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Synthesis and kinetic study of a series of chloro- and *m*-carboxypyridium triazinyl reactive dyes

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ABSTRACT

Five monochloro-*s*-triazinyl reactive dyes (MCT) and five *m*-carboxypyridium-*s*-triazinyl reactive dyes (NTR) were synthesised with the same red chromophore bearing an –NHCN, –OCH_3, –$CH_3NSO_2CH_3$, –*N*-methyl phenyl or –OH group as 'second-leg' substituents. A kinetic study of the hydrolysis of these dyes was conducted, and the rate constant (k_{obs}) and half-life time values were determined. The k_{obs} of the MCT and NTR dyes was found to follow the order –OCH_3 > –$CH_3NSO_2CH_3$ > –*N*-methyl phenyl > –NHCN > –OH, which was approximately in agreement with the values obtained for the Hammett substituent constants. Overall, the higher the electron-donating property of the substituent on *meta*-position to the leaving group in the triazine ring, the lower the hydrolysis rate constant.

1. Introduction

The use of triazine derivatives as functional groups for the attachment of dyes to cellulosic substrates is well established. Indeed, the first widely available reactive dyes for cotton were Procion, which are dichlorotriazine dyes developed by Imperial Chemical Industries in the 1950s. In particular, dichlorotriazines were highly reactive and suitable for cold pad-batch dyeing and exhaust dyeing at 40 °C; however, the resulting dyeing is unstable toward mild acids. This prompted the introduction of monochlorotriazines, which solved the issue of acid stability, although requiring more energetic application conditions. Procion dyes were followed by masked vinyl sulphones, such as CI Reactive Black 5 by Hoechst AG and fluorotriazines such as Cibacron F dyes by Ciba Geigy. Both classes of dyes are more reactive than monochlorotriazines and, as such, can be applied at lower temperature, which enables energy saving. The difficult handling of fluorotriazines has driven the replication of their reactivity level using other leaving groups that were more suitable for commercial-scale manufacture. Among the leaving groups known to increase the reactivity of monohalogenotriazine reactive dyes, such as pyridine derivatives, trimethylamine and nicotinic acid [1–3], only 3-carboxypyridine achieved commercial success as a component of bis-3-carboxypyridinium-*s*-triazines, the so-called "nicotinic quats". Nippon Kayaku used bis(3-carboxypyridinium) to develop Kayacelon Reacts, which are applied to cellulosic substrates under disperse dyeing conditions. These dyes can be applied under mildly acidic conditions at high temperature (ca. 130 °C), alongside disperse dyes obviating the requirement for lengthy two-stage dyeing processes [4,5]. The reactivity of reactive dyes is important for cotton dyeing. Although the major determinant of the reactivity is the nature of the leaving group, the changes in the nature of the 4-substituents in the triazine ring also influence the reactivity. Several studies have demonstrated that the change in the structure of the 'second leg' in monochloro-*s*-triazine or *m*-carboxypyridinium-*s*-triazine reactive dyes can influence the reactivity of dye molecules for exhaust cotton dyeing. V. Kampyli et al. [6] investigated dyes containing a chlorine leaving group and an oxido group, which exhibited dyeing performance that is significantly inferior to that of dyes with nicotinic acid/oxido, chlorine/o-toluidine and nicotinic acid/o-toluidine combinations. E. Karapinar et al. [7] used methanol as a model for cellulose to investigate the reactivity of different substituents at the 4-position of 2-chloro-*s*-triazinyl reactive dyes. They found that the order of reactivity was 4-alkylthio > 4-methoxy > 4-dimethylamino. D. L. Liu et al. [8] studied the hydrolysis kinetics and dyeing properties of monochloro-*s*-triazinyl and *m*-carboxypyridinium-*s*-triazinyl reactive dyes containing aniline as a 'second-leg' substituent. They found that the pH value was a key factor at low temperature to achieve dyeing efficiency, whereas the hydrolysis of the dye molecule is important at high temperature. Although numerous 'second-leg' substituents have been

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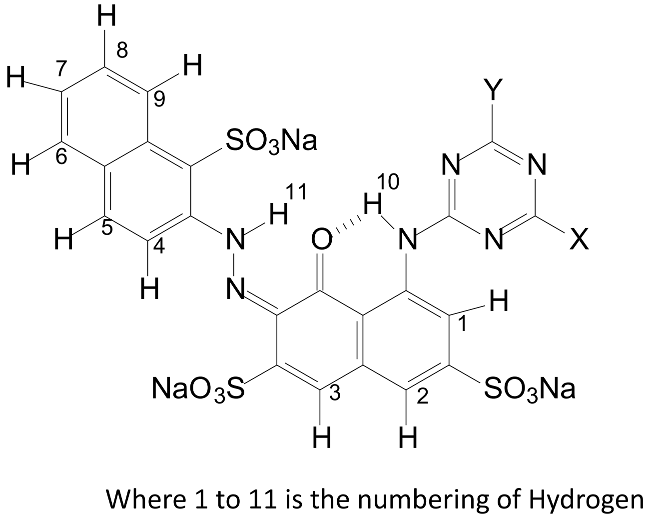
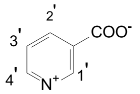
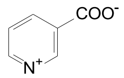
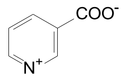
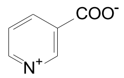


Fig. 1. General structure of the model dyes with different X and Y substituents.

Table 1
Model dyes and their substituents.

Name of Dye	X	Y
1A	Cl	NHCN
1B[a]		NHCN
2A	Cl	OCH_3
2B		OCH_3
3A	Cl	$N(CH_3)–SO_2CH_3$
3B		$N(CH_3)–SO_2CH_3$
4A	Cl	$N(CH_3)$-phenyl
4B		$N(CH_3)$-phenyl
5A	Cl	OH

[a] The numbering of 1' to 4' is represented the proton of Nicotinic acid.

investigated, they are mainly simple amines, including aliphatic, aromatic and mixed aliphatic/aromatic amines. Consequently, we were interested in evaluating the effect of the different 4-substituents on the reactivity of a series of 2-chlorotriazines and 2-(3-carboxypyridinium) triazines. In this paper, various substituents were selected and synthesised to represent a range of reactivity, including cyanoamino (–NHCN) [9], *N*-methyl methylsulfonylamino ($–NCH_3SO_2CH_3$) [10], methoxyl ($–OCH_3$), *N*-methylphenyl and hydroxyl (–OH) substituents.

2. Experimental section

2.1. Chemicals

1-Amino-8-hydroxynaphthalene-3,6-disulphonic acid (H-acid), acetic anhydride, cyanuric chloride (CC), 2-amino-1-naphthalenesulfonic acid (Tobias acid), *N*-methyl aniline, nicotinic acid, 32% hydrogen chloride solution, 45% sodium hydroxide solution, sodium carbonate (anhydrous), sodium bicarbonate (anhydrous) and toluene were obtained from Everlight Chemical Industrial Corp. (Taoyuan, Taiwan R. O·C.). Cyanamide was obtained from Acros Organics, and *N*-methyl methanesulfonamide was purchased from TCI. All reagents were used as received unless otherwise specified.

2.2. Instruments and analysis methods

Ultraviolet/visible (UV/Vis) absorption spectroscopy was performed using a Shimadzu UV-2700 UV/Vis spectrophotometer. Thin layer chromatography (TLC) was employed to monitor the reactions using aluminium plates coated with silica gel (60 F254, Merck) as a stationary phase and a mixture of *iso*-butanol/*n*-propanol/ethyl acetate/water at a volume ratio of 2:4:1:3 as a mobile phase. The developed plates were visualised under short and long UV light (254 and 365 nm, respectively). High-performance liquid chromatography (HPLC) was performed using the following conditions: (1) For the organic purity analysis, a WATERS e2695-2998 separation module with a 10-cm Purospher RP-18 column with 5 μm packing and Inertsil ODS 4.6 × 250-mm cartridges were used. The mobile phase was 0.005 M tetrabutylammonium bromide aqueous solution as solvent A and methanol (HPLC grade) as solvent B. These solvents were passed through the column at A/B gradient ratios from 50:50 to 75:25 at a gradient rate of 1 mL/min within 40 min at ambient temperature. The samples were analysed using a diode array detector at a wavelength ranging from 200 to 700 nm. (2) For the kinetic study, the hydrolysis product of the model dye was analysed *via* HPLC by detecting the product absorbance at a wavelength of 254 nm using a WATERS PDA u0416-2998 separation module with a 10-cm Mightysil RP-18 4.6 × 250 mm (5 μm) column. The mobile phase for the analysis of 1A, 2A, 3A, 5A, 2B, 3B, 4B and 5B was 0.005 M tetrabutylammonium bromide aqueous solution as solvent A and methanol (HPLC grade) as solvent B. These solvents were passed through the column at A/B gradient ratios from 50:50 to 34:66 at a gradient rate of 1 mL/min within 16 min at ambient temperature. For the analysis of 4A, the same mobile phase and column were used, but the A/B gradient was changed from 45:55 to 30:70 in 15 min. The mobile phase used for the analysis of 1B was 0.005 M tetrabutylammonium bromide aqueous solution with 0.01 M $(NH_4)_2HPO_4$ aqueous solution as solvent A and methanol (HPLC grade) as solvent B. These solvents were passed through the same column at A/B gradient ratios from 50:50 to 38:62 at a gradient rate of 1 mL/min within 12 min at ambient temperature. Analysis of all the samples was conducted using a diode array detector at a wavelength ranging from 200 to 700 nm. A German Elementar Vario EL cube analyser was utilised to conduct elemental analysis to determine N, C, S and H by digesting and burning 4–5 mg of the dye sample in a furnace at a temperature of up to 1200 °C to achieve 100% recovery even for samples that were difficult to burn. To ensure that the sample was completely burned, oxygen was directly injected into the combustion point of the sample. Mass spectra were recorded using a Q Exactive™ Plus Hybrid Quadrupole-Orbitrap™ mass spectrometer fitted with a thermo scientific ion max API HESI source operating with an advanced quadrupole technology and an Orbitrap mass analyser. Data were obtained by ultrafast real-time data acquisition using an instrument control system. Nuclear magnetic resonance (NMR) spectroscopy (^1H and ^{13}C) was performed using a Bruker-AVANCE III 400 MHz spectrometer at an operating temperature of 297.3 K using deuterated dimethyl sulfoxide (DMSO-d_6) and deuterated water (D_2O) as solvents and tetramethylsilane as the internal reference. Fourier transform infrared (FTIR) spectra were obtained using a PerkinElmer 100 FTIR spectrometer fitted with a universal attenuated total reflection (ATR) accessory for ATR-FTIR measurement. The working range was 7800–350 cm^{-1}, and the resolution was 0.5 cm^{-1}. The effective agent (e.a.) content of each dye was calculated using the following formula: (found% of carbon obtained by elemental analysis/ theoretical% of carbon in sodium form molecular weight of dyestuff) × 100%. The electron density of the dyes was simulated by HyperChem Release 7.52 using two models, i.e. MM + molecular mechanics for the optimisation of the molecular geometric configuration and PM3 semi-empirical quantum mechanics for the calculation of the electron density of the dye molecule [11].

2.3. Preparation of the dye molecules

A total of 10 model dyes were studied. Their general structure is presented in Fig. 1. The detailed names and components are listed in Table 1, and their synthesis was conducted as described below.

2.3.1. 5-amino-4-hydroxy-3-[(1-sulfo-2-naphthyl)azo]naphthalene-2,7-disulfonic acid (Compound 3, Red base)

Compound 3, Red base (0.117 mol), was prepared as described by J A Bone et al. in Colouration Technology [12]. The reaction solution (560 mL) was monitored *via* TLC (Compound 3, Rf = 0.50). When the reaction was completed, sodium chloride (84 g, 15% w/v) was slowly added over 30 min to the cooled solution (40 °C-45 °C) under stirring. The resulting precipitate was collected and oven-dried at 50 °C, affording 103 g of the product (82% conversion). The organic purity of the product was determined to be 100% *via* HPLC (Retention Time = 14.997 min). The e. a. content of dye was calculated to be 69.96%.

IR (KBr): –NH, –OH stretching 3550–3200 cm^{-1} (broad, s); aromatic –C═C– bending 1625, 1583 cm^{-1} (m, m); sp^2-C═O stretching 1210 cm^{-1} (s), sp^3-C–O– stretching 1048 cm^{-1} (s); ^{1}H NMR (DMSO-d_6): δ 6.935 (C2–1H, d, J = 1.2 Hz), 7.068 (C1–1H, d, J = 1.2 Hz), 7.337 (C3–1H, s), 7.402 (C7–1H, t, J = 7.6 Hz), 7.483 (C8–1H, t, J = 7.6 Hz), 7.842 (C6–1H, d, J = 7.6 Hz), 7.890 (C5–1H, d, J = 9.2 Hz), 8.0–8.2 (broad, azo hydrazone –HN–N═C–), 8.689 (C4–1H, d, J = 9.2 Hz), 9.011 (C9–1H, d, J = 8.4 Hz), 16.075 (sharp, intramolecular H-bonding C═O⋯H–N); Elemental analysis: Found: C 27.13%, N 4.64%. Calc. for $C_{20}H_{12}N_3Na_3O_{10}S_3$: C 38.78%, N 6.78%; HR mass: Found *m/z* 551.9852 $(M-H)^-$. Calc. for $C_{20}H_{15}N_3O_{10}S_3$ 551.9842 $(M - H)^-$.

2.3.2. 5-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-4-hydroxy-3-[(1-sulfo-2-naphthyl)azo]naphthalene-2,7-disulfonic acid (Compound 4, DCT dye)

Cyanuric chloride (22.00 g, 99%, 0.119 mol) was added to an ice-cold solution of Compound 3 (0.117 mol, pH 8) in 900 mL water under stirring. The reaction temperature was maintained at 15 °C-18 °C and the pH at 5.5–6.0 over 2–3 h; then, 45 mL of a 15% w/v sodium carbonate solution was added. The reaction was monitored *via* TLC until Compound 3 completely disappeared and Compound 4 was obtained. Due to its high instability, Compound 4 was used immediately for the next reaction without isolation.

2.3.3. 5-[[4-chloro-6-(cyanoamino)-1,3,5-triazin-2-yl]amino]-4-hydroxy-3-[(1-sulfo -2-naphthyl)azo]naphthalene-2,7-disulfonic acid (Dye 1A)

Cyanamide (5.57 g, 95%, 0.126 mol) was added to a solution of Compound 4 (0.117 mol in 850 mL water). The mixture was heated to 50 °C-55 °C for 4 h under stirring while maintaining the pH at 8.5–9.0 by adding 80 mL of a 15 wt% Na_2CO_3 aqueous solution. When TLC monitoring (Dye 1A, Rf = 0.43) demonstrated that the reaction had completed, the reaction solution was cooled down to room temperature, and 15% w/v of sodium chloride (140 g) was slowly added. The resulting precipitate was collected by filtration to give a red solid, which was dried at 50 °C to give Dye 1A as a red crude product (114 g, 83% conversion). The organic purity of Dye 1A was determined to be 96.02% *via* HPLC (RT = 21.296 min). The e. a. content of dye was calculated to be 65.92%.

IR (KBr): –NH, –OH stretching 3550–3200 cm^{-1} (broad, s); nitrile stretching 2179 cm^{-1} (m), aromatic –C═C– bending 1617 cm^{-1}, 1566 cm^{-1} (m, m); sp^2-C═O stretching 1210 cm^{-1} (s), sp^3-C–O– stretching 1052 cm^{-1} (s); ^{1}H NMR (DMSO-d_6): δ 7.478–7.570 (C3,7,8-4H, complex multiplets), 7.570 (C2–1H, s), 7.903 (C6–1H, d, J = 7.8 Hz), 7.972 (C5–1H, d, J = 9.2 Hz), 8.748 (C4–1H, d, J = 9.1 Hz), 9.075 (C9–1H, d, J = 8.7 Hz), 9.339 (broad, C1–1H), 12.719 (broad, azo hydrazone –NH–N═C–), 16.425 (sharp, intramolecular H-bonding –C═O⋯H–N–); Elemental analysis: Found: C 24.58%, N 9.75%. Calc. for $C_{24}H_{12}ClN_8Na_3O_{10}S_3$: C 37.29%, N 14.5%; HR mass: Found *m/z* 234.31660 $(M-3H)^{3-}$. Calc. for $C_{24}H_{15}ClN_8O_{10}S_3$ 234.31812 $(M-3H)^{3-}$.

2.3.4. 1-[4-(Cyanoamino)-6-[[8-hydroxy-3,6-disulfo-7-[(1-sulfo-2-naphthyl)azo]-1-naphthyl]amino]-1,3,5-triazin-2-yl]pyridin-1-ium-3-carboxylate (Dye 1B)

Dye 1B was made from Dye 1A. Dye 1A (0.097 mol) was dissolved in water (1000 mL), and nicotinic acid (59.97 g, >99%, 0.482 mol) was added. The pH was adjusted to 5.5–6.0 by adding 100 mL of a 15 wt% Na_2CO_3 aqueous solution. The resultant solution was heated to 60 °C-65 °C for 4 h. When TLC monitoring (Dye 1B, Rf = 0.38) indicated that the reaction had completed, the mixture was salted out with 15% w/v of sodium chloride (210 g) to give a red solid, which was isolated by filtration and oven-dried at 50 °C. Dye 1B was obtained as a red crude product (120 g, 91% conversion). The organic purity of Dye 1B was determined to be 93.51% *via* HPLC (RT = 18.498 min). The e. a. content of dye was calculated to be 63.44%.

IR (KBr): –NH, –OH, –COOH stretching 3550–3200 cm^{-1} (broad, s); nitrile stretching 2172 cm^{-1} (m), aromatic –C═C– bending 1628 cm^{-1}, 1564 cm^{-1} (m, m); sp^2-C═O stretching 1214 cm^{-1} (s), sp^3-C–O– stretching 1048 cm^{-1} (s); ^{1}H NMR (DMSO-d_6): δ 7.480–7.566 (C2,3,7,8,16-4H, cm), 7.897 (C6–1H, d, J = 8.0 Hz), 7.967 (C5–1H, d, J = 9.2 Hz), 8.269 (C3′, t, J = 6.8, 7.2 Hz), 8.735 (C4–1H, J = 9.2 Hz), 9.062 (C9–1H, d, J = 8.4 Hz), 9.177 (C2′-1H, d, J = 7.6 Hz), 9.315 (C1–1H, broad), 9.970 (C4′-1H, d, J = 6.4 Hz), 10.202 (C1′-1H, s), 12.813 (broad, azo hydrazone –NH–N═C–), 16.436 (sharp, intramolecular H-bonding –C═O⋯H–N–); Elemental analysis: Found: C 26.59%, N 9.23%. Calc. for $C_{30}H_{16}N_9Na_3O_{12}S_3$: C 41.92%, N 14.66%; HR mass: Found *m/z* 792.02374 $(M-H)^-$. Calc. for $C_{30}H_{19}N_9O_{12}S_3$ 792.0242 $(M-H)^-$.

2.3.5. 5-[(4-chloro-6-methoxy-1, 3, 5-triazin-2-yl)amino]-4-hydroxy-3-[(1-sulfo-2-naphthyl)azo]naph-thalene- 2,7-disulfonic acid (Dye 2A)

$NaHCO_3$ (15.14 g) was added to cold methanol (150 mL) at 10 °C, followed by cyanuric chloride (27.67 g, >99%; 0.15 mol) within 10 min while stirring. The mixture was maintained at 20 °C-25 °C for 1 h. Water (150 mL) was added, and the resulting mixture was stirred for further 2 h. The white dichloro methoxyl triazine (DCT-OCH_3) product was isolated by filtration and directly used for the following reaction [7]. DCT-OCH_3 was added to an aqueous solution of Compound 3 (66.36 g, 0.12 mol), and the pH was adjusted to 6.5–7.0 by adding 40 mL of a 15 wt% Na_2CO_3 aqueous solution. The mixture was heated to 40 °C-45 °C for 3 h at pH 6.5–7.0 with monitoring *via* TLC (Dye 2A, Rf = 0.55). Salting out with 10% w/v sodium chloride (120 g) afforded a dark red solid, which was isolated by filtration and oven-dried at 50 °C to give the product (121 g, 86% conversion). The organic purity of Dye 2A was determined *via* HPLC to be 90.95% (RT = 18.436 min). The e. a. content of dye was calculated to be 64.66%.

IR (KBr): –NH, –OH stretching 3550–3200 cm^{-1} (broad, s); aromatic –C═C– bending 1632 cm^{-1}, 1550 cm^{-1} (m, m); sp^2-C═O stretching 1211 cm^{-1} (s), sp^3-C–O– stretching 1051 cm^{-1} (s); ^{1}H NMR (DMSO-d_6): δ 4.133 (–OCH_3, 3H, s), 7.491–7.594 (C3,7,8-3H, cm), 7.674 (C2–1H, s), 7.915 (C6–1H, d, J = 7.8 Hz), 7.991 (C5–1H, d, J = 9.2 Hz), 8.734 (C4–1H, d, J = 9.2 Hz), 9.085 (C9–1H, d, J = 8.6 Hz), 9.281 (C1–1H, broad), 13.363 (s, azo hydrazone –NH–N═C–), 16.533 (sharp, intramolecular H-bonding –C═O⋯H–N–); Elemental analysis: Found: C 24.43%, N 7.04%. Calc. for $C_{24}H_{14}ClN_6Na_3O_{11}S_3$: C 37.78%, N 11.01%; HR mass: Found *m/z* 230.98740 $(M-3H)^{3-}$. Calc. for $C_{24}H_{17}ClN_6O_{10}S_3$ 230.98626 $(M-3H)^{3-}$.

2.3.6. 1-[4-[[8-hydroxy-3, 6-disulfo-7-[(1-sulfo-2-naphthyl) azo]-1-naphthyl]amino]-6-methoxy-1,3,5- triazin-2-yl]pyridin-1-ium-3-carboxylate (Dye 2B)

Dye 2B was prepared from Dye 2A (0.103 mol) as follows: Dye 2A was dissolved in 1400 mL water, followed by the addition of nicotinic acid (73.60 g, >99%, 0.60 mol). The pH was adjusted to 6.0 by adding 80 mL of a 15 wt% Na_2CO_3 aqueous solution. The resultant solution was heated to 60 °C-65 °C for 7 h. When TLC monitoring (Dye 2B, Rf = 0.33) demonstrated that the reaction had completed, the mixture was salted out with 10% w/v sodium chloride (160 g) to give a red solid, which was isolated by filtration and oven-dried at 50 °C to produce Dye 2B as a red crude product (105 g, 95% conversion). The organic purity of the product was determined to be 84.26% *via* HPLC (RT = 14.124 min). The e. a. content of dye was calculated to be 79.25%.

IR (KBr): –NH, –OH, –COOH stretching 3550–3200 cm^{-1} (broad, s); aromatic –C═C– bending 1630 cm^{-1}, 1557 cm^{-1} (m, m); sp^2-C═O stretching 1214 cm^{-1} (s), sp^3-C–O– stretch 1053 cm^{-1} (s); ^1H NMR (D_2O): δ 4.332 (-OCH_3, 3H, s), 7.311 (C3–1H, s), 7.427 (C2–1H, s), 7.464–7.607 (C8, C7–2H, cm), 7.633 (C6–1H, d, $J = 8$ Hz), 7.694 (C5–1H, d, $J = 9.2$ Hz), 7.777 (C3′-1H, t, $J = 6$ Hz), 7.946 (C4–1H, d, $J = 6.4$ Hz), 8.032 (C2′-1H, d, $J = 8.8$ Hz), 8.460 (C9–1H, d, $J = 8.4$ Hz), 9.193 (C1–1H, s), 9.518 (C1′-1H, s), 9.997 (C4′-1H, d, $J = 4.4$ Hz), 12.799 (s, azo hydrazone –NH–N═N–), 15.887 (s, intramolecular H-bonding –C═O···H–N–); Elemental analysis: Found: C 33.61%, N 9.17%. Calc. for $C_{30}H_{18}N_7Na_3O_{13}S_3$: C 42.41%, N 11.54%; HR mass: Found *m/z* 782.02686 $(M-H)^-$. Calc. for $C_{30}H_{21}ClN_7O_{13}S_3$ 782.02867 $(M-H)^-$.

2.3.7. 5-[[4-chloro-6-[methyl(methylsulfonyl)amino]-1,3,5-triazin-2-yl]amino]-4-hydroxy-3-[(1-sulfo-2-naphthyl)azo]naphthalene-2,7-disulfonic acid (Dye 3A)

3A was prepared according to the procedure reported by B. Stephen et al. [10]. A solution of *N*-methyl methanesulfonamide (6.35 g, >99%, 0.058 mol) in water (8 mL) was added to a sodium hydroxide (2.33 g, >99%, 0.058 mol) solution in water (3 mL). Toluene (20 mL) was added, and water was azeotropically removed. Then, cyanuric chloride (10.8 g, >99%, 0.058 mol) was added, and the mixture was stirred below 3 °C for 8 h, followed by stirring at room temperature for 12 h to give a suspension. A solid was filtered out from the suspension, and toluene was removed in vacuum to give 2,4-dichloro-6-(*N*-methanesulphonyl) methylamino s-triazine as a white crude solid (13.45 g). Subsequently, an aqueous solution of Compound 3 (0.029 mol) was added to a solution of 2,4-dichloro-6-(*N*-methanesulphonyl)methylamino s-triazine (9.70 g, 0.042 mol) in acetone (25 mL) under stirring. The pH was adjusted at 7.0–8.0 by adding 15 mL of a 15% w/v Na_2CO_3 aqueous solution, and the mixture was heated to 50 °C for 6 h until TLC monitoring (3A, Rf = 0.56) demonstrated complete consumption of Compound 3. The reaction solution was then filtered for the removal of insoluble materials, the filtrate was allowed to cool to room temperature, and 15% w/v sodium chloride (75 g) was added. The resulting precipitate was collected and oven-dried to give the title product as a red solid (19.14 g, 52% conversion). The organic purity of the product was determined to be 96.24% *via* HPLC (RT = 18.09 min). The e. a. content of dye was calculated to be 66.48%.

IR (KBr): –NH, –OH, –COOH stretching 3650–3200 cm^{-1} (broad, s); aromatic –C═C– bending 1635 cm^{-1}, 1559 cm^{-1} (m, m); sp^2-C═O stretching 1228 cm^{-1} (s), sp^3-C–O– stretching 1046 cm^{-1} (s); ^1H NMR (DMSO-d_6): δ 3.512 (–SO_2–CH_3, 3H, s), 3.658 (–N–CH_3, 3H, s), 7.469–7.571 (C3,7,8-3H, cm), 7.631 (C2–1H, s), 7.892 (C6–1H, d, $J = 7.6$ Hz), 7.962 (C5–1H, d, $J = 9.2$ Hz), 8.736 (C4–1H, d, $J = 9.2$ Hz), 9.076 (C9–1H, d, $J = 8.4$ Hz), 9.127 (C1–1H, broad), 13.410 (broad, azo hydrazone –NH–N═N–), 16.537 (sharp, intramolecular H-bonding –C═O···H–N–); Elemental analysis: Found: C 23.76%, N 8.11%. Calc. for $C_{25}H_{17}ClN_7Na_3O_{12}S_4$: C 35.74%, N 11.67%; HR mass: Found *m/z* 256.6527 $(M-3H)^{3-}$. Calc. for $C_{25}H_{20}ClN_7O_{12}S_4$ 256.6508 $(M-3H)^{3-}$.

2.3.8. 1-[4-[[8-hydroxy-3,6-disulfo-7-[(1-sulfo-2-naphthyl)azo]-1-naphthyl]amino]-6-[methyl(methyl-sulfonyl) amino]-1,3,5-triazin-2-yl]pyridin-1-ium-3-carboxylate (Dye 3B)

3A (0.015 mol) was dissolved in water (300 mL), nicotinic acid (7.67 g, 99%, 0.062 mol) was slowly added, and the pH was adjusted to 5.5–6.0 by adding 20 mL of a 15 wt% Na_2CO_3 aqueous solution. The resultant solution was heated to 50 °C-55 °C for 7–8 h. When TLC monitoring (Dye 3B, Rf = 0.47) indicated that the reaction had completed, the mixture was salted out with 10% w/v sodium chloride (35 g), and the resulting precipitate was isolated by filtration to give a red solid, which was oven-dried at 50 °C to give the product (17.52 g, 95% conversion). The organic purity of the product was determined to be 94.71% *via* HPLC (RT = 12.803 min). The e. a. content of dye was calculated to be 75.34%.

IR (KBr): –NH, –OH, –COOH stretching 3650–3200 cm^{-1} (broad, s); aromatic –C═C– bending 1631 cm^{-1}, 1557 cm^{-1} (m, m); sp^2-C═O stretching 1208 cm^{-1} (s), sp^3-C–O– stretching 1047 cm^{-1} (s); ^1H NMR (D_2O): δ 3.783 (–SO_2–CH_3, 3H, s), 3.790 (–N–CH_3, 3H, s), 7.453 (C3–1H, s), 7.476–7.645 (C7,8-2H, cm), 7.508 (C2–1H, s), 7.676 (C6–1H, d, $J = 7.6$ Hz), 7.766 (C5–1H, d, $J = 9.2$ Hz), 7.903 (C3′-1H, t, $J = 6.8$ Hz), 8.126 (C4–1H, d, $J = 9.2$ Hz), 8.169 (C2′-1H, d, overlapped with C4), 8.510 (C9–1H, d, $J = 8.8$ Hz), 9.126 (C1–1H, s), 9.700 (C1′-1H, s), 10.072 (C4′-1H, d, $J = 6$ Hz) 12.998 (s, azo hydrazone –NH–N═N–), 16.016 (s, intramolecular H-bonding –C═O···H–N–); Elemental analysis: Found: C 30.27%, N 9.16%. Calc. for $C_{31}H_{21}N_8Na_3O_{14}S_4$: C 40.18%, N 12.09%; HR mass: Found *m/z* 859.02167 $(M-H)^-$. Calc. for $C_{31}H_{24}N_8O_{14}S_4$ 859.02220 $(M-H)^-$.

2.3.9. 5-[[4-chloro-6-(N-methylanilino)-1,3,5-triazin-2-yl]amino]-4-hydroxy-3-[(1-sulfo-2-naphthyl) azo]naphthalene-2,7-disulfonic acid (dye 4A)

N-Methyl aniline (8.66 g, 99%, 0.080 mol) was slowly added to an aqueous solution of Compound 4 (0.078 mol). The pH of the reaction mixture was adjusted to 7.5–8.0 by sodium ash powder. The resultant solution was heated to 45 °C-50 °C for 4 h while being monitored *via* TLC (Dye 4A, Rf = 0.58). By salting out with 15% w/v sodium chloride (135 g), a dark red solid was produced, which was isolated by filtration and oven-dried at 50 °C to give Dye 4A as a red solid (79 g, 74% conversion). The organic purity of the product was determined to be 98.81% *via* HPLC (RT = 25.02 min). The e. a. content of dye was calculated to be 61.39%.

IR (KBr): –NH, –OH stretching 3500–3200 cm^{-1} (broad, s); aromatic –C═C– bending 1616 cm^{-1}, 1562 cm^{-1} (m, m); sp^2-C═O stretching 1234, 1209 cm^{-1} (s), sp^3-C–O– stretching 1052 cm^{-1} (s); ^1H NMR (DMSO-d_6): δ 3.624 (*N*-methyl,-3H, s), 7.343–7.572 (*N*-phenyl-5H, C7–1H, C8–1H, total 7H, cm), 7.535 (C3–1H, s), 7.592 (C2–1H, s), 7.985 (C6–1H, d, $J = 7.8$ Hz), 7.963 (C5–1H, d, $J = 9.2$ Hz), 8.752 (C4–1H, d, $J = 9.2$ Hz), 9.076 (C9–1H, d, $J = 8.7$ Hz), 9.456 (C1–H1, broad), 13.000 (azo hydrazone –NH–N═C–, broad), 16.470 (NH, sharp, intramolecular H-bonding –C═O···H–N–); Elemental analysis: Found: C 26.39%, N 7.17%. Calc. for $C_{30}H_{19}ClN_7Na_3O_{10}S_3$: C 42.99%, N 11.70%; HR mass: Found *m/z* 256.00357 $(M-3H)^{3-}$. Calc. for $C_{30}H_{22}ClN_7O_{10}S_3$ 256.00202 $(M-3H)^{3-}$.

2.3.10. 1-[4-[[8-hydroxy-3,6-disulfo-7-[(E)-(1-sulfo-2-naphthyl)azo]-1-naphthyl]amino]-6-(N-methyl-anilino)-1,3,5-triazin-2-yl]pyridin-1-ium-3-carboxylate (Dye 4B)

Dye 4B was prepared from Dye 4A (0.058 mol) as follows: Dye 4A was dissolved in water (1000 mL), followed by the addition of nicotinic acid (57.68 g, >99%, 0.460 mol). The pH was adjusted to 5.5–6.0 by adding 160 mL of a 15 wt% Na_2CO_3 aqueous solution. The resultant solution was heated to 60 °C-65 °C for 40 h while being monitored *via* TLC (Dye 4B, Rf = 0.5). The mixture was then salted out with 5% w/v sodium chloride (60 g) to give a red solid, which was isolated by filtration and oven-dried at 50 °C to give Dye 4B as a red product (41 g, 62% conversion). The organic purity of the product was determined to be 100% *via* HPLC (RT = 17.110 min). The e. a. content of dye was calculated to be 81.35%.

IR (KBr): –NH, –OH stretching 3500–3200 cm^{-1} (broad, s); aromatic –C═C– bending 1634 cm^{-1}, 1544 cm^{-1} (m, m); sp^2-C═O stretching 1238 cm^{-1} (s); ^1H NMR (D_2O): δ 3.846 (C12–3H, s), 7.531–7.726 (C5–1H,C6–1H,C7–1H,C8–1H, *N*-phenyl-5H, in total 9H, cm), 7.442 (C3–1H, s), 7.609 (C2–1H, s), 7.986 (C3′-1H, t, $J = 6$ Hz), 8.260 (C4–1H, d, $J = 8.8$ Hz), 8.301 (C2′-1H, d, $J = 7.2$ Hz), 8.488 (C9–1H, d, $J = 8.8$ Hz), 9.480 (C1–1H, s), 9.318 (C1′-1H, s), 10.036 (C4′-1H, d, $J = 5.2$ Hz),

Table 2

λ_{max}, ε_{max} and full width at half maximum (FWHM) of 10 model dyes.

Dye	λ_{max} nm (in water)	ε_{max} ($dm^3mol^{-1}cm^{-1}$)	Organic purity (HPLC %)	FWHM (nm)
1A	547	40011	96.02	86.08
1B	546	38595	93.51	87.93
2A	545	39594	90.95	87.61
2B	546	38192	84.26	92.11
3A	546	38612	96.24	89.19
3B	546	41119	94.71	92.06
4A	547	40901	98.81	93.48
4B	548	37995	100.00	89.72
5A	546	40760	99.45	87.66
5B	546	40653	97.14	87.40

12.832 (–NH, weak, –NH–N=N–), 16.103 (–NH, weak, intramolecular H-bonding of –C=O···H–N–); Elemental analysis: Found: C 38.04%, N 9.94%. Calc. for $C_{36}H_{23}N_8Na_3O_{12}S_3$: C 46.76%, N 12.12%; HR mass: Found *m/z* 857.07519 $(M-H)^-$. Calc. for $C_{36}H_{26}N_8O_{12}S_3$ 857.075409 $(M-H)^-$.

2.3.11. 5-[(4-chloro-6-hydroxy-1,3,5-triazin-2-yl)amino]-4-hydroxy-3-[-(1-sulfo-2-naphthyl)azo] naphthalene-2,7-disulfonic acid (Dye 5A)

Na_2CO_3 (15 g, >99%, 0.118 mol) was added to 1000 mL aqueous solution of Compound 4 (0.053 mol), and the mixture was heated to 80 °C under stirring for 2 h. When TLC monitoring (Dye 5A, Rf = 0.50) demonstrated that the reaction had completed, the mixture was allowed to cool down to room temperature, and 16% w/v sodium chloride (176 g) was slowly added. The resulting red solid was collected by filtration and oven-dried at 50 °C to give Dye 5A as a red product (44.82 g, 75% conversion). The organic purity of the product was determined to be 99.45% *via* HPLC (RT = 17.92 min). The e. a. content of dye was calculated to be 66.70%.

IR (KBr): –NH, –OH stretching 3600–3200 cm^{-1} (broad, s); aromatic –C=C– bending 1634 cm^{-1}, 1617 cm^{-1} (m, m); sp^2-C=O stretching 1214 cm^{-1} (s), sp^3-C–O– stretching 1049 cm^{-1} (s); ^1H NMR (DMSO-*d*$_6$): δ 7.419 (C3–1H, s), 7.449 (C2–1H, s), 7.469–7.557 (C7 and C8–2H, cm), 7.877 (C6–1H, d, *J* = 8.0 Hz), 7.897 (C5–1H, d, *J* = 9.2 Hz), 8.723 (C4–1H, d, *J* = 9.2 Hz), 9.042 (C9–1H, d, *J* = 8.8 Hz), 9.358 (C1–1H, sharp), 12.261 (NH, sharp, azo hydrazone hydrogen –NH–N=C–), 16.338 (NH, sharp, intramolecular H-bonding –C=O···H–N–); Elemental analysis: Found: C 24.60%, N 6.95%. Calc. for $C_{23}H_{12}ClN_6Na_3O_{11}S_3$: C 36.88%, N 11.22%; HR mass: Found *m/z* 226.31537 $(M-3H)^{3-}$. Calc. for $C_{23}H_{15}ClN_6O_{11}S_3$ 226.31437 $(M-3H)^{3-}$.

2.3.12. 1-[4-hydroxy-6-[[8-hydroxy-3,6-disulfo-7-[(E)-(1-sulfo-2-naphthyl)azo]-1-naphthyl]amino]-1,3,5-triazin-2-yl]pyridin-1-ium-3-carboxylate (Dye 5B)

An aqueous solution of Dye 5A (0.021 mol, 300 mL) was prepared by dissolving the dye in water under stirring, followed by the addition of nicotinic acid (9.78 g, 99%, 0.079 mol). The resultant solution was heated to 60 °C-65 °C for 8 h while being monitored *via* TLC (Dye 5B, Rf = 0.42), and the pH was adjusted to 5.5–6.0 by adding 20 mL of a 15 wt % Na_2CO_3 aqueous solution. The temperature was then decreased to 40 °C, and 10% w/v sodium chloride (39 g) was added. The resulting red solid was collected *via* filtration and re-dissolved in water (300 mL) at room temperature. Sodium chloride (5% w/v, 15 g) was then added, affording a red solid that was isolated by filtration and oven-dried at 50 °C to give Dye 5B (19.28 g, 83% conversion). The organic purity of the product was determined to be 97.14% *via* HPLC (RT = 15.62 min). The e. a. content of dye was calculated to be 75.38%.

IR (KBr): –NH, –OH stretching 3600–3200 cm^{-1} (broad, s); aromatic –C=C– bending 1630 cm^{-1} (m); sp^2-C=O stretching 1214 cm^{-1} (s), sp^3-C–O– stretching 1049 cm^{-1} (s); ^1H NMR (DMSO-*d*$_6$): δ 7.489 (C3–1H, s), 7.494 (C2–1H, s), 7.468–7.576(C7 and C8–2H, cm), 7.895 (C6–1H, d, *J* = 7.6 Hz), 7.964 (C5–1H, d, *J* = 9.2 Hz), 8.258 (C3′-1H, t, *J* = 7.2 Hz), 8.739 (C4–1H, d, *J* = 9.2 Hz), 9.062 (C9–1H, d, *J* = 8.8 Hz), 9.138 (C2′-1H, d, *J* = 7.6 Hz), 9.404 (C1–1H, sharp), 9.988 (C4′-1H, d, *J* = 6.4 Hz), 10.228 (C1′-1H, s), 12.542 (NH, sharp, azo hydrazone –NH–N=C–), 16.412 (NH, sharp, intramolecular H-bonding –C=O···H–N–); Elemental analysis: Found: C 31.42%, N 8.83%. Calc. for $C_{29}H_{16}N_7Na_3O_{13}S_3$: C 41.68%, N 11.73%; HR mass: Found *m/z*

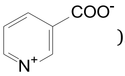
Table 3

Chemical shifts (ppm) of aromatic protons for 1A–5A (X = Cl) in DMSO-*d*$_6$.

	H1	H2	H3	H4	H5	H6	H7	H8	H9
1A (Y=NHCN)	9.339	7.570	7.542	8.748	7.972	7.903	7.478–7.524		9.075
2A (Y=OCH_3)	9.281	7.674	7.571	8.734	7.991	7.915	7.491–7.594		9.085
3A (Y=$NCH_3SO_2CH_3$)	9.127	7.631	7.524	8.736	7.962	7.892	7.469–7.571		9.076
4A (Y=N-methyl phenyl)	9.456	7.592	7.535	8.752	7.963	7.985	[a]7.343–7.572		9.076
5A (Y=OH)	9.358	7.449	7.419	8.723	7.897	7.877	7.469–7.557		9.042

[a] Five aromatic protons of the *N*-methyl phenyl moiety are also in the same area.

Table 4

Chemical shifts (δ ppm) of the aromatic protons of 1B–5B (X = ).

	1B(Y=NHCN) (in DMSO-d6)	2B(Y=OCH_3) (in D2O)	3B(Y=$NCH_3SO_2CH_3$) (in D2O)	4B(Y=NCH_3phenyl) (in D2O)	5B(Y=OH) (in DMSO-d6)
H1	9.315	9.193	9.126	9.480	9.404
H2	7.566	7.427	7.508	7.609	7.494
H3	7.513	7.311	7.453	7.442	7.489
H4	8.753	7.946	8.126	8.260	8.739
H5	7.967	7.694	7.766	7.531–7.726 (including five protons of *N*-phenyl)	7.964
H6	7.897	7.633	7.676		7.895
H7	7.480–7.539	7.464–7.607	7.476–7.645		7.468–7.576
H8					
H9	9.062	8.460	8.510	8.488	9.062
H1’	10.202	9.518	9.700	9.318	10.228
H2’	9.177	8.032	8.169	8.301	9.138
H3’	8.269	7.777	7.903	7.986	8.258
H4’	9.970	9.997	10.072	10.036	9.988

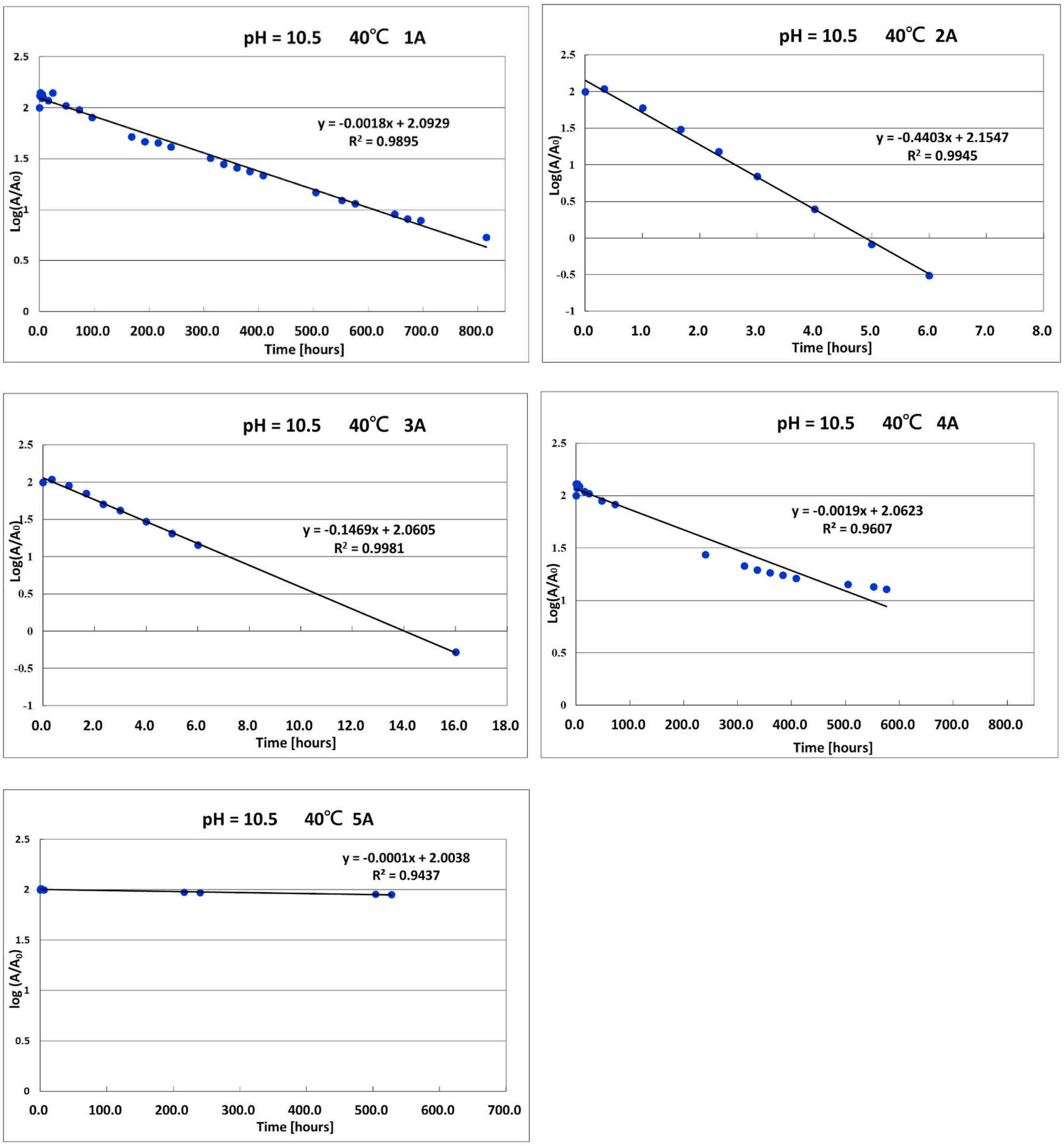


Fig. 2. Plots of the logarithms of the relative concentration (A/A_0) against time at 40 °C for 1A, 2A, 3A, 4A and 5A.

768.01210 (M−H)$^-$. Calc. for $C_{29}H_{19}N_7O_{13}S_3$ 768.012474 (M−H)$^-$.

2.4. *Kinetic study*

The kinetic study was conducted by modifying the OECD Guideline 111 (2004) ‘Hydrolysis as a function of pH’ [13]. Hydrolysis of the model dyes (Table 1) was performed by mixing approximately 5×10^{-5} mol dye with 5×10^{-3} mol reagent-grade sodium carbonate in water (100 mL, pH = 10.5) at 40 °C [14,15]. Samples (0.5 mL) were taken at suitable intervals and quenched with a pre-cooled 0.1 N HCL aqueous solution (0.5 mL), giving a pH of 6.0–7.0. The samples (1 mL) were kept in an ice bath before HPLC analysis.

3. Results and discussion

3.1. *Optical properties of model dyes*

The optical properties of the 10 model dyes are presented in Table 2. The values of the wavelength of the maximum absorbance (λ_{max}) of the monochloro-*s*-triazinyl dyes (MCT dyes) and the *m*-carboxypyridium-*s*-triazinyl dyes (NTR dyes) have a difference of only ±1 nm (close to the resolution of the spectrometer). Therefore, the absence of colour change when the chloro group was replaced with nicotinic acid on the triazinyl dye can be considered. The molar extinction coefficient (ϵ_{max}) of the model dyes were between 38000 and 41119, which are typical values for red chromophores based on naphthyl-azo-naphthalene sulfonic acid dyestuff. Meanwhile, the full width at half maximum (FWHM) indicates the shade brightness. The data demonstrate that the dyes with higher organic purity (by HPLC) afforded narrower FWHM values.

3.2. *Synthesis and ^{1}H NMR spectroscopic characterisation of the dye molecules*

Monochlorotriazines containing cyanoamino, *N*-methyl phenyl and hydroxy substituents in the ‘second leg’ were prepared from the reaction of an aqueous solution of dichlorotriazine (Compound 4) with cyanamide, *N*-methyl aniline and hydroxide, respectively, at 45 °C-55 °C in the presence of 15 w/w% sodium carbonate (aq.) as acid scavenger. *N*-methylphenylchlorotriazine (4A) and hydroxychlorotriazine (5A) were prepared under a normal pH condition, whereas the reaction of

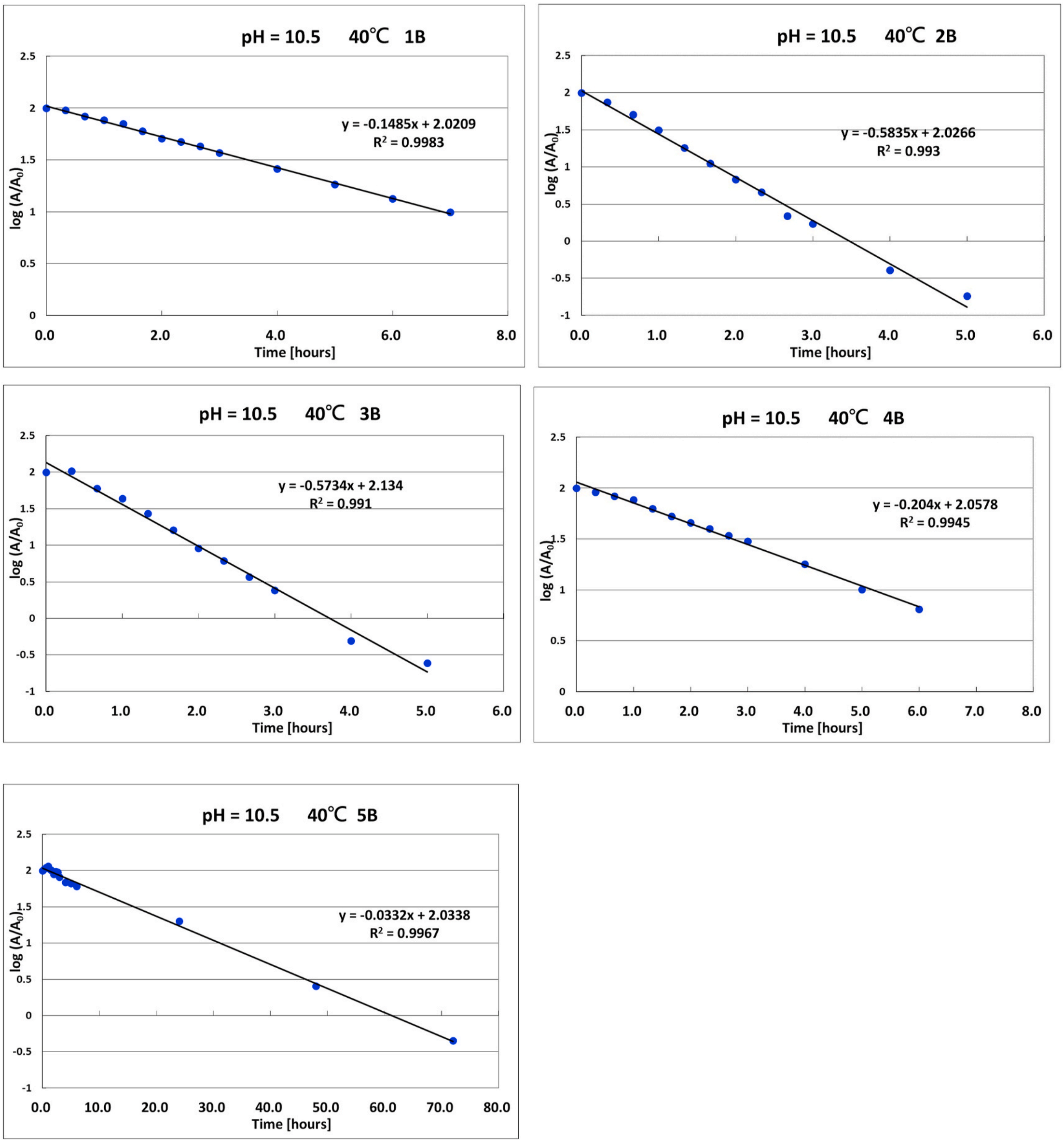


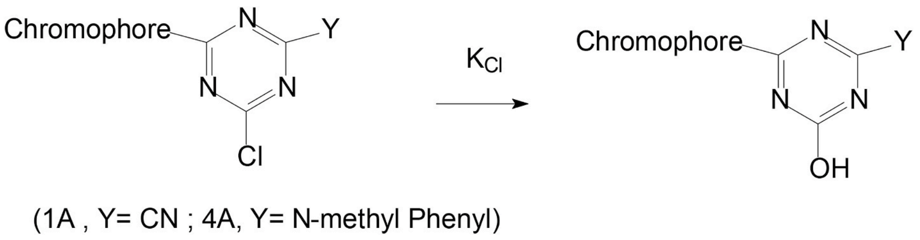
Fig. 3. Plots of the logarithms of the relative concentration (A/A_0) against time at 40 °C for 1B, 2B, 3B, 4B and 5B.

Table 5
Pseudo-first-order hydrolysis rate constants of Dyes 1A, 2A, 3A, 4A and 5A.

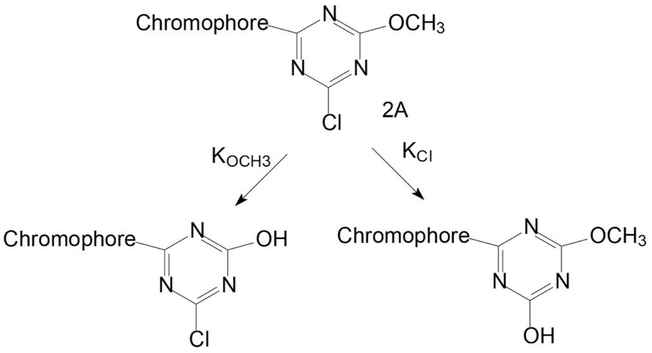
MCT Dye	Overall reactivity Rate constants (k_{obs}) [$hours^{-1}$]	Half-life time ($t_{½}$) [hours]	R^2 value
1A	4.15×10^{-3}	168	0.9895
2A	1.01×10^{0}	0.68	0.9945
3A	3.38×10^{-1}	2.00	0.9981
4A	4.38×10^{-3}	168	0.9607
5A	2.30×10^{-4}	3000	0.9437

Order of Reactivity: 2A > 3A > 4A > 1A > 5A

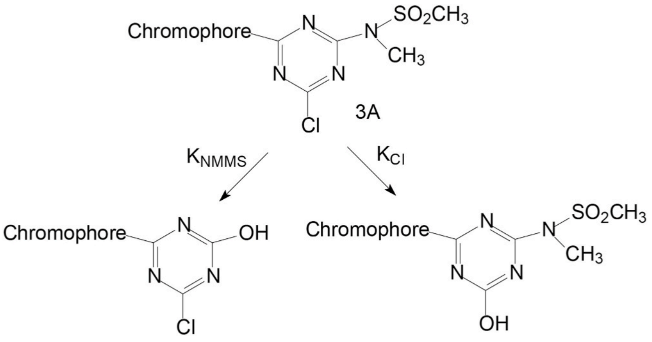
cyanamide with dichlorotriazine to produce cyanoaminochlorotriazine (1A) was performed at a fairly high pH to partly ionise the cyanamide, since the ionised form is the reactive nucleophile. Under these conditions, the desired product is relatively stable as the chlorotriazine is deactivated due to the ionisation of triazine–NH–CN. However, these conditions were not suitable for the reaction of methanol and *N*-methylmethanesulfonamide $HN(CH_3)SO_2CH_3$, probably due to the low nucleophilicity of methanol and sulfonamides compared to that of water. The reaction route to methoxychlorotriazine dye is well known and consists of a condensation of cyanuric chloride with aqueous methanol in the presence of sodium hydrogen carbonate to form methoxydichloro-*s*-triazine, followed by a second condensation reaction with Red base (Compound 3) to obtain methoxychlorotriazine (2A) with high yield and purity [7]. Likewise, sulfonamides are insufficiently nucleophilic to react cleanly with dichlorotriazine, and competitive hydrolysis to hydroxychlorotriazine occurs. This undesired side product cannot be easily removed when mixed with the desired product. To confirm this speculation, dichlorotriazine (Compound 4) was reacted with *N*-methylmethanesulfonamide at pH 7.5–9.0 and temperature of 40 °C-50 °C. The product was analysed *via* HPLC, and it was found that the hydrolysis compound (Dye 5A, 83.36% area by HPLC) was the major product, and a small amount of the desired Compound 3A (10.23% area by HPLC) was obtained. Therefore, the alternative synthetic route (see 2.3.7) was adopted *via* a condensation of cyanuric chloride with *N*-methylmethanesulfonamide sodium salt to form a dichloro-6-(*N*-methanesulphonyl)methylamino s-triazine, followed by a second condensation reaction with Red base (Compound 3) to obtain methyl (methylsulfonyl)aminochlorotriazinyl Compound 3A with high purity



Scheme 1. Hydrolysis of Dyes 1A and 4A



Scheme 2. Hydrolysis of Dye 2A



Scheme 3. Hydrolysis of Dye 3A

(93.64% area by HPLC).

For 1A, 2A, 3A, 4A, 5A, 1B and 5B, nice and clean ^1H and ^{13}C NMR spectra were obtained in DMSO-d_6, whereas 2B, 3B and 4B afforded messy spectra in the same solvent. Contrarily, clean NMR spectra were obtained for 2B, 3B and 4B when D_2O was used. The chemical shifts of the aromatic protons of dyes 1A–5A are presented in Table 3. Azo dyes are known to be in keto–enol tautomeric equilibrium, with the keto-hydrazone form being highly predominant in DMSO-d_6. For example, the ^1H NMR spectrum of 1A exhibits one downfield proton at 16.410 ppm, which is attributed to the nitrogen proton in the H-acid ring, thus forming a hydrogen bond with the –C═O group, affording a six-membered ring, and another at 12.704 ppm due to the nitrogen proton of the hydrazone. In the same spectrum, three singlet peaks can be attributed to the protons in the H-acid ring. Significant downfield shifts are observed for the H1 proton in the ortho position to the amino group compared with protons H2 and H3 due to the π-electron de-shielding effect of the triazinyl ring [16].

Table 6
Rate constants of 2A and 3A.

MCT Dye	Rate constants [hours^{-1}]				Ratio of rate constants	
	k_{obs}	K_{Cl}	K_{OCH3}	K_{NMMS}	K_{Cl}/K_{OCH3}	K_{Cl}/K_{NMMS}
2A	1.01×10^0	0.245	0.765	–	0.32:1	–
3A	3.38×10^{-1}	0.218	–	0.12	–	1.82:1

When D_2O was used as a solvent for 2B, 3B and 4B, downfield protons H10 and H11 were replaced with deuterium, and the corresponding resonances exhibited very low intensity in the ^1H NMR spectra (see Table 4).

3.3. Kinetic study

The hydrolysis reaction of the reactive dyes was considered to be a pseudo-first-order reaction in the presence of a large excess of hydroxide ions (pH 10.5). To quench the reaction, 0.1 N HCl solution was utilised to adjust the pH to 6.0–7.0. The hydrolysis products were then determined *via* HPLC.

For the kinetic study, the following pseudo-first-order equation was used:

$$\log(A_t/A_0 \times 100\%) = -a \times t + b,$$

where *t* denotes the time [hour]; *a*, the slope [h^{-1}]; *b*, the intercept; , A_0, the initial concentration of the dye; and A_t, the concentration of the dye after t hour of the reaction. The rate constant (k_{obs}) can be determined using the following equation:

$$k_{obs} = -a \times 2.303\ [h^{-1}],$$

where 2.303 is the conversion factor between natural and base 10 logarithms.

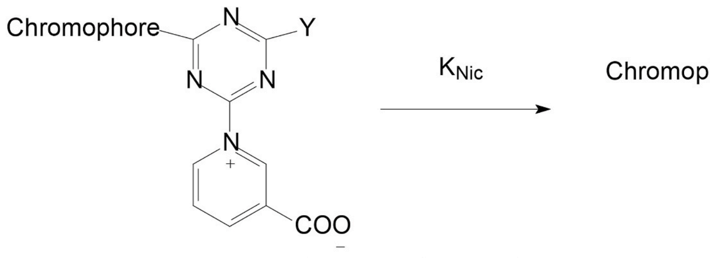
The half-life time ($t_{½}$), which is the time required for the concentration of the reactive dye in the test substance to decrease to 50% from its initial concentration for the first-order reaction, was calculated using the equation $t_{½} = \ln(2/k_{obs})$. The concentration change of the dye was calculated from the peak area percentage of the corresponding HPLC chromatogram, and the logarithmic plot of log (A/A_0) against time at 40 °C for the 10 model dyes (presented in Figs. 2 and 3) was used to calculate k_{obs} and $t_{½}$. The R^2 values obtained for the curves of the 10 model dyes confirmed the pseudo-first-order kinetic for this reaction.

The hydrolysis rate constants and $t_{½}$ of the MCT dyes are presented in Table 5. The methoxychlorotriazinyl compound (2A, OCH_3/Cl) exhibited the highest rate constant for the disappearance of the starting material (k_{obs}), followed by the methyl (methylsulfonyl)amino chlorotriazinyl compound (3A, $N(CH_3)SO_2CH_3$/Cl). The cyanoamino-chlorotriazinyl (1A, NHCN/Cl) and *N*-methylphenylchlorotriazinyl (4A, $N(CH_3)$phenyl/Cl) compounds exhibited similar reactivity and $t_{½}$ for the

Table 7
Pseudo-first-order hydrolysis rate constants of NTR Dyes (1B–5B) at 40 °C.

NTR Dye	Overall reactivity Rate constants (k_{obs}) [hours^{-1}]	Half-life time ($t_{½}$) [hours]	R^2 value
1B	3.42×10^{-1}	2	0.9983
2B	1.34×10^0	0.52	0.9930
3B	1.32×10^0	0.52	0.9910
4B	4.70×10^{-1}	1	0.9945
5B	7.65×10^{-2}	9	0.9967

Order of reactivity: 2B > 3B > 4B > 1B > 5B



Y: 1B=NHCN; 2B=OCH3; 3B=NMMS; 4B=NMA; 5B=OH

Scheme 4. Hydrolysis of NTR dyes 1B, 2B, 3B, 4B and 5B

Table 8
Reactivity enhancement from MCT (A series) to NTR (B series) dyes.

k_{obs} of Dye B / k_{obs} of Dye A	Ratio
k_{obs} 1 B/k_{obs} 1A	83
k_{obs} 2 B/k_{obs} 2A	1.32
k_{obs} 3 B/k_{obs} 3A	4
k_{obs} 4 B/k_{obs} 4A	107
k_{obs} 5 B/k_{obs} 5A	333

Table 9
Hammett substituent constants (σ_{meta}) of the ‘second-leg’ substituents.

2nd leg substituent	‘σ_{meta}’
-NHCN/–$(NCN)^-$	0.21/expected negative value
$-OCH_3$	0.11
$-N(CH_3)SO_2CH_3$	0.29
$-NHC_6H_5$/$-N(C_6H_5)_2$/$-N(CH_3)_2$	−0.12/−0.07/−0.15
-OH/$-O^-$	0.13/−0.47

hydrolysis reaction. As expected, a very small amount of the hydrolysis product of the hydroxylchlorotriazinyl compound (5A, OH/Cl) was obtained due to the deactivation of the chloride reactive group by the strong electron-donating substituent O^- in the triazine ring.

The displacement of chloride in the hydrolysis reaction was detected for Dyes 1A and 4A (Scheme 1), as demonstrated by HPLC and HR mass spectrometry. According to a previous study [15], the hydrolysis of Dye 2A proceeds *via* the displacement of chloride (K_{Cl}) and displacement of methoxide (K_{OCH3}) in an alkali aqueous solution (see Scheme 2). In this study, it was found that the hydrolysis of Dye 3A also involved two competing reaction steps, i.e. displacement of chloride (K_{Cl}) and displacement of *N*-methyl (methylsulfonyl)amino (K_{NMMS}) (see Scheme 3).

The individual rate constants K_{Cl}, K_{OCH3} and K_{NMMS} were calculated from a statistical average of the ratio between the amount of Dyes 2A or 3A that underwent chloride displacement and that with methoxide ($-OCH_3$) or methyl (methylsulfonyl)amino ($-N(CH_3)SO_2CH_3$) displacement obtained *via* HPLC. The rate constant ratios K_{Cl}/K_{OCH3} and K_{Cl}/K_{NMMS} are presented in Table 6. The results indicate that the displacement of methoxide was faster than that of chloride in Dye 2A, whereas the displacement of chloride was faster than that of methyl (methylsulfonyl)amino in Dye 3A. The K_{Cl} values of Dyes 2A and 3A were similar; however, the displacement of methoxide was about six times faster than that of methyl (methylsulfonyl)amino. This may be due to the steric hindrance of the methyl (methylsulfonyl)amino group, which renders it less prone to undergo nucleophilic attack by the hydroxide group.

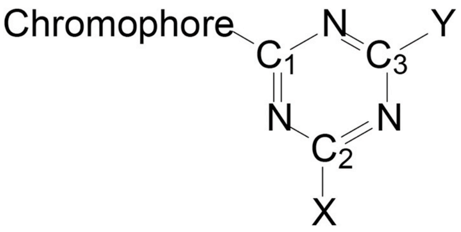


Fig. 4. Triazine carbon labels of the 10 model dyes.

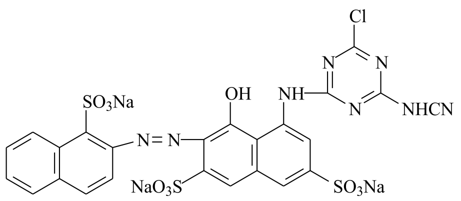
The rate constants (k_{obs}) of the NTR dyes (1B, 2B, 3B, 4B and 5B) are presented in Table 7. The HPLC data confirmed that the hydrolysis reaction of the NTR dyes mainly proceeded by the displacement of nicotinic acid by the hydroxide group (see Scheme 4). From Tables 5 and 7, it can be seen that the reactivity of the NTR dyes was faster than that of the MCT dyes, except for Dye 2B. However, the degree of rate enhancement when comparing chloride- and nicotinic acid-substituted dyes dramatically varies. For example, the reactivity of Dye 3B was four times faster than that of Dye 3A. Nevertheless, Dyes 1B, 4B and 5B were 83, 107 and 333 times faster than Dyes 1A, 4A and 5A, respectively ([NHCN] $k_{nic}/k_{Cl} \sim 83$, [OCH_3] $k_{nic}/k_{Cl} = 1.32$, [NMMS] $k_{nic}/k_{Cl} = 3.9$, [$N(CH_3)$ Phenyl] $k_{nic}/k_{Cl} = 107$, [OH] $k_{nic}/k_{Cl} = 333$; see Table 8). The order of the overall reactivity (k_{obs}) of the MCT and NTR dyes followed the same sequence: 2A > 3A > 4A > 1A > 5A and 2B > 3B > 4B > 1B > 5B. These results may be partly due to the relative efficiency of the substituents as leaving groups. The pk_a values of the cyanoamino and hydroxy protons in 1A, 1B, 5A and 5B were simulated using the Instant Cheminformatics Solution-Chemicalise tool [17], affording the values 10.93, 10.62, 7.29 and 1.55, respectively. It can be deduced that both the hydroxyl and cyanoamino groups would be deprotonated in alkali aqueous solution. The resulting negatively charged substituents, i.e. O^- and $-(NCN)^-$, would disfavour the nucleophile attack of the hydroxyl group to the reactive chloro or nicotinic acid group as the triazine ring would be more electron-rich. This explains why Dyes 5A and 5B have the lowest reactivity, followed by Dyes 1A and 1B, probably because of the partial ionisation of the cyanoamino group at pH 10.5, which would render the triazine ring more electron-rich, thus deactivating the reactive chloro or nicotinic acid group towards nucleophile attack. Contrarily, the most reactive dyes were 2A, 2B, 3A and 3B, which have electron-withdrawing groups that render the triazine ring more electron-poor, therefore favouring the nucleophile attack by OH^-.

To confirm the above hypothesis, the Hammett substituent constants [18], σ_{meta}, of the ‘second-leg’ substituents were compared (see

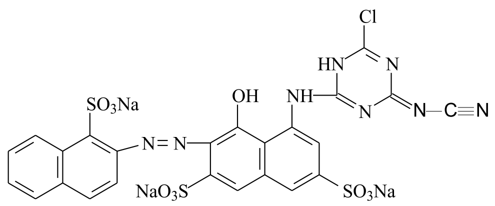
Table 10
Calculated electron density of the triazine carbon atom of Dyes 1A, 2A, 3A, 4A and 5A.

MCT Dye	Electron density			
	X	C_2	Y	C_3
1A	Cl	−0.001	-NHCN	0.014
1A[a](resonance)	Cl	−0.093	= N–CN	0.121
2A	Cl	−0.006	$-OCH_3$	0.195
3A	Cl	−0.002	$-NCH_3SO_2CH_3$	0.136
4A	Cl	−0.036	-*N*-methyl phenyl	0.051
5A	Cl	0.000	-OH	0.219
5A[a](resonance)	Cl	−0.142	= O	0.251

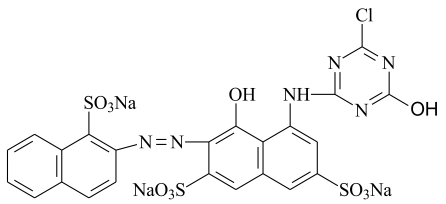
[a] Deprotonation structure of NHCN and OH in alkali solution.



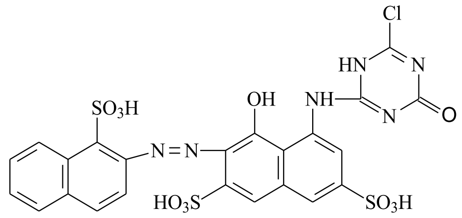
1A



$1A^a$ (resonance form at pH 10.5)



5A



$5A^a$ (resonance form in pH 10.5)

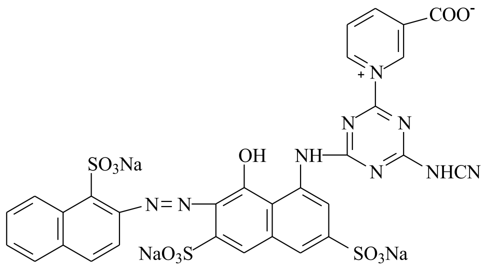
Fig. 5. The Structures and resonance structures of 1A and 5A

Table 11
Electron density of triazine carbon atom of Dyes 1B, 2B, 3B, 4B and 5B.

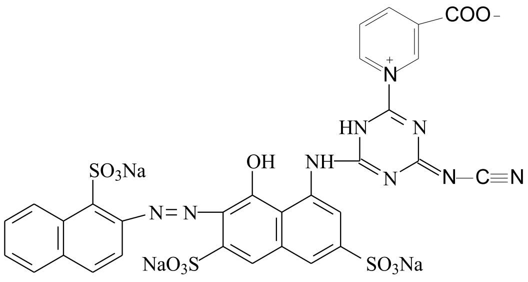
NTR Dye	Electron density			
	X	C_2	Y	C_3
1B	Nic	−0.068	-NHCN	0.034
$1B^a$(resonance)	Nic	−0.273	= N–CN	0.245
2B	Nic	−0.082	$-OCH_3$	0.210
3B	Nic	0.026	$-NCH_3SO_2CH_3$	0.258
4B	Nic	−0.095	-*N*-methyl phenyl	0.057
5B	Nic	−0.142	-OH	0.217
$5B^a$(resonance)	Nic	−0.210	= O	0.253

[a] Deprotonation structure of NHCN and OH in alkali solution.

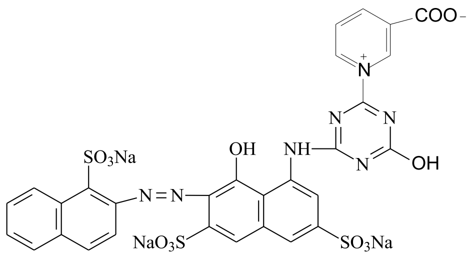
Table 9). High values of σ meta indicate strong electron-withdrawing property. It was found that the $–OCH_3$ and $–N(CH_3)SO_2CH_3$ substituents exhibited stronger electron-withdrawing ability than the others, which can explain the higher reactivity of 2A, 2B, 3A and 3B. It was assumed that the –NHCN group of 1A and 1B would be partially ionised in alkali solution, as in the case of the –OH group. Thus, the value of σ_{meta} of $–(NCN)^-$ would be expected to be negative, which indicates electron-donating property. The σ_{meta} values of the phenyl–N–Me group of 4A and 4B would be in-between those of $–NHC_6H_5$, $–N(C_6H_5)_2$ and $–N(CH_3)_2$. The least-reactive group would be the –OH substituent of 5A and 5B, which has the strongest electron-donating group ($–O^-$). As a result, the σ_{meta} values follow the order $–N(CH_3)SO_2CH_3$ > $–OCH_3$ > –*N*-methyl aniline > $–(NCN)^-$ > $–O^-$, which



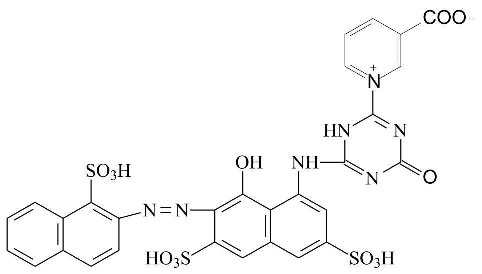
1B



$1B^a$ (resonance form at pH 10.5)



5B



$5B^a$ (resonance form in pH 10.5)

Fig. 6. The structures and resonance structures of 1B and 5B

approximately matches the trend observed for the hydrolysis constant (K_{obs}): Dye (OCH_3) > Dye ($N(CH_3)SO_2CH_3$) > Dye (*N*-methyl aniline) > Dye (NHCN) > Dye (OH).

The electronic effect of the substituents on the rate constant was also investigated by quantum mechanics calculation of the model dyes (see Fig. 4). The modelling data presented in Table 10 demonstrates the electron density of the carbon atom bonded to the chloro atom in Dyes 1A, 2A, 3A, 4A and 5A. The electron density was found to increase in the order 3A < 2A < 4A < 1A* < 5A* (1A* and 5A* are the resonance structures of 1A and 5A in alkali solution, respectively, as presented in Fig. 5). This sequence is nearly inverse to that of the K_{obs} value of the rate constant (2A > 3A > 4A > 1A > 5A). The higher K_{obs} of 2A compared with that of 3A is most likely due to the steric effects; $–OCH_3$ is smaller than $–N(CH_3)SO_2CH_3$, and therefore, Dye 2A is more reactive than Dye 3A.

Table 11 presents the electron density of the carbon atom bonded to the nicotinic acid in Dyes 1B, 2B, 3B, 4B and 5B. The electron density increased in the order 3B < 2B < 4B < 5B* < 1B* (1B* and 5B* are the resonance structures of 1B and 5B, respectively, in alkali solution, as presented in Fig. 6). However, the NHCN substituent on Dye 1B is only partially deprotonated at pH 10.5; thus, the electron density of the carbon atom connected to the nicotinic acid lies between −0.068 and −0.273, and the average electron density of 1B and 1B* is −0.171. The sequence of the electron density is also nearly inverse to that of the K_{obs} values of the NTR dyes (2B > 3B > 4B > 1B > 5B). Thus, the electron density of the carbon atom bonded to the nicotinic acid of 5B is the highest (−0.210 for C_2), whereas the K_{obs} value is the lowest.

4. Conclusions

Ten reactive dyes, i.e. five monochloro-*s*-triazinyl and five *m*-carboxypyridinium-*s*-triazinyl dyes, were prepared to examine the effect of the different substituents on the hydrolysis rate constant k_{obs} and the $t_{½}$ values of the reactive dyes. By replacing the chloro substituent in the MCT dyes with nicotinic acid in the NTR dyes, the reactivity was enhanced. The order of reactivity for both the MCT and NTR dyes followed the sequence $–OCH_3$ > $–N(CH_3)SO_2CH_3$ > –*N*-methyl phenyl > –NHCN > –OH, which is significantly related to the electronic effect of the ‘second-leg’ substituent in the triazine ring. The order of the K_{obs} values was explained by the Hammett substituent constants σ_{meta} and by the quantum mechanics calculation. It was found that the substituents with higher electron-donating property afforded lower hydrolysis rate constants.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109147.

References

[1] Sandro Ponzini S. Reactive azo dyes containing triazine group quarternized by nicotinic acid. GB 3519614 1970.
[2] Ponzini Sandro, Saronno, Castelli Paolo. Monza and Jean Stanislao Lawendel. Quarternized reactive phthalocyanice dyestuffs containing triazine and nicotinic acid groups. US 3642787 1972.
[3] Leng John Lindley, Parton Brian, Denis RAR, John RL. Dyesstuffs. US 3996221; 1976.
[4] Masakatsu Mikamoto, Suzuki Yoshiharu, Masayoshi Ojima, Yutaka Iizuka, Ryuzo Orita, Tadshi Matsuo. Disazo dyes.. GB 2165852 A; 1986.
[5] Masakatsu Mikamoto, Suzuki Yoshiharu, Masayoshi Ojima, Yutaka Iizuka, Ryuzo Orita, Tadshi Matsuo. Process for dyeing cellulose fibers of its union fibers with reactive triazine dye quaternized with nicotinic acid. US 4453945; 1984.
[6] Kampyli V, Phillips DAS, Renfrew AHM. Reactive dyes containing a 4-m-carboxy-pyridinium-1,3,5-triazine-2-oxide reactive group: exhaust dyeing of cotton under alkaline and neutral fixation conditions. Dyes Pigments 2004;61:165–75.
[7] Karapinar E, Phillips DAS, Taylor JA. Reactivity, chemical selectivity and exhaust dyeing properties of dyes possessing a 2-chloro-4-methylthio-s-triazinyl reactive group. Dyes Pigments 2007;75:491–7.
[8] Dongzhi L, Kunyu G, Lubai C. The hydrolysis kinetics and dyeing properties of 3′-carboxypyridino-triazine reactive dyes. Dyes Pigments 1997;33:87–96.
[9] Pedemonte R. Dye mixture of fiber reactive azo dyes and use thereof for dyeing material containing hydroxy and/or carboxamido groups. WO 02/08341 A2; 2002.
[10] Bostock Stephen B, Michael G, Hutchings JAT. Reactive dyes having a sulphonamide group. US5359043; 1994.
[11] Paluszkiewicz J, Czajkowski W. Reactive dyes derivatives of quinoline triazinium salts for dyeing cellulose fibres in neutral medium. Fibres Text East Eur 2007;15:101–3.
[12] Bone JA, Le TT, Phillips DAS, Taylor JA. One-bath dyeing of polyester/cotton blends with disperse and bis-3-carboxypyridinium-s-triazine reactive dyes. Part 2: application of substantive reactive dyes to cotton at 130°C and neutral pH. Color Technol 2008;124:117–26.
[13] OECD guidelines for the testing of chemicals. Test No. 111: hydrolysis as a function of pH. Organisation for Economic Cooperation and Development; 2004. https://doi.org/10.1787/9789264069701-en.
[14] Renfrew AHM, Taylor Ar JA. Reactive dyes for cellulose. concurrent methoxide-hydroxide reactions of triazinyl reactive systems: a model system for assessment of potential fixation efficiency. J Soc Dye Colour 1989;105:441–5.
[15] Taylor JA, Renfrew A, Lovis JN. Reactive dyes for cellulose. The reaction of alkoxychlorotriazinyl dyes with hydroxide ion. Color Technol 1991;107:455–9.
[16] Yang K, Clark M, Lewis DM. Synthesis of a di-(p-sulphophenoxy)-s-triazine reactive dye and its application in wool fabric ink-jet printing. Color Technol 2019;135(3):202–12. https://doi.org/10.1111/cote.12388.
[17] https://chemicalize.com/welcome/chemical-calculations-and-predictions.
[18] Perrin DD, Dempsey B, Serjeant EP. pKa prediction for organic acids and bases. https://doi.org/10.1007/978-94-009-5883-8; 1981.