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Triazinyl reactive dyes for the exhaust dyeing of cotton: Influence of the oxido group on the reactivity of chloro and *m*-carboxypyridinium leaving groups

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Abstract

A series of four triazinyl reactive dyes have been applied to cotton by exhaust dyeing in alkaline media. Two of the dyes employed *o*-toluidine as the reactivity modifying group, with either a chlorine or a nicotinic acid leaving group, and the other two used the same leaving groups but with an oxido group as the reactivity modifier. The dye containing the combination of a chlorine leaving group and an oxido reactivity modifying group (dye **IV**) proved greatly inferior in dyeing performance to that of the other combinations studied in the series. Dyeing at a higher salt level, to correct for the low substantivity of dye (**IV**), and at a higher temperature, furnished only a marginal improvement in visual colour yield indicating lack of reactivity to be the problem. The low reactivity of dye (**IV**) was confirmed by computational analysis.

Keywords: Triazinyl betaine; 6-Chloro-1,3,5-triazin-2(1*H*)-one; Cotton; Exhaust dyeing; Oxido; Computation

1. Introduction

Partial hydrolysis of dichlorotriazinyl dyes furnishes tautomeric 6-chloro-1,3,5-triazin-2(1*H*)-ones (chlorohydroxytriazines) (Scheme 1; R = a dyebase), which are regarded as "hydrolysed dye" and are essentially unreactive [1] under conventional cellulosic fixation conditions. 6-Chloro-1,3,5-triazin-2(1*H*)-ones (**Ic**; Scheme 1) are weakly acidic, e.g. 6-(*N*-methylpyrrol-2-yl)-4-chloro-1,3,5-triazin-2(1*H*)-one (**II**) has a pK_a of 5.2 [2], and are essentially fully deprotonated (**Ia**, Scheme 1) during any established alkaline fixation process for monochlorotriazinyl (MCT)-based reactive dyes.

Accordingly, it has been postulated [3] that the loss of reactivity for cellulose is due to deactivation of the remaining chlorine atom by the strongly electron-donating oxido group.

However in aqueous acidic media, 6-chloro-1,3,5-triazin-2(1*H*)-one compounds (**Ic**) are capable of reacting with a variety of nucleophilic compounds [4], including wool [1], but not cellulose. If the triazinyl ring also contains an amino substituent (as in all commercial triazinyl reactive dyes), then further activation of the remaining chlorine is possible via protonation of the system and resonance stabilization (Scheme 2). Nucleophilic attack at C-6 – as the first step of a chlorine displacement – is facilitated by a partial positive charge at this carbon.

6-Chloro-1,3,5-triazin-2(1*H*)-one dyes (**Ic**, R = a dyebase) are capable of acid catalysed fixation to cellulose, but high temperature baking conditions are required which lead to depolymerisation of the fibre and strength loss.

Another triazinyl reactive group which carries the powerfully deactivating oxido group is triazinyl betaine (**III**). While chlorohydroxytriazinyl dyes are believed to be incapable of chemical fixation to cellulose in alkaline media [3], it has

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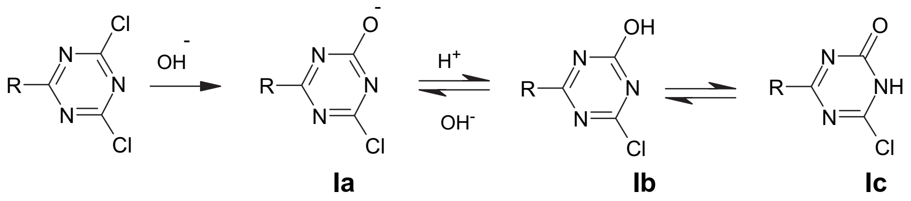
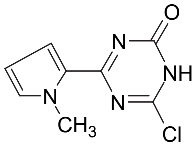
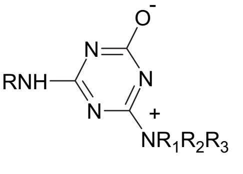


Scheme 1.



II



III

been shown that triazinyl betaine dyes [5] are fibre reactive, and in terms of fixation, behave like commercial triazinyl-based reactive groups. To investigate this apparent anomaly more fully, a series of four dyes (**IV**, **V**, **VI** and **VII**) have been applied to cotton and dyeing performances compared.

2. Experimental

HPLC was performed with a Hewlett Packard 1100 series fitted with a quaternary pump. The column was a 10-cm Purospher RP-18, with a 5-μm reversed-phase packing and a LiChrocart 125-4 HPLC column cartridge; solvent A, acetonitrile; solvent B, water with 0.25 wt% of dicyclohexylammonium phosphate; flow rate, 2 ml/min; temperature, 40 °C; injection volume, 5 μl; samples were analysed using a diode array detector. The following gradient programme was used:

t_R (min)	%A	%B
0	30	70
5	50	50
6	40	60
7	30	70

Stop time is 7.
Retention times are in minutes.

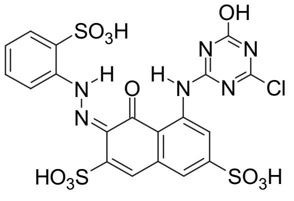
Mass spectra were recorded with a Micromass Instruments LCT orthogonal time-of-flight mass spectrometer fitted with a Z-spray electrospray ion source operating at 3 kV needle potential. Nitrogen was used as a drying and sheath gas. Data was stored in the continuum mode on a Micromass Instruments MassLynx data station utilizing Version 3.5 software pack. Infusion was at a rate of 20 μl/min with a Harvard Instruments syringe pump utilized for sample introduction.

Ultraviolet spectra were taken with a Camspec M350 Double Beam UV–Visible Spectrophotometer.

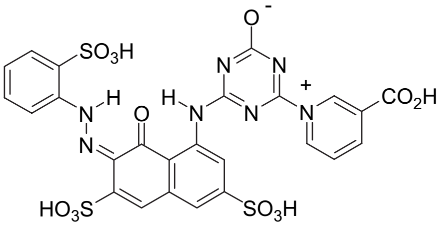
Visual colour strengths of the dyed fabrics (*K*/*S*) were measured with a Datacolor International, Spectroflash 600.

2.1. Procion Red P-4BN (VI)

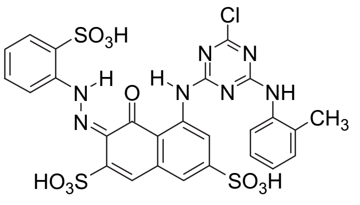
Procion Red P-4BN was supplied by DyStar.



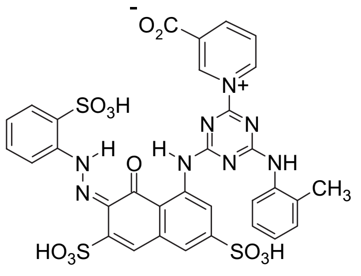
IV



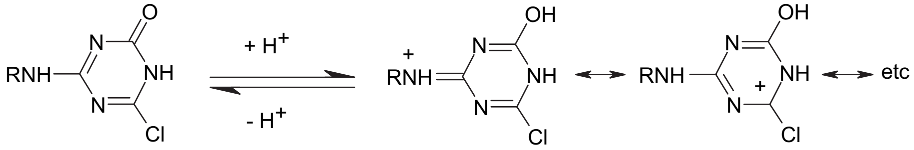
V



VI



VII



Scheme 2.

2.2. 8-(4′-o-Toluidinyl-6′-m-carboxypyridinium-s-triazinylamino)-2-o-sulphophenylhydrazo-1,2-dihydro-naphthalene-3,6-disulphonic acid (**VII**)

To Procion Red P-4BN (**VI**; 14.6 g, 0.018 mol) in water (300 ml) was added nicotinic acid (9.9 g, 0.081 mol), the pH adjusted to 6.9 at room temperature and the reaction mixture heated to 80–85 °C, with stirring, for 5 h. Sodium chloride (20% w/v) was added, the solution stirred overnight to give a precipitate which was filtered off, washed with 10% brine and dried in an electric oven at 40 °C to give the product (10 g). HPLC analysis gave a single peak at $t_R = 1.99$ and mass spectrometry (positive mode) gave a molecular ion at $m/z = 809$ $(M + H)^+$ (100).

2.3. Determination of optimum alkaline dyeing conditions for dye (**VII**)

Bleached, unmercerised, knitted cotton interlock (5 g) was dyed at 1, 2, 4 and 8% omf in sealed stainless steel dye pots housed in a MATHIS LABOMAT BFA dyeing machine. Each dyeing process was carried out at a liquor ratio of 10:1 and dyeings were performed at 50, 60, 70, 80 and 90 °C. The dyeing method is shown in Fig. 1 and the salt and alkali usage is summarised in Table 1. At the end of the dyeing process, the dyed samples were removed, rinsed in warm running water at 50 °C, boiled for 20 min in water containing CIBAPON R detergent (1 g/l), rinsed in cold water and air dried.

2.4. Dyeing process for triazinyl betaine dye (**V**)

As for dye (**VII**) above but the dyeings were performed at 60 °C [5].

2.5. Dyeing process for dye (**IV**)

As for dye (**VII**) above but the dyeings were performed at (a) 80 °C with salt and alkali usage as shown in Table 2; (b) at 80 and 90 °C with salt and alkali usage as shown in Table 3.

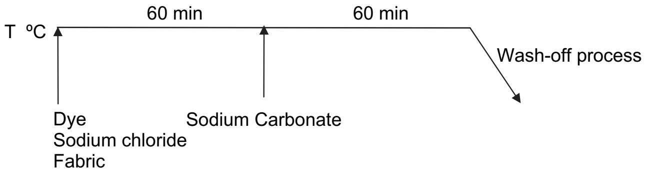


Fig. 1. Dyeing profile for dye (**VII**).

At the end of the 90 °C dyeing cycle, HPLC analysis of the spent dye liquors showed unfixed dye (**IV**) to be unchanged.

2.6. Determination of the substantivity of dye (**IV**)

Bleached, unmercerised, knitted cotton interlock (5 g) was dyed at 1% omf. Four separate dyeings were carried out at liquor ratio 10:1, for 60 min. Two dyeings were performed at 80 °C with salt usages of 40 g/l (Table 2) and 80 g/l (double salt; Table 3), respectively, using the process outlined in Fig. 2. The dyebath solution was measured by UV–vis spectroscopy at the start and at the end of the dyeing process.

2.7. Determination of the substantivity of dye (**VI**)

As for dye (**IV**) above but at 80 °C with 40 g/l sodium chloride.

2.8. Determination of the substantivity of dye (**V**)

As for dye (**IV**) above but at 60 °C with 40 g/l sodium chloride.

2.9. Determination of the substantivity of dye (**VII**)

As for dye (**IV**) above but at 50 °C (see Graph 1) with 40 g/l sodium chloride.

3. Results and discussion

Under alkaline fixation conditions (pH = 11), dyes (**IV**) and (**V**) both contain the strongly electron-donating oxido group attached to the triazinyl ring, but one has a chloro (**IV**) and the other a 3-carboxypyridinium (**V**) leaving group. Dyes (**VI**) and (**VII**), with chloro and 3-carboxypyridinium leaving groups, respectively, both employ *o*-toluidine as the reactivity modifying group.

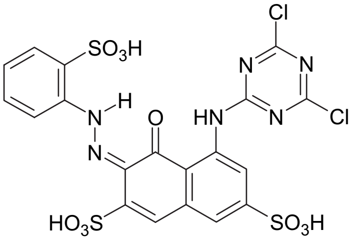
Table 1
Salt and alkali usage for dye (**VII**)

Depth of shade (%)	Sodium chloride (g/l)	Sodium carbonate (g/l)
1	40	15
2	50	20
4	60	20
8	65	20

Table 2
Salt and alkali usage for dye (**IV**) applied at 80 °C

Depth of shade (%)	Sodium chloride (g/l)	Sodium carbonate (g/l)
1	40	15
2	50	15
4	60	20
8	65	20

The four dyes selected for evaluation were based on Procion Red MX-2B (**VIII**), and the syntheses of dyes (**IV**) and (**V**) have been described previously [5].



VIII

A commercial sample of Procion Red P-4BN was used for the MCT dye (**VI**) and preparation of the derived 3-carboxypyridinium derivative (**VII**) is outlined in Section 2.

For the initial exhaust application work, dyes (**IV**) and (**VI**) were applied at 80 °C, this being the dye manufacturer's recommended dyeing temperature for MCT dyes. For triazinyl betaine dye (**V**), the optimum exhaust dyeing performance is known to be 60 °C [5]. The optimum exhaust dyeing temperature for the quaternary ammonium triazinyl dye (**VII**) was determined by dyeing cotton at temperatures of 50–90 °C, at 10 °C intervals, and the results are shown in Graph 1.

The optimum temperature for dye (**VII**) was found to be 50 °C, although very similar colour yields were obtained at 60 °C.

Graph 2 shows the exhaust dyeing results of the four dyes, three of which were dyed under optimum dyeing conditions. The chloro-1,3,5-triazin-2(1*H*)-one dye (CTO, **IV**) was initially treated as an MCT dye and dyed at 80 °C.

The performance of the CTO dye (**IV**) was particularly poor, and strikingly out of step with the other dyes of the series. While this can be rationalised in terms of the powerful deactivating effect of the O^- group, (from the hydroxychloro tautomer) formed in alkaline medium, the triazinyl betaine dye (**V**) has the same deactivating O^- group but the exhaust dyeing performance of this dye was significantly better.

Table 3
Salt and alkali usage for dye (**IV**) applied at 80 and 90 °C

Depth of shade (%)	Sodium chloride (g/l)	Sodium carbonate (g/l)
1	80	15
2	100	15
4	120	20
8	130	20

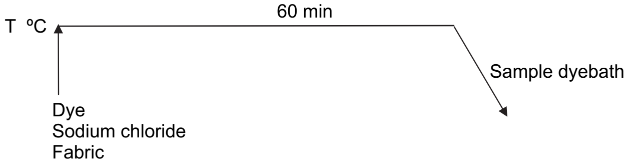


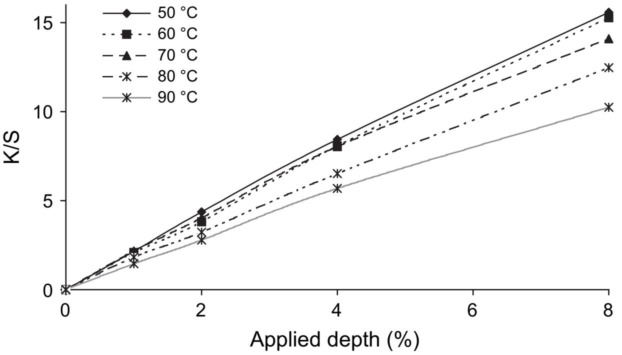
Fig. 2. Dyeing profile for the substantivity measurements of dye (**IV**).

Changing the reactive group attached to the Procion Red MX-2B chromophore not only alters the reactivity, but also the substantivity of each dye, as shown in Table 4.

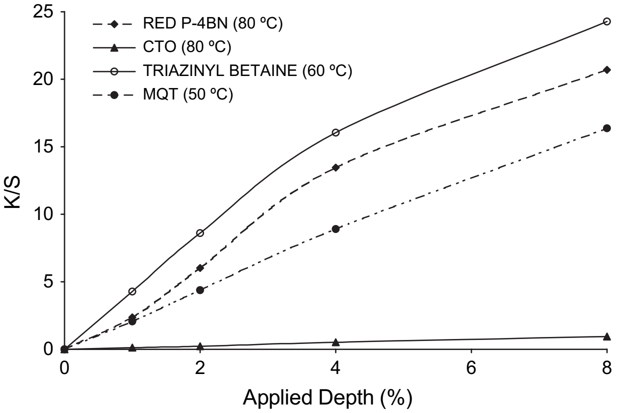
Table 4 shows the substantivity of the CTO dye at 80 °C, in the presence of conventional quantities of salt (40 g/l), to be significantly lower (9%) than the other dyes in the series. Accordingly, the substantivity of the CTO dye was re-measured using double salt (80 g/l) and was found to be 22%, i.e. similar to Procion Red P-4BN (**VII**). At 90 °C, in the presence of 80 g/l salt a value of 27% was obtained.

A comparison of the optimum dyeing temperatures for dyes (**VI**) and (**VII**) (Table 4) shows a 30 °C difference in optimum fixation temperature for a chloro versus a *m*-carboxypyridinium leaving group. Accordingly, the CTO dye (**IV**) was applied under exhaust dyeing conditions, both at 80 and 90 °C, with double salt, and the results are shown in Graph 3.

Graph 3 shows that a steady improvement in the dyeing performance of dye (**IV**) can be achieved by increasing the salt concentration and temperature. However, the colour value at 90 °C with double salt was still very poor despite the higher dyeing temperature and increased substantivity of the dye. The apparent contradiction [6] of a greater substantivity at 90 °C compared to 80 °C, is ascribed to a fall in pH at the higher temperature and a greater concentration of the ketonic tautomer (**Ic**, R = Procion Red MX-2B dyebase). Washing of the cotton fabric used for the substantivity determinations at 90 °C, with conventional and double salt concentrations, at 1% applied depth, gave *K*/*S* values of 0.15 and 0.24, respectively, showing negligible fixation had occurred under neutral conditions.



Graph 1. Relationship between colour yield (*K*/*S*) and applied depth of dye (**VII**) under alkaline fixation conditions.



Graph 2. Comparison of the visual colour yield (*K/S*) of Procion Red P-4BN (**VI**), CTO (chlorohydroxytriazine; **IV**), triazinyl betaine (**V**) and the monoquaternised dye (MQT) (**VII**) under alkaline fixation conditions.

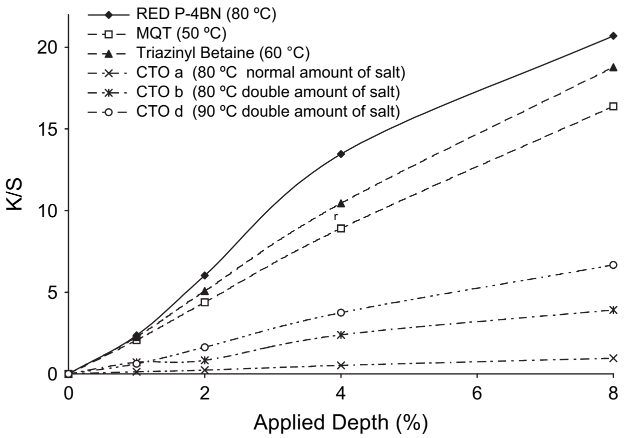
HPLC analysis of the spent liquors, from the 90 °C dyeing, failed to detect hydrolysed dye, indicating that poor fixation to cotton was not a consequence of dye hydrolysis but of low reactivity.

To shed some light on the unexpected reaction behaviour observed computational chemistry was employed. The chromophore in dyes (**IV**)–(**VII**) was replaced by NH_2, and nicotinic acid by pyridine, for computations.

For comparison with the experimental results, the electrostatic potential (EP), which correlates with positive and negative partial charges in a molecule and hence a safe indicator of reaction centres being attacked by either nucleophiles or electrophiles was mainly used. In the present case, the electrostatic potential values of the carbon atoms carrying the displaceable leaving group were compared with each other. The more positive the value, the more readily the compound should undergo nucleophilic attack at this carbon with concomitant substitution of the leaving group by the attacking nucleophile. The computational data can be correlated with the experimental observations only qualitatively, since solvent effects, alkalinity, type of attacking nucleophiles and the exact reaction mechanism, e.g. a monomolecular or bimolecular elementary step, are not considered. While the absolute values are of less significance, the relative values are supposed to agree well with an experimental reactivity gradation.

Table 4
Substantivities of CTO (**IV**), triazinyl betaine (**V**), monoquaternised triazine (**VI**) and Procion Red P-4BN (**VII**)

Dyes	Dyeing temperature (°C)	Salt (%)	Substantivity (%)
CTOa (**IV**)	80	40	9
CTOb (**IV**)	80	80	22
CTOc (**IV**)	90	40	14
CTOd (**IV**)	90	80	27
MQT (**VII**)	50	40	51
Triazinyl betaine (**V**)	60	40	32
Procion Red P-4BN(**VI**)	80	40	19

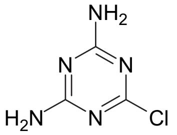


Graph 3. Visual colour yield (*K/S*) of dyes (**V**), (**VI**) and (**VII**), under optimum dyeing conditions and the CTO dye at (a) 80 °C with conventional amounts of salt, (b) 80 and 90 °C with double salt.

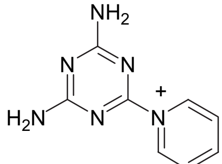
Preliminary calculations using semi-empirical methods (AM1, PM3) provided largely unsatisfactory results. The calculated charge distributions in both aminotriazines (**IX**) and (**X**) did not correspond to the observed reactivities.

A picture which agreed with the observed reaction behaviour was produced using higher levels of theory, employing the basis set as 6-311 + G(d,p) [7], which includes diffuse functions (one set of s- and p-functions for non-H atoms) and polarized functions (d-type function for non-H atoms, p-type for H atoms) [8], and which is known to treat anions and other molecules with negative charges more correctly.

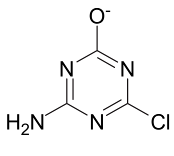
In the following, data are reported that were obtained using geometries pre-optimized by the semi-empirical PM3 method. For subsequent full geometry optimisation, the widely employed B3LYP hybrid method, which includes a mixture of HF and DFT exchange terms and the gradient-corrected correlation functional of Lee et al. [9], parametrized by Becke [10], was used, along with the above mentioned split valence basis set. Going to even higher levels of theory provided no improvements or changes. The differences in bond length, angles, energies and EP values, as compared to MP2/6-311 + G(d,p) calculations based on the B3LYP/6-311 + G(d,p) geometries, were negligibly small (<1%).



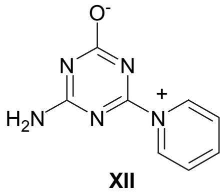
IX



X



XI



XII

The geometry of the compounds (**IX**) and (**XI**) is rather simple, with all atoms lying in a nearly perfect plane. Also, the pyridinium substituted compounds (**X**) and (**XII**) are planar with both rings lying in one plane. In the amino-substituted triazines (**IX**) and (**X**), the electrostatic potential of the carbon carrying the displaceable leaving group was 0.536 for the chloro compound (**IX**) and 0.601 for the pyridinium–triazine (**X**). This corresponds to the experimentally observed higher reactivity of the latter. In the oxido-substituted triazinyl betaine (**XII**), the corresponding value was 0.522 indicating a reactivity similar to compound (**IX**) {experimentally the analogue of compound (**XII**), dye (**V**) proved more reactive than dye (**VI**)}, but there was a significant decrease for the oxido-chlorotriazine (**XI**) giving a value of 0.318. This computational outcome thus correctly reflected the very low reactivity of the latter in nucleophilic substitution reactions.

4. Conclusions

The poor exhaust dyeing performance on cotton of the 6-chloro-1,3,5-triazinyl-2(1*H*)-one dye (**IV**) at 80 °C is attributed to low reactivity and low substantivity under alkaline fixation conditions. Raising the dyeing temperature to 90 °C and the substantivity to a value close to that of the triazinyl betaine dye (**V**) furnished only a marginal improvement in visual colour yield, indicating lack of reactivity to be the main problem. This was supported by HPLC analysis of the spent dye liquors, after the 90 °C dyeing, which showed no evidence of formation of the dihydroxytriazinyl dye.

Although the triazinyl betaine dye (**V**) has the same deactivating O^- group, the exhaust dyeing results were greatly superior to that of the 6-chloro-1,3,5-triazinyl-2(1*H*)-one dye (**IV**). High levels of computational analysis correctly reflected the observed reactivity differences between the two dyes, tracing back the low reactivity of dye (**IV**) to a low electrostatic potential value at C-6 in the triazine, which translates into a reduced susceptibility to nucleophilic attack at this position.

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