CXXI.—*A Series of Coloured Diazo-salts Derived from
Benzoyl-1 : 4-naphthylenediamine.*

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IN this communication the authors give the results of a further study of the diazo-derivatives of the monoacylated para-diamines, their experiments being devised with the view of ascertaining the joint influence of the acyl group and the aromatic nucleus on the nature of the products of diazotisation.

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It had already been ascertained that benzoyl-*p*-phenylenediamine furnished a series of stable diazonium salts including both a carbonate and a nitrite (Trans., 1905, 87, 933), but as the cyanides of this series had not been isolated satisfactorily the investigation was extended to benzoyl-1 : 4-naphthylenediamine, with the result that a very complete series of stable diazo-derivatives, including a well-defined cyanide, has been obtained, and the noteworthy fact discovered that all these compounds are distinctly coloured.

The diazotisation of benzoyl-1 : 4-naphthylenediamine hydrochloride leads to the production of a yellow, crystalline diazonium chloride which is so stable that it can be crystallised from hot water or boiling alcohol. The other diazonium salts of this series were usually made by double decomposition, as they are only sparingly soluble in water. The bromide, sulphate, nitrate, chlorate, thiocyanate, nitrite, carbonate and other salts described in the experimental section of the paper are all yellow, crystalline compounds. The perchlorate is the most insoluble and least coloured salt of the series; it separates from very dilute aqueous solutions as a pale yellow, crystalline precipitate, and is quite stable in the dry state.

These salts retain their colour when exposed to the temperature of liquid air, and when soluble in water their solution is distinctly yellow. They couple readily with alkaline β -naphthol and show the other properties of diazonium salts. The aqueous solution of the diazonium chloride is neutral to litmus, and when treated with a small proportion of alkali or even sodium acetate, a yellowish-brown nitrosoamine, $C_6H_5 \cdot CO \cdot NH \cdot C_{10}H_6 \cdot NH \cdot NO$, is precipitated. With excess of aqueous caustic alkali this substance gives an alkali derivative which, like the nitrosoamine itself, does not couple with alkaline β -naphthol. This property is, however, regained when the nitrosoamine is dissolved in mineral acids, the corresponding diazonium salt being formed.

When the foregoing diazonium salts are treated with alcoholic potash, the nitrosoamine produced at first dissolves to form the soluble potassium derivative, which then undergoes reduction in accordance with the following equation :

When alcoholic solutions of these diazonium salts are treated with aqueous potassium cyanide, a stable, red cyanide is immediately produced which, unlike the diazonium salts, does not couple with alkaline β -naphthol. The red cyanide, when allowed to remain for about twenty hours in alcoholic solution containing a trace of potassium cyanide, becomes transformed into a more soluble, yellow modification, which is precipitated on the addition of water. This substance also is

incapable of coupling with alkaline β -naphthol. Both cyanides dissolve in cold concentrated sulphuric acid, giving red solutions which rapidly assume a yellow tint. If at this stage the liquid is diluted with water and poured into alkaline β -naphthol, the azo-condensation occurs.

The existence of coloured diazo-salts has already been indicated by Hantzsch (*Ber.*, 1900, **33**, 2183, and 1901, **34**, 4168) in a comparative study of the chlorides, bromides, iodides, and thiocyanates of the simpler diazonium bases. He found that whereas the chlorides and bromides were almost invariably colourless, yet the iodides and thiocyanates were generally coloured and also very unstable. On this account, Hantzsch assumed that these coloured unstable products were equilibrium mixtures of diazonium and *syn*-diazo-compounds.

This equilibrium can be modified in the sense of increasing the proportion of diazonium salt either by dissolving the substance in water, when a colourless solution is obtained, or by cooling the solid considerably, when it undergoes an appreciable loss in colour.

More recently, Cain (*Trans.*, 1905, **87**, 5) has obtained from 4'-hydroxy-3-ethoxydiphenyldiazonium hydroxide a series of coloured salts possessed of considerable stability, to which in accordance with this author's views (this vol., p. 1040) the formula (I) should be ascribed :

It is manifest that the unstable coloured diazo-compounds obtained by Hantzsch differ considerably from those prepared by Cain and by the authors. In the former series the acid ion is the factor which apparently determines the colour, for with the same diazonium ion Hantzsch found that the chloride and bromide were colourless, whereas the iodide and thiocyanate were coloured. In the latter series described by Cain and the authors, the nature of the acid ion is certainly not the determining factor, for all the diazonium salts of this group are more or less coloured. Moreover, the appearance of colour is associated with an increase rather than a decrease in stability.

The assumption that these stable coloured diazo-salts are wholly or in part *syn*-diazo-derivatives is not justifiable from the experimental evidence available at present. The behaviour of these coloured

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diazonium salts derived from benzoyl-1:4-naphthylenediamine is in accord with Cain's formulation, and accordingly the series may be represented by the formula (III), in which these salts are given the same configuration as the colourless benzenediazonium chloride (II) :

The formula advocated by Cain is applicable both to the simpler colourless diazonium salts and also to the more complex coloured diazo-derivatives described in this communication, the development of colour in the latter series being attributed by the authors to the presence of a complex radicle in the para-position with respect to the diazo-nitrogen and to the substitution of a naphthalene for a benzene nucleus.*

The alternative configuration, (IV), for the 4-benzoylaminonaphthalene-1-diazonium salts has been suggested by Hewitt (Proc., 1907, 23, 181), according to which a base yielding coloured diazonium salts should contain a labile hydrogen atom * (V) which migrates to the diazo-nitrogen during the process of diazotisation.

It still, however, remains to be demonstrated that this migration of hydrogen is necessary for the development of colour among diazonium salts, and experiments bearing on this point are in progress. The converse statement that a coloured diazonium salt will result when a labile hydrogen atom is present, is certainly not generally true, for benzenesulphonyl-*p*-phenylenediamine (VI) yields colourless diazonium salts (chloride, sulphate, etc.) although it contains a very labile hydrogen atom (Morgan and Micklethwait, Trans., 1905, 87, 81).

In connexion with the hypothesis of a quinonoid structure for diazonium salts, it should be remembered that Griess originally held the view that two carbon atoms of the nucleus are in some way involved in the diazonium complex, or, in other words, that benzene-diazonium nitrate, " $\text{C}_6\text{H}_4\text{N}_2\text{HNO}_3$," and sulphate, " $\text{C}_6\text{H}_4\text{N}_2\text{H}_2\text{SO}_4$,"

* The influence of the naphthalene nucleus in intensifying the colour of diazonium salts is exemplified by the diazonium chlorides derived from α - and β -naphthylamines which are described respectively as orange and yellow compounds (Knoevenagel, Ber., 1895, 38, 2057).

are disubstituted derivatives of benzene (*Annalen*, 1866, 137, 47). Now inasmuch as both benzene and naphthalene nuclei can assume an ortho-quinonoid configuration, the possibility that their diazo-derivatives may have a similar structure must be taken into account. This view is expressed by the following formulæ (VII) and (VIII) :

in which the former represents the colourless benzenediazonium chloride, whilst the latter indicates the alternative ortho-quinonoid configuration for the coloured diazonium salts described in this communication.

In these two formulæ the diazo-nitrogens are represented as being attached to the ortho-quinonoid nucleus forming an unstable four-membered ring and hence readily detachable, as in the Sandmeyer reaction :

with the regeneration of a benzenoid nucleus.

A comparative study of the colourless and coloured diazonium salts is in progress, the object of the investigation being to arrive at some decision with regard to the several alternative quinonoid formulæ now proposed for this group of substances.

EXPERIMENTAL.

Diazo-derivatives of Benzoyl-p-phenylenediamine.

p-Aminobenzanilide hydrochloride, obtained by saturating a benzene solution of the recrystallised base with hydrogen chloride, was made into a thin paste with glacial acetic acid, and treated with amyl nitrite diluted with its own volume of the same solvent. Benzoyl-*p*-aminobenzenediazonium chloride was thus precipitated in the form of a pale brown, granular powder.

Benzoyl-p-aminobenzenediazonium thiocyanate,

was prepared by adding an excess of aqueous potassium thiocyanate to the clear solution produced by mixing the sparingly soluble diazonium

chloride with a saturated solution of sodium acetate. An almost white, amorphous precipitate was formed which gradually assumed a yellowish-brown tint, and separated into a bulky mass of long, filamentous needles. When recrystallised from alcohol, the compound separated in long, lustrous brown needles often one centimetre in length:

0.2081 gave 0.1807 BaSO₄. S = 11.91.

C₁₄H₁₀ON₄S requires S = 11.34 per cent.

This thiocyanate gave a scarlet coloration with alkaline β-naphthol, and hence may be regarded as a diazonium salt.

Benzoyl-p-aminobenzenediazonium picrate,

C₆H₅·CO·NH·C₆H₄·N₂·O·C₆H₂(NO₂)₃,

separated as a pale yellow precipitate on mixing a warm saturated solution of picric acid in 30 per cent. alcohol with an aqueous solution of the foregoing diazonium chloride. The yield is almost theoretical, and the product when crystallised from warm alcohol forms rosettes of yellow needles melting and decomposing at 132°:

0.2119 gave 31.2 c.c. nitrogen at 17° and 770 mm. N = 17.60.

C₁₉H₁₂O₈N₆ requires N = 18.58 per cent.

A similar compound, *acetyl-p-aminobenzenediazonium picrate*, obtained from *p*-aminoacetanilide, crystallised from boiling alcohol in glistening, yellow needles. As these picrates may be precipitated from solutions of the diazonium chloride even in the presence of excess of mineral acid, and as they couple readily with alkaline β-naphthol, they must be regarded as diazonium salts.

Diazo-derivatives of Benzoyl-1:4-naphthylenediamine.

Benzo-*α*-naphthalide was nitrated according to the method given by Worms (*Ber.*, 1882, 15, 1813), and the product when dissolved in hot glacial acetic acid yielded, on cooling, benzoyl-4-nitro-*α*-naphthylamine, whilst the isomeride, benzoyl-2-nitro-*α*-naphthylamine, was recovered from the mother liquors by diluting these with three volumes of water.

Benzoyl-1:4-naphthylenediamine was obtained by suspending 100 grams of the foregoing *p*-nitro-compound in 900 c.c. of boiling alcohol, and adding gradually 300 c.c. of concentrated hydrochloric acid, and 70 grams of tin foil. The nitro-compound dissolved completely in about two hours, and benzoyl-1:4-naphthylenediamine hydrochloride separated on cooling as a flocculent precipitate, which was crystallised from water acidified with hydrochloric acid. The base, set free with sodium carbonate, was crystallised from alcohol, when it was obtained in colourless needles melting at 187° (compare Hübner, *Annalen*, 1881, 208, 326).

Benzoylbenzylidene-1:4-naphthylenediamine,

produced on warming together in alcoholic solution equivalent quantities of benzoyl-1:4-naphthylenediamine and benzaldehyde, was recrystallised from alcohol and glacial acetic acid; it separated in yellow needles, and melted at 196—197°.

4-Benzoylaminonaphthalene-1-diazonium chloride,

—Benzoyl-1:4-naphthylenediamine hydrochloride is not readily diazotised with hydrochloric acid and sodium nitrite, and the following treatment was found to give the best result. Ten grams of the base dissolved in the least possible amount of a mixture of one part of glacial acetic acid and four parts of alcohol were treated with 16 c.c. of concentrated hydrochloric acid mixed with 32 c.c. of hot alcohol, when the mixture immediately set to a stiff paste. When the temperature of the mass had fallen to 40°, 20 c.c. of amyl nitrite were added in four lots of 5 c.c. each. The paste became reddish-yellow, and when kept for 10—15 minutes at 50° it changed to a clear liquid which was filtered from a slight impurity; the filtrate was warmed again and treated with several volumes of warm ether. The diazonium chloride rapidly separated in warty aggregates of straw-coloured needles, the yield being almost quantitative:

0.069 gave 0.0324 AgCl. Cl = 11.61.

0.1320 „ 15.6 c.c. nitrogen at 21° and 766 mm. N = 13.54.

$\text{C}_{17}\text{H}_{12}\text{ON}_3\text{Cl}$ requires Cl = 11.47, N = 13.57 per cent.

The diazonium chloride may be recrystallised either from hot water or from warm alcohol and ether, when it separates in glistening, yellow needles which are stable on exposure to light. It melts and decomposes at 140—143°. The yellow colour is retained even after repeated crystallisations, the palest specimens being obtained by fractionally precipitating its alcoholic solution with ether. The aqueous solution of this chloride is neutral to litmus paper, and this, together with the fact that the compound readily couples with alkaline β -naphthol to form an azo-derivative (compare p. 1322), supports the view that the substance must be regarded as a true diazonium salt.

The diazonium chloride also condenses with aniline to form an unstable, yellow diazamine, which rapidly changes to a red azo-derivative.

4-Benzoylaminonaphthalene-1-diazonium bromide,

separates in yellow needles on mixing aqueous solutions of potassium bromide and the diazonium chloride; it is non-explosive and melts at

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148—149°. Its colour is intermediate between that of the chloride and iodide:

0.2064 gave 0.1124 AgBr. Br = 23.15.

$C_{17}H_{12}ON_3Br$ requires Br = 22.67 per cent.

4-Benzoylaminonaphthalene-1-diazonium iodide,

which is precipitated in small, orange-coloured prisms on mixing aqueous solutions of potassium iodide and the diazonium chloride, is very sparingly soluble in water, and melts at 97—98°.

4-Benzoylaminonaphthalene-1-diazonium platinichloride,

is a dark yellow, microcrystalline powder, sparingly soluble in alcohol or water, obtained by adding excess of platinic chloride to an alcoholic solution of the diazonium chloride:

0.1751 gave 0.0363 Pt. Pt = 20.73.

$C_{34}H_{24}O_2N_6Cl_6Pt$ requires Pt = 20.39 per cent.

When suspended in alcohol and exposed to light, this compound undergoes decomposition.

4-Benzoylaminonaphthalene-1-diazonium sulphate,

—Amyl nitrite (3 c.c.) was added to the pasty mass obtained by dissolving benzoyl-1:4-naphthylenediamine (1.5 grams) in a warm mixture of glacial acetic acid and alcohol into which was introduced 1 c.c. of concentrated sulphuric acid mixed with two volumes of glacial acetic acid. The amorphous sulphate slowly changed into pale yellow plates of the diazonium salt, the precipitation of this substance being completed by the addition of absolute alcohol and ether:

0.2015 gave 18.9 c.c. nitrogen at 20° and 768 mm. N = 10.82.

0.3422 „ 0.2177 BaSO₄. S = 8.74.

$C_{17}H_{13}O_5N_3S$ requires N = 11.32; S = 8.63 per cent.

The diazonium sulphate dissolved in water but was insoluble in alcohol or ether. The aqueous solution, when evaporated over concentrated sulphuric acid, furnished well-defined, glistening needles often one centimetre in length.

4-Benzoylaminonaphthalene-1-diazonium nitrate,

was not readily obtained by direct diazotisation, but on adding dilute nitric acid to an aqueous solution of the diazonium chloride it separated in sparingly soluble yellow needles which melted and decomposed at 140—142°:

0.1688 gave 24.0 c.c. nitrogen at 24° and 778 mm. N = 16.66.

$C_{17}H_{12}O_4N_4$ requires N = 16.06 per cent.

4-Benzoylaminonaphthalene-1-diazonium nitrite,

was precipitated in yellow needles on mixing 10 per cent. aqueous solutions of the diazonium chloride and sodium nitrite; it darkened on exposure, sintered at 120° , and melted indefinitely at $145\text{--}155^\circ$:

0.1305 gave 19.0 c.c. nitrogen at 17° and 770 mm. $\text{N} = 17.13$.

$\text{C}_{17}\text{H}_{12}\text{O}_3\text{N}_4$ requires $\text{N} = 17.50$ per cent.

4-Benzoylaminonaphthalene-1-diazonium chlorate crystallised in long, iridescent, yellow needles on mixing aqueous solutions of the diazonium chloride and potassium chlorate. When heated at 130° , the salt darkened and then exploded; it also detonated on percussion or when dropped into concentrated sulphuric acid. This salt is, however, quite stable in the dry state, and is not sensitive to friction.

4-Benzoylaminonaphthalene-1-diazonium perchlorate was obtained as a pale yellow, microcrystalline precipitate on mixing cold aqueous solutions of potassium perchlorate and the diazonium chloride; it was almost insoluble in cold water and decomposed on warming with this solvent.

4-Benzoylaminonaphthalene-1-diazonium chromate, obtained as a yellowish-brown precipitate from potassium chromate and the diazonium chloride, darkened on exposure and deflagrated on heating.

4-Benzoylaminonaphthalene-1-diazonium carbonate, a yellow, microcrystalline precipitate formed on adding aqueous sodium carbonate to a solution of the diazonium chloride, was soluble in alcohol, but dissolved only sparingly in cold water. It dissolved with effervescence in hydrochloric acid and the solution developed a red coloration with alkaline β -naphthol. On heating on the water-bath, the salt darkened slightly. An estimation of carbon dioxide showed that about 90 per cent. of the substance consisted of the diazonium carbonate.

4-Benzoylaminonaphthalene-1-diazonium trichloroacetate,

separated on mixing aqueous solutions of trichloroacetic acid and the diazonium chloride as a gummy mass which rapidly changed on trituration into light yellow crystals:

0.1670 gave 0.1693 AgCl. $\text{Cl} = 25.07$.

$\text{C}_{19}\text{H}_{12}\text{O}_3\text{N}_3\text{Cl}_3$ requires $\text{Cl} = 24.44$ per cent.

4-Benzoylaminonaphthalene-1-diazonium thiocyanate,

was obtained as an amorphous, pale yellow precipitate, rapidly segregating into short, orange-coloured needles, on mixing dilute aqueous solutions of ammonium thiocyanate and the diazonium chloride; it darkened at 100° and melted at 103° :

0.1533 gave 0.1092 BaSO_4 . $\text{S} = 9.78$.

$\text{C}_{18}\text{H}_{12}\text{ON}_4\text{S}$ requires $\text{S} = 9.64$ per cent.

Action of Potassium Cyanide on 4-Benzoylaminonaphthalene-1-diazonium Chloride.

1. A blood-red coloration is developed on adding aqueous potassium cyanide to the diazonium chloride dissolved in alcohol, and if the solution is sufficiently concentrated a red precipitate makes its appearance. This red product is also deposited when water is added at once to the red solution, whereas a yellowish-brown, finely-divided precipitate is formed when the red liquid is kept overnight before dilution with water.

2. One gram of the diazonium chloride dissolved in 10 c.c. of warm alcohol was treated with 0.25 gram of potassium cyanide (98—99 per cent. KCN) dissolved in the same solvent, and the deposition of the deep red precipitate was completed by adding 65 c.c. of water. The precipitate, which retained water persistently, weighed 0.85 gram when dry :

0.1236 gave 0.3268 CO₂ and 0.0563 H₂O. C = 72.11 ; H = 5.06.

0.1439 „ 0.3804 CO₂ „ 0.0600 H₂O. C = 72.11 ; H = 4.63.

0.1116 „ 17.5 c.c. nitrogen at 17° and 762 mm. N = 18.35.

C₁₈H₁₂ON₄ requires C = 72.00, H = 4.00, N = 18.36 per cent.

4-Benzoylaminonaphthalene-1-diazocyanide,

when separating from a warm alcoholic solution appeared under the microscope ($\frac{1}{8}$ " objective) to consist of masses of fibrous curvilinear needles ; it sintered and darkened at 148° and decomposed very indefinitely at about 210°. When treated with cold concentrated sulphuric acid the diazocyanide developed a deep red coloration which faded in a few minutes to a pale yellow. The partially decolorised solution, when diluted and added to alkaline β -naphthol, gave the red azo- β -naphthol. An attempt to carry out this change quantitatively showed that the acid decomposed a portion of the cyanide. The red diazocyanide differs from all the preceding diazonium salts in not coupling with alkaline β -naphthol unless treated in the foregoing manner.

3. When the diazonium chloride and potassium cyanide (in slight excess) interacted at -10°, a bright yellow precipitate was formed, but on attempting to collect a portion of this product it became tarry. The remainder of the precipitate, suspended in its mother liquor at -10°, changed in succession to bright and dark red and became distinctly crystalline. The final product did not become tarry at the ordinary temperature, and was found to be identical with the red diazocyanide. An experiment made at the temperature of liquid air showed that the diazonium chloride and potassium cyanide did not interact,

but as the temperature was slowly raised the yellow primary product was formed which finally changed into the red diazocyanide.

4. The brown substance obtained when the diazonium chloride and potassium cyanide are left overnight in alcoholic solution before the liquid is diluted with water was dried over concentrated sulphuric acid until of constant weight; it then sintered at 77° and decomposed above this temperature, evolving much gas:

0.1120 gave 0.2840 CO_2 and 0.0536 H_2O . $\text{C} = 69.15$; $\text{H} = 5.32$.

0.1362 „ 0.3414 CO_2 „ 0.0634 H_2O . $\text{C} = 68.40$; $\text{H} = 5.17$.

0.1962 „ 27.2 c.c. nitrogen at 22° and 770 mm. $\text{N} = 15.93$ per cent.

These data indicate the presence in the brown product of a diazocyanide isomeric with the red cyanide, but the substance was not obtained in a state of purity. This substance does not couple with alkaline β -naphthol until it has first been dissolved in cold concentrated sulphuric acid, behaving in this respect quite like the stable red cyanide. Experiments were made with the view of ascertaining the conditions under which the red cyanide becomes transformed into the brown compound. The transformation does not take place when an alcoholic solution of the red cyanide is left for some time and it is, moreover, not induced by a caustic alkali. The change is, however, determined by the presence of potassium cyanide and the reaction occurs almost quantitatively; 0.2188 gram of red cyanide in alcoholic solution with 0.09 gram of potassium cyanide, when left for sixteen hours and then treated with water containing a little sodium acetate to accelerate the deposition of the precipitate, gave 0.2104 gram of the dry brown cyanide:

0.1545 gave 22 c.c. nitrogen at 20° and 768 mm. $\text{N} = 15.81$.

In many experiments it was, however, found that the reaction took a different course, tarry products only being obtained.

The two diazocyanides and several of the foregoing diazonium salts were exposed to the temperature of liquid air, but in no case was there any appreciable change of colour.

Action of Alkali Hydroxides on the Diazonium Chloride.

1. *Aqueous Caustic Alkalis.*—On slowly adding dilute aqueous caustic potash to a solution of the diazonium chloride, a slight amount of dark, viscid precipitate was first formed, and after removing this and adding more alkali a yellowish-brown substance separated, which did not darken on exposure and was dried in a vacuum desiccator over sulphuric acid:

0.2354 gave 29.8 c.c. nitrogen at 20° and 762 mm. $\text{N} = 14.48$.

$\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}_3$ requires $\text{N} = 14.43$ per cent.

This compound dissolved readily in caustic alkalis or in dilute acids;

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in the latter solvent it reverts to the diazonium salt, which then couples with alkaline β -naphthol. The substance itself does not yield an azo-derivative, and its properties are clearly those of 4-benzoyl-amino- α -naphthylnitrosoamine, $C_6H_5 \cdot CO \cdot NH \cdot C_{10}H_6 \cdot NH \cdot NO$.

The addition of sodium acetate to an aqueous solution of the diazonium chloride also determines the precipitation of this nitroso-amine.

2. *Alcoholic Potash*.—An aqueous solution of the diazonium chloride when added slowly to an excess of alcoholic potash produced a yellow precipitate (nitrosoamine), which immediately redissolved to a clear reddish-brown solution from which nitrogen was evolved, the liquid acquiring the odour of acetaldehyde and aldehyde resin. On diluting with water, a bulky precipitate of brown, felted needles was obtained, and this product, after repeated crystallisation, proved to be benzo- α -naphthalide (m. p. 156—157°).

Azo-derivatives of Benzoyl-1:4-naphthylenediamine.

4-Benzoylaminonaphthalene-1-azo- β -naphthol,
 $C_6H_5 \cdot CO \cdot NH \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_6 \cdot OH$.

This azo-compound, when obtained by the interaction of the foregoing diazonium salts and alkaline β -naphthol, formed a brick-red precipitate, sparingly soluble in the ordinary organic solvents. When crystallised from glacial acetic acid it separated in bulky masses of red felted needles having a green reflex (m. p. 249—250°):

0.2309 gave 19.2 c.c. nitrogen at 20° and 762 mm. $N = 9.53$.

$C_{27}H_{19}O_2N_3$ requires $N = 10.07$ per cent.

The compound was insoluble in aqueous alkalis, and with concentrated sulphuric acid it developed an intense violet coloration.

4-Benzoylaminonaphthalene-1:2'-azo-4'-benzoyl-1':4'-naphthylene-diamine.

On mixing alcoholic solutions of benzoyl-1:4-naphthylenediamine and its diazonium chloride, a bright red precipitate was immediately formed, and after adding aqueous sodium acetate a quantitative yield of the azo-derivative was obtained. This compound, although moderately soluble in the organic solvents, was not obtained crystalline; it decomposed at 148—150°:

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0.1959 gave 21.0 c.c. nitrogen at 20° and 773 mm. $N = 12.48$.

$C_{34}H_{25}O_2N_5$ requires $N = 13.08$ per cent.

With concentrated sulphuric acid, this azo-compound developed an intense violet coloration. When suspended in water and treated with acetic anhydride, it gave a red, amorphous, acetyl derivative darkening at 230° and melting at 248°. Hydrogen chloride, when passed into a glacial acetic acid solution of the azo-compound, produces an indigo-blue solution of the hydrochloride. This salt is diazotised on the addition of amyl nitrite, and its diazo-derivative can be condensed with β -naphthol or benzoyl-1 : 4-naphthylenediamine.

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