CLVIII.—*The Azo-derivatives of 2:2'-Diphenol.*

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It was first pointed out by Hewitt (*Ber.*, 1895, **28**, 799) that hydroxyazo-compounds tended to form characteristic hydrates which were of different colour from the original compounds. A list of such cases is given by Hantzsch and Robertson (*Ber.*, 1910, **43**, 106), and it is noteworthy that there is a general tendency for the hydrates to crystallise with half a molecule of water.

That this characteristic behaviour depends on some inherent property of the azo-grouping is supported by the fact that the alkali salts of these compounds also frequently crystallise with half a molecule of solvent of crystallisation. In some cases the hydrates are of quite exceptional stability, as, for example, in the case of benzeneazoresorcinol, which was for a long time regarded as existing in two modifications. Quite recently, however, Hantzsch (*Ber.*, 1913, **46**, 1556) has shown that the difference depends on the fact that one modification contains water, which is removed only after long heating at 120°.

Now that the nature of this substance has been settled, there appears to remain only one genuine case of a simple hydroxyazo-compound existing in two modifications, neither of which is a hydrate, and this substance is naphthaleneazophenol. McPherson and Gore (*Amer. Chem. J.*, 1901, **25**, 491) have shown that the ordinary yellow variety, on heating to 130°, changes its colour to red without loss of weight, and that this red modification may be recrystallised from petroleum unchanged.

In the course of some investigations on the azo-derivatives of 2:2'-diphenol, it was observed that 5:5'-bisbenzeneazo-2:2'-diphenol:

existed in a red and yellow modification, each containing half a molecule of water of crystallisation. The exact conditions which determined the stability of the two hydrates could not be ascertained, and both varieties were frequently observed to separate together, for example, on acidifying the aqueous alkaline solution, or on recrystallising from such different solvents as alcohol and glacial acetic acid. These hydrates were further characterised by their exceptional stability; they could be heated to 100° without losing water, and could be recrystallised from chloroform unchanged. On loss of water, which occurred slowly at 160° , the colour in each case was unchanged. The two varieties had the same melting point, namely, 184° , the yellow changing, just before melting, into the red. This, then, seems an ordinary case of

polymorphism, although the determining factor may be due possibly to stereoisomerism or the tendency of one or other variety to assume the quinonoid constitution. That this substance has the azo-constitution is made evident by the examination of its spectrum.

The deep band characteristic of the azo-group, shown by the curve for benzeneazophenol, which is also included, and entirely different from that observed in the corresponding quinonoid compounds, is noticed to be considerably flattened in the two bisazo-compounds that were photographed.* The reason for this is probably to be sought in the fact that the residual affinities of the azo-groupings in different parts of the same molecule tend to neutralise each other, so that the characteristic band which they cause in the spectrum is not so evident.

* We have much pleasure in expressing our indebtedness to Dr. I. M. Heilbron for these photographs.

This ready tendency to form two modifications was not noticed in the other bisazo-compounds of 2:2'-diphenol, although the dibromo-derivative of bisbenzeneazo-2:2'-diphenol was found to change under the influence of light from yellow to red when kept in a sealed tube under toluene. On the other hand, the tendency to form hydrates was frequently observed. Thus, 5:5'-bis-*p*-chlorobenzeneazo-2:2'-diphenol formed a red hydrate, which was stable at 100°, losing its molecule of water at 160° to form the yellow, anhydrous compound, and the isomeric *o*-chloro-compound formed a hydrate which was so stable that its water could be driven off only on melting. A further point of interest concerning these compounds was that substituents in the benzene nucleus tended to prevent the formation of bisazo-2:2'-diphenols, probably owing to steric hindrance. Thus, aniline and *o*-chloroaniline gave good yields of the bisazo-compounds, whereas *p*-toluidine and *p*-chloroaniline reacted less readily, producing also some monoazo-compound, and in the case of α -naphthylamine the monosubstituted derivative was the only product of the reaction.

This substance, 5- α -naphthaleneazo-2:2'-diphenol, was noticeable in that it formed a green hydrate, a colour rarely observed among azo-compounds.

Owing to the peculiar nature of the isomerism of *p*-azophenol, a substance of the constitution:

was prepared from *p*-aminophenol and 2:2'-diphenol. This compound was apparently obtained, although in a poor yield; unfortunately its slight solubility and its very high melting point (above 300°) caused difficulties which prevented a more detailed examination.

EXPERIMENTAL.

5:5'-Bisbenzeneazo-2:2'-diphenol.—A solution of 10 grams of aniline was diazotised and added slowly with constant stirring to a well-cooled solution of 10 grams of diphenol in 50 c.c. of 2*N*-sodium hydroxide diluted to about three litres. The mixture was left overnight, when the hydroxyazo-compound separated as a yellow precipitate. This was collected and freed from small quantities of tarry matter by solution in ammonia and reprecipitation with acid. The crude substance was crystallised from chloroform and light petroleum, and was obtained as a deep red, crystalline powder, which retained traces of chloroform even after

drying at 110° , but was obtained pure by recrystallisation from glacial acetic acid.

When crystallised from diluted alcohol, a pale yellow modification was obtained, which also separated at times from chloroform or acetic acid, often together with the red form. There seemed to be no method of controlling the form in which the compound separated, although chloroform seemed to favour the production of the red modification. From whatever solvent the substance separated, each modification always contained half a molecule of water.

The compounds were dried in a steam oven at 110° .

Red modification:

0.1275 gave 0.3352 CO_2 and 0.0546 H_2O . $\text{C}=71.6$; $\text{H}=4.7$.

0.2042, heated to 160° for four hours, lost 0.0043. $\text{H}_2\text{O}=2.1$.

Yellow modification:

0.1238 gave 0.3258 CO_2 and 0.0546 H_2O . $\text{C}=71.7$; $\text{H}=4.9$.

0.2004, heated to 160° for four hours, lost 0.0044. $\text{H}_2\text{O}=2.2$.

$\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires $\text{C}=71.4$; $\text{H}=4.7$; $\text{H}_2\text{O}=2.2$ per cent.

Both forms melted at 184° , the yellow changing to the red just before melting.

Hydrochloride of 5:5'-Bisbenzeneazo-2:2'-diphenol.—The base was dissolved in dry chloroform, and the solution saturated with dry hydrogen chloride. The hydrochloride separated as a bright red, crystalline powder, which was collected, washed with light petroleum, and dried in the air:

0.1604 gave 0.0995 AgCl . $\text{Cl}=15.3$.

$\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_4 \cdot 2\text{HCl}$ requires $\text{Cl}=15.2$ per cent.

The hydrochloride has no definite melting point, and is almost insoluble in concentrated hydrochloric acid.

3:3'-Dibromo-5:5'-bisbenzeneazo-2:2'-diphenol.—The bisbenzeneazodiphenol was dissolved in glacial acetic acid, anhydrous sodium acetate added, and then cautiously the requisite quantity of bromine dissolved in acetic acid. The bromo-compound separated almost at once, and was crystallised from glacial acetic acid, separating in golden crystals, melting at 222° :

0.1042 gave 0.1988 CO_2 and 0.0302 H_2O . $\text{C}=52.1$; $\text{H}=3.2$.

$\text{C}_{24}\text{H}_{16}\text{O}_2\text{N}_4\text{Br}_2$ requires $\text{C}=52.1$; $\text{H}=3.2$ per cent.

A solution of this substance in benzene in a sealed tube exposed to light slowly deposited dark red crystals.

5:5'-Bis-p-tolueneazo-2:2'-diphenol.—This substance was prepared in an analogous way to the unsubstituted compound from *p*-toluidine and diphenol. The product was only partly soluble in

ammonia, and the insoluble residue, after treatment with hydrochloric acid, gave the most satisfactory crop of pure substance after crystallisation from glacial acetic acid. The portion soluble in ammonia appeared to contain the monoazo-compound, which, however, could not be obtained in a pure condition:

0.1879 gave 20.8 c.c. N_2 at 19° and 760 mm. $N=13.0$.

0.2114, heated to 160° for twelve hours, lost 0.0041. $H_2O=1.9$.

$C_{26}H_{22}O_2N_4 \cdot \frac{1}{2}H_2O$ requires $N=12.9$; $H_2O=2.0$ per cent.

This compound forms pale yellow crystals, melting at 228° .

5: 5'-*Bis-p-chlorobenzeneazo-2: 2'-diphenol*.—This compound was obtained from *p*-chloroaniline and diphenol in the usual way, and was isolated from the portion insoluble in ammonia. It was crystallised from glacial acetic acid, and then from alcohol, when it was obtained in red crystals, melting at 226° :

0.2064 gave 20.8 c.c. N_2 at 17° and 754 mm. $N=11.8$.

0.3354 lost at 160° 0.0118. $H_2O=3.5$.

$C_{24}H_{14}O_2N_4Cl_2 \cdot H_2O$ requires $N=11.6$; $H_2O=3.7$ per cent.

The anhydrous substance was yellow.

5-*p-Chlorobenzeneazo-2: 2'-diphenol*.—This compound was obtained from the ammonia extract in the previous preparation. This was acidified with hydrochloric acid, the precipitate dissolved in glacial acetic acid, and reprecipitated by the cautious addition of water:

0.1160 gave 0.2800 CO_2 and 0.0451 H_2O . $C=65.9$; $H=4.3$.

$C_{18}H_{13}O_2N_2Cl$ requires $C=66.5$; $H=4.0$ per cent.

The compound is a yellow, crystalline powder, melting at 163° . A further proof that only one of the hydrogen atoms in the diphenol had been replaced in this compound was furnished by the fact that on bromination it yielded a tribromo-derivative.

5-*p-Chloro-3:3':5'-tribromobenzeneazo-2: 2'-diphenol*.—This was obtained by the bromination of the above compound in glacial acetic acid in the presence of anhydrous sodium acetate, and recrystallising the product first from glacial acetic acid and then from alcohol. It is a reddish-brown, crystalline powder, melting at 197° :

0.1402 gave 0.1991 CO_2 and 0.0259 H_2O . $C=38.7$; $H=2.0$.

$C_{18}H_{10}O_2N_2ClBr_3$ requires $C=38.4$; $H=1.7$ per cent.

5: 5'-*Bis-o-chlorobenzeneazo-2: 2'-diphenol*.—This substance was obtained as before from diphenol and *o*-chloroaniline, the yield in this case being particularly good, and the product completely soluble in ammonia. The ammoniacal solution was acidified with hydrochloric acid, and the precipitate crystallised from acetic acid, when it was obtained in yellow crystals, melting at 218° :

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0.1182 gave 0.2653 CO_2 and 0.0415 H_2O . $\text{C}=61.2$; $\text{H}=3.9$.

0.1177 „ 0.2636 CO_2 „ 0.0407 H_2O . $\text{C}=61.0$; $\text{H}=3.8$.

$\text{C}_{24}\text{H}_{14}\text{O}_2\text{N}_4\text{Cl}_2, \frac{1}{2}\text{H}_2\text{O}$ requires $\text{C}=61.0$; $\text{H}=3.6$ per cent.

It is of interest that these compounds retain water even at high temperatures; in the case of this substance the water appears to be driven off only on melting.

5 : 5'-*Bis-p-hydroxybenzeneazo-2 : 2'-diphenol*.—It was found that *p*-hydroxybenzenediazonium chloride would not condense with diphenol in an acid or neutral solution, so the diphenol was dissolved in sufficient alkali to leave the reaction mixture faintly alkaline. After twenty-four hours, excess of dilute sulphuric acid was added, and the red precipitate collected and crystallised from glacial acetic acid. The product was a dark red, crystalline powder, melting above 330° :

0.1346 gave 0.3334 CO_2 and 0.0514 H_2O . $\text{C}=67.5$; $\text{H}=4.2$.

$\text{C}_{24}\text{H}_{18}\text{O}_4\text{N}_4$ requires $\text{C}=67.5$; $\text{H}=4.2$ per cent.

The further investigation of this substance was prevented by the very small yield obtained and its extreme insolubility.

5-*Naphthaleneazo-2 : 2'-diphenol*.—This compound, prepared from diphenol and α -naphthylamine, was purified by solution in toluene and precipitation with light petroleum; it formed yellow crystals, melting at 150° :

0.1418 gave 10.8 c.c. N_2 at 23° and 758 mm. $\text{N}=8.7$.

$\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{N}=8.2$ per cent.

When obtained from its ammonium salt by the action of dilute acids, there was formed a green hydrate, which was unstable in air. A rapidly performed analysis indicated the presence of one molecule of water.

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