Dyes and Pigments 23 (1993) 179–196

Design of Chlorine-Fast Reactive Dyes. Part 2. The Role of Sulphonate Groups and Optimization of their Positions in an Arylazoarylamine System

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(Received 17 May 1993; accepted 11 June 1993)

ABSTRACT

The effect on colour fastness to chlorinated water caused by incorporating a sodium sulphonate (SO_3Na) group into the structure of reactive dyes based on an arylazoarylamine system has been investigated. The results of the study indicate that the SO_3Na group can play a vital role in increasing the colour fastness of 4-arylazo-1-naphthylamine dyes on cotton, and it is effective to incorporate this group into the 8-position. In contrast, the SO_3Na group in 4-arylazoaniline dyes plays only a minor role, because their chromogens are intrinsically chlorine-fast. The same structure–fastness relationships hold for their bisazo and trisazo analogues. The visible absorption spectra of these dyes are also described.

1 INTRODUCTION

The importance of a sulphonate (SO_3^-) group has been recognized in view of its ability to improve the colour fastness to chlorinated water (hereafter called chlorine fastness) of *o*-hydroxyazo dyes.[1,2] A previous paper in this series has examined reactive dyes based on arylazonaphthol.[2] In that study, it was found that differences in chlorine fastness arise primarily from differences in the positions of the sodium sulphonate (SO_3Na) groups, and thus it is quite effective to arrange an SO_3Na group on each of the aryl and naphthol rings so that the azo group is surrounded from both sides.

In the present study, this approach is extended to reactive dyes based on the arylazoarylamine structure. Unlike the arylazonaphthol dyes, commercially important arylazoarylamine dyes are those derived from arylamines by *p*-coupling, except for *o*-aminoazo dyes from aminonaphthosulphonic acids. Therefore, all dyes examined were limited to the *p*-coupled arylazoarylamine dyes and their analogous bisazo and trisazo dyes, of which each dye molecule has more than one SO_3Na group, and a fibre-reactive system linked to the terminal amino group.

The chlorine fastness of these dyes on cotton was assessed according to the ISO 105-E03 method. Since the covalent bond between such a dye and cotton, and that between its dye chromogen and an SO_3Na group are both stable to active chlorine under the test conditions,[3-5] the relationship between the position of the SO_3Na group and the chlorine fastness can be precisely assessed.

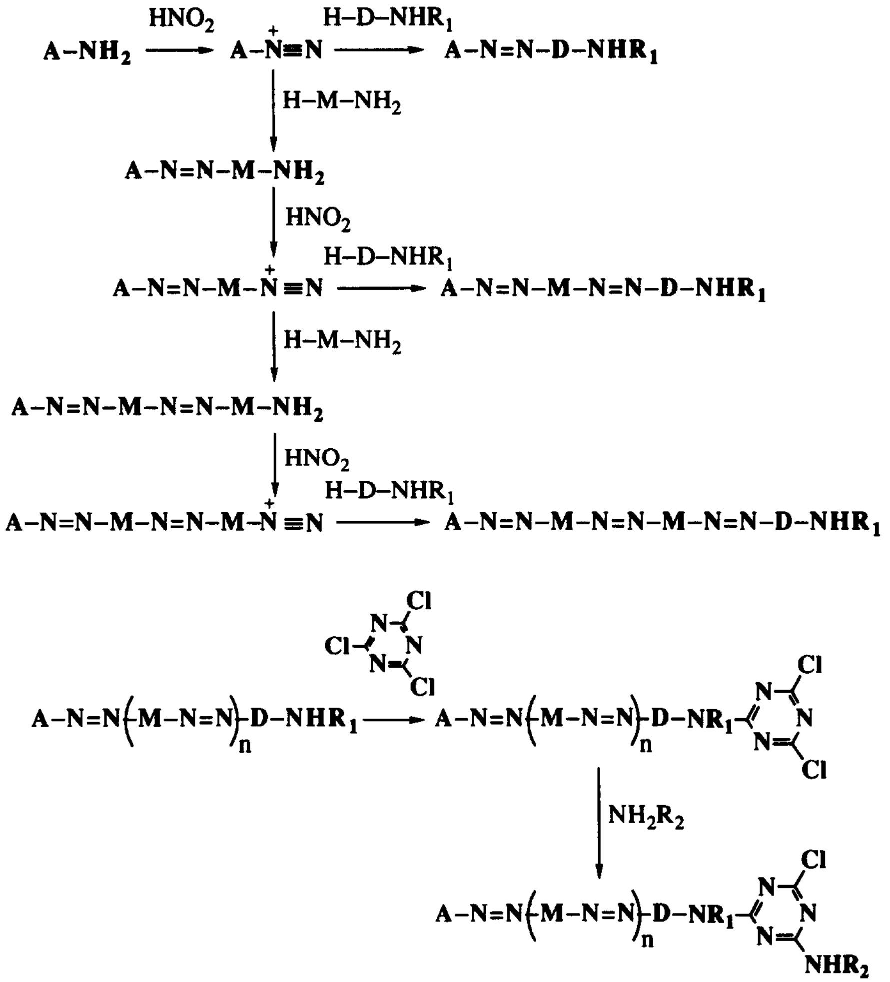
2 RESULTS AND DISCUSSION

The arylazoarylamine dyes and their analogous bisazo and trisazo dyes examined comprised a series of reactive dyes as shown in formula (I) (Fig. 1). These dyes are monofunctional with monochlorotriazine as a fibre-reactive group, or hetero-bifunctional with both monochlorotriazine and β-sulphatoethylsulphone, in which case an $SO_2C_2H_4OSO_3Na$ group is present as a part of R_2. All dyes contain more than one SO_3Na group incorporated into A, M and/or D as a potential way to impart chlorine-resistance to the dyes.

The reaction scheme used to synthesize these dyes is also given in Fig. 1. Essentially, they were synthesized by diazotizations and azo couplings using A—NH_2 and H—D—NHR_1, and additionally H—M—NH_2 when n is 1 or 2, and then subsequent condensations using the resulting dye bases, NH_2R_2 and cyanuric chloride. Of such dye bases, 4-aminoazobenzene-4′-sulphonic acid and 4-aminoazobenzene-3,4′-disulphonic acid were not synthesized, since they are commercially available.

2.1 4-Aminoazobenzene system

The 4-aminoazobenzene system (A = phenyl, D = 1,4-phenylene and $n = 0$ in formula (I)) provides the simplest chromogen giving a pale yellow colour; dyes of this sytem usually possess insufficient colour depth to be used. For example, dyes **1–4** ($X = R_3$) (Table 1) have λ_{max} in the 345–364 nm region, to which the human eye is insensitive, in contrast to λ_{max} in the 389–406 nm region for the corresponding dye bases (**1–4**; X = H), which lies in the visible region. The remarkable hypsochromic shift caused by incorporation of a



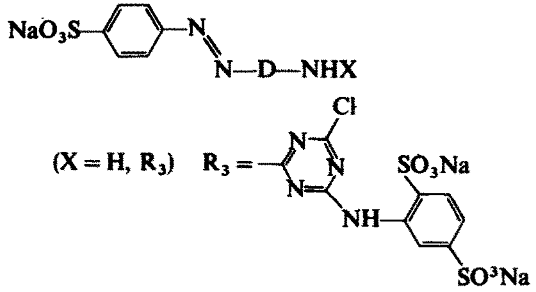
(I)

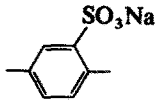
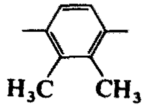
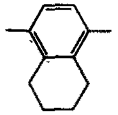
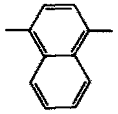
Fig. 1. Arylazoarylamine dyes and their analogous bisazo and trisazo dyes (I) examined, and reaction sequence used to synthesize these dyes. In the scheme, A is a phenyl or naphthyl group; M and D are each a 1,4-phenylene or 1,4-naphthylene group, all of which may be substituted; R_1 is hydrogen or an alkyl group; R_2 is a phenyl group substituted by two SO_3Na groups or an $SO_2C_2H_4OSO_3Na$ group; and *n* is 0, 1 or 2.

triazinyl group into the 4-amino group is a consequence of its strong electron-withdrawal nature. Therefore, few commercially important reactive dyes include this system, whereas in disperse dyes variation of electron-donating substituents at the 4-amino group, and of electron-withdrawing substituents in A is widely utilised technically.

Table 1 also shows that the SO_3Na group incorporated into the 3-position of D (dye **1**) is effective in imparting high chlorine fastness to the 4-

TABLE 1
Visible Absorption Spectral Data and Chlorine Fastness for 4-Aminoazobenzene Dyes **1**–**4** and 4-Phenylazo-1-naphthylamine Dye **5**

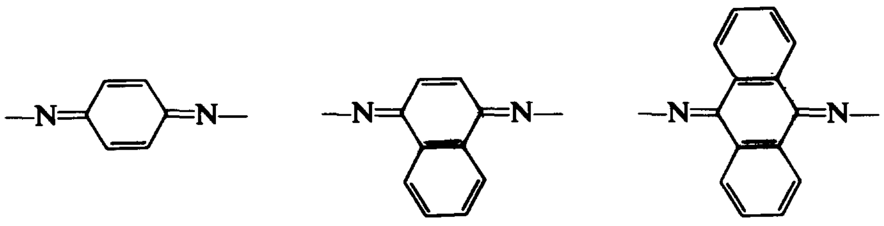


Dye no.	*D*	*λ_{max} (nm) ($\varepsilon_{max} \times 10^{-4}$)*[a]		*Chlorine fastness*
		X=H	*X=R_3*	*X=R_3*
1		389 (2·40)	359 (2·96)	4
2		394 (2·04)	364 (3·00)	3
3		389 (1·46)	345 (2·18)	3
4		406 (1·21)	350 (2·06)	3
5		477 (1·98)	397 (1·69)	1

[a] In dm^3 (mol cm).

aminoazobenzene system; however this system is intrinsically chlorine-fast, independent of the substituents in D (dyes **2**–**4**), so long as they do not form a conjugated ring. In contrast, dye **5** shows a significant decrease in the chlorine fastness, due to the presence of a naphthalene ring.

The most likely explanation for this difference lies in the low contribution of the hydrazone form in the azo-hydrazone tautomerism. Since this form is much more susceptible to oxidative decomposition by active chlorine than the azo form,[1,2] the hydrazone-form content is an important factor in



(II) (III) (IV)

Formula 1

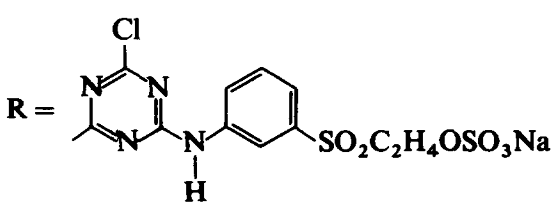
considerations of the chlorine fastness of azo dyes, particularly arylazoarylamine dyes. Experimental results[6,7] and quantum chemical calculations[8] indicate that the hydrazone form becomes progressively more preferable to the azo form as the size of a diiminoquinone ring increases in the sequence (II) < (III) < (IV) (Formula 1). Accordingly, 10-phenylazo-9-anthramine dyes are more likely to be in the hydrazone form, whereas 4-aminoazobenzene dyes exist almost completely in the azo forms. In 4-phenylazo-1-naphthylamine dyes, therefore, the hydrazone form tends to coexist in a mixture with the azo form.

2.2 4-Naphthylazoaniline system

The 4-naphthylazoaniline system (A = naphthyl, D = 1,4-phenylene and $n = 0$ in formula (I)) can be divided into two sub-systems: 4-(1-naphthylazo)aniline and 4-(2-naphthylazo)aniline systems. Of these, the latter system has found extensive use in anionic dyes such as acid, direct and reactive dyes, ranging in the yellow to orange shade areas.

The 4-(2-naphthylazo)aniline system examined in Table 2 comprised a series of reactive dyes having two or three SO_3Na groups and an NR_1R group in each dye molecule, where R_1 is hydrogen, methyl or ethyl, and R is a hetero-bifunctional reactive system comprising two different fibre-reactive groups, i.e. a β-sulphatoethylsulphone group and a monochlorotriazine group as in (V) (Formula 2).[3]

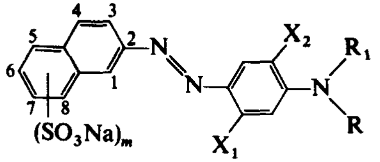
Table 2, in conjunction with Table 1, shows that the change of A from



(V)

Formula 2

TABLE 2
Visible Absorption Spectra Data and Chlorine Fastness for 4-(2-Naphthylazo)aniline Dyes[a]



Dye no.	*m*	*Orientation of SO_3Na*	*X_1*	*X_2*	*R_1*	*λ_{max} (nm) ($\varepsilon_{max} \times 10^{-4}$)[b]*	*Chlorine fastness[c]*
6	2	4,8-	CH_3	H	H	386 (2·40)	4
7	2	4,8-	CH_3	H	C_2H_5	362 (2·12)	4–5
8	2	4,8-	CH_3	OCH_3	H	408 (2·41)	4–5
9	2	4,8-	$NHCONH_2$	H	H	395 (2·84)	4
10	2	4,8-	$NHCOCH_3$	H	H	390 (3·08)	3
11	2	4,8-	$NHCOCH_3$	H	CH_3	387 (2·80)	4
12	3	3,6,8-	CH_3	OCH_3	H	404 (2·42)	3–4
13	3	3,6,8-	$NHCONH_2$	H	H	415 (2·91)	4

[a] R = hetero-bifunctional reactive system (V).
[b] In $dm^3/(mol\,cm)$.
[c] The data are cited from Ref. 11.

phenyl to 2-naphthyl and the incorporation of an auxochrome such as ureido and acetylamino into X_1 produce bathochromic and/or hyperchronic shifts; this system then leads to a deeper and stronger colour of greater practical value than the 4-aminoazobenzene system.

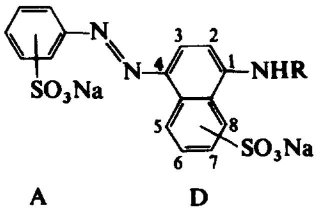
Table 2 also indicates that the 4-(2-naphthylazo)aniline dyes have almost the same chlorine fastness as the 4-aminoazobenzene dyes (Table 1); therefore the 1,4-phenylene group in both dyes exclusively governs their chlorine fastness, irrespective of the substituents in A and D. Furthermore, alkylation of the —NH— group linked to D results in higher chlorine fastness (dyes **7** and **11** versus dyes **6** and **10**). Complete fixation to the azo form is quite effective in rendering the resulting dye chlorine-fast. However, it should be kept in mind that such alkylation causes a hypsochromic and a hypochromic shift, leading to lower colour depth.

2.3 4-Phenylazo-1-naphthylamine system

The nine 4-phenylazo-1-naphthylamine dyes examined (Table 3) were isomeric, differing only in the positions of the two SO_3Na groups in A and D. Since the 3- and 5-SO_3Na in 1-naphthylaminesulphonic acids sterically restrict the *p*-coupling of diazotized anilinesulphonic acids with 1-naphthylaminesulphonic acids, 1-naphthylamine-2-, 6-, 7- and 8-sulphonic acids were used as coupling components. However, isomeric dyes from 1-naphthylamine-2-sulphonic acid could not be obtained, owing to the failure of the corresponding dye bases, 4-(sulphophenylazo)-1-naphthylamine-2-sulphonic acids, to condense with cyanuric chloride.

TABLE 3

λ_{max} in nm (ε_{max} in dm^3/(mol cm) × 10^{-4}) for 4-Phenylazo-1-naphthylamine Dyes **14–22**

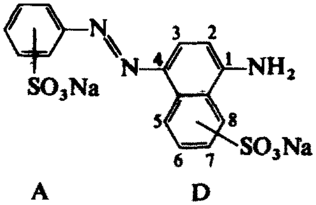


Orientation of SO_3Na A	D		
	6-	7-	8-
o	**14** 388 (1·73)	**17** 386 (1·70)	**20** 399 (1·55)
m	**15** 386 (1·72)	**18** 384 (1·72)	**21** 395 (1·58)
p	**16** 388 (1·82)	**19** 388 (1·84)	**22** 400 (1·80)

R = hetero-bifunctional reactive system (V).

TABLE 4

λ_{max} in nm (ε_{max} in $dm^3/(mol\,cm) \times 10^{-4}$) for Dye Bases **23–31**, the precursors of Dyes **14–22**



Orientation of SO_3Na A	*D*		
	6-	*7-*	*8-*
o	**23** 516(2·07)	**26** 440(1·97)	**29** 482(2·10)
m	**24** 452(1·76)	**27** 468(1·84)	**30** 475(1·67)
p	**25** 468(1·90)	**28** 469(1·96)	**31** 495(2·39)

The visible absorption spectra of dyes **14–22** (Table 3) are characterized by a single maximum at 384–400 nm, and are more bathochromic and hypochromic than those of dyes **1–4** ($X = R_3$) (Table 1). The SO_3Na group in A decreases the λ_{max} slightly in the sequence $p \geq o > m$; the SO_3Na group in D, 8- > 6- ≥ 7-. The electronic effect of the latter group on λ_{max} is larger than that of the former group. The lower ε_{max} of this system, compared to the 4-(2-naphthylazo)aniline system, decreases the practical value of this system.

A comparison between Tables 3 and 4 indicates that the incorporation of R into the 1-amino group of dyes **23–31** (Table 4) results in a pronounced hypsochromic shift (*c.* 100 nm) and a small hypochromic shift, the generally observed shift of the absorption band to shorter wavelength being attributed to the powerful $-I$ inductive effect of R. In order to develop commercially available reactive dyes of this type, it is therefore important to design dye bases which are more bathochromic and hyperchromic, since a strong electron-withdrawing heterocyclic fibre-reactive group such as halogenated triazine and pyrimidine are substituted into the 1-amino group.

TABLE 5

Chlorine Fastness of 4-Phenylazo-1-naphthylamine Dyes

Orientation of SO_3Na A	*D*		
	6-	*7-*	*8-*
o	**14** 1	**17** 1	**20** 4–5
m	**15** 1	**18** 1	**21** 4–5
p	**16** 1	**19** 1	**22** 4–5

Table 5 shows, that unlike the previous systems, the chlorine fastness of the 4-phenylazo-1-naphthylamine system varies from minimal to maximal, depending only on the position of the SO_3Na group in D. This system becomes intrinsically unstable to active chlorine under the test conditions, as a result of the change of D from 1,4-phenylene to 1,4-naphthylene. It must be emphasized that only the SO_3Na group at the 8-position can impart high chlorine fastness to this system.

2.4 4-Naphthylazo-1-naphthylamine system

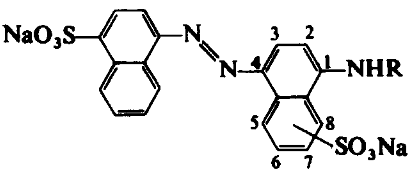
The 4-naphthylazo-1-naphthylamine system (A = naphthyl, D = 1,4-naphthylene and $n = 0$ in formula (I)) can also be divided into two sub-systems: 4-(1-naphthylazo)-1-naphthylamine and 4-(2-naphthylazo)-1-naphthylamine systems. Tables 6 and 7 show that the SO_3Na groups in both sub-systems have the same effect on chlorine fastness as those in the 4-phenylazo-1-naphthylamine system, irrespective of whether A is a phenyl or naphthyl group; only the SO_3Na group at the 8-position in D imparts high chlorine fastness to these sub-systems.

2.5 Bisazo system

Because of the structure–fastness relationship observed in the previous monoazo series when the arylazoarylamine dyes (A = phenyl or naphthyl, D = 1,4-phenylene or 1,4-naphthylene and $n = 0$ in formula (I)) were used, a further series of bisazo dyes of this system (A = phenyl or naphthyl, M and D = each 1,4-phenylene or 1,4-naphthylene and $n = 1$ in formula (I)) was examined.

TABLE 6

Chlorine Fastness of 4-(1-Naphthylazo)-1-naphthylamine Dyes

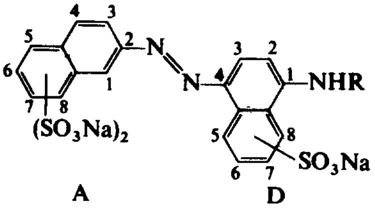


Dye no.	Orientation of SO_3Na	λ_{max} (nm) ($\varepsilon_{max} \times 10^{-4}$)	Chlorine fastness
32	6-	421 (1·96)	1
33	7-	416 (1·94)	1
34	8-	427 (1·95)	4

R = hetero-bifunctional reactive system (V).

TABLE 7

Chlorine Fastness of 4-(2-Naphthylazo)-1-naphthylamine Dyes

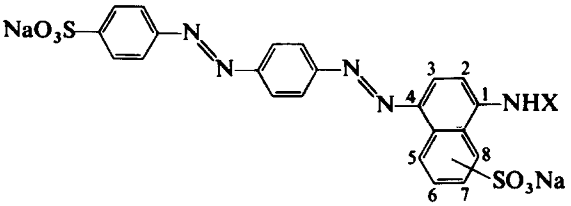


Dye no.	*Orientation of SO_3Na*		λ_{max} *(nm)* ($\varepsilon_{max} \times 10^{-4}$)	*Chlorine fastness*
	A	*D*		
35	4,8-	6-	398(2·26)	1
36	4,8-	7-	396(2·30)	1
37	4,8-	8-	407(2·26)	4
38	3,6-	7-	402(2·18)	1
39	3,6-	8-	413(1·87)	4

R = hetero-bifunctional reactive system (V).

TABLE 8

Visible Absorption Spectral Data and Chlorine Fastness for Bisazo Dyes



Dye no.	*Orientation of SO_3Na*	λ_{max} *(nm)* ($\varepsilon_{max} \times 10^{-4}$)		*Chlorine fastness*
		X═H	*X═R*[a]	*X═R*[a]
40	6-	514(2·83)	412(2·82)	1
41	7-	515(3·09)	412(2·84)	1
42	8-	535(3·61)	421(2·66)	4–5
43	2-	498(2·86)	—[b]	—[b]

[a] R = hetero-bifunctional reactive system (V).

[b] The dye could not be obtained owing to failure of **43** (X═H) to condense with cyanuric chloride.

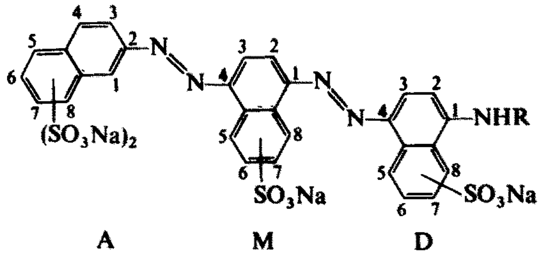
Table 8 summarizes the visible absorption spectral data for a set of bisazo dyes and their dye bases, and their chlorine fastness. As could be anticipated, insertion of a 1,4-phenylene group as an M-component into the 4-phenylazo-1-naphthylamine system causes a bathochromic and hyperchromic shift of the first absorption band. The values of $\lambda_{X=H} - \lambda_{X=R}$ and $\varepsilon_{X-H}/\varepsilon_{X-R}$ for dyes **40–42** (102–114 nm and 1·00–1·36 times) are similar to those observed for the corresponding 4-phenylazo-1-naphthylamine dyes (80–95 nm and 1·04–1·33 times for dyes **25**, **28** and **31** versus dyes **16**, **19** and **22**). This similarity relates to the fact that in these bisazo dyes, as well as in the monoazo dyes derived from 1-naphthylamines, the SO_3Na group in D governs their chlorine fastness.

Table 9 gives another representative example of bisazo dyes. The table, combined with Table 8, shows that the 8-SO_3Na group in D imparts high chlorine fastness, irrespective of whether A and M are a benzene or naphthalene ring; the other SO_3Na groups have an insignificant effect.

Table 10 indicates that the ^{15}N chemical shifts of the four azo-nitrogen atoms in dye **50** (X=R) have values of 113·0–130·8 ppm, and are shifted much more downfield than those in dye **51** (X = H), as a result of the change of X from H to R. The values are typical of almost all azo compounds, since azobenzene, a true azo compound, gives the ^{15}N chemical shift of 129 ppm in

TABLE 9

Chlorine Fastness for Bisazo Dyes Having Naphthalene Rings in A, M and D

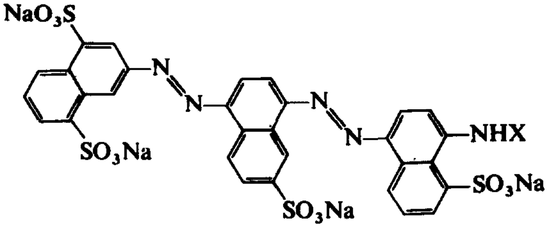


Dye no.	Orientation of SO_3Na			Chlorine fastness
	A	*M*	*D*	
44	4,8-	6-	6-	1
45	4.8-	6-	7-	1
46	4,8-	6-	8-	4–5
47	3,6-	6-	8-	4–5
48	5,7-	6-	8-	4–5
49	6,8-	6-	8-	4–5
50	4,8-	7-	8-	4–5

R = hetero-bifunctional reactive system (V).

TABLE 10

^{15}N NMR and Visible Absorption Spectral Data for Dye **50** and its Dye Base **51**



Dye no.	*Chemical shifts of azo-nitrogen atoms (ppm)*[a]				λ_{max} *(nm)* ($\varepsilon_{max} \times 10^{-4}$)
50 (X=R)[b]	113·0	121·2	125·6	130·8	487 (3·25)
51 (X=H)	56·2	105·1	117·7	122·4	578 (3·96)

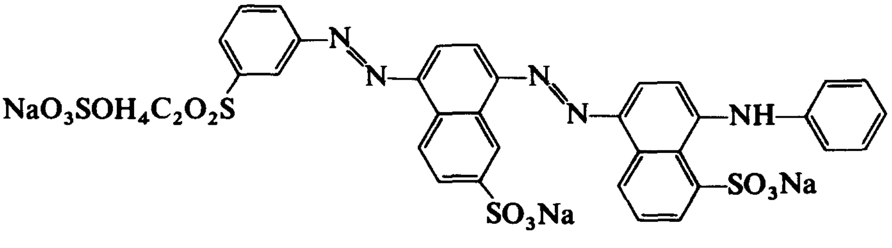
[a] In DMSO/DMSO-d_6 (9/1) solution at 27°C.

[b] R = hetero-bifunctional reactive system (V).

The chemical shifts were not assigned to each azo-nitrogen atom.

the same solvent, DMSO.[9,10] In contrast, dye **51** exists as a mixture of the azo and hydrazone forms in either or both the two azo groups. The results are supported by the visible absorption spectral data (Table 10). The predominance of the azo form in dye **50** is probably due to the fixation of the mobile NHR hydrogen atom by both intramolecular hydrogen-bonding with the 8-SO_3Na group in D and the strong electron-withdrawing of R.[6] The high chlorine fastness can, therefore, be explained in terms of these results. In fact, the replacement of this hydrogen atom by a methyl group for the analogous bisazo dye of dye **50** gives high chlorine fastness.[1] High chlorine fastness of the other monoazo and bisazo dyes having an 8-sulpho-1,4-naphthylene group as D can be ascribed to the same reason.

In contrast, dye **52** (Formula 3), having an N-phenyl group, gives much lower chlorine fastness, being rated at 1 on the same scale, compared to dye



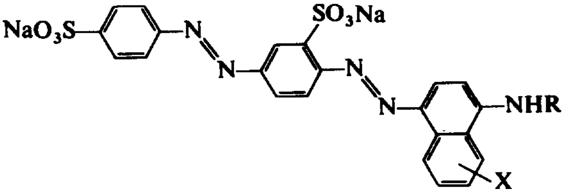
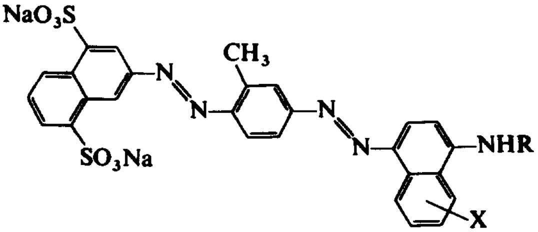
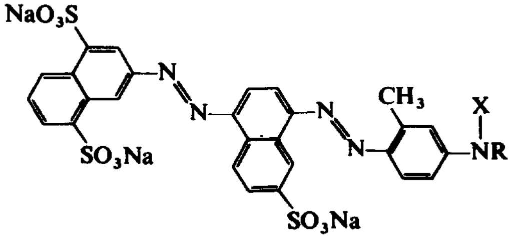
52 (λ_{max} 582 nm, ε_{max} 31 700)

Formula 3

50, having an N-triazinyl group. Besides these N-substituents, the structures of the two dyes differ from each other in A. However, since it is not essential for conjugation to proceed through A as it is for M and D in the structure of formula (I) when *n* is 1,[6] the bathochromic shift of 95 nm relative to dye **50** is primarily attributed to the N-phenyl group being more weakly electron-withdrawing than R. Therefore, the hydrazone-favouring dyes such as dye **52** have lower chlorine fastness.

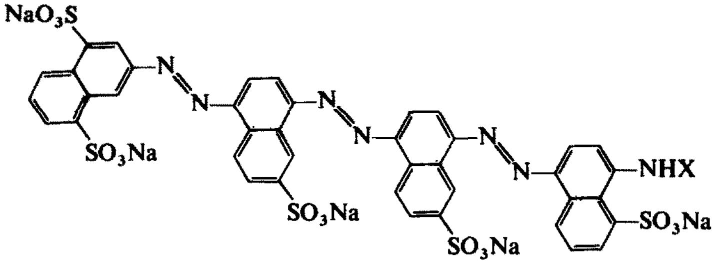
The chlorine-fastness-improving effect of the 8-SO_3Na group is also apparent in the bisazo dyes **56** and **60**, where M is a 1,4-phenylene group, as shown in Table 11. It is noteworthy that the presence of the 1,4-phenylene group in D (dye **61**) results in high chlorine fastness, similar to that of the 4-aminoazobenzene and 4-naphthylazoaniline dyes. Further, alkylation of the NHR group in dye **61** leads to high chlorine fastness (dyes **62** and **63**), similar to that of dyes **7** and **11** (Table 2).

TABLE 11
Chlorine Fastness for Bisazo Dyes

Structure	*Dye no.*	*Chlorine fastness*
	**53** (X=H)	1
	54 (X=6-SO_3Na)	1
	55 (X=7-SO_3Na)	1
	56 (X=8-SO_3Na)	4–5
	**57** (X=H)	1
	58 (X=6-SO_3Na)	1
	59 (X=7-SO_3Na)	1
	60 (X=8-SO_3Na)	4
	**61** (X=H)	4
	62 (X=CH_3)	4–5
	63 (X=C_2H_5)	4–5

R = hetero-bifunctional reactive system (V).

TABLE 12
Visible Absorption Spectral Data and Chlorine Fastness for Trisazo Dyes



Dye no.	λ_{max} (nm) ($\varepsilon_{max} \times 10^{-4}$)	Chlorine fastness
64 (X=R)[a]	526(4·73)	3–4·
65 (X=H)	610(4·88)	—[b]

[a] R = hetero-bifunctional reactive system (V).
[b] No data because a non-reactive dye.

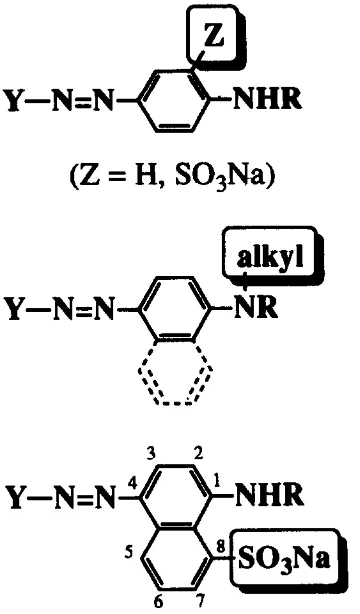
2.6 Trisazo system

Table 12 shows that the structure–fastness relationship found in the monoazo and bisazo systems is maintained in this system, after comparison of dyes **64** and **65** with dyes **50** and **51**.

2.7 Design of chlorine-fast reactive dyes

Unlike the arylazonaphthol system which exists predominantly in the hydrazone form, the arylazoarylamine system exists primarily in the azo form, as noted above. Accordingly, concepts for designing chlorine-fast reactive dyes must be distinguished clearly between the two systems. The former system requires steric protection of an intrinsically cleavable —NH—N= group in the hydrazone form against attack of active chlorine,[2] whereas the latter system requires fixation of the azo–hydrazone tautomerism to the azo form which is chlorine-fast. The ring size of the arylamine residue, its N-substituents and an SO_3Na group in the residue are all important considerations which render this system chlorine-fast, because this residue plays the most important role in increasing the azo-form content.

The characteristic structural features of chlorine-fast reactive dyes based on arylazoarylamine are shown schematically in Fig. 2. The 1,4-phenylene group linked to NHR (formula (**VI**)) gives high chlorine fastness, which further increases when Z = SO_3Na. Replacement of the 1,4-phenylene group by a 1,4-naphthylene group, used to deepen the colour, usually leads to a



(VI)

(VII)

(VIII)

Fig. 2. Basic structures of chlorine-fast reactive dyes based on arylazoarylamine. The 1,4-phenylene group and additionally Z = SO_3Na in Formula (VI), the alkyl group in Formula (VII), and the 8-SO_3Na group in Formula (VIII) all lead to high chlorine fastness. Y is an aryl, arylazoaryl or arylazoarylazoaryl group, where aryl is phenyl or naphthyl. R is a hetero-bifunctional reactive system (V).

significant decrease in chlorine fastness, but this can be increased by alkylation of the NHR group (formula (VII)), or by incorporation of an SO_3Na group into the 8-position (formula (VIII)). These molecular designs are applicable to analogous bisazo and trisazo dyes, where Y is an arylazoaryl or arylazoarylazoaryl group (aryl = phenyl or naphthyl).

Additional SO_3Na groups can be introduced into suitable positions to increase the water-solubilizing properties, to improve other fastness properties and to adjust substantivity to cellulose. The role of the SO_3Na group in chlorine fastness will also be the same as for other metal sulphonate groups such as an SO_3Li and SO_3K.

Figure 3 illustrates a flow diagram for designing chlorine-fast reactive dyes.

3 EXPERIMENTAL

3.1 Materials

First or technical grade reagents were used for the syntheses. Special grade reagents or their equivalents and water purified by ion exchange were used

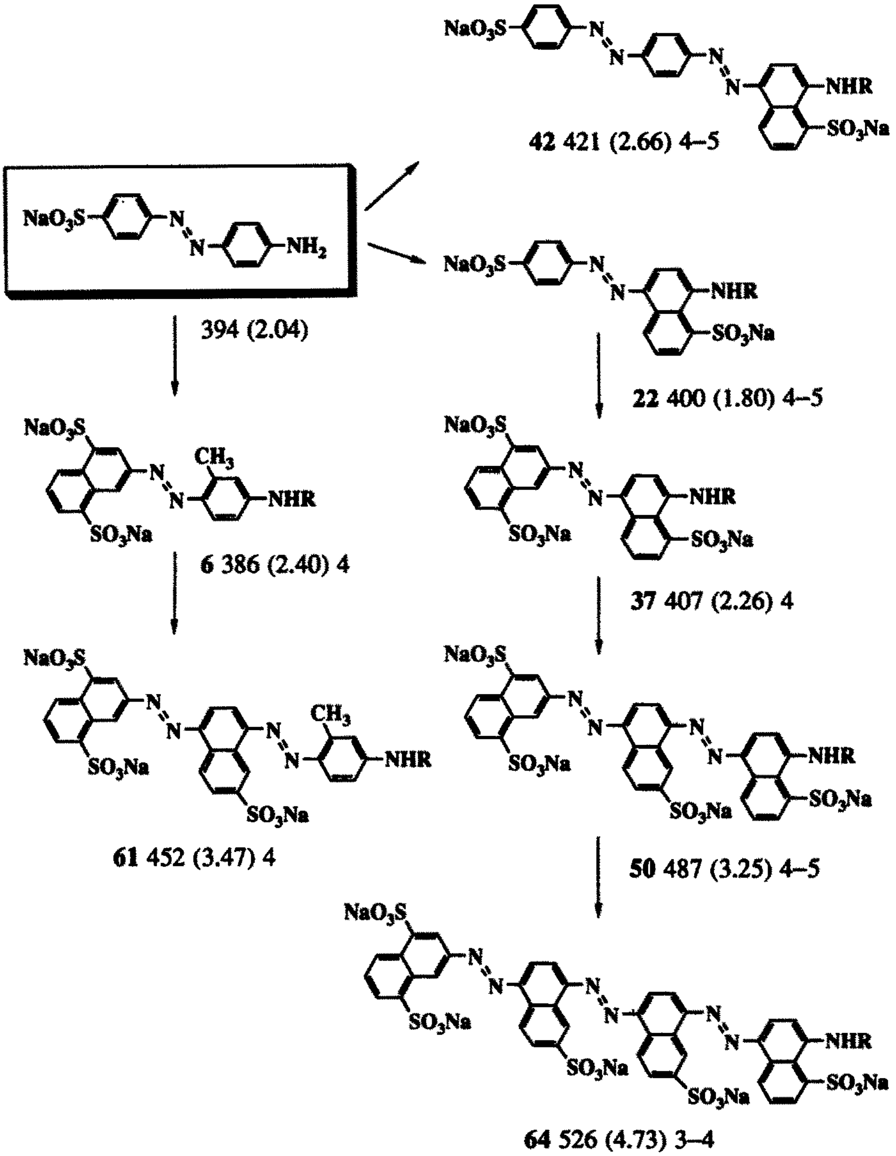


Fig. 3. Design process for chlorine-fast reactive dyes. The notation under each structure shows dye No., λ_{max} in nm (ε_{max} in dm^3/(mol cm) × 10^{-4}) and chlorine fastness, whereas that under the structure framed shows only λ_{max} and ε_{max} because of a non-reactive dye. *R* is a hetero-bifunctional reactive system (V).

for analysis, dyeing and the chlorine fastness test. The scoured and bleached unmercerized cotton knitted fabrics for dyeing were obtained from Nitto Boseki Co. Ltd.

3.2 Measurement

Visible absorption spectra were recorded on a Hitachi UV-Visible spectrophotometer model 228A, using water as solvent. [^{15}N] NMR spectra were recorded on a JOEL GX-270 spectrometer at 27°C, using DMSO containing 10% of DMSO-d_6 as solvent and nitromethane as external standard.

3.3 Synthesis

All dyes except **1** and **2** were synthesized as sodium salts following the method published previously[11,12] and purified by repeated recystallization.

Dye **1** was synthesized as follows: 4-aminoazobenzene-3,4′-disulphonic acid (10·7 g) and the disodium salts of 2,4-dichloro-6-(2,5-disulphoanilino)-1,3,5-triazine (14·0 g) were stirred in water (200 ml) for 10 h at 50°C under weak acidic conditions. Sodium chloride was added to give a yellow precipitate, which was collected by filtration and then dried. Dye **2** was synthesized similarly.

3.4 Dyeing

Each of the dyes **14–22**, **32–42**, **44–50** and **52–64** (0·1 g) was dissolved in water (200 ml), and sodium sulphate (10 g) and cotton (10 g) were added to the dye solution, which was then heated to 60°C. After 20 min with stirring, sodium carbonate (4·0 g) was added, and dyeing was carried out at the same temperature for 60 min. The dyed cotton was rinsed with cold water, and then thoroughly with boiling water to remove unfixed dyes, and finally dried at 80°C. Of the respective controls for comparison, those giving dyeings of relatively high or low colour depth were redyed so as to give dyeings having a similar colour depth to each other.

The above method was repeated using **1–5**, but the dyeing temperature was 80°C instead of 60°C.

3.5 Chlorine fastness testing

The test was carried out on the dyeings prepared in Section 3.4 according to the ISO method (ISO 105-E03: effective chlorine 20 mg/dm^3, 25°C, 4 h). The results were assessed in ratings: 1, poor; 2, fair; 3, good; 4, very good; 5, excellent.

4 CONCLUSIONS

Although the arylazoarylamine system exists primarily as the azo form, the scarcity of the hydrazone form is an important consideration when designing chlorine-fast reactive dyes of this system, because this form is much more susceptible to oxidative decomposition by active chlorine than the azo form. The chlorine fastness of the arylazoarylamine dyes varies from minimal to major, depending on the structure of the arylamines used. Consequently, three molecular designs for imparting high chlorine fastness to these dyes have been established. The results are applicable to the design of chlorine-fast bisazo and trisazo dyes ranging in shade from yellow through orange to brown.

ACKNOWLEDGEMENTS

The author is indebted to Messrs Y. Kayane and N. Kunimi and Dr N. Harada for their cooperation in this project and to Mr K. Yamamoto for the [^{15}N] NMR spectral analysis.

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