

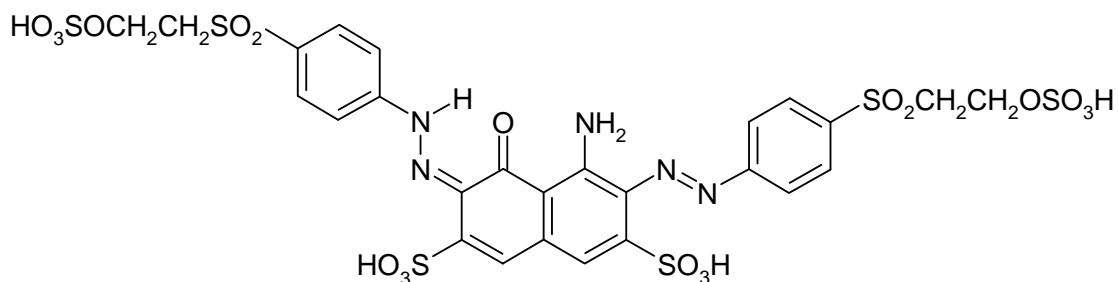
## Triazinyl Betaines as Fibre Reactive Groups

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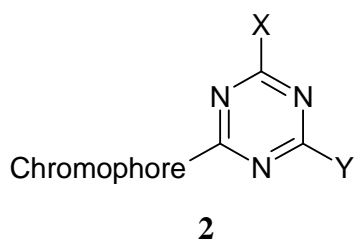
### Introduction

The first reactive dye range for cellulose, launched in 1956, comprised a single chromophore and a single triazinyl fibre reactive group. However, the advantages conferred by the presence of two reactive groups were quickly recognised as CI Reactive Black 5 **1** (whose introduction pre-dated the formal recognition of the reactive dye class) proved to be an outstanding and enduring commercial success.



**1**

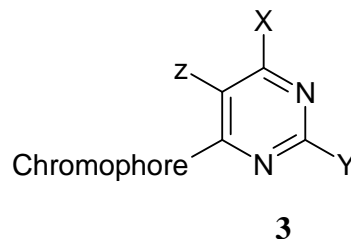
Over the intervening 50 years, a large range of electrophilic compounds have been evaluated as fibre reactive groups, but of these only a few classes have found commercial success, viz triazines, pyrimidines (relatively minor) and vinyl sulphones. Within each class of fibre reactive group many variations have been studied and the best candidates selected. Structures **2** and **3** below show some of the triazines, and pyrimidines respectively which have been exploited commercially.



**2**

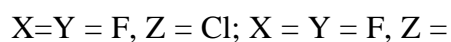
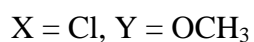
X = Y = Cl; X = Cl/F, Y = NHR

CN



**3**

X = Y = Z = Cl; X=Y = Cl, Z =

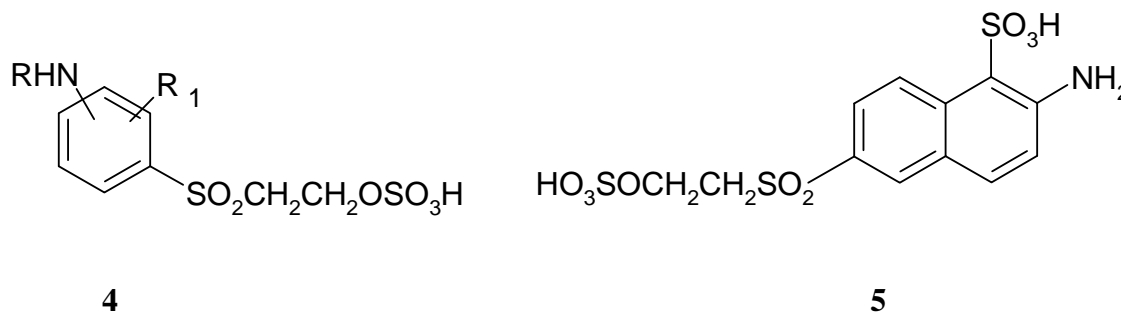


H

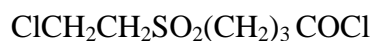


Vinyl sulphones in dye structures are generally, but not always, present in a masked or protected form. Intermediates used to insert this reactive group, into a dye structure, can be aromatic or aliphatic and usually also contain an amino group. Where an amino group is present in the vinyl sulphone intermediate, introduction is either by diazotisation and coupling or by reaction with an electrophilic compound, e.g. a halotriazinyl ring, which forms part of the dye structure. Aliphatic vinyl sulphones also use attachment *via* an electrophilic group. A selection of the many (masked) vinyl sulphone compounds used is shown below **4,5,6,7**. Vinyl sulphones can also be “built” into a coupling component, e.g. a pyrazolone.

At the present time, reactive dyes are designed to address the twin objectives of improving cost effectiveness for the dyer and reducing the environmental impact of dyeing with reactive dyes, while not compromising on fastness. Accordingly, new products are now much more sophisticated and often contain two and sometimes three chromophores together with at least two reactive groups. The reactive groups can be the same or different.



(R = H or alkyl; R<sub>1</sub> = H, methoxyl or SO<sub>3</sub>H)



**6**

**7**

The application and technical properties of a reactive dye are influenced by the choice and position of the reactive group and **Table 1** shows some of the issues involved.

**Table 1: Dye properties influenced by the reactive group.**

Solubility

Hue

Dye stability

Fastness

Substantivity

Selectivity

Application method

Dye-fibre bond stability

Dischargeability (position)

Levelness

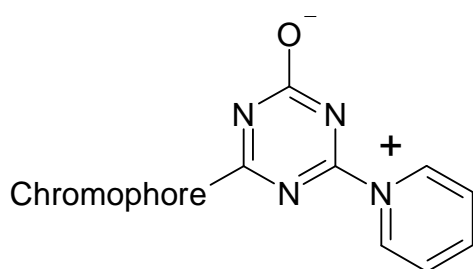
Ease of wash-off

Brightness

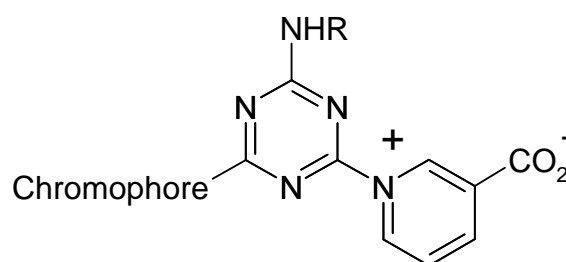
Cost

This can be exemplified by Tulative XLE dyes (Atul). This range of dyes, for exhaust dyeing, employs triazinyl reactive groups, not only to confer levelness through moderate substantivity and high migration, but also to render the products suitable for post mercerisation as the triazinyl-cellulose covalent bond displays good stability to strong alkali treatment.

One triazinyl group, which has been overlooked in the context of reactive dyes, is the triazinyl betaine group **8**.



**8**

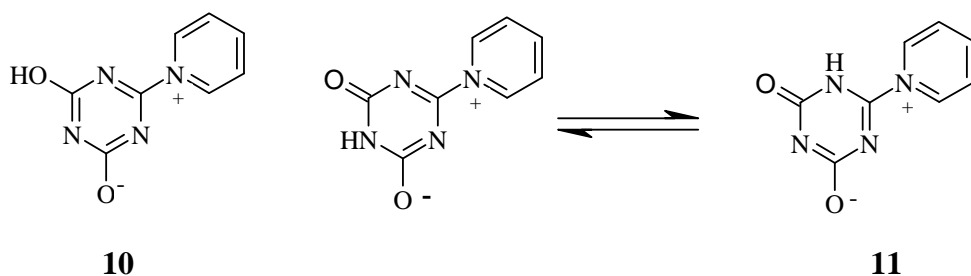


**9**

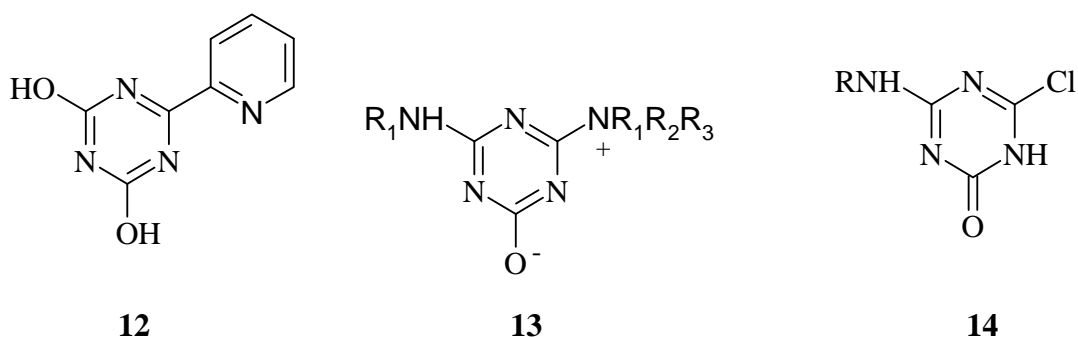
The diionic triazine **8** has both a nucleophilic and an electrophilic centre and is closely related to the conventional quaternary ammonium triazines **9** used in Kayacelon React dyes.

### Discussion

Triazinyl betaines were first reported in the literature, in 1965, by Tsujikawa, who assigned structure **10** to the reaction product of pyridine and cyanuric chloride. This particular hydroxytriazinyl betaine **10**, can exist in two 1,3,5-triazin-2(1H)-one tautomeric forms 11 and had been synthesised some years earlier by Saure and by Menon but the structure was wrongly assigned. The earlier workers believed the pyridine ring to be attached to the

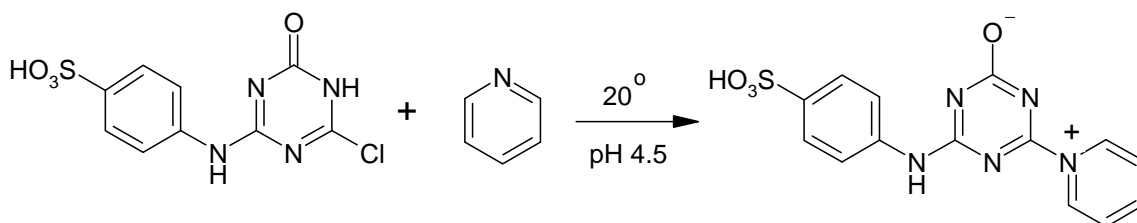


triazine *via* a C-C bond (**12**; or the corresponding *para* isomer) although Saure observed that the colourless product turned yellow in alkaline solution. This was a strong indication of the presence of a pyridinium-s-triazinyl compound as such colour forming reactions were well established by Zincke and Fujiwara.

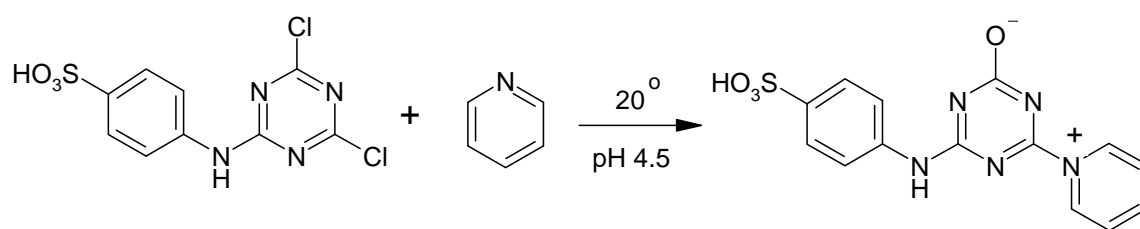


Pyridinium and 3-carboxypyridinium triazinyl betaines (**13**; where  $R_1R_2R_3$  = pyridinium or 3-carboxypyridinium) can readily be prepared from 6-chloro-1,3,5-triazin-2(1H)-ones **14** **Scheme 1**.

However, a general and more direct method of preparation of triazinyl betaines is *via* dichlorotriazinyl (DCT) compounds, e.g. triazinyl betaines (**13**; where  $R_1R_2R_3$  = independently alkyl, or form part of an alicyclic or heterocyclic ring;  $R_4$  = an aromatic ring) can readily be prepared by reaction with an appropriate tertiary, in either weakly acidic or weakly alkaline solution depending on the  $pK_a$



**Scheme 1**



## Scheme 2

of the base **Scheme 2**.

The reaction of DCT compounds with tertiary amines to form triazinyl betaines is a general reaction as shown in Table 2. The failure of triethylamine to react is ascribed to steric factors.

**Table 2: Mechanism of Formation of triazinyl betaines from dichlorotriazines**

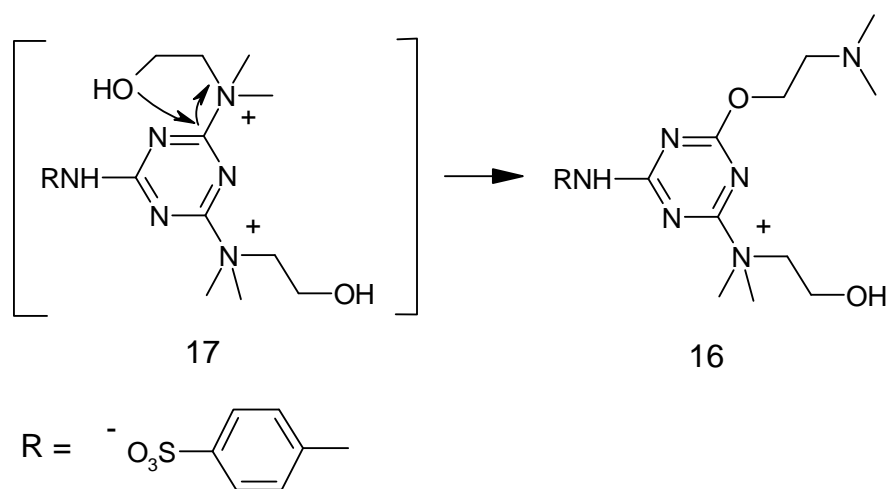
No	Amine	Product
1	trimethylamine	betaine
2	triethylamine	no reaction
3	<i>N</i> -methylpyrrolidine	betaine
4	<i>N</i> -methylmorpholine	betaine
5	1,4-diazabicyclo[2,2,2]octane	betaine
6	Hexamethylenetetramine	betaine
7	<i>N,N</i> -dimethylethanolamine	mixture

The mass spectrum clearly shows a peak that consisting molecular mass of 426 Da and consistent with a molecular formula of  $C_{17}H_{26}N_6O_5S$ , indicating a stable reaction product was formed from two moles of *N,N*-dimethylethanolamine and one mole of the DCT compound. This stable zwitterionic compound is assigned the triazinyl ether where the counter ion is  $SO_3^-$ .

Not only was the expected triazinyl betaine formed but also a triazinyl ether as a major product and under conditions (20-26°C; pH 7-8) unfavourable for deprotonation of the alcohol group and for conventional ether formation. For alcohols as

nucleophiles, that the rate of formation of a  $\sigma$ -complex in an  $S_NAr$  reaction is linearly dependent on the concentration of the alkoxide anion.

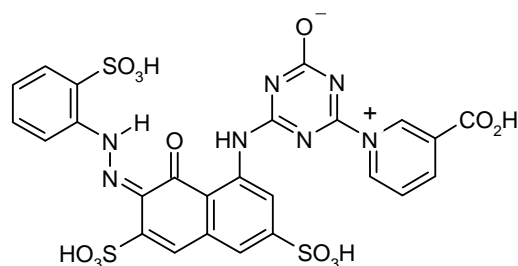
The origin of the triazinyl ether can be readily explained if a bis-quaternary ammonium intermediate **17**; **Scheme 4** is involved in the reaction. An intramolecular  $S_NAr$  reaction (Smiles rearrangement) of this activated heteroaromatic species would give this product. Such a highly electrophilic triazinyl intermediate, with both quaternary ammonium activating groups separated from the nucleophilic hydroxyl groups by two carbon atoms, is ideally set up for such a reaction to occur. Generally, Smiles rearrangements require alkali to proceed. However, for this structure, the high reactivity of the bis-quaternary ammonium intermediate **17**; **Scheme 4** renders unnecessary a deprotonation of the hydroxyl group. Only one quaternary ammonium group rearranges under the “neutral” conditions of the reaction since the electrophilicity of the triazinyl ring in compound **16**; **Scheme 4** is now reduced by the attached electron donating oxygen atom.



**Scheme 4**

Although many electrophilic triazinyl compounds have been evaluated in the context of fibre reactive dyes during the second half of the twentieth century, the triazinyl betaine group was overlooked. While recent interest by workers at the University of Manchester in the UK, in the triazinyl betaine group, was primarily in the context of fibre treatment rather than reactive dyeing, a reactive dye offers a convenient visual

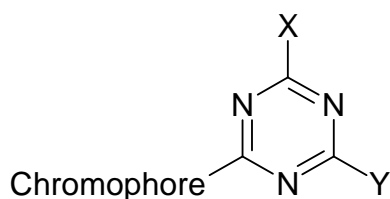
assessment of the performance of the covalent bond forming reaction with cellulose. Accordingly, an H-acid based red reactive dye **18**,



**18**

was synthesised and applied to cotton under exhaust dyeing conditions using a range of different application temperatures **Figure 1**.

The highest visual colour yields (K/S values) were recorded at 60 and 70 ° C. **Figure 2** shows the K/S values of a series of dyes, all with the same chromophore as for dye **18**, but employing different reactive groups **19**.



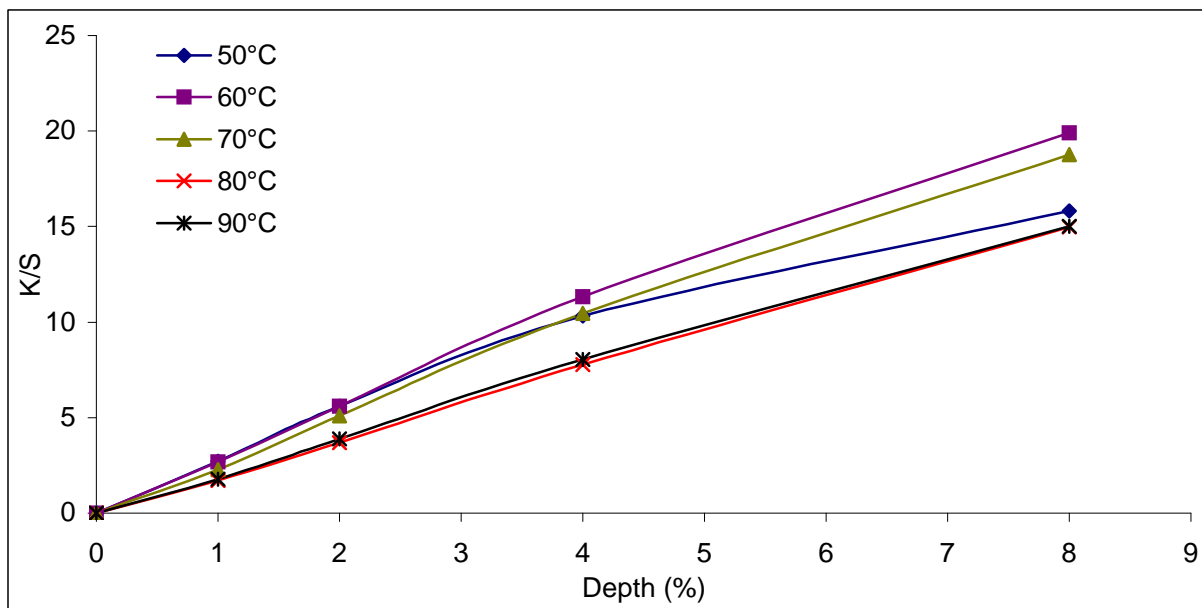
**19**

- A ; X = Cl, Y = o-toluidinyl:      B; X = OH, Y = HNC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub>H (para)  
 C ; X = OH, Y = Cl:                      D = triazinyl betaine **18**  
 E; X = Y = Cl:

Dyeings were by an exhaustion method, in the presence of alkali, and at 10:1 liquor ratio, using the manufacturer's recommended dyeing methods. The triazinyl betaine was dyed at 70° C.

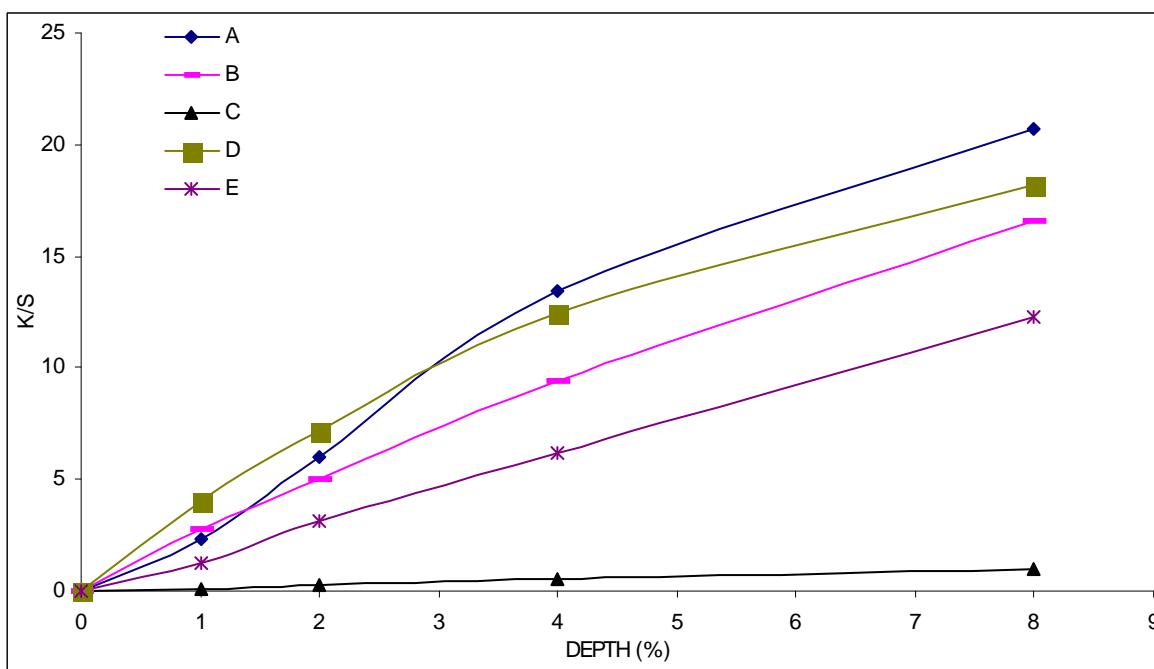
**Figure 1**

**Dyeing profiles of dye (18), on cotton, at different temperatures**



**Figure 2**

Dyeing profiles of the red series on cotton



C = chlorohydroxytriazine (80° C); E = dichlorotriazine (50° C); B = vinyl sulphone (60° C); D = triazinyl betaine; A = monochlorotriazine MCT (80° C)



**Figure 2** shows that the chlorohydroxytriazinyl (C) group is not fibre reactive under typical base catalysed monochlorotriazinyl fixation conditions, i.e. the strongly electron donating oxido group completely deactivates the remaining chlorine atom on the triazinyl ring. On the other hand, the triazinyl betaine dye (D), which also contains an oxido group, is fibre reactive and under alkaline fixation conditions is capable of giving comparable yields to other “conventional” reactive groups.

### **Conclusions**

The triazinyl betaine group has been shown to be fibre reactive and capable of forming covalent bonds with cellulose, under base catalysed conditions. It is cheap, easy to synthesise and AOX free, but preliminary work on dyes carrying this group, indicates no superiority over existing, established reactive groups, used for cellulose dyeing. Moreover, the betaine group occupies two positions on the triazine ring thereby reducing the flexibility of the heterocyclic reactive group, and a limited study to date, suggests it is unlikely to be of interest as a new reactive group for cellulose reactive dyes.

The chemistry of reactive groups is now well developed and it is difficult to justify research into this area for reactive dyes. One hundred percent fixation will not be achieved by this technology but rather the industry will continue to see a slow improvement in fixation, wash-off, fastness and application technology.