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Dyes and Pigments 64 (2005) 163–170

DYES and PIGMENTS

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Synthesis and evaluation of a series of trisazo hetero bi-functional reactive dyes for cotton

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Received 20 February 2004; received in revised form 15 May 2004; accepted 17 May 2004

Abstract

Three linear trisazo derivatives, of the type A–N=N–M^1–N=N–M^2–E, incorporating both a sulphatoethylsulphone and a monochlorotriazine reactive group were prepared and evaluated as reactive dyes for the exhaust dyeing of cotton. The products were generally strong chromophorically but were dull in shade. All three dyes displayed good build-up in the presence of reduced levels of salt and the measured migration indices were similar to those of some commercial dyes. Although the fixation efficiencies of two of the dyes were similar to those of the commercial controls, their higher $E-F$ (exhaustion–fixation) values resulted in poor wash-off performance.
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Keywords: Hetero bi-functional; Reactive dyes; Trisazo dyes; Salt; Exhaust dyeing

1. Introduction

In an earlier study [1] we reported the synthesis and evaluation of some novel trisazo monochloro-*s*-triazinyl (MCT) reactive dyes, as potentially high build-up, high wet fastness products which could be applied to cotton by an exhaustion process in the presence of reduced levels of salt (0–30 g/l). However, it was found that all the dyes exhibited modest technical properties, especially relatively low fixation, probably resulting from the presence of a single reactive group in the molecule.

We now report the synthesis and evaluation of related novel hetero bi-functional reactive dyes, containing both a monochloro-*s*-triazinyl (MCT) and a β-sulphatoethylsulphonyl (SES) reactive group. These were synthesised by coupling the diazonium salts derived from the disazo intermediates **1**, **2** and **3** (Table 1), onto 1-hydroxy-6-(4-chloro-6-[4-β-sulphatoethylsulphonyl] phenylamino triazin-2-yl-amino-)naphthalene-3-sulphonic acid to yield bi-functional reactive dyes **4**, **5** and **6** (Table 2).

2. Experimental

2.1. Instrumental and analytical methods used

Instrumental and analytical methods used for characterisation of novel dyes and intermediates were as reported earlier [1]. The high performance liquid chromatography (HPLC) analyses were performed using a Hewlett–Packard 1100 liquid chromatograph with a 10 cm column length, Purospher RP-18 (5 μm) packing and a LiChroCART 125-4 HPLC column cartridge. The mobile phases used were 0.25% CHAP solution (cyclohexylammonium phosphate) as solvent A and acetonitrile (HPLC grade) as solvent B. These eluents were passed through the column, maintained at 40 °C, in either a fixed ratio (70:30) or the standard gradient rate at 2 ml/min, and the samples were analysed spectroscopically using a diode array detector at a wavelength range from 250 nm to 650 nm.

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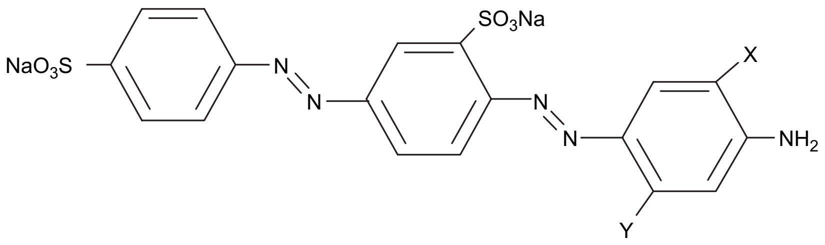
0143-7208/$ - see front matter
doi:10.1016/j.dyepig.2004.05.007

Table 1
Structures of disazo intermediates



Structure	X	Y
1	$-CH_3$	$-CH_3$
2	$-H$	$-OCH_3$
3	$-SO_3Na$	$-OCH_3$

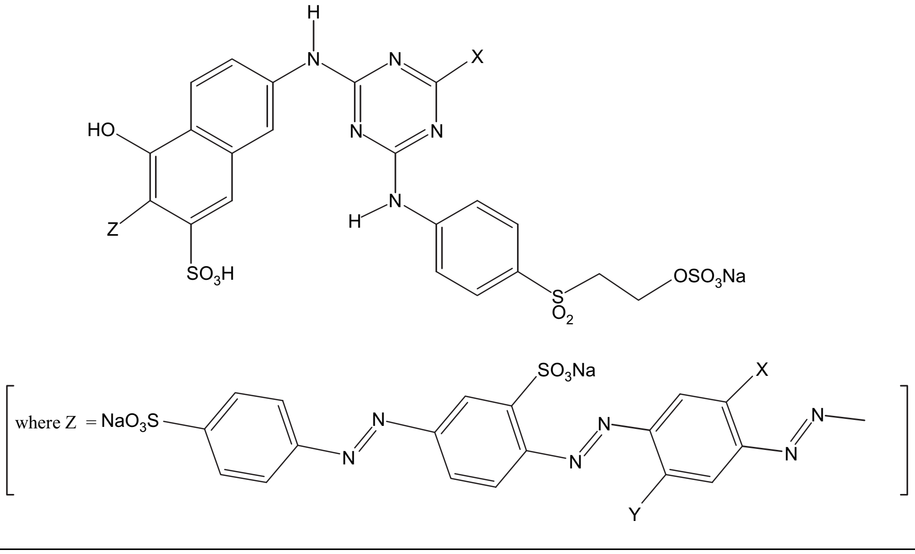
2.2. Synthesis and characterisation of dyes

Materials: 4-Amino-1,1′-azobenzene-3,4′-disulphonic acid, 2,5-dimethylaniline, 3-methoxyaniline, oleum, cyanuric chloride, 7-amino-4-hydroxy naphthalene sulphonic acid and other chemicals were supplied by Aldrich Chemical Company Limited (UK). *p*-Aminobenzene-sulphatoethylsulphone (PABSES) was supplied by Everlight Chemical Industrial Corporation (Taiwan). The cotton fabric used for dye evaluation was a plain weave bleached cloth. Visking tubing used for dialysis was supplied by Merck.

2.2.1. Synthesis of 1-hydroxy-6-(4-chloro-6-[4-β-sulphatoethylsulphonyl] phenylamino triazin-2-yl-amino-)naphthalene-3-sulphonic acid

A solution of cyanuric chloride (19.32 g, 0.105 mol) in acetone (80 ml) was poured into a vigorously stirred mixture of crushed ice (200 g) and water (200 ml). An aqueous solution (200 ml, pH 6.5) of 4-(β-sulphatoethylsulphonyl) aniline (29.6 g, strength 95%, 0.1 mol) was added dropwise at 0–5 °C, over 60 min, with the pH maintained between 3.5 and 4.5 using sodium carbonate solution (10% w/v). The solution was stirred for a further 60 min to complete the reaction.

Table 2
Structures of hetero bi-functional reactive dyes synthesised



Structure	X	Y
4	$-CH_3$	$-CH_3$
5	$-H$	$-OCH_3$
6	$-SO_3Na$	$-OCH_3$

To the resulting solution, an aqueous solution (200 ml, pH 6.5) of J-acid (6-amino-1-hydroxynaphthalene-3-sulphonic acid) (25.7 g, strength 93%, 0.1 mol) was added dropwise at 35 °C over 60 min with the pH maintained between 4 and 4.5 using sodium carbonate solution (10% w/v). The mixture was stirred for a further 60 min to complete the reaction. The product (ZH, Table 2) was then used without isolation for conversion to dyes.

The progress of the reaction was followed by HPLC, which indicated a purity of 93% and a retention time of 2.60 min for the product compared with retention times of 0.77 and 2.40 min for J-acid and the intermediate dichlorotriazine, respectively.

2.2.2. Synthesis of reactive dye 4 (see Table 2)

The sodium salt of the disazo dye (**1**) (6.58 g, strength 81%, 0.01 mol) was diazotised as described previously [1]. A solution of the coupling component (ZH, Table 2) (0.0105 mol) was adjusted to pH 5–6 at 25–30 °C. The diazonium salt was then added very slowly to the stirred solution over 2 h, while maintaining the pH in the range 5–6, and the mixture stirred for an additional 30 min. The product (**4**) was precipitated by adding industrial ethanol, filtered off and dried (12.6 g, strength 76%, yield 79%). The progress of the reaction was followed using TLC and HPLC. TLC showed an R_f of 0.77 for the starting material and 0.74 for the product. HPLC analysis indicated a purity of 100%, retention time 4.10 min; starting material 1.51 min. The product was desalinated by dialysis using Visking tubing; λ_{max} = 539 nm, ε_{max} = 66,200 l mol^{-1} cm^{-1}.

2.2.3. Synthesis of reactive dye 5 (see Table 2)

The sodium salt of the disazo dye (**2**) (6.08 g, strength 88%, 0.01 mol) was diazotised, and the diazonium salt added to the coupling component (ZH, Table 2) (0.0105 mol) in water at pH 5–6, 25–30 °C. After completion of the coupling, the product (**5**) was collected and dried (15.3 g, strength 57%, yield 71%).

Starting material, R_f 0.68; product, R_f 0.72. HPLC analysis showed a single peak, retention time 3.84 min; starting material 0.86 min; λ_{max} = 538 nm, ε_{max} = 68,200 l mol^{-1} cm^{-1}.

2.2.4. Synthesis of reactive dye 6 (see Table 2)

The diazonium salt of the disazo dye (**3**) (13.0 g, strength 49%, 0.01 mol) was added to the coupling component (ZH, Table 2) (0.0105 mol) in water at pH 5–6, 25–30 °C. After completion of coupling, the product (**6**) was filtered off and dried (13.7 g, strength 72%, yield 75%). Starting material R_f 0.65; product R_f 0.70. HPLC analysis showed a purity of 94%, retention time 3.49 min; starting material 1.09 min; λ_{max} = 534 nm, ε_{max} = 55,500 l mol^{-1} cm^{-1}.

2.2.5. Determination of the colour strength of trisazo reactive dyes 4–6

The strengths of the dyes were determined by titration with titanium (III) chloride [2] and the results are shown in Table 4.

2.2.6. Determination of the spectroscopic characteristics of reactive dyes 4–6

Solutions of the three reactive dyes **4–6** in the concentration range 0–0.05 g/l were prepared in water buffered to pH 7 and the visible absorbance values (optical densities) were measured at the wavelength of maximum absorption in a 1 cm cell using a Philips model PU8720 spectrophotometer. The half-band widths and the molar extinction coefficients (ε_{max}) of the dyes were determined and are shown in Table 5.

2.3. Evaluation of the application properties of reactive dyes 4–6

In order to evaluate and compare the application properties of the novel hetero bi-functional dyes **4–6** with those of a series of commercially available dyes, it was necessary to define their optimum dyeing conditions. For this purpose, a series of dyeings were conducted using various amounts of salt at different temperatures, in a Mathis Labomat dyeing machine. Because the combination of reactive groups (MCT and SES) are the same as those of several commercial hetero bi-functional ranges of reactive dyes, the amount of alkali used was similar to that recommended for Sumifix Supra dyes [3].

The technical properties of dyes **4–6** were assessed against four commercial reactive dyes: two Cibacron LS (low salt) dyes, namely Cibacron Navy LS-G and Cibacron Orange LS-BR, and two bis MCT Procion H-E/H-EXL dyes, namely Procion Red H-E7B and Procion Crimson H-EXL. The two Procion dyes were chosen because they exhibit different level dyeing properties. Procion Crimson H-EXL possesses a higher migration index [4] than Procion Red H-E7B, indicating superior level dyeing characteristics.

2.3.1. Effect of salt concentration and dyeing temperature on the visual colour yield of dyes 4–6

The effect of salt concentration and both the (neutral) exhaustion and fixation temperature on the visual colour yield of the dyes was studied. For this purpose, a series of dyeings were carried out at 2% dye o.m.f. using 0–60 g/l salt, 20 g/l soda ash, liquor ratio 10:1, 60 min at neutral exhaustion temperatures of 80 and 90 °C and 60 min fixation time at temperatures of 60, 70, 80 and 90 °C. The visual colour yield was expressed as a K/S value [5], measured at the λ_{max} of each dye, using a Spectroflash 600 spectrophotometer from Datacolour International. The results are listed in Tables 6–8.

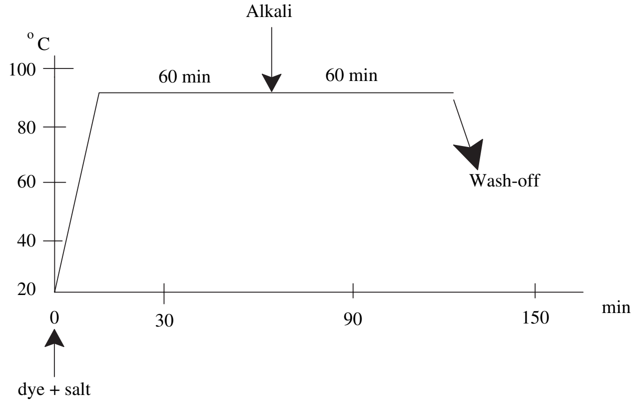


Fig. 1. Dyeing profile for reactive dyes **4–6**.

2.3.2. Build-up properties of dyes **4–6**

The build-up properties of the dyes were assessed under their optimum dyeing conditions (see Section 2.3.1), viz. using the dyeing profile shown in Fig. 1. The commercial dyes were applied using the manufacturer's recommended conditions [1]. The compositions of the various dyebaths are summarised in Table 3 and the build-up curves are shown in Fig. 2.

2.3.3. Measurement of the SER$_5$F profiles of dyes **4–6**

The SER$_5$F profiles [6] of the dyes were compared at the same visual colour yield (K/S = 14–15), determined from the build-up curves shown in Fig. 2.

Hence, dyes **4** and **5** were determined at 2% o.m.f.; **6** at 2.6%; Procion Red H-E7B at 2.8% and Cibacron Navy LS-G at 1.45%; the results are shown in Table 9.

The substantivity (S) of the novel dyes and Cibacron Navy LS-G was determined by measuring the exhaustion of the dyebath after 60 min at 90 °C using 15 g/l salt. The corresponding value for Procion Red H-E7B was determined after 60 min at 80 °C in the presence of 45 g/l salt.

The exhaustion (E) was measured 60 min after the addition of 15 g/l soda ash at 90 °C in the case of dyes **4–6**; at 80 °C for Procion H-E7B and 70 °C for Cibacron Navy LS-G.

Table 3
Dyebath compositions when examining the build-up properties of dyes **4–6** and the control dyes

Depth of shade (% o.w.f)	Salt concentration (g/l)							Soda ash (g/l)	LR
	4	**5**	**6**	PR	PC	CO	CN		
1	15	15	30	45	45	15	15	15	10:1
2	20	20	40	60	60	25	25	20	10:1
4	25	25	50	70	70	35	35	20	10:1
6	30	30	60	90	90	40	40	20	10:1

PR: Procion Red H-E7B, PC: Procion Crimson H-EXL, CN: Cibacron Navy LS-G, CO: Cibacron Orange LS-BR.

2.3.4. Determination of the migration indices of dyes **4–6** and the control dyes

The migration properties of reactive dyes were readily estimated using a simple test, which seeks to define a migration index (MI) for an individual dye when applied under a given set of conditions [7]. Each dye was applied at the same depth as for the determination of its SER$_5$F profile, K/S approximately 15, using 15 g/l soda ash for fixation but different salt levels, viz. 15 g/l for dyes **4–6** and Cibacron Navy LS-G and 45 g/l for Procion H-E7B. The migration indices are given in Table 10.

2.3.5. Comparison of the ease of wash-off of dyes **4–6** and the control dyes

The dyes to be compared were applied at a depth of shade, which gave a K/S value of approximately 15 (see Table 11). Each dyed pattern was then treated as follows.

Each one was removed from the dyebath and rinsed in cold running water (2–3 min, three squeezings by hand during rinsing) to reduce the salt concentration of the dye liquor in the fabric to less than 2 g/l. Each fabric was hydroextracted and placed in a rotadyer tube, set with 4 g/l of salt (liquor ratio 10:1 based on 4 g of fabric), for 25 min at 95 °C. Each was then rinsed in cold running water (2–3 min, three squeezings by hand during rinsing), hydroextracted, hot air dried and submitted to the ISO 105 CO6/C2S wash fastness test [8]. The stain on the cotton portion of the multi-fibre strip was assessed visually using grey scales. The results are shown in Table 11; the quoted K/S values refer to the dyed fabric, which was submitted to the test.

3. Results

3.1. Colour strength of dyes **4–6**

The colour strength of the three novel dyes varied from 58 to 77%, indicating strong products for evaluation (Table 4).

Table 4
Colour strength (effective agent content) of dyes **4–6** and the control dyes

Dye	MW	MI	Strength (%)
4	1219.5	1605	76
5	1221.5	2129	57
6	1323.5	1839	72
PR	1741	3307	53
PC	1755	2621	67
CN	1370	2605	53
CO	1621	2205	74

PR: Procion Red H-E7B, PC: Procion Crimson H-EXL, CN: Cibacron Navy LS-G, CO: Cibacron Orange LS-BR.

Table 5
Spectroscopic properties of dyes **4–6**

Dye	ε_{max} (l mol^{-1} cm^{-1})	λ_{max} (nm)	$\Delta\nu_{1/2}$ (nm)
4	66,200	539	108
5	68,200	537	109
6	55,500	534	109
PR	70,700	546	86
PC	62,200	547	88
CO	57,100	439	114
CN	90,300	620	107

3.2. Spectroscopic characteristics of dyes **4–6**

As expected, the results obtained fall in the range of that of their mono-functional analogues [1]. All three dyes **4–6** exhibited a *dull* violet shade, in keeping with their broad half-band width (Table 5).

3.3. Evaluation of the technical properties of dyes **4–6**

The technical properties of the synthesised and the control dyes are summarised in the following sections.

3.3.1. Effect of salt concentrations and dyeing temperature on the visual colour yield

Table 6
Variation in the colour yield of dye **4** with changes in salt concentrations and dyeing temperature

Salt (g/l)	K/S values for dye **4** (2% depth, 20 g/l soda ash, LR 10:1)						
	Exhaustion at 90 °C				Exhaustion at 80 °C		
	Fixation at T (°C)				Fixation at T (°C)		
	90	80	70	60	80	70	60
0	11.5	9.5	6.8	7.4	9.4	6.9	6.2
15	13.9	14.2	12.8	13.9	13.1	11.3	10.4
30	14.0	13.0	12.7	13.7	12.4	10.0	9.4
40	13.2	12.4	12.0	12.9	11.8	9.8	9.6
60	11.8	10.9	10.3	11.2	10.1	8.2	8.1

Table 7
Variation in the colour yield of dye **5** with changes in salt concentration, temperature of exhaustion and temperature of fixation

Salt (g/l)	K/S values for dye **5** (2% depth, 20 g/l soda ash, LR 10:1)						
	Exhaustion at 90 °C				Exhaustion at 80 °C		
	Fixation at T (°C)				Fixation at T (°C)		
	90	80	70	60	80	70	60
0	13.5	12.3	11.1	11.3	10.6	10.2	9.6
15	14.2	14.0	13.7	13.6	12.5	12.3	12.1
30	13.9	13.5	13.1	13.0	11.9	11.1	11.6
40	13.5	12.9	12.7	12.9	11.6	10.5	9.6
60	13.1	11.8	10.0	11.6	10.8	8.7	8.4

Table 8
Variation in the colour yield of dye **6** with changes in salt concentration, temperature of exhaustion and temperature of fixation

Salt (g/l)	K/S values for dye **6** (2% depth, 20 g/l soda ash, LR 10:1)						
	Exhaustion at 90 °C				Exhaustion at 80 °C		
	Fixation at T (°C)				Fixation at T (°C)		
	90	80	70	60	80	70	60
0	11.7	11.0	9.9	10.7	11.4	9.2	9.2
15	15.0	14.0	13.9	13.2	13.8	13.6	13.1
30	15.3	14.0	15.0	13.4	14.2	14.1	13.4
40	15.4	14.0	14.7	13.7	14.4	14.2	14.0
60	15.4	14.5	14.7	14.0	14.4	14.0	13.8

3.3.2. Build-up curves

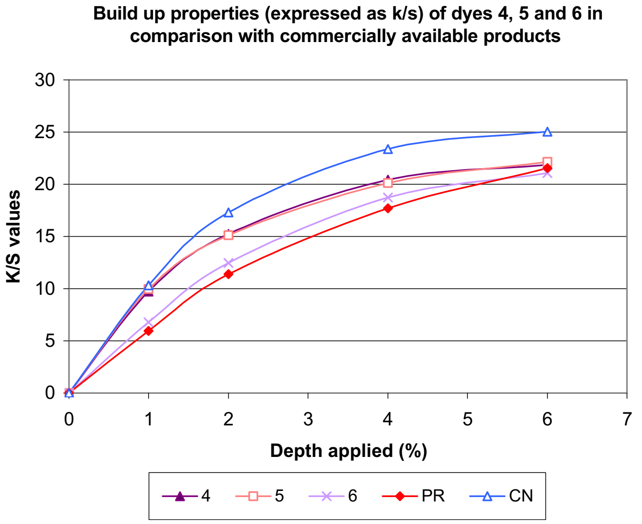


Fig. 2. Build-up curves (expressed as K/S) of dyes **4–6** and the control dyes.

3.3.3. SER$_5$F profiles

Table 9
SER$_5$F profiles of dyes **4–6** and control dyes

Dye	K/S values	S (%)	E (%)	F (%)	R_5 (%)	$E-F$ (%)
4	14.6	67	86	65	80	21
5	14.4	85	97	77	86	20
6	14.3	72	91	74	95	17
PR	14.4	80	88	73	48	15
CN	14.7	74	91	78	95	13

S: substantivity; E: exhaustion; F: fixation, R_5: fixation after 5 min/the final fixation, expressed as a percentage.

3.3.4. Migration indices

Table 10
Migration indices (MI) of dyes **4–6** and the control dyes

Dye	S (%)	MI (%)
4	67	48
5	85	54
6	72	64
PR	80	52
CN	74	55

PR: Procion Red H-E7B, CN: Cibacron Navy LS-G.

3.3.5. Comparison of the ease of wash-off of dyes **4–6** and the control dyes

Table 11
ICI short liquor ratio wash-off test results

Dyes	K/S value	Depth (%)	Salt (g/l)	Soda ash (g/l)	Staining on cotton
4	15.2	1.6	15	20	1–2
5	16.8	2.0	15	20	1–2
6	14.4	1.9	15	20	2–3
CN	14.3	1.4	15	20	3–4
PR	15.3	2.8	45	20	4

CN: Cibacron Navy LS-G, PR: Procion Red H-E7B.

4. Discussion

Three novel hetero bi-functional trisazo reactive dyes **4–6** were synthesised and their dyeing behaviour was investigated. The effect of salt concentration, the temperature of the neutral exhaustion phase and the temperature of the fixation phase of the dyeing process on colour yield were examined, in order to define their optimum application conditions. Subsequently, the build-up properties, SER$_5$F profiles, migration indices and wash fastness properties of the dyes were evaluated in order to judge whether such hetero bi-functional trisazo structures represented a commercially viable approach to producing low salt, high colour strength, highly fixation efficient, bright reactive dyes. The results are discussed in the following sections.

4.1. Spectroscopic characteristics of the dyes

Table 5 shows the spectroscopic characteristics of dyes **4–6** and the control dyes. The molar extinction coefficients of the novel dyes varied within the range 55,500–68,200 $\mathrm{l\,mol^{-1}\,cm^{-1}}$, those of the commercial control dyes within the range 57,100–90,300 $\mathrm{l\,mol^{-1}\,cm^{-1}}$. Dye **6** exhibited a lower extinction coefficient than either **4** or **5**, possibly due to the electronic effect of the additional sulphonic acid group in the molecule [9].

4.2. Effect of salt concentrations and dyeing temperature on colour yield

Because each of the dyes possesses a monochlorotriazinyl (MCT) group (usual fixation temperature 80–90 °C), and a β-sulphatoethylsulphone (SES), which fixes at 60 °C, the effect of a range of fixation temperatures, from 60 to 90 °C, on the visual colour yield was assessed. Also, different salt concentrations were examined using neutral exhaustion temperatures, 80 and 90 °C, with 2% dye o.m.f.

Tables 6–8 show the effect of variations in the salt concentration, neutral exhaustion temperature and fixation temperature on the visual colour yield of dyes **4–6** at 2% o.m.f. depth of shade, respectively. The colour yield of dye **6** initially increases with salt concentration, reaching a 'plateau' in the presence of 15 g/l. However, dyes **4** and **5** show a maximum colour yield at 15 g/l salt, further increases in the amount of salt, reducing the colour yield.

The role of salt in the dyeing process is to suppress the repulsion between the negative charge on the surface of the cellulose and the anionic dye, thereby increasing its substantivity for the cotton. This effect will progressively increase as the concentration of salt is increased, leading to a higher colour yield. In the case of dye **6**, this mechanism appears to operate. However, dyes **4** and **5** behave in a different manner. The reduction in colour yield when the concentration of salt is increased above 15 g/l could be due to pronounced aggregation of the dye molecules in the bath, leading to reduced solubility (even partial precipitation) and prevention of the dye being adsorbed onto the cotton.

Consideration of the molecular structure of the dyes (Table 2) shows that the only difference between the dyes is the nature of substituents X and Y. Since the solubility would be expected to increase with the introduction of an additional sulphonic acid group, it is not surprising that dye **6** should be less 'salt sensitive' than both dyes **4** and **5**.

It would be expected that problems associated with aggregation would be less pronounced if the 'salting phase' of the dyeing process was carried out at temperatures higher than 80 °C, with the temperature subsequently lowered to 80 °C to effect fixation. The beneficial effect of a higher 'neutral exhaustion' temperature is partially shown in Tables 6–8, the decrease in colour yield with increasing salt concentration being slightly less pronounced at 90 °C than at 80 °C, particularly at the higher (2%) applied depth. Increasing the fixation temperature from 60 to 90 °C, at any level of salt concentration within the range 0–60 g/l, increases the visual colour yield of the dyes on cotton (see Tables 6–8). This could be due to reacting additional fixation taking place in the MCT group at higher temperatures.

4.3. Build-up properties of the dyes

Fig. 2 shows the build-up properties of the dyes alongside two commercial products used as controls. All the three novel dyes exhibited better build-up characteristics than those of their mono-functional analogues, which tailed off at paler depths of shade [1]. The build-up properties of dyes **4–6** are comparable with those of the control dyes. All three novel dyes exhibited better build-up than Procion Red H-E7B. Dyes **4** and **5** were similar in strength to Cibacron Navy LS-G up to 1% depth of shade but thereafter build-up tailed off.

4.4. Dyeing properties of the dyes

In order to predict the (likely) level of dyeing and fastness properties of the trisazo dyes **4–6** under (bulk) exhaust dyeing conditions, the SER_5F profile and reactivity (R_5) of the dyes were measured and compared against a series of commercially available products. The results are shown in Table 9. Dyes **5** and **6** both exhibit higher substantivity (85%–72%) and higher exhaustion (97%–91%) levels than dye **4** (67% and 86%, respectively), the former dyes being similar to Procion Red H-E7B and Cibacron Navy LS-G. High substantivity and exhaustion are desirable properties of dyes from an environmental and economical point of view, provided high fixation of the exhausted dye also occurs. However, high substantivity can lead to unlevelness, unless careful control of the neutral/salting stage of the dyeing process is carried out. All the three dyes exhibited commercially acceptable substantivity and exhaustion levels.

The fixation levels of dyes **5** (77%) and **6** (74%) are similar to those of both Procion Red H-E7B (73%) and Cibacron Navy LS-G (78%), dyes of similar substantivity. However, dye **4** exhibited a lower fixation level (65%). This may be a reflection of its lower substantivity.

The reactivity of a dye (R_5) is defined as the fixation that occurs 5 min after the addition of alkali compared with the final fixation, expressed as a percentage. It is therefore an indication of how quickly a dye fixes to cellulose; a high value suggests a *risk* of unlevelness if the level of secondary exhaustion ($E-S$) is high and the need for gradual addition of alkali. Examination of the R_5 values of the novel dyes (Table 9) show that dyes **5** and **6** (86% and 95%, respectively) exhibit similar rates of fixation to that of Cibacron Navy LS-G (95%) and much greater than that of Procion Red H-E7B (48%). The rate of fixation of dye **4** (80%) is lower than that of the other two novel dyes and Cibacron Navy LS-G and much greater than that of Procion Red H-E7B. All the three novel dyes and Cibacron Navy LS-G showed a high rate of fixation, suggesting that careful alkali addition is required to achieve level dyeing properties.

A useful indicator of the ease of washing off of the hydrolysed reactive dye, in order to achieve good wet fastness properties, can be obtained by examination of the difference between the exhaustion (E) and fixation (F) values. A high '$E-F$' value means a large amount of hydrolysed dye needing to be washed out during the rinsing and 'soaping' stages. This results in potentially lengthy washing sequences, especially if the dye exhibits a high substantivity (S). Table 9 clearly shows that the $E-F$ levels of dyes **4** and **5** (21% and 20%, respectively) are greater than those of the commercial dyes (13–15%), products which themselves may be regarded as needing relatively long washing off sequences. The $E-F$ level of dye **6** (17%) is almost similar to that of Procion Red H-E7B (15%) but greater than that of Cibacron Navy LS-G (13%). Hence, one would suspect that dyes **4** and **5** would require a longer washing off sequence than the control dyes to achieve good wet fastness properties (see Section 3.3.3). Dye **6** would probably require shorter washing times that the other two novel dyes to achieve a given level of wet fastness.

*4.5. Migration indices of dyes **4–6***

The migration index of a dye is often a reflection of its substantivity, highly substantive dyes exhibiting a low migration index and vice versa. Table 10 shows that the migration index of dye **6** (64%) is much better than those of dyes **4** (48%) and **5** (54%) and control dyes (Procion Red H-E7B, 52%; Cibacron Navy LS-G, 55%). The migration properties of dyes **4** and **5** are similar to those of Procion Red H-E7B (C.I. Reactive Red 141, 52%) and Cibacron Navy LS-G (55%). Hence, dye **6** is likely to represent better level dyeing properties than the other two novel dyes as well as the control dyes.

*4.6. Comparison of the ease of wash-off of dyes **4–6** and the control dyes*

Table 11 shows the ICI short liquor ratio washing fastness for the three trisazo dyes in comparison with the commercial dyes used as 'controls'. The level of cotton staining (1–2 for **4** and **5**; 2–3 for **6** versus levels of either 3–4 or 4 for the 'controls') is commensurate with the higher levels of hydrolysed dye ($E-F$) to be washed off—see Table 9.

Although the fixation efficiencies of dyes **5** and **6** were almost similar to those of the control dyes (**5** similar to Cibacron Navy LS-G; **6** similar to Procion Red H-E7B), their higher level of exhaustion led them to exhibit higher $E-F$ levels resulting in poor washing off properties.

5. Conclusions

Three novel trisazo dyes (**4–6**) have been synthesised and their technical properties compared with a series of commercial products. Dyes **4** and **5** exhibited higher molar extinction coefficients (66,200–68,200 $\mathrm{l\,mol^{-1}\,cm^{-1}}$) than **6** (55,500 $\mathrm{l\,mol^{-1}}$). All three dyes gave a *dull* violet shade when applied to cotton. However, they could be applied to cotton by exhaust dyeing using relatively low salt quantities (15–30 g/l) because of their high substantivity. They exhibited good build-up properties and better migration indices. Dyes **4** and **5** exhibited better build-up properties than **6** and Procion Red H-E7B but lower than that of Cibacron Navy LS-G. However, all the three dyes required a longer washing off process than the control dyes, but displayed good build-up properties and moderate migration index values.

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