Diffraction Methods in Modern Structural Chemistry.

THE TILDEN LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY IN LONDON ON JANUARY 18TH, 1945, AND AT BRISTOL UNIVERSITY ON FEBRUARY 8TH, 1945.

By J. MONTEATH ROBERTSON.

IN his Tilden Lecture last year, Thompson [1] described the application of infra-red measurements to chemistry; this year I wish to go to the other end of the spectrum and deal with an entirely different method. In *X*-ray or electron-diffraction experiments we usually try to build up a picture of the object under investigation by recombining the waves which it scatters. If the object is much smaller than the wave-length, it is well known that we can at best get a blurred picture. Detail on a finer scale than the wave-length is lost, and hence arises the necessity for using short waves. However, we have this much in common with the subject of last year's lecture : in both cases an attempt is made to use as delicate a probe as possible to explore the structure of the molecule. In infra-red radiation we have a delicate energy probe, for the longer the wave-length the smaller is the energy quantum. In *X*-rays or electron waves, on the other hand, we have a delicate measuring rod for ascertaining interatomic distances and other structural data in a rather direct manner.

I. DIFFRACTION METHODS.

It would be out of place here to attempt any detailed account of diffraction methods.[2] We are concerned rather with their application to problems of chemical interest; but something should be said about their present scope and limitations and also about possible future developments. With regard to problems of molecular structure, two main methods have been very extensively developed and employed : electron diffraction, applied to what are effectively single molecules in the gaseous state; and *X*-ray diffraction, applied to crystals. Until recently each of these methods has been confined to a considerable extent to its own particular province. The electron method is most easily applied to gases or to easily volatile substances, and these are just the ones from which it is most difficult to prepare and preserve the well-formed single crystals that are necessary for a detailed study by the *X*-ray method. Between them, therefore, these two methods have covered or can cover nearly the whole field which is of interest in structural chemistry. Where there has been overlap the results have generally been concordant.

When we look a little more closely at these methods we find that the observational data from which the analysis proceeds differ very much in the two cases. In the electron method we get a number of rather minor gradations of intensity on the continuously receding background of the photographic film. But the human eye is a better instrument than most photometers, and by means of what Sutton calls a " singularly impressive optical illusion " a number of well-defined bands can be seen whose relative positions and intensities can be estimated. Quantitative intensity measurements are rather out of the question, and have seldom or never been employed, although improvements in technique may make this possible. For very simple structures, involving one or two parameters, these meagre data are sufficient for a complete and very accurate solution, for the method is very sensitive. Unfortunately, however, as the complexity of the structure increases, the available observations do not multiply in like proportion.

With the *X*-ray crystal method we appear to be in a much happier position. Again, the diffracted beams are generally recorded on photographic films; but this time we can, if we wish, get discrete spots instead of circular bands, and these spots can be related to the angular setting of the crystal. Their positions can be measured accurately to one part in a thousand, or even much better if we care to take the necessary trouble. Their intensities can also be measured, both relatively and absolutely, with an accuracy which depends mainly on the type of photometer or other instrument available.[3] Background scattering is again the limiting factor, but it does not worry us unduly until the method is pushed to the extreme regions of very small or very large angles of incidence. Most important of all, the number of independent measurements which we can make increases with the complexity of the structure under review. Thus, if the unit of structure contains about 10 atoms of carbon, nitrogen or oxygen, together with an appropriate number of hydrogen atoms, then with copper radiation ($\lambda = 1{\cdot}54$ A.) there will be over 500 possible reflections, and we should be able to make intensity measurements on most of them; but if the structure is more complicated and contains 100 such atoms, then about 5000 possible reflections will be available for observation. We have therefore the possibility of making about 50 observations per atom of the structure. Further, we can in principle increase this number as much as we please by using shorter wave-lengths, although in practice background limitations and other difficulties would soon be encountered. So far as I know, this extreme wealth of data has never been fully employed in any structural investigation, with the possible exception of a few elementary substances. One of the most promising and most interesting lines of development undoubtedly lies in the more complete utilisation of these data for the purpose of making really detailed and exact structural analyses.

The comparison so far made between the electron diffraction and the *X*-ray crystal method may appear unfavourable to the former, but our treatment has been superficial because we have not yet considered the nature of the problem which presents itself for analysis in the two cases. For diffraction by gas molecules, this problem is in some ways much simpler than the corresponding crystal problem. The gas molecules are widely separated, and scatter independently. The result can be calculated by treating a single molecule and averaging over all possible orientations. It is thus possible to set up a model for any molecule, and test it directly by comparing the observed and the calculated diffraction patterns. The parameters can be varied systematically until the best agreements are found.

With a crystal we cannot do this. The molecules or structural units co-operate in scattering, and the whole essence of the experiment is to take advantage of this co-operation in order to build up diffracted or " reflected " rays which are strong enough to measure or record. We must therefore take account of the relative positions of the molecules in the crystal, their distances apart and mutual orientation. If we can work the problem out, we are rewarded with all this additional information about intermolecular distances, information which is beyond the reach of the gas-diffraction experiments; but it makes the problem very much more complex : it is no longer possible to set up a simple model for the molecule and carry out a direct test, for every such model would have an infinite number of different orientations, all of which would require to be tested before that particular model could be either established or eliminated.

The nature of these two different problems becomes very clear if stated in terms of the so-called " direct " methods of analyses which are available in the two cases. The electron scattering $I(s)$ can be represented by the integral

$$I(s) = \kappa\int_0^\infty (r^2D(r)/s^4)[(\sin sr)/sr]\mathrm{d}r$$

where $r^2D(r)$ represents the product of scattering powers in all volume elements at the distance r apart; s is a function of the scattering angle. This integral can be inverted to give

$$D(r) = \kappa'\int^\infty s^6I(s)[(\sin sr)/sr]\mathrm{d}s$$

from which $D(r)$, the radial distribution function of the scattering matter, can be calculated from the observations.[4] If the structure consists of atoms, and if most of the scattering takes place at or near the nuclei, then maxima in $D(r)$ correspond to interatomic distances. The complete function represents the superposition of all the interatomic distances in the molecule, and so in principle at least it presents in a very concise form all the information provided by the diffraction pattern.

In crystal-structure work the methods of Fourier analysis,[2b] and in particular Patterson's method, are very similar. The structure amplitude F_{hkl} for any crystal plane (hkl), the absolute value of which can be obtained from the observed intensity of the diffracted beam, is given by the triple integral

$$F_{hkl} = \kappa'\int_0^a\int_0^b\int_0^c \rho(xyz)\exp 2\pi i(hx/a + ky/b + lz/c)\mathrm{d}x\mathrm{d}y\mathrm{d}z$$

where $\rho(xyz)$ is the density of scattering matter at x, y, z; a, b, and c are axial lengths, and hkl Miller indices. A somewhat similar inversion gives the density of scattering matter in terms of the structure amplitudes as

$$\rho(xyz) = \kappa'\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F_{hkl}\exp - 2\pi i(hx/a + ky/b + lz/c)$$

only in this case the triple series is the correct representation. In the electron-diffraction problem a series is generally used for convenience, but the integral is the correct form. The difference arises from the essentially periodic nature of the crystal. It will be noted also that in the crystal the complete expressions are always triple integrals or triple series because the orientation is fixed and we can explore the structure in three dimensions.

The X-ray crystal problem, however, is not really so simple as this. The F_{hkl} as defined above is a complex quantity, with an amplitude and a phase constant, and the observed intensities in general only enable us to calculate the amplitudes. If we confine ourselves to these observed quantities, Patterson [5] showed that we can calculate a function $\mathrm{A}(uvw)$ from them which is given by the analogous expression

$$\mathrm{A}(uvw) = \kappa''\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F^2_{hkl}\exp 2\pi i(hu/a + kv/b + lw/c)$$

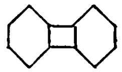
Lines joining the origin to peaks in this function give interatomic vectors, and the complete function thus represents the superposition of all the interatomic vectors in the crystal, which, of course, include the vectors between the atoms of adjoining molecules as well as those within the molecule itself. Like the radial distribution function for electron diffraction, the Patterson function again presents in a concise form all the direct information about interatomic distances which is provided by the diffraction pattern.

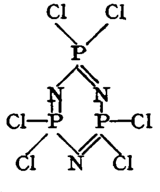
The information obtained from the crystal gives a picture of the structure in three dimensions, and so it is much more detailed than that provided by the gas-diffraction experiments. Nevertheless, in both cases, as soon as we pass beyond the simplest structural units containing three or four atoms, the direct methods of analysis tend to break down because of the complexity of the resulting diagrams and the difficulty of resolving separate peaks. In general it is found necessary to resort to the more indirect but more critical tests of trial and error methods based on the testing of preconceived models of the structure under investigation, and, as we have already seen, the gas-diffraction method enjoys a great advantage here, because scattering from the molecule is automatically averaged over all possible orientations. With a crystal we may predict the interatomic vectors of any molecule, but the vectors between the atoms of adjoining molecules, which are intermingled with these, are usually much less easy to predict.

This greater simplicity of the gas-diffraction method is reflected in the results already achieved. In its own field it has probably led to a larger number of accurate determinations of interatomic distances than the crystal method. Particularly important for structural chemistry is the way in which it can be employed to compare long series of closely similar compounds, *e.g.*, the work on the chloro- and fluoro-methanes, and on the chlorobenzenes [7] by Brockway and Palmer, and the recent work on halogen derivatives of tin, arsenic, and nitrogen by Skinner and Sutton.[8] With more complicated molecules the method is, of course, limited by the comparative meagreness of its data, but with recent improvements in technique some very striking results have been obtained, in the direction of checking and testing structures. The recent very interesting work by Schomaker and others on the hitherto doubtful structures of pirylene (I) [9] and diphenylene (II),[10] and the full structural determination by Brockway and Bright [11] on the trimer of phosphonitrile chloride (III), are significant examples. If further refinements of the method can be achieved, to give still more detailed diffraction patterns, it seems quite possible that the gas-diffraction method may rival the crystal method in dealing with moderately complex structures. The comparative speed and simplicity of its application are also great advantages.

(I.) $CH_3{\cdot}C{\equiv}C{\cdot}CH{:}CH_2$

(II.)

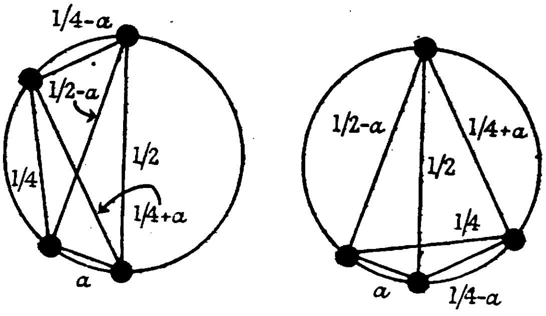




(III.)

FIG. 1.

Homometric pair (4 points) with one variable parameter (Patterson).[13]



In comparing these two methods, one final question should be considered. If, in any investigation, excellent agreement is finally obtained between the observed diffraction pattern and the calculated intensities, does this constitute a unique solution of the problem? For gas-diffraction experiments the answer is almost certainly no if the structure contains more than two or three atoms. Even four atoms in general positions involve 12 parameters, which is probably about as great as the number of diffraction maxima which can be observed on the photograph. The process is rather one of showing that a certain assumed model is compatible with the experiments and that other slightly different models lead to inconsistencies. The testing and eliminating of various molecular models is a most important and essential part of the analysis.

In the X-ray crystal method we have seen that the number of observed diffraction maxima is very great. In single-crystal work it can always be made very much greater than the number of parameters involved in the structure, even when the atoms are placed in their most general positions. It might then be thought that, once good agreements are obtained between the observed and the calculated values throughout the whole range of the intensities, the structure so determined would constitute a unique solution of the problem.* This is perhaps usually the case but it is by no means always necessarily so. The problem may contain inherent ambiguities which no amount of accurate intensity data alone will solve. The first evidence of this state of affairs in a special case was obtained by Pauling and Shappell,[12] and recently the mathematics of the general one-dimensional problem has been studied by Patterson.[13] He finds that various periodic distributions of points along a line may have the same vector distance set, and that consequently they will give rise to the same X-ray diffraction pattern. Such sets of points are termed " homometric." A linear periodic distribution is conveniently represented by plotting the points on the circumference of a circle, and one such homometric pair for four points with one variable parameter is shown in Fig. 1. There is difficulty in developing any general mathematical theory for this problem, and only special cases have so far been investigated. The easiest examples are obtained by arranging the points at r of the n vertices of a regular polygon, and out of 2664 " cyclotomic " sets examined in this way Patterson has found 390 homometric pairs, 7 sets of homometric triplets, and 3 sets of quadruplets. These results are very significant because they show that, even if perfect agreements are obtained between all the calculated and observed X-ray intensities, the result may not constitute a unique solution to the problem.

---

* If the problem is treated as a continuous distribution of scattering matter, without the fundamental assumption that it is concentrated into a limited number of atoms, then it is easy to show that there are always an infinite number of solutions. These may be obtained by assigning arbitrary values to the unknown phase constants, and evaluating the appropriate Fourier series.

In view of this, one may be inclined to regard the outlook rather pessimistically, but it should be emphasised that the real question to be asked about any diffraction problem is whether a unique solution is possible *in terms of reasonable structures*. In practice this is the question always put when structures are analysed in terms of preconceived molecular models. It is important, too, that the solution be supported by other kinds of physical evidence, such as may be furnished by optical and magnetic properties, dipole-moment measurements, etc. All these various lines of evidence should agree and converge before we finally accept a structure as being true.

It should also be emphasised that the above discussion of the *X*-ray problem refers to the general case where complete ignorance of the relative phase constants of the diffracted beams is assumed. In practice, this gap in our knowledge can sometimes be overcome. In the phthalocyanine structures [14] a method was developed for determining the phase constants directly by the comparison of members of an isomorphous series. Again, the " heavy atom " method for settling the phase constant problem has often been used,[15] and promises to become increasingly important. In such cases the results are free from the possibility of such ambiguities as those mentioned above, and they do represent unique solutions. In the most favourable cases, such as that represented by the metal-free phthalocyanine structure, the solution obtained does not even involve the elementary assumption that the molecule is composed of discrete atoms.

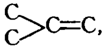
II. Application to Molecular Structure.

Bonds between Like Atoms.

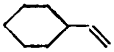
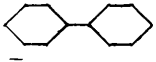
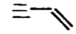
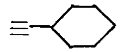
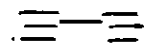
Since their inception about 30 years ago, diffraction measurements have been responsible for transforming a large part of both the subject matter and the theory of chemistry. We can hardly imagine what the subject was like when the structures of simple substances like diamond, graphite, and rock-salt were still unknown. With the successful analyses of more complicated structures like the silicates, whole new chapters of inorganic chemistry came to be written. Later, from about 1930, the subject began to branch in two main directions. On the one hand, it became possible to investigate still more complicated structures like cellulose, rubber, and proteins, and in this direction a great deal of progress has been made. On the other hand, it became necessary to examine a larger number of simple structures more accurately to provide a sound experimental basis for the striking developments of theoretical chemistry. The very great part played by diffraction methods in the latter direction is clearly evident in such authoritative reviews of the subject as have been given by Sidgwick [16] and Pauling.[17]

In these simple structures the relative positions of the atoms are usually well known to chemistry; the object of the diffraction experiments is to provide accurate information on interatomic distances and valency angles. At the present time this subject of interatomic distances is rather more suited to a general discussion than to a lecture, for after a period of reasonable stability, when definite rules were formulated, the number of exceptions has gradually increased until now the whole subject is again more or less in the melting pot. This is probably a good thing, because we hope that it will ultimately mean a further advance. All I can do at present is to provide a few rather scanty notes on the position.

About 10 years ago Pauling and Huggins [18] formulated a table of covalent radii which were intended to be applicable to normal structures when the bonds were largely covalent, like those in ethane, chlorine, or carbon tetrachloride. For other valency configurations, such as pure double and triple bonds, other values of the radii were employed. These empirical values were found to be extremely useful in predicting the structures of simple molecules and crystals, and also for drawing attention to special structures where the observed distances differed from the predicted values. Such special cases could usually be explained in terms of resonance, and, in fact, the observed departures from normal distances provided a method for estimating rather accurately the contributions of various postulated structures to the normal state of the molecule.

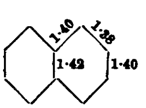
If we confine ourselves first to the case of bonds between like atoms, the process appears to be fairly reliable. By far the largest and most important group concerns bonds between carbon atoms, for these constitute the main framework of organic chemistry. The normal covalent radii for single, double, and triple carbon bonds are 0·77, 0·67, and 0·60 A., derived from measurements on diamond and numerous aliphatic compounds, on ethylene and on acetylene. In practice we find C–C distances which range practically all the way from 1·34 A. (double bond) to 1·54 A. (single bond), and these can be interpreted as representing various states of resonance between single- and multiple-bonded structures. For instance, in benzene, the C–C distance is found to be about 1·39 A., and if we consider the contributions of the two Kekulé structures only, this distance will correspond to a state of 50% double-bond character. In graphite we have to consider many indefinitely extended structures of the type  $\genfrac{}{}{0pt}{}{C}{C}\!\!>\!C{=}C$, which gives a 33% double-bond character, and the corresponding distance is now 1·42 A. The amount of double-bond character can be estimated from the empirical curve of Pauling, Brockway, and Beach,[19] which is obtained by plotting these distances against the corresponding bond character.

Some familiar types of conjugation for which reasonably accurate measurements are now available are listed on p 258, the observed C–C distance referring to the " single bond " between the multiple bonds or benzene rings.

Type.	Compound.	Measured C–C distances, A.	Double-bond character, %.*
	Butadiene [20]	1·46 ± 0·03	18 ± 10
	*cyclo*Pentadiene [20]	1·46 ± 0·03	18 ± 10
	Phenylethylene, Stilbene [21]	1·44 ± 0·02	25 ± 7
	Diphenyl [22]	1·48 ± 0·04	13 ± 12
	p-Diphenylbenzene [23]	1·46 ± 0·04	18 ± 12
	Vinylacetylene, Pirylene [9]	1·42 ± 0·03	25 ± 12
	Tolan	1·40 ± 0·02	33 ± 8
	Diacetylene [25]	1·36 ± 0·03	44 ± 13
	Dimethyldiacetylene [25]	1·38 ± 0·03	34 ± 13
	Cyanogen [25]	1·37 ± 0·02	33 ± 10

* For structures involving triple bonds a correction of 0·02 A. is applied for each triple bond, to allow for a small postulated contraction in the covalent radius.

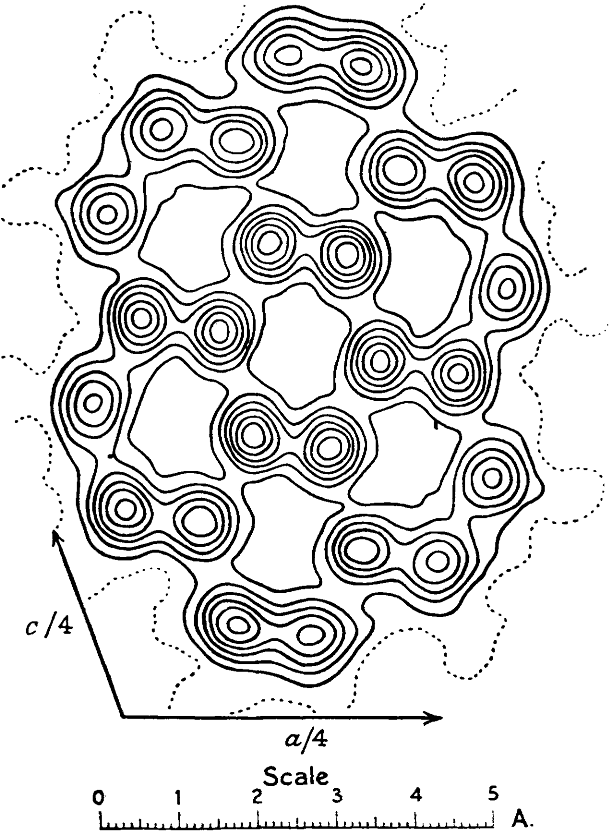
When we wish to make quantitative predictions of the bond lengths in such systems, more accurate calculations are necessary. These have been carried out for a number of cases by Lennard-Jones,[26] Penney,[27] and Coulson [28] by both the "molecular orbital" and the "electron pair" method. A "bond order" can be derived which is linearly related to the bond energy, and then bond lengths may be obtained by interpolation from the standard values in diamond, graphite, ethylene, and acetylene. Calculated in this way, the length of the connecting "single" bond in butadiene comes out at 1·43 A., and in phenylethylene at 1·45 A., figures which are in quite good agreement with the observed values. For the condensed-ring aromatic hydrocarbons similar calculations can be made, and the results indicate certain small variations in the C–C distances for different bonds. The calculated results for naphthalene are shown in (IV). The average, 1·40 A., is in excellent agreement with the measured value of 1·41 A. The individual variations are rather beyond the reach of experiment at present, although there is some indication that the central bond may be slightly larger than the others.



(IV.)

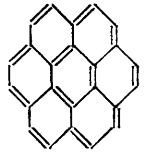
The high symmetry of the coronene molecule makes it an interesting one to study in this connection. The crystal measurements are not yet very complete, but the preliminary results [29] which have been obtained (Fig. 2) indicate that the average C–C distance is slightly greater than in benzene (1·39 A.) and probably nearer the graphite value of 1·42 A.

FIG. 2.

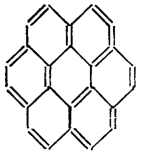


Electron density map for coronene. The plane of the molecule is inclined at about 45° to the projection plane, with consequent distortion of the hexagonal symmetry.

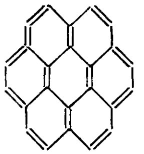
Five groups of stable valency-bond structures (V)—(IX) can be written, which contain the number of individuals shown. If we take a linear sum of these structures and compute the average double-bond character we find, for the 18 outer bonds, 43% ; for the 6 " spokes," 40% ; and for the 6 inner bonds, only 30% double-bond character, as compared with 50% in benzene and 33% in graphite. The overall average for coronene is



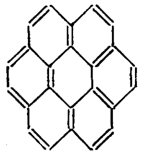
(V.)
4 Structures.



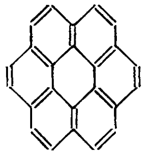
(VI.)
6 Structures.



(VII.)
3 Structures.



(VIII.)
6 Structures.



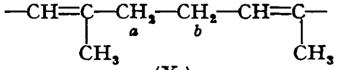
(IX.)
1 Structure.

40%, which is nearer to graphite than to benzene. These calculations are rather crude, but they may have some measure of success for this particular molecule because of its high symmetry. Coulson [30] has recently examined the coronene problem in detail by the molecular orbital method, and has calculated the bond energies and bond orders. He finds the mean length of all the bonds to be 1·406 A., with the central bonds 1·418 A., compared with 1·417 A. (assumed) in graphite and 1·389 A. (assumed) in benzene.

The theoretical calculations for systems containing mainly one kind of atom thus appear to be capable of considerable refinement. It should be emphasised that the diffraction measurements on bond lengths at present available are not nearly accurate enough to provide a really critical test of the theories. For the systems we have been discussing, the most interesting variations all lie within the limits of experimental error, which are usually about ±0·02 or ±0·03 A. in the best determinations, and may be much greater in some cases. There is a great deal of scope for future refinement in this direction.

In other cases the measurements are quite accurate enough to reveal large departures from the expected distances which are difficult to explain in terms of resonance with multiple-bonded structures. Here there would appear to be scope for further development of the theories. For example, in the methylacetylenes the C–C single bond to the methyl group shows a contraction of about 0·07 or 0·08 A.[25, 31] In methyl cyanide the contraction is rather less at about 0·05 A.[32] Resonance with double-bond structures such as $\overset{+}{H}CH_2{=}C{=}\overset{-}{C}H$ which involve the rupture of a C–H link has been proposed to explain the contraction, but there is evidence against this view from a study of the heats of hydrogenation of acetylene and its methyl derivatives.[33] Further, if the bond to the methyl group had any double-bond character, we might expect some evidence of this in restricted rotation, and perhaps also in the behaviour of the methyl hydrogens, but such evidence appears to be lacking. Looking at the matter from a crudely chemical point of view, one might expect some contraction on general grounds. If the triple bond engages six of the electrons on one side of the carbon atom, the other side will be unusually positive and the effective radius should decrease; but it is very difficult to explain all the contraction by a change of radius alone.

Another novel and difficult case arises in geranylamine hydrochloride, recently studied by Bateman and Jeffrey.[34] The two isoprene units in this structure are found to have normal configurations and bond distances except for the central linking bond *ab* (X), for which a contraction of 0·10 or 0·09 A. is reported. This seems considerably greater than any probable experimental error, and it is suggested that a hyperconjugation process involving the C–H bonds may be responsible; but discussion should be deferred until the result can be further established by other examples.



$$—CH{=}\underset{CH_3}{C}—CH_2\overset{a}{—}\overset{b}{}CH_2—CH{=}\underset{CH_3}{C}—$$

(X.)

Bonds between Unlike Atoms.

When we come to consider bond distances between atoms of different kinds, the problems arising are obviously much more complicated. If there are n different kinds of atom, we might in general expect about $\frac{1}{2}n^2$ different distances for all combinations. It will be a great simplification if we can derive these distances from only n different radii. There is no doubt that this can be done approximately, but departures from the rules are more numerous and their causes more complex than before.

These departures are generally in the direction of a decrease from the predicted values, which may be explained in terms of contributions from double-bonded structures, or by the partly ionic character of the bonds. The former explanation has been made, in part at least, for the shortened bond distances observed in the halogen compounds of various elements, the oxides and oxy-acids, and in the covalent complexes of the transition elements.[17] In all discussions of these theories accurate measurements of bond distance are of extreme importance.

The basis for such discussions involving bond length are the tables of covalent radii derived by Pauling and Huggins [18] mainly from crystal data. In addition to the ordinary covalent radii, given below, which apply to atoms forming their usual number of bonds (as given by their place in the Periodic Table), there are tables of tetrahedral covalent radii and octahedral covalent radii for use in crystals of these types. The tetrahedral radii do not differ much from the normal covalent radii, which apply to a large variety of compounds including some with considerable ionic character. For true ionic crystals (alkali halides, etc.) quite a different set of ionic radii must be used.

Single-bond covalent radii.

	H.	Li.	B.	C.	N.	O.	F.	Na.	Si.	P.	S.	Cl.
r^a	0·37	1·34	—	—	0·74	0·74	0·72	1·54	—	—	—	—
r^b	0·30	—	0·88	0·77	0·70	0·66	0·64	—	1·17	1·10	1·04	0·99
x^c	2·1	1·0	2·0	2·5	3·0	3·5	4·0	0·9	1·8	2·1	2·5	3·0

	K.	Ge.	As.	Se.	Br.	Rb.	Sn.	Sb.	Te.	I.	Cs.
r^a	1·96	—	—	—	—	2·11	—	—	—	—	2·25
r^b	—	1·22	1·21	1·17	1·14	—	1·40	1·41	1·37	1·33	—
x^c	0·8	1·7	2·0	2·4	2·8	0·8	1·7	1·8	2·1	2·4	0·7

[a] Value of r as revised by Schomaker and Stevenson.[35] [b] Former value of r due to Pauling and Huggins.[18]
[c] Electronegativity values (Pauling [17]).

There is an enormous mass of consistent evidence in support of the covalent radii, derived mainly from diffraction studies on various compounds. One may mention, as an example, the extensive series of measurements on methyl compounds made by Brockway and Jenkins [35] and others. By subtracting the well-known carbon radius from the observed distances, the radii of the other elements can be obtained, in excellent agreement with the Pauling–Huggins figures.

In spite of all these agreements, however, it has recently become clear that a revision of the long-accepted values is necessary for the three elements nitrogen, oxygen, and fluorine. This arises from recent accurate measurements of what must be regarded as true single bonds between the atoms of these elements in hydrogen peroxide,[36, 37] hydrazine,[37] and fluorine.[38] The distances obtained are O–O = 1·47 ±0·02 A., N–N = 1·47 ±0·02 A., and F–F = 1·435 ±0·01 A., giving radii of 0·74, 0·74, and 0·72 A., respectively. This rather drastic upward revision means that many observed bond lengths for compounds involving these elements are now significantly less than their radius sum, even where no double-bond character is likely to exist. In such cases Schomaker and Stevenson [39] attribute the deviation to the extra ionic character of the bond between the unlike atoms as compared with whatever ionic character there may be in normal bonds between like atoms of the kinds respectively involved. In an attempt to predict the distance r_{AB} from the radii r_A and r_B they employ the empirical relation

$$r_{AB} = r_A + r_B - \beta|x_A - x_B|$$

where x_A and x_B are the Pauling electronegativities for the atoms concerned, and the constant β is given the value 0·09. The deviations are thus found to be proportional to the absolute value of the electronegativity differences. These electronegativities are defined by Pauling [17] in terms of bond energies, and are linearly related to the square roots of the differences between the actual bond energies for unlike atoms A–B and the expected bond energies for normal covalent bonds, the latter being taken as the arithmetical mean of the bond energies for A–A and B–B.

Schomaker and Stevenson have tested this relation fairly extensively. Although it tends to give low values for the bond distances in many cases, they consider that there is enough general agreement to warrant its adoption as a basis for the rediscussion of bond distances between unlike atoms. Much of this rediscussion is presumably still to come, and also further comparisons with more accurately determined distances, so it would be out of place to attempt any adequate review here. We may note, however, that as a result of the revised radii there has been rather a shift of emphasis in regard to explanations of bond contractions. Bond character as expressed by the electronegativity difference becomes more important, perhaps at the expense of bond multiplicity theories.

This is particularly the case with halogen compounds, and attention should be directed to the recent interesting work of Skinner and Sutton [8] on the halogen derivatives of various elements. It is a very general phenomenon that, as the number of halogen atoms attached to some central atom is increased, so the bond length progressively contracts. This contraction is small but fairly definite for a large variety of atoms. Any straightforward explanation of this in terms of either multiple character of the links or electronegativity differences seems difficult; but each substitution by halogen will tend to put some positive charge on the central atom, which in turn will tend to decrease its radius. The countereffect on the halogen may tend to increase its radius, but this effect will decrease progressively as further halogens are added. There will also tend to be a net increase in the attractive forces during this process of halogen addition, and so on both counts we should expect a small progressive decrease in bond distances. It is to be hoped that a more quantitative expression of this theory will be developed.

III. POSSIBLE EXTENSIONS OF THE DIFFRACTION METHODS.

Although, as we have seen, distance measurements are extremely important, it is clear that they are not in any way a sufficient basis for full and detailed discussions of the structure and nature of bonds. What we require most of all is a detailed picture of the electron distribution in bonds of various kinds. Dipole-moment measurements can furnish much valuable information in this direction,[40] but we should like to be able to supplement this by other and if possible more detailed information derived from the study of individual linkages.

In principle, diffraction measurements can furnish information of this kind, if they are pushed far enough. The complete solution of a crystal structure is expressed by a map which gives the electron density at every point in the structure. It is true that this information is not, in general, furnished directly by the experimental measurements of structure amplitudes. We have seen that these quantities lead only to the corresponding vector diagram, which is frequently too complicated to be of direct assistance. Nevertheless, once the structure has been roughly established, by whatever means, then the true electron-density maps can be calculated and further and further refined by successive approximations.

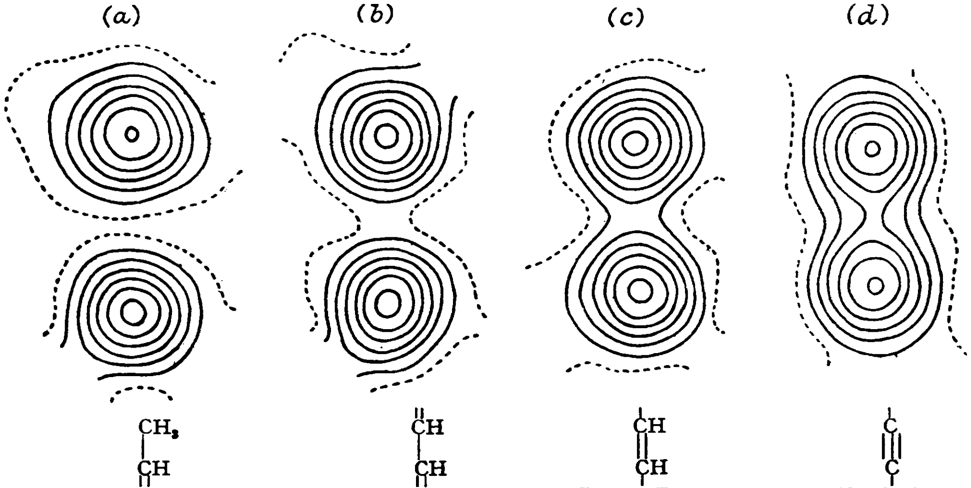
We have also seen that in hardly any case has full use yet been made of all the available data in *X*-ray crystal analysis. Results regarding atomic positions are usually obtained from two-dimensional projections of the structure, which utilise only about $n^{\frac{2}{3}}$ of the n available observations. A partial three-dimensional analysis is sometimes made for complicated structures for the better location of atoms,[41] but I do not know of any case where it has been carried to the limit, with the full use of quantitative intensity measurements.

Thorough-going analyses of this kind will become necessary if we wish to gain any detailed information about electron distribution. Considerable difficulties are involved in the accurate measurement of intensities and their correction for various disturbing factors such as the perfection of crystal specimens; also in the calculation of the results and their correction for spurious diffraction effects of various kinds. These difficulties, however, are not fundamental and there is no doubt that they can be overcome, largely by the proper planning and organisation of the research, which will have to be on a fairly large scale.

It is more difficult to say just how much information would be obtained from a comprehensive investigation of this kind. The inner electrons are concentrated in a relatively small space and are the most effective in scattering. Because of this we can determine atomic positions with accuracy. Much of the spread of electron density which we see in contour maps is due to thermal movement of the atoms. At lower temperatures the peaks sharpen and the outer effects diminish. Consequently, it is very difficult to reach conclusions about these outer effects. The situation is rather similar to that which arises when we try to locate light atoms in the presence of heavy ones, and this is difficult in all diffraction experiments.

The presence of hydrogen atoms, for example, has very little effect in *X*-ray crystal analysis and they are usually neglected in the preliminary calculations. In the final representation of the results, however, they probably have some effect, although they tend to become submerged in the outer parts of the carbon atoms. If we examine the contour map for coronene,[29] shown in Fig. 2, which is only a preliminary two-dimensional projection of the structure, we see that there are distinct bulges around every outer carbon atom to which we expect to find a hydrogen atom attached. This is very apparent in the dotted contour line which represents a density of about one electron per A.^{2}. Similar effects have been observed in many other hydrocarbon structures; but I have never directed much attention to these effects in the past because they are obviously far from precise, and they await confirmation from more detailed and exact analyses. The position of the one-electron density line is very easily changed because the slope is very gradual in this region of the map. Diffraction effects arising from the incompleteness of the Fourier series used, or lack of convergence, have large effects on the position of the dotted line, but evidence is accumulating, and on the whole the coronene hydrogen effect would appear to have some significance.

FIG. 3.
Carbon–carbon bonds.



Single Bond. 1·54 A. Conjugated. 1·44 A. Double Bond. 1·34 A. Triple Bond. 1·20 A.

With regard to electron distribution in the bonds themselves, some fairly detailed work has been briefly reported by Brill and his co-workers.[42] They find that in the sodium chloride crystal the electron density falls to zero between the ions, but that in diamond a small residual density remains between the carbon atoms, which is attributed to the covalent linkage. The latter result may unfortunately be vitiated by uncertainty regarding some of the phase constants, and in general the work appears to require further confirmation. Some interesting intermolecular effects are also reported for hexamethylenetetramine and oxalic acid dihydrate.[43]

In our own analyses there are many bond effects to which attention might be directed, but as in the case of the hydrogen atom, these effects are not precise. Two-dimensional Fourier projections are very misleading with regard to electron-density distribution because the amount of overlapping which is shown between a pair of atoms obviously depends primarily on the angle which the bond between them makes with the projection plane, *i.e.*, the angle from which they are viewed. There may also be atoms belonging to other molecules in the structure which prevent any clear projection of a particular pair. In general, it would be much better to employ sections of three-dimensional syntheses.

However, in special cases normal or nearly normal projections of a particular pair of atoms can be obtained. Fig. 3 shows (*a*) a $CH_3{-}CH{=}$ single bond in the sorbic acid structure[44] (C–C distance, 1·54 A.); (*b*) a shortened $={CH}{-}{CH}=$ bond, situated between two double bonds, in the same structure (C–C distance, about 1·44 A.);

(*c*) one of the sorbic acid double bonds, $-\mathrm{CH{=}CH}-$ (C–C distance, 1·34 A.); (*d*) a triple bond, $-\mathrm{C{\equiv}C}-$, from the tolan structure[24] (C–C distance, 1·19 A.). In each case the bond is tilted at a small angle (12—15°) to the projection plane, which gives an apparent additional shortening of about 3% in the bond length.

The above results are therefore fairly comparable with one another, and it is seen that the electron density between the atoms rises fairly steadily from something under one electron in the single bond to just over four electrons per A.^{3} in the triple bond. (Each contour line represents a density increment of one electron per A.^{3}, the one electron line being dotted.) It is to be emphasised that these are the actual distributions found, and that no correction has been made for the thermal movements of the atoms, which have a very large effect in spreading the observed electron densities.

Calculation shows that the overlapping effect observed in the first three cases is just about the same as would result from bringing pairs of average carbon atoms in these structures to within the specified distances. In the triple bond there appears to be a small additional effect, *i.e.*, the bridge density is a little higher than can be explained by normal overlapping for the given separation of the atoms. However, it is clear that in order to obtain useful information a much better resolution is required, with correction for temperature factor, etc. Considerable further development appears to be possible in these directions. The gas-diffraction method, too, may be employed, especially when improvements in technique make quantitative intensity measurements possible, particularly in the direction of small angle scattering. This method would have the great advantage of being readily applied to certain very simple and critical types of molecule. In such directions as these we may ultimately hope to gain a far more intimate and detailed view of the structure of molecules.

This account of the part played by diffraction methods in modern chemistry has necessarily been very inadequate and confined almost entirely to covalent bond types. No reference has been made to the large amount of exact work on ionic crystals and metals, or to general stereochemical problems. Sidgwick and Powell's recent paper[45] shows very clearly the great part played by diffraction methods in the latter direction. Again, no reference has been made to the large and growing amount of work on the weaker type of intermolecular bonds, on the structure of molecular compounds, hydrogen bridges, surface structures, and so on. Indeed, a complete survey of the scope of the subject at the present time would mean nothing less than a complete survey of practically the whole of modern chemistry.

References.

[1] J., 1944, 183.
[2] (*a*) For electron diffraction, see Brockway, *Rev. Mod. Physics*, 1936, **8**, 231; Sutton, *Ann. Reports*, 1940, **37**, 37.
(*b*) For *X*-ray analysis, see Robertson, *Repts. Progr. Physics*, 1937, **4**, 332.
[3] Robertson, *J. Sci. Instr.*, 1943, **20**, 175.
[4] Pauling and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 2684.
[5] *Physical Rev.*, 1934, **46**, 372; *Z. Krist.*, 1935, **90**, 517; Robertson, *Nature*, 1943, **152**, 411.
[6] Brockway, *J. Physical Chem.*, 1937, **41**, 185, 747.
[7] *J. Amer. Chem. Soc.*, 1937, **59**, 2181.
[8] *Trans. Faraday Soc.*, 1944, **40**, 164.
[9] Spurr and Schomaker, *J. Amer. Chem. Soc.*, 1942, **64**, 2693.
[10] Waser and Schomaker, *ibid.*, 1943, **65**, 1451.
[11] *Ibid.*, p. 1551. [12] *Z. Krist.*, 1930, **75**, 128. [13] *Physical Rev.*, 1944, **65**, 195.
[14] Robertson, J., 1935, 615; 1936, 1195; 1937, 219; 1940, 36.
[15] *Idem, Nature*, 1939, **143**, 75; J., 1940, 36.
[16] "The Covalent Link in Chemistry," Cornell Univ. Press, 1933.
[17] "Nature of the Chemical Bond," Cornell Univ. Press, 1939.
[18] *Z. Krist.*, 1934, **87**, 205.
[19] *J. Amer. Chem. Soc.*, 1935, **57**, 2705.
[20] Schomaker and Pauling, *ibid.*, 1939, **61**, 1769.
[21] Robertson and Woodward, *Proc. Roy. Soc.*, 1937, *A*, **162**, 568.
[22] Dhar, *Indian J. Physics*, 1932, **7**, 43.
[23] Pickett, *Proc. Roy. Soc.*, 1933, *A*, **142**, 333.
[24] Robertson and Woodward, *ibid.*, 1938, *A*, **164**, 436.
[25] Pauling, Springall, and Palmer, *J. Amer. Chem. Soc.*, 1939, **61**, 927.
[26] *Proc. Roy. Soc.*, 1937, *A*, **158**, 280, 297. [27] *Ibid.*, p. 306. [28] *Ibid.*, 1939, *A*, **169**, 413.
[29] Robertson and White, *Nature*, 1944, **154**, 605.
[30] *Ibid.*, 1944, **154**, 797.
[31] Herzberg, Patat, and Verleger, *J. Physical Chem.*, 1937, **41**, 123.
[32] See ref. (25), p. 931.
[33] Conn, Kistiakowski, and Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 1868.
[34] *Nature*, 1943, **152**, 446; Jeffrey, *Proc. Roy. Soc.* (in press).
[35] *J. Amer. Chem. Soc.*, 1936, **58**, 2036.
[36] Lu, Hughes, and Giguère, *ibid.*, 1941, **63**, 1507.
[37] Giguère and Schomaker, *ibid.*, 1943, **65**, 2025.
[38] Rogers, Schomaker, and Stevenson, *ibid.*, 1941, **63**, 2610. [39] *Ibid.*, p. 37. [40] Sutton, J., 1940, 544.
[41] See, *e.g.*, Goodwin and Hardy, *Proc. Roy. Soc.*, 1938, *A*, **164**, 369; *Phil. Mag.*, 1938, **25**, 1096; Crowfoot and Carlisle, *Proc. Roy. Soc.*, *A* (in press).
[42] *Naturwiss.*, 1938, **26**, 29, 479; *Angew. Chem.*, 1938, **51**, 277.
[43] Brill, Hermann, and Peters, *Naturwiss.*, 1939, **27**, 677; Robertson, *Trans. Faraday Soc.*, 1940, **36**, 917.
[44] Lonsdale, Robertson, and Woodward, *Proc. Roy. Soc.*, 1941, *A*, **178**, 43, and further unpublished calculations.
[45] *Ibid.*, 1940, *A*, **176**, 153.