the present study was to synthesise disazo acid dyes (cf. form I to IV) which would not contain carcinogenic amines of the MAK III A1 and A2 groups.



(I)

where :

	Sulphonic group position	R_1	R_2
D – 1	4	OH	OH
D – 2	4	CN	H
D – 3	3	OH	OH
D – 4	3	CN	H
D – 5	3	CN	CN

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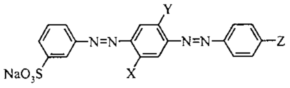
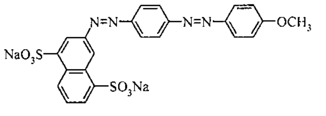


(II)

	X	Y	Z
D - 6	NHCOCH$_3$	H	OCH$_3$
D - 7	CH$_3$	H	OCH$_3$
D - 8	OCH$_3$	OCH$_3$	OC$_2$H$_5$
D - 9	OCH$_3$	OCH$_3$	OCH$_3$

D - 10



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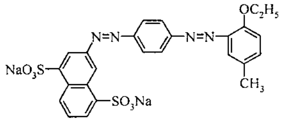


(IV)

2. Experimental

Metanilic, sulphanilic and 2-aminonaphthalene-4,8-disulphonic acids were diazotised in water and coupled with aniline-N-methanesulphonic acid in water at pH 3.5–4.0 (acetate buffer) and 7–10°C for several hours. The product was hydrolised in water at pH 10.8–11.2 and 95–98°C for 3–4 h. The resultant aminomonoazo dyes were precipitated by salting out with sodium chloride at pH 7.5–8.0. For comparison, diazotised metanilic acid was coupled with 2,5-dimethoxyaniline, m-aminoacetanilide and m-toluidine in water with pH 3.2–3.7 at a temperature of 5–10°C.

The resultant aminomonoazo dyes were diazotised *by the intermediate method* in an aqueous medium at 30–40°C and then coupled with dialkylaniline derivatives at pH 3.5–4.5 and 10–15°C for several hours. The coupling with phenol was carried out at pH 8.5–9.0 and that with *p*-cresol at pH 10.0–10.5.

Disazo dyes that were derivatives of phenol and *p*-cresol were alkylated with dimethyl or diethyl sulphate in water at pH 10.5–11.0 and 60–65°C. The resultant dyes were precipitated by salting out with sodium chloride, filtered off, washed with brine, and dried at 50–60°C. The yields were 80–90%.

3. Examples of the syntheses

3.1. Dye B-4

The sodium salt of 4’aminoazo benzene-3-sulphonic acid (14.95 g, 0.05 mol) was dissolved, in water (250 cm^3) at 60°C. Then, sodium nitrite (3.6 g) dissolved in water (10 cm^3) was added. After cooling to 35–40°C, the resultant mixture was added dropwise over 1 h to 50 cm^3 of cold water containing hydrochloric acid (12.5 g, 30%). The diazotisation process was carried out at 25–30°C for 3 h, maintaining excess sodium nitrite. At that point, excess sodium nitrite was destroyed by adding sulphamic acid (0.4 g).

N-cyanoethyl-N-ethylaniline (9 g) was dissolved in glacial acetic acid (10 g) and Surfynol 104 (0.5 g) was added, and the solution was added dropwise to water (50 cm^3). To the aqueous emulsion of the coupling component, the diazo component was added over 0.5 h with vigorous stirring. At 10–15°C the pH of the reaction was slowly raised to 3.5 by the dropwise addition of sodium carbonate (100 cm^3, 20%) over 1 h. The reaction mixture was stirred overnight, allowing temperature rise to 20°C. Next day, the pH of the mixture was increased to 8.5–8.8 by adding dropwise sodium hydroxide (4.5 g, 50%), and then the reaction mixture was stirred at 60°C for another hour. After cooling to 50°C, the dye was collected by filtration, washed several times with 2% brine, and dried to give 22.3 g solid (83.1%).

3.2. Dye B-9

Metanilic acid (8.65 g, 0.05 mol) was dissolved in water (30 cm^3) containing NaOH (2.0, pH 7.2–7.5) and ice, and hydrochloric acid (12.5 g, 30%) was added. Then, sodium nitrite (3.5 g) dissolved in water (10 cm^3) was added dropwise. Diazotisation was carried out at 2–7°C for 40 min, maintaining a slight excess of sodium nitrite. Afterwards excess nitrite was destroyed by sulfamic acid (10.15 g). 2,5-Dimethoxyaniline (7.65 g) was dissolved in water (50 cm^3) containing hydrochloric acid (6 g, 30%). The solution was cooled to 5–10°C by adding ice and diazotised metanilic acid was added. The pH of the solution was raised to 3.2–3.6 over

20 min by the dropwise addition of sodium acetate (11 g, 30%). The reaction was stirred for 1 h at 5–10°C and the pH was raised to 8.0–8.5 by adding NaOH (4.0–4.5 g, 50%) dropwise. The mixture was stirred for 30 min at 15–18°C and the dye was filtered to give 35 g dye paste (0.0478 mol per amine group).

The dye paste was dissolved in water (300 cm^3) at 60°C and the resultant solution was cooled to 30°C. Sodium nitrite (3.7 g) was added, followed by hydrochloric acid (14 g of 30%). Diazotisation was carried out for 1 h at 30–35°C and the reaction mixture was cooled to 14–20°C. Excess sodium nitrite was destroyed by adding sulphamic acid (0.4 g).

Phenol (4.7 g) was dissolved in water (20 cm^3) containing sodium hydroxide (4.0, 50%). To the phenol solution, the suspension of the diazotized monoazo dye was added over 30 min with vigorous stirring. During the coupling step, the temperature was maintained at 10–15°C, by adding ice and the pH was kept at 8.5–9.0 by adding sodium carbonate (20%, 90 ml). Stirring was continued overnight, at room temperature. The mixture was heated to 60–65°C and the pH was increased to 10.5–10.8. To this mixture, dimethyl sulphate (17.6 g) was added dropwise over 3 h, maintaining a pH of 10.5–10.8 by adding sodium hydroxide (50%, 10 g). The reaction was monitored by paper chromatography, using Whatman No. 3 paper and an eluent consisting of pyridine:20% ammonia:1% sodium chloride (1:1:8).

Once the reaction was complete, the resultant dye was precipitated by salting out with sodium chloride (5% v/v). The mixture was cooled to 40°C and the dye was collected by filtration and washed with 2% brine. The dry dye weighed 23.8 g (89.3%).

3.3. Dye purity

The purity of the dyes was determined by HPLC, using a Water 996 Photodiode Array Detector and a Column Purospher^R RP-18e (5 μm). Samples were prepared in HPLC grade. Conditions: linear gradient, injection 10 μl, flow 0.65 ml/min, run time 29.5 min, delay time 13.5 min. The gradient used was:

Time (min)	A	B
0–15	40%	60%
16–30	85%	15%
31–43	40%	60%

A = CH_3CN B = 0.01 m. $(C_4H_9)_4\ N^+Br^-$ in water HPLC

The sodium chloride content in the dyes prepared was determined by potentiometry. The results are given in Table 1.

3.4. Absorption spectra

Spectroscopic determination of λ_{max} values in water and 50% ethanol were conducted at pH 2–7

Table 1
Reaction yield and purity of dyes D-1-D-11

Dye no	Molecular weight	Yield of reaction	HPLC		Contents of NaCl [%]	Color
			Time of retention [min]	Purity [%]		
D-1	491	84.3	3,850	98.84	9.0	Red
D-2	484	82.7	9,993	94.84	7.0	Reddish Orange
D-3	491	87.3	4,312	98.72	6.8	Red
D-4	484	83.1	14,763	95.16	9.7	Reddish Orange
D-5	509	79.7	7,762	93.27	4.7	Orange
D-6	475	87.1	13,970	97.73	9.7	Reddish Yellow
D-7	432	86.2	16,665	98.49	9.3	Reddish Yellow
D-8	492	89.4	15,272	97.05	10.2	Reddish Orange
D-9	478	89.3	13,620	97.91	10.3	Reddish Orange
D-10	570	79.8	14,525	97.56	14.3	Reddish Yellow
D-11	598	83.1	15,600	96.97	12.7	Reddish Yellow

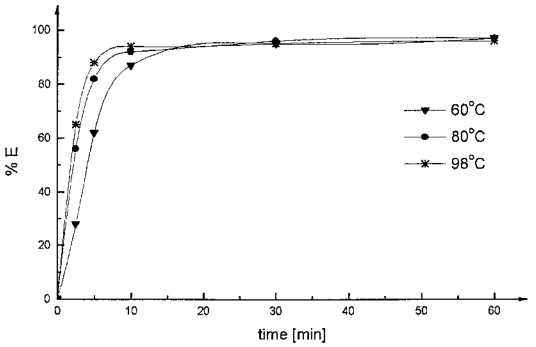


Fig. 1. Absorption curves for dye D-9 on polyamide fibers.

and a dye concentration of 4×10^{-5} mol/dm^3. This work employed a Hitachi U-300 Spectrophotometer.

3.5. Dyeing studies

Polyamide fibres were dyed in a Roaches dyeing machine at PH 5.0 (acetate buffer) using 1% dye in relation to fibres and a liquor ratio (LR) of 20:1. Percent exhaustion (E) was calculated from Eq. (1):

$$E = \frac{C_{S_1} - C_{S_2}}{C_{S_1}} \cdot 100\% \qquad (1)$$

where:

C_{S_1} dye concentration in the dyebath before dyeing,
C_{S_2} dye concentration in the bath after dyeing.

Dyes absorption curves were prepared for the application of each dye to polyamide fibres at 60°C, 80°C and 98°C. Representative data is presented in Fig. 1.

To determine the saturation point of polyamide 6 fibres, the fibres were dyed at concentrations of 3–60 milliequivalents of dye per 1 kg of fibre. Dyeing conditions were pH 5.0, 98°C, 20:1 LR, and 2h dyeing time. Polyamide 6 with a degree of crystallinity of 0.49 and containing 27.5 milliequivalents of amine end groups in the amorphous portion of the fibre was used.

The dye concentration in the fibre (C_f) was calculated as the difference in dye concentrations before (C_{S_1}) and after dyeing (C_{S_2}).

$$C_f = C_{S_1} - C_{S_2} \qquad (2)$$

Using the Kubelka-Munk equation, the relationship between the dye concentration in fibre and the colour strength of dyeing was determined, with the aid of a Datacolor reflectance spectrophotometer:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} = kC_f \qquad (3)$$

The measurements were performed in relation to standard dyeings where $C_{S_1} = 10$ milliequivalent of dye/1 kg of fibre.

$$\frac{(K/S)_X}{(K/S)_{10}} = \frac{C_{f_x}}{C_{f_{10}}} \qquad (4)$$

Representative data is presented in Fig. 2.

3.6. Fastness measurements

Polyamide 6 fibres dyed with a 1/1 strength of the auxiliary standard were used to test color fastness to water, acidic perspiration, alkaline perspiration, dry and wet rubbing and washing at 40°C. Fastness to light was measured using a Xenotest 150S apparatus (Heraus Hanau). The results are given in Table 3.

4. Discussion of the results

A group of disazo yellow, orange and red dyes have been obtained. The absorption spectra of dye solutions in water and 50% ethanol showed one absorption band in most cases. Exceptions were D-8 and D-9, derivatives of 2,5-dimethoxyaniline, which had absorption bands at 377–380 nm and 483–486 nm. As expected, the dyes had high molar absorption coefficients. The values were 38,000–39,000 for D-1 to D-4, derivatives of N,N-dialkylaniline, and 28,000–33,000 for phenol-based dyes D-6, D-7, D-10 and D-11. Some of the yellow dyes had absorption bands in the UV region. Examples

Table 2
Spectrophotometric properties and dyebath exhaustion of the acid dyes prepared in this study

Dye no.	Absorption maxima and extinction								
	Water		pH7		50% alcohol pH2		pH3		
	λ_{max} (nm)	ε_{max} (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	ε_{max} (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	ε_{max} (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	ε_{max} (dm^3 mol^{-1} (dm^3 mol^{-1} cm^{-1})	Dyebath exhaustion *at pH 5.0
D-1	501.4	34600	501.0	38100	536.0	22950	503.6	35500	98.2
D-2	494.4	35700	484.2	38900	498.8	38000	487.6	38800	99.2
D-3	498.4	36950	497.2	37800	537.2	46200	503.4	37100	98.1
D-4	491.4	30800	486.2	39250	499.2	36150	489.0	37750	99.5
D-5	484.2	33600	484.2	33800	478.8	31950	483.2	33450	99.4
D-6	384.2	28400	386.2	30650					98.9
D-7	379.8	29400	380.6	33000					99.4
	380.6	20000	379.6	20000					97.8
D-8	483.4	18800	477.6	18800					
	377.4	19400	376.8	19600					98.2
D-9	485.6	18300	481.2	18400					
D-10	387.8	24500	390.6	28650					99.0
D-11	371.6	28900	368.4	30100					96.2

were D-11 (371.6 nm) D-7 (379.8 nm), D-6 (384.2 nm), and D-10 (387.8 nm), which caused a decrease in the colour yield in fibres. The position and types of substituents in the dye molecules also affected colour, as illustrated in Table 2.

Comparison of absorption spectra in water and 50% ethanol showed that some of the dyes (D-1, D-2, D-3, D-4, D-6 and D-7) gave lower molar absorption values in water, which indicates their aggregation in water.

Spectroscopic studies conducted on dyes D1–D5 in water at pH 2 and 50% ethanol at pH 3, revealed pH-induced colour changes known as halochromism. The halochromism was caused by protonation of the azo bond and by resonance interactions involving the protonated species (see *a,b,c*).

Table 3
Fastness properties of dyes D-1-D-11

							Perspiration fastness									
	Water fastness			Wash fastness			Alkeline			Acid			Rubbing fastness		Light fastness	
Dye no[a]	1	2	3	1	2	3	1	2	3	1	2	3	Dry	Wet	1/1	1/3
D-1	5	4	5	5	4	5	4–5	3	3–4	5	3–4	4–5	5	5	5	4
D-2	5	4–5	5	4–5	4–5	5	4–5	4	4–5	5	4–5	5	5	5	6	6
D-3	5	4	4–5	5	4	4–5	5	3	3–4	5	3–4	4–5	5	5	5	4
D-4	5	4	4–5	5	4	4–5	5	3	3–4	5	4	4–5	5	5	6	6
D-5	5	4	4–5	5	4–5	5	5	4–5	4–5	5	4	4–5	5	5	6	6
D-6	5	4	4–5	5	4	4–5	4–5	4	4	5	4	4–5	5	5	7	7
D-7	5	4–5	5	4–5	4	4–5	4–5	4–5	4–5	5	4–5	5	5	5	6–7	6
D-8	5	3–4	4	4–5	4–5	5	4–5	3	3–4	5	3	3–4	5	5	6–7	6
D-9	5	3–4	4–5	4–5	4–5	5	4–5	3	3–4	5	3–4	4–5	5	5	6–7	6
D-10	5	4–5	5	5	4–5	5	5	4–5	4–5	5	4–5	5	5	5	6–7	6
D-11	5	4–5	5	5	5	5	5	4–5	4–5	5	4	4–5	5	5	6–7	6

[a] 1. Change of shade of a dyed fabric; 2. Staining of nylon; 3. Staining of wool.

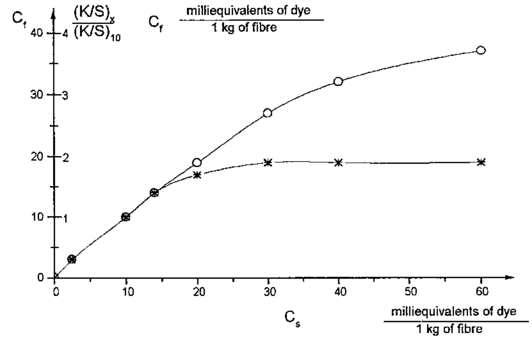
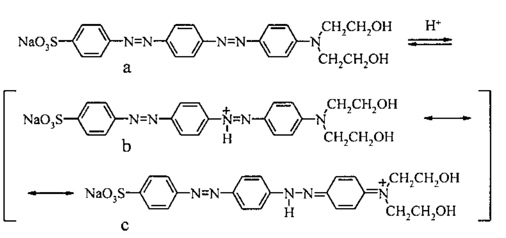


Fig. 2. Relationship between D-3 dye concentration in the bath and dye concentration in the fibres (o), and relative color strength of dyeing (∗).



The substituents placed in pendant alkyl chains have a clear influence on the magnitude of this effect. A strong batochromic effect at pH 2 was observed in dyes based on bis(β-hydroxy ethyl) aniline-35 nm for D-1 and 40 nm for D-3. This indicates a considerable proportion of structure c. At pH (3), the bathochromic effect was decreased to 2.6 nm for D-1 and 6.2 nm for D-3. At pH 2, dye D-1 is aggregated and the molar absorption coefficient was reduced by a factor of 2. A considerably lower bathochromic effect was shown by dyes derived from N-cyanoethyl-N-ethylaniline. The shift was only to 11 nm for dye D-2 and 13 nm for dye D-4. At pH 2, dye D-5 underwent a slight hypsochromic shift of 5.4 nm, which indicates a higher proportion of structure b.

Dye application studies showed that the dyes were nearly 100% exhausted from the dyebath at pH 5.0, which would lead to a practically colorlesseffluent. Even the disulphonic derivatives were characterised by high % exhaustions, namely 99% for dye D-10 and 96.2% for dye D-11. The high affinity to polyamide fibres is due to the presence of linear molecules that are terminated with a sulphonic group, the dyes were characterised by a high dyeing rate as illustrated in Fig. 1 for dye B-9.

Absorption measurements also showed an overdyeing effect for all the dyes in this investigation. At dye concentrations above 14 milliequivalents/kg of fibre, the relative colour strength of dyeing was not proportional to the quantity of dye in fibres. For example, this aspect for dye D-3 is illustrated in Fig. 2. It is probable that the decrease in the relative colour strength of dyeing was caused by dye aggregation in the polyamide fibres.

The colour fastness of the dyes to various treatments was high. In the group of dialkylamine derivatives, the highest fastness to wet treatment was exhibited by dyes D-2 (N-cyanoethyl-N-ethylaniline derivative) and D-5 (N,N-dicyanoethylaniline derivative).

Colour fastness to light was also very high, ranging from 6 to 7 with a standard strength of 1/1. Only the derivatives of N,N-diethanoloamine, D-1 and D-3, have lower light fastness, namely 5 with the strength 1/1.

5. Conclusion

A group of inexpensive and easy to synthesise disazo dyes, yellow, orange, and red have been prepared. The dyes were characterised by quantitative exhaustion from weakly acidic dyebaths and had high fastness to light and wet treatments. Some of the dyes may serve as replacements for disazo acid dyes that are derived from amines in the MAK III A1 and MAK III A2 groups.

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