

Progress in the Technique of Crystal Analysis*

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THREE years ago, Sir Gowland Hopkins in his presidential address spoke with admiration of the work of the organic chemist and in particular of the "emergence of power to grasp the architecture of complex invisible entities such as organic molecules and the ability to construct them at will". He told how under modern methods of investigation the picture which the chemist had formed of the invisible molecule had actually taken shape. His picture-making had been amply justified. His stereometry was not, as some thinkers had maintained, to be swept away in favour of a mathematical symbolism.

This anticipation has been fully realized during the last few years, mainly through the remarkable increase in the accuracy with which the structure of molecules, molecular aggregates and solid bodies in general can be determined. For this the methods of X-ray analysis of crystalline structure have been largely responsible. Moreover, other methods have been greatly strengthened by the example set by X-ray analysis and by its reactions upon themselves. Optical, electrical, magnetic and other properties have been successfully studied with the same great purpose, namely, the correlation between the properties of a substance and the spatial arrangements of its components.

While the X-ray methods have been mainly useful in describing the arrangement of the atoms in assemblages surrounded by others of like nature and conditions, the methods of electron-diffraction are giving a remarkable insight into the modifications of arrangement that are to be found on surfaces. The extraordinary interest of such knowledge arises from the fact that natural processes so largely depend on surface actions.

For many years after its inception, the X-ray analysis was, as might be expected, engaged in trying its own powers and learning how to apply them. It cleared up many structural problems on which older methods had little to say that was definite, as for example the distinction between ionic, metallic, adamantine, and molecular compounds. Many crystalline structures were determined, and the results, as is well known, have been serviceable in a wide field of scientific research, and in many industrial processes. The methods of analysis, the technique and the interpretation of results have been greatly improved, as might be expected, by the researches of many hundreds

of workers. The increase in accuracy is so great that new possibilities of usefulness come into view.

The improvement appears in two ways. In the first of the two, the measurements of the dimensions of the unit of pattern of a structure can now be made to one part in several thousand. Consequently, the determination of the electron charge e , made by the X-ray method, can stand beside the older determinations of the oil-drop method. There is a persistent discrepancy of about one part in two hundred, the former giving the value 4.80×10^{-10} , the latter 4.77×10^{-10} ; but it is clear that the larger value is at least as near the true value as the smaller. A full discussion of the X-ray method is given by Compton and Allison in their recent book on "X-rays in Theory and Experiment", and a critical examination of some outstanding points is made by du Mond and Bollman (*Phys. Rev.*, Sept. 1936).

Again, as has been observed by Bernal, the use of high-precision determinations of the lattice constants of metals will soon become the most reliable gauge of purity of a metallic element. Accuracy has here been pushed to one or two parts in forty thousand. The phase boundaries of an alloy also can be very closely and conveniently defined by observations of such a character. Accuracy has been of great importance to the well-known work of Hume-Rothery on alloy structures, and to the curious and very important relations between order and disorder in alloys which have been specially studied at Manchester.

The accuracy with which the position of each atom in the unit cell can be measured is of quite a different order. Thanks in particular to the use of Fourier analyses by J. M. Robertson and others, the distances separating the atoms, centre to centre, can be found to about 1 per cent, even when the complicated molecules of organic crystals are under examination. This is a great advance on the possibilities of even a few years ago, and it has important consequences. In particular, fresh light is thrown upon the problem of the chemical bond. At one time, single, double, and triple bonds were considered to be distinct and definite phenomena. The tetravalency of carbon, for example, was described as an assemblage of four equal powers of combination, of which one or more might be exercised in the same direction. When the diamond structure was found by the X-ray methods, it was no matter of surprise that

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the four separate single bonds were displayed in the attachment of each carbon to four neighbours. In the structure assigned by the chemist to benzene, the fact that each atom had but three neighbours presented difficulties; various theories have been suggested in explanation, mostly little more than different ways of drawing diagrams, in which four single bonds were made to act somehow. In recent years, it has been more usual to propose that bonds may alternate between single and double, and that the tetravalency of carbon in the benzene ring is satisfied because three of the six links are double and three single, the two kinds alternating both in time and in order round the ring. The conception can be extended to cases much more complicated provided that the two forms between which alternation occurs do not differ much either in form or energy. The effect is described as one of 'resonance', a term due to Hund but applied to organic chemistry mainly by Pauling and his collaborators. Its bearing on structural chemistry was discussed by Sidgwick a few months ago in a presidential address to the Chemical Society.

When substances in which this 'resonance' is supposed to occur are examined by the X-rays, it is found that the actual centre to centre distance of two atoms connected by a link alternating between single and double is characteristic of neither of the two extremes. These last two are definite quantities, and the length of the varying link lies between them. An actual link is rarely a pure single or double or triple link. Pauling and Sidgwick both discuss a number of cases in which the centre to centre distances can be correlated with a probable or possible amount of resonance. An excellent example is furnished by oxalic acid, which was examined by Zachariasen in 1934, but has just been remeasured by Robertson, using the powerful Fourier method of analysing the observations. The distance between the carbon atoms is 1.43 Å. The length of the single link of diamond is 1.54 Å. The length of a double bond is very nearly 1.33 Å. It might seem that in oxalic acid the link is actually more nearly double than single; but this is not so. A small proportion of double linking seems to shorten the distance considerably. For example, each link in the hexagonal network of graphite must be two-thirds single and one-third double, yet its length is 1.41 Å. In benzene, the half and half arrangement (following Kekulé) is correlated with a length of 1.39 Å. or 1.40 Å. Thus the actual length of a bond may prove to be a safe indication of its nature. Robertson points out that the oxalic acid molecule is always planar, which may be accounted for on the ground that rotation is restricted round a link which is even partially of a double character.

It has recently been shown by Bernal and Megaw (*Proc. Roy. Soc., A*, 151, 384; 1935) that in all probability there are two types of bond linking oxygen atoms through intermediary hydrogens. One is the 'hydrogen bond'; it is found, for example, in acids, and it corresponds to a separation distance, oxygen to oxygen, of 2.55 Å. The other is the hydroxyl bond; it is found in a number of hydroxides, and its length is about 2.8 Å. By the use of this conception it has been found possible to locate the positions of the hydrogen atoms in several hydroxide structures, particularly in the clayey mineral hydrargillite. The oxalic structure of Robertson seems to supply a new and interesting example of the difference between the two kinds of bond. One of the oxygens at each end of the oxalic acid molecule is bound to a water molecule in the crystal by a link 2.87 Å., the other by a link 2.52 Å.

It has been pointed out (Fricke, *Koll. Z.*, 69, 312; 1934) that the linking up of hydroxyl bonds explains the properties of the gels that are formed by neutral hydroxides.

These few examples may serve to show how improvements in the technique of X-ray analysis are sharpening a tool which has already been of assistance to research in many directions and now seems to be acquiring a new usefulness.

The chemist has already shown that the properties of the molecule depend on the internal disposition of its atoms. The characteristics of the solid state depend also on spatial relations, and in a manner which is even more complicated, much more complicated than in the case of the independent molecule. Accurate measurement of the spatial arrangements lays a firm foundation for the study of the properties of a substance in relation to its structure and its composition. The problems to be solved are, of course, extremely complex, but it is surprising how much can be done towards the examination of intricate molecular associations when the spatial relations between the most commonly occurring atoms are known. This applies, for example, to the study of the proteins, which has already gone far; to the clays, and to the glasses and other extended structures. At one time it seemed hopeless to expect to learn much of the structure of bodies which were so irregular as to give no sign of crystallinity. But it is now possible to work from the regularity in occurrence of a few definite separation distances, even when regularity in orientation does not exist: and methods have been devised by which these distances can be determined by the X-ray methods.

It is clear that the stereometry which the chemist has developed so successfully is acquiring new powers which will have the widest applications.