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Synthesis and evaluation of a series of trisazo, monochloro-*s*-triazinyl (MCT) reactive dyes for cotton

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Abstract

Three novel trisazo, monochloro-*s*-triazinyl (MCT) reactive dyes were synthesised with a view to achieving heavy bright shades on cotton by exhaust dyeing using low concentrations of salt. Unfortunately, the dyes proved to be dull violet in shade, exhibiting modest build-up and poor level of dyeing and wash fastness properties, although two of them exhibited their optimum colour yield using low salt quantities (0–30 g/l).

Keywords: Reactive dyes; Trisazo dyes; Salt; Monochloro-*s*-triazinyl (MCT) reactive group; Exhaust dyeing

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1. Introduction

Ayyangar et al. [1,2] reported that disazo dyes are tinctorially stronger than monoazo dyes, making them potentially more economic. For example, the monoazo red reactive dye, Procion Red P-4BN (C I Reactive Red 3.1 ex DyStar), has an extinction coefficient ($\varepsilon_{\max}$) of 30,000 $dm^3\,mol^{-1}\,cm^{-1}$ [3], whereas Levafix Brilliant Red E-2GN (DyStar), a very bright disazo reactive dye, has an extinction coefficient of about 50,000 $dm^3\,mol^{-1}\,cm^{-1}$. It might be expected that trisazo dyes would be tinctorially even stronger, though dullness of shade sometimes accompanies high chromophoric strength.

The objectives of the current investigation were to synthesise and evaluate tinctorially strong, bright reactive dyes, which could be applied to cotton by exhaust dyeing using low salt (0–30 g/l) quantities. To this effect three novel monochloro-*s*-triazinyl (MCT) trisazo reactive dyes (**RD1**, **RD2** and **RD3**) were synthesised by coupling a series of diazotised disazo intermediates onto 1-hydroxy-6-(4′-chloro-6′-[4″-sulphophenylamino-] triazin-2-yl) aminonaphthalene-3-sulphonic acid (**Structure 1**).

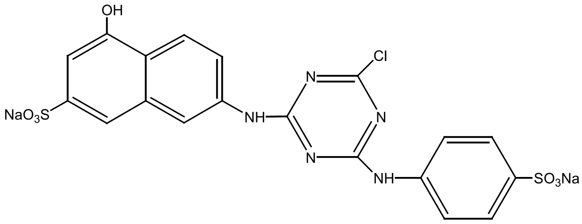

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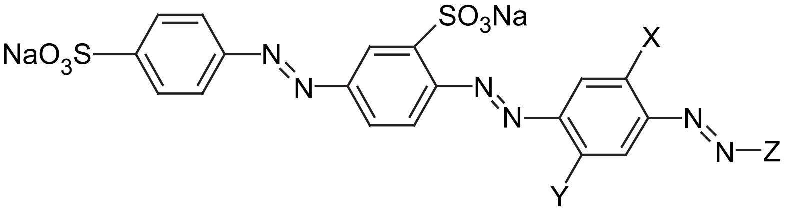
Table 1
Structures of novel dyes



Dye	X	Y	ZH
RD1	$-CH_3$	$-CH_3$	**Structure 1**
RD2	$-H$	$-OCH_3$	**Structure 1**
RD3	$-SO_3Na$	$-OCH_3$	**Structure 1**

The structures of the synthesised trisazo dyes are summarised in Table 1.

2. Experimental

2.1. Instrumental and analysis methods

2.1.1. UV/visible spectrometry

The visible absorption spectra of dyes were recorded using a Phillips model PU 8700 UV/visible spectrophotometer.

2.1.2. Thin layer chromatography (TLC)

Thin layer chromatography (TLC) was used for monitoring reactions. This technique was performed using aluminium plates coated with silica gel 60 F_{254} (Merck) as stationary phase and a mobile phase consisting of *n*-butanol:acetone: water (2:2:1). The developed plates were visualized under both short and long wavelength ultraviolet light (254 nm, 365 nm).

2.1.3. High performance liquid chromatography (HPLC)

The high performance liquid chromatography (HPLC) analyses were performed using a Hewlett–Packard 1100 liquid chromatograph with a 10 cm, Purospher RP-18 (5 μm) packing and LiChroCART 125-4 HPLC column cartridges. 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.

2.1.4. Elemental analysis

Elemental analyses for carbon, hydrogen, nitrogen and sulphur were carried out at the Department of Chemistry, UMIST, on a Carlo Erba 1108 elemental analyser.

2.1.5. Mass spectrometry

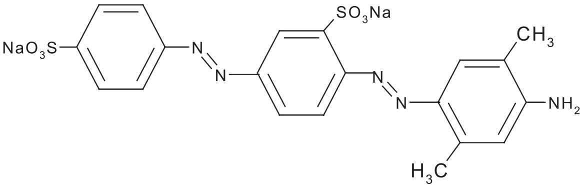
Mass spectrometry was performed using two different techniques, i.e. FAB (fast atomic bombardment) and MALDI (matrix assisted laser desorption ionisation) at the Department of Chemistry, UMIST.

2.2. Synthesis and characterisation of dyes

2.2.1. Materials

4-Amino-1,1′-azobenzene-3,4′-disulphonic acid, 2,5-dimethylaniline, 3-methoxy aniline, oleum, cyanuric chloride, 4-aminobenzene sulphonic acid, 7-amino-4-hydroxy naphthalene sulphonic acid and other chemicals were supplied by Aldrich Chemical Company Limited (UK). The cotton fabric used for the dye evaluation was a plain weave bleached cloth. Visking tubing used for dialysis was supplied by Merck.

2.2.2. Synthesis of (4-amino-2,5-dimethylphenyl-) azo-1,1′-azobenzene-3,4′-disulphonic acid (**Structure 2**)



The sodium salt of 4-amino-1,1′-azobenzene-3,4′-disulphonic acid (10.02 g, 0.025 mol) was dissolved in water (300 ml) at pH 7–8, and 20–25 °C. Sodium nitrite (1.79 g, 0.026 mol), dissolved in water (10 ml), was added and the resultant mixture was added dropwise to cold water (50 ml) containing hydrochloric acid (6.21 g, 37%, 0.063 mol) during 45 min. The diazotisation process was carried out at pH <2, and 0–5 °C over 75 min, after which excess nitrous acid was destroyed by the addition of sulphamic acid.

2,5-Dimethyl-aniline (3.15 g, 0.026 mol) was dissolved in glacial acetic acid (5 g) and the solution was then added dropwise to water (50 ml). The solution was then cooled to 0–5 °C by external cooling. To the aqueous solution of the coupling component, the diazonium salt solution prepared above was added over 30 min, at 0–5 °C with vigorous stirring. On completion of the addition, the pH of the reaction mixture was slowly raised to ca. pH 6.5–7.0, at 0–5 °C, over 30 min, by the dropwise addition of sodium carbonate solution (5%). The reaction mixture was allowed to warm to room temperature and precipitated solid (**Structure 2**) was filtered off and dried (12.8 g, strength 81%, yield 78%).

The process was followed using HPLC (starting material: RT = 1.17 min; product: RT = 1.90 min) and TLC (starting material: $R_f = 0.77$; product: $R_f = 0.78$). The purity of the product was determined using HPLC, 100%. After desalination, by dialysis, the product was re-precipitated and dried.

Mass spectrometry: m/e 488.3 $[M-H]^-$

Microanalysis: $C_{20}H_{17}N_5Na_2O_6S_2$ requires C, 42.4%; H, 4.2%; N, 12.3%; Na, 4.1%.

Found: C, 41.9%; H, 3.5%; N, 11.7%; Na, 4.2%.

$\lambda_{max} = 447$ nm

2.2.3. Synthesis of (4-amino-2-methoxyphenyl-) azo-1,1′-azobenzene-3,4′-disulphonic acid (**Structure 3**)

The sodium salt of 4-amino-1,1′-azobenzene-3,4′-disulphonic acid (16.04 g, 0.04 mol) was diazotised as described above.

3-Methoxy aniline (5.17 g, 0.042 mol) was dissolved in water (30 ml) containing hydrochloric acid (4 g, 30%). The solution was cooled to 5–10 °C, and over 10 min, the diazonium salt previously prepared was added dropwise with stirring maintaining the temperature at or below 5 °C. The pH of the reaction mixture was raised to 2.5–3 over 30 min by dropwise addition of sodium acetate (7 g, 30%). The reaction was stirred for 2 h at 5–10 °C and then the pH was raised to 8.0–8.5 by the dropwise addition of sodium hydroxide solution (3–4 g, 50%). The reaction mixture was stirred for 30 min at 15–18 °C and then the solid (**Structure 3**) was filtered off and dried (17.9 g, strength 88%, yield 74%).

Process was followed using HPLC (starting material: RT = 1.17 min; product: RT = 0.83 min) and TLC (starting material: $R_f = 0.77$; product: $R_f = 0.76$). The purity of the product was determined using HPLC, >93%. After desalination, by dialysis, the product was re-precipitated and dried.

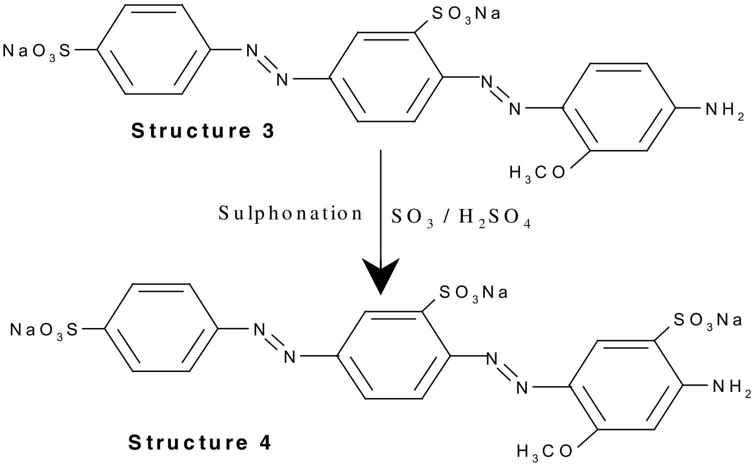
Microanalysis: $C_{19}H_{15}N_5Na_2O_7S_2$ requires C, 38.7%; H, 3.6%; N, 11.9%.

Found: C, 38.8%; H, 4.0%; N, 11.7%.

$\lambda_{max} = 475$ nm

2.2.4. Synthesis of (4-amino-2-methoxy-5-sulphophenyl-) azo-1,1′-azobenzene-3,4′-disulphonic acid (**Structure 4**)

Structure 4 was prepared by the sulphonation of **Structure 3** (Scheme 1).



Scheme 1

Structure 3 (10.7 g, strength 88%, 0.0176 mol) was dissolved in concentrated sulphuric acid (20 g) in 50 ml round-bottom flask at room temperature. To the solution, oleum (3.2 g, 0.04 mol) was then added and the temperature raised to 95–100 °C for 60 min. The reaction mixture was then poured into ice (the minimum amount predictable) and the resulting precipitate (**Structure 4**) was filtered off as a damp solid (16.6 g, strength 49%, yield 64%).

The progress of the reaction was followed step by step using HPLC (starting material: RT = 0.83 min; product: RT = 1.11 min) and TLC (starting material: $R_f = 0.76$; product: $R_f = 0.73$). The purity of the product was determined using HPLC, 95%. The product was characterised after desalination.

Mass spectrometry: m/e 572.4 $[M+H]^+$

Microanalysis: $C_{19}H_{14}N_5Na_3O_{10}S_3$ requires C, 32.2%; H, 2.8%; N, 9.9%.

Found: C, 32.3%; H, 3.5%; N, 9.7%.

$\lambda_{max} = 457.5$ nm

2.2.5. Synthesis of coupling component [1-hydroxy-6- (4′-chloro-6′-[4″-sulphophenylamino-] triazin-2-yl) aminonaphthalene-3-sulphonic acid] (**Structure 1**)

A solution of cyanuric chloride (9.75 g, 0.053 mol) in acetone (40 ml) was poured into a vigorously stirred mixture of crushed ice (100 g) and water (100 ml). A solution of 4-aminobenzene sulphonic acid (8.65 g, 0.05 mol) in water (100 ml, pH 6.5) was added dropwise at 0–5 °C over 30 min at pH 3.5–4.5, using sodium carbonate solution (10%w/v). The solution was stirred for a further 60 min to complete the reaction.

To the resulting solution of 4-(2,4-dichlorotriazin-6-ylamino-)benzene sulphonic acid, was added dropwise an aqueous solution (100 ml, pH 6.5) of 6-amino-1-hydroxynaphthalene-3-sulphonic acid (J acid) (12.86 g, 0.05 mol) at 35 °C over 60 min, at pH 4–4.5, using sodium carbonate solution (10% w/v). The mixture was stirred for a further 60 min to complete the reaction. The product (**Structure 1**) was used directly (see Section 2.2.6).

The progress of the reaction was followed using TLC and HPLC. The purity of the product was 92% by HPLC and the retention time of the product was 1.40 min.

2.2.6. Synthesis of dye **RD1** (see Table 1)

The sodium salt of the disazo dye (**Structure 2**) (5.33 g, strength 81%, 0.0081 mol) was diazotised using the inverse diazotisation method [4].

A solution of the reaction product described in the previous section containing 0.0085 mol of the coupling component (**Structure 1**) was measured out and the diazonium salt was then added very slowly to the solution over 2 h. The coupling reaction was completed after 30 min at pH 5–6, 25–30 °C, and then the product (**RD1**) was precipitated by adding industrial ethanol, filtered off and dried (7.8 g, strength 87%, yield 75%, $R_f = 0.73$).

The purity of the product was 90% by HPLC, retention time 3.50 min (1.45 min for the starting material).

The product was desalinated by dialysis.

$\lambda_{max} = 536$ nm, $\varepsilon_{max} = 64{,}100$ dm^3 mol^{-1} cm^{-1}.

2.2.7. Synthesis of dye **RD2** (see Table 1)

The sodium salt of the disazo dye (**Structure 3**) (5.35 g, strength 88%, 0.0088 mol) was diazotised using the inverse diazotisation method [4].

A solution of the coupling component (**Structure 1**) (0.0092 mol) was adjusted to pH 5–6, 25–30 °C. The coupling reaction was carried out as described in Section 2.2.6. The product (**RD2**) was filtered off and dried (8.51 g, strength 81%, yield 70%, $R_f = 0.71$).

The purity of product was 94% by HPLC, retention time 3.37 min (0.87 min for the starting material).

$\lambda_{max} = 536$ nm, $\varepsilon_{max} = 67{,}500$ dm^3 mol^{-1} cm^{-1}.

2.2.8. Synthesis of dye **RD3** (see Table 1)

The sodium salt of the disazo dye (**Structure 4**) (6.37 g, strength 49%, 0.0049 mol) was diazotised using nitrosylsulphuric acid [4].

A solution of the coupling component (**Structure 1**) (0.0051 mol) was measured out and the pH raised to pH 5–6 at 25–30 °C. The coupling process was followed as described in Section 2.2.6 and the product (**RD3**) was filtered off and dried (6.9 g, strength 60%, yield 70%, $R_f =$ 0.69).

The purity of the product was 80% by HPLC, retention time 3.36 min (1.12 min for the starting material).

$\lambda_{max} = 531$ nm, $\varepsilon_{max} = 43{,}400$ dm^3 mol^{-1} cm^{-1}.

2.2.9. Determination of the colour strength of **RD1**, **RD2** and **RD3**

The strengths of the dyes were determined by titration with titanium (III) chloride [5] and the results are shown in Table 3.

2.2.10. Determination of the spectroscopic characteristics of **RD1**, **RD2** and **RD3**

Solutions of the three novel dyes **RD1**, **RD2** and **RD3** in the concentration range of 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 width and the molar extinction coefficients (ε_{max}) of the dyes were determined and are shown in Table 4.

2.3. Evaluation of the application properties of dyes **RD1**, **RD2** and **RD3**

The technical properties of **RD1**, **RD2** and **RD3** 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 of dyeing properties. Procion Crimson H-EXL possesses a higher migration index [6] than Procion Red H-E7B, indicating superior level dyeing characteristics.

Samples of cotton (2 g pieces of unmercerized, scoured, bleached woven fabric) were dyed at different depths of shade in a Roaches dyeing machine. In the case of **RD1**, **RD2** and **RD3**, because the reactive group (MCT) is the same as that in the Procion dyes, the dyeing profile used was that recommended for Procion H-E dyes (Fig. 1). Dyeing with the Cibacron LS dyes was carried out as described in the manufacturer's pattern card (Fig. 2).

2.3.1. Effect of salt concentration on the visual colour yield of **RD1**, **RD2** and **RD3**

In order to determine the effect of various salt (NaCl) concentrations on the visual colour yield of **RD1**, **RD2** and **RD3**, a series of dyeings of both these and the Cibacron LS dyes were carried out at 2% depth of shade using 0 g/l–75 g/l salt and 10:1 liquor ratio, employing the dyeing sequences shown in Figs. 1 and 2. The visual colour yield was expressed as a K/S value [7], measured at the λ_{max} of each dye, using a Spectroflash 600 spectrophotometer from Datacolor International. The results are shown in Fig. 3.

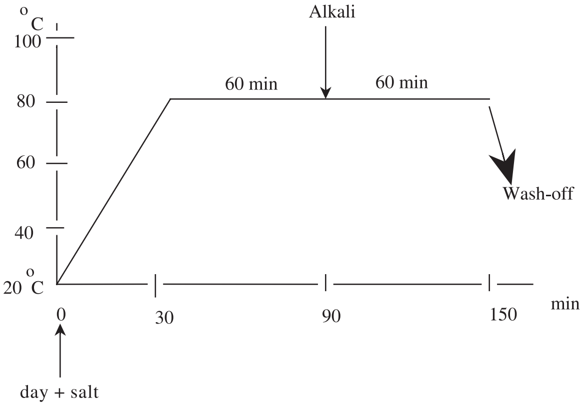


Fig. 1. Dyeing profile for **RD1**, **RD2**, **RD3** and the Procion dyes.

2.3.2. *Effect of neutral exhaustion temperature on the colour yield of* ***RD1*** *and* ***RD2***

RD1 and **RD2** were applied to cotton at 1% and 2% depth of shade in the presence of different salt quantities and using 15 and 20 g/l soda ash, respectively, for fixation at a liquor ratio of 10:1. Temperatures of 80 °C and 90 °C were used for the neutral (salt) exhaustion stage, cooling to 80 °C, in the latter case, to effect fixation. The results are shown in Figs. 4 and 5.

2.3.3. *Build-up properties of* ***RD1, RD2*** *and* ***RD3***

The build-up properties of the control dyes were examined using the dyeing profiles shown in Figs. 1 and 2. For the novel dyes, Procion H-E/H-EXL conditions were used together with salt concentrations selected from the previously described study (Section 2.3.1). The composition of the various dyebaths is summarised in Table 2 and the build-up curves are shown in Fig. 6.

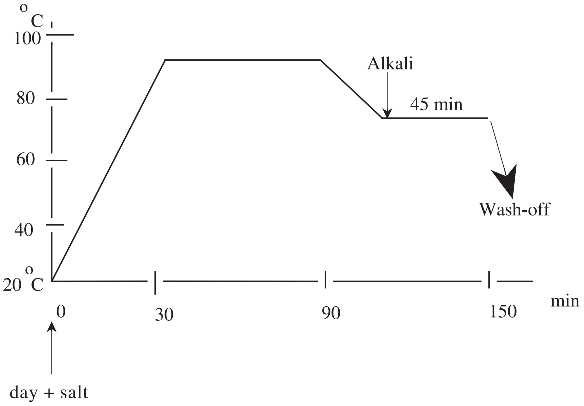


Fig. 2. Dyeing profile for the Cibacron LS dyes.

2.3.4. *Measurement of the SER$_5$F profiles of* ***RD1, RD2, RD3*** *and the control dyes*

The SER$_5$F profiles [8] of the dyes were compared at the same visual colour yield ($K/S = 10$). These values were determined from Fig. 6.

Hence the SER$_5$F profiles of **RD1**, **RD2** and Cibacron Navy LS-G were determined at 1% o.m.f., Procion Red H-E7B and Procion Crimson H-EXL at 1.6% and Cibacron Orange LS-BR and **RD3** at 2%.

The substantivity (*S*) of **RD1**, **RD2** and **RD3** and Procion dye controls was determined by measuring the exhaustion of the dyebath after 60 min at 80 °C using 15 g/l and 45 g/l salt, respectively. The corresponding values for the two Cibacron LS dyes were determined after 60 min at 90 °C in the presence of 15 g/l salt.

The exhaustion (*E*) was measured 60 min after the addition of 15 g/l soda ash at 80 °C in the case of the novel and Procion dyes and at 70 °C for the Cibacron LS controls.

2.3.5. *Determination of the migration indices of* ***RD1, RD2, RD3*** *and the control dyes*

Migration refers to the movement of a dye molecule from one site to another on the textile substrate via a desorption process into the dyebath. By this means, a uniform dyeing over the whole of the textile substrate can be achieved. Because a reactive dye forms a covalent bond with cellulose under alkaline conditions, migration must take place primarily during the neutral salting phase in order to achieve a uniform dyeing. This is particularly the case with high substantivity (*S*) dyes. Opportunity for migration after the addition of alkali will be limited.

The migration properties of reactive dyes can be 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 [9].

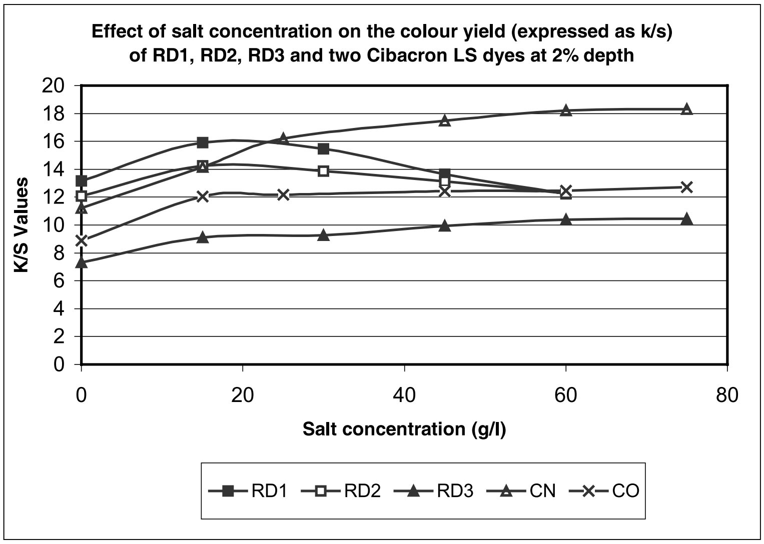


Fig. 3. Effect of salt concentration on the colour yield (expressed as K/S) of **RD1**, **RD2**, **RD3** and the control dyes at 2% applied depth. CN: Cibacron Navy LS-G; CO: Cibacron Orange LS-BR.

As for the determination of the SER_5F profiles, each dye was applied at $K/S = 10$ on unmercerized plain woven cotton using 15 g/l soda ash to fix each dye but different salt levels, viz. 15 g/l for dyes **RD1**, **RD2**, **RD3** and the Cibacron LS dyes; 45 g/l for the Procion H-E(XL) dyes. The migration index results are given in Table 6.

2.3.6. *Wash fastness properties of **RD1**, **RD2**, **RD3** and the control dyes*

The wash fastness properties of dyes were assessed using the ISO 105 CO6/C2S wash fastness test [10].

The change in shade and the degree of cross staining were assessed visually using grey scales and the results are presented in Table 7. The fastness

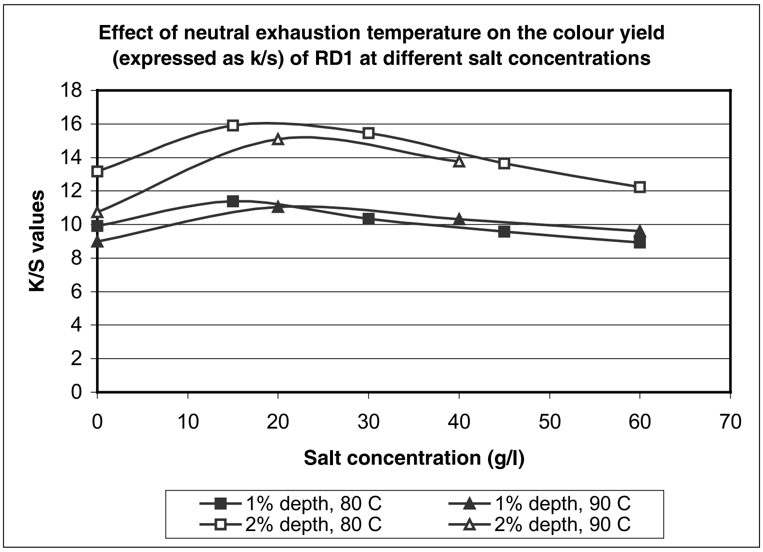


Fig. 4. Effect of neutral exhaustion temperature on the colour yield (expressed as K/S) of **RD1** at different salt concentrations.

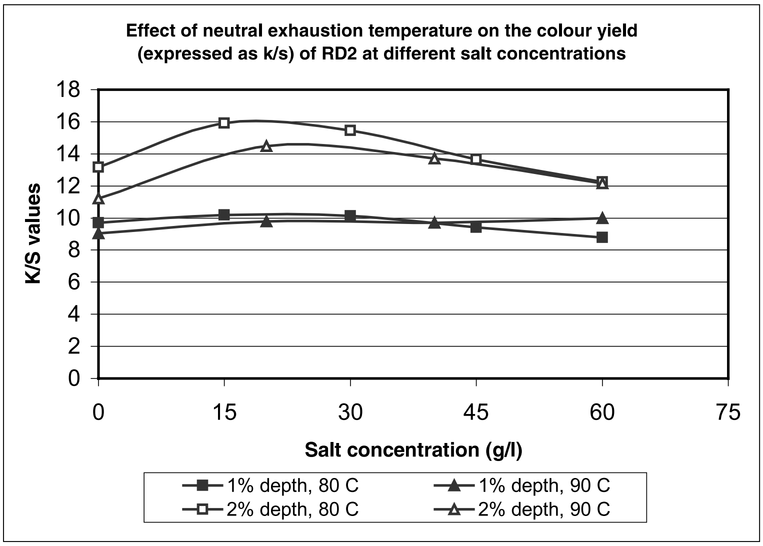


Fig. 5. Effect of neutral exhaustion temperature on the colour yield (expressed as K/S) of **RD2** at different salt concentrations.

tests were carried out after a similar washing off sequence had been applied to all the cotton samples, dyed to the same visual depth of shade ($K/S = 10$), viz. 3 cold (20 °C) rinses at L:R 20:1 for 5 min; 1 soap boil (L:R, 20:1, 15 min), 1 cold rinse.

3. Results

3.1. Colour strength of ***RD1***, ***RD2*** and ***RD3***

The colour strength of the three novel dyes varied from 60–87%, indicating strong products for evaluation (see Table 3).

3.2. Spectroscopic characteristics of ***RD1***, ***RD2*** and ***RD3***

The three novel dyes exhibited a **dull** violet shade, in keeping with their broad half-band width compared with the bright bluish-red Procion dyes (see Table 4).

3.3. Evaluation of the application properties of ***RD1***, ***RD2*** and ***RD3***

The application properties of the dyes are summarised below.

The effect of salt concentration on the visual colour yield of **RD1**, **RD2**, **RD3** and the two Cibacron LS dyes is shown in Fig. 3.

The effect of neutral exhaustion temperature on the colour yield of **RD1** and **RD2** is shown in Figs. 4 and 5.

The build-up curves of **RD1**, **RD2**, **RD3** and the control dyes are shown in Fig. 6.

The SER$_5$F profiles of **RD1**, **RD2**, **RD3** and the control dyes are shown in Table 5.

Table 2
Dyebath compositions when examining the build-up properties of **RD1**, **RD2**, **RD3** and the control dyes

Depth of shade (% o.m.f.)	Salt concentration (g/l)							Soda ash (g/l)	L:R
	RD1	**RD2**	**RD3**	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	30	30	60	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.

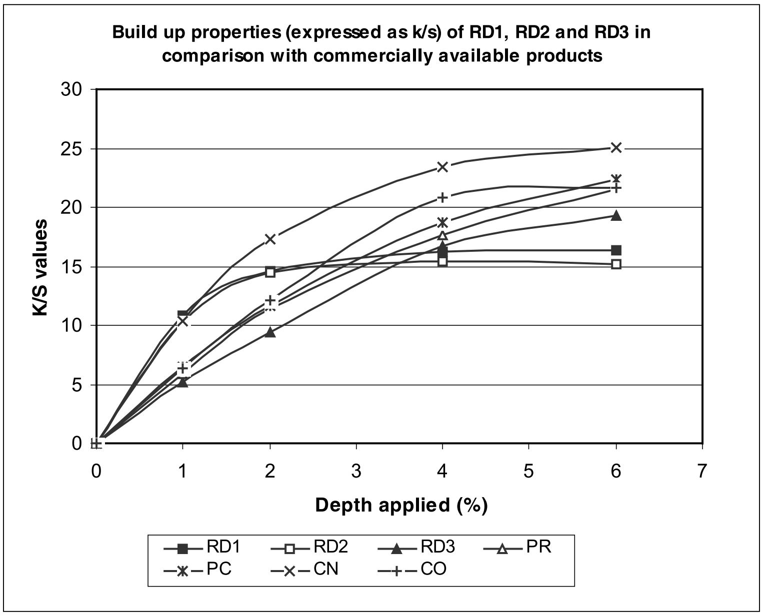


Fig. 6. Build-up curves (expressed as K/S) of **RD1**, **RD2**, **RD3** and the control dyes.

The migration indices of **RD1**, **RD2**, **RD3** and the control dyes are shown in Table 6.

The wash fastness properties of **RD1**, **RD2**, **RD3** and the control dyes are shown in Table 7.

4. Discussion

Three novel mono-functional (MCT) trisazo reactive dyes **RD1**, **RD2** and **RD3** were synthesised and their dyeing behaviour was investigated. The effect of salt concentration and the temperature of the neutral exhaustion phase of the dyeing process on colour yield was examined in order to define the optimum application conditions for the dyes. Subsequently, the build-up properties, SER_5F profiles, migration indices and wash fastness properties of the dyes were evaluated in order to judge whether such mono-functional trisazo structures represented a commercially viable approach to producing low salt, high colour strength, high fixation efficient, and bright reactive dyes. The results are discussed in the following sections.

Table 3
Colour strength of synthesised and control dyes

Dye	Molecular weight (MW)	Mole In (MI)	Strength (%)
RD1	1111.5	1277	87
RD2	1113.5	1380	81
RD3	1215.5	2026	60
PR	–	3307	–
PC	–	2621	–
CN	–	2605	–
CO	–	2205	–

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

4.1. Spectroscopic characteristics of the dyes

Table 4 shows the spectroscopic characteristics of both the novel dyes **RD1**, **RD2**, **RD3** and the control dyes. The molar extinction coefficients of

Table 4
Spectroscopic properties of **RD1**, **RD2** and **RD3**

Dyes	ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)	λ_{max} (nm)	$\Delta\nu_{1/2}$ (nm)
RD1	64,100	536	101
RD2	67,500	536	103
RD3	43,400	531	119
PR	70,700	546	86
PC	62,200	547	88
CO	57,100	439	114
CN	90,300	620	107

Table 5
SER$_5$F profiles of **RD1**, **RD2**, **RD3** and control dyes

Dye	*S* (%)	*E* (%)	*F* (%)	R_5 (%)	*E*−*F* (%)
RD1	87	96	70	57	26
RD2	90	98	69	56	29
RD3	60	78	55	77	23
PR	88	90	75	63	17
PC	58	72	59	66	13
CO	65	75	65	62	10
CN	87	94	82	86	12

S: Substantivity; *E*: Exhaustion; *F*: Fixation; R_5: Fixation after 5 min/the final fixation, expressed as a percentage.

the synthesised dyes varied within the range of 43,400–67,500 dm^3 mol^{-1} cm^{-1}, those of **RD1** and **RD2** falling within the range of the control dyes (57,100–90,300).

The lower extinction coefficient of **RD3**, relative to both **RD1** and **RD2**, is attributed to the electronic effect of the additional sulphonic acid group, *ortho* to an azo linkage within the trisazo structure [11].

4.2. Effect of salt concentration and neutral exhaustion temperature on the colour yield of the dyes

Fig. 3 shows the effect of variations in the salt concentration on the colour yield of the novel dyes at 2% depth of shade. The colour yield of the control dyes and **RD3** initially increases with salt concentration, reaching a ‘plateau’ in the presence of either 15 g/l (**RD3** and Cibacron Orange LS-BR) or 40 g/l in the case of Cibacron Navy LS-G. However, **RD1** and **RD2** show a maximum colour yield at 15 g/l salt, further increases in the amount of salt leading to a reduction in colour yield.

Table 6
Migration index (MI) results of **RD1**, **RD2**, **RD3** and the control dyes

Dye	S (%)	MI (%)
RD1	87	54
RD2	90	57
RD3	60	66
PR	88	52
PC	58	80
CN	87	55
CO	65	73

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

The role of salt in the dyeing process is both to suppress the repulsion between the negative charge on the surface of the cellulose and the anionic dye and to allow the anionic dye to form small aggregates, thereby increasing its substantivity for the cotton. These two effects will progressively increase as the concentration of salt is increased, leading to a higher colour yield. In the case of the control dyes and **RD3**, this mechanism appears to operate. However, **RD1** and **RD2** 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 dyebath, leading to reduced solubility (even partial precipitation) and prevention of the dye being adsorbed onto the cotton.

Consideration of the molecular structures of the dyes (Table 1) 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 **RD3** should be less ‘salt sensitive’ than both **RD1** and **RD2**.

It might 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 being lowered to 80 °C to effect fixation. The beneficial effect of a higher ‘neutral exhaustion’ temperature is partially shown in Figs. 4 and 5; the decrease in colour yield with increasing salt concentration being slightly less pronounced at 90 °C than at 80 °C; particularly at the heavier (2%) applied depth.

4.3. Build-up properties of the dyes

Fig. 6 shows the build-up properties of the synthesised dyes in comparison with two commercially available products.

RD1 and **RD2** build-up well to 2% but thereafter the build-up tails off. **RD3** continues to build-up beyond 2% applied depth but exhibits inferior build-up characteristics to the commercial

Table 7
Wash fastness results of **RD1**, **RD2**, **RD3** and the control dyes in the ISO 105 CO6/C2S test

Dye	Grey scale staining assessment						Change of shade
	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	Acetate	
RD1	5	5	5	5	3–4	5	4
RD2	5	5	5	5	3–4	5	4
RD3	5	5	5	5	4	5	4
PR	5	5	5	5	4–5	5	4–5
PC	5	5	5	5	4–5	5	4–5
CN	5	5	5	5	4	5	4–5
CO	5	5	5	5	4	5	4–5

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

products. To exhibit acceptable build-up properties, a dye should have a high extinction coefficient, a high level of exhaustion and a high degree of fixation. Since all three novel dyes have extinction coefficients in the range of 43,000–67,000 (see Table 4), their relatively poor build-up properties are probably a reflection of their inferior exhaustion and fixation properties at heavy applied depths, particularly **RD1** and **RD2**.

4.4. Dyeing properties of the dyes

In order to predict the likely (level) dyeing and fastness properties of the trisazo dyes under (bulk) exhaust dyeing conditions, the SER$_5$F profiles of the dyes were measured and compared against a series of commercially available products. The results are shown in Table 5. **RD1** and **RD2** both exhibit higher substantivity (87–90%) and higher exhaustion (96%–98%) levels than **RD3** (60% and 78%, 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 an economical point of view, provided that 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, precautions would seem necessary if both **RD1** and **RD2** were to be applied under bulk conditions.

The fixation levels of **RD1** (70%) and **RD2** (69%) are lower than those from both Procion Red H-E7B and Cibacron Navy LS-G, dyes of similar substantivity. This may be attributed to the fact that the two trisazo dyes contain only one reactive group, whereas the commercial dyes are bi/poly-functional. The lower fixation of **RD3**, relative to **RD1** and **RD2**, is probably 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 suggesting a *risk* of unlevelness if the level of secondary exhaustion ($E-S$) is high and the need for slow addition of alkali under bulk processing conditions. Examination of the R_5 values of **RD1** and **RD2** (Table 5) show that they exhibit slower rates of fixation than most of the commercial dyes, suggesting that the alkali addition stage should not represent a threat to achieving level dyeing properties. **RD3** could, however, present a greater level dyeing problem with its fast rate of fixation!

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 will result in potentially lengthy washing sequences, especially if the dye possesses a high substantivity (S). Table 5 clearly shows that the $E-F$ levels of the trisazo dyes (23–29%) are greater than those of the commercial dyes (10–17%), products which themselves may be regarded as needing relatively long washing off sequences. Hence, one would suspect that **RD1** and **RD2** would require a longer washing off sequence than the commercial dyes to achieve good wet fastness properties (see Table 5). **RD3** would probably require shorter washing times than the other two novel dyes to achieve a given level of wet fastness.

4.5. Migration indices of the dyes

The migration index (MI) of a dye is often a reflection of its substantivity; highly substantive dyes exhibiting a low migration index and vice versa. Table 6 shows that the migration indices of **RD1** and **RD2** (54–57%) are similar to that of Procion Red H-E7B (52%) and much inferior to the more level dyeing Procion Crimson H-EXL (80%). Hence, **RD1** and **RD2** are likely to represent more of a level dyeing problem than **RD3**. For example, the dyeing of pale-medium shades with **RD1** and **RD2** would probably require the use of portion-wise addition of salt and elevated (migration) temperatures to maximise the chances of achieving a good level dyeing performance.

4.6. Wash fastness properties of the dyes

Table 7 shows the (60 °C) washing fastness for the three trisazo dyes in comparison with the commercial dyes as ‘controls’. The level of cotton staining (3–4 for **RD1** and **RD2**; 4 for **RD3** versus levels of either 4 or 4–5 for the ‘controls’) is commensurate with the higher levels of hydrolysed dye ($E-F$) to be washed off and the relatively higher substantivity values (S) of **RD1** and **RD2**—see Table 5 and Table 7.

Hence, high substantivity dyes exhibiting relatively low levels of fixation efficiency (**RD1** and **RD2**), by virtue of their one reactive group, will struggle to meet commercial fastness specifications without the use of extended washing off sequences (and the use of cationic after-treatment agents). The three trisazo dyes certainly exhibit inferior wash fastness to the commercial dyes, many of which might be regarded as products, which exhibited slow washing off characteristics!

5. Conclusions

Three novel trisazo dyes (**RD1**, **RD2** and **RD3**) have been synthesised and their technical properties compared with a series of commercial products. **RD1** and **RD2** exhibited higher molar extinction coefficients (64,000–67,000 $dm^3 mol^{-1} cm^{-1}$) than **RD3**, 43,000 $dm^3 mol^{-1} cm^{-1}$. All three dyes gave a *dull* violet shade when applied to cotton. **RD1** and **RD2** can be applied to cotton by exhaust dyeing using relatively low salt quantities (0–30 g/l) because of their high substantivity. However, they exhibited poor build-up properties, probably as a result of their limited aqueous solubility and the presence of only one reactive grouping in the molecule. Nevertheless, **RD1** and **RD2** could be regarded as low salt dyes, requiring similar salt levels to the Cibacron LS dyes, although their build-up properties were markedly inferior. In addition, their exhaust application in pale-medium shades is likely to result in level dyeing problems because of their high substantivity and poor migration properties. **RD3**, by virtue of its lower level of substantivity, required higher salt concentrations to achieve modest build-up properties, levels that were also inferior to those of the commercial products. All three dyes, by virtue of being mono-functional, exhibited poor wash fastness properties, the inferior performances of **RD1** and **RD2** relative to **RD3** being accounted for by their higher substantivity.

Since all three dyes were inferior to the commercial products, the exploitation of trisazo structures, even for dull shades, would not seem to be techno-commercially attractive unless the level of fixation efficiency could be significantly increased, probably by the incorporation of additional reactive groups into the molecule.

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