LXVII.—*The Relation Between the Chemical Constitution and Colour of Azo-compounds.*

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FROM an examination of the colour of the dyeings obtained from, and the chemical constitution of the commercial azo-dyestuffs, and also from other experiments (Sircar and Watson, *J. Soc. Chem. Ind.*, 1912, **31**, 968), it is clear that increasing the complexity of the molecule does not necessarily deepen the colour of an azo-compound, and instances are not wanting where bisazo-, trisazo-, or even tetrakisazo-dyestuffs containing one or more naphthalene nuclei and having the most complex structures give only yellow, orange, or brown dyeings. The real cause of the deepening of the colour of azo-compounds must therefore be looked for elsewhere. From an examination of their constitutional formulæ it is seen that in order that an azo-dyestuff should give dyeings of a deeper

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shade than orange or brown* the auxochrome should be contained, not in a benzene, but in a naphthalene nucleus. It is further found that with a given complexity of the molecule the relative positions of the auxochromic and chromophoric groups have an obvious effect on the colour of an azo-compound, the ortho-position favouring red, violet, and blue shades, and the para-position giving orange or brown shades. Thus one arrives at the conclusion that to deepen the colour of an azo-compound the first condition to be satisfied is to have the auxochrome in a naphthalene nucleus, preferably in the ortho-position with respect to the azo-linking.

Hewitt and Mitchell (T., 1906, **89**, 18) showed that all *p*-nitrohydroxyazo-compounds exhibit remarkable changes of colour when dissolved in alkali, and suggested that in such cases no simple salt-formation, but transformation of the nitroazo-structure into the *isonitro-isoazo*-form (with a diquinonoid structure) takes place. In a subsequent paper (T., 1907, **91**, 1251) these authors drew the conclusion that in an azo-compound the chief oscillation frequency is less, that is, the colour is deeper the longer the chain of alternative double and single linkings in the molecule, and explained the difference in the colour of the alkaline solutions of *p*-nitrobenzeneazophenol and *p*-nitrobenzene-1-azo-4-naphthol as due to the potassium salt of the former containing a chain in which there are 6 double and 5 single bonds placed alternately, and that of the latter a similar chain of 8 double and 7 single bonds respectively in their molecules:

In view of these observations, it seemed interesting to examine whether *p*-nitrohydroxyazo-compounds containing the auxochrome in the benzene nucleus and a long chain of alternate double and single linkings in their molecules will exhibit the same changes of colour as are shown by *p*-nitrobenzene-1-azo-4-naphthol and *p*-nitrobenzene-1-azo-4-naphthol-3-carboxylic acid when dissolved in alkali.

p-Nitrobenzeneazobenzeneazophenol (Pope and Willett, T., 1913, **103**, 1258) dissolves in alkali with a purple colour, and *p*-nitrobenzeneazo-*m*-xyleneazophenol (Meldola, T., 1883, **43**, 430) does so with a reddish-violet colour. These facts, instead of supporting (compare Pope and Willett, *loc. cit.*), seem rather to militate against Hewitt and Mitchell's theory, for, according to these

* The colours are arranged in the following order:—yellow, orange, scarlet, crimson, violet, blue, and green, and the colour is said to deepen as it passes from one on the left- to one on the right-hand side of the order.

authors, as the following potassium salts contain chains with alternately 9 double and 8 single bonds in their molecules, they should dissolve in alkali with a blue or even a deeper colour.

In order to test the point further, 4-nitronaphthalene-1-azophenol and 4-nitronaphthalene-1-azosalicylic acid have been prepared. These two compounds are isomeric with, and should possess exactly similar diquinonoid arrangements in alkali as, *p*-nitrobenzene-1-azo-4-naphthol and *p*-nitrobenzene-1-azo-4-naphthol-3-carboxylic acid:

Comparing I and II, it is seen that in alkaline solutions they contain the same number of alternate double and single bonds in their molecules, and therefore they should dissolve in alkali with the same (blue) colour and produce absorption spectra similar and alike in nature.

The two *p*-nitronaphthalene-1-azophenolic compounds are found to dissolve in alkali only with a red colour. This fact and the nature of the absorption spectra produced by these two compounds are directly in opposition to Hewitt and Mitchell's conclusions (T., 1907, **91**, 1251). It may be mentioned here that Baly, Tuck, and Marsden (T., 1910, **97**, 1494) have shown that alkali salts of *p*-nitro-*p*-hydroxyazo-compounds are not quinoneazines as supposed by Hewitt and Mitchell.

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The colour of the alkaline solutions and the dyeings obtained on wool of the various *p*-nitroazo-compounds just discussed are compared below:

<i>p</i> -Nitroazo-compound.	Colour of the alkaline solution.	Colour of the dyeings on wool with 2 per cent. dye-stuff.
<i>p</i> -Nitrobenzeneazophenol.....	Red	Orange-yellow.
4-Nitronaphthalene-1-azophenol	Deep-red	"
<i>p</i> -Nitrobenzene-1-azo-4-naphthol	Blue	Orange-red.
<i>p</i> -Nitrobenzeneazosalicylic acid	Red	Orange-yellow.
4-Nitronaphthalene-1-azo-salicylic acid ...	Deep-red	"
<i>p</i> -Nitrobenzene-1-azo-4-naphthol-3-carb- oxylic acid	Blue	Brownish-red.
<i>p</i> -Nitrobenzeneazobenzeneazophenol	Purple	Rich brown.
<i>p</i> -Nitrobenzeneazo- <i>m</i> -xyleneazophenol ...	Reddish-violet	Orange-brown.

It is found that the azonaphthols give red dyeings, whilst the azophenols give yellow or orange dyeings. Such a difference in the colour of the dyeings obtained from the isomeric pairs of substances is quite in agreement with the view already expressed, namely, that to deepen the colour of an azo-compound the first condition to be satisfied is to have the auxochrome in a naphthalene and not in a benzene nucleus.

Now, naturally the question arises why, in order to produce an azo-dyestuff giving deeper colour than orange or brown, the auxochrome should necessarily be contained in the naphthalene nucleus. The argument that the deepening of colour in such cases is due to the auxochrome being contained in a complex nucleus is scarcely tenable. Many dyestuffs are known in which the auxochromes are contained in nuclei more complex than naphthalene, but which scarcely give dyeings of deeper colour than red. Again, any difference in the structure of the molecules of the azophenols and the azonaphthols as the cause of the difference in their colours cannot be accepted.

On examining the molecular structures of phenol and naphthol, it is found that the molecule of the latter, as compared with the molecule of the former, contains a larger number of alternate double and single bonds, and it is found (see below) that in an azo-compound the longer the chain of alternate double and single bonds in the part of the molecule containing the auxochrome, proceeding from the auxochrome up to the azo-linking, taking the longest possible route, the deeper is the colour. Comparing the formulæ of benzeneazophenol and benzeneazo-*α*-naphthol,

it is seen that the chain in the former consists of alternating 3 double and 2 single bonds, whereas in the latter case it consists alternately of 5 double and 4 single bonds. The former gives yellow and the latter orange-red dyeings on wool. In counting such alternate double and single bonds, one should not go beyond the azo-linking, as proposed by Hewitt and Mitchell in the case of *p*-nitroazo-compounds (T., 1907, **91**, 1257).

In order to test the validity of the conclusion, benzene-1-azo-1' : 2' : 3' : 4'-tetrahydro-4-naphthol, *p*-nitrobenzene-1-azo-1' : 2' : 3' : 4'-tetrahydro-4-naphthol, *p*-bromobenzene-1-azo-1' : 2' : 3' : 4'-tetrahydro-4-naphthol, and *p*-sulphobenzene-1-azo-1' : 2' : 3' : 4'-tetrahydro-4-naphthol have been prepared and examined. These compounds contain the auxochromes in the naphthalene nuclei, but the length of the desired chain in them is shorter and consists of only 3 double and 2 single bonds :

They are in this respect comparable with the azophenols. These azotetrahydronaphthols are all yellow, and give dyeings almost identical in colour with those given by the corresponding azophenols.

The difference in the lengths of the chain of alternate double and single bonds in the nuclei containing the auxochrome being the primary cause of the difference of colour of any two azo-compounds, it cannot be maintained that in order to produce azo-dyestuffs giving deeper colours than orange or brown the auxochrome should necessarily be contained in a naphthalene nucleus. The naphthalene nucleus is only advantageous in providing such a long chain. Green and Sen (T., 1912, **101**, 1171) prepared phenetoleazosulphophenyldihydroxydiphenylmethanedicarboxylic acid (I) :

It dyes wool yellow, but its oxidation product (II) dyes wool red. The cause of the deepening of colour in the latter case is evident when it is considered that it contains a chain of 6 double and 5 single bonds placed alternately, but that in the former such a chain is not conceivable.

The reason why the azo-derivative obtained by using such complexes as 2:2'-dihydroxydiphenyl (Robertson and Brady, T., 1913, **103**, 1484), catechin (A. G. Perkin and Yositate, T., 1902, **81**, 1160), substituted pyrazoles (Bülow and Hecking, *Ber.*, 1911, **44**, 467), and phenylisooxazolone (Meyer, *Compt. rend.*, 1913, **156**, 1992) as end components do not give dyeings of deeper colours than orange or brown is now obvious. In none of these cases is the length of the required chain in the nucleus containing the auxochrome very great, it being naturally short or broken.

As a further test of the theory, the preparation of azoanthrols suggested itself. Some azo-derivatives of β -anthrol are known (Liebermann, D.R.-P., 21178 of 1882), but in these compounds the auxochromic and chromophoric groups are in the ortho-position with respect to each other, and, as has been said before, such relative positions favour the formation of deep colours. It may be argued that deeper colours are obtained when the auxochromic and chromophoric groups are in the ortho-position, and comparatively lighter colours when they are in the para-position with respect to each other, because in the former case there is a comparatively longer chain of alternate double and single bonds running from the auxochrome to the chromophore, thus:

It is, however, premature to draw any such conclusions before further experimental work has been done on the subject, and only *p*-hydroxyazo-compounds have been chosen for the present investigation.

Lagodinski (*Ber.*, 1906, **39**, 1717) has shown that α -anthrol combines with diazonium salts to form bluish-red azo-compounds,

but he did not isolate any of them. Benzene-1-azo-4-anthrol, *p*-nitrobenzene-1-azo-4-anthrol, *p*-bromobenzene-1-azo-4-anthrol, and *p*-sulphobenzene-1-azo-4-anthrol have now been prepared and examined. They dye wool in reddish-violet shades, whereas the corresponding azo- α -naphthols dye wool only in orange or reddish-orange shades. This is quite in agreement with the view already expressed, for the chain in the case of the azo- α -naphthols consists alternately of 5 double and 4 single bonds, and in the case of the azo- α -anthrols of 7 double and 6 single bonds alternately:

As a still further test of the theory, the dyeing properties of benzeneazoanthranol and *p*-nitrobenzeneazoanthranol (Kaufler and Suchaunell, *Ber.*, 1907, **40**, 518) have been examined. That in these compounds the azo-linking occupies the para-position with respect to the hydroxyl group is evident from the preparation of benzeneazoanthranol by the condensation of 9:9'-dibromoanthrone with alcoholic phenylhydrazine (Meyer and Zahn, *Annalen*, 1913, **396**, 152). These compounds are isomeric with, and have the same molecular complexity as, the corresponding azo- α -anthrols. It will be seen from their formulæ that although the total number of alternate double and single bonds in the molecules of the azo- α -anthrols and azoanthranols are equal,

in the case of the azoanthranols the chain of alternate double and single bonds, proceeding one way or the other, from the auxochrome to the chromophore consists of only 5 double and 4 single bonds, that is, is equal to that in the azo- α -naphthols. The dyeings with the azoanthranols should therefore be lighter in colour than those obtained with the azo- α -anthrols. In fact, the azoanthranols dye wool in yellow shades.

On account of the very sparing solubility of the azo- α -anthrols and azoanthranols in water, they were first dissolved in sulphuric

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acid, precipitated by water, collected, and the precipitate washed until free from acids, and afterwards used for dyeing. Full shades were, however, not obtained, as much of the colouring matter was left in the dye-bath.

A comparison of the colour of the dyeings obtained on wool with the various azotetrahydronaphthols, azo- α -anthrols, azo-anthranols, and the corresponding azophenols and azo- α -naphthols is made below:

Formula.	M. p.	Colour of the dyeing obtained on wool with 2 per cent. dye-stuff.
$\text{NH}\cdot\text{N}:\text{C}_6\text{H}_4\text{:O}$	157°	Yellow.
$\text{NH}\cdot\text{N}:\text{C}_{10}\text{H}_7\text{:O}$	146°	Yellow.
$\text{NH}\cdot\text{N}:\text{C}_{10}\text{H}_7\text{:O}$	206°	Orange.
$\text{NH}\cdot\text{N}:\text{C}_{14}\text{H}_9\text{:O}$	—	Reddish-violet.
$\text{NH}\cdot\text{N}:\text{C}_{14}\text{H}_9\text{:O}$	—	Yellow.
$\text{NO}_2\text{C}_6\text{H}_4\text{NH}\cdot\text{N}:\text{C}_6\text{H}_4\text{:O}$	212—213°	Yellow.
$\text{NO}_2\text{C}_6\text{H}_4\text{NH}\cdot\text{N}:\text{C}_{10}\text{H}_7\text{:O}$	205—217°	Yellow.
$\text{NO}_2\text{C}_6\text{H}_4\text{NH}\cdot\text{N}:\text{C}_{10}\text{H}_7\text{:O}$	277—279°	Orange-red.
$\text{NO}_2\text{C}_6\text{H}_4\text{NH}\cdot\text{N}:\text{C}_{14}\text{H}_9\text{:O}$	—	Reddish-violet.

Formula.	M. p.	Colour of the dyeing obtained on wool with 2 per cent. dye-stuff.
—	Yellow.
155°	Yellow.
147—148·5°	Yellow.
237—238°	Reddish-orange.
—	Reddish-violet
—	Yellow.
—	Yellow.
—	Fiery-orange.
—	Reddish-violet.

It is seen from the table that in an azo-compound the longer the chain of alternate double and single bonds in the part of the molecule containing the auxochrome, going from the auxochrome to the azo-linking, taking the longest possible route, the deeper is the colour, and vice versâ.

An examination of the absorption spectra (Figs. 3, 4, 5, and 6) also reveals the fact that in an azo-compound as the length of

the chain referred to before is increased, so is the head of the absorption band gradually shifted towards the red end of the spectrum, and vice versa.

On the other hand, the absorption curves of the potassium salts

FIG. 1.

----- *p*-Nitrobenzeneazophenol.
 p-Nitrobenzene-1-azo-4-naphthol.
 - - - - - 4-Nitronaphthalene-1-azophenol.

Scale of oscillation frequency.

Scale of oscillation frequency.

----- *p*-Nitrobenzeneazosalicylic acid.
 p-Nitrobenzene-1-azo-4-naphthol-3-carboxylic acid.
 - - - - - 4-Nitronaphthalene-1-azosalicylic acid.

of azotetrahydronaphthols and azoanthranols (Figs. 7, 8, 9, and 10) are found to be much like the absorption curves of the potassium salts of the corresponding azo- α -naphthols and azo- α -anthranols respectively. These facts seem fully to support the view expressed by Hantzsch (*Ber.*, 1899, **32**, 3089), that the salts of

p-hydroxyazo-compounds are true derivatives of hydroxyazobenzene.

The absorption spectra produced by the azo-dyestuffs under examination in the visible part of the spectrum only have been

FIG. 2.

- *p*-Nitrobenzeneazophenol (potassium salt).
 p-Nitrobenzene-1-azo-4-naphthol (potassium salt).
 - - - - 4-Nitronaphthalene-1-azophenol (potassium salt).

Scale of oscillation frequency.

Scale of oscillation frequency.

- *p*-Nitrobenzeneazosalicylic acid (potassium salt).
 p-Nitrobenzene-1-azo-4-naphthol-3-carboxylic acid (potassium salt).
 - - - - 4-Nitronaphthalene-1-azosalicylic acid (potassium salt).

considered, as in judging the colour of a dyestuff we are concerned only with the absorption produced by it in the visible part of the spectrum.

All the solutions examined were alcoholic, the solutions of the

FIG. 3.

FIG. 4.

FIG. 5.

FIG. 6.

FIG. 7.

FIG. 8.

FIG. 9.

FIG. 10.

potassium salts being prepared by adding three or four drops of 50 per cent. potassium hydroxide solution to 100 c.c. of the alcoholic solution of the parent substance.

It is also interesting to note that the melting points of the azo-tetrahydronaphthols are very near to the melting points of the corresponding azophenols and much lower than those of the corresponding azo- α -naphthols.

EXPERIMENTAL.

4-Nitro- α -naphthylamine.—Aceto- α -naphthalide was nitrated (Lillmann and Remfry, *Ber.*, 1886, **19**, 797), and by selective hydrolysis of the product a mixture, containing two forms of crystals fairly distinguishable by their colour and appearance, of 4-nitro- α -naphthylamine and 2-nitroaceto- α -naphthalide was obtained. The two substances could not be separated by following the original directions (*loc. cit.*), but it was found that on adding to the mixture sodium nitrite in the presence of concentrated hydrochloric acid, 4-nitro- α -naphthylamine was diazotised and passed into solution, leaving the 2-nitroaceto- α -naphthalide in suspension. The latter substance was separated by filtration, washed, crystallised from alcohol, and identified. A blank experiment showed that the mixture contained 50 per cent. of 4-nitro- α -naphthylamine, and in preparing the two azo-compounds described below appropriate quantities of the second components were employed.

4-Nitronaphthalene-1-azophenol, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$.—Two grams of the above mixture were made into fine paste with 15 c.c. of concentrated hydrochloric acid, cooled, and diazotised with a solution of 0.5 gram of sodium nitrite in 2 c.c. of water. After twenty minutes the mixture was filtered, and the solution added slowly to a cold alkaline solution of 0.7 gram of phenol in 250 c.c. of water, when a brown precipitate of the azo-compound was formed. Next day the mixture was warmed with excess of hydrochloric acid, when the dirty-brown precipitate became orange-brown. After collecting and drying, it crystallised from dilute alcohol in pale red needles melting at $182\text{--}183^\circ$, the yield being 1.2 grams.

The compound is soluble in alcohol, acetic acid, acetone, benzene, or nitrobenzene, moderately so in ether, chloroform, or methyl alcohol, and insoluble in water or cold alkali hydroxide. In a boiling solution of alkali hydroxide it dissolves with a deep red, and in concentrated sulphuric acid with a magenta colour. It dyes wool bright yellow:

0.1241 gave 16 c.c. N_2 (moist) at 30° and 760.9 mm. $N=14.32$.
 $C_{16}H_{11}O_2N_3$ requires $N=14.30$ per cent.

4-Nitronaphthalene-1-azosalicylic acid,
 $NO_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_6H_3(OH) \cdot CO_2H$.

—A diazotised solution of 4-nitro- α -naphthylamine was added to an alkaline solution of slightly more than the theoretical quantity of salicylic acid, and the product worked up as before. A brownish-yellow precipitate was obtained, which crystallised from nitrobenzene in yellowish-red needles softening at 199 — 200° and melting at 222 — 223° . It is fairly readily soluble in methyl and ethyl alcohols, benzene, acetone, chloroform, ether, acetic acid, or nitrobenzene, but insoluble in water or cold dilute alkali hydroxide. It dissolves in boiling alkali hydroxide solution with a deep red, and in concentrated sulphuric acid with a violet colour. It dyes both unmordanted and chrome-mordanted wool orange-yellow:

0.1295 gave 14.4 c.c. N_2 (moist) at 26° and 763.2 mm. $N=12.61$.
 $C_{17}H_{11}O_5N_3$ requires $N=12.46$ per cent.

p-Sulphobenzene-1-azo-1':2':3':4'-tetrahydro-4-naphthol.—Bamberger and Bordt (*Ber.*, 1890, **23**, 217) prepared the sodium salt of this compound, but not the free acid.

A diazotised solution of 0.865 gram of sulphanilic acid was added to 0.74 gram of 1':2':3':4'-tetrahydro- α -naphthol dissolved in excess of sodium hydroxide. After a few minutes the whole was exactly neutralised with glacial acetic acid, when an orange precipitate of the sodium salt was produced, which was collected, dried, and crystallised from boiling water, separating in bronzy plates (1 gram).

To the filtrate concentrated hydrochloric acid was added drop by drop, when a turbidity appeared. The addition of acid was stopped when the turbidity was at its maximum, and, after two hours, the orange needles of the free acid were collected and dried (0.5 gram).

The compound dissolves in methyl and ethyl alcohols, acetone, acetic acid, or water, but is almost insoluble in light petroleum, benzene, or chloroform. It dissolves in alkali hydroxide with an orange-red, and in concentrated sulphuric acid with a red colour. It dyes in full yellow shades:

0.1029 gave 8 c.c. N_2 (moist) at 24° and 752 mm. $N=8.73$.
 $C_{16}H_{16}O_4N_2S$ requires $N=8.47$ per cent.

p-Nitrobenzene-1-azo-1':2':3':4'-tetrahydro-4-naphthol.—A diazotised solution of 0.69 gram of *p*-nitroaniline was combined as in the last experiment with an alkaline solution of 0.74 gram of

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1':2':3':4'-tetrahydro- α -naphthol. After a few minutes the precipitate formed was treated with concentrated hydrochloric acid, and the orange-coloured flocks obtained in this way were collected and dried on a porous plate. Amyl alcohol was the only solvent from which the substance could be crystallised; it separated in aggregates of orange prisms, softening at about 205° and melting at 217°. It is soluble in methyl, ethyl, or amyl alcohols, nitrobenzene, benzene, toluene, acetone, chloroform, or acetic acid, but is insoluble in light petroleum or water. It dissolves in alkali hydroxide solution with an orange-red, and in concentrated sulphuric acid with a red colour, and dyes wool in full yellow shades:

0.1210 gave 15 c.c. N₂ (moist) at 23° and 762 mm. N=14.0.

C₁₆H₁₅O₃N₄ requires N=14.14 per cent.

p-Bromobenzene-1-azo-1':2':3':4'-tetrahydro-4-naphthol.—A diazotised solution of 0.86 gram of *p*-bromoaniline was combined with 0.74 gram of 1':2':3':4'-tetrahydro- α -naphthol in alkaline solution. After thirty minutes the mixture was acidified, and the brown precipitate collected and dried. It crystallises from alcohol with the addition of a few drops of water in orange-yellow needles melting at 147–148.5° (yield 1.3 grams). It is soluble in acetic acid, benzene, chloroform, acetone, or ether, but almost insoluble in light petroleum or water. It dissolves in alkali hydroxide solution with an orange-red, and in concentrated sulphuric acid with a red colour. It dyes wool yellow:

0.1400 gave 10.6 c.c. N₂ (moist) at 27° and 760.2 mm. N=8.66.

C₁₆H₁₅ON₂Br requires N=8.48 per cent.

Anthracene- α -monosulphonic Acid.—Anthraquinone was sulphonated as directed by Schmidt (*Ber.*, 1904, **37**, 67), but the best yield was obtained by using fuming sulphuric acid containing 25–30 per cent. of sulphur trioxide. The reduction of the potassium salt of anthraquinone- α -monosulphonic acid thus formed by zinc dust and ammonia required only twenty-five to thirty minutes (compare Schmidt, *ibid.*, p. 70). As the yield of the crystals appearing on cooling was rather poor, the whole of the clear, filtered solution was evaporated to dryness, and the potassium anthracene- α -monosulphonate utilised for the next operation.

α -Anthrol (Dienel, *Ber.*, 1905, **38**, 2868; Schmidt, *Ber.*, 1904, **37**, 70).—Two grams of potassium anthracene- α -monosulphonate were fused with 10 grams of potassium hydroxide at 250–260°, the fusion being kept at that temperature for twenty-five minutes,

and afterwards allowed to cool. Four or 5 c.c. of water, and then 6—7 c.c. of concentrated hydrochloric acid, were added, and the whole was poured into about 100 c.c. of water, when a brown precipitate separated. This crystallised in yellowish-white, shining plates, melting at 152° (1 gram), by dissolving in the smallest quantity of boiling acetic acid, and then shaking with about thrice its volume of water. It was further purified by a second crystallisation from dilute alcohol.

Benzene-1-azo-4-anthrol.—A diazotised solution of 0.2 gram of aniline was added to a solution of 0.4 gram of α -anthrol in 6 c.c. of alcohol. After some time a precipitate separated from the deep red solution; this was collected next day and dissolved in an excess of 25 per cent. aqueous potassium hydroxide, forming a magenta-violet solution. The solution was next acidified with concentrated hydrochloric acid, when the free azo-compound separated. After being collected and dried, it crystallised from benzene in violet-red, shining needles melting and decomposing at 234 — 235° . The substance is soluble in methyl or ethyl alcohols, acetone, chloroform, benzene, toluene, xylene, acetic acid, nitrobenzene, or ether, but insoluble in water, light petroleum, or aqueous potassium hydroxide. It dissolves in concentrated sulphuric acid to a violet-black solution, and in alcoholic potassium hydroxide with a reddish-violet colour. It dyes wool reddish-violet:

0.1076 gave 9.2 c.c. N_2 (moist) at 30° and 759 mm. $N=9.26$.

$C_{20}H_{14}ON_2$ requires $N=9.39$ per cent.

p-Bromobenzene-1-azo-4-anthrol.—A diazotised solution of 0.355 gram of *p*-bromoaniline was combined, as in the last experiment, with 0.4 gram of α -anthrol dissolved in 10 c.c. of alcohol. On repeated crystallisation from xylene it separated in dark, reddish-violet, microscopic needles melting and decomposing at 248 — 249° . The compound is soluble in methyl or ethyl alcohols, acetic acid, acetone, benzene, toluene, xylene, chloroform, nitrobenzene, or amyl alcohol, but insoluble in water or aqueous alkali hydroxide; it dissolves in concentrated sulphuric acid to a blue-black solution, and in alcoholic potassium hydroxide with a violet colour. It dyes wool reddish-violet:

0.1226 gave 8.5 c.c. N_2 (moist) at 27° and 764.5 mm. $N=7.80$.

$C_{20}H_{13}ON_2Br$ requires $N=7.45$ per cent.

p-Nitrobenzene-1-azo-4-anthrol.—A diazotised solution of 0.214 gram of *p*-nitroaniline was added to an alcoholic solution of 0.3 gram of α -anthrol. Next day the red precipitate was collected

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and treated with dilute aqueous potassium hydroxide, when it turned black. The precipitate was collected, treated with concentrated hydrochloric acid, warmed, again collected, and dried. For purification it was dissolved in nitrobenzene and precipitated with light petroleum. It forms a dark red powder melting at above 285° . It is soluble in acetone, chloroform, or nitrobenzene, moderately so in ethyl or methyl alcohols, acetic acid, benzene, or ether, and dissolves in concentrated sulphuric acid to a blue-black solution and in alcoholic potassium hydroxide with a greenish-blue colour. It dyes wool reddish-violet:

0.1302 gave 13.4 c.c. N_2 (moist) at 22° and 764 mm. $N=11.88$.

$C_{20}H_{13}O_3N_3$ requires $N=12.24$ per cent.

p-Sulphobenzene-1-azo-4-anthrol.—A diazotised solution of 0.447 gram of sulphanilic acid was combined with a solution of 0.5 gram of α -anthrol in excess of alkali hydroxide. On acidifying the solution next day, a purple-coloured precipitate separated, but it could not be crystallised. The compound forms a dark red powder, which is moderately soluble in alcohol, nitrobenzene, or water, insoluble in benzene, light petroleum, or ether, and soluble in concentrated sulphuric acid with a blue-black, and in alcoholic potassium hydroxide with a violet colour. It dyes wool bright violet:

0.1116 gave 7 c.c. N_2 (moist) at 25° and 761.5 mm. $N=7.12$.

$C_{20}H_{14}O_4N_2S$ requires $N=7.40$ per cent.

In conclusion, I beg to express my best thanks to Dr. E. R. Watson for the kind help and encouragement which he has given me during the course of this investigation.

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[Received, October 13th, 1915.]