C.—*The Constitution of the Diazo-compounds.*

By John Cannell Cain.

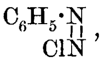
Although the long controversy between Hantzsch and Bamberger on this subject apparently came to an end some few years ago, and many chemists have accepted the views of the former, yet it would appear that there is still some uncertainty of opinion with regard to the constitution of these substances.

The stereochemical hypothesis of the constitution of the metallic diazo-derivatives (also cyanides, &c.), so stoutly advocated by Hantzsch, has been sharply criticised by Bamberger, von Pechmann, Blomstrand, and Armstrong, but the re-introduction of Blomstrand's formula for the diazo-salts by Bamberger in 1895 has met with hardly any opposition.

Although this formula, for example, $C_6H_5{\cdot}NCl{\vdots}N$, advocated, as it has been, by no less than three chemists independently (Blomstrand, 1869, Strecker, 1871, and Erlenmeyer, 1874), was rejected on the ground that it did not explain the formation of phenylhydrazine from diazobenzene chloride by reduction as did Kekulé's formula,

$$C_6H_5{\cdot}N{:}NCl,$$

it must be admitted that the reasons given by Bamberger for discarding the latter were slight. This chemist indeed only advanced the old criticism of Blomstrand that Kekulé's formula was that of a chloride of nitrogen and as such was improbable. Apparently Bamberger was not quite sure as to which of the two formulæ, $C_6H_5{\cdot}NCl{\vdots}N$ and $C_6H_5{\cdot}N{\vdots}NCl$, was the more preferable, but finally chose the former. Hantzsch did not at first agree with this view; he regarded diazobenzene chloride as a *syn*-diazo-compound,



$$\begin{array}{r}C_6H_5{\cdot}N\\ \|\\ ClN\end{array},$$

but soon rejected this and agreed with Bamberger in adopting the Blomstrand formula.

It is necessary to point out here that Blomstrand's formula was used, not so much that the reactions of the diazo-salts demanded it, but from the analogy with the ammonium salts, and that the Kekulé formula was required for the metallic diazo derivatives. Later, Hantzsch adduced much evidence, chiefly from the physical side, in favour of the so-called diazonium formula, from the resemblance which existed between these salts and the ammonium salts in solution. It is true, of course, that diazobenzene chloride results from aniline hydrochloride by replacement of three atoms of hydrogen, but by no means does it follow that the constitutions of the two are analogous. Moreover, the diazo-compounds are in a class entirely by themselves; their behaviour and reactions are different from those of any other series of compounds, and straining after analogous constitutions in cases like this is dangerous. The whole framework of this supposed resemblance is shaken when we remember that the commonly accepted constitution of the ammonium compounds is by no means certain and is very different from that which is probably the true one.*

In the whole of the literature bearing on the constitution of the diazo-compounds it is remarkable that, with one important exception which will be referred to presently, they are treated solely from the point of view of nitrogen derivatives: they are compared with either nitrogen chloride (argument against Kekulé's formula), with metallic salts (ammonium, potassium, &c.), or with aliphatic substituted quaternary ammonium derivatives. In no discussion of their constitution (with the above exception) is the condition of the benzene ring taken into consideration; this is tacitly assumed to remain in exactly the same condition as it was in the aniline hydrochloride before being converted into the diazo-chloride. In view of our modern ideas on the extreme mobility of the benzene nucleus it is surprising that conceptions of mobility have been practically confined to the diazo-part of the molecule. When, however, we regard such a compound as diazobenzene chloride as a substituted benzene derivative $C_6H_5(N_2Cl)$ and consider its properties in this light, we cannot but be impressed, *inter alia*, by the remarkable ease with which it loses the whole of its nitrogen. Those derivatives of benzene which contain only one atom of nitrogen in the substituting group (for example,

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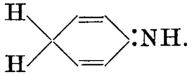
* Compare Werner, *Annalen*, 1902, **322**, 261; Cain, *Mem. Manchester Phil. Soc.*, 1904, **48**, No. 14; *Ber.*, 1905, **38**, 2715. It is, perhaps, not out of place here to point out that at the time of the inception of the ordinary ammonium theory by Ampère (1816) nitrogen was regarded as being the only element which could exhibit variable valency; the unitary formula, $H_3N{<}^{Cl}_{H}$, for ammonium chloride was therefore obvious. Had it been known, as it is now, that chlorine and oxygen could also become tervalent and quadrivalent respectively, it is highly probable that the formulæ for ammonium chloride and hydroxide respectively would have been written as I have suggested (*loc. cit.*), namely, $H_3N{:}ClH$ and $H_3N{:}OH_2$.

aniline) manifest a very great resistance to parting with it. Such compounds withstand the action of almost all reagents with the singular exception of oxidising agents. Moreover, it is very often the case that when an atom or group is introduced into a nucleus with great ease, it is also readily removed ; we might therefore expect that as an atom of nitrogen is easily substituted for three atoms of hydrogen in aniline hydrochloride, this atom would be easily eliminated. There is, however, nothing to indicate in either of the formulæ, $C_6H_5\cdot NCl\vdots N$ or $C_6H_5\cdot N\colon NCl$, that the union of the nitrogen atom with the benzene ring would be easily broken. It would, indeed, be reasonable to expect that only the second nitrogen atom would be readily split off by the various reagents.

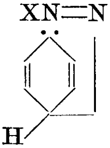
In seeking for an explanation of this fact we are driven to examine the case, already referred to, in which the nitrogen attached to the benzene ring is easily removed. This happens, of course, in the formation of *p*-benzoquinone by the oxidation of aniline. Now recent work by Ostrogowich and Silbermann (*Bull. Soc. Sci. Bucharest*, 1906, **15**, 281) has shown that there is considerable evidence in support of the view of these authors that when oxidising agents or free halogens act on amines, quinoneimides are first formed, and that the parent substance of benzoquinone is the tautomeric form of aniline,



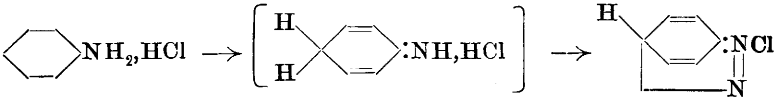
It is evident that a compound of this constitution would readily tend to split off the nitrogen at the double linking.

Now the diazotising process bears a considerable resemblance to the foregoing reaction, and it seems likely, therefore, that in this case also the tautomeric form of aniline may be the first result of the action of nitrous acid.

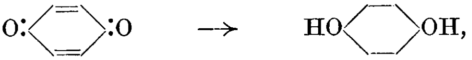
Further, it would seem necessary that any formula for the diazo-salts should contain a quinquevalent nitrogen atom, and the only formula which can satisfy the foregoing conditions is



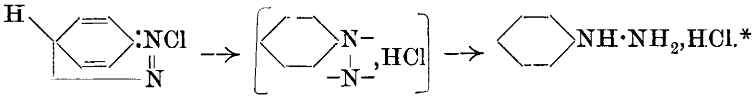
Diazobenzene chloride thus results from aniline hydrochloride as follows :



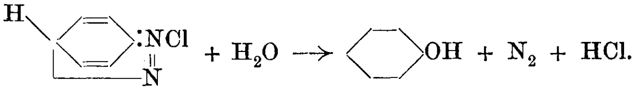
It will be seen at once that this formula readily explains those properties of diazobenzene chloride which have been already discussed. Just as benzoquinone, on reduction, loses its quinonoid configuration



so does diazobenzene chloride, in its conversion to phenylhydrazine, undergo the same change:

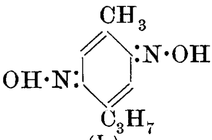


Further, the decomposition with water, as would be expected, takes place with rupture of the double linking, thus:

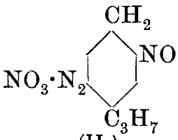


The various other decompositions are explained in the same way. It must be noted that this formula being "ring-quinonoid" or "semi-quinonoid" does not represent diazobenzene chloride as a true quinone, consequently there is no reason why, according to this formulation, this compound should be coloured, although, of course, coloured diazo-salts are well-known (compare Hantzsch, Proc., 1905, **21**, 298).

An important reaction in connexion with this constitution is the production of diazo-compounds directly from substances possessing undoubtedly the quinonoid structure. By acting on quinonedioximes with nitrogen peroxide, Oliveri-Tortorici found (*Gazzetta*, 1900, **30**, i, 526) that nitrosodiazo-compounds resulted; thus thymoquinonedioxime (I) yields the compound (II).

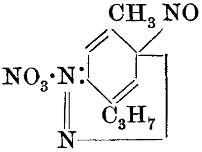


(I.)



(II.)

It is difficult to imagine why the quinonoid configuration should disappear in this reaction, and the simplest explanation of this change is offered by the formula here suggested, namely,



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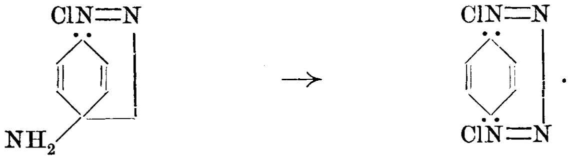
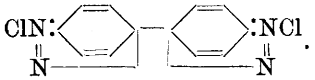
* In order to make this transformation clearer I have written phenylhydrazine hydrochloride as $C_6H_5{\cdot}NH{\cdot}NH_2,HCl$.

This formula also indicates why both N·OH groups are not changed into the diazo-group, for when we consider the case of *p*-phenylenediamine, which, as is well known, can only be converted into the bisdiazo-compound under special conditions, we find that the reason of this is that the linking of the second nitrogen atom with the para-carbon atom must first be broken in order to allow the second aminic nitrogen to become attached by two bonds, the final condition probably being that the second nitrogen atoms in each case are united thus:



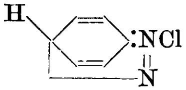
This may well explain the difference in the behaviour of *p*-phenylenediamine and diamines of the type of benzidine which are converted into the bisdiazo-compounds without difficulty, thus:



Applying this reasoning to the case of thymoquinonedioxime it is reasonable to suppose that the para-linking of the second nitrogen atom of the diazo-group cannot be broken under the conditions of the reaction.

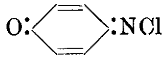
It is interesting at this point to compare the properties of diazobenzene chloride with those of, for example, quinonechloroimide, when a surprising similarity is apparent.

Diazobenzene chloride.



Readily soluble in water; decomposes by heating with water, fission taking place at the double-linked nitrogen atom. With concentrated hydrochloric acid gives chlorobenzene. Explodes on heating.*

Quinonechloroimide.



Readily soluble in hot water; decomposes by heating with water to 100°, fission taking place at the double-linked nitrogen atom.

With concentrated hydrochloric acid gives chlorophenol. Detonates above 85°.

There is, so far as I am aware, no record in the literature as to the behaviour of quinonechloroimide in solution. I am greatly indebted, therefore, to Prof. James Walker for light on this point. At Prof. Walker's request Miss H. H. Beveridge prepared a specimen of quinonechloroimide and determined its conductivity. Prof. Walker writes:

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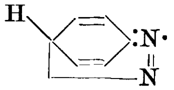
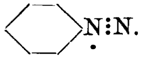
* On one occasion recorded by Hantzsch (*Ber.*, 1897, **30**, 2342), diazobenzene chloride exploded spontaneously with very great violence.

"The solution gave no precipitate with silver nitrate, indicating absence of chloridion, and had a conductivity only six times as great as that of the water employed. The solution was 0·16*N*, so that it had a conductivity only about 0·3 per cent. of a corresponding solution of an ordinary saline chloride."

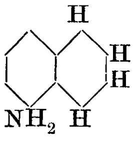
The fact that diazobenzene chloride is electrolytically dissociated in solution is thus a strong argument in favour of the presence of quinquevalent nitrogen, and there is no reason why the radicle diazonium, should not possess the constitution



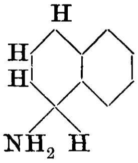
instead of



Not only does this formula explain satisfactorily the reactions of diazobenzene salts, but it throws new light on many phenomena which have hitherto been unexplained. For example, it is obvious that diazo-salts (chlorides, &c.) can only be formed from those amines which are capable of allowing the quinonoid formation to take place; thus *ar*-tetrahydronaphthylamine (I) forms diazo-salts, whilst the *ac*-compound (II) does not.

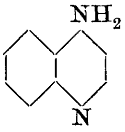


(I.)

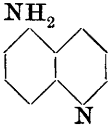


(II.)

Another example is furnished by the aminoquinolines,

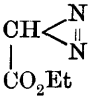


gives no diazo-salt



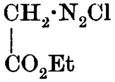
gives a crystalline diazo-chloride.

It is obvious also that one cannot expect the formation of a diazo-chloride from an aliphatic amine, as no quinonoid structure is possible, but it has hitherto remained unexplained why the diazo-compound prepared, for example, from aminoacetic ester should have the composition



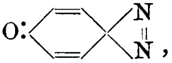
$$\begin{array}{l}\mathrm{CH}<\begin{array}{c}\mathrm{N}\\ \| \\ \mathrm{N}\end{array}\\ | \\ \mathrm{CO_2Et}\end{array}$$

and not

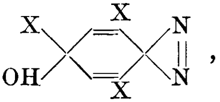


$$\begin{array}{l}\mathrm{CH_2{\cdot}N_2Cl}\\ | \\ \mathrm{CO_2Et}\end{array}$$

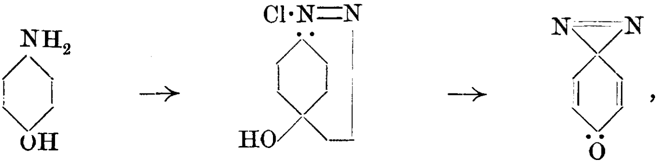
It has been indicated in the earlier portion of this paper that in one class of diazo-compounds the configuration of the benzene ring had already been taken into consideration in discussing the constitution of the diazo-nucleus. This is, of course, the class of the quinonediazides. Wolf has shown (*Annalen*, 1900, **312**, 119) that the so-called diazophenols must have the constitution



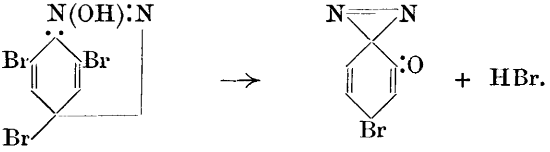
and Orton (*Proc. Roy. Soc.*, 1902, **71**, 153; Trans., 1903, **83**, 796) has shown that, in the various transformations which halogen substituted diazobenzene salts of weak acids undergo in aqueous solution, the benzene ring assumes the (ortho)quinonoid state. He even makes the interesting suggestion that such compounds when in solution may become paraquinonoid in structure, thus:



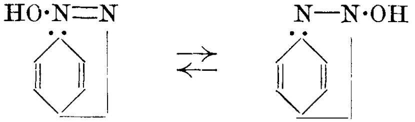
and adds that "there is a strong and increasing weight of evidence in favour of the view that in isomeric rearrangements of this type the benzene nucleus transiently assumes a quinonoid linking." These phenomena are evidently very satisfactorily explained if the first phase is of a quinonoid character; thus, in the case of the aminophenols we have



and the transformation described by Orton may be written, for example:

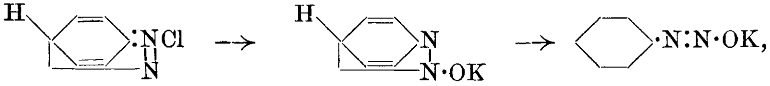


Constitution of the Metallic Diazo-compounds.—Although in the formula here suggested for the diazo-salts it may be regarded as certain that the acidic nucleus is firmly united with the quinquevalent nitrogen atom, when we investigate the case of the corresponding hydroxide it is evident that tautomerism may occur, thus:



the hydroxyl group being capable of migrating to the other nitrogen atom.

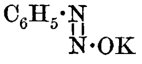
The latter formula provides an exceedingly probable constitution for the so-called *syn*-diazohydroxides and the corresponding metallic derivatives, for when one considers that the diazo-chloride yields the metallic derivative simply by admixture with caustic alkali at a very low temperature, in some cases below 0°, it seems reasonable to suppose that this change is accompanied by the smallest possible alteration in the constitution, such as is indicated above. When, however, the reaction is carried out at a high temperature, the quinonoid configuration is lost and the *iso*-salt is produced, thus:



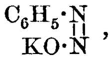
which is more in accord with the tautomeric nitrosoamine form than is the *anti*-configuration of Hantzsch.

From the above reasoning it is apparent that, as the constitution of the various diazo-compounds may readily be interpreted without the aid of the stereochemical theory, the terms *syn* and *anti* cannot be used. At the same time it is convenient to retain the name "diazonium" for what have up to this point been designated "diazo"-salts, and instead of "*syn*" and "*anti*" we have now "normal diazo-oxide" (for *syn*-diazotate) or simply "diazo-oxide" and "*iso*diazo-oxide" (for *anti*-diazotate), reverting to the older names.

The close chemical relationship between the diazo-oxides and the *iso*diazo-oxides are all readily explained by the formulæ here developed. The very slight capacity for coupling with phenols which is manifested by the *iso*-salt is explained by the fact that this is already an azo-compound, and the process may be regarded, not as a condensation, but as a displacement of the OK group by the C_6H_4·OK group. This difference in coupling power cannot, however, be explained by the stereochemical theory; indeed, one would almost expect the *anti*- to couple more readily than the *syn*-compound, for it is conceivable that if these really represented the configurations of the respective compounds



$$\begin{array}{l} C_6H_5\cdot N \\ \| \\ N\cdot OK \end{array}$$



$$\begin{array}{r} C_6H_5\cdot N \\ \| \\ KO\cdot N \end{array},$$

the *syn*-compound should couple more slowly than the *anti*-, owing to a greater possibility of steric hindrance.