

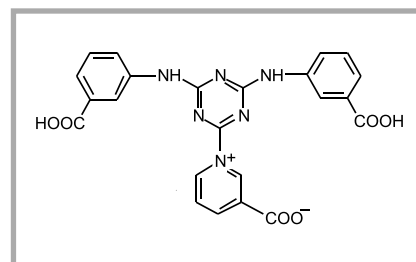
# Reactive Dyes Derivatives of Quinoline Triazinium Salts for Dyeing Cellulose Fibres in Neutral Medium

## Abstract

A number of bi-functional fibre-reactive dye derivatives of C.I. Reactive Red 120 containing quinolino-s-triazine groups were synthesised and their application properties during the dyeing of cotton fabrics were determined. Lower fixation values of new dyes with cellulose fibre in comparison with reference dye derivatives of pyridino-s-triazine were obtained.

**Key words:** reactive dyes for cellulose fibres, nicotinic acid, 3-carboxypyridino-s-triazine dyes, quinolino-s-triazine dyes.

differed in shade [5]. This phenomenon was especially visible in the case of pale greenish-yellow and yellow dyes. An attempt to explain these observations was made by the synthesis of the colourless model substance of the structure presented in Figure 1.



**Figure 1.** Model compound with 3'-carboxypyridinium-s-triazine residue prepared during the work.

## Introduction

In the 60's of the last century it was discovered that certain tertiary amines such as pyridine, trimethylamine and others can significantly increase the reactivity of monohalogenotriazine reactive dyes [1, 2]. It was found that this phenomenon had been the result of intermediate quaternary ammonium salts formation which exhibits higher reactivity to the dyed fibre. In 1983 this discovery was commercialised by the Japanese company Nippon Kayaku, which under the brand name 'Kayacelon React' introduced dyes containing reactive quaternary ammonium groups based on nicotinic acid built into the triazine residue. Dyes of such structure exhibit higher affinity to cellulose and are able to react with this fibre in a near neutral medium at elevated (100 °C) temperatures. Such properties are positive from a practical point of view because effluents after the application process contain a lower amount of dyes, alkalis and inorganic salts.

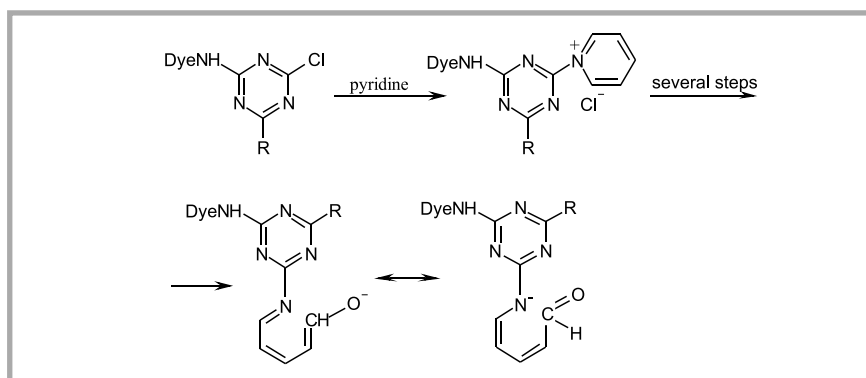
In other work on the synthesis of such types of dye various tertiary amines were examined [3, 4] but so, only products with nicotinic acid have found practical use.

During our research on this field, it was found that sometimes samples of the cotton fabric dyed with the use of a monochlorotriazine dye, and the same dye in which a chlorine atom in triazine residue was substituted by nicotinic acid, slightly

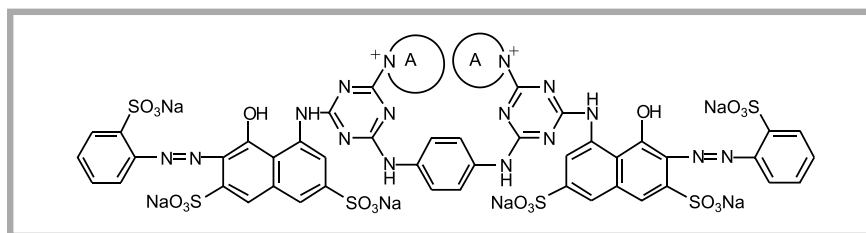
During TLC monitoring of the condensation process of 6-chloro-2,4-bis-(3'-carboxyphenyl)amino-1,3,5-triazine with nicotinic acid, it was found that the appearance of the main colourless product of reaction was accompanied by the presence of a yellow impurity. The amount of this impurity increased at elevated pH values of the reaction (above pH = 6.5).

A similar phenomenon was observed by Renfrew and co-authors [6] in the case

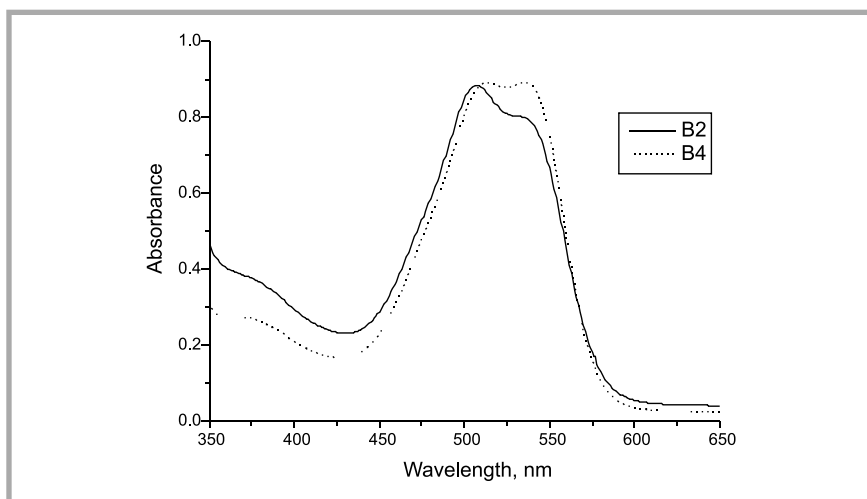
of substituted pyridinium triazine salts and explained that this was the result of a nucleophilic attack on the pyridine nucleus proceeding with its ring opening (Figure 2). The same behaviour was also previously reported in the case of other pyridinium salts [7 - 9]. It is then possible



**Figure 2.** Suggested decomposition of substituted triazine salt as the result of nucleophilic attack on the pyridine ring.[6].



**Figure 3.** General structure of bifunctional reactive dyes synthesised during present research.



**Figure 4.** Absorption curves of B2 and B4 dyes (water, approx. concentration  $2 \times 10^{-4}$  mole/dm<sup>3</sup>).

that such a process may also take place in the case of triazine derivatives of nicotinic acid and that the presence of various decomposition products could influence the colour shade of final dyeing.

During synthesis of the above-mentioned model compound (Figure 1) and its derivatives, it was found that the use of quinoline instead of pyridine and nicotinic acid did not result in the formation of yellow impurities. The purpose of our work was then the synthesis of a new group of reactive dyes of the structure presented in Figure 3, which contained reactive quaternary ammonium salts based on various derivatives of quinoline.

## Experimental

During this work, 6 new dyes were synthesised, in which tertiary amines were

used: 6-quinoxalinesulphonic acid (A3), quinoline (A4), isoquinoline (A5), 2-hydroxyquinoline (A6), 8-hydroxyquinoline (A7), and quinaldine (A8). Dyes synthesised with the use of pyridine (A1) and nicotinic acid (A2) were treated as reference.

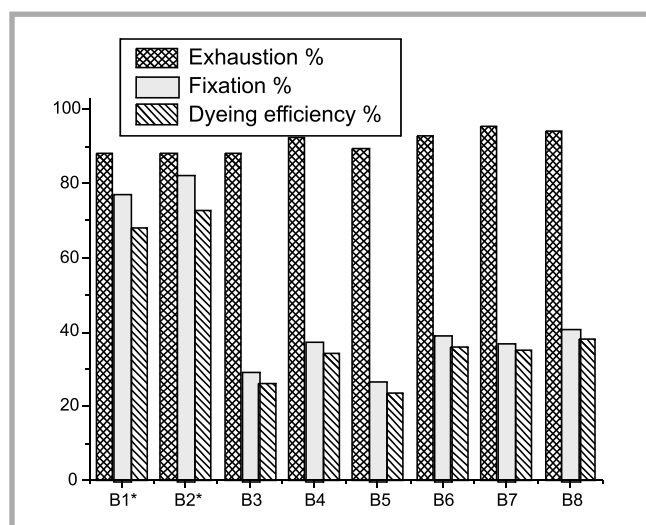
All dyes prepared during this work were based on the typical structure of C.I. Reactive Red 120 and synthesised in the usual way, during which condensation of 1,3,5-trichloro-s-triazine (cyanuric chloride) with 1-amino-8-hydroxy-3,6-naphthalene-disulphonic acid ("H acid") at 0-5 °C and pH = 1.2 - 1.5 was followed by the coupling of the resulted intermediate ("triazine-H acid") with diazotized 2-aminobenzenesulphonic acid at a temperature within the range of 5 - 10 °C and pH = 5 - 6. Monoazo dichloro-s-triazinyl dye was then condensed with 1,4-phe-

nylenediamine at a temperature within the range of 30 - 40 °C and pH =  $6.5 \pm 0.2$ . The final step of the synthesis was the condensation of bis-monochloro-s-triazinyl dye with appropriate tertiary amine at a temperature of between 85 - 90 °C and pH = 6.0 - 6.5. All reaction steps were monitored by TLC chromatography. The structures of the selected final products were confirmed by MALDI mass spectrometry. Structure, synthetic and colouristic properties of the prepared dyes are presented in Table 1.

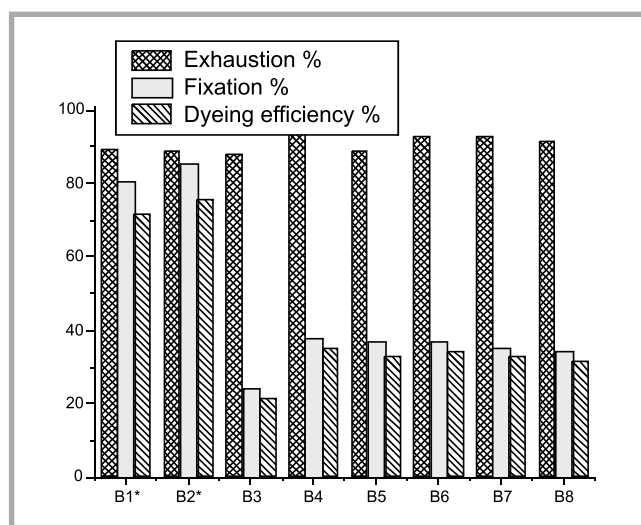
## Results and discussion

It can be seen from the data presented in Table 1 that both derivatives of pyridine and quinoline are characterised with a double-peak light absorption band within the range of 510 - 540 nm. The intensity of these absorption peaks differs slightly in the case of individual dyes as is presented in Figure 4. The observed phenomenon is probably the result of various degrees of dye self-association in the aqueous medium.

In order to determine the application properties of prepared dyes, they were used for dyeing cotton fabric by the exhaust method (1% dyeings, dyebath ratio 1:10 in the presence of 20 g/dm<sup>3</sup> sodium chloride). The required near-neutral pH of the dyebath was obtained by the use of an appropriate phosphate buffer. The dyeing process was carried out for 1 hour at a temperature of 100 °C. Percentage exhaustion and fixation degrees on dyed cellulose fabric were determined spectrophotometrically



**Figure 5.** Exhaustion and fixation degrees of synthesised dyes and total efficiency of dyeing process at pH = 7.0.



**Figure 6.** Exhaustion and fixation degrees of synthesised dyes and total efficiency of dyeing process at pH = 7.5.

**Table 1.** Structure of synthesised dyes presented in Figure 3; \*reference dyes, \*\* in water, \*\*\* on Merck Cellulose F<sub>254</sub> plates, eluent: benzyl alcohol:DMF:water - 4:2:1,

Symbol of the dye	Structure of used amine A	$\lambda_{\max}$ **	R <sub>f</sub> ***
B1*	pyridine	512.7 539.3	0.55
B2*	nicotinic acid	507.1 535.2	0.27
B3	6-quinoxalinesulphonic acid	511.0 534.3	0.10
B4	quinoline	512.5 535.2	0.61
B5	isoquinoline	517.9 544.0	0.65
B6	2-hydroxyquinoline	513.7 537.1	0.69
B7	8-hydroxyquinoline	515.0 537.0	0.66
B8	quinaldine	513.8 537.3	0.66

**Table 2.** Exhaustion and fixation degrees during dyeing of cotton fabric at near neutral pH dyebaths.

Symbol of the dye	pH=7.0		pH=7.5	
	Exhaustion %	Fixation %	Exhaustion %	Fixation %
B1*	88.4	77.1	89.3	80.4
B2*	88.5	82.4	88.8	85.3
B3	88.4	29.4	88.0	24.4
B4	92.4	37.2	93.6	37.8
B5	89.5	26.6	89.1	36.9
B6	93.2	38.9	92.8	37.1
B7	95.4	36.9	93.1	35.4
B8	94.1	40.7	91.6	34.4

**Table 3.** Charge density distribution and bond length data of selected model compounds of structure presented in Figure 6.

Used amine Bond length 2-7 Bond order 2-7	Compound's structure (A)	Charge density distribution			
A1 1.4717 1		1 -0.299 4 0.250 7 -0.003 10 -0.154	2 0.173 5 -0.275 8 0.044 11 -0.159	3 -0.294 6 0.246 9 0.028 12 -0.002	
A2 1.4731 1		1 -0.295 4 0.247 7 -0.007 10 -0.163	2 0.161 5 -0.280 8 0.094 11 -0.137	3 0.147 6 0.246 9 0.052 12 0.046	
A4 1.4721 1		1 -0.285 5 -0.265 8 0.088 11 -0.195 14 -0.105	2 0.156 6 0.236 9 0.075 12 0.030 15 -0.048	3 -0.292 4 0.240 7 -0.002 10 -0.084 13 -0.081 16 -0.136	
A5 1.4707 1		1 -0.294 6 0.244 10 0.031 14 -0.047	2 0.169 7 0.097 11 -0.029 15 -0.103	3 -0.307 4 0.245 8 -0.001 9 -0.106 12 -0.113 13 -0.13 16 -0.080	

and are presented in Figure 5, Figure 6 and in Table 2.

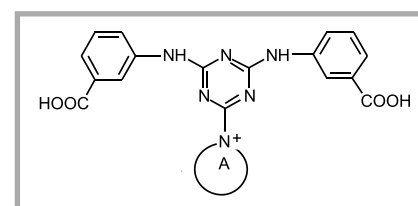
It can be observed that all the prepared dyes exhibited similar affinity to dyed fabric and introducing quinoline residue to dye molecule in some cases even increased dye exhaustion on the cellulose fibre as compared with reference dyes. Nevertheless, these properties were not accompanied by an increase in dye

fixation in the fibre. Much lower than expected fixation degrees of all derivatives of quinoline are not clear at the present moment and this problem would probably require more detailed investigation. From the results of the quantum-mechanical structure calculations with the use of the AM1 HyperChem method for quaternary ammonium salts based on the model compound (Figure 7) presented in Table 3, similar values of electron

density distribution were obtained for all examined amines. One might then expect that the reactivity of dyes B3-B8 should be comparable with model dyes B1 and B2, derivatives of pyridine.

## Conclusion

One of the possible explanations for the observed phenomena might be that large quinoline residues substituted to the triazine ring cause some steric hindrance during the nucleophilic attack of ionised



**Figure 7** Model compounds used for charge density calculations by AM1 HyperChem method.

cellulose into the quaternary active centre of the dye. However, these quaternary ammonium salts are still accessible to smaller hydroxyl ions which may result in an increased degree of dye hydrolysis.

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