Reaction of 1-Amino-8-hydroxynaphthalene-3,6-disulphonic Acid and its *N*-Acyl and *N*-*s*-Triazinyl Derivatives with Cyanuric Chloride and 6-Substituted 2,4-Dichloro-*s*-triazines. Formation of *O*-*s*-Triazinyl Derivatives and *peri*- O- ⟶ N-*s*-Triazinyl Rearrangements

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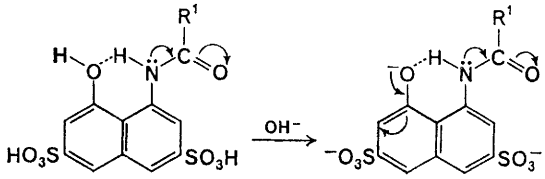
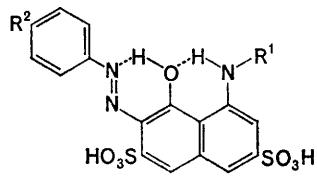
N-Acyl and *N*-*s*-triazinyl derivatives of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid react with cyanuric chloride and with 6-substituted 2,4-dichloro-*s*-triazines to give the unstable or moderately stable *O*-*s*-triazinyl compounds. In the presence of alkali the *O*-*s*-triazinyl groups rearrange to the *peri*-nitrogen atom to give *N*-*s*-triazinyl-*N*-acyl or *NN*-bis-*s*-triazinyl derivatives which are hydrolysed to 1-hydroxy-8-*s*-triazinylaminonaphthalene-3,6-disulphonic acid. 1-(2,4-Dichloro-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid undergoes self-condensation at pH 7 to form highly soluble polymeric products which rearrange so that there are hydroxy-groups and *NN*-bis-*s*-triazinyl groups present in the molecules.

1-AMINO-8-HYDROXYNAPHTHALENE-3,6-DISULPHONIC acid and its *N*-acyl and *N*-*s*-triazinyl derivatives are important intermediates in dyestuff chemistry.[1] During the reactions of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid with cyanuric chloride and with 6-substituted 2,4-dichloro-*s*-triazines to form *N*-*s*-triazinyl intermediates, undesirable side reactions may occur to a greater or lesser degree depending on reaction conditions. Closer study of these side reactions revealed that many of them were associated with the formation of unstable *O*-*s*-triazinyl derivatives and with intramolecular O ⟶ N *s*-triazinyl rearrangement. The object of this work was to isolate the unstable intermediates and to identify their decomposition products by conversion into azo-derivatives.

There are considerable steric interactions between two bulky substituents located in the *peri*-positions in naphthalene.[2] 1-Acetylamino- and 1-benzoylamino-8-hydroxynaphthalene-3,6-disulphonic acids are relatively stable in mild aqueous alkaline solution at room temperature, but 8-acetylamino-3,6-disulpho-1-naphthyl benzoate is unstable, the benzoyl group rearranging to the *peri*-nitrogen atom carrying the acetyl group with subsequent displacement of one of the acyl groups [3] in a reaction similar to that of the acetyl-benzoyl derivatives of *o*-aminophenols.[4] Acylation of the amino-group in 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid with the resultant intramolecular hydrogen bonding (HO · · · H–N) has the effect of lowering the pH at which the hydroxy-group will ionise (pK_{OH} lowered from 8·5 to *ca.* 7) to form the naphthoxide ion [(1) ⟶ (2)], which is readily attacked by the diazonium cation, such as that from *p*-chloroaniline, below or at pH 7 to give the known bluish-red 7-arylazo-derivatives (3), or by other species which possess an electron-deficient atom or centre such as benzoyl chloride [3] or cyanuric chloride.[5] 1-Acetylamino- and 1-benzoylamino-8-hydroxynaphthalene-3,6-disulphonic acids reacted readily with cyanuric chloride and with 6-arylamino-2,4-dichloro-*s*-triazines to give highly soluble *s*-triazinyl-*N*-acyl derivatives. The inability of these freshly prepared *s*-triazinyl-*N*-acyl compounds (particularly the *s*-triazinyl-*N*-benzoyl derivative) to couple with diazotised *p*-chloroaniline below or at pH 7 indicated that originally the *s*-triazinyl group was located on the oxygen atom of the hydroxy-group, as shown by structure (4), rather than on the acylamino-nitrogen atom, as shown by structure (10), since the latter compound would be expected to couple as readily as, for example, 1-hydroxynaphthalene-3,6-disulphonic



(1) R¹ a; Me b; Ph (2)



(3)

a—s Table 1

acid.[6] In contrast to the stability of the 1-acetylamino- and 1-benzoylamino-8-hydroxynaphthalene-3,6-disulphonic acids in mild aqueous alkali, the *N*-acyl groups

[1] K. Venkataraman, 'The Chemistry of Synthetic Dyes,' Academic Press, New York, 1952, vol. I, p. 488; W. F. Beech, 'Fibre-reactive Dyes,' Logos Press, London (in course of publication); W. E. Stephen, *Chimia* (*Switz.*), 1965, **19**, 261.

[2] V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, 567; G. M. Oksengendler and E. P. Gendrikov, *J. Gen. Chem.* (*U.S.S.R.*), 1959, 3857.

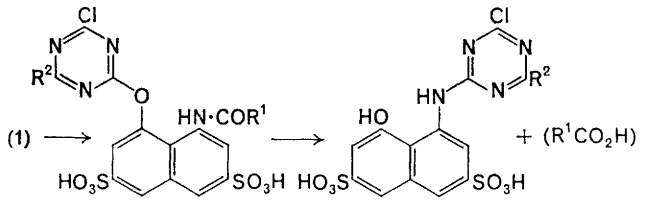
[3] R. Budziarek, *Chem. Comm.*, 1968, 1427; *cf.* L. C. Raiford and E. P. Clark, *J. Amer. Chem. Soc.*, 1926, **48**, 483.

[4] W. Böttcher, *Ber.*, 1883, **16**, 629; K. Auwers and F. Eisenlohr, *Annalen*, 1909, **369**, 209; L. C. Raiford, *J. Amer. Chem. Soc.*, 1919, **41**, 2068; L. C. Raiford and J. R. Couture, *ibid.*, 1924, **46**, 2305; L. C. Raiford and H. P. Lankelma, *ibid.*, 1925, **47**, 1111; L. C. Raiford and J. H. Scott, *J. Org. Chem.*, 1937, **2**, 213; F. Bell, *J. Chem. Soc.*, 1931, 2346; 2962; C. B. Pollard and R. E. Nelson, *J. Amer. Chem. Soc.*, 1931, **53**, 996; *cf.* J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 362.

[5] E. M. Smolin and L. Rapoport, 'The Chemistry of Heterocyclic Compounds),' Interscience, New York, 1959, p. 52.

[6] Von O. A. Stamm, A. Zenhäusern, and H. Zollinger, *Chimia* (*Switz.*), 1965, **19**, 224.

were very labile in the *O*-*s*-triazinyl-*N*-acyl derivatives, which rearranged readily above pH 7 to the *N*-*s*-triazinyl derivatives (5) with the displacement of the *N*-acyl group [as (6), see Scheme 1].

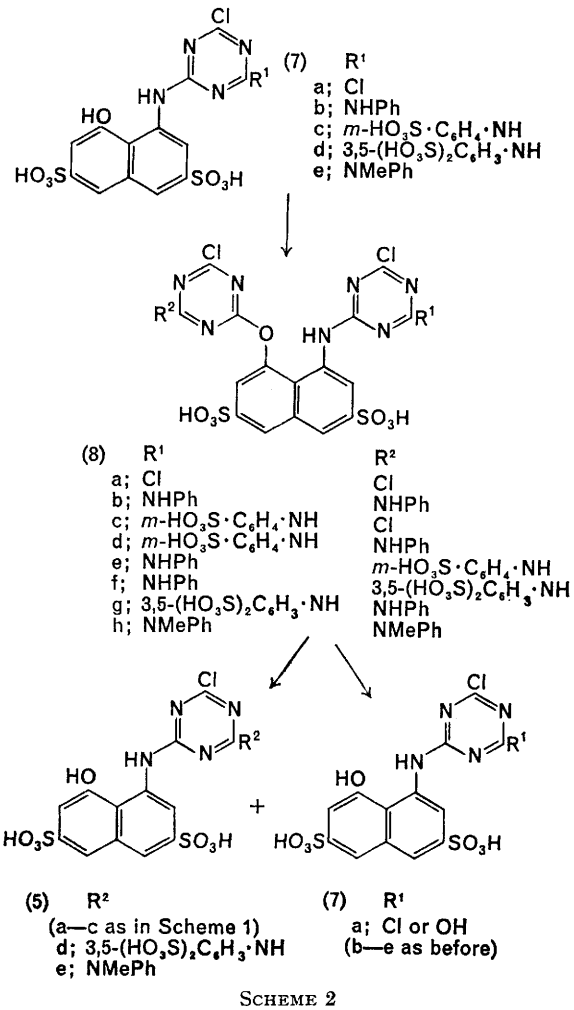


(4) R¹ R²
a; Me Cl
b; Me NHPh
c; Me *m*-HO₃S·C₆H₄·NH
d; Ph NHPh
e; Ph *m*-HO₃S·C₆H₄·NH

(5) R²
a; OH
b; NHPh
c; *m*-HO₃S·C₆H₄·NH
(d—e, Scheme 2)

(6) R¹
a; Me
b; Ph

SCHEME 1



SCHEME 2

Titrations of the freshly prepared *O*-*s*-triazinyl-*N*-acyl derivatives with diazotised *p*-nitroaniline at pH 7—8·5 showed, however, that new highly soluble orange-red azo-derivatives were formed before the final hydrolysis to the less soluble bluish-red 7-arylazo-derivatives of 1-*s*-triazinylamino-8-naphthol (3). The analytical data indicated that the new orange-red azo-compounds still contained both the *s*-triazinyl and the *N*-acyl groups and n.m.r. spectra showed a resonance at δ 15—16 p.p.m. (in most cases) associated with the hydroxy-group hydrogen bonded to the *ortho* azo-group as in structure (3).[7] This suggested that coupling took place at C-7, *ortho* to the hydroxy-group, and that during coupling in mild alkali intramolecular O ⟶ N *s*-triazinyl rearrangement occurred so that now both groups, the *s*-triazinyl and the acyl, were located on the *peri*-nitrogen atom in compounds such as (10) (*cf.* ref. 8), with subsequent hydrolysis of the more labile *N*-acyl group.

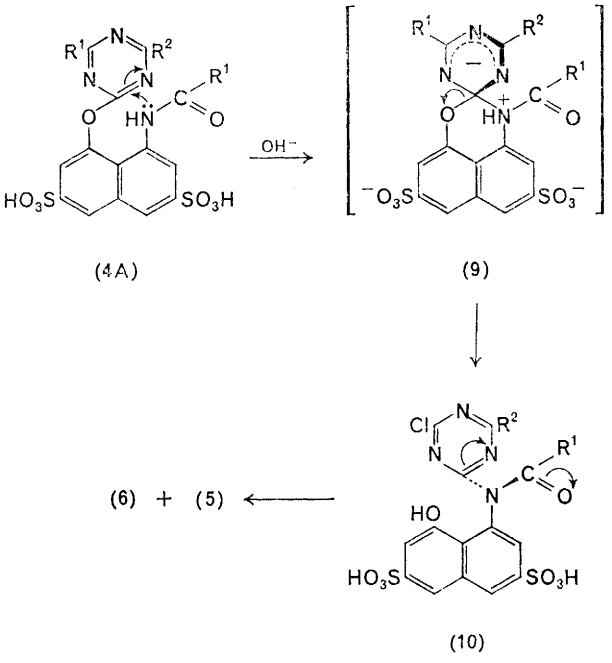
Similarly 1-*s*-triazinylamino-8-hydroxynaphthalene-3,6-disulphonic acids (7b—e) (pK_{OH} *ca.* 6·9—7·1 depending on substituent R¹) were found to react with cyanuric chloride and with 6-substituted 2,4-dichloro-*s*-triazines at pH 7 to give the *NO*-bis-*s*-triazinylamino-naphthols (8), which did not couple with diazotised *p*-chloroaniline below or at pH 7. These *NO*-bis-*s*-triazinyl derivatives were generally more stable towards alkali than the *O*-*s*-triazinyl-*N*-acyl compounds, but they were hydrolysed at pH 9—11·5 to the 1-*s*-triazinyl-amino-8-naphthols. Treatment with diazotised *p*-nitro-aniline above pH 7 revealed the formation of orange-red azo-compounds containing two *s*-triazine rings per molecule and showing an n.m.r. signal at δ 15—16 p.p.m., as in the case of the *O*-*s*-triazinyl-*N*-acylaminonaphthols (4). Instead of the expected outright hydrolysis of the *O*-*s*-triazinyl group in alkali, intramolecular *peri*-O ⟶ N rearrangement occurred to give first the *NN*-bis-*s*-triazinylaminonaphthols (12), which were then hydrolysed to *s*-triazinylaminonaphthols. *NO*-bis-*s*-triazinylaminonaphthols containing different substituents on the triazine rings [*e.g.* (8f and g)] gave two *N*-*s*-triazinyl derivatives [(7b) and (5d); see Scheme 2] with sodium hydroxide, and two 7-arylazo-derivatives [(3i) and (3m) in approximately equal proportions] after coupling with diazotised *p*-chloroaniline and alkaline hydrolysis. This reaction was, therefore, analogous to the alkaline hydrolysis of the acetyl-benzoyl derivative of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid reported earlier,[3] which gave a mixture of both *N*-acyl derivatives.

In the light of these results, a reaction mechanism represented by Schemes 3 and 4 is suggested. Catalin molecular models showed that the *O*-*s*-triazinyl derivatives (4) and (8) were not planar molecules and that the *s*-triazine ring can approach very closely to the nitrogen atom in the *peri*-position [as in (4A) and (8A)]. Since the nitrogen atom, with its unshared pair of electrons, is able to act as an internal nucleophile towards the neighbouring electron-deficient *O*-carbon atom of the *s*-triazine ring, the large *O*-*s*-triazinyl group may interfere

[7] A. H. Berrie, P. Hampson, S. W. Longworth, and A. Mathias, *J. Chem. Soc.* (*B*), 1968, 1308.

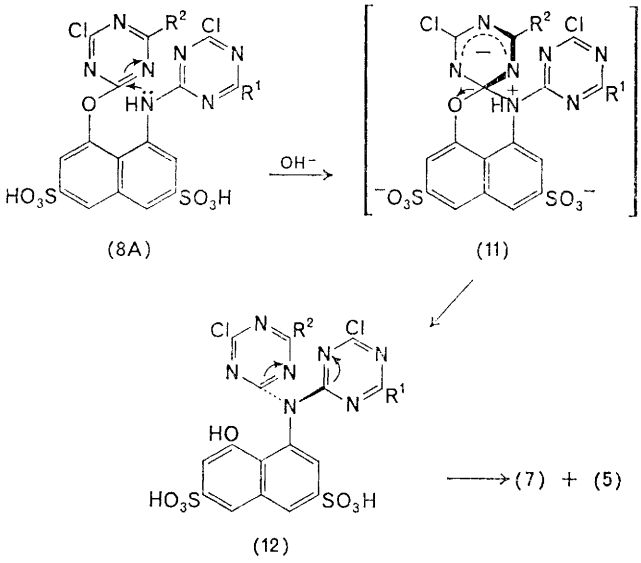
[8] B. S. Joshi, R. Srinivasan, R. V. Talavdekar, and K. Venkataraman, *Tetrahedron*, 1960, **11**, 133; P. Madhavan Nair, R. Srinivasan and K. Venkataraman, *ibid.*, 1960, **11**, 140.

sterically with the *peri*-acylamino- (or *s*-triazinylamino-) group so that withdrawal of electrons from the nitrogen atom by the acyl (or *s*-triazinyl) group becomes inhibited [9] and the nitrogen atom is able to satisfy the electronic demand of the *s*-triazine *O*-carbon atom more fully than the oxygen atom. The first step in the *peri*-O ⟶ N *s*-triazinyl transfer would be the formation of an unstable cyclic intermediate such as (9) and (11), followed by a loss of a proton from a nitrogen atom and cleavage of the O–C(triazine) bond to form the three-dimensional *N*-*s*-triazinyl-*N*-acyl intermediate (10) or *NN*-bis-*s*-triazinyl intermediate (12), which is then hydrolysed to the *s*-triazinylaminonaphthol. The preferential hydrolysis of the *N*-acyl group rather than the *N*-*s*-triazinyl group in (10) suggests that the carbonyl carbon atom may be more electropositive in character and more easily accessible by the hydroxide ion than the *N*-*s*-triazine carbon atom.



SCHEME 3

1-(2,4-Dichloro-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid (7a) is best prepared by treating 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid (pK_{NH_2} 3·54; pK_{OH} 8·55) [10] with cyanuric chloride (1 mol.) below pH 3·5; [11] it couples quantitatively with diazotised *p*-chloroaniline at pH 5—6·8 to give the bluish-red 7-arylazo-derivative (3e). The presence of the strongly electron-withdrawing 2,4-dichloro-*s*-triazinyl group and the strong intramolecular hydrogen bonding (HO · · · H–N) is responsible for the increased acidity of the hydroxy-group (pK_{OH} 6·6) and partial ionisation in neutral and weakly acid solutions. The intermediate (7a) reacted rapidly with a further molar equivalent of cyanuric chloride at pH 6—7 to give the unstable *NO*-bis(dichloro-*s*-triazinyl)aminonaphthol (8a) which



SCHEME 4

coupled slowly with diazotised *p*-chloroaniline at pH 7—8·5 (readily with diazotised *p*-nitroaniline at pH 6—8 *) to give a very soluble orange-red 7-arylazo-derivative of the *NN*-bis-*s*-triazinylaminonaphthol (12; $R^1 = R^2 = Cl$). In the absence of cyanuric chloride at pH 6—7, however, 1-(2,4-dichloro-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid (7a) underwent self-condensation † to give a highly water-soluble polymeric product. The inability of the polymer to couple with more than, for example, 8—20% of diazotised *p*-chloroaniline below pH 7 indicated self-condensation of the intermediate (7a) through the ionised hydroxy-group to polymeric compounds of the type (13; average $n = 4$—12 depending on reaction conditions). The freshly prepared polymer was found to couple readily, however, at pH 7·5—8·5 without any significant decomposition into *N*-*s*-triazinylaminonaphthol molecules to yield very soluble polymeric orange-red azo-derivatives. The n.m.r. spectrum indicated the presence of more than one strongly hydrogen-bonded hydroxy-group (δ 15 p.p.m.) in the molecule, which can be explained by the occurrence of intramolecular O ⟶ N

* Whereas the *NO*-bis-*s*-triazinylaminonaphthol [*e.g.* (8a)] and also some *O*-*s*-triazinyl-*N*-acyl-(*e.g.* benzoyl)-aminonaphthols coupled reluctantly with diazotised *p*-chloroaniline above pH 7, they coupled readily with diazotised *p*-nitroaniline and at lower pH. This could be interpreted as reflecting either the capability of some of the *O*-*s*-triazinyl derivatives to form a stabilised transition state with strong diazo-components before the O→N *s*-triazinyl rearrangement, or the ability of the stronger diazo-component to promote the O→ N *s*-triazinyl rearrangement, or both.

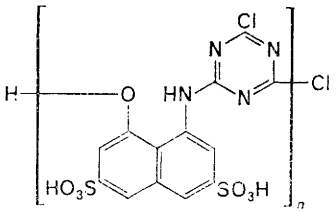
† This reaction was first observed in 1947 by Dr. W. E. Stephen (this laboratory), who suggested self-condensation through the hydroxy-group.

[9] B. M. Wepster, *Progr. Stereochem.*, 1958, **2**, 105; L. K. Dyall and J. E. Kemp, *Spectrochim. Acta*, 1966, **22**, 483; P. J. Krueger, *ibid.*, 1963, **19**, 705; J. W. Smith, *J. Chem. Soc.*, 1961, 4700; H. Kessler and A. Rieker, *Annalen*, 1967, **708**, 57.

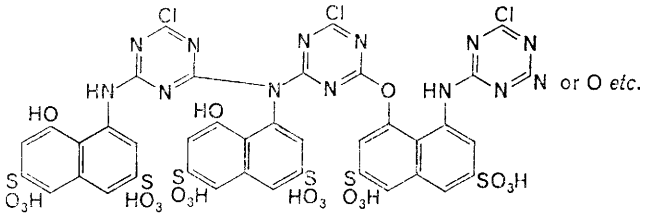
[10] H. Zollinger and C. Wittwer, *Helv. Chim. Acta*, 1952, **35**, 1209.

[11] B.P. 785,222/1955 and 834,304/1960.

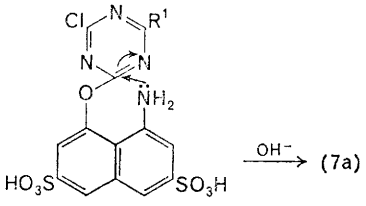
s-triazinyl rearrangement in the polymer (13) during coupling in mild alkali, so that there were present free hydroxy-groups and *NN*-bis-*s*-triazinyl groups, as represented by a partial structure such as (14).



(13)



(14)



(15)

It is known that treatment of the naphthoxide ion of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid with toluene-*p*-sulphonyl chloride gives the *O*-tosyl derivative,[12] so an attempt was made to prepare the *O*-*s*-triazinyl derivative (15) of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid by a similar reaction. In contrast to the relatively sluggish reaction of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid with cyanuric chloride in mild acid medium, it reacted with cyanuric chloride (1 mol.) in aqueous acetone at pH 8·5—10·5 and 0° as soon as mixed. Although it seemed obvious that two different mechanisms were operating in acid and in alkali, the product consisted essentially of the usual 1-(dichloro)- and some (chlorohydroxy)-*s*-triazinylamino-8-hydroxynaphthalene-3,6-disulphonic acid (7a; R^1 = Cl and some R^1 = OH), together with smaller amounts of by-products related to (13) and (14). Estimations of the free amino-group, however, revealed small but significant amounts of a *s*-triazinylaminonaphthol (presumably 15; R^1 = Cl or OH) (the presence of ionised OH 'deactivating' the triazine ring towards a nucleophilic attack)[13] in the reaction mixture. It appears, therefore, that at pH ⩾ 8·5 the reaction proceeded partly or mainly by attack of cyanuric chloride on the naphthoxide ion to give first the labile *O*-(dichloro-*s*-triazinyl)-aminonaphthol (15; R^1 = Cl), which rearranged to the *N*-(dichloro-*s*-triazinyl)aminonaphthol (7a) in a reaction similar to the O ⟶ N rearrangements of the acyl group in *o*-aminophenyl benzoate,[14] β-aminoethyl benzoate, and related compounds.[15]

EXPERIMENTAL

1-Amino-8-hydroxynaphthalene-3,6-disulphonic acid crystallised from water (as a monosodium salt), and cyanuric chloride crystallised from light petroleum (b.p. 100—120°), m.p. 145—146°, were used as starting materials. The suspension of cyanuric chloride in aqueous acetone was obtained by dissolving the solid in AnalaR acetone (usually 1 g. in 5—10 ml.) and adding the solution dropwise to deionised water at 0—4° with stirring. Diazo-PCA and -PNA stand for diazotised *p*-chloroaniline and *p*-nitroaniline: couplings were carried out at 0—6° with a spot of a neutral aqueous solution of 1-amino-8-hydroxy-2-(3-nitro-4-sulphophenylazo)naphthalene-3,6-disulphonic acid (*cf.* ref. 16) as indicator (purple ⟶ green-blue). Aqueous 2N-sodium carbonate was used as an acid binder and to control the pH unless stated otherwise.

Several chromatographic methods were used, *e.g.* (*a*) glass plates, 3MM Whatman paper (30 × 30 cm.) or no. 1 Whatman paper (32·0 cm.) for quick, qualitative work, 0·05—2·0% aqueous sodium chloride as eluant; (*b*) glass tank, ascending method, no. 20 Whatman paper (31·5 × 33·5 cm.), ethyl cellosolve–water (20%) as eluant; (*c*) column, Whatman CF 11 fibrous cellulose powder, 0·5—2·0% aqueous sodium chloride as eluant, used for separations and purifications of larger quantities of material; (*d*) t.l.c. on silica gel G, n-butanol–acetone–water–ammonia (*d* 0·88) (5 : 5 : 2 : 1) as eluant.

Since most of the water-soluble compounds examined contained inorganic salt and moisture, Mol. in (the weight of material in grams containing one gram molecule of the compound in question) was estimated by finding the salt and moisture content; Mol. in of an azo-compound was found by titration with 0·1N-titanous chloride.

N.m.r. spectra were recorded with a Varian 100 MHz machine for solutions in dimethyl sulphoxide with tetramethylsilane as internal reference; i.r. spectra were taken for Nujol mulls.

7-(p-*Substituted Phenylazo*)-*derivatives of* N-*Acyl and* N-s-*Triazinyl*-1-*amino*-8-*hydroxynaphthalene*-3,6-*disulphonic Acids* (3).—The known [1,11] reference compounds (3a—n) (Table 1) were prepared by coupling a diazotised *p*-substituted aniline with an *N*-acyl or *N*-*s*-triazinyl-1-amino-8-hydroxynaphthalene-3,6-disulphonic acid at pH 6—7.

[12] B.P. 14,248/1907; R. H. Wilson, 1941, this laboratory (unpublished work).
[13] S. Horrobin, *J. Chem. Soc.*, 1963, 4130.
[14] A. Einhorn and B. Pfyl, *Annalen*, 1900, **311**, 34; K. Auwers, *ibid.*, 1904, **332**, 159.
[15] S. Gabriel and T. Heymann, *Ber.*, 1890, **23**, 2501; S. Gabriel, *Annalen*, 1915, **409**, 326; T. Immediata and A. R. Day, *J. Org. Chem.*, 1940, **5**, 512; L. H. Welsh, *J. Amer. Chem. Soc.*, 1947, **69**, 128; 1949, **71**, 3500; A. P. Phillips and R. Baltzly, *ibid.*, 1947, **69**, 200; G. Fodor and J. Kiss, *ibid.*, 1950, **72**, 3495; E. E. van Tamelen, *ibid.*, 1951, **73**, 5773.
[16] H. Zollinger, 'Chemie der Azofarbstoffe,' Birkhäuser Verlag Basel and Stuttgart, 1958, p. 174; H. Otsuka, O. Manabe, and H. Hiyama, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1968, **71**, 2023.

Compounds (3o and p) and (3r and s) were obtained from compounds (3e and f) by treatment (room temperature) with aqueous sodium hydroxide and hydrochloric acid respectively. The bluish-red azo-compounds were moderately strongly adsorbed on cellulose from aqueous solutions containing sodium chloride. N.m.r. spectra (solutions in dimethyl sulphoxide) showed resonances at δ 15—16 p.p.m. (C-8 OH hydrogen-bonded to the *ortho* azo-group irrespective of the hydroxyazo–hydrazone tautomerism [7]). For example compound (3b) showed δ 7·6 (4- and 5-H), 8·0 (2H, phenyl protons α to the azo-group), 8·3 (2H, phenyl protons α to the nitro-group), 8·9 (2-H), 12·3 (hydrogen-bonded 1-NH), and 15·3 p.p.m.(hydrogen-bonded 8-OH).

TABLE 1

N-Acyl and *N*-*s*-Triazinyl-1-amino-8-hydroxy-7-(*p*-substituted phenylazo)naphthalene-3,6-disulphonic acids (3)

p-Substituent (R^2)	Acyl or *s*-Triazinyl group (R^1)
(a) Cl (b) NO_2	Ac
(c) Cl (d) NO_2	Bz
(e) Cl (f) NO_2	2,4-Dichloro-*s*-triazinyl
(g) Cl (h) NO_2	2-Chloro-4-(3-sulphoanilino)-*s*-triazinyl
(i) Cl (j) NO_2	2-Chloro-4-anilino-*s*-triazinyl
(k) Cl (l) NO_2	2-Chloro-4-*N*-methylanilino-*s*-triazinyl
(m) Cl (n) NO_2	2-Chloro-4-(3,5-disulphoanilino)-*s*-triazinyl
(o) Cl (p) NO_2	2-Chloro-4-hydroxy-*s*-triazinyl [a]
(r) Cl (s) NO_2	2,4-Dihydroxy-*s*-triazinyl [b]

Hydrolysable Cl per mol.: [a] (o) 1·05 and (p) 0·95; [b] (r) and (s) nil.

O-s-*Triazinyl Derivatives from* 1-*Acylamino- and* 1-s-*Triazinylamino*-8-*hydroxynaphthalene*-3,6-*disulphonic Acids* (4 and 8).—(a) *Preparation. Method A.* A neutral aqueous solution of 1-acylamino-8-hydroxynaphthalene-3,6-disulphonic acid (1a or b) or 1-(4-arylamino-2-chloro-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid (7b—e) (0·01 mol.; 50—80 ml.) was added dropwise to a suspension of cyanuric chloride (1·94 g.) in aqueous acetone (1 : 1; 60 ml.) at 0—2° and the mixture was stirred at pH 6·9—7·1 (2N-Na_2CO_3) for 30—60 min., until no starting material remained (no coupling with diazo-PCA below or at pH 7). The solution containing the *O*-(2,4-dichloro-*s*-triazinyl) derivative (Table 2) was filtered, and a small sample of the solid was isolated by partial evaporation of the solution (8—15°) and dilution with acetone. Yields were nearly quantitative and depended on the solubility of the product; the presence of the *O*-*s*-triazinyl group in the molecule was confirmed by analysis, in particular by the C : N ratio [*e.g.* ratio C : N = 15·1 : 3·9 for derivative (4a)].

Method B. The aqueous solution containing the *O*-(2,4-dichloro-*s*-triazinyl) derivative [(4) or (8), Table 2] prepared according to method A was either mixed with a neutral aqueous solution of sulphonated aniline [*e.g.* *m*-aminobenzenesulphonic acid (1·75 g.)] or treated dropwise with a solution of aniline (0·95 g.) in acetone, and the mixture was stirred at 15—30° for 2—4 hr. at pH 6·0—6·8 (2N-Na_2CO_3) until a negative test for the presence of the dichloro-*s*-triazinyl group was obtained (absence of a deep yellow colour after crossing a spot of the solution on filter paper with pyridine followed by 2N-sodium hydroxide). The products (Table 2) did not couple with diazo-PCA below pH 7. Some were isolated by precipitation with potassium acetate, filtration, and removal of the salt from the product with ethanol [*e.g.* (4e), Table 2], but this procedure caused extensive decomposition in most cases [*e.g.* (4c)]; the products were usually isolated either by concentration of the solution and dilution with acetone (yilds >90%) or by precipitation with sodium (or potassium) chloride, filtration, extraction of the product with aqueous ethanol (to remove some of the salt), and evaporation to dryness.

Method C. Cyanuric chloride (1·94 g.) was first treated with a sulphonated aniline (0·01 mol.) in aqueous acetone at 0—4° and pH 5—6 to give a clear solution of 2-arylamino-4,6-dichloro-*s*-triazine, which was then mixed with a neutral aqueous solution of 1-acylamino- or 1-(4-arylamino-2-chloro-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid (1a or b, or 7b—e) and the mixture was stirred at 20—25° and pH 7 for 1—2 hr., until a negative test with diazo-PCA was obtained. [Derivative (8h) showed only one exchangeable proton (δ 9·4 p.p.m.) in its n.m.r. spectrum].

(b) *Reactions.* (i) *With alkali.* The *O*-*s*-triazinyl derivative (4a—e or 8b—h) was dissolved in water (1 g. in 5—10 ml.) and treated with 2N-sodium hydroxide at room temperature and pH 10·5—11·0 for 6—16 hr.; the pH was then lowered to 5—6 (HCl). The *N*-*s*-triazinyl derivatives present in the reaction mixtures (Table 2) were identified by coupling with diazo-PCA (or -PNA) and comparison (chromatography and i.r. spectra) with the reference azo-compounds [(3a—s) Table 1]. The sparingly soluble (2-chloro-4-anilino-*s*-triazinylamino)naphthol and its azo-derivatives (3i and j) usually precipitated from the solutions, and benzoic acid [from (4d and e)] was isolated by extraction of the mixtures (before coupling) with ether.

(ii) *With diazonium compounds.* An aqueous solution of *O*-*s*-triazinyl derivative [(4) or (8)] was either titrated with

TABLE 2

O-*s*-Triazinyl derivatives from 1-acylamino- and 1-*s*-triazinylamino-8-naphthol-3,6-disulphonic acids

		Found (%)						Mol.	Required (%)					Products	Identified as azo-derivatives
	Method	C	H	Cl	N	S	Formula	in	C	H	Cl	N	S	from NaOH	
(4a)	A	22·3	1·6		6·7		$C_{15}H_8Cl_2N_4Na_2O_8S_2{,}2H_2O$	810	22·2	1·5		6·9		(5a)	(3o and p)
(4b)	B	30·5	2·4		8·5		$C_{21}H_{14}ClN_5Na_2O_8S_2{,}2H_2O$	830	30·4	2·2		8·4		(5b)	(3i)
(4c)	C	23·9	2·3	3·7	6·5	8·6	$C_{21}H_{13}ClN_5Na_2O_{11}S_3{,}3H_2O$	1050	24·0	2·4	3·4	6·7	9·1	(5c)	(3g)
(4d)	B	38·8	2·4	4·2	8·9	7·5	$C_{26}H_{16}ClN_5Na_2O_8S_2{,}2H_2O$	805	38·8	2·5	4·4	8·7	7·95	(5b) + (6b)	(3i)
(4e)	B	35·3	2·5	4·3	7·8	11·1	$C_{26}H_{15}ClK_3N_5O_{11}S_3{,}3H_2O$	875·5	35·7	2·4	4·1	8·0	11·0	(5c) + (6b)	(3g)
(8b)	B	40·0	2·4	8·1	14·7	7·3	$C_{28}H_{17}Cl_2K_2N_9O_7S_2{,}2H_2O$	840	40·0	2·3	8·45	15·0	7·6	(7b)	(3i)
(8c)	A	22·5	1·5		9·8		$C_{22}H_{10}Cl_2N_8Na_2O_{10}S_3{,}3H_2O$	1160	22·8	1·4		9·7		(7c) + (5a)	(3g) + (3o)
(8d)	B	33·2	2·3	6·7	12·4	9·2	$C_{28}H_{16}Cl_2K_3N_9O_{10}S_3{,}3H_2O$	1010	33·3	2·2	7·0	12·5	9·5	(7b) + (5c)	(3i) + (3g)
(8e)	C	34·4	2·5	7·1	12·8	9·4	$C_{28}H_{16}Cl_2K_3N_9O_{10}S_3{,}3H_2O$	976	34·5	2·3	7·3	12·9	9·8	(7b) + (5c)	(3i) + (3g)
(8f)	C	20·0	1·2	4·05	7·3	7·2	$C_{28}H_{15}Cl_2N_9Na_4O_{13}S_4{,}4H_2O$	1700	19·8	1·4	4·2	7·4	7·5	(7b) + (5d)	(3i) + (3m)
(8g)	B	20·6	1·5	4·1	7·8	7·6	$C_{28}H_{15}Cl_2N_9Na_4O_{13}S_4{,}4H_2O$	1640	20·5	1·4	4·3	7·7	7·8	(7b) + (5d)	(3i) + (3m)
(8h)	B	39·0	2·7	7·6	13·8	6·7	$C_{30}H_{21}Cl_2N_9Na_2O_7S_2{,}2H_2O$	920	39·2	2·7	7·7	13·7	6·95	(7e)	(3k and l)

0·05N-diazo-PCA or -PNA or mixed with the diazo-component (1 mol.) and stirred at pH 7—8·5 (aqueous Na_2CO_3) at 2—6° for 1—2 hr. until the theoretical amount of the diazo-component was consumed. The orange-red solution was concentrated and filtered through a short column of cellulose powder (to remove traces of strongly adsorbed bluish-red decomposition products), and the very soluble orange-red azo-derivatives were isolated by evaporation at room temperature to a syrup and dilution with acetone (yields >90%). Most of the new azo-derivatives (Table 3) showed a broadened singlet peak at δ 15—16 p.p.m. in the n.m.r. spectrum (C-8 OH), although some products [*e.g.* from (4a—e)] showed no such signal, possibly because it was too broad to be observed. Hydrolysable chlorine was estimated by boiling with aqueous sodium hydroxide and titration with 0·1N-silver nitrate.

An aqueous solution of the orange-red azo-derivative (1g. in 5 ml.) was treated with 2N-sodium hydroxide at room temperature (pH 9·0—10·5) for 6—16 hr., after which time the pH was lowered to 4—6 (HCl). The blue-red azo-derivatives (3g—n) present in the reaction mixtures (Table 3) were separated by use of their difference in solubility and by column (cellulose) chromatography, and identified by comparison with the reference azo-compounds listed in Table 1. Benzoic acid [from coupled (4d and e)] was isolated by extraction with ether.

Reaction of 1-*Amino*-8-*hydroxynaphthalene*-3,6-*disulphonic Acid with Cyanuric Chloride* (2 *Mol.*).—A faintly acid solution (pH 6·0—6·2) of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid (3·19 g.) in water (60 ml.) was added dropwise to a suspension of cyanuric chloride (1·92 g.) in aqueous acetone (1 : 1; 40 ml.) at 0—2° and the pH was allowed to fall to 1·8. The mixture was stirred for 1 hr. without addition of alkali (no starting material present by HCl–$NaNO_2$ test) and the solution (100 ml.) was filtered from unchanged cyanuric chloride.

A part of the solution (25 ml.) was added to acetone (0·5 l.) and the white precipitate was collected and dried (1·4 g.) to give 1-(2,4-*dichloro*-s-*triazinylamino*)-8-*hydroxynaphthalene*-3,6-*disulphonic acid* (7a; R^1 = Cl) [Found: C, 27·0; H, 2·1; Cl, 11·9; N, 10·0; S, 11·6. $C_{13}H_6Cl_2N_4Na_2O_7S_2,2H_2O$ (Mol. in 575) requires C, 27·15; H, 1·75; Cl, 12·3; N, 9·7; S, 11·1%]. Another part of the solution (25 ml. diluted with water to 210 ml.) was mixed with 0·05N-diazo-PCA (25 ml.) and the pH was raised very slowly to 6·8—7·0 at 0—4° by dropwise addition of aqueous 0·5N-sodium carbonate solution during 45 min. with stirring. The theoretical amount of the diazonium compound was consumed to give a blue-red solution of the corresponding 7-*p*-chlorophenylazo-derivative [Table 1 (3e)].

The remaining solution (50 ml.) containing the 1-(dichloro-*s*-triazinylamino)-8-naphthol derivative was added dropwise to a suspension of cyanuric chloride (0·96 g., 1·03 mol.) in aqueous acetone (1 : 1; 20 ml.) at 0° with the pH maintained at 6·5—7·0 (N-Na_2CO_3). After 15 min. the solution (80 ml.) was filtered (no coupling with diazo-PCA below pH 7) and a part (20 ml.) was diluted with acetone to give the NO-*bis*-(*dichloro*-s-*triazinyl*) *derivative* (8a) (0·95 g.) (Found: C, 21·4; H, 1·4; Cl, 15·2; N, 10·9; S, 6·9. $C_{16}H_5Cl_4N_7Na_2O_7S_2,2H_2O$ (Mol. in 890) requires C, 21·6; H, 1·0; Cl, 15·95; N, 11·0; S, 7·2%). This product decomposed in solution and as a solid to 1-(2,4-dihydroxy-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid. The freshly prepared *NO*-bis(dichloro-*s*-triazinyl) derivative (in solution; 20 ml.) was coupled with 0·05N-diazo-PNA at pH 7·0—8·0 and the orange-red solution was filtered through a column of cellulose to remove the blue-red impurity. Evaporation to dryness gave a solid (2·3 g.) containing salt mixed with an *orange-red azo-compound* (Found: C, 12·9; H, 0·8; N, 6·5. $C_{22}H_8Cl_4N_{10}Na_2O_9S_2,2H_2O$ (Mol. in 2050) requires C, 12·9; H, 0·6; N, 6·8%. Ratio C : N 22 : 9·5), δ 15·0br p.p.m. The blue-red decomposition product was characterised as the azo-derivative of 1-(2-chloro-4-hydroxy-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid [Table 1 (3 p)].

Self-condensation of 1-(2,4-*Dichloro*-s-*triazinylamino*)-8-*hydroxynaphthalene*-3,6-*disulphonic Acid* [*to* (13)].—1-Amino-8-hydroxynaphthalene-3,6-disulphonic acid (3·19 g.) was treated with cyanuric chloride (1·92 g.) as already described. After 1·5 hr. the solution was filtered (no starting material present) and the pH was adjusted to 6·8—7·0 by titration with aqueous 0·5N-sodium hydroxide (40 ml.) at 20—25°. The pH of the solution fell rapidly and was repeatedly adjusted to 7 by the addition of the alkali during 1—1·5 hr., after which time the pH remained unchanged near 7 and there was no 1-(2,4-dichloro-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid left in the solution (traces of the partially hydrolysed 2-chloro-4-hydroxy-*s*-triazinyl analogue might have been present). The volume of the solution was adjusted to 250 ml. and portions (25 ml.) were titrated with 0·05N-diazo-PCA and -PNA at pH 5·5—6·5 (0·5N-Na_2CO_3); the readings corresponded to only 7·5—15% of the diazo-component consumed. [In a number of experiments the polyermised product (13; n = 4—12) coupled with up to 20—25% of the diazo-component below pH 7. Molecular weights of the polymer (solid obtained by removal of water and slurrying with acetone) determined by short channel equilibrium ultracentrifugation in aqueous sodium chloride solutions varied between 2000 and 5000.] Titrations with 0·05N-diazo-PCA and -PNA at pH 8·5 and

TABLE 3

Azo-derivatives from O-*s*-triazinyl derivatives [(4) and (8), Table 2]

	Diazo-component	Found (%) C	H	N	S	Hydrolysable Cl per mol.	Formula	Mol. in	Required (%) C	H	N	S	Azo-compounds from NaOH
(4a)	PNA	19·4	1·4	7·6		1·92	$C_{21}H_{11}Cl_2N_7Na_2O_{10}S_2,2H_2O$	1290	19·55	1·2	7·6		(3s)
(4c)	PCA	19·3	1·6	5·9		0·96	$C_{27}H_{16}Cl_2N_7Na_3O_{11}S_3,3H_2O$	1680	19·3	1·3	5·8		(3g)
(4d)	PNA	22·6	1·3	6·5		0·98	$C_{32}H_{19}ClN_8Na_2O_{10}S_2,2H_2O$	1700	22·6	1·4	6·6		(3j)
(4e)	PNA	23·7	1·5	7·1	5·6	1·04	$C_{32}H_{18}ClN_8Na_3O_{13}S_3,3H_2O$	1620	23·7	1·5	6·9	5·9	(3h)
(8b)	PCA	35·0	2·3	12·9	5·2	2·01	$C_{31}H_{20}Cl_3N_{11}Na_2O_7S_2,2H_2O$	1175	34·75	2·0	13·1	5·45	(3i)
(8d)	PCA	23·8	1·6	8·8	5·3	1·95	$C_{34}H_{19}Cl_3N_{11}Na_3O_{10}S_3,3H_2O$	1720	23·7	1·5	8·95	5·6	(3g) + (3i)
(8f)	PCA	21·9	1·7	8·0	6·6	2·05	$C_{34}H_{18}Cl_3N_{11}Na_4O_{13}S_4,4H_2O$	1865	21·9	1·4	8·3	6·9	(3i) + (3m)
(8g)	PCA	22·7	1·6	8·5	7·0	1·97	$C_{34}H_{18}Cl_3N_{11}Na_4O_{13}S_4,4H_2O$	1785	22·9	1·5	8·6	7·2	(3i) + (3m)
(8h)	PNA	38·2	2·4	14·2	5·6	1·92	$C_{36}H_{24}Cl_2N_{12}Na_2O_9S_2,2H_2O$	1140	37·9	2·5	14·7	5·6	(3l)

7·5—8·5 respectively showed 60 and 75% couplings with the diazo-components after 30 min. The very soluble orange-red *p*-nitrophenylazo-derivative, isolated by column chromatography and evaporation, showed a broad n.m.r. peak at δ *ca.* 15 p.p.m., (hydrogen-bonded OH) (ratio of the intensities of aromatic protons at δ 7—9 p.p.m. to OH protons *ca.* 12 : 1). The product (and its azo-derivative) decomposed in aqueous solutions to 1-(2,4-dihydroxy-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid; a part of the polymer in which the chlorine atoms had been hydrolysed to OH appeared to be stable in aqueous alkali at room temperature.

Reaction of 1-*Amino*-8-*hydroxynaphthalene*-3,6-*disulphonic Acid with Cyanuric Chloride above pH* 7.—Several experiments were carried out at pH 8·5—10·5 (20 sec. to 2 min.). For example, a neutral aqueous solution (50 ml.) of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid (3·19 g.) was treated with 2N-sodium hydroxide (5 ml.) and 2N-sodium carbonate (5 ml.) and cooled to −2° (pH 10·5). This was added in a stream together with a chilled solution (below 0°) of cyanuric chloride (1·95 g.) in acetone (30 ml.) through a cooling and mixing system to aqueous acetone (1 : 1; 50 ml.) with vigorous stirring at 0°. After 2 min. (pH 8·2; trace of starting material removed by adding a few drops of cyanuric chloride in acetone) the pH was lowered to 2·1 with hydrochloric acid, and the volume of the solution was adjusted to 200 ml.; titration of a portion (50 ml.) with aqueous 0·05N-sodium nitrite solution showed the presence of an amino-containing product (*e.g.* 9%; values of 6—17% obtained from several experiments). Coupling of the product with diazo-PCA and chromatography showed the main product to be the 7-phenylazo-derivative of 1-(dichloro- and some chlorohydroxy-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid [Table 1 (3e and o)] together with smaller amounts of an orange-red azo-derivative of self-condensed 1-(dichloro-*s*-triazinylamino)-8-hydroxynaphthalene-3,6-disulphonic acid [related to (14)].

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