45. *Substitution Reactions of the Naphthylenediamines. Part I. The Coupling of Diazobenzene to* 1 : 5- *and* 1 : 8-*Naphthylenediamines.*

By J. S. WHITEHURST.

The coupling of diazobenzene to 1 : 5- and 1 : 8-naphthylenediamines has been investigated over a range of pH values and found to occur at position 2 in the former and at position 4 in the latter substance. In almost neutral solution 1 : 8-naphthylenediamine tends to undergo bisazo-coupling. The dissociation constants of naphthalene-1 : 2 : 5- and -1 : 4 : 5-triamines have been determined and compared with those of the diamines from which they are derived.

THE importance of the naphthylenediamines in the dye industry may be judged from the number of patents dealing with their uses. Tetrazotised 1 : 5-naphthylenediamine and its 3 : 7-disulphonic acid yield direct cotton dyes (B.A.S.F., G.P. 39,954, " Friedländer," **1**, 525; Cassella & Co., G.PP. 58,617, 61,174, " Friedländer," **3**, 784), and as a coupled component this diamine has been claimed for the preparation of black acid dyes (Cassella & Co., G.P. 71,329, " Friedländer," **3**, 551). Because 1 : 8-naphthylenediamine was until recently difficult to tetrazotise (Hodgson and Whitehurst, *J.*, 1947, 80), the azo-dyes derived from it were made by using it as a second coupling component (Cassella & Co., G.P. 71,329; B.A.S.F., G.PP. 94,074, 140,955, *Chem. Centr.*, 1898, I, 231; A.-G. f. Anilinf., G.P. 84,657, " Friedländer," **4**, 1022).

The technological use of these compounds has, however, progressed without a fundamental knowledge of their chemistry (see Saunders, " The Aromatic Diazo-Compounds," 2nd edn., 1949, p. 202). For instance, the orientation of diazo-groups when coupled to these diamines has received scant attention. Finzi (*Ann. Chim. Appl.*, 1925, **15**, 55) made a brief study of the coupling reactions with diazotised *p*-toluidine in aqueous hydrochloric acid–sodium acetate and concluded that monocoupling occurred at position 2 in 1 : 5-naphthylenediamine and at position 4 in 1 : 8-naphthylenediamine. Some of the evidence he adduced was of a negative nature, *e.g.*, that the triamine hydrochloride obtained from 1 : 8-naphthylenediamine by coupling and reduction (the intermediates were not crystallised) failed to give a sparingly soluble phenazine with phenanthraquinone. But, as Sachs has shown (*Annalen*, 1909, **365**, 53), ketones can react with the amino-groups of 1 : 8-naphthylenediamine forming perimidines and dihydroperimidines, and these are not necessarily less soluble than the reactants. Finally, Friedländer and Silberstein (*Monatsh.*, 1902, **23**, 518) coupled diazotised sulphanilic acid with 1 : 8-naphthylenediamine, reduced the resulting dye, and then oxidised the products with atmospheric oxygen. Naphthazarin was obtained and as this is now known to be 5 : 8-dihydroxy-1 : 4-naphthaquinone (Dimroth and Ruck, *Annalen*, 1926, **446**, 129) coupling must have occurred at both positions 4 and 5. The naphthazarin was identified merely by its physical appearance and a few colour reactions, a derivative possessing a melting point not being prepared.

In the present investigation, diazotised aniline was coupled with both 1 : 5- and 1 : 8-naphthylenediamine in aqueous hydrochloric acid–sodium acetate, acetic acid–sodium acetate, pyridine containing calcium carbonate, aqueous ethanol–sodium carbonate, and aqueous ethanol–potassium hydroxide. Under all conditions 1 : 5-naphthylenediamine yielded a mono- and a bis-azo-compound, and as the latter was less soluble in ethanol than the former, a separation was readily effected. The proportion of bisazo-compound increased as the medium became more basic and, as with 1 : 8-naphthylenediamine, an excess of caustic alkali produced intractable tars. Reduction of the monoazo-1 : 5-naphthylenediamine furnished a naphthalenetriamine dihydrochloride (Finzi, *loc. cit.*, describes the formation of a chlorostannate blackened instantly by alkalis) from which a naphthalenetriamine, m. p. 147°, and a tribenzamidonaphthalene, m. p. 282°, were obtained. These compounds would be expected to be 1 : 2 : 5- or 1 : 4 : 5-derivatives. 1 : 4 : 5-Trinitronaphthalene, obtained by nitrating 1 : 5-dinitronaphthalene (de Aguiar, *Ber.*, 1872, **5**, 904; Beilstein and Kuhlberg, *Annalen*, 1873, **169**, 97; Pascal, *Bull. Soc. chim.*, 1920, **27**, 397; Dimroth and Ruck, *loc. cit.*) on reduction and benzoylation yielded 1 : 4 : 5-tribenzamidonaphthalene, m. p. 312°, evidently not identical with the tribenzamidonaphthalene obtained from 1 : 5-naphthylenediamine. Clearly, unless anomalous *meta*-substitution has occurred, the monocoupling of diazobenzene occurs at position 2 over the whole pH range.

The results of coupling diazobenzene with 1 : 8-naphthylenediamine under differing conditions are illustrated qualitatively in Table II (p. 219), and briefly it may be stated that in acid or alkaline solution monocoupling predominated, whilst in acetic acid–sodium acetate the bisazo-compound alone was isolated. It is understandable that attack by the electrophilic coupling reagent on the diamine should be hindered under strongly acid conditions as the diamine will then, in all probability, be doubly protonised, but as the acidity is reduced the degree of protonisation will be lowered and the molecule will become more susceptible to electrophilic attack. With regard to coupling in alkaline media, it would appear that the attacking reagent is not so actively electrophilic as that which functions in neutral or mildly acid circumstances since the diamine can no longer be deactivated by protonisation. A complete explanation cannot be given because of the general obscurity concerning the nature of the coupling entity in alkaline media (Hodgson and Marsden, *J.*, 1945, 207).

Monophenylazo-1 : 8-naphthylenediamine, on reduction, yielded a naphthalenetriamine trihydrochloride, converted by aqueous potassium hydroxide into a crystalline naphthalenetriamine (cf. Finzi, *loc. cit.*). The tribenzoyl derivative of the latter gave no depression of melting point when mixed with an authentic specimen of 1 : 4 : 5-tribenzamidonaphthalene. Thus the monocoupling of diazobenzene to 1 : 8-naphthylenediamine occurs at position 4.

It is of interest to compare these results with the coupling reactions of other similarly constituted naphthalene compounds. According to Heller and Kretzschmann (*Ber.*, 1921, **54**, 1098), 1 : 8-dihydroxynaphthalene gives mono- and bis-azo-compounds, with the azo-links at positions 4 and 5. Apparently no data exist for 8-amino-1-naphthol itself; although its *N*-acetyl compound couples *para* to the hydroxyl group with diazotised aniline (Fichter and Gageur, *Ber.*, 1906, **39**, 3331), the *N*-toluene-*p*-sulphonyl compound produces a mixture of mono- and bis-azo-compounds of undetermined structure (Fichter and Kuhnel, *Ber.*, 1909, **42**, 4748). It is difficult to attach more than one azo-link to 1 : 5-dihydroxynaphthalene, and it couples in position 2 or 4 according to the nature of the diazonium compound and the conditions of coupling. Diazobenzene attacks position 4 (Fischer and Bauer, *J. pr. Chem.*, 1917, **95**, 261) whilst the important dye Diamond Black PV (C.I. 170) is made by the coupling of the diazo-oxide of 2-aminophenol-4-sulphonic acid at position 2. Porai-Koshits *et al.* have more recently made the important discovery that the attack of diazo-compounds on 5-amino-1-naphthol never occurs *para* to the amino-group, the only exception being diazotised H-acid (*J. Gen. Chem. Russia*, 1945, **15**, 446; 1947, **17**, 1758, 1807). It is clear that in the naphthalene series amino-groups have a greater tendency to bring about *ortho*-coupling than have hydroxyl groups.

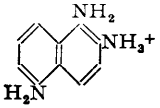
4-Phenylazo-1 : 8-naphthylenediamine reacted very slowly with boiling 90% formic acid yielding the perimidine, and could only be monoacylated with *p*-toluenesulphonyl chloride in pyridine solution, the product being, most likely, 1-amino-4-phenylazo-8-*p*-toluenesulphonamidonaphthalene. No isolable product was obtained by the action of *p*-toluenesulphonyl chloride on 2-phenylazo-1 : 5-naphthylenediamine in pyridine solution. This was surprising as it might have been reasonably expected that the chelating influence of the azogroup (Elkins and Hunter, *J.*, 1935, 1598; Hunter, *J.*, 1937, 320) on the one *ortho*-amino-group would have left the other free to react with the acylating agent. Attempts were made, without success, to determine the constitution of the bisazo-1 : 8-naphthylenediamine by reduction and benzoylation. 1 : 4 : 5 : 8-Tetrabenzamidonaphthalene, useful as a possible reference substance for future investigations, was made from 1 : 4 : 5 : 8-tetranitronaphthalene.

The dissociation constants of naphthalene-1 : 2 : 5- and -1 : 4 : 5-triamines were determined by potentiometric titration of their hydrochlorides in 50% aqueous ethanol. The hydrochlorides of 1 : 5- and 1 : 8-naphthylenediamines were titrated in like manner. The results are recorded in Table I. The constants for 1 : 5- and 1 : 8-naphthylenediamines are essentially in agreement with those found by Kuhn and Wassermann (*Helv. Chim. Acta*, 1928, **11**, 79). The discrepancy in the value of pK_2 for 1 : 5-naphthylenediamine is partly caused by the use by these authors of an empirical equation due to Bjerrum (*Z. Elektrochem.*, 1918, **24**, 321; *Z. physikal. Chem.*, 1923, **104**, 406), which is now known to be inaccurate.

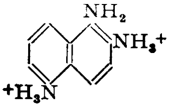
TABLE I.

		(14°).		Kuhn and Wassermann.	
	pK_3.	pK_2.	pK_1.	pK_2.	pK_1.
1 : 5-Naphthylenediamine	—	1·94	4·06	1·74 (19°)	4·07 (20°)
1 : 8-Naphthylenediamine	—	1·49	4·29	—	4·29 (17°)
Naphthalene-1 : 2 : 5-triamine	—	2·61	5·58	—	—
Naphthalene-1 : 4 : 5-triamine	*ca.* 2·4	*ca.* 2·4	5·89	—	—

The greater basicity of β-naphthylamine compounds compared with the corresponding α-compounds probably indicates structures (I) and (II) for the singly and doubly charged cations of naphthalene-1 : 2 : 5-triamine. The low value of K_1 for naphthalene-1 : 4 : 5-triamine ($1·29 \times 10^{-6}$) is near that for 1 : 4-naphthylenediamine ($2·88 \times 10^{-6}$), by far the strongest base among the naphthylenediamines investigated by Kuhn and Wassermann (*loc. cit.*). By analogy the first dissociation constant of naphthalene-1 : 4 : 5-triamine almost certainly involves the 1- or the 4-amino-group. As the second and third dissociation constants have been found to be virtually equal, the protonised amino-group of the singly charged cation must influence the other two amino-groups equally as regards the acceptance of hydrogen ions. A proton situated on the 1-amino-group would be unlikely to do this, and hence the structure of the singly charged cation of naphthalene-1 : 4 : 5-triamine is probably (III).



(I.)



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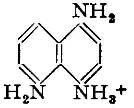

(III.)

EXPERIMENTAL.

(M. p.s are uncorrected.)

Dihydrochlorides of 1 : 5- *and* 1 : 8-*Naphthylenediamines*.—Benzene solutions of the pure diamines were treated with an excess of dry hydrogen chloride, and the white sludge was collected, washed with benzene, and dried at 50°. Both products were colourless solids, very soluble in water in contrast to the diamines which dissolve slowly in dilute hydrochloric acid.

Coupling of Diazobenzene to 1 : 5-*Naphthylenediamine*.—(a) *In aqueous hydrochloric acid–sodium acetate.* The diamine dihydrochloride (1·50 g.) in water (200 c.c.) was treated at 0° with benzenediazonium chloride [from 0·63 g. of aniline and 1·60 c.c. of hydrochloric acid (*d* 1·18), the solution having been freed from nitrous acid with urea]. Sodium acetate (10 g.) in water (100 c.c.) was then added at 0° with stirring, and after 1 hour the deep-red precipitate was collected, washed, and dried (1·5 g.). Crystallisation from ethanol yielded the less soluble *bisazo*-derivative (0·10 g.), which formed deep red needles, m. p. 240° (decomp.) (Found: C, 72·3; H, 5·1; N, 22·6. $C_{22}H_{18}N_6$ requires C, 72·1; H, 5·0; N, 22·9%), and the more soluble *monoazo*-derivative (0·94 g.), which separated in red needles, m. p. 148° (Found: C, 73·6; H, 5·5; N, 21·2. $C_{16}H_{14}N_4$ requires C, 73·3; H, 5·4; N, 21·4%).

The monoazo-compound imparted an orange-red colour to concentrated sulphuric acid, which changed to purplish-red in thin films and to pale orange on dilution with water. The bisazo-derivative gave a beautiful claret colour with the same reagent, turning to purplish-green in thin films and to blue on dilution with water.

(b) *In acetic acid–sodium acetate.* The addition of a nitrous acid-free solution of benzenediazonium chloride [from 0·61 g. of aniline and 1·60 c.c. of hydrochloric acid, *d* 1·18)] to a well stirred solution of the diamine (1 g.) in glacial acetic acid (125 c.c.), followed by the addition of sodium acetate (10 g.) in water (100 c.c.) at 0° and then 10% aqueous potassium hydroxide (*ca.* 200 c.c.), gave a precipitate of azo-compounds, which, crystallised from ethanol as above, gave the same amounts of mono- and bis-azo-derivatives.

(c) *In pyridine containing calcium carbonate.* 1 : 5-Naphthylenediamine (1 g.) in pyridine (80 c.c.) containing powdered calcium carbonate (1·5 g.) was treated at 0°, with stirring, with a solution of benzenediazonium chloride (from 0·62 g. of aniline, the solution having been freed from nitrous acid with urea and made neutral with calcium carbonate). After filtration, water (*ca.* 80 c.c.) was added to the solution, and the red crystalline precipitate which had a marked green reflex was collected (0·44 g.) and crystallised from ethanol. The bisazo-derivative separated in deep red needles (0·24 g.). Further addition of water (*ca.* 200 c.c.) to the pyridine solution precipitated the crude monoazo-compound (0·48 g.) which crystallised from ethanol in rosettes of needles (0·22 g.).

(d) *In aqueous ethanolic potassium hydroxide.* The diamine (1 g.) in ethanol (200 c.c.) containing sufficient potassium hydroxide to neutralise the mineral acid liberated in coupling, when treated with either one or two moles of benzenediazonium chloride, gave difficultly crystallisable mixtures of mono- and bis-azo-compounds.

Reduction of the Monoazo-compound.—The compound (0·70 g.) in ethanol (30 c.c.) was reduced, at 80°, with stannous chloride (1·75 g.) in *ca.* 12 c.c. of fuming hydrchloric acid. On cooling, the white precipitate of the *triamine dihydrochloride* (0·45 g.) was removed, washed with a little ethanol, and dried in a vacuum. A portion was crystallised by dissolution in the minimum quantity of aqueous ethanol and addition of alcoholic hydrogen chloride cautiously until precipitation of the colourless needles commenced (Found : C, 48·7; H, 5·5; N, 16·2; Cl, 27·4. $C_{10}H_{13}N_3Cl_2$ requires C, 48·8; H, 5·3; N, 17·1; Cl, 28·8%).

When the compound in a minimum quantity of water was treated cautiously with 20% potassium hydroxide solution at 0° it gave a colourless crystalline precipitate of *naphthalene*-1 : 2 : 5-*triamine*, m. p. 147° (Found : C, 68·7; H, 6·7; N, 24·0. $C_{10}H_{11}N_3$ requires C, 69·3; H, 6·4; N, 24·2%). Attempted crystallisation of this substance from ethanol gave a product less pure than the original material. Treatment of the hydrochloride with benzoyl chloride and aqueous potassium hydroxide gave the *tribenzoyl* derivative, which, though sparingly soluble, crystallised from glacial acetic acid in colourless needles, m. p. 282° (Found : C, 76·2; H, 5·0; N, 8·1. Calc. for $C_{31}H_{23}O_3N_3$: C, 76·7; H, 4·8; N, 8·7%) (Finzi, *loc. cit.*, gives m. p. 268°). The compound gave no depression of melting point when mixed with an authentic specimen of 1 : 4 : 5-tribenzamidonaphthalene, m. p. 312°, but the mixture decomposed with bubbling at 282°.

The triamine dihydrochloride (0·2 g.) was treated with toluene-*p*-sulphonyl chloride (0·44 g.) in hot (95°) pyridine. After 3 hours, dilution with water gave a precipitate which, crystallised repeatedly from ethanol (charcoal), gave a small yield of colourless crystalline material (needles), m. p. 145—155°, which analysed satisfactorily for 1 : 2 : 5-*tritoluene*-p-*sulphonamidonaphthalene* (Found : C, 57·6; H, 4·8. $C_{31}H_{29}O_6N_3S_3$ requires C, 58·6; H, 4·6%). The reaction between toluene-*p*-sulphonyl chloride and naphthalene-1 : 2 : 5-triamine dihydrochloride in aqueous sodium carbonate gave a similar product.

Coupling of Diazobenzene to 1 : 8-*Naphthylenediamine.*—Experiments, summarised in Table II, are considered in more detail below. 4-*Phenylazo*-1 : 8-*naphthylenediamine. Method A* (*a*). 1 : 8-Naphthylenediamine dihydrochloride (1·27 g.) in water (150 c.c.) was treated with a nitrous acid-free solution of benzenediazonium chloride, prepared from aniline (0·5 g.), hydrochloric acid (1·25 c.c.; *d* 1·18), and sodium nitrite (0·45 g.) in a minimum of water at 0°. A blue-violet colour developed but no precipitate appeared until sodium acetate (7·5 g.) in water (*ca.* 50 c.c.) was added. The red solid was collected, washed well with water and dilute aqueous ammonia, and dried in a vacuum (1·2 g.). It was dissolved in ethanol containing a few drops of ammonia (*d* 0·880) and water added until crystallisation commenced (1·03 g.). Recrystallisation from aqueous ethanol furnished light-scarlet plates of 4-*phenylazo*-1 : 8-*naphthylenediamine* (0·75 g.), m. p. 115° (Found : C, 73·1; H, 5·4; N, 21·2. $C_{16}H_{14}N_4$ requires C, 73·3; H, 5·4; N, 21·4%). The compound was soluble in most organic solvents, and very soluble in ether. It imparted an orange-yellow colour to concentrated sulphuric acid, which changed to violet-pink in thin films or on dilution with water.

Method B (*c*). The diamine (1·58 g.) in glacial acetic acid (150 c.c.) was treated with a neutral, nitrous acid-free solution of benzenediazonium chloride [from 0·93 g. of aniline, 2·40 c.c. of hydrochloric acid (*d* 1·18), and 0·75 g. of sodium nitrite in 12 c.c. of water]. Sodium acetate (7·5 g.) in water (100 c.c.) was then added with stirring. The violet precipitate (1·04 g.) was then worked up as described above.

Method B (*e*). This method was similar to *B* (*c*) except that conditions were kept as nearly anhydrous as possible, the sodium acetate (1·1 g.) being dissolved in the diamine–glacial acetic acid solution before the rapid addition of the benzenediazonium chloride solution. 4-*Phenylazo*-1 : 8-*naphthylenediamine monohydrochloride* separated from the solution in deep red needles possessing a green metallic lustre (m. p. >360°). It was extracted with boiling ethanol and dried (1·1 g.) (Found : C, 64·1; H, 5·2; N, 18·8; Cl, 12·0. $C_{16}H_{15}N_4Cl$ requires C, 64·3; H, 5·1; N, 18·8; Cl, 11·9%). The same compound was formed from the azo-compound and dry hydrogen chloride in glacial acetic acid solution.

Method D (*j*). A neutral nitrous acid-free solution of benzenediazonium chloride (from 0·93 g. of aniline) was added slowly to a vigorously stirred solution of 1 : 8-naphthylenediamine (1·58 g.) in 80% ethanol (400 c.c.) containing sodium carbonate (7 g.) at *ca.* 10°. The solution was then warmed to *ca.* 60° and water (*ca.* 300 c.c.) added until the red plates began to separate. Crystallisation from ethanol containing a few drops of aqueous ammonia (*d* 0·880) gave scarlet plates of 4-phenylazo-1 : 8-naphthylenediamine (1·02 g.; m. p. 115°).

The bisazo-compound. Method B (*d*). The procedure was similar to that of method *B* (*c*) except that the benzenediazonium chloride solution (2 moles), rendered free from nitrous acid with urea and from mineral acid with calcium carbonate, was run at 0° into the diamine (1·58 g.) in glacial acetic acid

(150 c.c.), to which sodium acetate (7·5 g.) in water (30 c.c.) had been added. The dark-violet precipitate was collected, washed, dried (vacuum), and crystallised four times from ethanol. The *bisphenylazo-*1 : 8-*naphthylenediamine* formed dark red needles (0·24 g.; m. p. 195°) (Found: C, 71·9; H, 5·1; N, 22·8. $C_{22}H_{18}N_6$ requires C, 72·1; H, 5·0; N, 22·9%). It was less soluble than the monoazo-derivative and gave a dark brown colour with concentrated sulphuric acid, becoming purplish-green in thin films and deep blue on dilution with water.

TABLE II.

	Diamine, moles.	PhN_2Cl, moles.	NaOAc, moles.	Mode of mixing.	Chief product.
Method A. 1 : 8-Naphthylenediamine dihydrochloride in water–benzenediazonium chloride–sodium acetate.					
(*a*)	1	1	10	Sodium acetate solution added to mixture of diamine and PhN_2Cl	Monoazo-compound
(*b*)	1	1	10	Diazonium solution run into diamine and sodium acetate	Bisazo-compound
Method B. 1 : 8-Naphthylenediamine in acetic acid–benzenediazonium chloride–sodium acetate.					
(*c*)	1	1	10	Sodium acetate added to diamine and PhN_2Cl	Monoazo-compound
(*d*)	1	1	10	Diazonium solution run into diamine–sodium acetate–acetic acid solution	Bisazo-compound
(*e*)	1	1	1½	Similar to (*d*). Rapid addition of diazonium solution	Monoazocompound monohydrochloride
(*f*)	1	2	6	Similar to (*d*)	Bisazo-compound
Method C. 1 : 8-Naphthylenediamine in pyridine containing calcium carbonate treated with a neutral solution of benzenediazonium chloride.					
(*g*)	1	1	—	—	Bisazo-compound
(*h*)	1	2	—	—	Bisazo-compound
(*i*)	1	3	—	—	Bisazo-compound
Method D. A neutral solution of benzenediazonium chloride added to an aqueous ethanolic solution of 1 : 8-naphthylenediamine containing sodium carbonate.					
(*j*)	1	1	—	—	Monoazo-compound
Method E. A neutral solution of benzenediazonium chloride added to an ethanol solution of 1 : 8-naphthylenediamine containing sufficient potassium hydroxide to permit the maximum degree of coupling.					
(*k*)	1	1	—	—	Monoazo-compound
(*l*)	1	2	—	—	Monoazo-compound
(*m*)	1	3	—	—	No cryst. product isolated

Reduction of 4-*Phenylazo*-1 : 8-*naphthylenediamine*.—The compound (1 g.) in hot ethanol (50 c.c.) was reduced with stannous chloride (3·5 g.) in fuming hydrochloric acid (20 c.c.). The initial violet precipitate became colourless and the crystalline *triamine trihydrochloride* (0·72 g.) was collected on cooling. A portion was crystallised from aqueous ethanol by adding alcoholic hydrogen chloride. The compound formed colourless needles (Found: C, 43·0; H, 5·0; N, 14·4; Cl, 36·8. $C_{10}H_{14}N_3Cl_3$ requires C, 42·5; H, 5·0; N, 14·9; Cl, 37·6%). 10% Sodium hydroxide solution furnished the crystalline *triamine*, m. p. 156° (Found: C, 69·0; H, 6·4; N, 23·5. $C_{10}H_{11}N_3$ requires C, 69·3; H, 6·4; N, 24·2%), which rapidly became oxidised when moist but was quite stable when dry.

The *tribenzoyl* derivative was made by treating the triamine hydrochloride (0·5 g.) with benzoyl chloride in dilute potassium hydroxide solution. The yellow residue (0·87 g.) crystallised from glacial acetic acid in colourless needles, m. p. 312° (Found: C, 76·7; H, 5·1; N, 8·1. $C_{31}H_{23}O_3N_3$ requires C, 76·7; H, 4·8; N, 8·7%).

1 : 4 : 5-*Tritoluene*-p-*sulphonamidonaphthalene* was obtained from the triamine hydrochloride (0·3 g.) and toluene-*p*-sulphonyl chloride (0·78 g.) in hot pyridine. The solid was precipitated with dilute hydrochloric acid and several crystallisations from ethanol (charcoal) gave crystalline material, m. p. *ca.* 150°, raised to 248° by two further crystallisations from toluene, in which the *compound* is only sparingly soluble (0·057 g.) (Found: C, 58·1; H, 4·6. $C_{31}H_{29}O_6N_3S_3$ requires C, 58·6; H, 4·6%).

6(7)-Phenylazoperimidine was made by refluxing 4-phenylazo-1 : 8-naphthylenediamine (0·2 g.) with 90% formic acid (10 c.c.) for 3 hours. The solution was poured into water and rendered alkaline with aqueous ammonia, and the scarlet gelatinous precipitate collected. It crystallised from ethanol with some difficulty, forming small prisms, darkening and decomposing continuously above 180° (Found: N, 20·2. $C_{17}H_{12}N_4$ requires N, 20·6%). The compound gave a vivid blue-green colour with concentrated sulphuric acid.

1-*Amino*-4-*phenylazo*-8-*toluene*-p-*sulphonamidonaphthalene* was prepared by heating together 4-phenylazo-1 : 8-naphthylenediamine (0·17 g.), pyridine (7 c.c.), and toluene-*p*-sulphonyl chloride (0·1 g.) on the water-bath for 2 hours. Addition of water gave a dark red precipitate which, after extraction with hot ethanol, crystallised from pyridine in dark red, very small needles, m. p. 238° (Found:

C, 65·9; H, 4·8; N, 13·7. $C_{23}H_{20}O_2N_4S$ requires C, 66·3; H, 4·8; N, 13·5%). Attempts to prepare the ditoluene-*p*-sulphonyl derivative failed, both in pyridine solution and in hot aqueous sodium carbonate suspension.

1 : 4 : 5-*Trinitronaphthalene*.—The methods described by de Aguiar, and Beilstein and Kuhlberg (*locc. cit.*), gave considerable amounts of 1 : 4 : 5 : 8-tetranitronaphthalene, which hindered the purification of the trinitro-compound. That of Dimroth and Ruck (*loc. cit.*) was satisfactory but inconvenient and the following was adopted. 1 : 5-Dinitronaphthalene (5 g.) was stirred into sulphuric acid (100 c.c.; *d* 1·84) and nitric acid (20 c.c.; *d* 1·42) was added slowly. The dinitro-compound dissolved and the trinitronaphthalene was precipitated. After 30 minutes it was collected on sintered glass, washed, dried, and crystallised from benzene. 1 : 4 : 5-Trinitronaphthalene separated in long yellow needles (1·84 g.), m. p. 149°, the surface of which sintered on evaporation of the solvent (Found : C, 45·5; H, 1·9; N, 16·0. Calc. for $C_{10}H_5O_6N_3$: C, 45·6; H, 1·9; N, 16·0%) (de Aguiar, *loc. cit.*, gives m. p. 154°; Dimroth and Ruck, *loc. cit.*, give m. p. 148—149°; Desvergnes, *Monit. Scient.*, 1926, **16**, 73, gives m. p. 147·8—148·3°).

FIG. 1.

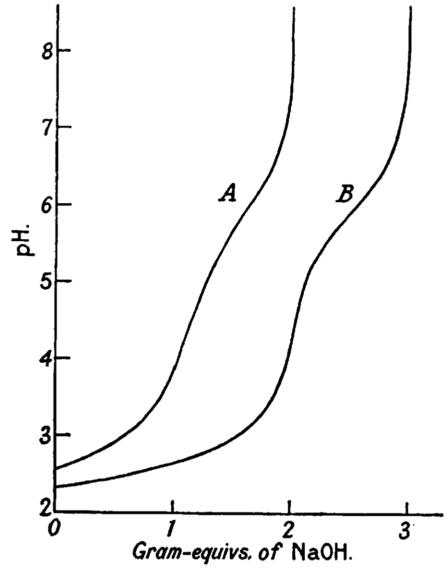

FIG. 2.

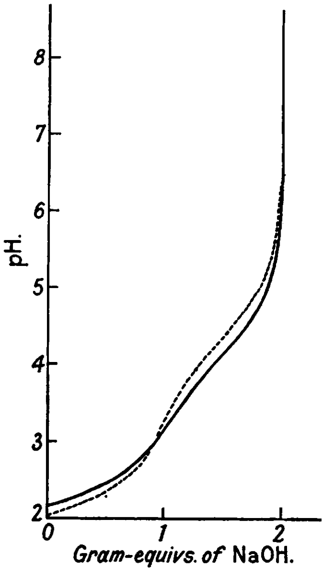

FIG. 1. A, *Naphthalene*-1 : 2 : 5-*triamine dihydrochloride* (38·2 *mg.*) *in* 50% (*v/v*) *ethanol* (20 *c.c.*).
B, *Naphthalene*-1 : 4 : 5-*triamine trihydrochloride* (35·4 *mg.*) *in* 50% (*v/v*) *ethanol* (20 *c.c.*).

FIG. 2. ———, 1 : 5-*Naphthylenediamine dihydrochloride* (69·9 *mg.*) *in* 50% (*v/v*) *ethanol* (20 *c.c.*).
– – – –, 1 : 8-*Naphthylenediamine dihydrochloride* (63·5 *mg.*) *in* 50% (*v/v*) *ethanol* (20 *c.c.*).

Hydrogen was bubbled through the solutions during the titrations.

Reduction of 1 : 4 : 5-*Trinitronaphthalene*.—The compound (1·5 g.) was warmed with ethanol (300 c.c. on the water-bath, and a solution of stannous chloride (14 g.) in fuming hydrochloric acid (45 c.c.) was added. The deep orange-coloured solution, on evaporation under reduced pressure in a stream of hydrogen, gave colourless crystals of a *stannichloride*, in which the triamine was presumably monoacidic (Found : Cl, 31·1, 31·4. $2C_{10}H_{11}N_3,H_2SnCl_6$ requires Cl, 31·3%) but the addition of concentrated hydrochloric acid or preferably ethanolic hydrogen chloride precipitated the triamine trihydrochloride (1·29 g.) (Found : C, 41·9; H, 5·1%). Basification gave the triamine, m. p. 156°, and the action of benzoyl chloride and aqueous potassium hydroxide on the latter produced 1 : 4 : 5-tribenzamidonaphthalene, m. p. 312° (Found : C, 76·0; H, 5·0. $C_{31}H_{23}O_3N_3$ requires C, 76·7; H, 4·8%).

1 : 4 : 5 : 8-*Tetrabenzamidonaphthalene*.—1 : 4 : 5 : 8-Tetranitronaphthalene (Will, *Ber.*, 1895, **28**, 367; Dimroth and Ruck, *loc. cit.*) was made by dinitrating 1 : 5-dinitronaphthalene. The latter (10 g.) was dissolved in nitric acid (100 c.c.; *d* 1·52) and sulphuric acid (100 c.c.; *d* 1·84) was added slowly at *ca.* 80°. After 30 minutes, ice was added to the solution until a crystalline precipitate appeared, which was collected on sintered glass, washed, and extracted with a little cold acetone. The residue (4·2 g.) was crystallised from nitrobenzene. 1 : 4 : 5 : 8-Tetranitronaphthalene (2·9 g.) formed pale yellow needles, darkening at *ca.* 280° and melting on rapid heating at *ca.* 340° (decomp.) (Found : C, 39·5; H, 1·3; N, 18·9. Calc. for $C_{10}H_4O_8N_4$: C, 39·0; H, 1·3; N, 18·2%) [Dimroth and Ruck, *loc. cit.*, give m. p. 340—345° (decomp.)].

The nitro-compound (0·5 g.) was heated under reflux with granulated tin (1·5 g.), hydrochloric acid (15 c.c.; *d* 1·18), and water (5 c.c.). After 1 hour the orange-brown solution was filtered, water (20 c.c.) was added, the solution was saturated with hydrogen sulphide, and the precipitated tin sulphides were removed. The solution was then evaporated under hydrogen at reduced pressure, neutralised with dilute potassium hydroxide solution (phenolphthalein), and poured into an emulsion of benzoyl chloride in dilute sodium carbonate solution. After 6 hours at 0°, the solution was acidified with dilute hydrochloric acid and filtered, and the residue was then extracted with warm (35°) dilute potassium hydroxide solution. Crystallisation from ethanol (charcoal) gave colourless prisms of 1 : 4 : 5 : 8-*tetrabenzamidonaphthalene* (0·023 g.), m. p. 233° (Found : C, 76·0; H, 4·0. $C_{34}H_{28}O_4N_4$ requires C, 75·5; H, 4·7%).

Bisphenylazo-1 : 8-naphthylenediamine (0·5 g.) was reduced with stannous chloride in aqueous ethanolic hydrogen chloride; the solution, added to a mixture of benzoyl chloride–aqueous potassium hydroxide at 0°, gave a product (0·7 g.), which on crystallisation from ethanol furnished benzanilide, m. p. 161°, alone and mixed with an authentic specimen.

Potentiometric Titration.—The cell employed was a glass electrode–calomel electrode system, the E.M.F. being measured by a Cambridge pH-meter. The glass electrode was first calibrated with solutions of known pH. The amine hydrochlorides were dissolved in 50% (v/v) air-free ethanol, and titrated with 0·1N-sodium hydroxide solution (carbonate-free) in an atmosphere of hydrogen at 14°. The results are shown graphically in Figs. 1 and 2. For the subsequent calculations, equations due to Britton (" Hydrogen Ions," London, Chapman and Hall, 1932, p. 198; cf. Noyes, *Z. physikal. Chem.*, 1893, **11**, 495) were employed. For the diacidic amines the ionic equilibria are

$$R(NH_2)(NH_3^+) \rightleftharpoons R(NH_2)_2 + H^+$$

$$R(NH_3^+)_2 \rightleftharpoons R(NH_2)(NH_3^+) + H^+$$

with dissociation constants $K_1 = \frac{[R(NH_2)_2][H^+]}{[R(NH_2)(NH_3)]^+}$ and $K_2 = \frac{[R(NH_2)(NH_3^+)][H^+]}{[R(NH_3^+)_2]}$ respectively.

If c = total concentration of the diamine, a = total concentration of the added alkali, and h = hydrogen ion concentration, then for any point on the titration curve parameters A, B, and D are given by $A = h(a + h - c)$; $B = 2c - (a + h)$; $D = h^2(a + h)$, and the dissociation constants by the expressions

$$K_1 = \frac{A_1D_2 - A_2D_1}{B_1D_2 - B_2D_1} \text{ and } K_2 = \frac{B_1D_2 - B_2D_1}{A_1B_2 - A_2B_1}.$$

Activity coefficients were not used in the calculations as at the dilution of the solutions under observation they would be approximately unity. In determining the three dissociation constants of 1 : 4 : 5-naphthalenetriamine, the shape of the pH titration curve made it obvious that the Henderson equation (*J. Amer. Chem. Soc.*, 1908, **30**, 954) was applicable, without serious error, over the last-third portion of the curve in order to evaluate K_1. K_2 and K_3 $\left\{= \frac{[R(NH_2)(NH_3^+)_2][H^+]}{[R(NH_3^+)_3]}\right\}$ were then determined by applying the Britton equations over the first-two-thirds portion of the curve.

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