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Design of Chlorine-Fast Reactive Dyes. Part 3: Structure–Fastness Relationship in Twice-Coupled H-acid Dyes and Their Analogues

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ABSTRACT

The substituent effects of the degradation of azo dyes by sodium hypochlorite have been investigated. A study of a series of sulphonated 1-amino-2,7-bisphenylazo-8-naphthol dyes suggests that the two phenylazo groups at the 2- and 7-positions make a large contribution to protecting the amino group at the 1-position, which is intrinsically very susceptible to electrophilic attack by a Cl^+ *ion, particularly in sulphonated 1-amino-2- or 7-phenylazo-8-naphthol dyes. The specific structural feature responsible for retarding the degradation of 1-amino-2,7-bisphenylazo-8-naphthol dyes is the incorporation of two* SO_3Na *groups into the 6-position and the 2'-position of the 7-phenylazo group. The replacement of the 2'-*SO_3Na *group by a 2'-*NO_2 *group is also effective. The other positions are of little significance.*

1 INTRODUCTION

H-acid (1-amino-8-naphthol-3,6-disulphonic acid) has been a prolific source of water-soluble azo dyes over the last 100 years, remaining dominant as a key intermediate to this day. The versatility of H-acid as a coupling components is exemplified by its use as an end component in monoazo reds and disazo blues. Even more important, on a volume basis, is its use as a middle component of disazo blues and blacks, formed by stepwise acid and alkaline coupling;[1,2] such twice-coupled H-acid dyes have found

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extensive use in most dye classes, e.g. acid dyes for nylon and wool, direct dyes for cellulose, leather and paper, and recently for jet-ink, and reactive dyes for cellulose and wool. The attractive features of twice-coupled H-acid dyes are high tinctorial strength, excellent dyeability and wide applicability. With the increasing economic relevance of blue to black dyes, the requirements for the dyes have also grown, particularly with respect to improvement in their fastness properties. In spite of the technical importance of the properties, the literature relating to structure—fastness relationships in these dyes is sparse and, in particular, little mention has been made of colour fastness to chlorinated water (hereafter called chlorine fastness) of such dyes.

The previous papers in this series examined the role of sulphonate (SO_3^-) groups in chlorine-fast reactive dyes based on arylazonaphthols[3] and arylazoarylamines.[4] In the present study, this approach is extended to 1-amino-2,7-bisphenylazo-8-naphthols, which combine 2-phenylazo-1-naphthols and 2-phenylazo-1-naphthylamines as chromogenic parts. The scope of this study was to assess the relationship between the structure and chlorine-resistance in such disazo dyes, compared with that in 2-phenylazo-1-naphthol and 2-phenylazo-1-naphthylamine dyes, and to design chlorine-fast reactive dyes. The dyes examined were twice-coupled H-acid dyes and related monoazo and disazo dyes, having systematically varied substituents and orientations.

2 RESULTS AND DISCUSSION

2.1 Synthesis and structure of twice-coupled H-acid dyes

Figure 1 gives the reaction scheme used to prepare the twice-coupled H-acid dye **III** and the related phenylazo-H-acid dyes **I** and **II**. Essentially, dye **III** was prepared by initially coupling diazotized anilines with H-acid under acidic conditions, and then further coupling the resulting dye **I** under weak acidic or alkaline conditions. A small amount of the isomeric dye **II**, formed as a by-product, could not be isolated from the reaction mixture. Coupling of the diazotized anilines with N-acetyl-H-acid and subsequent hydrolysis of the acetyl group led to successful preparation of the dye. The analogous twice-coupled K-acid (1-amino-8-naphthol-4,6-disulphonic acid) and S-acid (1-amino-8-naphthol-4-sulphonic acid) dyes were also prepared similarly.

Dye **1** (Table 1) is a typical twice-coupled H-acid dye whose structure is shown as the azo form, with no implications concerning the equilibrium position, and has a hetero-bifunctional reactive system R comprising two

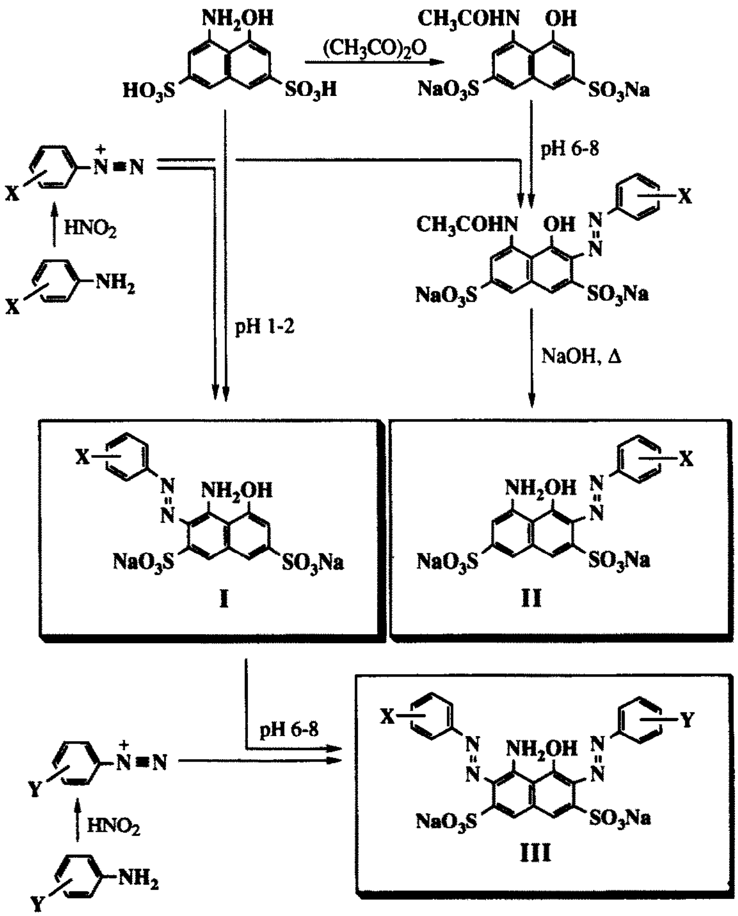
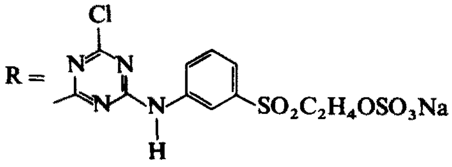


Fig. 1. Twice-coupled H-acid dye **III** and related phenylazo-H-acid dyes I and II, and the reaction sequence used to synthesize these dyes.

different fibre-reactive groups, a β-sulphatoethylsulphone group and a monochlorotriazine group, as in Formula IV.[5]

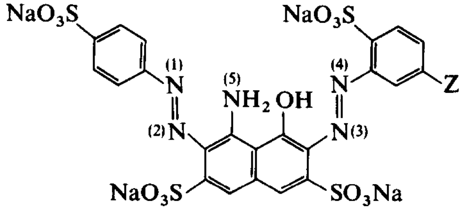


IV

The ^{15}N chemical shifts of the two azo groups indicate that the N^1 and N^2 nitrogen atoms favour an azo form,[6] in contrast to the N^3 and N^4 nitrogen atoms, which favour a hydrazone form.[3,7,8] These results are

TABLE 1

^{15}N NMR and Visible Absorption Spectral Data for Dyes 1–3



Dye No.	*Chemical shifts (ppm)*[a]					λ_{max} *(nm)*
	$\delta(N^1)$	$\delta(N^2)$	$\delta(N^3)$	$\delta(N^4)$	$\delta(N^5)$	$(\varepsilon_{max} \times 10^{-4})$[b]
1 (Z = NHR)[c]	140·3	81·8	2·5	−196·2	−293·1	599 (4·80)
2 (Z = NH$_2$)[d]	137·8	82·2	−5·4	−196·2	−291·8	597 (4·73)
3 (Z = H)	—	—	—	—	—	596 (4·76)

[a] In DMSO/DMSO-d$_6$ (9/1) solution at 27°C.

[b] In dm^3/(mol cm).

[c] *R* is the hetero-bifunctional reactive system **IV**.

[d] The chemical shifts δ(N^1)–δ(N^4) are cited from Ref. 8.

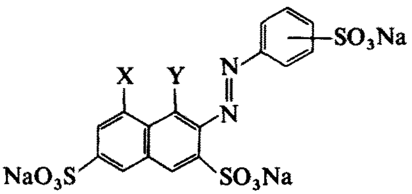
also supported by the PPP-MO calculations.[9] Thus, the azo-hydrazone tautomerism of dye **1** is consistent with the view that 2-phenylazo-1-naphthols exist predominantly in the hydrazone form rather than the azo form,[3,10] and that 2-phenylazo-1-naphthylamines exist conversely to this.[11]

Table 1 also shows that the chemical shifts δ(N^1)–δ(N^5) and the visible absorption spectra are little affected by a change in Z from NHR (dye **1**) through NH$_2$ (dye **2**) to H (dye **3**); the amino group makes negligible contributions to the conjugated system with respect to colour. On the other hand, the amino group on the H-acid moiety plays a vital role in giving an intense navy blue colour;[9] it is essential as an auxochrome of twice-coupled H-acid dyes. Therefore, it is reasonable to select sulphonated twice-coupled H-acids and phenylazo-H-acids as model dyes (X = Y = SO$_3$Na in Formulae **I–III**) in order to examine the relationship between the structure and chlorine-resistance of such dyes.

2.2 Degradation of phenylazo-H-acid dyes

The phenylazo-H-acid dyes **4–9** (Table 2) are isomeric, differing only in the position of the SO$_3$Na group on the phenylazo group and/or its coupling

TABLE 2
Visible Absorption for Phenylazo-H-acid Dyes and their Analogues in Water (pH 7·0), and Pseudo-first-order Rate Constant k (Half-life $t_{1/2}$) for their Degradation in Aqueous NaOCl[a]



Dye No.	*X*	*Y*	*Orientation of SO_3Na*	*λ_{max} (nm) ($\varepsilon_{max} \times 10^{-4}$)[b]*	*k (s^{-1}) ($t_{1/2}$ (s))*
4	NH_2	OH	*o*	528 (2·92)	$9{\cdot}5 \times 10^{-2}$ (7)
5	NH_2	OH	*m*	525 (2·95)	— (<7)
6	NH_2	OH	*p*	530 (3·20)	— (<7)
7	OH	NH_2	*o*	521 (2·49)	$8{\cdot}2 \times 10^{-2}$ (8)
8	OH	NH_2	*m*	509 (2·64)	— (<8)
9	OH	NH_2	*p*	511 (2·71)	— (<8)
10	H	OH	*o*	489 (2·52)	$5{\cdot}5 \times 10^{-4}$ (1 300)

[a] Dye concentration = $2{\cdot}0 \times 10^{-5}$ M, NaOCl/dye = 100 in molar ratio, pH 7·0 and 24°C.
[b] In $dm^3/(mol\ cm)$.

site to the H-acid. The visible absorption spectra of dyes **4–6** and **7–9** are characterized by a single maximum at 525–530 nm and at 509–521 nm, respectively; the former dyes are more bathochromic and hyperchromic. The SO_3Na group on the phenylazo group of dyes **4–6** reduces the λ_{max} and ε_{max} in the sequence $p > o > m$ and $p > m > o$, respectively, in contrast to that of dyes **7–9**, which has the sequence $o > p > m$ and $p > m > o$, respectively. All the sequences are in complete agreement with those of the two SO_3Na groups of bis(sulphophenylazo)-H-acid dyes.[12] Therefore, dyes **4–6** differ from dyes **7–9** in the azo-hydrazone tautomerism; the former dyes exist predominantly in the hydrazone form, whereas the latter dyes are in the azo form. The analogous dye **10** is more hypsochromic and hypochromic, because of the absence of the amino group as an auxochrome; this dye also exists predominantly in the hydrazone form. These results would be expected on the basis of previous studies.[3,8] It should be noted that in the following discussion, all dyes are conventionally referred to as azo forms.

The aqueous solutions of dyes **4–10**, ranging in concentration below 5×10^{-5} M, showed no deviations from the Lambert–Beer law of absorbance; all the dyes are nonaggregating in this range. This is a consequence of a higher degree of sulphonation, compared to disodium 8-acetylamino-2-phenylazo-1-naphthol-3,6-disulphonate (CI Acid Red 1), which tends to aggregate under the same conditions.[13-15] The nonaggregating dyes will not be significantly affected by a small amount of additives such as buffer and sodium hypochlorite (NaOCl).

Since the reaction of dyes **4–10** with NaOCl in aqueous solution yielded decoloured products, the reaction was followed spectrophotometrically, monitoring the absorbance at λ_{max} of each dye. The pH (7·0) employed was based on the range 7·0–8·5 in which chlorine fastness tests are usually carried out. The pseudo first-order rate constants obtained are also summarized in Table 2.

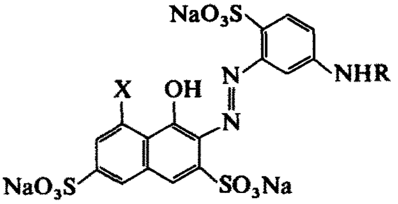
The high chlorine-resistance of dye **10** is well understood in terms of an azo-protecting ability arising mainly from the steric effect of the two SO_3Na groups adjacent to the azo group.[3] In spite of the presence of these groups, dyes **4–6** show a markedly accelerated degradation, approximately 200 times that of dye **10**; this is attributable to the amino group. It is surprising that the azo-protecting ability of the two SO_3Na groups does not prevent the degradation from occurring. Similar results were obtained for dyes **7–9**, irrespective of the coupling site to the H-acid.

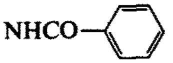
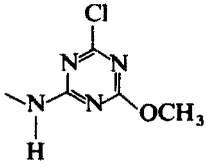
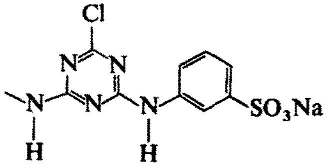
In this connection, the chlorine fastness of reactive dyes based on 2-(2'-sulphophenylazo)-1-naphthol-3,6-disulphonic acid has been examined (Table 3). These dyes are typical of hydroxyazo dyes ranging in shade from orange to red. All the dyes faded under the test conditions employed. Since no phenomena such as swealing and bleeding were observed, both the covalent dye–fibre bonds and the imino bridges are stable; thus the azo chromogens are the relatively weak sites which may be decomposed.

A deleterious effect of the amino group in dye **11** is evident from the anomalous decrease in chlorine fastness compared to that of dye **12**, which does not contain such a group. These results are relatable to the degradation rates of dyes **4** and **10** in aqueous solutions. The low chlorine fastness can, however, be raised by acetylation (dye **14**), benzoylation (dye **15**) and triazinylation (dyes **16** and **17**); thus the effective substituents are electron-withdrawing groups capable of reducing the electron density at the amino-nitrogen atom. These results suggest that the degradation of such amino-containing dyes involves initial attack at the amino group by the electrophilic Cl^+ ion as active species,[16] and then proceeds by cleavage of the azo chromogens.

TABLE 3

Chlorine Fastness for Hydroxyazo Dyes on Cotton



Dye No.	*X*	*Chlorine fastness*
11	NH_2	1
12	H	3–4
13	SO_3Na	4
14	$NHCOCH_3$	3–4
15		4–5
16		4–5
17		4–5

R is the hetero-bifunctional reactive system IV.

The chlorine-resistance-improving ability of such substituents exerted on cotton is probably the same as in aqueous solutions, since the dominance of the hydrazone form in hydroxyazo dyes does not vary with the differences in the two media.[17]

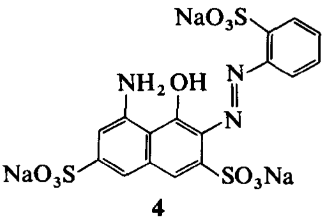
The degradation of dye **4** becomes progressively faster as the pH changes from 10·9 to 4·5 (Table 4). The pH-sensitivity is independent of the dye molecule, because the visible absorption of the dye is little affected within this pH range. Therefore, an increase in the degradation rate with a decrease in pH is relatable to an increase in Cl^+ with increase in the hydrogen on concentration,[16] VIZ:

$$OCl^- + H_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} OH^- + HOCl$$

$$HOCl + H^+ \rightleftharpoons H_2O + Cl^+$$

TABLE 4

pH-Dependence of Visible Absorption for Dye **4** in Water, and the Pseudo-first-order Rate Constant k and Half-life $t_{1/2}$ for its Degradation in Aqueous NaOCl Solution[a]



4

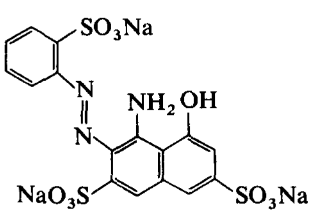
pH	λ_{max} (nm)	$\varepsilon_{max} \times 10^{-4}$ [b]	k (s^{-1})	$t_{1/2}$ (s)
4·5	528	2·87	—	<7
7·0	528	2·92	$9{\cdot}5 \times 10^{-2}$	7
9·2	528	2·92	$3{\cdot}7 \times 10^{-3}$	190
10·9	528	2·92	$8{\cdot}8 \times 10^{-5}$	7 900

[a] Dye concentration = $2{\cdot}0 \times 10^{-5}$ M, NaOCl/dye = 100 in molar ratio and 24°C.
[b] In $dm^3/(mol\ cm)$.

Comparison between Table 4 and 5 indicates that the hydroxy group in dye **7** is more readily ionized than that in dye **4**, because dye **7** is more sensitive to pH. This explains one greater susceptibility to degradation of dye **7** by the Cl^+ ion in an alkaline medium. This tendency will be the same as in dyes **8** and **9**.

TABLE 5

pH-Dependence of Visible Absorption for Dye 7 in Water, and the Pseudo-first-order Rate Constant k and Half-life $t_{1/2}$ for its Degradation in Aqueous NaOCl Solution[a]



7

pH	λ_{max} (nm)	$\varepsilon_{max} \times 10^{-4}$ [b]	k (s^{-1})	$t_{1/2}$ (s)
4·5	516	2·17	—	<8
7·0	521	2·49	$8{\cdot}2 \times 10^{-2}$	8
9·2	544	2·98	$6{\cdot}5 \times 10^{-2}$	11
10·9	544	2·97	$1{\cdot}6 \times 10^{-3}$	430

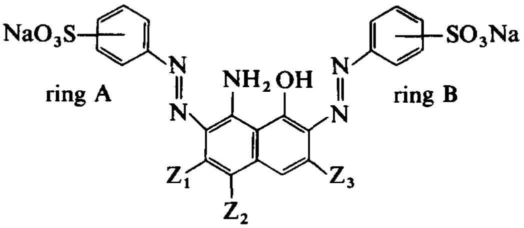
[a] Dye concentration = $2{\cdot}0 \times 10^{-5}$ M, NaOCl/dye = 100 in molar ratio and 24°C.
[b] In $dm^3/(mol\ cm)$.

2.3 Degradation of twice-coupled H-, K- and S-acid dyes

The twice-coupled H-acid dyes **3** and **18–25** (Table 6) used as model dyes are isomeric, differing only in the positions of the two SO_3Na groups on rings A and B. Additionally, the twice-coupled K-acid dye **26** and S-acid dye **27** were examined as their analogues. The aqueous solutions of these

TABLE 6

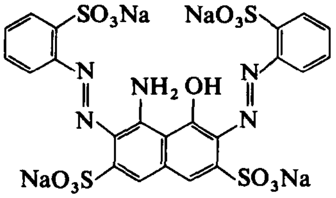
Effect of SO_3Na Groups on the Visible Absorption for Twice-coupled H-, K- and S-acid Dyes in Water (pH 7·0),[a] and the Pseudo-first-order Rate Constant k (Half-life $t_{1/2}$) for their Degradation in Aqueous NaOCl Solution[b]



Dye No.	Z_1	Z_2	Z_3	*Orientation of SO_3Na*		λ_{max} *(nm)* ($\varepsilon_{max} \times 10^{-4}$)[c]	$k \times 10^3$ *(s^{-1})* ($t_{1/2}$ *(s)*)
				Ring A	*Ring B*		
18	SO_3Na	H	SO_3Na	*o*	*o*	601 (4·36)	3·6 (190)
19	SO_3Na	H	SO_3Na	*o*	*m*	600 (4·58)	10 (69)
20	SO_3Na	H	SO_3Na	*o*	*p*	603 (4·65)	12 (58)
21	SO_3Na	H	SO_3Na	*m*	*o*	592 (4·52)	4·0 (170)
22	SO_3Na	H	SO_3Na	*m*	*m*	589 (4·68)	13 (53)
23	SO_3Na	H	SO_3Na	*m*	*p*	594 (4·84)	11 (63)
3	SO_3Na	H	SO_3Na	*p*	*o*	596 (4·76)	5·4 (130)
24	SO_3Na	H	SO_3Na	*p*	*m*	595 (4·86)	21 (33)
25	SO_3Na	H	SO_3Na	*p*	*p*	599 (5·08)	16 (43)
26	H	SO_3Na	SO_3Na	*o*	*o*	573 (4·24)	3·8 (180)
27	H	SO_3Na	H	*o*	*o*	572 (4·21)	41 (17)

[a] Cited from Ref. 12.
[b] Dye concentration = 2·0 × 10^{-5} M, NaOCl/dye = 100 in molar ratio, pH 7·0 and 24°C.
[c] In $dm^3/(mol\ cm)$.

TABLE 7
pH Relationship between the Visible Absorption for Dye **18** in Water, and the Pseudo-first-order Rate Constant *k* and Half-life $t_{1/2}$ for its Degradation in Aqueous NaOCl Solution[a]



18

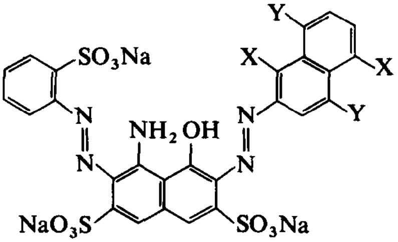
pH	λ_{max} *(nm)*	$\varepsilon_{max} \times 10^{-4}$ [b]	*k* (s^{-1})	$t_{1/2}$ *(s)*
4·5	601	4·36	2.4×10^{-2}	29
7·0	601	4·36	3.6×10^{-3}	190
9·2	601	4·36	1.4×10^{-4}	5 000
10·9	602	4·33	7.4×10^{-5}	9 400

[a] Dye concentration = 2.0×10^{-5} M, NaOCl/dye = 100 in molar ratio and 24°C.
[b] In $dm^3/(mol\ cm)$.

dyes, ranging in concentration below 5×10^{-5} M showed no deviations from the Lambert–Beer law of absorbance; all the dyes were also non-aggregating in this range. The relationship between the positions of the two SO_3Na groups and the visible absorption was discussed in the previous work.[12]

The pH-insensitivity of dye **18** (Table 7) explains that the mobile OH-

TABLE 8
Visible Absorption for Twice-coupled H-acid Dyes in Water (pH 7·0), and the Pseudo-first-order Rate Constant *k* and Half-life $t_{1/2}$ for their Degradation in Aqueous NaOCl Solution[a]

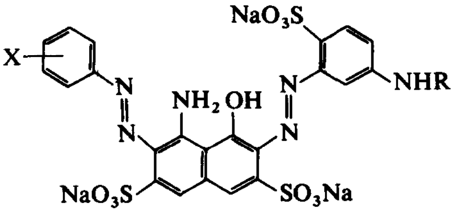
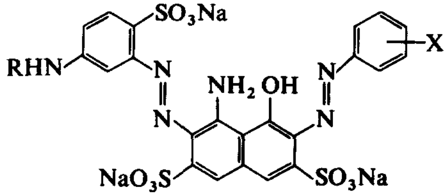
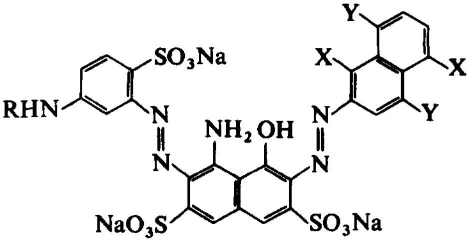
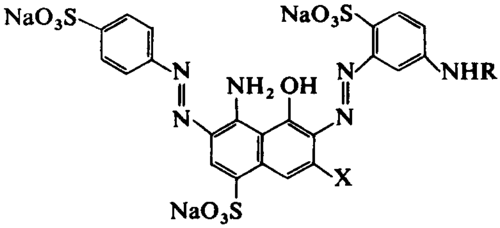


Dye No.	*X*	*Y*	λ_{max} *(nm)*	$\varepsilon_{max} \times 10^{-4}$ [b]	$k \times 10^{3}$ (s^{-1})	$t_{1/2}$ *(s)*
28	H	SO_3Na	615	5·09	7·4	94
29	SO_3Na	H	608	5·17	2·0	350

[a] Dye concentration = 2.0×10^{-5} M, NaOCl/dye = 100 in molar ratio, pH 7·0 and 24°C.
[b] In $dm^3/(mol\ cm)$.

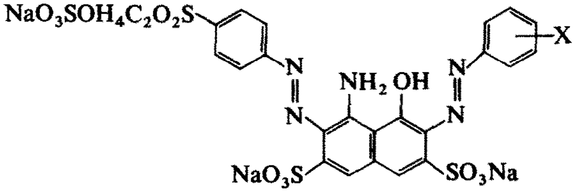
proton of dye **7** is fixed by incorporation of another phenylazo group into the dye; the hydroxy group conjugates to the phenylazo group so as to undergo azo-hydrazone tautomerism, and the resulting hydrazone form forms a strong intramolecular hydrogen-bonding between the hydrazo-hydrogen atom and the carbonyl-oxygen atom. The existence in the tinctorially stronger hydrazone form and the pH-insensitivity make disazo dyes such as this ideal colourants. As seen from Tables 5 and 7, the phenylazo group produces an extreme hyperchromic shift (ε_{max} 24,900 → 43,600).

TABLE 9
Chlorine Fastness of Reactive Dyes Based on Twice-coupled H-, K- and S-acids

Structure	*Dye No.*	*Chlorine fastness*
	**30** (X = *o*-SO_3Na) **31** (X = *m*-SO_3Na) **1** (X = *p*-SO_3Na)	3–4 3–4 3–4
	**32** (X = *o*-SO_3Na) **33** (X = *m*-SO_3Na) **34** (X = *p*-SO_3Na)	3–4 1 1
	**35** (X = SO_3Na, Y = H) **36** (X = H, Y = SO_3Na)	4 1–2
	**37** (X = SO_3Na) **38** (X = H)	3–4 1

R is the hetero-bifunctional reactive system **IV**.

TABLE 10
Substituent-dependence of Chlorine Fastness for Reactive Dyes Based on Twice-coupled H-acids



X	*Chlorine fastness*[a]
H	1
o-OH, *o*-CH_3	1
m-CO_2Na, *m*-Cl, *m*-CH_3, *m*-OCH_3, *m*-NO_2, *m*-SO_3Na	1
m-$SO_2C_2H_4OSO_3Na$	1
p-NO_2, *p*-CO_2Na, *p*-$SO_2C_2H_4OSO_3Na$, *p*-$NHCOCH_3$	1
p-SO_3Na, *p*-OCH_3, *p*-Cl, *p*-benzoyl, *p*-CH_3	1
o-Cl, *o*-OCH_3, *o*-C_2H_5, *o*-phenyl, *o*-Br	1–2
o-CO_2Na, *o*-$SO_2C_2H_4OSO_3Na$	3
o-SO_3Na, *o*-NO_2	3–4

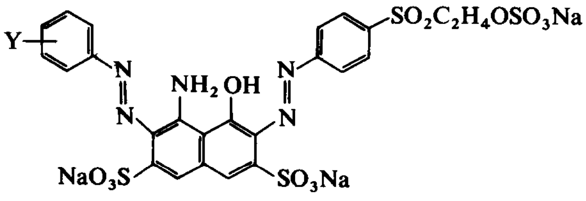
[a] Cited partially from Ref. 19.

The degradation of these dyes by NaOCl yielded yellow products having λ_{max} of *c*. 450 nm, then all of which changed to decoloured compounds. The pseudo first-order rate constants obtained under the same conditions as in dyes **4–10** are also summarized in Tables 6 and 7.

Table 6 shows that the degradation rate depends strongly on the positions of SO_3Na groups. The effective positions for retarding the degradation are the *o*-position of ring B and the Z_3 position (dyes **18**, **21**, **3** and **26**); arrangements of two SO_3Na groups so as to surround the OH-side azo group (more strictly, the hydrazo group) from both sides exert an extremely beneficial chlorine-resistance-improving effect. The role of SO_3Na groups in twice-coupled H-, K- and S-acid dyes coincides with that in phenylazonaphthol dyes.[3] Interestingly, the SO_3Na groups at the *o*-position on ring A and the Z_1 position play a minor role in this case, whereas these play a central role in imparting high formaldehyde resistance.[12] It is worth noting that the two phenylazo groups in dyes **3** and **18–25**, and most likely in dye **26**, contribute to reducing the rate, being about one-tenth that of the phenylazo-H-acid dyes **4–9**, as a result of excluding the contribution of the *o*-SO_3Na group on ring B. Thus, these groups also play an important role in chlorine-resistance.

The degradation rate of dye **18** is also directly proportional to pH-

TABLE 11
Substituent-dependence of Chlorine Fastness for Reactive Dyes Based on Twice-coupled H-acids



Y	*Chlorine fastness*[a]
H	1
o-SO_3Na, *o*-CO_2Na, *o*-NO_2, *o*-Cl	1
m-SO_3Na, *m*-CO_2Na, *m*-NO_2, *m*-Cl	1
p-SO_3Na, *p*-CO_2Na, *p*-NO_2, *p*-Cl	1

[a] Cited partially from Ref. 19.

dependent Cl^+ concentration (Table 7). However, the dye is much more resistant to degradation than the corresponding phenylazo-H-acid dyes (4 and 7) in the pH range of 4·5–10·9, because of the incorporated phenylazo group.

Table 8 shows that in the retarding ability of the SO_3Na groups, the same conclusion can be drawn from twice-coupled H-acid dyes where the phenylazo group *ortho* to the hydroxy group is replaced by a 2-naphthylazo group. The 2-naphthylazo group is more effective than the phenylazo group within the range of dyes examined.

2.4 Chlorine-fast reactive dyes from twice-coupled H-acids

The chlorine fastness of reactive dyes based on twice-coupled H-, K- and S-acids (Table 9) is in agreement with the pseudo-first-order kinetic estimation of the corresponding model dyes. However, since the chlorine fastness test employed was under severe conditions (ISO 105–E03), pseudo-first-order rate constants of the order of 10^{-2} s^{-1} correspond to poor chlorine fastness, being rates at 1 on a 1–5 scale.

The effect of various substituents on the chlorine fastness was examined. Table 10 shows that substituents on the phenylazo group *ortho* to the hydroxyl group markedly affect the chlorine fastness. The importance of the steric effect is evident from the increase in chlorine fastness which is produced by relatively large size substituents located only *ortho* to the azo group, irrespective of whether they are electron-donating or electron-withdrawing. It is important to note that the dye where X = *p*-$SO_2C_2H_4OSO_3Na$

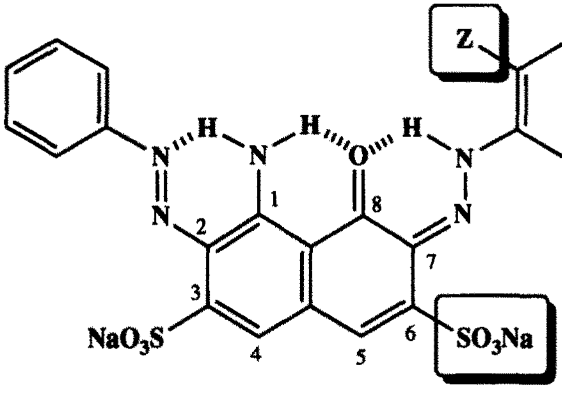


Fig. 2. Basic structure of chlorine-fast dyes derived from 1-amino-2,7-bisphenylazo-8-naphthol. The formula is shown as mixed forms which predominate in the azo-hydrazone tautomerism. The 6-SO_3Na group and a bulky substituent Z such as SO_3Na and NO_2 effectively protect the —NH—H = group against electrophilic attack of Cl^+.

is a widespread commercial product (CI Reactive Black 5); the poor chlorine fastness, rated at 1, can be improved when a bulky substituent such as SO_3Na and NO_2 is introduced into the *o*-position in place of X.

Table 11 shows that substituents on the phenylazo group *ortho* to the amino group have no chlorine-fastness-improving abilities.

2.5 Design of chlorine-fast reactive dyes

Figure 2 shows the most stable conformations of the two phenylazo groups at the 2- and 7-positions in 1-amino-2,7-bisphenylazo-8-naphthol-3,6-disulphonic acid dyes.[12] The conformations and the resulting intramolecular hydrogen-bonding formations meet a prerequisite for protecting the amino group at the 1-position against electrophilic attack of a Cl^+ ion.

Therefore, in designing chlorine-fast reactive dyes based on twice coupled H-acids, it is concluded, as shown in Fig. 2, that the introduction of a bulky substituent such as SO_3Na and NO_2 into the Z position is essential in improving the chlorine fastness. This chlorine-fastness-improving effect will also be relevant to chromogens where the benzene rings are replaced with naphthalene rings. An NHR group, or its analogous reactive systems, can be introduced into chromogens to lead to chlorine-fast reactive dyes. Since the other positions do not substantially affect chlorine fastness within the range of dyes examined, additional SO_3Na groups can also be introduced to suitable positions to increase water-solubilizing properties, to adjust substantivity to cellulose or to improve other fastness properties. The role of SO_3Na groups in giving chlorine-resistance will also be the same with other metal sulphonate groups such as an SO_3Li and SO_3K.

3 EXPERIMENTAL

3.1 Materials

First-grade reagents or technical-grade ones were used for the syntheses. Special-grade reagents or their equivalents, and water purified by ion exchange, were used for analysis, dyeing and fastness tests. Scoured and bleached unmercerized cotton knitted fabrics for dyeing were obtained from Nitto Boseki Co., Ltd.

3.2 Measurements

Visible absorption spectra were recorded on a Hitachi UV-Visible spectrophotometer model 228A, using water as solvent, unless otherwise noted. ^{15}N NMR spectra were measured 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 were synthesized following the previously reported methods.[18–21] The dyes were purified by repeated recrystallization until chromatographically pure.

3.4 Pseudo-first-order rate constant

A $2{\cdot}0 \times 10^{-5}$ M solution of each of the dyes **3–10** and **18–29** was prepared, using aqueous buffer solutions at the given pH values. A known amount of freshly estimated NaOCl solution (100 mol per mol of dye) was added to the solution, while ensuring homogeneity by vigorous stirring. The reaction mixture was then quickly transferred to a 1 cm quartz cell in the spectrophotometer, and absorbance at λ_{max} was monitored over 50–80% reaction.

The pseudo-first-order rate constant k was obtained from the initial slope of ln $A_0/A_t v.t$ plot, where A_0 and A_t are the absorbance at times 0 and t (in seconds), respectively. Half-life $t_{1/2}$ was calculated from the equation of $t_{1/2} = (1/k) \ln 2$.

The reactions were carried out at 24°C, and the following buffer systems were used: pH 4·5 M/15 KH_2PO_4, pH 7·0 M/15 KH_2PO_4–M/15 Na_2HPO_4 (4:6 in a volume ratio), pH 9·2 M/15 Na_2HPO_4, pH 10·9 0·02 M Na_2CO_3.

3.5 Dyeing

Each of the dyes **1**, **11–17** and **30–38** (0·1 g) was dissolved in water (200 ml). 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 continued at the same temperature for 1 h. The dyed cotton was rinsed with cold water, then thoroughly washed with boiling water to remove unfixed dye, 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 at 50°C instead of 60°C, using the dyes shown in Tables 10 and 11.

3.6 Chlorine fastness testing

The test was carried out for the dyeings so obtained, according to 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 CONCLUSION

Substituents and chromogenic parts of twice-coupled H-acid dyes make large contributions to their chlorine-resistance; many of the structural units responsible for high chlorine-resistance are the same as in arylazonaphthol and arylazoarylamine dyes, but some are different. In particular, the two phenylazo groups in twice-coupled H-acid dyes can overcome the deleterious influence of the amino group on chlorine resistance. In contrast, the phenylazo group in phenylazo-H-acid dyes can not overcome it; acylation of the amino group is essential. The results are applicable to the design of chlorine-fast reactive dyes based on twice-coupled H-acids, ranging in shade from blue to black.

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