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Old and New Views on Some Chemical Problems

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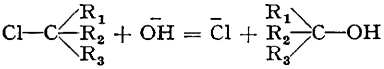
The chemists of my generation have lived through a wonderful period in the history of science. Brought up in the old chemistry, they have seen the great increase in our knowledge of molecular structure that followed on the nuclear theory of the atom and the electronic theory of valency.

I think nothing illustrates better the contrast between the new and the old views than the changed attitude towards the Walden inversion. The old view is well illustrated bya drawing in a paper of Emil Fischer (*Annalen*, **1911**, **381**, 131). We see an impenetrable atom with its surface marked off into valency areas. Fischer regarded the Walden inversion as " the most surprising observation which had been made in the field of optically active compounds since the fundamental investigations of Pasteur."

The new conception of the atom as an open structure with a central nucleus—and particularly G. N. Lewis's octet theory of valency in which the eight valency electrons were regarded as arranged in pairs at each corner of a tetrahedron—opened the way to a new view of the phenomenon. As Lewis himself said (" Valence," p. 113) : " There seems to be but one possible way of accounting for this peculiar behaviour." The carbon core must move out of the tetrahedron formed by the four radicals of the original compound into a new tetrahedron whose base is formed by three of the original radicals and its apex by the entrant radical.

The process is illustrated by this model which represents an anionic exchange reaction such as :

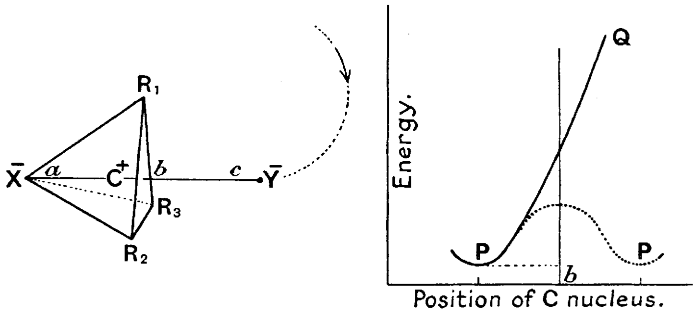


$$\text{Cl}-\text{C}\!\left\langle\begin{matrix}R_1\\R_2\\R_3\end{matrix}\right. + \bar{\text{O}}\text{H} = \bar{\text{Cl}} + \left.\begin{matrix}R_1\\R_2\\R_3\end{matrix}\right\rangle\text{C}-\text{OH}$$

The four spheres at the corners of a regular tetrahedron represent the four radicals, and the smaller sphere at the centre represents the core of the central carbon atom. On bringing up this sphere (illuminated to indicate the ionic charge) into the appropriate position we see the carbon core swing into the centre of a new tetrahedron, and the illumination is transferred to the sphere which formed the apex of the original tetrahedron and now represents a newly liberated anion.

It is not difficult to see in a general way the kind of energy relationships involved. The curve *PQ* (Fig. 1) indicates the increase of energy of the system as the carbon core C$^+$ is moved out of the tetrahedron along the axis *abc*. The curve rises sharply from the minimum *P* at the centre of the tetrahedron, finally reaching a level corresponding with the work of disrupting the molecule. If now an anion Y$^-$ should reach the position *c*, corresponding with the apex of the inverted tetrahedron—and, on account of the interaction between the ionic charge and the $\overset{+}{\text{C}}\text{——}\overset{-}{\text{X}}$ dipole, anions will tend to take up positions on the *ac* axis, favouring attack on this face of the tetrahedron—a second minimum will be created at *P'* and the energy curve will have to take a new course between *P* and *P'* as indicated by the dotted line.

Fig. 1.



Hence through the presence of Y$^-$ the energy of the system when the carbon nucleus is at *b* is greatly diminished, the potential barrier between the minima at *P* and *P'*, which the carbon core has to surmount, is made comparatively low, and the inversion reaction needs only a moderate energy of activation.

This view, based on the movement of the carbon core, gives an exceedingly simple picture of the process, and the inversion of configuration, which was regarded as so surprising at the beginning of the century, now seems a natural and inevitable concomitant of reactions due to anionic exchange.

Of all the papers I have read I think none roused more interest or surprise than Werner's first account of the optical resolution of co-ordination compounds of cobalt. But whilst Werner's remarkable series of investigations left no doubt of the six-fold co-ordination and the octahedral configuration of a very large group of compounds, they did nothing to remove the great difficulties of interpretation which their structure presented. Here was a great class of substances which seemed to lie outside the ordinary laws of valency, and Werner had to introduce the idea of *subsidiary valencies.*

The electron theory of valency however provided a simple solution of the difficulty. It removed the need for introducing a new and mysterious kind of valency. It enabled us to see that the link which binds the co-ordinated group to the central atom is a two-electron bond, similar in nature to the nitrogen–oxygen bond in the amine oxides, or the carbon–nitrogen bond in the organic ammonium radicals. This was pointed out by G. N. Lewis (" Valence," p. 114) and very clearly by Sidgwick in our Journal (J., **1923**, **123**, 725). Sidgwick also made the interesting and important observation that, in the most stable and characteristic 6-co-ordinate complexes, the electron duodecet was related to the next following inert gas in the same kind of way as was the octet of 4-covalent compounds.

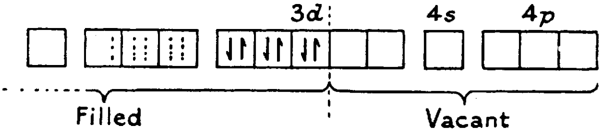
All the radicals which enter into co-ordination complexes possess lone pairs of electrons. The formation of a co-ordinate link between, for example, ammonia and a metal M is conceived to take place by the passage

$$\mathrm{M}\boxed{} + \boxed{:}\mathrm{NH_3} = \mathrm{M}\overset{-}{\boxed{\cdot}}\ .\ .\ \overset{+}{\boxed{\cdot}}\mathrm{NH_3}$$

of one of the electrons of the lone pair of ammonia into a vacant orbital of the metallic atom. This process conveys a formal charge of -1 to the metal and leaves one of $+1$ on the ammonia, giving it the ammonium structure. A bond then arises from the resonance energy of the two electrons between the two orbitals, provided that the energy thus obtained is more than that required to bring about the electron transference.

Since the 6-co-ordinated complexes have octahedral configuration, we shall find the most stable compounds where the electron structure thus acquired by the central atom is that which is best adapted to give a set of octahedrally disposed bonds. Pauling has shown that in the last three transition elements of each period (where the *d*-orbitals have about the same energy as the *s*- and *p*-orbitals of next higher quantum number) six equivalent, strongly bonding, octahedrally arranged orbitals can be obtained by appropriate hybridisation from two *d*-orbitals and the set of four provided by the next following *s*- and *p*-orbitals.

In the fourth period, for example, to obtain the necessary vacant orbitals to yield the strongest set of octahedral bonds for six co-ordinated groups we should require the following electron scheme :



which can be obtained from Fe^{++} or Co^{+++}. Similarly, in the sixth period the corresponding arrangement can be got from Os^{++}, Ir^{+++}, or Pt^{++++}. These are the systems which, speaking generally, are in fact found to give rise to the most stable and characteristic co-ordination compounds—this is particularly apparent in the metallic carbonyls and nitrosyls—and it seems probable that in this theory of Pauling the foundation for Sidgwick's rule is to be found.

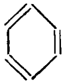
With regard to organic compounds, probably the most interesting theoretical advances made during the present century have been those relating to the structure and reactivity of aromatic compounds.

Though various formulæ have been proposed from time to time for benzene, most chemists have probably always felt that the original Kekulé formula provided the nearest approach which the structure theory could provide to a representation of the benzene molecule.

At the same time it was evident that constitutional factors existed in benzene to which the structure theory could give no expression. The simple Lewis form of the electron theory of valency threw no light on this question, but advances followed rapidly on the discovery that electrons had a wave aspect and that atomic electrons behaved as standing waves represented by solutions of Schrödinger equations. Soon after this discovery Heitler and London gave a satisfactory explanation of the covalent bond, and Slater and Pauling developed the concept of resonance in relation to molecular structure. We are indebted to Pauling especially for showing on a broad basis the great value of this concept in enabling us to interpret the structure of molecules which could only be represented imperfectly by the unmodified structure theory.

The conception of the benzene molecule as a resonance hybrid of (mainly) two structures closely resembling the two Kekulé formulæ must now be universally familiar to organic chemists.

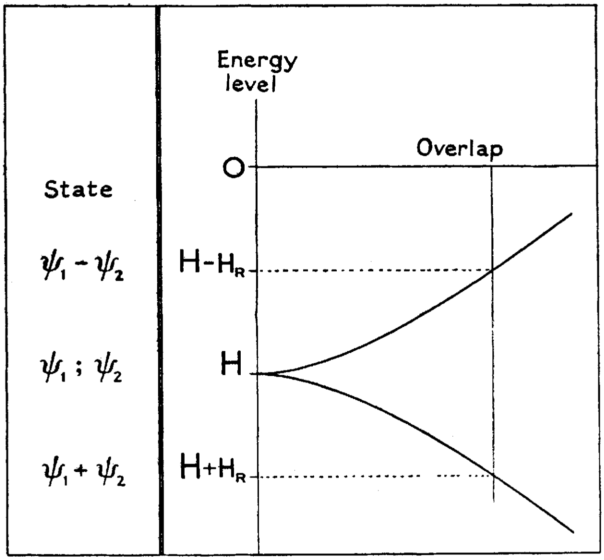
When it is a question of finding quantitative solutions for problems of this kind no doubt the method of molecular orbitals provides the more elegant and powerful instrument. For organic chemists however who have in the structure theory their principal means of interpreting a highly complex mass of experimental data the concept of resonance is of particular value. In effect, it provides an extension of the structure theory which enables it to be applied to cases to which, in its simple form, it is inapplicable.

The Schrödinger equation is a second-order, linear, homogeneous, differential equation and equations of this type have the property that if they have two or more independent solutions then any linear combination of these is also a solution. The Schrödinger equation for the possible distributions of the electrons in a molecule is determined by the positions of the atomic nuclei. We know from experimental data that the atomic nuclei in the benzene molecule have a regular hexagonal arrangement. In the two structures represented by the Kekulé formulæ   the single and double bonds must therefore have the same length and the arrangement of the nuclei must consequently be the same in both these structures. The wave functions ψ_1 and ψ_2 corresponding with the two structures are therefore solutions of the same Schrödinger equation and the general solution is a linear combination of these, $(\alpha\psi_1 + \beta\psi_2)$.

This expression represents a superposition of two modes of vibration of the same system, and since the two wave *functions* ψ_1 and ψ_2 evidently have equal energies, H_{11} and H_{22}, the behaviour of the system is determined by a general theorem easily proved by perturbation theory. The theorem may be stated in the following way. If in a system there are two unperturbed wave functions, ψ_1 and ψ_2, having equal energies, H_{11} and H_{22} (which we may put equal to H) their mutual perturbation will result in a splitting of this energy level into two $(H + H_R)$ and $(H - H_R)$, and the system will assume one or other of two allowed states corresponding with these levels (Fig. 2). The state which corresponds with the level $(H + H_R)$ is $a(\psi_1 + \psi_2)$ and that corresponding with $(H - H_{12})$ is $b(\psi_1 - \psi_2)$. In the former state ψ_1 and ψ_2 are vibrating in unison; in the latter they are in exactly opposite phases.

The new term H_R which appears in these expressions and determines the extent of the splitting is known as an " exchange integral." The perturbation is due to the overlapping of the wave functions and the magnitude of H_R is determined by the extent of the overlapping.

FIG. 2.



Since H_R like H is always negative, $(H + H_R)$ is the lower of the two levels and the corresponding state $a(\psi_1 + \psi_2)$ accordingly represents the ground state of the system (Fig. 2).

In the benzene molecule the wave functions ψ_1 and ψ_2, representing the two Kekulé formulæ, evidently overlap. They will therefore undergo mutual perturbation and, in consequence, the system will have to assume one or other of two new states—either $a(\psi_1 + \psi_2)$ of energy $(H + H_R)$, or $b(\psi_1 - \psi_2)$ of energy $(H - H_R)$, where H_R, as above, denotes the exchange integral.

Of these states $a(\psi_1 + \psi_2)$, representing the resonance hybrid of the two Kekulé formulæ, has the lower energy and is therefore the state which the molecule must normally assume; * the other is an excited state. The energy H_R by which the ground state is stabilised relatively to the individual Kekulé structures is the " resonance energy."

There is another important effect which is always associated with the mutual perturbation of electronic states of equal energy. The system behaves in some respects like a pair of loosely coupled pendulums of equal frequency. It pulsates between the two states and it can be shown—quite generally—that the frequency of the pulsation is $2H_R\boldsymbol{h}/$, where ***h*** is Planck's constant.

Kekulé's suggestion that the system of double bonds in the benzene molecule oscillated between their two possible positions was therefore to a large extent correct, though Kekulé was of course ignorant of the essential point that this oscillation is associated with a large amount of resonance energy which stabilises the molecule and thus causes the observed reduction of the unsaturation normally associated with double bonds.

The frequency of this oscillation, calculated from the estimated value of the benzene resonance energy, is of the order of a thousand times the vibration frequency of the carbon nuclei. The molecule can therefore never settle down into one of the states which the Kekulé formula really denotes with alternate distances of 1·54 A. and 1·33 A. between the carbon nuclei, but remains in an intermediate form with a uniform internuclear distance of 1·39 A. Similar considerations evidently apply to other resonating systems, such as the nitro-group, or the anions of the carboxylic acids.

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* Actually the ground state includes small contributions from other less important structures.

We may note in passing that the foregoing principle provides a general explanation of the covalent link. In the hydrogen molecule, for example, where we have two nuclei, *a* and *b*, and two electrons, (1) and (2), there must be two states of equal energy; u_1, in which electron (1) is on *a* and electron (2) on *b*, and u_2, in which the two electrons are interchanged, so the (2) is on *a* and (1) on *b*. The equal unperturbed energies of these states (H_{11} and H_{22}) are made up of the energies of two isolated hydrogen atoms together with the potential energy due to their electrostatic interaction.

The mutual perturbation of these states splits the energy level so that the system has to assume either the symmetrical state $a(u_1 + u_2)$ in which the energy is $(H_{11} + H_{12})$ or the antisymmetrical state $b(u_1 - u_2)$ in which the energy is $(H_{11} - H_{12})$, H_{12} being the exchange integral. The symmetrical state, having the lower energy, is the ground state of the system.

As the distance between the two atoms is diminished the overlap of u_1 and u_2 becomes greater and the magnitude of H_{12} is accordingly increased. In the symmetrical state this increase of H_{12} as the distance between the atoms is lessened produces an attraction which draws the atoms together until an equilibrium position is reached where this attraction is balanced by the electrostatic effect, the major term in which is the repulsion between the two nuclei. This repulsion increases very rapidly with the diminution of the internuclear distance when this is less than about 1 A.

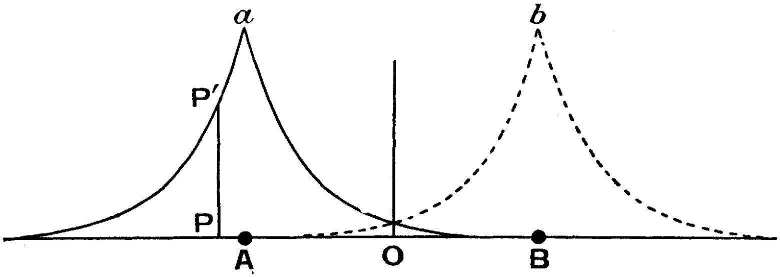
In the antisymmetrical state, in which the energy includes the term $-H_{12}$, the atoms evidently repel one another.

It is, I think, profitable to consider these questions also from another, more elementary and less generalised point of view—one which has the advantage however of being more indicative of the physical nature of the processes concerned. If we take, for example, the simplest of all chemical compounds, the hydrogen molecule ion—in which two protons are linked by one electron—we may regard the bond energy as resonance energy arising from resonance of the electron between the two states :

(I.) H-----H^+ H^+-----H (II.)

But we may also regard the bonding as brought about in the following manner. In a hydrogen atom in its ground state the electron forms a spherically symmetrical standing wave centred on the nucleus, the amplitude of the wave along any line through the nucleus A (Fig. 3*a*) being represented by a curve of the type *a*.

FIG. 3*a*.



If a second hydrogen nucleus B is placed on this line at such a distance that there is an appreciable overlap between *a* and the corresponding curve *b* for B, as indicated in the diagram, there will be a finite probability that the electron centred on A will find itself to the right of O, the midpoint between A and B. It will then be in a region where the field of B is the stronger, and when this occurs the electron will be captured by B and a transition from structure (I) to structure (II) will result.

There will then be the same probability of transition back to structure (I), so that a continuous exchange of the electron between the two nuclei will proceed at an average rate determined by the overlap of the two wave functions, and the probability of finding the electron on B will be equal to that of finding it on A.

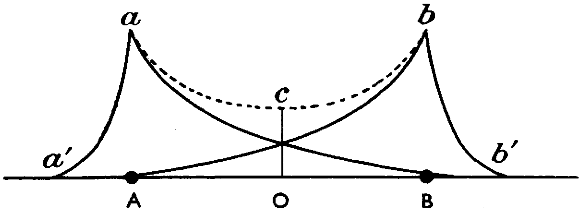
In the absence of B the probability of finding the electron at a point *P* is given by the square of the amplitude *PP′* of the wave at that point. When the second nucleus is brought up to B this probability is halved (to a first approximation) and thus the ordinate of the curve at *P* is reduced to $P/\sqrt{2}$.

Hence to represent the compound H_2^+ we must begin by re-drawing Fig. 3*a*, reducing the vertical scale by the factor $1/\sqrt{2}$ and removing the distinction between curves *a* and *b*. We must also take into account the fact that the presence of the nucleus B destroys the spherical symmetry of the field round A, increasing the probability of finding the electron on the side towards B; the form of the wave centred on B is of course correspondingly distorted. We thus get a diagram of the type indicated in Fig. 3*b*.

We have now to consider the superposition of the waves represented by *a* and *b*, and this depends on their relative phases. We have already seen that there are only two possibilities; the phases have to be either the same (as shown in the figure), or exactly opposite. We are concerned now with the former condition, since the latter does not lead to compound formation.

We may begin then by adding the amplitudes of the components *a* and *b* in accordance with the law for compounding waves, thus obtaining the dotted curve *a′acbb′* of Fig. 3*b*. This curve represents an element of a standing electron wave enveloping both nuclei. We have however also to take into account another fundamental principle of wave-motion, namely that the intensity of a wave is proportional to the square of its amplitude. The intensity ψ^2 of an electron wave at a point is interpreted as the probability of finding the electron there—or, more precisely, the probability of finding the electron in the element of volume dv at P is ψ^2 dv. Hence, if the electronic charge is taken as unity, ψ^2 can alternatively be regarded as the time-average of the negative charge density at P.

FIG. 3*b*.



Covalent bonding is a consequence of the two elementary principles of wave-motion : (1) that when waves are superposed the resultant amplitude is the *sum* of the component amplitudes, and (2) that the intensity of a wave is proportional to the *square* of its amplitude. For if u is the amplitude of each of the component waves a and b at the midpoint O between the two nuclei (Fig. 3*b*) the resultant amplitude there will be $2u$ and the corresponding charge density will be $4u^2$. But if we had merely added the individual charge densities (u^2) of the two components—as we should have done if electron clouds behaved like gas clouds—the resulting density would only have been $2u^2$. Hence the resonance between the two halves of the electron wave produces an amplification of the charge density at O which, to a first approximation, doubles its value there.

It will now be seen that the vertical scale of the curve $a'acbb'$ must be modified. The diagram as it stands—with the component and resultant curves drawn to the same scale—indicates an increase of negative charge density wherever there is an appreciable overlap of the wave functions without any compensatory decrease. The increase of charge density in the region of maximum overlap however clearly requires a decreased density elsewhere in order that the total electronic charge may remain constant.

It can readily be shown that the reduction factor for the vertical scale of the curve representing the resultant wave should be $1/\sqrt{2(1 + S)}$, where S is the value of the "overlap integral," $\int ab\,dv$, taken over the whole of space.

The changes which the resonance effect brings about in the charge distribution along the line through the nuclei AB (which are representative of those along parallel lines) can be seen from Fig. 4. In Fig. 4*a* the continuous curve indicates the actual density distribution (obtained by squaring the ordinates of $a'acbb'$ after applying the proper reduction factor). The dotted curve shows what the distribution would be if there were no resonance effect (*i.e.*, it represents the sum of the squares of the ordinates of the curves a and b of Fig. 3*b*). Fig. 4*b* shows the difference between the two distributions on an enlarged vertical scale and it can be seen from this how the charge is drawn out of the regions about the nuclei into the space between them. The general distribution of the electronic charge brought about in this way is indicated in Fig. 5. The negative charge drawn by resonance into the central space attracts both nuclei and causes them to move towards one another till an equilibrium position is reached at which this attraction is balanced by their more rapidly increasing

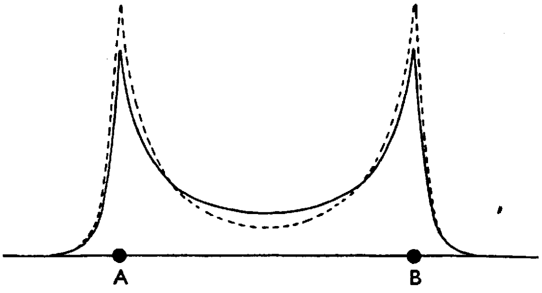


FIG. 4*a*.

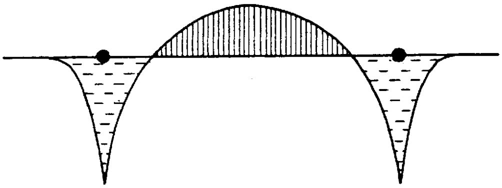


FIG. 4*b*.

mutual repulsion. Thus, in consequence of its wave-nature, the electron forms a bond between the two nuclei and the compound $[H_2]^+$ results.

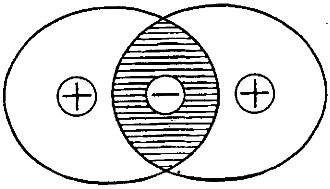


FIG. 5.

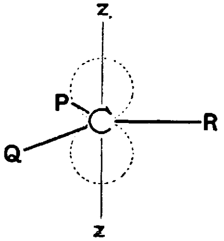
We may next consider the hydrogen molecule. In this the bond is formed by two electrons of opposite spins and the bonding is brought about by processes of the same kind as are operative in the molecule-ion. When the two atoms are near enough together to allow of an appreciable overlap of their 1*s* wave functions, each electron wave spreads round both nuclei and in each wave self-amplification takes place in the region between the nuclei, causing an accumulation of negative charge there in the manner already explained. The total accumulation of negative charge in this region, arising from both electrons, then exerts an attraction on the nuclei, as in the molecule-ion, and thus bonds the two atoms together.

The contribution of each electron to the bond strength is less in the molecule than in the molecule-ion since, when two electrons are present, each lessens the strength of the field in which the other is moving. Otherwise the two electrons do not greatly interfere with one another—they are rarely (only about 4% of the time) both on the same nucleus—and the bond-energy of the hydrogen molecule, instead of being twice, is 1·7 times that of the molecule-ion. Also—on account of the greater total resonance attraction due to two electrons—the bond-length is considerably less in the molecule (0·74 A.) than in the molecule-ion (1·06 A.).

The increased bond energy which results from the resonance of the two Kekulé structures for benzene can be interpreted in a similar way as arising from the amplification of charge density which takes place in the regions between the nuclei when an electron wave spreads round more than one nucleus.

It is convenient to regard the benzene nucleus as built up of carbon atoms whose valency systems are based on the trigonal wave functions of carbon. These wave functions (which result from the hybridisation of one 2*s*- with two 2*p*-wave functions) give three strong coplanar bonds, *P, Q, R,* with intervalency angles of 120° (Fig. 6*a*), the fourth valency being derived from a 2*p*-electron having its symmetry axis *zz'* perpendicular to the plane of the trigonal bonds.

FIG. 6*a*.



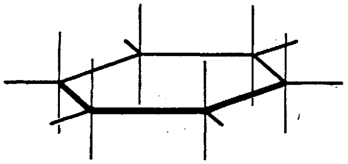


FIG. 6*b*.

When a benzene nucleus is constructed from carbon atoms with valencies thus arranged the trigonal bonds will yield a strainless hexagonal frame-work and in addition there will be a 2*p*-electron on each carbon atom as indicated in perspective in Fig. 6*b*. These 2*p*-electrons with symmetry axes perpendicular to the plane of the hexagon are termed π-electrons (Hückel), or mobile electrons (Lennard-Jones). They form dumb-bell-shaped electron clouds as indicated in Fig. 6*a* and they are represented in Fig. 6*b* for simplicity by their symmetry axes only.

The unique character of the aromatic hydrocarbons is thus chiefly dependent on two factors; the first of these is the number of atoms in the ring—a ring of this type can only be plane and strainless if it contains *six* atoms—the second is the presence of an even number of mobile electrons, one for each atom of the ring, giving strong additional bonding between the ring atoms and at the same time conferring a special type of reactivity.

The manner in which a pair of π-electrons on two adjacent carbon atoms give rise to a bond (forming the second component of a double bond in the Kekulé formula) is indicated in Fig. 7.

Each of the two electrons is shared equally by both nuclei and in consequence resonance amplification of the negative charge density takes place in the regions of overlap of the dumb-bell-shaped electron clouds in the manner which has been explained for the electrons of the hydrogen molecule. In this way a distribution of negative charge is brought about which will evidently tend to draw the (partially screened) positively charged nuclei together.

A Kekulé formula with the three double bonds in a fixed position implies that an electron found momentarily on, for example, carbon atom 2 is shared only between this and carbon atom 1. Such a limitation is however evidently unjustifiable; there is an equal probability of its being shared with carbon atom 3. This would mean that the electron wave, instead of spreading round two atoms only, 1 and 2, spreads round three atoms, 1, 2, and 3. Still further extensions of the wave of a mobile electron are possible; there is a certain probability of its extending round all six carbon atoms.

Between each pair of nuclei round which the electron wave extends, amplification of the charge density will be brought about by resonance in the manner already explained. This causes, as we have seen, a withdrawal of charge from the regions of maximum density into the bonding regions between the nuclei.

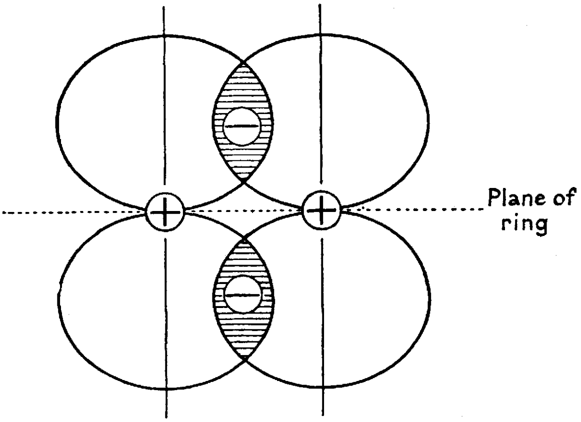


FIG. 7.

Now the greater the number of nuclei round which the electron wave spreads the greater is the proportion of the electronic charge drawn by resonance into the bonding regions and the greater the total contribution made by that electron to the bond energy. From the present point of view then we can see in this effect the cause of the additional bond energy in the benzene molecule compared with that which a single Kekulé structure would yield. Each electron wave spreads on the average over more than two ring atoms and thus makes a greater contribution to the bond energy than it would if subject to the restraint implied in the Kekulé formula.

I turn now to the question of the reactivity of aromatic compounds. During the present century there has been a great advance in our understanding of the factors controlling the entry of substituents into the benzene nucleus and in this advance much of the pioneer work has been due to British chemists.

A fundamental step—which we owe in great measure to Lapworth—was the recognition of the importance of the *polarity* of the substituent group. Since most of the groups capable of direct introduction into aromatic compounds belong to the class which Lapworth termed *kationoid*, they would be expected to attack preferentially carbon atoms having negative relative polarity.

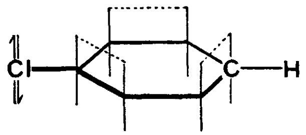
The way in which a substituent group could influence the polarities of the benzene ring atoms through inductive, and especially through electromeric effects was pointed out by Robinson. Robinson also showed how these effects could be expressed in terms of Lewis's electron theory of valency. His conclusions were strikingly confirmed by Sutton's comparisons of the electric dipole moments of corresponding aliphatic and aromatic compounds. These showed that the electron shifts required by Robinson's theory did in fact take place.

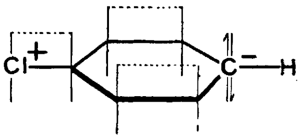
During the last decade the fundamental features of aromatic chemistry have received great illumination from the theory of resonance and we are indebted especially to Pauling for very clear explanations of the application of this theory to carbon compounds.

In chlorobenzene, for example, from the *o*-*p*-orientation of an entering second substituent we infer the presence of excess negative charges on the *o*- and *p*-carbon atoms. We know that these cannot arise through the inductive action of the chlorine–carbon dipole, since this would have the contrary action. We must conclude therefore that they come from the chlorine atom through an electromeric shift, and this is confirmed by the fact that the molecular dipole of chlorobenzene is less than that of the alkyl chlorides, showing the existence in the aromatic chloride of a dipole opposing the chlorine–carbon dipole.

In terms of the theory of resonance we should accordingly regard the chlorobenzene molecule as a resonance hybrid of the conventional structure (III) with three electromeric modifications formed from (III) by the loss of an electron from the chlorine atom and the gain of one by an *o*- or *p*-carbon atom of the ring. The *p*-form is shown in (IV). In these diagrams the benzene ring is shown in perspective; a vertical line represents a mobile electron (its symmetry axis) and a pair of vertical lines represents two paired electrons in a single orbital. The horizontal dotted lines indicate coupling between the electrons; the coupling shown in the conventional structure should be understood to comprise the five canonical structures included in the benzene ring.

(III.)





(IV.)

We have then in (III) and (IV) two states of the same system, whose wave-functions we may denote by ψ_1 and ψ_2. Since the energy H_1 corresponding with ψ_1 is evidently much lower than that H_2 corresponding with ψ_2 we have a case of the mutual perturbation of two states of unequal energy. It can be shown that the results of this must always be to cause the system to assume one or other of two allowed states whose wave-functions are linear combinations of ψ_1 and ψ_2. One of these is a stable state $(\alpha\psi_1 + \beta\psi_2)$ of energy $(H_1 + H_R)$, the other is an activated state $(\alpha\psi_2 - \beta\psi_1)$ of energy $(H_2 - H_R)$. The resonance energy H_R, which enters into these expressions, is, like H_1 and H_2, always negative. The effect of the perturbation is therefore to push the energy levels further apart.

The magnitude of H_R depends partly on the extent of the overlap of ψ_1 and ψ_2 and partly on the difference between their energies. H_R increases as the overlap increases; it also increases as H_1 and H_2 become more nearly equal. These relationships are illustrated in Fig. 8, which shows how the energy of the system varies with the relative contributions, α^2 and β^2, of the two states. The system assumes the state of minimum energy, and in order to do this it has—at first sight paradoxically—to obtain a contribution from the state of higher energy. This is however a necessary consequence of the wave nature of the electron and the laws which govern the interaction of vibrating systems. These principles explain why the electromeric changes take place and thus how it comes about that substituents influence the polarity of the carbon atoms of the benzene ring.

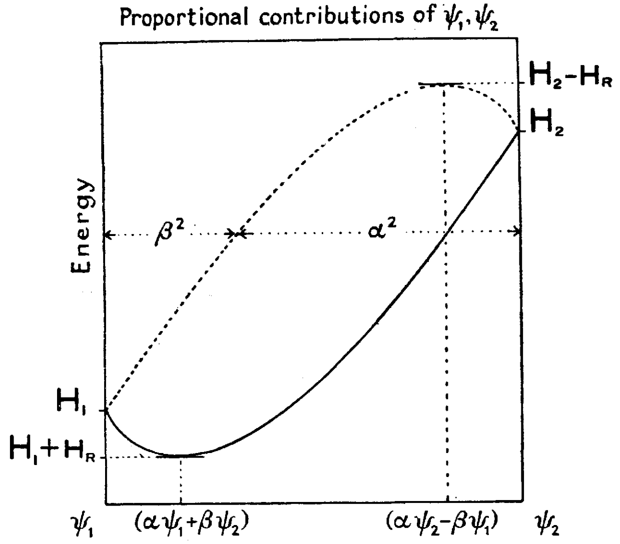
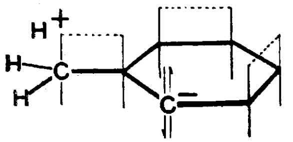


FIG. 8.

Experimental evidence that the chlorobenzene structure does indeed include a contribution from structure (IV), which shows a double bond between chlorine and carbon, is given by electron diffraction measurements. These indicate a shortening of the chlorine–carbon link corresponding with about 15% double-bond character.

The presence in the chlorobenzene structure of a contribution from structure (IV) also gives the reason for one of the most distinctive characters of aromatic halogen derivatives—their resistance to reagents which normally bring about anionic exchange. On the one hand, the partial double character of the chlorine–carbon link gives a stronger binding of the chlorine atom to the nucleus; on the other hand, the formal positive charge on the chlorine atom lessens its tendency to escape as an anion.

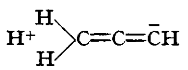
The toluene molecule formerly presented difficulties of interpretation. It was not easy to see what process could bring about a passage of negative charge from the methyl group into the aromatic nucleus—yet the behaviour of toluene towards substituting agents, as well as its dipole moment, indicates that such a passage does take place. There now however seems reason to believe that we may assume an appreciable probability for the existence of ionic structures like that represented in (V), in which a hydrogen atom of the methyl group has lost an electron and the *para-* or (as shown in the diagram) one of the *ortho*-carbon atoms has gained one. The toluene molecule would then be a resonance hybrid in which the carbon atoms would have acquired the requisite polarities.



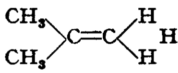
(V.)

If we grant that a methyl group can change in this way when attached to a system capable of taking up an electron, we can explain, not only the behaviour of toluene, but also the abnormal bond lengths in methylacetylene [through resonance of the conventional structure with structures like (VI)] and the greater tendency of *tert.*-butyl, compared with other alkyls, to form a kation [through resonance of CMe_3^+ with several structures of the form (VII)].

(VI.)



$$H^+ \begin{matrix} H \\ H \end{matrix}\!\!>C{=}C{=}\bar{C}H$$



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C{=}C\!\!<\begin{matrix} H \\ H \end{matrix} H^+$$

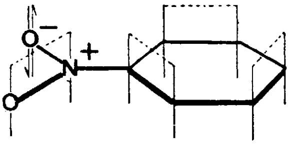
(VII.)

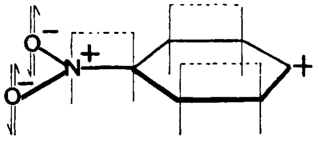
That the configuration of CH_2 is not quite the same in methyl as in doubly-linked methylene should only partially affect the energy due to resonance between such structures.

The influence of a nitro-group on the reactivity of benzene is of special interest. This substituent is characterised by the presence of a dipole having its positive end towards the ring. Though the dipole must have an inductive action on the mobile electrons similar to that of a positive pole (like NMe_3^+ in trimethylanilinium salts), its effect will be much weaker, and the effects of the group on the relative polarities of the ring atoms, causing *meta*-substitution, are attributed chiefly to the electromeric transformations made possible by the presence in it of a double bond.

Thus the nitrobenzene molecule can be represented as a resonance hybrid in which the conventional structure (VIII) (which includes resonance within the nitro-group) receives contributions from structure (IX) and its two *ortho*-analogues.

(VIII.)

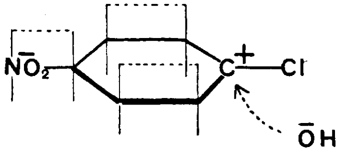




(IX.)

The view that the nitrobenzene structure includes contributions from these electromeric forms requires that the two oxygen atoms of the nitro-group should lie in the plane of the benzene ring. It thus finds interesting support in the observation of Birtles and Hampson that the presence of two *ortho*-substituents largely inhibits the normal electromeric effects in an aromatic nitro-compound as indicated by the dipole moment—presumably by keeping the plane of the nitro-group out of the plane of the ring.

The behaviour of the halogen derivatives of nitrobenzene gives particularly strong support to the polarity theory. If a nitro-group brings about *meta*-substitution by giving the *ortho*- and *para*-carbon atoms a resultant positive charge, then, whilst making them less reactive to kationoid groups, it should make them more reactive to anionoid reagents—and it is very well known that they are.

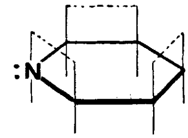


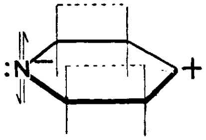
(X.)

Thus the *p*-carbon atom in *p*-nitrochlorobenzene is readily attacked by anions, such as the hydroxyl ion, with the ejection of a chloride ion—as is also the *o*-carbon atom in *o*-nitrochlorobenzene—whilst the *m*-chlorine atom in *m*-nitrochlorobenzene shows the immobility normally characteristic of aromatic chloro-derivatives. Since the loss of an electron by the *p*-carbon atom in the structure (X) not only leaves it with a positive charge, but also with a " sextet " valency system like that in boron trichloride, it seems clear that a contribution from (X) to the molecular structure should increase the mobility of the chlorine atom.

It has long been recognised that the influence of the nitrogen atom in pyridine on the reactivity of the rest of the molecule resembles that of the $:C(NO_2)$ complex in nitrobenzene. This resemblance can be clearly

(XI.)

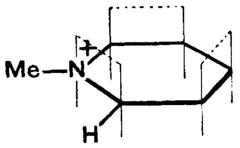


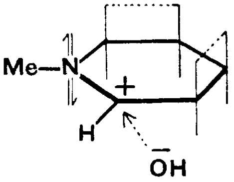


(XII.)

explained if we regard pyridine as a resonance hybrid of the conventional structure (XI) with contributions from the structure (XII) and its two α-analogues. Similarly the readiness with which the methyl-

(XIII.)



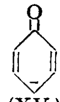


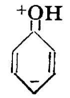
(XIV.)

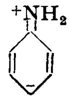
pyridinium ion is attacked by the hydroxyl ion with the formation of a " pseudo-base " is at once intelligible if methylpyridinium (XIII) is a resonance hybrid containing a contribution from structure (XIV). No doubt a corresponding process plays a part in determining the oxidisability of nitro-substituted benzenes in alkaline solution.

Thus the resonance theory provides a rational explanation of the principal substitution phenomena in aromatic compounds. These compounds have however other distinguishing features. Of these the chief are: (1) the stability of the halogen derivatives, (2) the acidity of the hydroxyl derivatives, (3) the feeble basicity of the amino-compounds, and (4) the convertibility of the amino-compounds into diazonium salts.

The stability of the halogen derivatives we have already considered. The acidity of phenol is an immediate consequence of the stabilisation of the phenoxide ion by resonance with structures like (XV), since the electrolytic dissociation constant of a compound at a given temperature is determined by the free-energy change of ionisation. The resonance energy which phenol itself obtains from the corresponding electromeric processes is much less, since the production of its electromeric forms [*e.g.*, XVI)], requiring the separation of electric charges, involves a greater energy change; and we have seen that the greater the energy difference of two states the less their resonance energy.


(XV.).

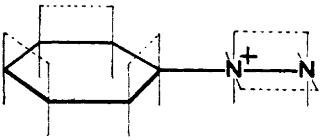

(XVI.)

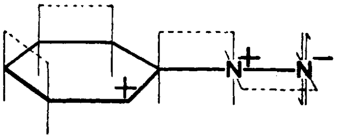

(XVII.)

The feeble basicity of aniline can be accounted for in a similar way. In the free base electromeric changes [*e.g.*, (XVII)] are possible, leading to resonance stabilisation. Conversion of the amino-group into the ammonium residue, $-NH_3^+$, stops these changes by fixing the lone pair on the nitrogen atom. Thus the base is stabilised relatively to the ion and ionisation is diminished.

The fourth characteristic—that aromatic amines can be diazotised—can be referred to the stabilisation of the diazonium ion by resonance between the conventional structure (XVIII) and electromeric modifications, an *ortho*-form of which is represented by (XIX). This explanation is supported by the well-known exchange reactions of *o*- and *p*-substituent halogen atoms in diazonium salts, which take place too readily to be accounted for by the presence of the positive pole. In aromatic compounds such anionic exchanges seem only to occur when there is resonance with an electromeric modification which has a formal positive charge on the ring atom carrying the halogen, as in halogen-substitution derivatives of nitrobenzene or pyridine, or of the triphenylmethyl kation.

(XVIII.)

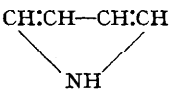




(XIX.)

A long-standing problem whose solution—in its main outlines—is clearly indicated by the resonance theory is that presented by the remarkable relationship which certain five-membered heterocyclic compounds—notably thiophen, and in a lesser degree pyrrole and furan—show to the aromatic series.

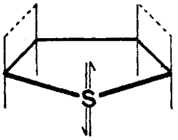
In these compounds the conventional formula shows a butadiene residue with its terminal carbon atoms linked through a bivalent atom or group (=S, =NH, or =O)—as in pyrrole (XX). It is evident however that some interaction takes place between the butadiene residue and the bridging atom which cannot be expressed by the unaided structure theory. In thiophen, for example, the butadiene residue has lost its usual additive properties and reagents like bromine or sulphuric acid act on it substitutively; the sulphur atom also has lost the power which it would normally have in a thio-ether of yielding a sulphonium salt with methyl iodide, and of giving a sulphoxide or a sulphone with oxidising agents.

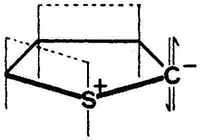


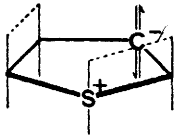
(XX.)

Now the heats of combustion of thiophen, pyrrole, and furan are considerably smaller than would be expected for compounds of their conventional formulæ—Pauling and Schomaker (*J. Amer. Chem. Soc.*, **1939**, **61**, 1769) estimate the differences as 31, 23, and 23 kg.-cals./mol. respectively.

The substances are therefore presumably resonance hybrids and the structures with which the conventional structures resonate are not far to seek. In each of these compounds the bridging atom has at least one lone pair of electrons and we may assume a finite probability for electronic arrangements in which this pair is resolved and a pair is found on one of the ring carbon atoms as indicated in diagrams (XXI), (XXII), and (XXIII) for thiophen. Along with the conventional structure (XXI) there are two possible structures of type (XXII) and two of type (XXIII), and the actual structure results from resonance between the five forms. This view of the constitution of thiophen explains its more characteristic properties. The formation of an addition product with bromine, for example, would abolish the resonance by making the ring carbon atoms incapable of accepting an additional electron. Hence on treatment with bromine it is the more stable substitution products which result.


(XXI.)


(XXII.)

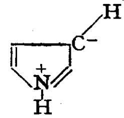

(XXIII.)

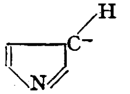
That kationoid substitution is more readily effected in thiophen than in benzene is evidently to be attributed to the resultant negative charges on the carbon atoms due to the presence of contributions from the structures (XXII) and (XXIII). Thiophen does not combine with methyl iodide because the resulting sulphonium iodide would lack most of the resonance energy by which thiophen itself is stabilised. The corresponding electromeric changes would be resisted by the formal positive charge on the sulphur atom and probably also by a firmer binding of the remaining lone pair of electrons. The energy differences between the conventional and the electromeric structures would thus be large and the resonance energy correspondingly small.

The chief characters of pyrrole can also be explained. When pyrrole forms a salt with acids the addition of the proton fixes the lone pair on the nitrogen atom and thus abolishes the resonance. Hence pyrrole is a very weak base and its salts are highly unsaturated and consequently rapidly undergo condensation and resinification.

On the other hand when pyrrole is treated with potassium the removal of the nucleus of the N-hydrogen atom leaves an anion in which the resonance energy is greater than in pyrrole itself for reasons similar to those already given in connexion with the phenoxide ion and phenol, as will be apparent from the following formulæ :

(XXIV.)





(XXV.)

In pyrrole itself the production of the electromeric forms ([*e.g.* (XXIV)] requires the separation of opposite electric charges; in the pyrrole anion (XXV) it does not. The acidic properties of pyrrole are thus explained.

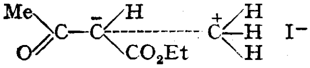
There is also a distinct similarity between the electromeric forms of the pyrrole anion (XXV) and those of the phenoxide anion, and the presence of contributions from these forms will cause the two anions to resemble one another in having comparatively large resultant negative charges on the ring carbon atoms (α- and β- in the pyrrole anion; *o*- and *p*- in the phenoxide ion). We may see in this resemblance the cause of the remarkable analogy which pyrrole in many of its reactions shows to phenol.

The third member of the group, furan, shows distinctly less relationship to the aromatic series. This we should expect. It is evidently, as Pauling has pointed out, because the very electronegative oxygen atom has a smaller tendency than nitrogen or sulphur to assume the positive charge which the resonating structure requires.

Experimental evidence in support of these structures is given by the bond lengths between the hetero-atom and the α-carbon atoms, which have been measured by electron diffraction (Pauling and Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 1769). A shortening, showing that these bonds actually have a partial double-bond character as the resonating structures require, was in fact indicated by these observations, and the amount of the shortening showed that the contribution from the electromeric forms was greatest in thiophen (*ca.* 17%) and least in furan (*ca.* 5%).

We can thus interpret the broader outlines of the chemistry of the aromatic series in terms of a picture representing the ground states of aromatic compounds as resonance hybrids in which the conventional structure is stabilised by contributions from electromeric modifications.

We know however that, in order to react, the compounds must take up energy of activation. Hence to understand their reactivity it is essential to know the structure of the activated forms. One cannot help noticing that reactions of aromatic compounds can frequently be most simply represented when we assign to the reactants—not the conventional structure—but that of an electromeric modification although this contributes in only a minor proportion to the ground state. In the aliphatic series also one may find the same thing—resonance hybrids seeming to react in the form of one of the less stable contributors to the ground state. A well-known example is the anion of acetoacetic ester which seems to react with alkyl halides in the modification which has the negative charge on the α-carbon atom (the alkyl radical presumably undergoing inversion, see inset).



One might be tempted therefore to suppose that the reactive forms were the activated states $(\alpha\psi_2 - \beta\psi_1)$ represented in Fig. 8 (in which the electromeric modifications form the major contributions) were it not that the energy differences between these and the ground states are presumably far greater than the energies of activation indicated by the temperature coefficients of the reaction velocities. We have however to remember that the immediate precursor of a reaction is the intermediate compound existing at the summit of the energy pass through which the reactants travel to yield the products, and it is perhaps not impossible that a resonance hybrid may enter into this intermediate compound in the activated form of Fig. 8.

Chemistry is more interesting now than it ever was. There is more logical connexion between the facts. But the amount the student has to learn is greater and the temptation to overspecialise much increased. Our deeper knowledge enables us now to see things in truer perspective and the teacher needs more than ever to seek out the essentials and to find the simplest methods of presentation and so to help the student on the long road he has to travel to the stage where he can undertake independent research.