PRESIDENTIAL ADDRESS.

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Hybrid Molecules.

IN my remarks at the annual meeting at Bristol last year, I said something about the modifications which structural chemistry has undergone in the last few years through the introduction of the concept of resonance. These modifications are so important to all sides of chemistry that I think I cannot do better this year than say something more about them.

I may briefly repeat what is meant by resonance in organic chemistry. If a molecule can be represented by two (or more) structural formulæ (in the ordinary sense of that term), and if these formulæ ascribe approximately the same positions to the atoms and are of about the same stability or energy content, then it is found that the actual state of the molecule is not that represented by either of the formulæ, but is something between them, which cannot be expressed by means of the ordinary structural symbols; it has to some extent the properties of both, but is more stable than either, and also the linked atoms are rather nearer together than is usual. If the structures differ in stability, the actual state will lie nearer to the more stable. This phenomenon is known as resonance, and the molecule is then said to be a resonance hybrid of the two (or more) forms.

The idea that a molecule may have a structure intermediate between those represented by two ordinary formulæ is certainly not new: Kekulé's conception of the benzene nucleus, and Conrad Laar's idea of tautomerism in general involve something like this, and a more definite approach to it is the " valency tautomerism " of Wieland and others (Wieland, *Ber.*, 1920, **53**, 1318; see also Arndt and Eistert, *Z. physikal. Chem.*, 1935, *B*, **31**, 125).

But the theory of resonance differs from these general notions in two specific particulars. It demands that the two formulæ should have their atoms in very nearly the same positions, and makes resonance impossible if the change from one to the other involves any serious shift even of a hydrogen atom. Further it shows that when resonance occurs the resulting molecule is more—often much more—stable than either of the component structures. Now this conclusion is one which could not have been anticipated from general considerations, or calculated by classical mechanics. It is impossible to understand why these things are so unless one has some knowledge of the principles of wave mechanics, and it is impossible to discover the quantitative results of the theory unless one is familiar with the methods of wave-mechanical calculations.

This at once raises a difficulty. The general conclusions of the theory of resonance are of great practical importance, especially to the organic chemist. But it is not to be expected that more than a very few organic chemists will have either the time or the ability to master these mathematical operations. It is therefore obviously our duty to express—or to induce the wave-mechanicians to express—the results in the simplest terms that are possible, and this can really be done quite easily. The use of the technical language of wave mechanics for this purpose is quite unnecessary and in fact misleading, for it makes the non-mathematical reader think that as he can't understand the language he can't understand the conclusions either, which is quite untrue; and not uncommonly, I think, it leads the non-mathematical writer to believe that if he knows the technical terms he must understand their meaning, which is by no means always the case. It was well said by Clerk Maxwell :* " For the sake of persons of different types of mind scientific truth should be presented in different forms, and should be regarded as equally scientific whether it appears in the robust form and colouring of a physical illustration, or in the tenuity and paleness of a symbolical expression."

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* Quoted by Sir J. J. Thomson, " Recollections," p. 392.

For example, with carbon dioxide we have the three formulæ

$$\mathrm{O{=}C{=}O} \qquad \mathrm{O}\underset{=}{\rightarrow}\mathrm{C}\rightarrow\mathrm{O} \qquad \mathrm{O}\leftarrow\mathrm{C}\underset{=}{\leftarrow}\mathrm{O}$$

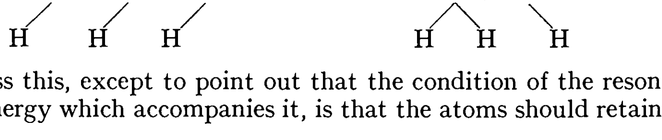
According to the theory of resonance, since all these formulæ represent linear molecules, and should have about the same stability or heat of formation, resonance must occur, and the actual state of the molecule will be something intermediate between them which we call a resonance hybrid, which will have a greater stability and heat of formation, and a rather smaller distance between the atoms, than correspond to any one of the formulæ. Experiment shows that this is so. Further, since the last two formulæ are really the same, they must be represented to the same extent in the actual state of the hybrid, which therefore should be non-polar, as it is found to be.

These ideas are simple enough, and they gain nothing in clearness for the ordinary chemist if they are expressed in the technical language of wave mechanics—if I say that in the carbon dioxide molecule we have a superposition of eigenfunctions, that the three formulæ I have given are the unperturbed canonical structures, and that the last two are completely degenerate : it is better to say that these are the three constituent formulæ, that the last two are the same, and that carbon dioxide is a resonance hybrid between the three.

Another terminological difficulty arises from the word resonance itself. This undoubtedly suggests to the ordinary man a rapid alternation between two structures, an idea that presents itself the more readily since we are already familiar with it in tautomerism. But this is not what resonance means : it must be sharply distinguished from rapid tautomerism. In tautomerism, the substance is a mixture of two kinds of molecules in equilibrium after the manner of a reversible chemical reaction; the rate of change may be too quick to be measured, but it is quite definite, and further there is no reason why some of the atoms, especially of the hydrogen atoms, should not change their positions in going from one tautomeric form to the other. Also the occurrence of tautomerism is not necessarily a sign of greater stability, but rather the opposite. In resonance on the other hand there is no chemical change, quick or slow : the substance is not a mixture, but all the molecules are in a state intermediate between those represented by the constituent formulæ : the positions of the atoms in these formulæ must be nearly the same, and the occurrence of resonance necessitates an increase in the stability of the molecule.

It would therefore I think be better if we could adopt another name, and mesomerism, which has been applied to the phenomenon by Prof. Ingold, seems to be the most suitable. It is however of little use for the chemist to adopt this unless the physicists who are specially concerned with the problem will do the same.

Some of the more important applications of the idea of resonance I considered last year, especially its close relation to the modern theories of organic reactivity. Another point is the so-called co-ordination of hydrogen, which accounts for the association of hydroxyl compounds. There is no doubt that a hydrogen atom is able to hold two oxygen atoms together, and the crystallographers have actually measured the length of this O—H··O link (about 2·5 A.), which they call the hydrogen link,* but the idea which formerly prevailed, that this link, like co-ordinate links in general, was due to the hydrogen taking up two more shared electrons (so that it had four in all), is now known to be impossible, since a hydrogen atom cannot hold four electrons with sufficient firmness. The only alternative explanation is that we have resonance between the ordinary form and one in which there is an oxonium cation and an R–O anion :



I will not discuss this, except to point out that the condition of the resonance, and hence of the gain of energy which accompanies it, is that the atoms should retain their positions;

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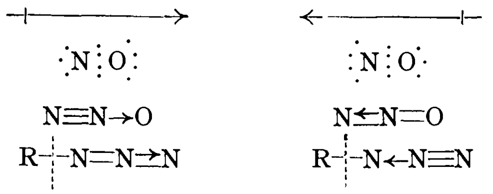
* For further details, see Bernal and Megaw, *Proc. Roy. Soc.*, 1935, **151**, 384.

hence the ions in the ionised structure are not free to move, and so cannot contribute to the electrical conductivity of the liquid.

One advantage which we have in these days is that any theory of structure can be tested by the measurement of a whole series of properties. This is eminently true of resonance. When the attempt was first made, some eight or ten years ago, to determine the magnitude of the various properties of covalent links, it was evident that this could only be successful if these properties were at least approximately constant—if they were more or less independent of the other links in the molecule. It is now clear that to a large extent this is so, but that the properties are considerably modified when there is resonance in the molecule. Conversely the departure of these properties of links from their normal values provides the best evidence we have of the occurrence of resonance. The properties which are most frequently used for its detection are, as we have seen, the heats of formation and the internuclear distances; but in addition we can use the dipole moments, the force constants of the links, and the general reactivity. These points are best illustrated by taking a series of examples.

It happens with several molecules that there is a possibility of two structural formulæ, conforming to the conditions of resonance, both of which have large dipoles, but in opposite directions, and that the actual molecule can be shown to have a very small moment : as for example with nitric oxide, nitrous oxide, and the organic azides :



Dipole moment.

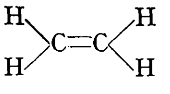
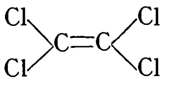
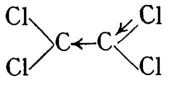
0·16 D

0·17 D

N_3 *ca.* 0

The very small moment observed is impossible not only for each structure separately, but also for any mixture of the two in tautomeric equilibrium in the ordinary sense : a mixture of two highly polar substances, even if their moments are in opposite directions, will itself be highly polar, as it does not matter to the dielectric constant which way the dipole is pointing; but if the molecule is in a state intermediate between the two structures, their opposing dipoles will tend to neutralise one another.

With some molecules we can make use of the force constants of the links. These constants, which are derived from the absorption spectra, are a measure of the resistance of the link to deformation, and may be said to throw more light on the actual state of the molecule than the heats of formation, since they can be determined for individual links and not merely for the molecule as a whole. A comparison of the values of these properties for ethylene and for tetrachloroethylene is very instructive. In ethylene itself no resonance is possible : every hydrogen atom already carries its maximum load of electrons, and they are all shared. But in tetrachloroethylene there is a possibility of the formation (as in chlorobenzene) of a double link between a chlorine and a carbon, as shown below :

The values of the force constants are (see Duchesne, *Nature*, 1937, **139**, 288; Linnett and Thompson, *ibid.*, p. 509) :

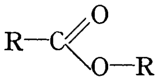
C—H in methane	$4{\cdot}98 \times 10^5$	C=C in ethylene	$9{\cdot}0 \times 10^5$	C—Cl in CCl_4	$3{\cdot}8 \times 10^5$
C—H in ethylene	4·85 ,,	C=C in C_2Cl_4	5·8 ,,	C—Cl in C_2Cl_4	5·2 ,,

There could not be clearer evidence that while the C—H link is the same in ethylene as it is in methane, the C—Cl link is stronger in tetrachloroethylene than it is in carbon tetrachloride, and becomes so at the expense of the double carbon link. The measurements of the length of the C=C link appear to be in agreement with this; in ethylene it has been found (Scheib and Lueg, *Z. Physik*, 1933, **81**, 764) to be 1·34 A., and in tetrachloroethylene 1·38 A. (Brockway, *Rev. Mod. Physics*, 1936, **8**, 261).

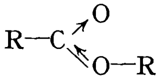
Of the large number of organic structures whose behaviour is determined by resonance we may consider two, the carbonyl group $>C=O$, and the most important of all, the aromatic ring. The most familiar examples of carbonyl compounds are : (1) aldehydes and ketones, (2) carboxylic acids and their derivatives, such as the esters and amides, (3) carbon dioxide (carbon monoxide might be included, but its resonance does not concern us at the moment). Organic chemists have long been aware that the carbonyl group in an ester is very different in behaviour from that in an aldehyde or ketone, and much less active. It does not give the carbonyl reactions with hydroxylamine or phenylhydrazine, it is much less easily reduced, and its refractive power and its parachor are less than we should expect. Again, two adjacent carbonyls in the α-diketones give the compound an intense yellow colour, as we see in diacetyl, glyoxal, and benzil; but pyruvic acid and oxalic acid are colourless. Carbon dioxide behaves in general like the acids and esters rather than the aldehydes and ketones.

It was at one time supposed that these peculiarities of the acids were due to the hydrogen of the carboxyl group being in some way joined to both oxygens; but nearly all these properties are shared by the esters, where no such explanation is possible. There should obviously be some explanation applicable to the acids and their esters and to carbon dioxide, but not to aldehydes and ketones. This is given quite simply by the theory of resonance. We have already seen how this is possible in carbon dioxide, and its occurrence is proved both by the heat of formation, which is 30 kg.-cals. higher than one would calculate, and by the O . . . O distance, which is found to be only 2·30 A., whereas one would calculate it on any of the three formulæ to be 2·56 A.

With the acids and their derivatives there is a similar possibility of resonance between the structures



and

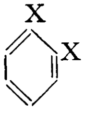


This is supported by their heats of formation; Pauling and Sherman (*J. Chem. Physics*, 1933, **1**, 606) have shown that the resonance energy, that is, the excess of the observed over the calculated heat of formation, is on the average about 27 kg.-cals. for the carboxylic acids and about 23 kg.-cals. for their esters, and rather less for their amides (the heat of formation of a single link is usually between 50 and 100 kg.-cals.).

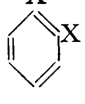
One important point must be mentioned here. The result of the resonance is, as we have seen, an increase in the heat of formation and therefore in the stability of the molecule. Hence the resonance hybrid will in general be less reactive than the usual formula would imply, even when the second formula looks as if it would be more reactive; this appears very clearly in these acid derivatives, where the CO group is much less active when resonance is possible than it is in the ketones where it is not.

At the same time we must recognise that the resonance, while it increases the stability and heat of formation of the molecule as a whole, may diminish that of a particular link, as we have seen in tetrachloroethylene.

The most extensive group of organic substances whose behaviour is determined by resonance is that of the aromatic compounds. It was recognised from the beginning that the two difficulties in the way of Kekulé's formula for benzene are, first, that we should expect two ortho-di-derivatives



and

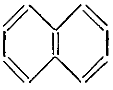
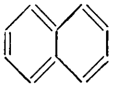
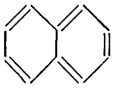


and secondly, that benzene should have the reactivity of an ethylene derivative, whereas in fact it behaves almost always as a saturated compound. The conception of resonance removes both of these objections at once : the first because we assume the state of the ortho-compound to be permanently half way between the two formulæ, and the second on account of the increased stability which the resonance must produce. The last point can be determined experimentally from the heats of formation, and the following table gives the values of the resonance energy, as found by Pauling and Sherman (*loc. cit.*), first the value for the whole molecule, and secondly the amount per aromatic ring : it will be seen that the values of this last figure are approximately constant.

Resonance Energy of Aromatic Compounds.

Compound.	Resonance energy, in kg.-cals.	$\frac{\text{Resonance energy}}{\text{Number of rings}}$, in kg.-cals.	Compound.	Resonance energy, in kg.-cals.	$\frac{\text{Resonance energy}}{\text{Number of rings}}$, in kg.-cals.
Benzene	37·6	37·6	Acenaphthene ...	70·8	35·4
Toluene	39·2	39·2	Anthracene	104·7	34·9
Ethylbenzene ...	39·7	39·7	Phenanthrene ...	110·2	36·7
Propylbenzene ...	41·3	41·3	Chrysene	150·6	37·7
Naphthalene	74·7	37·4			

These results are based on the heats of combustion. The theoretical calculation (Pauling and Wheland, *J. Chem. Physics.*, 1933, **1**, 362) shows that in benzene three other structures, more or less corresponding to the Dewar formulæ, have to be taken into account, but that over 80% of the resonance energy is due to the two Kekulé structures. In the same way in naphthalene, where there are altogether 42 structures to be taken into account, 68% of the resonance energy is due to the three obvious formulæ

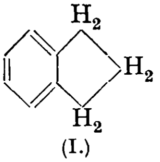




This conception of the aromatic ring explains many of its peculiarities, and especially its extreme adaptability. This is indeed proved directly by the high refractive power, but it is shown in many other ways as well. Thus the electrons attaching atoms to the ring can be moved towards or away from it; it has been shown (Sutton, *Proc. Roy. Soc.*, 1931, **133**, 668) that the electron drift, as indicated by the difference in electrical dipole moments between an aromatic compound and its aliphatic analogue, is what determines the position of further substitution, a conclusion which the organic chemists had already reached on grounds of reactivity alone.

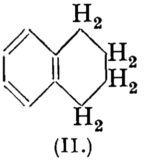
An interesting question is how far the resonance in benzene is affected by the presence of other groups in the molecule. Normally a substituent if it produces any effect will cause an increase, by providing new resonance structures. Pauling and Sherman (*loc. cit.*) have given a series of values (derived from the heats of formation) of the extra energies of the compounds $C_6H_5 - X$: some of these are quoted below.

X.	Extra energy.	X.	Extra energy.	X.	Extra energy.
$—CH_3$	1·6	$—O—CH_3$	6·0	$—NH_2$	4·4
$—C_2H_5$	1·9	—CHO	3·5	$—NHCH_3$	6·2
$—CH{=}CH_2$	6·7	$—CO—CH_3$	7·2	—CN	4·8
$—C{\equiv}CH$	10·4				

On the other hand it would appear that it is sometimes possible to reduce the resonance by steric effects. This was first suggested by Mills and Nixon (J., 1930, 2510) before the resonance theory had been developed. They pointed out that on stereochemical grounds we might expect that in hydrindene (I) (with a reduced 5-ring attached to the nucleus) the most stable form would be that which had a single link common to the two rings, while in tetralin (II) (with a 6-ring) the common link should be double. They obtained experimental confirmation of this by showing that if 5-hydroxyhydrindene (III) is brominated or coupled with diazo-compounds, reaction takes place at carbon atom 6, whereas in the corresponding tetralin derivative (IV) it occurs in the α-position. Both these reagents would be expected to attack the carbon atom joined to the hydroxylic carbon atom by a double link. This work has been carried further by Fieser and Lothrop (*J. Amer. Chem. Soc.*, 1936, **58**, 2050), who tried the effect on the coupling with diazo-compounds of blocking the natural positions with methyl groups. They found that with the hydrindene compound (V) no coupling occurred at all, whereas the tetralin derivative (VI) coupled readily in the position shown by the arrow.



(I.)



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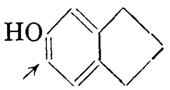

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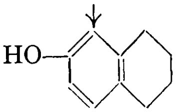
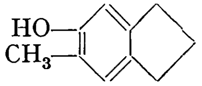
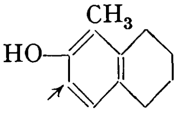


(IV.)

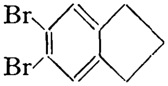
(V.)



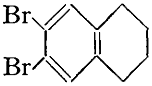


(VI.)

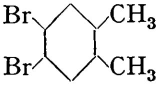
These results suggest that Mills and Nixon's conclusions are valid for hydrindene but not for tetralin; this is what we might expect, since the strain in tetralin can be relieved if the reduced ring is not planar, whereas no such relief is possible in hydrindene. Further confirmation is afforded by the dipole moments of the dibromo-derivatives of the two systems (VII and VIII).



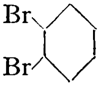
(VII.)



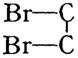
(VIII.)



(IX.)



(X.)

It is evident that if the double links are fixed in the positions suggested (as shown in the diagram) the angle between the C—Br valencies will be greater (and hence the moment smaller) in the hydrindene compound, and least in the tetralin, while in the benzene and *o*-xylene derivatives (IX and X), where resonance must prevail, it should have an intermediate value. Experiment showed (Sidgwick and Springall, J., 1936, 1532) that the moment of the  $\begin{matrix}\mathrm{Br—C}\\ \mathrm{Br—C}\end{matrix}$ system was practically the same in the benzene, xylene, and tetralin derivatives (X), (IX), and (VIII) (2·12, 2·13, 2·11 D, respectively), but markedly lower (1·78 D) in the hydrindene compound (VII), thus entirely confirming the results of Fieser and Lothrop.

It is to be noticed that the evidence of Fieser and Lothrop, like that of Mills and Nixon, is based on the reactivity, and so depends on the heat of activation, a relatively small change in which may account for the whole effect. Sutton and Pauling (*Trans. Faraday Soc.*, 1935, **31**, 939) have discussed this question from the theoretical side, and conclude that a difference of 6% in the ratio of the coefficients (*i.e.*, in the predominance) of the two Kekulé forms is enough to account for the experimental results of Mills and Nixon. On the other hand the dipole moments express the mean positions of the atoms in the resting molecules, and they certainly show the difference to be expected if the links were fixed in hydrindene but not in tetralin.

It is too early to say definitely whether this conclusion is to be accepted; but if it is, it leads to a remarkable result. The peculiarities of the aromatic compounds—the "aromatic character"—are due partly to the alternation of single and double links, and partly to the resonance. If these conclusions are correct, then in hydrindene the resonance is stopped, while the alternation of links of course remains. The properties of hydrindene and its derivatives should therefore be those which depend on the alternation, and those which are due to the resonance should be absent.