Bond Character and Interatomic Distance.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON NOVEMBER 18TH, 1937.

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THE precise determination of interatomic distance has become possible during the last 25 years owing to a number of major advances in physical science. Of these, the most important have been the discovery of the diffraction of *X*-rays, and later of electrons, by matter, and the application of quantum theory to the analysis of spectra. Thus we have three powerful and independent methods for studying the distances between atoms in molecules, but none of these methods is capable at present of general application to the whole range of molecules known to chemistry. Each is to some extent restricted to a special field.

The analysis of band spectra, for example, leads to some of the most accurate determinations of internuclear distance, but difficulties of calculation tend to restrict the results at present to certain simple and highly symmetrical types of molecule. Some preliminary figures recently given by Sutherland (*Nature*, 1937, **140**, 239), however, promise an interesting extension of band-spectral methods to the halogenomethanes and other polyatomic molecules which have hitherto been studied only by diffraction methods.

In the diffraction of electrons by gas molecules we have a method with wider application, but the analysis is limited in this case by the comparative meagreness of the experimental data which can be recorded for a given compound. A typical photograph is shown in Fig. 1, for which I am indebted to Professor L. O. Brockway, and it will be noted that only a small number of rather diffuse rings are visible. More detail can be distinguished on the negative, but it is seldom that the positions of as many as 10 diffraction maxima can be determined with accuracy against the heavy background. With a molecule of even moderate complexity the number of parameters required to define the structure may actually be greater than the number of intensity maxima recorded on the electron-diffraction photograph, in which case there is, of course, no hope of completely establishing the structure. This limitation, however, does not destroy the usefulness of the method when it is applied to sufficiently simple structures, or even to moderately complex structures, when, by virtue of previous knowledge, they can be described in terms of a few parameters.

A good example is provided by the analysis of benzene (Pauling and Brockway, *J. Chem. Physics*, 1934, **2**, 867) where the C–C distance has been determined with an accuracy which is probably better than 0·01 A., by making use of the geometry of the molecule to limit the number of parameters. But if we knew nothing about the benzene molecule except that it consisted of some arrangement of 6 carbon and 6 hydrogen atoms, it would evidently be quite hopeless to try to determine all the 36 parameters by analysis of the electron-diffraction results. We know that the 6 carbon atoms are equivalent in benzene, not by diffraction experiments, but by the experiments of organic chemistry.

The most powerful method for the metrical study of complex molecules is provided by diffraction experiments on the solid, crystalline material. As the molecules in general possess a fixed and definite orientation in the solid, there is no need to average the diffraction effect over all possible orientations, as in the case of gases. Instead, the structure can be explored in three dimensions. If single crystals of the material are available, there is practically no limit to the number of observations, in the form of intensity measurements on the diffracted beams, which can be made; and each of these observations gives a relation amongst the parameters of the structure. For example, if a is the cell edge, the number of diffracted beams will be proportional to a^3/λ; so that, as the molecule gets larger, the number of possible observations increases in like proportion, and in any case we can always make this number as large as we please by using a sufficiently small wave-length λ. This is illustrated in Figs. 2 and 3, which show a small portion of the *X*-ray spectra obtained from a single crystal of oxalic acid dihydrate compared with an exactly similar portion of the spectra from a single crystal of one of the phthalocyanines. In the first case there are 8 atoms in the molecule (including water but neglecting hydrogen), and in the second case there are 41, and it will be seen that the reflections are now about five times as numerous.

There are, however, very considerable difficulties in the interpretation of all these data. Just as in electron-diffraction work, it is usually (though not always) necessary to start with some preconceived model for the molecule, and in the solid we have the additional complication of testing various possible orientations of this model. But the method has this outstanding advantage. Any proposed structure can be tested very exhaustively, and if it is the correct one, the agreements obtained with the experimental observations can be made sufficiently numerous to exclude other possible models. The method is thus extremely suitable for the study of complex structures.

With simple compounds, especially of the light elements, the experimental difficulties of obtaining good single crystals are often very great, and consequently not much accurate *X*-ray diffraction work has been done on such solids. This is unfortunate because it limits the opportunities for making comparisons between the results of the *X*-ray crystal method and those of band-spectra analysis and electron diffraction. Now the last two methods deal with the relative configuration of the atomic nuclei, while the *X*-ray diffraction method deals essentially with the electron distribution. In certain cases, involving multiple bonds, we might anticipate some very small but interesting differences in the results, and it would seem that more work might usefully be done in making accurate comparisons along these lines.

These are, very briefly, the methods which can be employed to measure the distances between atoms in molecules. In the last seven or eight years a very large number of results have been obtained, and it is difficult to make a selection of those which are of most interest. The carbon–halogen distances in simple compounds have been studied very extensively, and the recent results of Brockway (*J. Physical Chem.*, 1937, **41**, 185, 747) on the fluoromethanes show how such measurements lead to a differentiation of bond type which can be correlated with chemical reactivity. Carbon–oxygen and carbon–nitrogen distances have given some unexpected results, and more work requires to be done on such structures. Again, there is the very interesting question of the distances between atoms in neighbouring molecules in the solid state, leading to the detection of hydrogen bonds and other kinds of intermolecular resonance. But the field is too wide, and in this discussion I wish to confine myself chiefly to certain carbon–carbon distances which are of interest in connection with the problem of resonance in certain aromatic and conjugated systems.

There are three normal types of covalent link, called single, double, and triple bonds according as one, two, or three pairs of electrons take part, and the interatomic distance and energy are found to depend on the kinds of atom and the multiplicity of the bond, being approximately constant from one compound to another. Thus Pauling and Brockway (*Proc. Nat. Acad. Sci.*, 1932, **18**, 293; *J. Amer. Chem. Soc.*, 1937, **59**, 1223) have given a table of covalent radii, compiled from crystal-structure and other data, which can be used with a good deal of reliance to predict the distances in many compounds. The revised figures for the first-row elements are as follows.

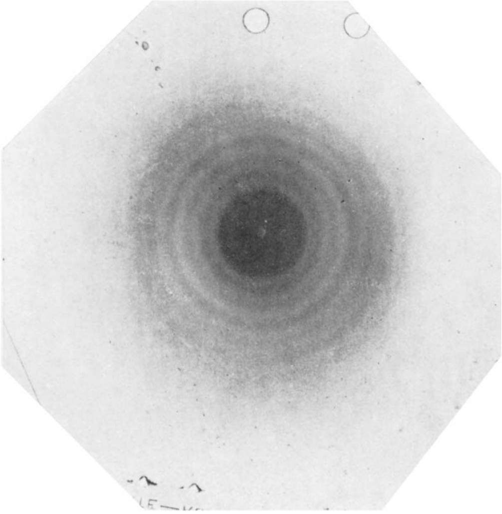
Covalent Radii (A.).

	C.	N.	O.	F.
Single bond	0·77	0·70	0·66	0·64
Double bond	0·67	0·61	0·57	0·55
Triple bond	0·60	0·55	0·51	—

For example, the normal C–C distance is 1·54 A., C=C is 1·34, C—N is 1·47, C=N is 1·28, etc. Very soon, however, the application of this table breaks down. This happens for those structures in which there is no longer a unique way of drawing the bonds, and which can be described in terms of resonance. The most notable examples are, of course, the aromatic compounds, for which it has long been known that the representation in terms of single and double bonds is inadequate.

Before considering this matter in detail, we may survey briefly some results obtained by *X*-ray analysis in which these exceptional distances are displayed. In oxalic acid dihydrate (Robertson and Woodward, J., 1936, 1817) the C–C distance is 1·43 A. The accurate measurement is not easy, and the result may be in error by 0·03 A., but there is no doubt that this " single " bond has undergone a severe contraction from the standard value of

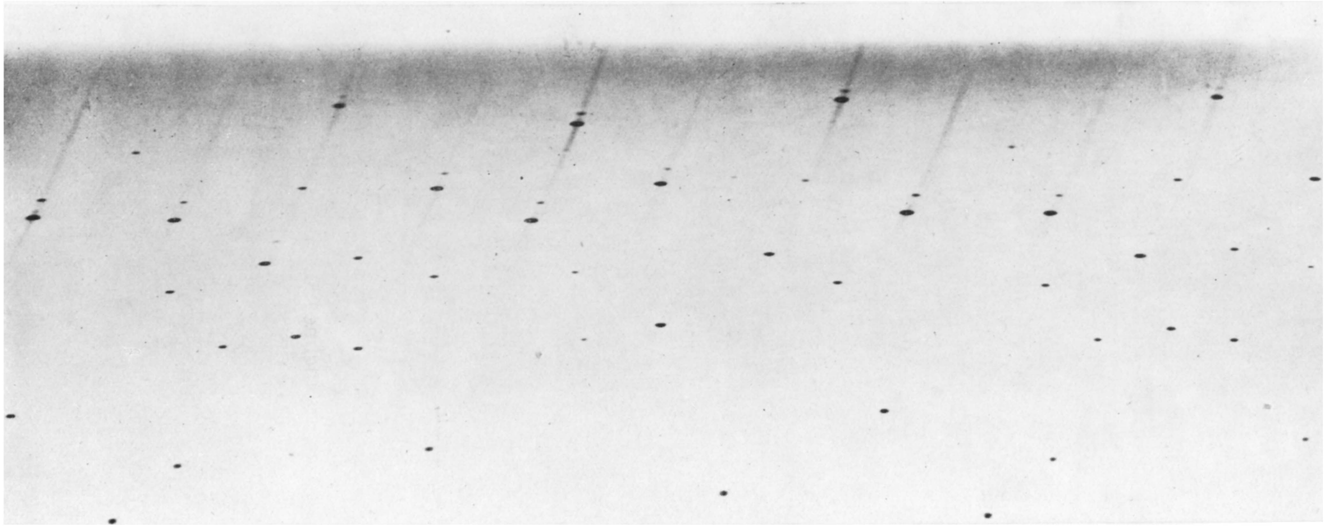
FIG. I.



Carbon tetrachloride vapour. Electron diffraction.

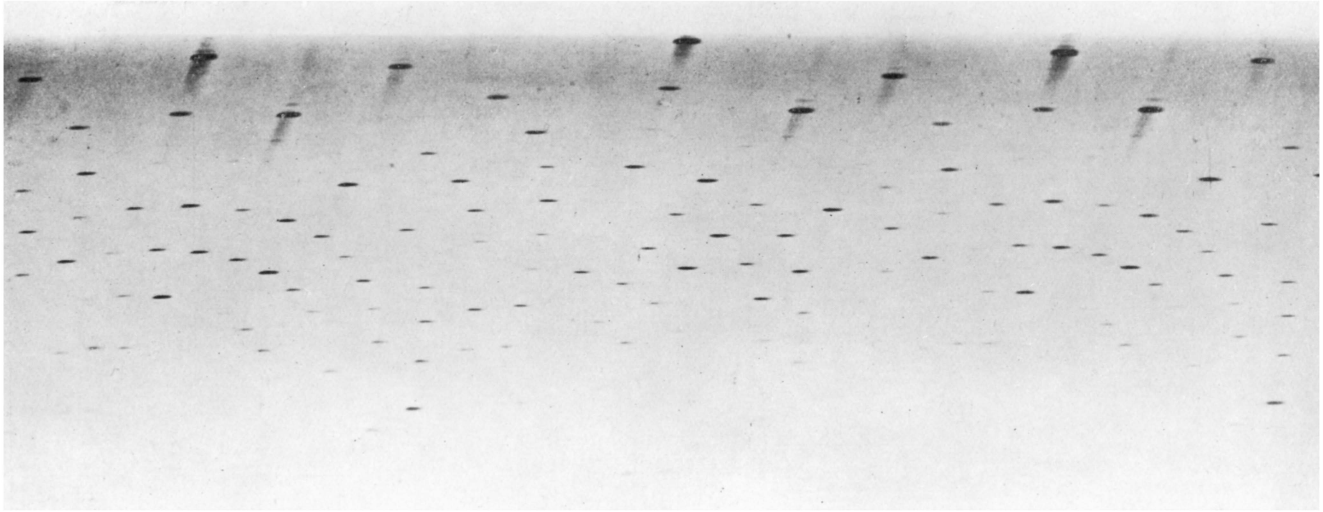
[*To face p.* 132.

Fig. 2.



Oxalic acid dihydrate crystal, {h0l} : X-*ray spectra*.

Fig. 3.

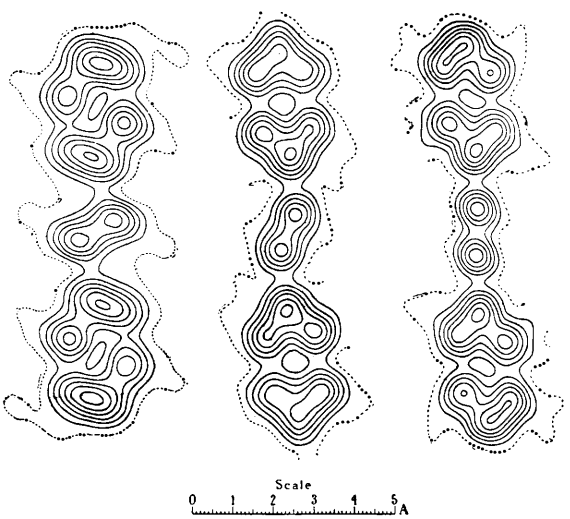


Nickel phthalocyanine crystal, {h0l} : X-*ray spectra*.

1·54 A. The great phthalocyanine molecule provides an excellent example of abnormal distances (Linstead, J., 1934, 1016; Robertson, J., 1935, 615; 1936, 1195; Robertson and Woodward, J., 1937, 219). In the benzene rings the C–C distance averages 1·39 A., the C–C links connecting these rings to the inner conjugated system are 1·45—1·49 A., while the C–N links of this inner system are 1·34—1·37 A. These figures apply both to free phthalocyanine and to its metal derivatives, and we note that none of these distances can be predicted by the table of covalent radii—they all lie *between* the single- and the double-bond values.

I wish to mention one other set of structures which are of particular interest in this connection. Although not yet quite fully worked out, all the significant distances have been determined with some accuracy. The compounds belong to the dibenzyl series (Robertson, *Proc. Roy. Soc.*, 1934, *A*, **146**, 473; 1935, *A*, **150**, 348; Robertson and Woodward, *ibid.*, 1937, *A*, **162**, 568), and the final results of the *X*-ray analysis for three members are represented by the electron-density maps of Fig. 4. These diagrams are projections of the structures along important crystal directions, and although the long axes of the molecules lie almost in the planes of the projections, the short cross axes are inclined at high angles of 50—60° to these planes. The benzene rings therefore appear to be distorted, certain pairs of atoms coming so close together in the projection that they are not separately resolved, but coalesce to form oval concentrations of density. Before the distances and valency angles can be accurately determined it is necessary to reduce these results to normal projections. But the central pairs of carbon atoms are quite clearly defined, and we can see at once how the valency angle changes from near the tetrahedral value in dibenzyl (single bond) on the left, through stilbene (double bond), where the reduced figure is about 130°, to the accurately linear arrangement imposed by the triple bond of tolan on the right.

FIG. 4.


Dibenzyl. *Stilbene.* *Tolan.*

These results are an interesting example of a partly direct *X*-ray analysis based upon the use of an isomorphous series of crystals. It is necessary in the first place to assume some model for the molecule, and then refine the results by the application of Fourier series methods. But it is only necessary to assume *one* model. Thus, if we begin with the tetrahedral dibenzyl model, the other structures can be obtained directly from the *X*-ray intensity measurements by successive approximation with Fourier series methods. Or we might begin by assuming the linear tolan model, whereupon the stilbene and dibenzyl structures could be obtained directly. In practice there are several complications; for example, the size of the unit cell is doubled in passing from dibenzyl to the other members, and the calculations are difficult and tedious, but the above statement is correct in principle.

When the complete orientations of the molecules are obtained, by the use of other projections, etc., it is found that the distances between the central pairs of carbon atoms are near the standard values given by the table of covalent radii for single, double, and triple bonds. But for the links joining these central atoms to the benzene rings we find abnormal values. In dibenzyl the distance, 1·47—1·50 A., appears to be somewhat less than the true single bond value. In stilbene, at 1·45 A., it is definitely less, while in tolan the distance is only 1·40 A., as small as in many aromatic molecules.

These results, and others of a similar kind, are collected below (in A.), and we see that the internuclear distance, or bond length, can vary considerably in different compounds, and in fact may adopt almost any value between that of a pure single bond and a pure double bond.

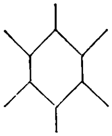
C—C	diamond, aliphatic hydrocarbons	**1·54** single bond.
C—C_6H_5	diphenyl, phthalocyanines	1·48—1·49
C—C_6H_5	stilbene	1·44—1·45
C—C	oxalic acid	1·43
C—C	graphite	1·42
C—C	naphthalene, anthracene	1·41
C—C_6H_5	tolan	1·40
C—C	benzene	1·39
C=C	stilbene	1·33—1·35
C=C	ethylene	**1·33** double bond.
C≡C	acetylene, tolan	**1·20** triple bond.

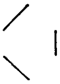
We must now consider the classification of these results, and how they can be used to obtain information regarding the electronic structure of the molecules concerned. Such a classification might in the first place be a purely formal one, enabling some kind of a correlation to be made between different structures. On the other hand, it might be possible to give it more of a theoretical basis, so that when a few standard distances have been measured experimentally the distances to be expected in other kinds of molecules might be predicted. We now give a brief outline of the attempts which have been made in these directions.

The molecules for which we find the exceptional distances are those which cannot be represented satisfactorily by a single structural formula or bond diagram. To explain their chemical and physical properties it is necessary to assume the simultaneous existence of several structures, and the theory of this " resonance " phenomenon has been developed very largely by Pauling (*J. Amer. Chem. Soc.*, 1932, **54**, 3570; *J. Chem. Physics*, 1933, **1**, 280, 362, etc.). He (*Proc. Nat. Acad. Sci.*, 1932, **18**, 293) also pointed out the importance of interatomic-distance measurements in estimating the relative probability of the several structures which contribute to the normal state of the molecule.

For a molecule such as benzene, three of the bonds of each carbon atom can be accounted for in the usual way (I), as pure single bonds, and these can for the present be neglected in a discussion of the resonance problem. We are then left with what is effectively a system of six univalent atoms between which we can draw three bonds (II).

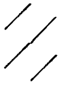
Now a very extensive mathematical treatment for systems of this kind has been developed (Slater, *Physical Rev.*, 1931, **38**, 1109; Hückel, *Z. Physik*, 1931, **70**, 204; **72**, 310; 1932, **76**, 628; Pauling, *loc. cit.*; Van Vleck and Sherman, *Rev. Mod. Physics*, 1935, **7**, 167; Penney, " The Quantum Theory of Valency," Methuen and Co., 1935). The problem is a very general one and has many applications, *e.g.*, to the cohesion of a system of univalent metal atoms, activation energies, and so on. It is important to notice that this mathematical treatment concentrates on the energy relations of the complex, and that the description of the system in terms of bonds appears to be rather vague. For a system of six univalent atoms there are 15 ways of drawing the bonds, and the actual state of the system will be represented by some superposition pattern of these diagrams. The wave function which corresponds to a diagram with crossed bonds, however, can be shown to be given by the sum or difference of the wave functions of certain of the simpler diagrams without crossed bonds. The number of these simple uncrossed bond diagrams for which the wave functions are independent is much less, being only five in the case of six univalent atoms. These five independent bond diagrams (II—VI) are termed the " canonical " structures by Pauling.


(I.)


(II.)


(III.)


(IV.)


(V.)


(VI.)

The wave function for the whole system can be given in terms of these canonical structures by

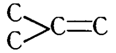
$$\psi = a_1(\psi_{\mathrm{II}} + \psi_{\mathrm{III}}) + a_2(\psi_{\mathrm{IV}} + \psi_{\mathrm{V}} + \psi_{\mathrm{VI}})$$

and the coefficients, a_1 and a_2, of the different sets of structures (which can be grouped together on account of symmetry) have been calculated by Pauling and Wheland (*J. Chem. Physics*, 1933, **1**, 362).

Pauling, Brockway, and Beach (*J. Amer. Chem. Soc.*, 1935, **57**, 2705) now define the fractional character of a given bond in terms of the coefficients of the canonical structures by the relation

$$x = \Sigma' a_i^2 / \Sigma a_i^2$$

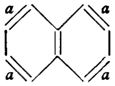
the primed sum being taken over those structures in which there is a bond between the atoms in question. Hence for each structure they assess the probability of there being a bond between the atoms, and sum the result.

The bond character for a few simple substances like benzene can be derived in this way and an empirical relation established between interatomic distance and bond character. In calculating the bond character of benzene and graphite, however, Pauling, Brockway, and Beach actually employ a simpler definition than that given above, by taking only a linear sum of the non-excited canonical structures. Thus in benzene, by giving equal weights to the two Kekulé structures, the bond character is half single and half double, or 1·5, and in graphite, by considering many structures of the type  $\begin{matrix}\mathrm{C}\\ \mathrm{C}\end{matrix}\!\!>\!\mathrm{C}{=}\mathrm{C}$ the bond character is 1·33. The valency of carbon is simply divided by the number of available bonds.

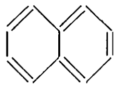
The C–C distances in benzene and graphite are accurately known, and so are the distances for pure single and pure double bonds. When these distances are plotted against the bond character given by the above methods it is found that a smooth curve can be drawn through the four points. By the use of this empirical relation, Pauling, Brockway, and Beach have discussed and classified a large number of interatomic distance measurements in relation to the information they give regarding the degree of resonance in the molecules concerned. By a suitable translation and change of scale, they apply the curve to discussing the resonance effect on bonds other than C–C bonds, as for example the C–Cl bonds in carbonyl chloride and the chloroethylenes. They find a small amount of double-bond character in the C–Cl bonds when conjugated to a double bond, a fact which can be correlated with chemical reactivity; C–N bonds are also discussed, and in urea, for example, they appear to have about 20% double-bond character.

We see, therefore, that this conception of the fractional character of a bond enables us to classify the results of interatomic-distance measurements and draw conclusions regarding the relative extent of the resonance phenomenon in different molecules. We now come to the more quantitative aspect. Can this classification be used as a basis for predicting the distances in other molecules? A large amount of mathematical work has been done on the resonance problem in recent years, and it should be possible to employ accurate distance measurements as an experimental test of this work.

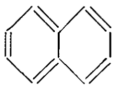
Take, for example, the naphthalene molecule. If we assume a linear sum of the non-excited canonical structures (VII–IX) we see that all the bonds except *a* are double bonds for $\frac{1}{3}$ of the time, but *a* is a double bond for $\frac{2}{3}$ of the time. The fractional characters are thus 1·33 and 1·66, corresponding to distances, on Pauling's curve, of 1·42 and 1·38 A., the results being shown by (X). It is possible, however, to go further and take account of the



(VII.)



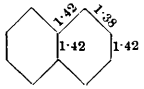
(VIII.)

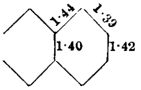


(IX.)

excited structures as well, on the basis of their coefficients in the approximate wave function for the naphthalene molecule calculated by Sherman (*J. Chem. Physics*, 1934, **2**, 488). The results are then given by (XI).

(X.)





(XI.)

The experimental measurements on the naphthalene molecule·(referred to more fully later) are hardly yet of sufficient accuracy to reflect such small distortions from a regular structure, but such results as have been obtained are not in favour of (X) or (XI). Although the method of defining fractional bond character outlined above has proved useful in the general discussion of resonance in related groups of molecules, it would appear to be unsuitable for quantitative predictions of the kind now required. This failure may perhaps be ascribed to a certain over-emphasis on the physical significance of the canonical structures. We have already seen that the mathematical treatment of these problems concentrates on the energy relations, and that the description in terms of bonds is rather vague. The canonical structures are the different ways of drawing the bonds between an imaginary set of univalent atoms that lead to the simplest independent set of wave functions, and the complete wave function will be some linear combination of these. But this complete wave function might also be expressed as a different combination of another set of structures, some of them involving crossed bonds, and these two expressions would not necessarily lead to the same value for the fractional bond character between a given pair of atoms.

But whatever set of structures are used to define the problem, the energy levels calculated from them must be invariant, and Penney (*Proc. Roy. Soc.*, 1937, *A*, **158**, 306) has recently employed a new definition of bond " order " based on the energy relations. This treatment is not so general as Pauling's, being restricted at present to C–C bonds only, but it has led to some very promising calculations of distance, and these are also in agreement with other recent calculations by Lennard-Jones (*Proc. Roy. Soc.*, 1937, *A*, **158**, 280, 297) by the method of molecular orbitals.

In the benzene problem, Pauling and Wheland (*J. Chem. Physics*, 1933, **1**, 362) find that the energy of the normal state of the molecule is given by $W = Q + 2{\cdot}61J$. Here the energy of the electrons forming the system of single bonds (I) is neglected, and certain simplifying assumptions are made. Q is the additive Coulomb integral, which we can neglect, and J is the exchange integral—the two types of binding energy which appear in the hydrogen molecule problem (Heitler and London, *Z. Physik*, 1927, **44**, 455). These integrals themselves cannot be calculated for a system of carbon atoms, but the energy can be expressed in terms of them. If we take, for example, a single Kekulé structure (II), when the atoms are linked by a bond the contribution to the energy is J, and when they are not so linked the interaction is expressed by $-\frac{1}{2}J$. (The non-binding interaction of $-\frac{1}{2}J$ can also be derived from a consideration of the results of the hydrogen molecule problem; see Penney " Quantum Theory of Valency," Chapter II, Methuen and Co., 1935.) Hence for one Kekulé structure, the energy, the Coulomb integral being neglected, is $W = 3J - 1{\cdot}5J = 1{\cdot}5J$, and the difference between this result and the value of $2{\cdot}61J$, calculated by Pauling and Wheland by solving the secular equation for the complete system, represents the " resonance energy " for benzene. The existence of this resonance energy can be demonstrated from the thermochemical data (Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606)

Now Penney defines the " order " of a bond in terms of the exchange integral in such a way that the energy relation is satisfied. If there are k equivalent pairs of neighbouring orbits, the average energy per pair is W/k, and if p is the bond order

$$W/k = p(J) + (1 - p)(-\tfrac{1}{2}J)$$

or

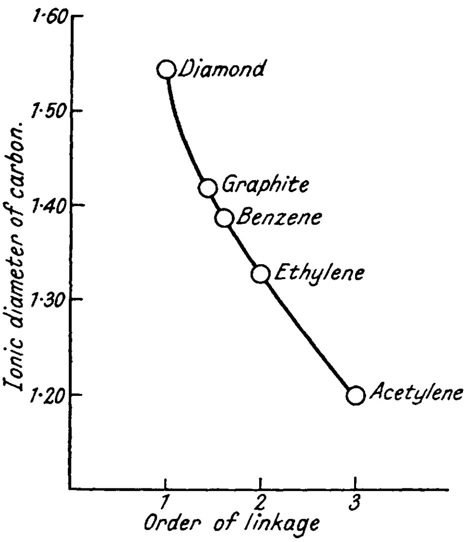
$$p = (1 + 2W/kJ)/3$$

A more profound definition of p, based on the Dirac vector model, is possible, for which reference should be made to Penney's paper (*Proc. Roy. Soc.*, 1937, *A*, **158**, 306). But we see that if W can be calculated in terms of J, the bond order may be obtained immediately from the above relation. If the exchange energy for benzene were $1{\cdot}5J$, as for a single Kekulé structure, the bond order would be 0·5, or, adding 1 for the system of single bonds, 1·5, as in the calculations of Pauling, Brockway, and Beach. But the energy state for the complete system is actually $W = 2{\cdot}61J$, which gives a bond order of 1·623. Penney's definition thus makes the bond order in benzene greater than 1·5 on account of the extra resonance energy. For graphite the calculations are more involved, but by a method of successive approximation Penney obtains an exchange energy per atom in the sheet of $0{\cdot}27J \pm 0{\cdot}01J$, which gives an energy per bond of $0{\cdot}18J$, and a bond order of 1·45.

We can now plot these calculated bond orders against the measured distances in diamond graphite, benzene, and ethylene (Fig. 5), and it is found that a smooth curve can be drawn through the points, and that this curve now passes through the triple-bond point (acetylene) as well. If the C–C bond order for other substances can be calculated, the internuclear distance to be expected may be estimated from this relation.

Benzene and graphite were chosen as intermediate points to define this curve because in these substances the bonds are all equivalent, and the calculations are relatively simple. When the bonds are not necessarily all equivalent the calculations become more difficult, but Penney has recently obtained definite results for a number of structures. Without describing these detailed calculations, we may now compare the results with the experimental measurements given earlier in this discussion.

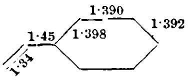
FIG. 5.



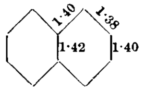
The ionic diameter of carbon as a function of bond order (Penney).

The calculated distances for some typical cases are shown by (XII)—(XIV). The resonance effect on a single bond situated between two double bonds is illustrated by butadiene, where the length of 1·43 A. is in exact agreement with the molecular orbital calculations of Lennard-Jones (*loc. cit.*, p. 280). There do not appear to be any accurate experimental data on butadiene at present, but in oxalic acid, where the C–C bond provides the path of conjugation between the two carboxyl groups, the situation is evidently similar, and for this structure the measured length of the link is 1·43 A.

(XII.)



(XIII.)



(XIV.)

Phenylethylene has been chosen for the calculation of the effect on a single bond conjugated between a double bond and a benzene ring. The contraction of the single bond is now not quite so great, the length obtained being 1·45 A. This figure is in quantitative agreement with the experimental measurements on stilbene.

In both butadiene and phenylethylene the calculations show that the double bonds are increased by only 0·01 A. from the measured value of 1·33 A. in ethylene. Similarly, in phenylethylene, the links in the benzene rings deviate only very slightly from the normal values. These small effects are quite beyond the reach of experiment at present, the stilbene measurements, for example (Robertson and Woodward, *Proc. Roy. Soc.*, 1937, *A*, **162**, 568), merely indicating approximately regular benzene rings of the usual size.

Penney's calculations for the naphthalene molecule, based upon an extension of Pauling's treatment of resonance energies, are shown in (XIV), and we note that they differ from the previous results (X and XI) in predicting the greatest length for the central bond between the rings. The calculations are complicated, and may not even yet be very accurate. The mean value of 1·40 A., however, is in good agreement with the experimental value of 1·41 A. The deviations from this mean are of small order, but it is interesting to note that when the experimental work was reported (Robertson, *ibid.*, 1933, *A*, **142**, 674, 686) one of the Fourier projections gave a value of 1·44 A. for the middle link. This may be due to experimental error, but the result indicates that a more accurate examination would now be useful.

The importance of diffraction measurements as an aid to the determination of chemical structure, in indicating the symmetry and shape of complex molecules, the absolute configuration of geometrical isomers, and so on, has often been stressed. In this discussion I have tried to show, on the other hand, how really accurate measurements of interatomic distance by these methods can be used as an experimental test of some of the new developments in theoretical chemistry which are becoming so important.