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Structural Chemistry.

THERE are two ideas about the progress of science which are widely prevalent, and which appear to me to be both false and pernicious. The first is the notion that when a new discovery is made, it shows the previous conceptions on the subject to be untrue; from which unscientific people draw the very natural conclusion that if to-day's scientific ideas show those of yesterday to be wrong, we need not trouble about them, because they may themselves be shown to be wrong to-morrow. It is difficult to imagine any statement more opposed to the facts. The progress of knowledge does indeed correct certain details in our ideas, but the main result of every great discovery is to establish the existing doctrines on a firmer foundation, and give them a deeper meaning.

The second false notion is that the progress of research involves increasing specialisation : and specialisation, we are told, means knowing more and more about less and less. This last phrase has undoubtedly brought comfort to many people who know practically nothing about absolutely everything. But it is entirely untrue that as knowledge grows, its conclusions are based on a narrower range of observations. Nothing is more remarkable in the immense development of physics and chemistry during this century than the way in which it has brought to bear on the same problems the results of the investigation of widely different properties, obtained by widely different experimental methods.

These points are well illustrated by the subject I have chosen for my remarks to-day—the development of structural chemistry from its origin to the present time. We do not always realise what a remarkable history this theory has had. It was laid down in the 50's and 60's of last century, mainly through the work of Kekulé and Cannizzaro; it was extended to three dimensions by van 't Hoff and Le Bel in 1874, 62 years ago. Since then, at any rate until the last three or four years, it has undergone no serious modifications. A few minor developments have been introduced, such as the recognition of the distinction between ionised and non-ionised links, and of the co-ordinate or semipolar bond. But in essence it remains to-day what it was 60 years ago, and Cannizzaro, if he read the last (1935) volume of Richter's textbook, would find no difficulty in understanding the formulæ and the equations.

This structural theory is of extreme simplicity. It assumes that the molecule is held together by links between one atom and the next : that every kind of atom can form a definite small number of such links : that these can be single, double, or triple : that the groups may take up any position possible by rotation round the line of a single but not round that of a double link : finally that with all the elements of the first short period, and with many others as well, the angles between the valencies are approximately those formed by joining the centre of a regular tetrahedron to its angular points. No assumption whatever is made as to the mechanism of the linkage.

Through the whole development of organic chemistry this theory has always proved capable of providing a different structure for every different compound that can be isolated. Among the hundreds of thousands of known substances, there are never more isomeric forms than the theory permits.

At the same time our knowledge of the meaning of these structures has developed, especially in the last 20 years, to an enormous extent. We have applied to their investigation a whole series of physical methods, based on the examination of the absorption spectra in the infra-red, the visible, and the ultra-violet, and of the Raman spectra : on the measurement of specific heats and heats of combustion, of the dielectric properties, and of the scattering of X-rays and electron waves, as well as on the study of chemical dynamics : to mention only the most important. To Kekulé the links had no properties beyond that of linking; but we now know their lengths, their heats of formation, their resistance to deformation, and the electrostatic disturbance which they involve. Throughout all this work the starting point has always been the structural formula in the ordinary organic sense. There is no better example of the effect of new discoveries in giving new meaning to a theory while they leave the truth of the theory unaffected, and of the way in which modern research, instead of being content with evidence of one kind, as were the older organic chemists with that of chemical reaction, draws its material from every side, and from every branch of chemistry and physics.

The position of the structural theory is peculiar both in its extent and in its limitations. In predicting the number of isomeric forms that can exist it is infallible; it may not always be possible to obtain all the forms, for the theory says nothing about stability, but wherever a new form can be obtained, there is a new formula ready for it. On the other hand the theory gives a very limited representation of the properties of the linked atoms, and in particular of the reactivity. We write the link of carbon to chlorine in the same way C–Cl in chlorobenzene, where the chlorine can scarcely be removed by anything short of metallic sodium, and in acetyl chloride, which is hydrolysed almost explosively by water. In fact we know that the properties of a link are not determined solely by the atoms which form it (which are all that the structural theory takes into account), but are modified by all the other atoms in the molecule.

In the light of modern knowledge it should be possible to explain both the successes and the failures of the theory. We may take the successes first—the power which the theory has of predicting the number of separable isomeric forms of a molecule which can exist. If a compound is to be separable, it must not change as soon as it is formed into something else; we may fairly say that unless a molecule lives in one form for a few seconds, before it changes over into another, the two will be regarded as one substance. Now we know that if a change is slow, that is because the molecules need to acquire extra energy before they can react. Recent work, especially that of Eyring and Polanyi, has shown that this extra energy—the heat of activation—is mainly devoted to stretching the links so as to bring the atoms into the positions required for the production of the new molecule; the consequent rearrangement of the electronic orbits takes place relatively easily. Hence the change from one form to another will occur the more rapidly, the less the differences of position of the atoms in the two molecules: if this difference is very small, the change will occur at once, and we shall not be able to separate the less stable form at all. Thus the number of separable forms is the number of different arrangements in space of the atoms that are possible.

It would seem, then, that the structural theory owes its success to the fact that it prescribes all the possible arrangements in space that a given group of atoms can assume. This conclusion is entirely supported by the physical evidence. We know that the distance between two linked atoms is a very constant magnitude; it is very little affected by the other atoms in the molecule; it is only reduced about 10% by the conversion of a single link into a double or of a double into a triple. Recent work has indeed shown that these distances are capable of certain highly significant modifications, to which I shall return later, but these also are all small—of the order of 10%. Also the valency angles are fairly constant; on the tetrahedral theory, that between two single links is 110°, and that between a single link and a double 125°. The experimental evidence shows that the establishment of a covalent link between two atoms, which is the foundation of the structural theory, is actually the fundamental process in molecular structure, and that its dimensions are little affected by variations in the rest of the molecule.

The conclusions of wave mechanics are in support of this view, and at the same time go far to explain the failure of the structural theory to account for the variations in reactivity. The complete calculation of the properties by wave mechanics is not yet possible except for a few of the simplest molecules, but by a variety of approximations and short cuts we can arrive at something more than a qualitative solution of the structural problem in general: we can get a picture of the mechanism by which the atoms are held together in a molecule, and what we find is this. The primary covalent linkage can be explained as being due to the sharing of two electrons between the atoms, as Lewis supposed, and moreover the theory provides a mechanism for this sharing, which the earlier theory did not; this forms the most important part of the interatomic forces, but it can be shown that it is not sufficient to take into account the reaction of each electron with the two particular adjacent nuclei, and that we have to consider the effect of all the electrons on all the nuclei in the molecule : in other words there is a force—a kind of bond—between every atom and every other. This is in entire agreement with our chemical experience, which shows that the properties of any particular link are to some extent dependent on all the atoms in the molecule.

Thus both the theoretical and the experimental evidence lead to the conclusion that in the formation of a molecule we have to distinguish two factors : first, the simple linkage between the atoms, and, secondly, the further influence on these links of the other atoms in the molecule which are not directly attached. The first of these determines the positions of the atoms in space, and therefore, in accordance with what I have said, the individuality of the compound; it is this factor which is expressed in the ordinary structural theory, and that is why that theory is able to determine the number of possible—that is, isolable —forms. The second factor has a large effect on the reactivity of the molecule; it is not regarded by the structural theory, which therefore cannot make any statement about the reactivity, except in the organic sense of showing in what order the atoms are linked, which depends on the first factor and not on the second.

It is not indeed to be expected that any simple theory should express so complicated a phenomenon as the interaction of all the nuclei and all the electrons of a molecule with one another, which even in benzene is a 54- or at least a 42-body problem. The full theoretical solution must wait until the application of the equations of wave mechanics has been made much easier than it now is; and we shall have to wait a long time before this becomes possible for molecules of any complexity. At the same time we may hope that the progress of wave mechanics will give us new principles of structure and of reactivity which will be applicable even where a complete calculation cannot be carried out.

One such principle has already been discovered, and it constitutes the most important development of structural chemistry since the days of van 't Hoff. This is the principle of resonance, due originally to Hund, but applied to organic chemistry mainly by Pauling and his school. The conclusions of this theory can only be reached by wave mechanics, but they can fortunately be expressed in very simple terms.

It has long been known that if we synthesise substances with structural formulæ which are different, but which can pass into one another by a mere rearrangement of single and multiple links, without either separating two linked atoms, or joining two that were separate, we get the same substance, which has the reactions of both formulæ. The classical example is that of the two Kekulé formulæ for benzene. This is explained by the relation between reaction velocity and spatial position : the two structures will have their atoms in nearly the same positions, and so the rate of change will be very great.

But the resonance theory takes this much further. The equations of wave mechanics show that if a molecule can be represented, on the ordinary structural theory, by two different formulæ, then under certain conditions its actual state is not either one or the other, nor is it a mixture of the two in chemical (tautomeric) equilibrium, but it is a hybrid structure intermediate between them, which cannot be represented by the ordinary symbols and has to some extent the properties of both. This phenomenon is known as resonance; the name is a bad one, because it suggests that the molecule is oscillating between the two states, which is not true; it would be better to give it some such name as mesomerism, if that is not already otherwise occupied; but for the present we have to accept the terminology of the physicists.

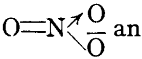
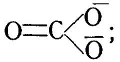
The conditions which must be satisfied for the resonance to be possible are two : (1) the positions of the atoms in the two structures must be nearly the same; the actual positions in the hybrid will be somewhere between them, and so involve a certain amount of strain with respect to either, but this must not be large : (2) the stabilities of the two must not differ greatly, or, to put it crudely, neither structure must be too improbable. The state of the hybrid is not necessarily half way between the two structures : it lies nearer to the more stable one. The occurrence of the resonance produces two important physical effects. (I) The energy content of the molecule is smaller, or its stability greater, than that of either form; this is of fundamental importance, because it follows that resonance must always occur whenever it is possible under the conditions (1) and (2). The resonance energy may be very considerable, amounting sometimes to as much as the energy of a single link (up to 70,000 calories). This affords one means of detecting the occurrence of resonance, since the heat of combustion of the hybrid must be smaller, or its heat of formation larger, than we should calculate for either of the two formulæ. (II) The second effect, which again is important for detecting the resonance, is that the linked atoms come rather nearer together than in either of the separate forms, owing to the greater strength of the link.

These wave-mechanical conclusions, as I have said, can only be reached by making certain assumptions and approximations, the validity of which cannot be judged by the non-mathematician, and so it is essential for us to check them by experiment. I will give one or two examples, in which the criteria are the heats of formation from the atoms, and the interatomic distances.

Carbon dioxide can have three formulæ, which are given below together with the calculated values of the distances and the heats of formation :

	$O{=}C{=}O$	$O \leftarrow C \equiv O$	$O \equiv C \rightarrow O$	Observed.
Distance	$\underbrace{1{\cdot}28 \quad 1{\cdot}28}_{2{\cdot}56\text{ A.}}$	$\underbrace{1{\cdot}43 \quad 1{\cdot}13}_{2{\cdot}56\text{ A.}}$	$\underbrace{1{\cdot}13 \quad 1{\cdot}43}_{2{\cdot}56\text{ A.}}$	$\underbrace{0 \;.\;.\;.\; 0}_{2{\cdot}30\text{ A.}}$
Heat of formation (kg.-cals.)	348	*ca.* 350	*ca.* 350	380

These structures satisfy condition (1), because they are all linear, and the distances between the atoms do not differ much : and condition (2), because the heat of formation of the link of carbon to oxygen is very nearly proportional to its multiplicity, and the electrostatic disturbance produced by the co-ordination does not seem to have much effect on the energy. Resonance is therefore possible, and that it occurs is shown by the two characteristic results : (I) the heat of formation of the carbonyl group in aldehydes and ketones is 174 kg.-cals., and so that of $O{=}C{=}O$ should be twice this, or 348 kg.-cals. : the observed value is 380, an excess of 30 kg.-cals. (II) The distance from oxygen to oxygen should be, in any of the three forms, 2·56 A. : it is found to be 2·30 A.

Many other examples could be quoted.* The most obvious are those in which there are two or more atoms similar except for a difference of linking, and where the resonance causes this difference to vanish. Thus the crystallographic evidence shows that the NO_3' and CO_3'' ions are plane structures, as the tetrahedral theory requires for the two formulæ  $O{=}N\!\begin{matrix}\nearrow \bar{O} \\ \searrow O\end{matrix}$ and  $O{=}C\!\begin{matrix}\diagup \bar{O} \\ \diagdown \bar{O}\end{matrix}$; but it further shows that in both ions the three oxygen atoms are at the points of an equilateral triangle, with the nitrogen or carbon at the centre. It is clear that the three oxygens share the double link, which is not localised on any one of them. Here too we find the characteristic shortening of the link. The values are : for NO_3', N—O 1·36, $N{=}O$ 1·22, mean 1·31 ; obs. 1·23 : for CO_3'', C—O 1·43, $C{=}O$ 1·28, mean 1·38 ; obs. 1·23.

There are many important applications of this theory, for example, to the co-ordination of hydrogen, to triphenylmethyl, to the triphenylmethane dyes and the *meri*-quinoid compounds in general, to the inactivity of the carbonyl group in acids and esters, and so forth, which I must pass over. But there is one application of such far-reaching importance that something must be said about it. The views of reactivity put forward by organic chemists during the last 20 years or so find in the theory of resonance their physical justification. These views agree in ascribing the changes of reactivity to a drift of the electrons from their normal positions, not amounting to a complete transference. Now this electronic drift is exactly what the theory of resonance requires. To express the organic doctrines in terms of resonance we have only to imagine the drift extended to the point where a new structural formula is reached. This gives us the second resonance structure, and the actual state of the molecule is somewhere between the two.

I cannot discuss this in detail, but I may give one example where the evidence is peculiarly complete. In chlorobenzene (I) it is assumed by the organic theorists, to

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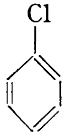
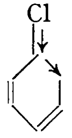
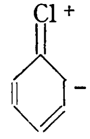
* For references see *Ann. Reports*, 1934, **31**, 38.

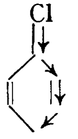
account for the ortho- and para-substitution, that there is a drift of electrons from the chlorine atom towards the ring (II). If we suppose this drift to go to the limit, we get a new formula (III; the two ways of writing it, III*a* and III*b*, mean the same thing); by a further change of the same kind the negative charge is transferred from the ortho- to the para-carbon atom (IV*a*, IV*b*). The properties implied by (II) are exactly those of

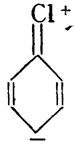

(I.)


(II.)


(III*a*.)


(III*b*.)

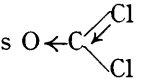
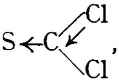

(IV*a*.)


(IV*b*.)

a resonance hybrid of the structures (I) and (III). Physical evidence of two kinds has been obtained in support of this view. It has been shown by Sutton (*Proc. Roy. Soc.*, 1931, **133**, 668) that the dipole moment of chlorobenzene is less than that of a chloro-paraffin, and so indicates an electronic drift towards the ring: he showed that wherever a substituent causes a drift in this direction it gives ortho- and para-substitution. The difference of moment in chlorobenzene is 0·6 D., which is about a tenth of what we should get by the complete transference of an electron from one atom to the next, so that the state of the hybrid must lie nearer to (I), and (III) must be the less stable form, which is what any organic chemist would expect.

Further evidence of the existence of links of the type of $\mathrm{C}\mathrel{\overset{\leftarrow}{-}}\mathrm{Cl}$ has been obtained by the measurement (by electron diffraction) of the X—Cl distances in a variety of chlorides. The radii of the atoms in question are already known from other compounds in which resonance does not occur; if there is resonance in any of these compounds, it should be shown by the X—Cl distance being less than the sum of the normal radii of X and chlorine. The distances in the tetrachlorides of carbon, silicon, germanium, and tin were measured by Brockway (*J. Amer. Chem. Soc.*, 1935, **57**, 958). He finds that the distance in carbon tetrachloride is what we should expect, but in all the other compounds is markedly less :

X—Cl	CCl_4.	$SiCl_4$.	$GeCl_4$.	$SnCl_4$.	$O{=}CCl_2$	$S{=}CCl_2$.
Calc.	1·76	2·16	2·21	2·39	1·76	1·76
Obs.	1·76	2·02	2·10	2·29	1·68	1·70
Diff.	±0	−0·14	−0·11	−0·10	−0·08	−0·06

Now resonance with the form $\mathrm{Cl_3X}\mathrel{\overset{\leftarrow}{-}}\mathrm{Cl}$ is not possible with carbon tetrachloride, because the carbon atom cannot hold more than 8 electrons, but it can happen with the tetrahalides of silicon, germanium, and tin, which are not limited in this way, and the results show that it does so. Strong evidence in favour of this view is afforded by the measurements of Brockway, Pauling, and Beach (*J. Amer. Chem. Soc.*, 1935, **57**, 2704) of the C—Cl distance in carbonyl chloride and thiocarbonyl chloride. Here the resonance is possible without contravention of the covalency rule, since the carbon still has the octet in the structures  $\mathrm{O}\leftarrow\mathrm{C}{\swarrow\atop}\!\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}$ and  $\mathrm{S}\leftarrow\mathrm{C}\!\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}$, and accordingly we find that the link is shortened, as the above table shows. A further confirmation is given by the measurements of Brockway and F. T. Wall (*ibid.*, 1934, **56**, 2373) of the X—F distances in the hexafluorides of sulphur, selenium, and tellurium. The covalency limit for sulphur and selenium is 6, and for tellurium 8, so that only the last of these compounds can resonate. The calculated values here are not to be expected to agree with the observed for any of these compounds, because we have to use the radii of the dicovalent atoms; but we find a much larger difference with the tellurium compound than with the others. The figures are :

X—F	SF_6.	SeF_6.	TeF_6.
Calc.	1·68	1·81	2·01
Obs.	1·58	1·70	1·84
Diff.	−0·10	−0·11	−0·17

Those few examples will serve to illustrate the importance of the resonance theory, which has certainly come to stay, and which may be expected, in conjunction with the views of the organic theorists, to extend enormously our ideas of structural chemistry, and of its relation to reactivity.

I hope I have said enough to show that the modern development of the structural theory, far from destroying the older doctrine, has given it a longer and a fuller life; and further that the tendency of modern research is not to contract the scope of its material, but on the contrary to call in to its assistance an increasingly wide range of properties, and to bring to bear on its problems the results of every kind of physical and chemical investigation.