482. *The Formation of Isomeric Azo-compounds in the Coupling of Diazonium Salts with* 1-*Naphthylamine.*

By Harold S. Turner.

The mixtures of 2- and 4-arylazo-1-naphthylamines formed by coupling benzene- and substituted benzene-diazonium salts with 1-naphthylamine have in several cases been separated by adsorption chromatography, and the components isolated and characterised. The absorption spectra of these compounds over the range 220—580 mμ. have been determined.

Gattermann and Liebermann (*Annalen*, 1912, **393**, 198) coupled various substituted benzenediazonium compounds with 1-naphthylamine-5-sulphonic acid (Laurent's acid) and determined the ratio of the 2- and 4-isomers produced by reducing the mixture and separating the 1 : 2- and 1 : 4-naphthylenediamine-5-sulphonic acids by fractional crystallisation. They concluded that, in the coupling of benzenediazonium compounds with this acid, (*a*) the more negative the substitution of the diazo-component the greater the tendency to coupling in the 4-position (sulphanilic acid, coupling exclusively in the 2-position, was an exception), and (*b*) an increase in the acidity of the coupling medium favours coupling in the 2-position. The 2-isomers were not isolated from the mixtures which were usually produced.

It has long been realised that, similarly, when diazonium compounds are coupled with 1-naphthylamine a mixture of the 2- and 4-aminoazo-compounds is produced, in which the latter is the major component. The formation of the 2-aminoazo-compound is a source of loss when the aminoazo-compound is required as an intermediate in the preparation of polyazo-compounds, since the 2-aminoazo-compounds do not diazotise normally, and it has been claimed that suitable modification of the amino-group of 1-naphthylamine will suppress *o*-coupling. For example, formation of the methyl-ω-sulphonate or of the toluene-*p*-sulphonyl derivative is said to have this effect, and it is claimed that 1-sulphaminonaphthalene couples exclusively in the 4-position (Bayer, B.P. 238,683). Nevertheless, the simple 2-arylazo-1-naphthylamines have not been described in the literature, only those with additional substituents in the naphthalene nucleus having been obtained.

The mixtures of isomers obtained by coupling diazotised aniline and several substituted anilines (*p*-methyl-, *p*-methoxy-, *m*- and *p*-chloro-) with 1-naphthylamine have now been separated by adsorption chromatography on alumina. With the exception of diazotised *m*-chloroaniline, which was coupled in dilute hydrochloric acid, the couplings were carried out in aqueous acetic acid–sodium acetate. The chromatograms obtained were generally complex, often containing more than 12 distinct zones, the *o*- and *p*-aminoazo-compounds being the principal components. Most of the products of decomposition and of side reactions which gave rise to the minor zones were more strongly adsorbed than the two main products, and of these the *p*-compound was the more strongly adsorbed. The large number of products formed in addition to the *o*- and *p*-aminoazo-compounds can be ascribed to all the possibilities of diazo-interchange, of decomposition of the diazonium to hydroxyl compounds, and of subsequent coupling. In no case did the material recovered from these zones exceed 2·5% of the total weight of crude coupling product. There was no indication that diazoamino-compounds were present in the crude coupling products, even where coupling was carried out in aqueous acetic acid–sodium acetate, though trace quantities cannot be excluded. In general, the formation

FIG. 1.

Thermal diagram of 2- *and* 4-p-*chlorobenzeneazo*-1-*naphthylamine.*

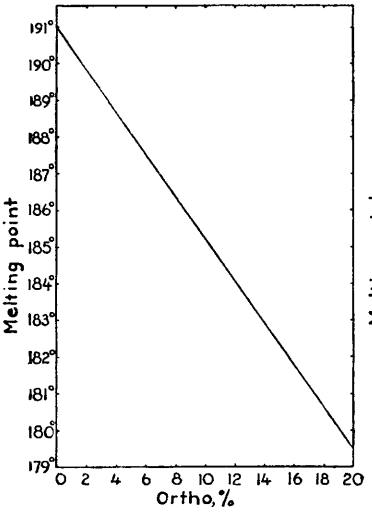
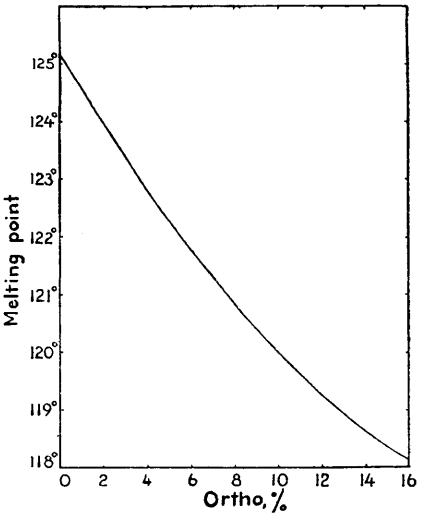


FIG. 2.

Thermal diagram of 2- *and* 4-p-*methoxybenzeneazo*-1-*naphthylamine.*



of 1-phenyl-3-naphthyltriazens occurs under these conditions only when the reactivity of the naphthyl radical is reduced by suitable substitution or direct blocking (cf. Dwyer, *J. Roy. Soc. N.S.W.*, 1940, **74**, 99; Morgan, *J.*, 1905, **87**, 86, 935). 1-Phenyl-3-naphthyltriazen has, however, been prepared by the interaction of α-azidonaphthalene and phenylmagnesium bromide (Dimroth, *Ber.*, 1906, **39**, 3905).

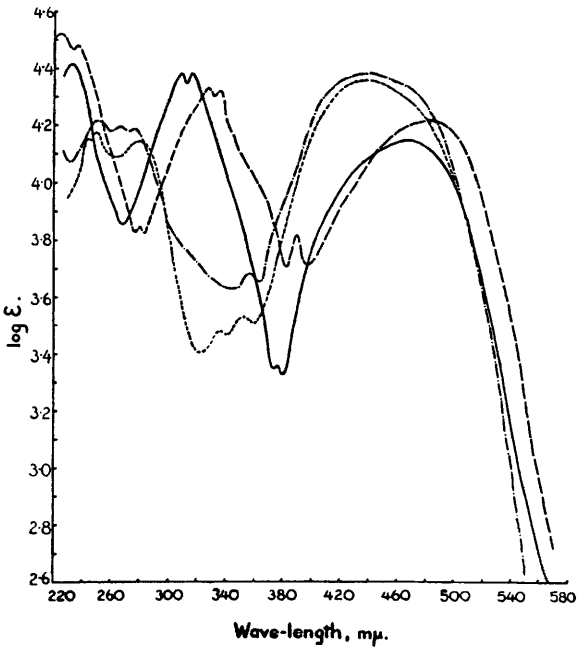
In the case of aniline, *p*-toluidine, and *m*-chloroaniline the recovery of combined *o*- and *p*-compounds from the coupling product was 95—100%, and here the proportion of the isomers was obtained by direct weighing. In the case of *p*-chloroaniline and *p*-anisidine the *p*-isomers appeared to decompose rapidly on the alumina, and the total recovery was 80 and 41%, respectively, though pure samples of each isomer were obtained. No extensive attempt was made to find a more suitable adsorbent. The proportions of the isomers were determined by constructing thermal diagrams (Figs. 1 and 2) from the pure isomers and referring to these the melting points of the crude coupling mixtures. This procedure suffers from the disadvantage that the coupling mixture contains compounds other than the *o*- and *p*-isomers, and so a falsely high value for the *o*-content would be expected. A rapid chromatographic separation was, therefore, attempted with the object of separating the combined adjacent *o*- and *p*-zones from the other products. The product, however, had a lower melting point than the crude mixture. There was, nevertheless, such a close correspondence between the apparent *o*-content of the crude coupling mixture as obtained from the melting point (which would in any case be in the nature of an upper limit) and as estimated from the actual quantity of *o*-isomer isolated from the

coupling mixture by the chromatographic separation (which would set a lower limit) that the method seems justified. Further, it may be deduced that the *o*-isomers were not appreciably decomposed during the separation.

The results obtained are summarised in Table I. From this it may be seen that, over the small range of compounds investigated, when a *p*-substituted benzenediazonium salt coupled with 1-naphthylamine in acetic acid–sodium acetate, the proportion of *o*-coupling increased with the electron-releasing character of the substituent. This parallels Gattermann and Liebermann's generalisation based on the coupling of Laurent's acid.

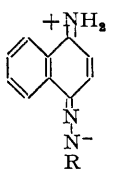
The simple 2-*benzeneazo*-1-*naphthylamines* have not previously been described. The orientation of the 2- and the 4-isomers was determined by conversion into the phenanthrazine, and into *NN'*-diacetyl-1 : 4-naphthylenediamine, respectively.

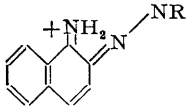
FIG. 3.



———— 2-*Benzeneazo*-1-*naphthylamine*.
— — — — 2-p-*Methoxybenzeneazo*-1-*naphthylamine*.
- - - - - - 4-*Benzeneazo*-1-*naphthylamine* (*cf., for example, Krüss*, Z. physikal. Chem., 1905, **51**, 257; *Shatenshtein*, Acta Physicochim. U.R.S.S., 1938, **10**, 121; 1940, **12**, 73).
— · — · — 4-p-*Methoxybenzeneazo*-1-*naphthylamine*.

In the analysis of the crude coupling mixtures obtained from diazotised *p*-toluidine and *p*-chloroaniline, three major zones were obtained instead of the usual two. The two more strongly adsorbed zones in each case gave the ordinary 4-isomer on elution and isolation. Here it would appear that partial (at least) separation into labile *cis*- and *trans*-isomers of the 4-isomer took place on the column (cf. Hartley, *J.*, 1938, 633; Cook, *J.*, 1938, 876; 1939, 1309; Zechmeister, Frehden, and Jörgensen, *Naturwiss.*, 1938, **26**, 495).

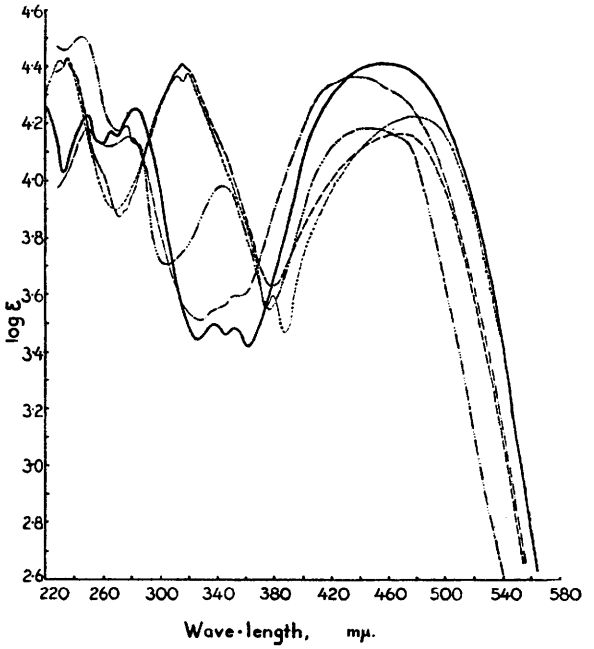
(I.) 


(II.)

The absorption spectra of these compounds in methanol have been determined over the range 220—580 mμ. The principal maxima are listed in Table II, and the spectra reproduced in Figs. 3 and 4. No attempt is made to analyse these spectra in detail, in the absence of the

spectra of suitable reference substances, but it is pointed out that, relatively to the *p*-isomers, there is in the *o*-isomers a general shift of the absorption maxima to longer wave-lengths. The *o*-isomers have a much greater total absorption in the ultra-violet region than the *p*-, and this probably indicates the presence of greater strain in their molecules. This would be expected from the ionic resonance structures possible in the two cases (I and II) (cf. Bergmann and Weizmann, *Trans. Faraday Soc.*, 1936, **32**, 1318), electromeric displacements in the former case involving the longer path. In the case of 2- and 4-nitro-1-naphthylamines, there are similar tendencies, the *o*-isomer having a much greater ultra-violet absorption (Hodgson and Hathway, *ibid.*, 1945, **41**, 115).

FIG. 4.



– – – – – – – – – 2-p-*Chlorobenzeneazo*-1-*naphthylamine*.
— — — — — 2-p-*Tolueneazo*-1-*naphthylamine*.
———————— 4-p-*Chlorobenzeneazo*-1-*naphthylamine*.
— · — · — · — 4-p-*Tolueneazo*-1-*naphthylamine* (*cf.* e.g., *Krüss*, loc. cit.).
— · · · — · · · — 1-p-*Tolueneazo*-2-*naphthylamine* (*cf.* e.g., *Krüss*, loc. cit.).

TABLE I.

Azo-1-*naphthylamines*, R·N:N·$C_{10}H_6$·NH_2.

R =	Recovery, *o*- + *p*-, %.	Yield based on total, *o*- + *p*-. *o*-, %.	*p*-, %.	M. p., *o*-.	M. p., *p*-.	M. p., acetyl deriv. of *p*-.	Note.
Phenyl	94·75	7	93	161—161·5°	125°	242—243°	(1)
p-Tolyl	99·5	7	93	126	149—150	240—241	(1)
p-Methoxyphenyl	41	9·9	90·1	150·5—151·5	125·2	226—227	(1) (3)
p-Chlorophenyl...	80	5·8	94·2	171·5—172	191·0	254—255	(1) (3)
m-Chlorophenyl	96·5	8·1	91·9	151	121	240—241	(2)

(1) Acetate–acetic acid coupling medium.
(2) Dilute hydrochloric acid medium.
(3) Percentages of isomers from thermal diagrams.

EXPERIMENTAL.

(Microanalyses are by Mr. E. S. Morton. All m. p.s are uncorrected.)

Carefully purified intermediates were used in preparing the aminoazo-compounds. The alumina used was Spence's Grade " O ".

Coupling Procedure.—Diazotised *m*-chloroaniline was coupled by method B, all other diazotised amines by method A.

Method A. 1-Naphthylamine hydrochloride (0·025 g.-mol.) in water (80 c.c.) was added slowly to a sodium acetate–acetic acid solution (3·3N-sodium acetate, 0·33N-acetic acid; 25 c.c.) containing as a dispersing agent a polyglycerol oleic ester (50%; 1·0 c.c.) at 0° (external ice-cooling).

The amine hydrochloride (0·0251 g.-mol.), hydrochloric acid (*d* 1·18; 1·5 × 0·0251 g.-mol.), ice (10 g.), and water (30 c.c.) were treated with 2N-sodium nitrite to a starch–iodide end-point. The very slight excess of nitrous acid was removed by a little aqueous sulphamic acid. The diazonium solution thus obtained was added dropwise during ½ hour to the stirred ice-cold suspension of 1-naphthylamine, and stirring continued overnight at 0—2°. 2N-Sodium hydroxide was added to the suspension until it was alkaline to Clayton-yellow. The azo-compound was filtered off, washed very thoroughly, and the moist cake transferred with water (100 c.c.) to a Kilner jar. 2N-Sodium hydroxide (5 c.c.) was added, and the whole milled with porcelain beads for 24 hours. After being warmed to effect coagulation, the mixture was filtered, and the azo-compound thoroughly washed and vacuum-dried. The use of the dispersing agent to disperse the 1-naphthylamine minimises contamination by products of side reactions, but the final milling process with alkali is necessary to remove it as otherwise it appears to form a benzene-insoluble material with the aminoazo-compounds.

Method B. The diazonium solution was added dropwise during ½ hour to an ice-cold solution of 1-naphthylamine hydrochloride (0·025 g.-mol.) in water (150 c.c.), N-hydrochloric acid (2·0 c.c.), and polyglycerol oleic ester (50%; 1·0 c.c.). The mixture was stirred overnight at 0—2° and then worked up as before.

Separation of the Crude Coupling Mixtures.—(a) *Aniline → 1-naphthylamine.* The crude product (7·50 g.; m. p. 116—119°) in benzene (400 c.c.) was separated on a column (6·5 × 41 cm.). Development with benzene (22 l.) gave a chromatogram consisting of 2 main zones and several more strongly adsorbed minor zones. The zones were separated by draining and extrusion, and the adsorbed material extracted by pure methanol and isolated by evaporation *in vacuo*. The more strongly adsorbed zone gave 4-benzeneazo-1-naphthylamine (6·60 g.), and the less strongly adsorbed zone gave 2-*benzeneazo*-1-*naphthylamine* (0·50 g.). Both were chromatographically pure. The recovery was *ca.* 95%, of this *ca.* 93% being the *p*-, and 7% the *o*-isomer. The latter separated from benzene–light petroleum in deep orange-red plates, m. p. 161—161·5° (Found: C, 78·0; H, 5·35; N, 16·6. $C_{16}H_{13}N_3$ requires C, 77·75; H, 5·26; N, 17·0%). 2-Benzeneazo-1-naphthylamine was converted into the phenanthrazine as follows. A solution of the compound (0·05 g.) in 50% acetic acid (5·0 c.c.) and 10N-hydrochloric acid (0·25 c.c.) was boiled under reflux and treated carefully with zinc dust until colourless. The hot solution was filtered into sodium acetate solution (3·3N; 1·0 c.c.), and the residue rinsed with boiling water (0·5 c.c.). The combined filtrates were mixed with a solution of phenanthraquinone (0·05 g.) in sodium hydrogen sulphite solution (40%; 1·5 c.c.) and water (3·0 c.c.) and heated on the water-bath. A yellow precipitate of 1 : 2-3 : 4-5 : 6-tribenzphenazine was deposited, and crystallised from benzene as a yellow microcrystalline powder, m. p. 277—277·5° (Found: C, 87·3; H, 4·0; N, 8·3. Calc. for $C_{24}H_{14}N_2$: C, 87·4; H, 4·3; N, 8·5%), identical with an authentic specimen prepared from 1-*p*-tolueneazo-2-naphthylamine (Lawson, *Ber.*, 1885, **18**, 2421, gives m. p. 273°). Both samples dissolved in sulphuric acid to give an intense blue coloration, and their solutions in benzene showed a strong blue fluorescence.

The *p*-isomer was crystallised from carbon tetrachloride–light petroleum, and several times from benzene–light petroleum. It formed deep-red needles, m. p. 125° (Michaelis and Erdmann, *Ber.*, 1895, **28**, 2197, give m. p. 123°). The *N*-acetyl derivative separated from glacial acetic acid in deep-orange needles, m. p. 242—243° (Michaelis and Erdmann give m. p. 233°) (Found: C, 74·85; H, 5·5. Calc. for $C_{18}H_{15}ON_3$: C, 74·7; H, 5·22%). When this was reduced by sodium hydrosulphite (dithionite) and acetylated, *NN'*-diacetyl-1 : 4-naphthylenediamine was formed, identical with an authentic sample.

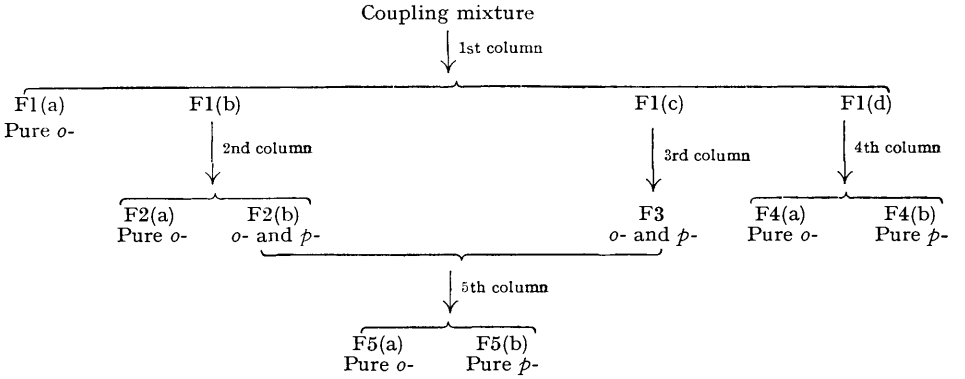
(b) p-*Toluidine → 1-naphthylamine.* The mixture of isomers (6·74 g.; m. p. 142—143°) was separated on a column (7 × 38 cm.). The chromatogram was developed (*a*) by carbon tetrachloride containing 3% by volume of ethyl acetate (7·5 l.), (*b*) by carbon tetrachloride containing 3% by volume of chloroform (7·5 l.), and (*c*) by carbon tetrachloride (2·5 l.) Separation into several minor and three well-defined major zones had occurred, the most strongly adsorbed of the latter being orange-yellow, the next maroon, and the next orange. The first of these on elution with methanol, followed by evaporation gave a product which was further separated on a small column, giving 3 small and a major red zone. The last yielded 4-*p*-tolueneazo-1-naphthylamine (0·50 g.). The second zone of the original chromatogram was chromatographically pure, and also gave the *p*-isomer (5·745 g.). The third zone gave a product which on further chromatographic separation gave a number of minor products and a major fraction, 2-p-*tolueneazo*-1-*naphthylamine* (0·465 g.), which crystallised from light petroleum (b. p. 80—100°) in red needles, m. p. 126° (Found: C, 78·1; H, 5·9; N, 16·35. $C_{17}H_{15}N_3$ requires C, 78·2; H, 5·75; N, 16·1%). It was converted into the phenanthrazine (m. p. 276—277°) as described above.

The *p*-isomer was crystallised from benzene–light petroleum, giving very deep-red needles, m. p. 149—150° (Weselsky and Benedikt, *Ber.*, 1879, **12**, 229, give m. p. 145°) (Found: C, 78·0; H, 5·65; N, 16·2%). The N-*acetyl* derivative crystallised from glacial acetic acid in orange-yellow needles, m. p. 240—241° (Found: C, 75·5; H, 5·7. $C_{19}H_{17}ON_3$ requires C, 75·2; H, 5·3%). This was converted into *NN'*-diacetyl-1 : 4-naphthylenediamine, identical with an authentic sample.

The recovery of *o*- and *p*-isomers was 6·71 g. or 99·5%, of which 93% was *p*- and 7% *o*-.

(c) p-*Anisidine → 1-naphthylamine.* The mixture of isomers (7·50 g.; m. p. 120·0°, shrinking above 105°) in benzene (250 c.c.) was separated on a column (65 × 7 cm.). Development with benzene (145 l.) gave a chromatogram showing 7 zones, the two principal zones, corresponding to the *o*- and the *p*-isomer, being most weakly adsorbed. The separation of the zones was not nearly complete, and a fractionation procedure was adopted as shown below. The chromatogram was divided into 4 fractions: F1(a) of pure *o*-isomer; F1(b), and *op*- mixture, largely *o*-; F1(c), an *op*-mixture, largely *p*-; F1(d), an *op*-mixture, containing only traces of *o*-, together with traces of zones corresponding to products of side reactions. These were treated as indicated in the scheme. F1(c) could not be separated on the third column, owing to the narrowness of the poorly defined zones; when it was combined with F2(b), a sharp and easy separation was achieved. Fractions F1(a), F2(a), F4(a), and F5(a) were chromatographically

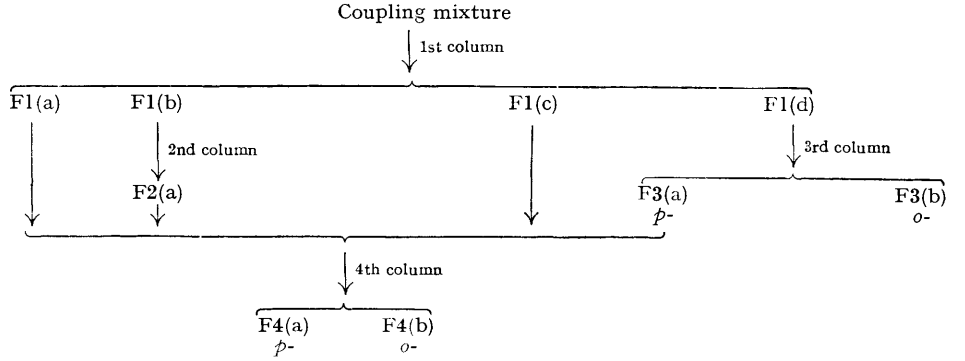
pure *o*-isomer (total : 0·73 g.). 2-p-*Methoxybenzeneazo*-1-*naphthylamine* crystallised from benzene–light petroleum in orange plates, m. p. 150·5—151·5° (not raised by further crystallisation from a variety of solvents) (Found : C, 73·4; H, 5·0; N, 15·3. $C_{17}H_{15}ON_3$ requires C, 73·65; H, 5·45; N, 15·15%). A sample was converted into the phenanthrazine, m. p. 277—278°, identical with an authentic specimen.



Fractions F4(b) and F5(b) consisted of *p*-isomer, but owing to decomposition during separation they were isolated in a tarry condition. A rapid re-separation on alumina, using benzene as developing solvent, gave a very complex chromatogram of 19 zones. Of these, 15 narrow zones, mainly purple or brown, were more strongly adsorbed than the principal zone of the *p*-isomer. This zone only was isolated, giving the *p*-isomer (2·33 g.) in a chromatographically pure condition. Crystallisation from light petroleum gave red needles, m. p. 125·2°. 4-p-*Methoxybenzeneazo*-1-*naphthylamine*, although mentioned in the literature, has not hitherto been analysed (cf. Vorländer, *Z. angew. Chem.*, 1930, **43**, 13; Weygand *et al.*, *J. pr. Chem.*, 1941, **158**, 266) (Found : C, 73·7; H, 5·35; N, 15·2%). The N-*acetyl* derivative, orange needles from glacial acetic acid, had m. p. 226—227° (Found : C, 71·35; H, 5·35; N, 13·4. $C_{19}H_{17}O_2N_3$ requires C, 71·5; H, 5·36; N, 13·16%). Reduction and acetylation gave *NN'*-diacetyl-1 : 4-naphthylenediamine, identical with an authentic sample.

The recovery of the isomers was only 41%. The recovery of *o*-isomer was equivalent to an *o*-content in the crude coupling of at least 9·7%.

(d) p-*Chloroaniline* → 1-*naphthylamine*. The mixed isomers (5·00 g.; m. p. 187·6°) in benzene (1 l.) were analysed on a column (7·5 × 40 cm.), benzene (23 l.) being used as developer. The incompletely resolved bands of *o*- and *p*-isomers were separated from impurities forming separate bands, and the adsorbed material recovered normally. It was re-separated on a similar column, and developed with benzene (30 l.). The three adjacent principal bands, red, maroon, and orange (in order of decreasing affinity for the adsorbent), were poorly defined. After extrusion, they were separated into 4 fractions (see following scheme), and the adsorbed materials recovered. F1(a) comprised most of the red zone with a little of a more strongly adsorbed zone of impurity. F1(b) included the remainder of the red zone and part of the maroon; F1(c) contained the rest of the maroon, together with a little of the orange; and F1(d) contained a little of the maroon plus all that remained of the orange zone.



A further separation of F1(b) was attempted on a smaller column. No separation took place under the same conditions as gave a separation of the crude mixture, and it appeared to be chromatographically pure. It was eluted from the column and recovered, giving F2(a). The red and the maroon zone are probably labile geometrical isomers of 4-*p*-chlorobenzeneazo-1-naphthylamine, incompletely separated on the column and isomerised by the isolation procedure here adopted. F1(d) was completely separated into 2 zones, F3(a) and F3(b), being *p*- and *o*-isomer, respectively. Finally, F1(a), F2(a), F1(c) and F3(a) were combined and re-separated on a column (7·5 × 40 cm.) and developed with benzene (75 l.). The two main zones were clearly defined and easily separated from one another and from 2 additional narrow zones of impurities.

In this way 2-p-*chlorobenzeneazo*-1-*naphthylamine* (0·28 g.) and its 4-isomer (3·71 g.) were isolated. The former crystallised from light petroleum in red needles, m. p. 171·5—172° (Found : C, 68·25; H, 4·2; N, 14·8; Cl, 12·75. $C_{16}H_{12}N_3Cl$ requires C, 68·25; H, 4·26; N, 14·9; Cl, 12·6%). It was converted into the phenanthrazine, m. p. 278—279°, identical with an authentic specimen.

The *p*-isomer separated from benzene–light petroleum in bright orange needles, m. p. 191·0° (Tröger and Petrowski, *Arch. Pharm.*, 1887, **225**, 160, give m. p. 187·5—188°) (Found : C, 68·0; H, 4·25; N, 14·55; Cl, 12·5%). The *acetyl* derivative, yellow-orange felted needles from glacial acetic acid, had m. p. 254—255° (Found : C, 66·85; H, 4·3; Cl, 10·85. $C_{18}H_{14}ON_3Cl$ requires C, 66·75; H, 4·35; Cl, 10·95%). Reduction and acetylation gave *NN'*-diacetyl-1 : 4-naphthylenediamine, identical with an authentic sample. The recovery of *o*- and *p*-isomers from the original mixture was 80%. The quantity of *o*-isomer isolated represents a minimum original content of 5·6%.

(e) m-*Chloroaniline* → 1-*naphthylamine*. The mixed isomers (6·00 g.; m. p. 109·5—112·5°) in benzene (250 c.c.) were added to a column (6·5 × 30 cm.) and developed by the same solvent (11 l.). A good separation took place into the two main and a number of minor zones. 4- (5·30 g.) and 2-*m*-chlorobenzeneazo-1-naphthylamine (0·47 g.) were thus obtained in 96·5% yield, with 8·1% *o*- and 91·9% *p*-. The *p*-compound separated from light petroleum in deep red prisms with a brilliant deep-green reflex, m. p. 121° (Tröger and Schaefer, *J. pr. Chem.*, 1926, **113**, 268, give m. p. 116°). From light petroleum (b. p. 80—100°) containing 20% of benzene the compound first crystallised in light-red needles. On being kept at room temperature these gradually dissolved and were replaced by the deep-red prisms (Found : C, 67·95; H, 3·9; N, 14·95; Cl, 12·45. Calc. for $C_{16}H_{12}N_3Cl$: C, 68·25; H, 4·3; N, 14·9; Cl, 12·6%). The *acetyl* derivative, orange-yellow felted needles from glacial acetic acid, had m. p. 240—241° (Found : C, 66·85; H, 4·05; Cl, 10·8. $C_{18}H_{14}ON_3Cl$ requires C, 66·75; H, 4·35; Cl, 10·95%). Reduction and acetylation of this compound gave *NN'*-diacetyl-1 : 4-naphthylenediamine, identical with an authentic sample. The 2-m-*chlorobenzeneazo*-1-*naphthylamine* separated from carbon tetrachloride–light petroleum in deep red needles, m. p. 151° (Found : C, 68·05; H, 4·35%). The phenanthrazine had m. p. 279°, and was identical with an authentic sample.

Thermal Diagrams.—Synthetic mixtures of the pure *o*- and *p*-isomers were prepared so as to cover the desired range and fused in carefully cleaned ignition tubes by immersion in an oil-bath approximately 10° above the m. p. of the pure *p*-isomer. The mixtures of *p*-chlorobenzeneazo-1-naphthylamines solidified to crystalline masses immediately on cooling; those of *p*-methoxybenzeneazo-1-naphthylamines formed glasses which became crystalline when scratched and kept at 40—50° for 12 hours. Owing to the intense colour of these mixtures it was not possible to detect the final disappearance of the solid phase in a conventional apparatus. The m. p.s were, therefore, taken on a heated-stage polarising microscope, the finely powdered specimens being spread thinly and uniformly between two carefully cleaned and dried microscope cover-glasses. The microscope was focussed on the edge of the aperture through the stage, and the specimen viewed between crossed polarisers. The stage could be heated at a rate of about 0·2° per minute in the desired region, and the m. p. was taken when a definite wave of extinction spread across the field of view from the edge of the aperture. Results were repeatable to within 0·1—0·2°. The diagrams obtained are reproduced in Figs. 1 and 2.

The mixture of isomers obtained by coupling *p*-anisidine with 1-naphthylamine was, without further purification, fused and ground in exactly the same manner as the synthetic mixtures; it melted at 120·0°. This corresponds to an *o*-content of 9·9%, in close agreement with the minimum value of 9·7% set by actual isolation. An attempt to separate the combined *o*- and *p*-isomers from impurities by means of a rapid chromatographic separation on alumina gave a product of m. p. 117·0—117·3° (corresponding to about 20% of *o*-), much lower, instead of higher, than the crude coupling mixture. The product so obtained was chromatographically less pure that the starting material.

The coupling mixture from *p*-chloroaniline was similarly treated. It melted at 187·6°, corresponding to 5·8% of *o*-, agreeing well with the 5·6% actually isolated. Here again a rapid chromatographic separation gave a more impure product, with a considerably lower m. p. (186·3—186·5°) than the crude coupling mixture.

TABLE II.

*Absorption Maxima of Arylazo-*1*-naphthylamines*, $R{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH_2$.

R.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε
2-C_6H_5	232	4·413	—	—	—	—	309	4·385	377	3·36	468	4·16
							315·5	4·385				
2-*p*-C_6H_4Me	235·5	4·43	—	—	273	3·88	315	4·415	—	—	468	4·17
					275 *	3·895						
2-*p*-$C_6H_4{\cdot}OMe$	223·5	4·52	—	—	279	3·845	327·5	4·327	389	3·815	469	4·219
	235·5	4·48					335·5	4·320				
2-*p*-C_6H_4Cl	230	4·42	—	—	—	—	312	4·37	379	3·60	480	4·23
	235	4·43					319	4·38				
4-C_6H_5	—	—	244·5	4·155	279	4·146	—	—	336·5	3·485	438	4·36
			249·5	4·18					352	3·53		
4-*p*-C_6H_4Me	—	—	247 *	4·175	278	4·155	—	—	340 *	3·55	440	4·37
			249	4·19					353 *	3·60		
4-*p*-$C_6H_4{\cdot}OMe$	—	—	250	4·215	265	4·195	—	—	357	3·685	455	4·385
					275	4·185						
4-*p*-C_6H_4Cl	—	—	249·5	4·23	265	4·175	—	—	338	3·495	458	4·408
					283	4·255			351·5	3·48		
1-*p*-Tolueneazo-2-naphthylamine	—	—	246	4·505	276	4·195	—	—	346	3·88	446	4·18
					283 *	4·14			373 *	3·58		

* = Point of inflexion.

Absorption Spectra.—The compounds, crystallised as described, were amply pure for these determinations. The solvent in every case was absolute methanol (AnalaR quality). The spectra of 2- and 4-*p*-tolueneazo-1-naphthylamine and of 1-*p*-tolueneazo-2-naphthylamine (added for comparison) were determined on a Beckman Photoelectric Spectrometer (Model DV) over the range 220—400 mμ. All other determinations in this region were carried out on an Adam Hilger " Spekker " Quartz Spectrophotometer. The author is indebted to Mr. I. Seltzer, who determined the absorption curves in the visible region (400—700 mμ.) on a Hardy Recording Spectrophotometer, using the same solutions as were used in the ultra-violet determinations. The maxima are listed in Table II, and the curves are reproduced over the range 220—580 mμ. (Figs. 3 and 4).

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