Some Studies in Molecular Orbital Theory I. Resonance Structures and Molecular Orbitals in Unsaturated Hydrocarbons

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DISCUSSION

It would be of considerable interest to obtain a value of the energy involved in the sintering process. This process in which the spheroidal particles coalesce undoubtedly proceeds by a process of self-diffusion.[10] ϵ'', the energy required for self-diffusion by the vacancy mechanism in a crystalline lattice, is equal to the sum of ϵ' and ϵ, where ϵ' is the energy required to move an atom from an interior lattice site to the surface, and ϵ is the activation energy required for an atom to move from one site in the lattice to an adjacent vacant site. ϵ' would thus be given by the difference in ϵ'' and ϵ. Also since the equilibrium ratio of the number of vacant sites to the total number of atoms is

$$N_e'/N \simeq \exp(-\epsilon'/kT) \qquad (14)$$

a knowledge of the magnitude of ϵ' would permit calculation of the equilibrium number of vacant sites.

Unfortunately, it has not been possible to relate satisfactorily the change in resistance or reflectance observed during the sintering process to any mechanism involving the coalescence of the particles.

If ϵ has the same value for massive gold as for gold smoke, then ϵ' for massive gold would be 27.5 kcal./g

atom, since ϵ'' for massive gold is 51 kcal./g atom.[11] This value of ϵ' is to be compared with the value of 28 kcal./g atom, calculated by Huntington[6] for the energy required to move a copper atom from an interior site to the surface. The energies for the copper lattice should be somewhat higher than for gold since the measured value of self-diffusion in copper is 57 kcal./g atom.[12] For gold smoke, however, ϵ' must be considerably smaller than 27.5 kcal./g atom in order to account for the rapid changes observed at temperatures below 200°C. When a smoke deposit is stabilized by heating below 80°C, the number of vacant sites is decreased and ϵ' is increased correspondingly. The difference in behavior above 100°C, shown in Fig. 4 at 150°C, between an untreated and a stabilized deposit indicates that the increase in energy required for the process after stabilization is probably of the order of magnitude of 5 to 10 kcal./g atom.

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[10] J. Frenkel, J. Phys. U.S.S.R. 9, 385 (1945).
[11] H. McKay, Trans. Faraday Soc. 34, 845 (1938).
[12] Steigman, Shockley, and Nix, Phys. Rev. 56, 13 (1939).

Some Studies in Molecular Orbital Theory

I. Resonance Structures and Molecular Orbitals in Unsaturated Hydrocarbons*

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(Received June 13, 1949)

The predictions of qualitative resonance theory, as to the electronic structures of unsaturated hydrocarbons, are analyzed in terms of LCAO molecular orbital theory. The following results are proved for "alternant" hydrocarbons, that is, hydrocarbons containing no odd-membered unsaturated rings:

(1) The number of unpaired electrons present in the ground state is at least as great as the number of carbon atoms having a deficiency of valence bonds in any principal resonance structure.

(2) With a few special exceptions, these odd electrons are distributed over just those atoms which have a deficiency of valence bonds in one or more of the principal resonance structures.

(3) In singly charged hydrocarbon anions or cations the ionic charge is located on just those atoms which bear charges in the various principal resonance structures.

It follows that enumeration of the principal resonance structures of a hydrocarbon molecule or ion gives much valuable information as to its electronic structure; and in particular, an alternant hydrocarbon possessing no normal Kekulé-type structure must have a paramagnetic ground state, and behave as a radical or multiradical.

These results do not depend on the neglect of overlap, or the assumption of a constant carbon-carbon resonance integral.

1. NOTATION

THE following is a summary of the notation used in this paper:

ϕ_t, ϕ_u are $2p$ atomic orbitals (AO) on the carbon atoms t, u.
N is the number of such AO.

T is the maximum number of double bonds (a triple bond being counted as two double bonds) occurring in any resonance structure.

ψ is a molecular orbital (MO) of form $\sum_t c_t \phi_t$; its binding energy is ϵ.

r is any "starred" carbon atom in an alternant hydrocarbon.

s is any "unstarred" carbon atom.

μ is any "active" carbon atom.

ν is any "normal" carbon atom.

R is the total number of starred atoms.

N_μ is the total number of active atoms.

N_ν is the total number of normal atoms.

R_ν is the number of normal starred atoms r_ν.

S_ν is the number of normal unstarred atoms s_ν.

A is the matrix formed by the resonance integrals β_{tu}.

A_μ is the matrix formed by the resonance integrals $\beta_{t\mu}$.

B is the matrix formed by the resonance integrals β_{rs}.

B_μ is the matrix formed by the resonance integrals $\beta_{rs\mu}$.

B_ν is the matrix formed by the resonance integrals $\beta_{rs\nu}$.

C is the matrix formed by the resonance integrals β_{sr}.

C_μ is the matrix formed by the resonance integrals $\beta_{sr\mu}$.

U is the rank of A.

U_μ is the rank of A_μ.

$\Pi^P\beta_{rs}, \Pi^Q\beta_{sr}, \Pi^{P\mu}\beta_{rs\mu}, \Pi^{Q\mu}\beta_{sr\mu}$, are products of P, Q, P_μ, Q_μ finite terms from different rows and columns of B, C, B_μ, C_μ.

2. INTRODUCTION

Because of their great simplicity and appeal to intuition, classical valence structures will probably long continue to be used for the description of molecules in the ground state. For this reason it is important to examine theoretically the various empirical rules which are used for correlating the properties of molecules with their classical valence structures.

An outstanding question in this connection is the following: Why are there relatively few stable molecules for which it is impossible to write some classical valence structure? This is perhaps the most fundamental problem in structural chemistry, and still awaits complete solution. In this paper it will be shown that the question can be answered more or less completely for unsaturated hydrocarbons containing no odd-membered rings, and that the answer throws much light on the theory of hydrocarbon free radicals and ions.

3. NOMENCLATURE

Before discussing the problem in detail, it is necessary to establish an unambiguous nomenclature.

For simplicity we shall restrict attention at first to unsaturated hydrocarbons in which all the carbon and hydrogen atoms lie in one plane, every carbon atom being of the sp^2-type, bonded to three other atoms. From this class we shall further select (for reasons that will appear shortly) those hydrocarbons which contain no odd-membered rings; and these will be referred to as *alternant hydrocarbons*.[1] According to this definition benzene, naphthalene, butadiene, and cyclobutadiene are alternant hydrocarbons, and so are most known planar hydrocarbons, but azulene and fulvene are not alternant.
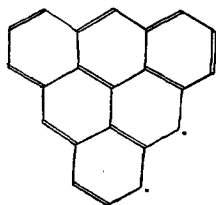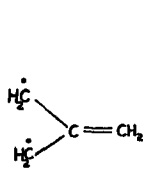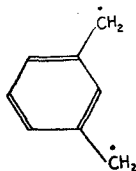

(I)   (II)   (III)

[1] See C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. A192, 16 (1947).

If hyperconjugation is neglected, an alternant hydrocarbon may have two kinds of resonance structure, namely (i) Kekulé-type or *K-structures*, in which each hydrogen atom is attached by a single bond to the adjacent carbon atom, and each carbon atom is involved in three single bonds and one double bond, and (ii) excited or *E-structures*, in which at least one carbon atom is joined to its three neighbors by single bonds only.

According to this nomenclature, benzene has two K-structures and several E-structures, whereas triphenylmethyl and the allyl radical have only E-structures. In the general case, an alternant hydrocarbon will have K-structures if and only if $N = 2T$, where N is the number of carbon atoms in the molecule and T is the maximum number of double bonds occurring in any resonance structure. This is because in a K-structure each carbon atom is involved in one double bond, and each double bond links two carbon atoms.

Those resonance structures which contain the greatest possible number, T, of double bonds will be described as *principal resonance structures*. In benzene ($T = 3$, $N = 6$) the principal resonance structures are just the two Kekulé structures, whereas in the allyl radical the principal resonance structures are of the E-type, namely,

$$CH_2 - CH = CH_2 \quad \text{and} \quad CH_2 = CH - CH_2.$$
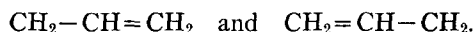
A further concept will be found useful later on. Carbon atoms which are doubly bonded in *all* the principal resonance structures will be described as *normal* carbon atoms, and all others will be described as *active* carbon atoms, to anticipate later results. Thus in benzene, all the carbon atoms are normal, whereas in allyl the two terminal atoms are active.

4. SCOPE OF THIS PAPER

The first problem to be discussed may now be formulated as follows: Why are alternant hydrocarbons with no K-structures so rarely stable? Consider, for example, the hydrocarbons (I), (II), and (III), none of which has hitherto been prepared. The only anomaly in their structures is the fact that they have no K-structures; each one has an unstrained skeleton of σ-bonds and an even number of π-electrons. Clar,[2] who first drew attention to molecule (I), supposed that it would be impossible to prepare because of having no Kekulé structures. As far as the author is aware, the attempt has not been made, and it would be of great interest to know the outcome; but (II) and (III), at any rate, are almost certainly unstable, according to the experimental evidence. The question is, why?

In approaching this problem theoretically, either the valence bond method or the method of molecular orbitals might be used. Superficially, the following answer, in

[2] E. Clar, *Aromatische Kohlenwasserstoffe* (Verlag. Julius Springer, Berlin, 1941), p. 311.

FIG. 1.
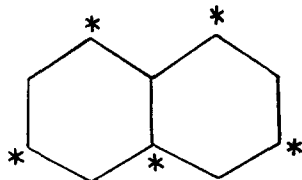
terms of the valence bond method, might appear plausible:

It is known that in benzene most of the resonance energy arises from the K-structures, the E-structures being relatively unimportant. One might therefore expect that in (I), where there are no K-structures, the resonance energy would be considerably reduced, and that this molecule would be relatively unstable. However, calculations by the French school[3] show that as a molecule becomes bigger the contribution of K-structures to its ground state becomes less and less significant; and that even in molecules the size of anthracene almost all the resonance energy arises from E-structures.

The breakdown of this argument suggests that the valence bond method is not a very promising approach to the problem in hand; so the molecular orbital method has been used as a basis for discussion, in spite of the apparent lack of connection between resonance structures and molecular orbitals. As will be seen, it can be proved by MO theory (i) that an alternant hydrocarbon must have at least $N - 2T$ unpaired electrons in its ground state, and (ii) that of these, at least $N - 2T$ will be distributed over the active carbon atoms only, in the sense of Section 3. It follows that any diamagnetic alternant hydrocarbon must have $N = 2T$, and must therefore possess at least one K-structure. In view of the fact that paramagnetic molecules usually behave as free radicals, these results provide a theoretical explanation for the rarity of stable alternant hydrocarbons possessing no Kekulé-type structures.

5. BASIS OF ARGUMENT

In discussing the electron configuration of an unsaturated hydrocarbon, it is usual to begin by dividing the electrons into two classes, σ and π. In the ground state the σ-electrons will form a closed shell since their orbitals have lower energy than the upper π-orbitals; and any unpaired electrons which may be present in the ground state will tend to occupy π-orbitals. The σ-electrons will therefore be ignored in the following discussion.

In determining the configuration of the π-electrons, each π-orbital is expressed as a linear combination of atomic orbitals of the correct symmetry. In this approximation (LCAO approximation) the total number of π-molecular orbitals in a hydrocarbon equals the total number of π-electrons, since both are equal to the number of available carbon $2p$ atomic orbitals.

There is one particular kind of unsaturated hydrocarbon in which the π-orbitals are distributed in a

specially simple way, namely, the alternant hydrocarbons defined earlier. It has been shown[4] that in an alternant hydrocarbon the π-molecular orbitals of nonzero binding energy occur in pairs with opposite energies; for example, in benzene the orbital energies are $\pm 2\beta$, $\pm \beta$, $\pm \beta$. In an alternant hydrocarbon with N carbon atoms, there will be N π-electrons and N π-molecular orbitals, in LCAO approximation. Therefore, if there are M π-orbitals of negative energy, there will be $N - 2M$ π-orbitals of zero energy. In the ground state the electrons tend to occupy the orbitals of lowest energy, so as a rule each MO of negative energy will contain two electrons with opposed spins, leaving $N - 2M$ to be distributed among the $N - 2M$ orbitals of zero energy. By Hund's rule, the most stable configuration is that with the highest multiplicity; so in the ground state there will be just one electron in each zero-energy molecular orbital. The number of unpaired electrons in an alternant hydrocarbon therefore equals the number of π-molecular orbitals of zero energy.

There is one loophole in the above argument. It is possible that there may be a pair of MO with binding energies $+\epsilon$ and $-\epsilon$, where ϵ is very small but not equal to zero. In such cases an electron will overflow from the lower into the upper MO if the exchange integral between the two is numerically greater than 2ϵ. Thus in the ground state there may be more unpaired electrons than indicated in the last paragraph. However, the following discussion is mainly concerned with finding a lower limit to the number of unpaired electrons, so this possibility does not matter.

6. MOLECULAR ORBITALS IN AN ALTERNANT HYDROCARBON

The electronic structures of alternant hydrocarbons have been studied by Coulson and Rushbrooke,[4] and by Coulson and Longuet-Higgins.[1] The distinguishing feature of an alternant hydrocarbon is that its sp^2 carbon atoms can be divided into two sets, such that no two carbon atoms in the same set have their $2p$ orbitals overlapping. This is illustrated by naphthalene in Fig. 1, where the carbon atoms of one set have been marked with stars, and the unstarred ones constitute those of the other set. This classification into "starred" and "unstarred" atoms has nothing to do with our earlier classification of carbon atoms into "normal" and "active;" thus all the carbon atoms in naphthalene are normal, but only half (which half does not matter) are starred.

Let us label the $2p$ orbitals of the starred atoms ϕ_1 to ϕ_R, and those of the unstarred atoms ϕ_{R+1} to ϕ_N. If the π-orbitals are now expressed in the form

$$\psi = \sum_{i=1}^{N} c_i \phi_i, \tag{1}$$

then the secular equations for the binding energy ϵ and

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[3] A. and B. Pullman, Rev. Sci. Inst. 84, 145 (1946).

[4] C. A. Coulson and S. Rushbrooke, Proc. Camb. Phil. Soc. 36, 193 (1940).
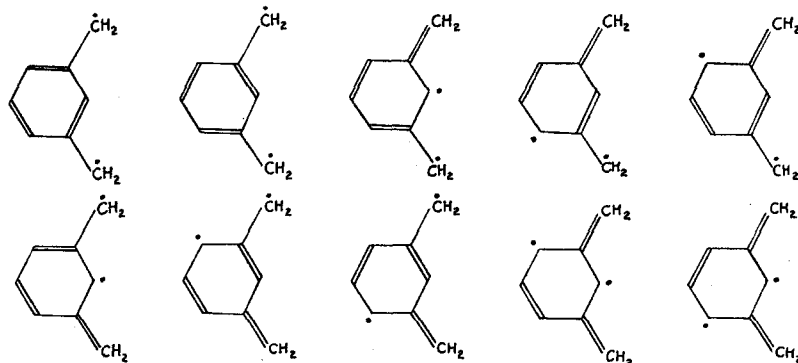
FIG. 2.

the coefficients c_t fall into two sets, namely,

$$-\epsilon c_r + \sum_{s=R+1}^{N} \beta_{rs}c_s = 0, \quad r=1, 2, \cdots, R \qquad (2)$$

and

$$-\epsilon c_s + \sum_{r=1}^{R} \beta_{sr}c_r = 0, \quad s=R+1, \cdots, N. \qquad (3)$$

These two sets of equations correspond to the two sets of atomic orbitals, those of the starred atoms being denoted collectively by ϕ_r, and those of the unstarred atoms by ϕ_s. It can now easily be seen why the MO of non-zero energy occur in pairs with opposite energies. For if $\epsilon = \epsilon^i \neq 0$, $c_r = c_r{}^i$, $c_s = c_s{}^i$ is a solution of (2) and (3), then $\epsilon = -\epsilon^i \neq \epsilon^i$, $c_r = c_r{}^i$, $c_s = -c_s{}^i$ is also a solution, distinct from the first.

As for the MO of zero energy, these are obtained by

solving Eqs. (4) and (5), obtained by putting $\epsilon = 0$ in (2) and (3).

$$\sum_{s=R+1}^{N} \beta_{rs}c_s = 0, \quad r=1, 2, \cdots, R, \qquad (4)$$

$$\sum_{r=1}^{R} \beta_{sr}c_r = 0, \quad s=R+1, \cdots, N. \qquad (5)$$

The number of zero-energy MO equals the number of linearly independent solutions of (4) and (5); and this is given[5] by $N-U$, where U is the rank of the matrix A in Eq. (6). The rank of a matrix is said to be U if all its minors of order $U+1$ or greater have vanishing determinants, while there is at least one minor of order U whose determinant does not vanish. An upper limit for the rank of A may be obtained as follows:

$$A = \begin{bmatrix} 0 & | & B \\ - & - & - \\ C & | & 0 \end{bmatrix} = \begin{bmatrix} 0, & \cdots, & 0 & | & \beta_{1,R+1}, & \cdots, & \beta_{1,N} \\ \cdot & & \cdot & | & \cdot & & \cdot \\ 0, & \cdots, & 0 & | & \beta_{R,R+1}, & \cdots, & \beta_{R,N} \\ - & - & - & - & - & - & - \\ \beta_{R+1,1}, & \cdots, & \beta_{R+1,R} & | & 0, & \cdots, & 0 \\ \cdot & & \cdot & | & \cdot & & \cdot \\ \beta_{N,1}, & \cdots, & \beta_{N,R} & | & 0, & \cdots, & 0 \end{bmatrix}. \qquad (6)$$

Consider a typical non-vanishing term in the expansion of any one of the minors of A. Such a term will be of the form (7)

$$\pm \Pi^P \beta_{rs} \Pi^Q \beta_{sr}, \qquad (7)$$

where $\Pi^P \beta_{rs}$ represents a product of P non-vanishing terms from B, and $\Pi^Q \beta_{sr}$ is a product of Q factors from C. Neither r nor s can take the same value more than once in either product; furthermore, each factor β_{rs} or β_{sr} must correspond to a pair of adjacent atomic orbitals ϕ_r and ϕ_s, or (7) would vanish. Therefore if the P pairs of atoms represented in $\Pi^P \beta_{rs}$ are joined by formal double bonds, we obtain a possible resonance structure for the molecule, and similarly for $\Pi^Q \beta_{sr}$. Conversely, any permissible resonance structure containing P double bonds defines a P-fold product of elements from B (or C), such that no two elements lie in the same row or

column. Now T was defined as the maximum number of double bonds occurring in any resonance structure.
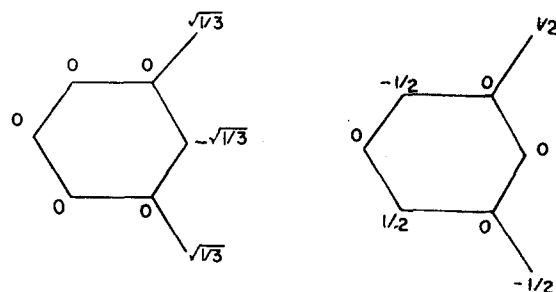

FIG. 3.

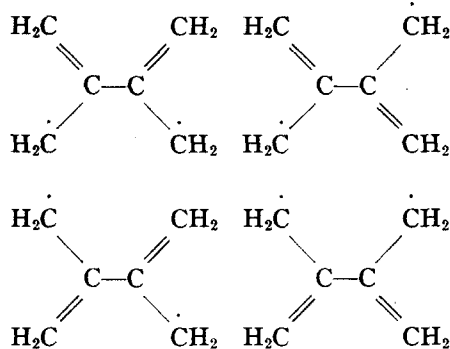[5] See, for instance, H. A. Bôcher, *Higher Algebra* (The Macmillan Company, New York, 1922).

FIG. 4.

Therefore neither P nor Q can exceed T, and so the number of factors in (7) cannot exceed $2T$. Therefore A has no non-vanishing minors of order greater than $2T$, and the rank of A cannot exceed $2T$. Hence there are at least $N-2T$ MO of zero energy.

This proves our first result, namely, that the number of unpaired electrons in the ground state of an alternant hydrocarbon is not less than $N-2T$; this being just the number of carbon atoms without double bonds in any principal resonance structure.

In the important case that the number R of starred atoms is not equal to the number $N-R$ of unstarred atoms, it can simply be shown that $N-2T$ is not less than the difference between these numbers. Suppose, without loss of generality, that R exceeds $N-R$. Then T is not greater than $N-R$, since any double bond must join a starred atom to an unstarred atom. Therefore $N-2T$ is not less than $N-2(N-R)=R-(N-R)$. From this result it can be seen at once that all the molecules (I), (II), and (III) contain not fewer than two unpaired electrons each.

7. EXAMPLES

(1) The hypothetical molecule m-phenylene-di-methylene (III) has no K-structures; its principal resonance structures are shown in Fig. 2. The dots denote π-electrons with unspecified spin functions. For this molecule $N=8$, $T=3$, so there must be at least two MO of zero energy, each containing one unpaired electron in the ground state. It turns out that there are just two such MO, and Fig. 3 gives their AO coefficients c_i, normalized to unity.

(2) The molecule tetramethylene-ethylene (IV) would have $N=6$, $T=2$; its principal resonance structures are
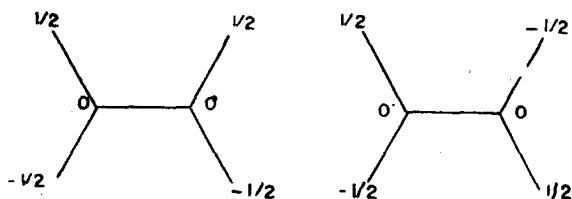

FIG. 5.

shown in Fig. 4. Each of these structures has just two carbon atoms which lack double bonds, and there are in fact exactly two zero-energy MO, with coefficients shown in Fig. 5.

(3) Clar's hydrocarbon (III) has $N=22$, and it is quite easily verified that this molecule has no resonance structures with more than 10 double bonds. Therefore there must be at least $22-20=2$ MO of zero energy, each containing one unpaired electron in the ground state. Hence, if it could be prepared, this molecule would be paramagnetic, having the character of a biradical. The AO coefficients for the two MO of zero energy are given in Fig. 6. Any two orthonormal combinations of these would, of course, do equally well.

(4) Cyclobutadiene (V), for which $N=4$, has two K-structures, each having two double bonds, so $N=2T$, and no conclusion can be drawn as to its number of zero-energy MO. Calculation shows that in fact this molecule has two zero-energy MO, with AO coefficients as shown in Fig. 7.

This last example shows that the absence of K-structures in an alternant hydrocarbon is a sufficient but not a necessary condition for the molecule to be paramagnetic in the ground state. This is an important point to be borne in mind when free radical character is being discussed from the point of view of qualitative resonance theory.

8. FORM OF THE ZERO-ENERGY MOLECULAR ORBITALS

In the above examples there is one point which is immediately striking, namely, that in three of the four examples quoted, the AO coefficients in the zero-energy MO vanish at the normal carbon atoms, in the sense of Section 2. In other words, according to MO theory, the unpaired electrons in these molecules are associated with just those carbon atoms at which, from the principal resonance structures, one would expect them to be located. This fact was noted as a curiosity by Coulson and Longuet-Higgins[1] for the particular case of the benzyl radical, but there seemed no obvious reason why it should be true in general.

We shall now show, as an extension of what has already been proved, that if N and T have their usual meanings, then any alternant hydrocarbon has at least $N-2T$ zero-energy MO of the form (8)

$$\psi = \sum_{\mu} c_{\mu} \phi_{\mu}, \tag{8}$$

where μ denotes an active carbon atom.

Since the active carbon atoms are by definition those which are not normal any MO can certainly be written in the form (9),

$$\psi = \sum_{\mu} c_{\mu} \phi_{\mu} + \sum_{\nu} c_{\nu} \phi_{\nu}, \tag{9}$$

where ν refers to a normal carbon atom. Therefore it will be sufficient to prove that there are at least $N-2T$ zero-
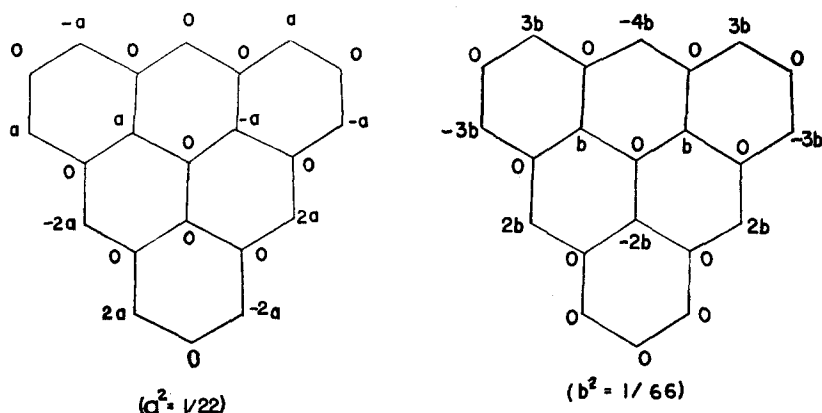
$(a^2 = 1/22)$

$(b^2 = 1/66)$

FIG. 6.

energy MO satisfying the condition that $c_r = 0$ for every normal carbon atom. Inserting this condition into Eqs. (4) and (5), we obtain (10) and (11),

$$\sum_{s_\mu} \beta_{r s_\mu} c_{s_\mu} = 0, \quad r = 1, 2, \cdots, R \tag{10}$$

$$\sum_{r_\mu} \beta_{s r_\mu} c_{r_\mu} = 0, \quad s = R+1, \cdots, N \tag{11}$$

where r_μ, s_μ denote active carbon atoms in the starred and unstarred sets, respectively. The matrix A_μ of the β's in Eqs. (10) and (11) may be written in the form (12),

$$A_\mu = \left[\begin{array}{c|c} 0 & B_\mu \\ \hline C_\mu & 0 \end{array} \right], \tag{12}$$

where B_μ and C_μ are obtained from B and C by striking out those columns which correspond to the normal carbon atoms. A_μ is therefore an N by N_μ matrix, N_μ being the total number of active carbon atoms; and the number of zero-energy MO of form (8) equals $N_\mu - U_\mu$ where U_μ is the rank of A_μ.

An upper limit may be obtained from U_μ by considering a typical non-vanishing term in the expansion of any minor of A_μ. Such a term will be of the form (13),

$$\pm \Pi^{P_\mu} \beta_{r s_\mu} \Pi^{Q_\mu} \beta_{s r_\mu}, \tag{13}$$

where $\Pi^{P_\mu} \beta_{r s_\mu}$ is a product of P_μ terms from B_μ, and $\Pi^{Q_\mu} \beta_{s r_\mu}$ is a product of Q_μ terms from C_μ. In the next section it will be proved that $P_\mu \leqslant T - S_\nu$, $Q_\mu \leqslant T - R_\nu$, where R_ν and S_ν are the numbers of normal carbon atoms in the starred and unstarred sets, respectively. Taking this for granted, it follows that no non-vanishing term in the expansion of a minor of A can contain more than $2T - S_\nu - R_\nu = 2T - N_\nu$ factors, where N_ν is the total number of normal carbon atoms. Hence U_μ cannot exceed $2T - N_\nu$, and the number of zero-energy MO of the form $\sum_\mu c_\mu \phi_\mu$ cannot be less than $N_\mu - (2T - N_\nu) = N - 2T$. This is the required result.

A zero-energy MO which is not of this form will be called a *supernumerary* zero-energy MO, and in this sense the zero-energy MO in cyclobutadiene are supernumerary.

9. PROOF THAT $P_\mu \leqslant T - S_\nu$

We shall now show that if $P_\mu > T - S_\nu$, it must be possible to construct a principal resonance structure in which not all the normal carbon atoms are doubly bonded.

We first introduce the idea of a "zigzag." Denote the product $\Pi^{P_\mu} \beta_{r s_\mu}$ by E_1; and denote by E_0 any product of T elements from B corresponding to the double bonds in a principal resonance structure. Then the factors of E_0 and E_1 are grouped into sets such that (a) a factor of E_0 and a factor of E_1 lie in the same set if they lie in the same row or in the same column, or are identical; (b) the number of elements in each set is a minimum, subject to condition (a). These sets are appropriately called zigzags, and have the following properties:

(i) Every element of E_0 or E_1 lies in exactly one zigzag, if it is allowed that a zigzag may consist of one element only.

(ii) The numbers of elements of E_0 and E_1 in a given zigzag cannot differ by more than one, since such elements occur alternately in the zigzag.

(iii) No two separate zigzags can contain elements in the same row or column.

Now E_0 has T factors, and E_1 has $P_\mu (\leqslant T)$; therefore by (ii) there must be $T - P_\mu$ zigzags ζ', or more, containing one more element of E_0 than of E_1. Define E_2 as the product of those elements of E_0 which lie in the zigzags ζ' with those elements of E_1 which lie in all the other zigzags ζ''.

By taking the elements of E_0 rather than those of E_1 from the zigzags ζ', we have made the number of factors of E_2 greater by $T - P_\mu$ than the number of factors of E_1. Therefore the total number of factors in E_2 is $P_\mu + (T - P_\mu)$, $= T$. Further, since the zigzags ζ' and ζ'' span different rows and columns, E_2 cannot contain
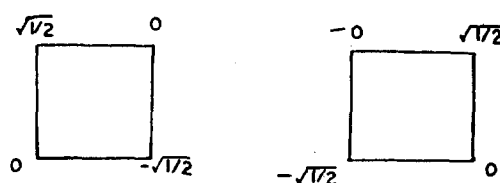

FIG. 7.

more than one element in any row or column. E_2 therefore corresponds to a principal resonance structure.

Denote by B_ν the S_ν columns of B which correspond to normal carbon atoms, these being excluded from B_μ. Then E_1 contains no factors in B_ν, and all those factors of E_2 lying in B_ν must be derived from E_0. But all such factors occur in the $T - P_\mu$ zigzags ζ', and no zigzag can have more than one element in B_ν. Therefore E_2 cannot have more than $T - P_\mu$ elements in B_ν. But by hypothesis $P_\mu > T - S_\nu$: that is, $T - P_\mu < S_\nu$; so at least one column of B_ν contains no factor of E_2.

Hence E_2 corresponds to a principal resonance structure in which at least one normal carbon atom is not doubly bonded; and this is absurd. It follows, by *reductio ad absurdum*, that $P_\mu \leqslant T - S_\nu$; and it can similarly be shown that $Q_\nu \leqslant T - R_\nu$.

10. SUMMARY OF RESULTS

The results so far obtained are:

(1) In LCAO approximation an alternant hydrocarbon has at least $N - 2T$ π-molecular orbitals of zero energy, this being the number of carbon atoms (if any) lacking double bonds in any given principal resonance structure.

(2) At least $N - 2T$ of these zero-energy MO are of the form $\sum_\mu c_\mu \phi_\mu$, the summation being confined to those carbon atoms which lack a double bond in one or more principal resonance structures.

(3) In the ground state there will be just one electron in each MO of zero energy, and if there are two or more such electrons, their spins will be parallel.

In proving these results it has not been assumed that the carbon-carbon resonance integral has the same value for all bonds. On the other hand, overlap has been neglected, and all the carbon atoms have been assumed to be in the (sp^2, p) state of hybridization. It will now be shown that neither of these latter assumptions is necessary to the validity of the results.

11. INCLUSION OF OVERLAP

If overlap is taken into account, the secular equations for the π-molecular orbitals take the form (14),

$$(\alpha - E)c_t + \sum_{u \neq t} (\beta_{tu} - S_{tu}E)c_u = 0, \qquad (14)$$

where α is the Coulomb integral for a carbon atomic $2p$ orbital (assumed constant), E is the absolute energy of an electron in the molecular orbital, and S_{tu} is the overlap integral between ϕ_t and ϕ_u.

If it is assumed‡ that

$$S_{tu} = k\beta_{tu}, \qquad (15)$$

where k is the same for all the bonds tu, then (14) may be written

$$-\epsilon c_t + \sum_{u \neq t} \beta_{tu} c_u = 0, \qquad (16)$$

---

‡ This assumption is certainly much better than the assumption that $S_{tu}=0$; and R. S. Mulliken (private communication) has found that it is quite accurately true in various two-center cases.

where now ϵ is understood to mean the quantity $(E - \alpha)/(1 - kE)$. It follows that the "true" binding energy $E - \alpha$ of a MO is given by the expression $\epsilon(1 - k\alpha)/(1 + k\epsilon)$, where ϵ is the "apparent" binding energy, calculated on the assumption that $S_{tu}=0$. Hence the sign of $E - \alpha$ is the same as that of ϵ, and the numbers of MO of positive, zero, and negative binding energy are correctly given by the secular equations in which overlap is formally neglected.

Equations (16) show that the ratio of the coefficients c_t is not affected by the inclusion of overlap, although the absolute values of c_t will in general depend on S_{tu} because of the normalization condition

$$\sum_t \sum_u c_t S_{tu} c_u = 1.$$

Hence any molecular orbital which vanishes at the normal carbon atoms when overlap is neglected will still do so when overlap is taken into account; and result (2) of the last section remains true.

## 12. EXTENSION TO MORE COMPLEX HYDROCARBONS

It is possible to extend the results of Section 10 to hydrocarbons containing sp^3 and sp carbon atoms, provided due account is taken of geometrical considerations. If hyperconjugation is neglected, a tetrahedral sp^3 carbon atom will not contribute to the π-molecular orbitals, and may be ignored in discussing the π-electrons. For example, it is a good approximation to take the π-molecular orbitals of diphenyl-methane as being identical with those of two benzene molecules.

On the other hand, an (sp, p^2) carbon atom—that is, an acetylenic or allenic carbon atom—has two $2p$ atomic orbitals, and both of these may take part in π-conjugation. So the number of $2p$ atomic orbitals differs from the number of unsaturated carbon atoms, and N will be used to denote the former quantity, not the latter. An alternant hydrocarbon is redefined as one which contains no odd-membered ring of mutually overlapping $2p$ atomic orbitals; so that according to this definition the secular equations for an alternant hydrocarbon may still be written in the form (2), (3), where r and s now refer to the two sets of *atomic orbitals*. In discussing molecular orbitals in relation to resonance structures, it is necessary to exclude from consideration any formal resonance structures whose multiple bonds do not correspond to non-zero elements of B and C. The quantity T is then redefined as the maximum number of such factors in any product of such elements; and since a triple bond corresponds to two pairs of overlapping $2p$ orbitals, T equals the maximum value of (the number of double bonds plus twice the number of triple bonds) occurring in any permissible resonance structure.

The importance of geometrical considerations is well illustrated by the example of allene, C_3H_4. This molecule is known to have its CH_2 groups in perpendicular planes,

and is assigned the K-structure (VI).

$$H_2C = C = CH_2.$$
(VI)
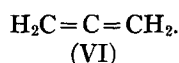
The double bonds correspond to two mutually over-lapping pairs of $2p$ orbitals: the central carbon atom has two perpendicular $2p$ orbitals, one of which overlaps the $2p$ orbital of the left-hand carbon atom, and the other of which overlaps the $2p$ orbital of the right-hand carbon atom. However, if allene were planar, the K-structure (VI) would be inadmissible; this is because only one of the $2p$ orbitals of the central atom would have the correct symmetry to overlap either of the terminal $2p$ orbitals, so that the above K-structure would not correspond to a non-vanishing product of terms from the matrix B. Instead, the principal resonance structures would contain one double bond each, and be as shown in Fig. 8. So in the ground state there would be two

$$H_2\dot{C} - \dot{C} = CH_2 \qquad H_2C = \dot{C} - \dot{C}H_2$$

FIG. 8.

unpaired electrons, distributed over the "active" $2p$ orbitals, namely, the $2pz$ orbital of the central atom and the $2py$ orbitals of the terminal carbon atoms. (The z axis is taken perpendicular to the molecular plane, and the x direction along the molecular axis.) Therefore if allene were planar, it would have a paramagnetic (triplet) ground state.

Two other examples will be given, to illustrate what happens in molecules containing triple bonds.

In phenyl-acetylene, $N = 10$, and $T = 5$ since the conventional K-structure does correspond to a possible division of the $2p$ orbitals into mutually overlapping pairs. There is therefore no reason to expect unpaired electrons in the ground state, and this molecule is indeed diamagnetic. The second example is the hypothetical linear molecule C_3H_2, which has the following principal resonance structures:

$$H - \dot{C} = C = \dot{C} - H$$

$$H - \dot{C} - C \equiv C - H$$

$$H - \dot{C} \equiv C - \dot{C} - H.$$
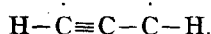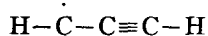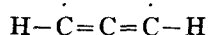
For this molecule $N = 6$, $T = 2$, so there must be two unpaired electrons in the ground state, and these will be
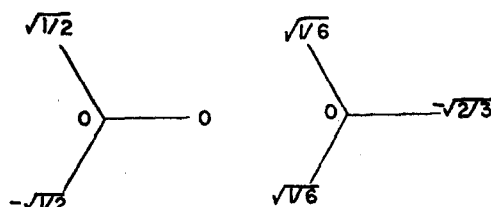

FIG. 9.

distributed over the $2p$ atomic orbitals of the terminal carbon atoms.

13. DISCUSSION OF RESULTS

The results established above provide what has been lacking for a long time in the theory of conjugated systems, namely, a bridge between molecular orbital theory and the essentially different concepts of classical resonance theory. There are, it is true, certain divergences between the two theories, as noted already in the case of cyclobutadiene, for which molecular orbital theory predicts a triplet ground state. However, from the principal resonance structures of an alternant hydrocarbon, it is possible to derive a correct lower limit for the number of unpaired electrons in the ground state, and in general to decide at which atoms these electrons are located.

The question at once arises: What experimental predictions can be made on the basis of these theoretical results?

One prediction, following immediately from Section 10, is that an alternant hydrocarbon with no classical structure of the K-type should be paramagnetic in the ground state. For a molecule with an odd number of valence electrons this is trivial; but for Clar's hydrocarbon (I) and such molecules as (II) and (III), the result is of great interest, and leads to further conclusions. One feature in common between paramagnetic molecules is their tendency to react with one another. For example, methyl, triphenyl-methyl, nitrogen dioxide, and chlorine trioxide all dimerize to varying extents, and most free radicals react with oxygen and nitric oxide, although the last two molecules themselves show little tendency to polymerize. In particular, there seems to be no exception to the rule that paramagnetic hydrocarbon molecules (radicals or multiradicals) react extremely easily with oxygen; so that any attempt to prepare such molecules in the presence of air will probably be unsuccessful. However, it is to be hoped that the hydrocarbon (I) will be prepared, and its magnetic susceptibility measured.

Another interesting prediction concerns the effect of bond twisting on the ground state of an alternant hydrocarbon. The discussion of the last section shows that if allene is twisted into a planar configuration, its ground state becomes a triplet. This is a special case of a more general phenomenon: if a diamagnetic alternant hydrocarbon undergoes internal twisting through 90° about a carbon-carbon bond that is formally double in *all* the principal resonance structures, the twisted molecule will have a triplet ground state. This is because twisting the molecule about the bond in question destroys the overlap between the $2p$ orbitals forming the double bond, so that all the principal resonance structures of the undistorted molecule become inadmissible when the molecule is twisted. Therefore T is decreased by one, and $N - 2T$ is raised from zero to two. From this it follows that excitation of the undistorted molecule into a triplet level will lower the barrier to rotation
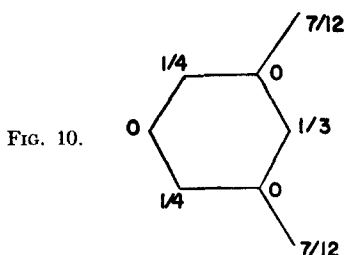
FIG. 10.

about any double bond; and it may be possible to induce *cis-trans*-isomerization by irradiation with photons whose energy is considerably less than the energy that would be required to twist the molecule if it remained all the time in the singlet state.

It can also be predicted, though with less certainty, which positions should be involved in the polymerization or oxidation of an unsaturated hydrocarbon radical. It is reasonable to suppose that those positions at which the density of unpaired electrons is highest will be the initial points of attack. Generally these positions are the "active" carbon atoms, which may be identified by enumerating principal resonance structures, if so desired. However, a more reliable procedure for predicting the reactive positions, is actually to solve the secular equations for the zero-energy molecular orbitals (this is not at all difficult or laborious as will be shown in the Appendix). One can then calculate the *odd-electron density* at atom t from the equation

$$q_t^* = \sum_z (c_t^z)^2, \tag{17}$$

the summation being taken over the zero-energy MO ψ^z. This procedure has the advantage of being quantitative; but, more important, it avoids the omission of supernumerary unpaired electrons such as occur in cyclobutadiene. Equation (17) is suitable as a definition of odd-electron density, as q_t^* is then invariant under an orthogonal transformation applied to the MO ψ^z, any set of orthogonal combinations of the ψ^z being equally valid as a description of the zero-energy MO.

To illustrate this procedure, consider molecules (II), (III), and (I), in that order.

The zero-energy MO of (II) are as shown in Fig. 9, if all the atoms are supposed to lie in one plane. The odd-electron density is therefore two-thirds at each external carbon atom, these being the active carbon atoms. Molecule (II) will therefore tend to polymerize through these atoms, or, more likely, to undergo ring closure with formation of methylene-cyclopropane (VII), which is known to be stable.

$$
\begin{array}{c}
CH_2 \\
| \qquad \diagdown \\
| \qquad \qquad C\!=\!CH_2. \\
| \qquad \diagup \\
CH_2
\end{array}
$$

(VII)
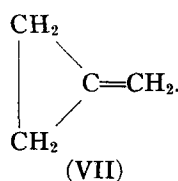
The odd-electron densities in (III) may be calculated from the orbitals shown in Fig. 3. They are given in Fig. 10. It is reassuring to find that the unpaired electrons are most dense at the external positions; one would be very surprised to find that polymerization involved the carbon atoms in the ring.

Clar's hydrocarbon (I) has odd-electron densities as shown in Fig. 11. The most active positions in free radical reactions should therefore be the meso positions.

A third prediction which can be made concerns the behavior of carbonium ions derived from alternant hydrocarbon radicals by loss of one electron. The ionized electron will be one that was unpaired in the radical, because the orbitals of the unpaired electrons are less stable than the other occupied orbitals. Now in a neutral alternant hydrocarbon the net charge at every carbon atom is zero, as proved by Coulson and Rushbrooke.[4] Therefore ionization of an electron in an orbit $\sum_\mu c_\mu \phi_\mu$ will leave a net positive charge of c_μ^2 at each active carbon atom. We conclude that in the cation the positive charge will be distributed entirely over the active carbon atoms, if the parent radical contained no supernumerary unpaired electrons. But the ionized electron is equally likely to have come from any one of the zero-energy orbitals ψ^z, so the probable net charge in ϕ_μ is given by $(1/Z) \sum_z (c_\mu^z)^2$, where Z is the number of zero-energy MO. A similar argument can be used for anions. For example, if Clar's hydrocarbon could be singly ionized, the probable net charges at the various atoms would be half the numbers given in Fig. 11.

Our third prediction may therefore be stated as follows: In singly charged anions or cations derived from alternant hydrocarbon radicals containing no supernumerary zero-energy MO, the ionic charge is distributed entirely over those carbon atoms which bear formal charges in one or more of the principal resonance structures. This prediction depends on the tacit assumption that the Coulomb integrals of the carbon atoms are the same in an ion as in a neutral hydrocarbon, and this cannot be strictly true; but it will be a better approximation the larger the ion.

14. SUPERNUMERARY ZERO-ENERGY MO

One further comment should be made on the generality of the results obtained in this paper. The proofs given in
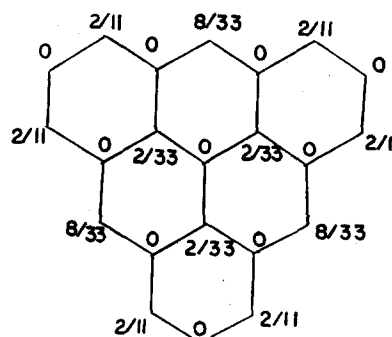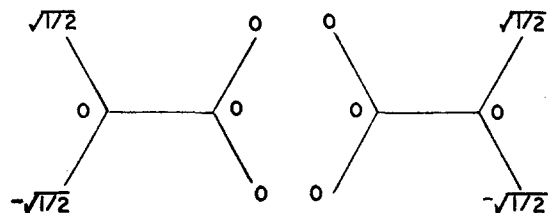

FIG. 11.

FIG. 12.

Sections 6 and 8 depend on the fact that a determinant vanishes if all the terms in its expansion vanish; and the existence of supernumerary MO arises from the fact that the converse is not true in general. It might therefore reasonably be asked: Is it not possible to find a stronger condition for the vanishing of one of the minors of B or C, which will give the exact number z of zero-energy MO in the general case? The answer seems to be as follows. Any stronger condition for the vanishing of a minor of B must necessarily imply some numerical relationship between the elements of B, and hence between the resonance integrals of the various carbon-carbon bonds. However, none of the arguments in this paper depend on the assumption of equal or related resonance integrals for the various bonds, so it would be necessary to sacrifice a certain amount of generality in order to obtain an exact expression for the total number of zero-energy MO in an alternant hydrocarbon. As an illustration, the conclusion that cyclobutadiene has two zero-energy MO depends on the assumption that all four carbon-carbon bonds have equal resonance integrals, so that there is an "accidental" cancellation of the terms of B corresponding to the two K-structures. However, if this molecule were rectangular instead of square (which is by no means out of the question), the energy of the corresponding MO would not be zero any longer. A precisely similar argument can be applied to cyclo-octatetraene; if this molecule were a regular octagon it would have two zero-energy MO, and therefore behave as a diradical. On the other hand, if it has a non-planar configuration with alternating bond lengths, there is no reason to anticipate a paramagnetic ground state.

To sum up, the conventional procedure of enumerating principal resonance structures in order to determine the number and distribution of unpaired electrons or electric charges in hydrocarbon molecules and ions, is justified with remarkable completeness by molecular orbital theory; and in particular, it is now possible to understand more deeply why hydrocarbon molecules without normal classical structures are so rare.

APPENDIX

It is usually much easier to determine the form of the zero-energy MO in an alternant hydrocarbon than to do the same for a MO of finite energy. This is because one can always obtain the solutions of (4) and (5) in the form $\sum_r c_r\phi_r$ or $\sum_s c_s\phi_s$ to begin with,* and then express the zero-energy MO as linear combinations of these, having the symmetry appropriate to some irreducible representation of the molecular symmetry group. To show that this is possible, consider the general solution of (4) and (5), namely,

$$\psi = \sum_r c_r\phi_r + \sum_s c_s\phi_s,$$

where at least one coefficient c_r and one coefficient c_s do not vanish. Then, by the arguments of Section 6, another solution of (4) and (5) is
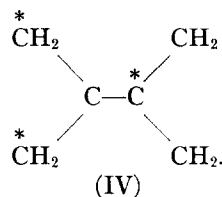
$$\psi' = \sum_r c_r\phi_r - \sum_s c_s\phi_s,$$

linearly independent of ψ. It follows that, with suitable normalization factors, the combinations

$$\sum_r c_r\phi_r \quad \text{and} \quad \sum_s c_s\phi_s$$

are also solutions of (4) and (5), and may be linearly combined to give again ψ and ψ'.

As an example of the use of this procedure, consider again the molecule (IV).

(IV)

It is easy to verify that (4) and (5) have one solution of the form $\sum_r c_r\phi_r$ and one of the form $\sum_s c_s\phi_s$, these being as shown in Fig. 12. To obtain MO of the correct symmetry properties with respect to the molecular group, it is merely necessary to take the sum and the difference of these, suitably normalized; this gives the forms shown in Fig. 5.

The author would like to express his gratitude to Professors J. R. Platt and R. S. Mulliken for much helpful discussion and criticism.

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* As before, the starred atoms are denoted collectively by r, and the unstarred ones by s.