XCI.—*A Space Formula for Benzene.*

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IN any space formula representing the benzene molecule the following facts should be accounted for :

1. The equal value of the six carbon atoms.
2. The equal value of the six hydrogen atoms.

3. The existence of only one mono-substitution product, and of three di-substitution derivatives, &c.
4. The existence of di-, tetra-, and hexa-hydro derivatives.
5. Why six carbon atoms are necessary for the production of the so-called "benzene nucleus."
6. The peculiarity of benzenoid compounds in contradistinction to paraffinoid compounds.

If any six solid figures are symmetrically arranged in space equidistantly from a point, their centres will lie on the surface of a sphere at points which may be regarded as the middle points of the six edges of a tetrahedron, the centres of the six faces of a cube, or the six corners of the six solid angles of an octahedron. If these solid figures be all of equal mass, this point will evidently be the centre of gravity of the system. Now let tetrahedra representing carbon atoms be so disposed. In order to satisfy the requirements of a space formula for benzene so that any one carbon atom is always connected with two others in a precisely similar manner, and so that the connections are from two of the four symmetrically placed points of attraction that every carbon atom is supposed to possess, then there seems to be only one configuration which will allow of this. (Plate I.*)

Moreover, if six hydrogen atoms are arranged symmetrically on these spheres or tetrahedra on six of the remaining twelve points of attraction, there is only one symmetrical way of doing this also. (Plate II.)

Movement in this figure could take place in two ways—

1. Movement of each sphere or tetrahedron about its centre.
2. Movement of each sphere or tetrahedron about the centre of gravity of the whole mass.

In the first case, the simultaneous rotation of each sphere or tetrahedron about its centre (and in the same direction) would bring the combined hydrogen atoms towards the centre of the mass in *two distinct sets*, those on the 1, 3, 5 carbon atoms, and those on the 2, 4, 6 carbon atoms. That is to say, when one set are inside or near the centre of the mass, the other three are outside and further away from the centre of the mass.

In the second case, namely, the vibratory movement of each sphere or tetrahedron about the centre of gravity of the mass, any movement would alter the relative positions of the spheres or tetrahedra with regard to one another, bringing into play alternatively the six unsaturated points of attraction on these spheres or tetrahedra. These different phases are very interesting to follow. (See Plate III. p. 1016).

* The connecting links between the carbon atoms are represented as from the centres of the faces of tetrahedra, and not, as is usual, from the corners. (Of course, these points are situated at the angles of the inscribed tetrahedra.)

Front view.

Side view.

PLATE III.

FIG. 1.

First phase.

FIG. 2.

Intermediate phase seen in the plane at right angles to that seen in Figs. 1 and 3.

FIG. 3.

Last phase.

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PLATE II.

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Symmetrical.

Unsymmetrical.

NOTE.—It will be seen in Fig. 2 that the carbon atoms are so arranged that at present neither the hydrogen atoms nor the vacant points of attraction are pointing towards the centre of the figure. But if they are rotated about their centres so that the hydrogen atoms and the vacant points of attraction of each atom are always in a plane drawn through the centre of the system, then the two sets of hydrogen atoms will always be separated from one another by an angle of 120° . In other words, when the hydrogen atoms on 1, 3, 5 are all pointing directly to the centre, by turning the tetrahedra through an angle of one-third of the circle, or 120° (not 180°), the other set, 2, 4, 6, will be pointing directly towards the centre.

In the first phase, Fig. 1 (Plate III), there is shown an extreme position of the carbon atoms. If any three carbon atoms are taken, for instance, 1, 2, 3, the position 2 will tend to take will be between 1 and 3. Similarly, if 2, 3, 4 are taken, the position 3 will tend to take will be between 2 and 4. Hence carbon atom 2 will move to the right, and 3 will move in the opposite direction, namely, the left.

The intermediate phase between Fig. 1 and Fig. 3 is seen in Fig. 2. In this figure, however, the view is taken sideways on a plane lying at right angles to that seen in Figs. 1 and 3.

FIG. 4.

FIG. 5.

As carbon atom 1, Fig. 4, moves in the direction indicated by the dotted line (to the left), and carbon atom 2 in the direction of the other dotted line to the right, a small rotation of the two carbon atoms about their centres will bring the vacant point of attraction on each into play for an instant, as shown in Fig. 5. The vacant points of attraction are on the faces abc on both carbon atoms, the faces abd on 1, and acd on 2, being occupied by the hydrogen atoms. Thus for a brief moment there will *almost* be a double bond between the carbon atoms 1 and 2, and also between 3 and 4, 5 and 6.

Continuing this movement when the six carbon atoms are all in one plane, as shown in Fig. 2, then by the same rotation about their centres

either three or six of the vacant points of attraction would point towards the centre together; and finally, in the return movement from Fig. 3 to Fig. 1, owing to the twist given to the carbon atom 2, there will be conversely *almost* a double bond between it and carbon atom 3, and also between 4 and 5, 6 and 1.

Taking the projections of these phases, we get the following:

This space formula for benzene, therefore, is in complete accord with that of Kekule and the centric formula, showing that both are mutually convertible the one into the other. It also shows how the supposed double linkings in the Kekule formula shift between the carbon atoms, rendering two ortho-chlorobenzenes incapable of existence. But it differs from both, in that, in two out of five, there are *two distinct sets of hydrogen atoms* (the 1, 3, 5 set, and the 2, 4, 6 set), and that when one set is inside the molecule, the other set is outside the molecule.

It seems also probable that reaction with such a grouping would only be effected when the reacting molecule had been actually drawn into or towards the centre of the mass. The combined attraction of three hydrogen atoms arranged symmetrically round a chlorine molecule, (see fig., next page) and the near proximity of the hydrogen and chlorine, should be sufficient to dissociate such a molecule, and produce free atomic

chlorine. It would then be capable of adding itself on to the benzene nucleus, and then, in order to restore stability to the system, monochlorobenzene would be formed by the elimination of hydrogen chloride.

It would be easy to give numberless illustrations of the simple manner in which this formula accounts for the peculiarities of benzenoid derivatives; they can, however, be summed up in the statement that everything that can be explained by the ordinary formula and by the centric formula can be explained by this space formula, because it embodies both; it is both joined together *plus the hypothesis that there are two distinct sets of three hydrogen atoms.*

Any formula for benzene must also be applicable to naphthalene and the other hydrocarbons which are supposed to consist of more than two benzene nuclei. The space formula renders it highly improbable that two nuclei could exist together. The two carbon atoms that join the two halves could only form part of one such nucleus at a time, that is to say, if six of the carbon atoms in the naphthalene molecule at any moment possessed the configuration shown in the space formula for benzene, then the remaining four would probably exist joined together in the same way as they are supposed to be in olefinoid compounds.

Naphthalene.

It is probable, however, that an interchange of the two central carbon atoms takes place, and under certain conditions the second half of the molecule becomes benzenoid in character, whilst the other four carbon atoms that are left become olefinoid in their character.

A formula for pyridine could of course also be suggested which would account for its similarity to benzene in its properties, also such

reactions as the formation of α - and γ -picoline by heating pyridine methiodide.

As has already been seen from the space formula, there are two sets of three hydrogen atoms, which, by rotation or oscillation of the carbon atoms, alternately come towards the centre of the molecule. These hydrogen atoms are in the 1, 3, 5 and 2, 4, 6 positions; and it seems possible that this may perhaps explain the fact that some mono-substituted benzene derivatives, when subjected to further substitution, give a mixture of the *ortho*- and *para*-di-derivatives, whilst others under the same conditions yield scarcely anything but *meta*-compounds. Crum Brown and Gibson (*Trans. Chem. Soc.*, 1892, **61**, 367) have formulated a rule by which we can predict which of these two sets of compounds is likely to be produced. And they point out that if the hydrogen compound HX of the radicle X (already united to the benzene molecule) is capable of *direct oxidation* in one step to the compound HOX, then

Pyridine.

that particular mono-derivative of benzene, when converted into a di-derivative, will yield a *meta*-compound.

If we arrange these groups in two series according as they give *ortho*- and *para*-di-derivatives or *meta*-di-derivatives, a marked difference between them can at once be seen—

First set.

$R \cdot CH_3$ RCl RBr ROH RNH_2 $R \cdot CH_2 \cdot COOH$ &c.
these yield chiefly *ortho*- and *para*-di-derivatives, whilst,

Second set.

yield scarcely anything but *meta*-di-derivatives.

In the second set of groups, the various elements directly united to the benzene nucleus are all, in a sense, unsaturated, or, in other words, their hydrogen compound HX (where X stands for the group) is capable of

directly adding on oxygen. This fact has already been pointed out by Armstrong (*Trans. Chem. Soc.*, 1887, 51, 259), in a slightly different manner; to quote, "Whereas in compounds subservient to the meta-law the grouping elements of the radicle (X) is associated with one or more polyad atoms—with N in CN, with O in NO_2 , COH, COCH_3 , and COOH."

There is one group, however, in the first set which is, in a sense, unsaturated, and that is the NH_2 group, but as it is difficult to produce a di-derivative from such a substance as aniline itself and it is always a salt or an anilide that is used, at present it is impossible to say whether it would give meta-derivatives. It is, however, a curious fact that dimethylaniline, which is a much more feeble base than aniline, does, on nitration and sulphonation, yield meta-derivatives.

All these groups, therefore, that favour the production of meta-di-derivatives are groups that possess a certain amount of what has been called "residual affinity," and, again to quote Armstrong, "Herein, I would suggest, lies the explanation of the meta-law, my opinion being that the additive compound which generates the meta-derivative is formed by the combination of the reacting molecule *with the radicle* of the mono-derivative, and not with the carbon atom which carries that radicle." If this be so, it is then easy to answer the question why a meta-di-derivative is produced.

Taking the projection of the space formula for benzene, an ordinary graphic representation can easily be substituted that will show how three hydrogen atoms are inside the molecule whilst three are outside.

From which it is seen that when the hydrogen atoms attached to the carbon atoms 1, 3, 5 are all in the centre together, then the hydrogen atoms attached to the carbon atoms 2, 4, 6 are all on the outside, also when, by oscillation, the hydrogen atoms on the 1, 3, 5 carbon atoms are on the outside, those attached to the 2, 4, 6 carbon atoms will move towards the middle of the molecule.

If nitrobenzene, therefore, is capable of forming first a very unstable additive product, $\text{C}_6\text{H}_5 \cdot \text{NO}_2 - \text{Cl}_2$, the NO_2Cl_2 group would,

when near the centre of the molecule, meet the two hydrogen atoms attached to the 3, 5 carbon atoms, and so a meta-derivative would be formed. But, on the other hand, in the case of chlorobenzene, if nitric acid be allowed to react with it, no such additive compound

would be produced, and the attraction* of the three hydrogen atoms attached to the 2, 4, 6 carbons might be just sufficient to determine its reaction with them.

This can be expressed as follows :

In the formation of meta-di-derivatives, this supposed residual affinity cannot be very great, for at present it is doubtful whether any compounds such as $\text{C}_6\text{H}_5\cdot\text{NO}_2\text{—Cl}_2$ have been produced ; still the residual affinity of the group —NO_2 might reasonably be supposed to be sufficient to overcome the tendency to form ortho- and para-derivatives, and direct the chlorine in towards those hydrogen atoms which come towards the centre of the molecule at the same moment that it does itself.

There is, however, an alternative explanation. Perhaps in the chlorination of nitrobenzene the “residual affinity” of the NO_2 -group might direct the addition of the entering chlorine to the partially free

* This idea of the “attraction” of combined hydrogen for electro-negative elements or groups of elements has been of the greatest value in the hands of J. Wislicenus, helping him to extend the hypothesis of Van’t Hoff and Le Bel on the arrangement of the atoms in space.

fourth point of attraction on the carbon atoms 1, 3, 5 (the NO_2 group being united to carbon atom 1). The additive compound would then be : *

Of course, the reverse would be the case with the nitration of chlorobenzene. The directing influence being the three hydrogen atoms on the 2, 4, 6 carbon atoms. The additive compounds first produced would be :

The first, on elimination of water, would yield the ortho-compound, the second the para-compound. There is, however, a possible objection to this explanation. The entering group would be attached to the carbon atom on the side opposite to that occupied by the original hydrogen atom, and in order that the whole molecule should be symmetrical would have to shift over. This change of place, however, is not at all impossible, and might easily take place, as it only involves the movement of a group to another *unoccupied* point of attraction on the *same* carbon atom.

As, in the preparation of tri- and further substituted derivatives of

* The production of such a chloro-additive product is rendered highly probable by the results of Ador and Rilliet, who obtained metabromobenzoic acid and metaphthalic acid by oxidising the compounds formed by the action of zinc ethyl on the product of the action of bromine on benzene at the ordinary temperature (*Ber.*, 1875, **8**, 1286).

benzene, the entering groups seem on the whole to follow the same laws as in di-substituted derivatives, it is unnecessary to give more examples. There are, however, some curious facts which need elucidation. For instance, why should a meta- di-substituted derivative, such as metanitrophenol, on further nitration, yield only compounds where the entering nitro-group is entirely directed by the OH, and not by the NO_2 group. This so-called directing influence of the OH group (and it occurs also with the NH_2 group) is certainly a curious fact. A possible explanation may, however, be given :

from which it will be seen that it is the combined influence of the three hydrogen atoms that tends to attract the entering molecule, and not the OH-group that determines how the tri-substituted compound is going to be formed.

Many interesting cases of isomeric change can also be partially explained by this space formula.

The production of hydrochloride of toluidine from methylaniline hydrochloride (at 350°). The production of sodium salicylate from sodium phenoxide and carbon dioxide. Also the isomeric changes that α -naphthalenesulphonic acids undergo when heated. In all these case of isomeric change, heat is required, and dissociation probably precedes recombination. A few other reactions, which do not receive any explanation from other benzene formulæ, might be mentioned. For instance, when sodium phenoxide is oxidised by means of fused caustic soda, resorcinol and phloroglucinol are formed; but if aniline is oxidised by chromic acid quinone alone is formed. If the ONa group and the NH_2 exert any determining influence on the entering oxygen, we should expect the sodoxyl group to have a greater attraction for the entering oxygen than the amido-group, and hence meta-di-derivatives would be formed.

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