

The Nature of the Chemical Bond. V. The Quantum-Mechanical Calculation of the Resonance Energy of Benzene and Naphthalene and the Hydrocarbon Free Radicals¹

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(Received March 21, 1933)

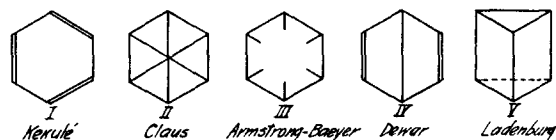
The secular equations corresponding to the five canonical structures for benzene and the forty-two for naphthalene, considered as six and ten-electron systems, respectively, are set up and solved with certain simplifying assumptions, leading to energy values differing by 1.1055α and 2.0153α , respectively, from those corresponding to unexcited (Kekulé-type) structures, α being a single exchange integral involving neighboring carbon atoms. Equating these values to the empirical values of the resonance energy, α is found to be about -1.5 v.e.

It is pointed out that the dissociation of certain substituted ethanes into free radicals is due not to weakness of the carbon-carbon bond in the ethane but to the stabilization of the free radicals resulting from resonance among the structures in which the unpaired electron is located on the

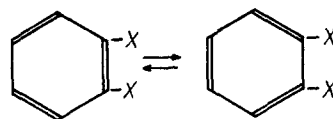
methyl carbon and those in which it is on other atoms (ortho, para, etc., to the methyl carbon). The secular equations for a number of such radicals have been solved, neglecting excited structures. The experimentally determined heat of formation of hexaphenylethane from triphenylmethyl, 0.5 v.e., when equated to the calculated value $C-C+2.2156\alpha$, with $C-C=3.65$ v.e., leads to $\alpha=-1.4$ v.e. The calculated tendencies towards dissociation are in satisfactory agreement with observation, such features as the smaller dissociating power of β -naphthyl than of α -naphthyl and of biphenylene than of diphenyl being accounted for, so that resonance among the structures considered may be accepted as the principal effect causing the stability of the hydrocarbon free radicals.

THE STRUCTURE OF BENZENE AND NAPHTHALENE

A NUMBER of structural formulae have been proposed for benzene, but none of them is free from very serious objections.



The oldest and best known structure is that proposed by Kekulé (I). The objections to it are twofold. First, it suggests that ortho-disubstituted derivatives should exist in two isomeric forms—a phenomenon which has never been observed. Kekulé avoided this difficulty, however, by assuming that the double bonds were in a state of constant oscillation such that any two adjacent carbon atoms were connected part of the time by a single bond and part of the time by a double bond. For example:



Second, the Kekulé structure suggests that benzene should be a highly unsaturated and comparatively unstable compound, in complete contradiction to the observed facts. Since this point has been discussed in considerable detail in various places, we shall not go into it here. The two centric structures (II and III) were proposed to avoid both of the above difficulties. They are indeed successful in eliminating the necessity for the oscillation hypothesis, but they can hardly account for the stability of the molecule. In the Claus structure the diagonal bonds would be very weak, as a result of the large distance between the atoms in the para positions, and the structure would probably represent a molecule less stable even than the Kekulé structure. In the Armstrong-Baeyer structure the meaning of the six lines pointing toward the center is not at all clear. If these

¹ The fourth paper of this series appeared in the *J. Am. Chem. Soc.* **54**, 3570 (1932).

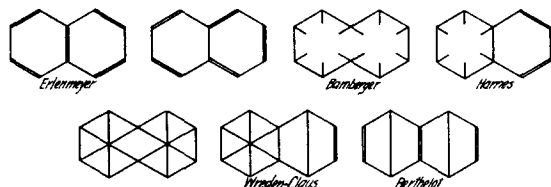
"central bonds" are left undefined, the structure is essentially meaningless; if they are considered to represent free valences, the molecule should be highly unsaturated.

The Dewar structure (IV) has never been seriously considered since it suffers from the same defects, in an accentuated form, as the Kekulé structure. Its advantage over the other structures is largely that it explains the intimate relationship that usually obtains between the para positions in the benzene ring.

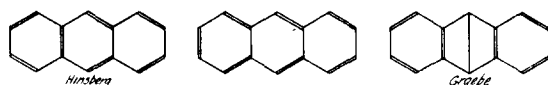
The Ladenburg prism structure (V) can be definitely ruled out, since we know that the benzene ring lies in a plane, or very nearly in a plane. The chemical evidence is also unfavorable in this case.

This by no means exhausts the list of structures proposed for benzene. The remainder, however, such as the structure of Thiele based upon his theory of partial valence and that of Collie based upon a dynamic model, are usually complicated and cannot be represented in any simple valence scheme.

In the case of the aromatic hydrocarbons with condensed ring systems the state of affairs is quite similar. Thus the following structures have been proposed for naphthalene:



for anthracene:



and so on for the other aromatic hydrocarbons. As in the case of benzene, however, the proposed structures are all unsatisfactory, on account both of the non-occurrence of predicted types of isomerism and of the unexpected stability of the molecules.

Apparently here we have a case where the classical ideas of structural organic chemistry are inadequate to account for the observed properties of a considerable group of compounds. With the

development of the quantum mechanics and its application to problems of valence and molecular structure, it became evident to workers² in this field that the resonance of benzene between the two equivalent Kekulé structures was an essential feature of the structure of this molecule, accounting for the hexagonal symmetry of the ring and for its remarkable stability; and it seemed probable that the quantum mechanical treatment of aromatic molecules would lead to a completely satisfactory explanation of their existence and characteristic properties. E. Hückel³ has made a valuable start in this direction in a series of papers on the quantum mechanics of benzene. His method of attack, however, is very cumbersome. In this paper we present a treatment of the problem which is rather closely similar to that of Hückel's and which leads to the same result in the case of benzene, but in which the calculations are simplified to such an extent that the method can be extended to the naphthalene molecule without undue labor. Furthermore, with the aid of additional simplifications and approximations we have been able to treat the problem of free radicals and to obtain results in surprisingly good qualitative agreement with experiment. We shall leave the discussion of these latter calculations to the second part of the paper.

We shall set up the problem in essentially the same way as Hückel. We assume that each of the six carbon atoms possesses two *K* electrons, and four *L* electrons, one for each of four orbital functions formed by linear combination of the *2s* and the three *2p* orbitals. Three of these *L* orbitals, each a combination of the *2s* orbital and the two *2p* orbitals in the plane of the ring, form single bonds to the attached hydrogen atom and the two adjacent carbon atoms. The fourth orbital for each atom remains a pure *p*-orbital, projecting at right angles to the ring. We neglect the energy of the electrons forming the system of single bonds in the plane and of their interaction with the electrons occupying the pure *p*-orbitals (these energy quantities occurring in the same way for all the structures considered, and hence leading to only a change in the arbitrarily-chosen zero of

² As, for example, J. C. Slater, *Phys. Rev.* **37**, 489 (1931).

³ E. Hückel, *Zeits. f. Physik* **70**, 204; **72**, 310 (1931); **76**, 628 (1932).

energy), and consider only the interaction energy of the latter electrons, which may interact with one another in different ways. That is, we treat benzene simply as a six-electron system with spin degeneracy only, and naphthalene as a ten-electron system with spin degeneracy only.

Considerable justification for this choice of orbital functions and of bond distribution is provided by the fact that each of the single exchange integrals between a pure p -orbit and an orbit in the plane of the ring is positive (arising from the e^2/r_{ij} term in the Hamiltonian only), and the chosen distribution of bonds causes these integrals to occur with the negative sign in the expression for the energy of the molecule, while the bonding exchange integrals, which are negative, occur with the positive sign.

In carrying out the calculations we make certain further simplifying assumptions. We neglect all exchange integrals of unity, and all exchange integrals of the energy H except single exchange integrals involving two adjacent atoms. The single exchange integrals involving adjacent atoms, $(abcdef/H/bacdef)$, $(abcdef/H/acbdef)$, etc., are represented by the symbol α . These integrals are seen to be equal in benzene; in naphthalene and other aromatic molecules, in which they are not all required to be equal by the symmetry of the molecule, the reasonable assumption is made that no serious error is introduced by giving them all the same value. The Coulomb integral $(abcdef/H/abcdef)$ is represented by the symbol Q .

$$\begin{vmatrix} (Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 \\ \frac{1}{4}(Q-W)+3\alpha/2 & (Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 \\ \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & (Q-W) & \frac{1}{4}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 \\ \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & (Q-W) & \frac{1}{4}(Q-W)+3\alpha/2 \\ \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & (Q-W) \end{vmatrix} = 0.$$

This quintic equation is easily reduced to three linear factors and one quadratic factor, the roots being -2α , -2α , 0 , $(-13)^{1/2}-1\alpha$, and $((13)^{1/2}-1)\alpha$. Since α is negative, the last of these roots, $((13)^{1/2}-1)\alpha = 2.6055\alpha$, represents the normal state of the molecule. The eigenfunction corresponding to this is (before normalizing) $\psi = \psi_A$

Benzene

The benzene molecule can now be treated very simply by the Slater method, with the help of the rules formulated by one of us⁴ for finding the matrix elements occurring in the secular equation. The bonds between the six eigenfunctions can be drawn so as to give the independent canonical structures shown in Fig. 1. Any other

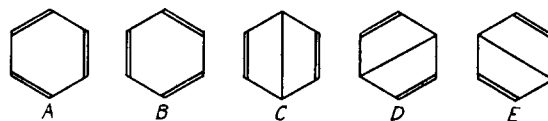
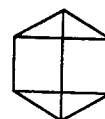


FIG. 1. The five canonical structures contributing to the normal state of the benzene molecule.

structures that can be drawn can be represented by eigenfunctions which are linear combinations of the five above. It will be seen that structures A and B are simply the two Kekulé structures, and C , D and E are three different forms of the Dewar structure. The Claus centric structure does not belong to the canonical set, but it can be represented as a linear combination of canonical structures; and the same is true of the Ladenburg structure if it be considered spread out in a plane, as:



(The Claus structure $= A + B - C - D - E$; the Ladenburg structure $= A + B - D - E$.)

As can be easily verified, the secular equation is

$+ \psi_B + 0.4341(\psi_C + \psi_D + \psi_E)$. If we had neglected the resonance phenomenon and calculated the energy for one of the structures A or B , we would have obtained the value $W' = Q + 1.5\alpha$. Hence the extra energy of the molecule resulting from resonance among the five independent structures

⁴L. Pauling, J. Chem. Phys. 1, 280 (1933).

is 1.1055α . It is interesting to see how much of this extra energy is due to resonance between the two Kekulé structures and how much is contributed by the excited structures *C*, *D* and *E*. A simple calculation shows that 0.9α or approximately 80 percent of the resonance energy comes from the Kekulé structures alone and only about 20 percent from the three excited structures.

In the following paper of this series⁵ a value of about 1.7 v.e. has been found from thermochemical data for the resonance energy of benzene. Equating the negative of this quantity to 1.1055α , we calculate the value of α to be about -1.5 v.e. This value may not be very reliable, however, since it is based on the assumption that values of bond energies obtained from aliphatic compounds can be applied directly to aromatic compounds.

The results of the calculation for benzene are summarized in Table I. They are identical with those obtained by Hückel.

The conclusions we draw regarding the structure of the normal benzene molecule are the following. The principal contributions to the structure are made by the two Kekulé structures, resonance between them stabilizing the molecule

	Total energy	Resonance energy	<i>a</i> : <i>b</i>
Single Kekulé structure	$Q+1.5\alpha$	0	
Resonance between two Kekulé structures	$Q+2.4\alpha$	0.9α	1 : 0
Resonance among all five structures	$Q+2.6055\alpha$	1.1055α	1 : 0.4341

The ratio *a* : *b* is the ratio of the coefficient of structures *A* and *B* to that of the singly-excited structures *C*, *D*, and *E*.

to the extent of 0.9α or about 1.35 v.e. over a ring with three double bonds. In addition, however, the excited structures contribute appreciably both to the energy (0.2055α) and to the eigenfunction.⁶ In a sense it may be said that all structures based on a plane hexagonal arrangement of the atoms—Kekulé, Dewar, Claus, etc.—play a part, with the Kekulé structures most important. It is the resonance among these structures which imparts to the molecule its peculiar aromatic properties.

Naphthalene

With naphthalene the calculation is very much more involved. The number of canonical structures is here forty-two (Fig. 2), so that the

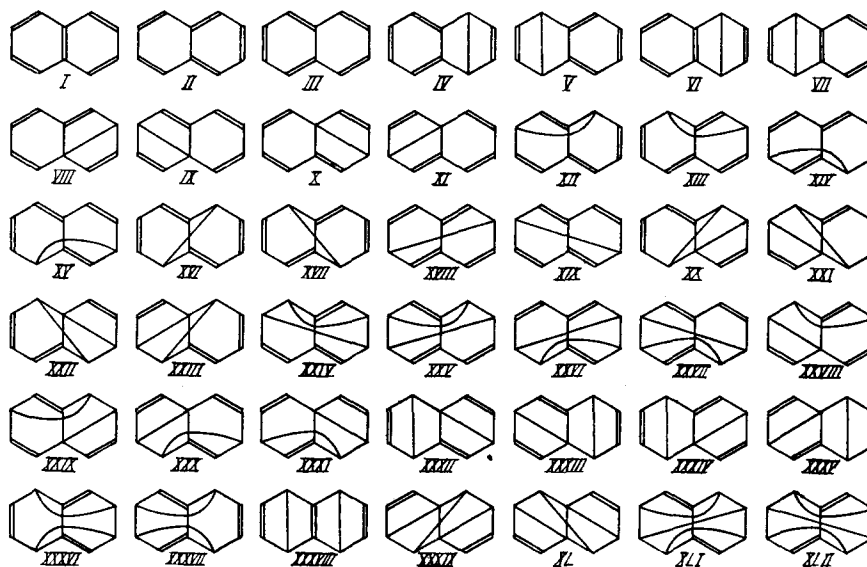


FIG. 2. The forty-two canonical structures contributing to the normal state of the naphthalene molecule.

⁵ L. Pauling and J. Sherman, *J. Chem. Phys.*, July, 1933.

⁶ The Claus centric structure, an old-quantum-theory analogue of which was suggested several years ago by one

of us (L. Pauling, *J. Am. Chem. Soc.* **48**, 1132 (1926)), is found to make a less important contribution to the normal state of benzene than do the Kekulé structures.

secular equation is of the forty-second degree. We have evaluated the matrix elements in the secular equation by the graphical method, but do not reproduce them because of their great number. For convenience the structures with the maximum number of bonds between adjacent atoms are called unexcited structures and those with one, two, etc., fewer such bonds first excited, second excited, etc., structures. From con-

siderations of symmetry, we can set a number of coefficients equal in the complete eigenfunction, and thereby reduce the secular equation to the fifteenth degree. To obtain an approximate solution of this we then assume that all of the first excited structures have the same coefficient, and similarly for all of the second and all of the third excited structures. The resultant secular equation, corresponding to the function

$$\psi = a\psi_I + b(\psi_{II} + \psi_{III}) + c(\psi_{IV} + \dots + \psi_{XIX}) + d(\psi_{XX} + \dots + \psi_{XXXVIII}) + e(\psi_{XXXIX} + \dots + \psi_{XLII})$$

is

$$\begin{vmatrix} (Q-W) + 2\alpha & (1/2)(Q-W) + 13\alpha/4 & (35/8)(Q-W) + 163\alpha/8 \\ (1/2)(Q-W) + 13\alpha/4 & (17/8)(Q-W) + 43\alpha/8 & (19/2)(Q-W) + 169\alpha/4 \\ (35/8)(Q-W) + 163\alpha/8 & (19/2)(Q-W) + 169\alpha/4 & (557/8)(Q-W) + 2035\alpha/8 \\ (27/8)(Q-W) + 165\alpha/8 & (21/2)(Q-W) + 159\alpha/4 & (525/8)(Q-W) + 2169\alpha/8 \\ (5/8)(Q-W) + 31\alpha/8 & 2(Q-W) + 7\alpha & (95/8)(Q-W) + 397\alpha/8 \\ & (27/8)(Q-W) + 165\alpha/8 & (5/8)(Q-W) + 31\alpha/8 \\ & (21/2)(Q-W) + 159\alpha/4 & 2(Q-W) + 7\alpha \\ & (525/8)(Q-W) + 2169\alpha/8 & (95/8)(Q-W) + 397\alpha/8 \\ & (633/8)(Q-W) + 1911\alpha/8 & (57/4)(Q-W) + 189\alpha/4 \\ & (57/4)(Q-W) + 189\alpha/4 & (19/4)(Q-W) - 7\alpha/4 \end{vmatrix} = 0.$$

To solve this we first neglect entirely the second and third excited structures. We then solve the secular equation, which is now only a cubic, and evaluate the ratio of the coefficients, $a : b : c$. Finally, we assume that this same ratio holds in

the complete eigenfunction, thus obtaining another cubic secular equation, the solution of which is an approximate solution of the original secular equation. The results are summarized in Table II.

TABLE II.

	Total energy	Resonance energy	$a : b : c : d : e$
Single unexcited structure	$Q + 2\alpha$	0	1 : 0 : 0 : 0 : 0
Resonance among three unexcited structures	$Q + 3.3703\alpha$	1.3703 α	1 : 0.8757 : 0 : 0 : 0
Resonance among unexcited and singly excited structures	$Q + 3.9760\alpha$	1.9760 α	1 : 0.8513 : 0.3026 : 0 : 0
Resonance among all structures	$Q + 4.01533\alpha$	2.01533 α	1 : 0.8513 : 0.3026 : 0.0919 : 0.0077

It will be noticed that the singly excited structures contribute somewhat over 30 percent to the total resonance energy instead of only about 20 percent as in benzene. The doubly and triply excited structures, however, make only a very small contribution.

Pauling and Sherman have found empirically⁵ that the ratio of the resonance energy of naph-

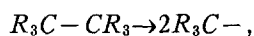
thalene to that of benzene is 1.90, while the present calculation gives the ratio of 1.82. The agreement is really quite satisfactory. It would have been somewhat, but probably not a great deal, better if the secular equation in the naphthalene calculation had been solved rigorously. The discrepancy must be attributed to the crudity of the method of calculation, and partly

also to the fact that, as mentioned above, the resonance energy calculated by Pauling and Sherman is not strictly comparable with that found by the present method. The value of α obtained from this calculation is -1.6 v.e., in good agreement with the value of -1.5 v.e. obtained from the benzene calculation.

This treatment could be applied to anthracene and phenanthrene, with 429 linearly independent structures, and to still larger condensed systems, though not without considerable labor. It is probable that the empirical rule⁵ of approximate proportionality between the resonance energy and the number of benzene rings in the molecule would be substantiated.

THE STRUCTURE AND STABILITY OF HYDRO-CARBON FREE RADICALS

The dissociation of a hexaarylethane into free radicals,



first observed by Gomberg about thirty years ago, can be considered formally to take place in two steps. First, the bond connecting the two halves of the original molecule breaks; and second, the free radicals formed thereupon stabilize themselves to a certain extent by means of a change in structure. Most theories which have been proposed to explain the existence and stability of free radicals have more or less tacitly assumed that the first of these steps is of primary importance and that the influence of the second upon the dissociation is negligible in comparison. Consequently these theories have concerned themselves very largely with attempts to explain why the ethane linkage in the undissociated molecule should be weakened by the presence of aryl groups. Of these various attempts, two stand out most prominently, one based upon the theory of "affinity-demand" (Valenzbeanspruchung), and the other upon the consideration of steric influences. According to the theory of affinity-demand, the aryl groups use up so much of the available affinity of the methyl carbon atoms that there is very little left over for the ethane linkage. This is not a very satisfactory explanation, however, for several reasons. It does not show why aryl groups should have such a great affinity-demand—as compared, for ex-

ample, with alkyl groups, nitro groups, etc.—nor does it enable one to predict which aryl groups should be relatively more effective and which relatively less effective in promoting dissociation. Furthermore, it leads to definitely incorrect predictions in some cases. Thus, tetraphenylmethane would be expected to be rather unstable, while actually it is an extraordinarily stable compound, boiling at 431° without decomposition.

The steric theory of free radical dissociation is based upon the assumption that the aryl groups are so large that they prevent the two halves of the undissociated molecule from coming close enough together to permit the formation of a strong bond. There are, however, some difficulties with this explanation as well. It is roughly true, to be sure, that the effectiveness of a group in promoting free radical dissociation runs parallel to its size, but why, for example, should the linear biphenyl group have a greater steric effect than the phenyl group, and why should there be an appreciable difference between the α and the β -naphthyl groups? In addition the stability of tetraphenylmethane is about as irreconcilable with this theory as with that of affinity-demand.

We may conclude from this discussion that it is apparently impossible to base a satisfactory theory of the free radicals upon the assumption that the C—C bond in the undissociated molecule is weakened by the influence of the aryl groups. We avoid the necessity of making this assumption, however, by considering that the energy necessary to carry through the first step of breaking the bond is the same in all cases, but that the subsequent stabilization of the radicals, resulting from the second step of changing the structure, may vary widely. Thus we attribute the dissociation not to the instability of the undissociated molecule but to the stability of the radicals formed in the dissociation.

This idea has been developed by Burton and Ingold,⁷ but not upon a very satisfactory theoretical basis. From their work it is not clear why the postulated redistribution of charge should occur after, but not before, dissociation,

⁷ H. Burton and C. K. Ingold, Proc. Leeds Phil. Soc. 1, 421 (1929); C. K. Ingold, Ann. Reports Chem. Soc. 25, 154 (1928).

nor is the mechanism by which this redistribution stabilizes the radical definitely established. In the following pages we describe the extension to the free radical problem of the quantum-mechanical methods which we used with benzene and naphthalene. It is shown that a straightforward calculation of the resonance energy for the undissociated ethane and for the free radical leads to values of the dissociation energy of various substituted ethanes in excellent qualitative and semiquantitative agreement with experiment. This theory of the stability of free radicals may be considered as a refinement and extension of Burton and Ingold's general views, for which it provides a sound theoretical basis.

Before going into our methods of calculation we shall first discuss briefly the nature of the experimental results which we wish to explain. In spite of the vast amount of work which has been done on free radicals in the last thirty years, the information available regarding the degree of dissociation of most hexaarylethanes is meager, and exceedingly inaccurate. Ziegler and Ewald⁸ have carried out precise photometric determinations in the cases of hexaphenylethane and tetraphenyldi- β -naphthylethane. In other cases the only data at hand are derived from determinations of the apparent molecular weights by the cryoscopic method. That this method is undependable is shown by the fact that it frequently indicates degrees of dissociation of 130 percent or even higher, and in the case of the slightly dissociated tetraphenyldi- β -naphthylethane it indicates a degree of dissociation two or three times greater than that found by Ziegler and Ewald. In some cases even this source of information is lacking, and then recourse must be had to such data as the intensity of the color of solutions, the temperature at which the color first appears, the number of times the color will reappear after having been discharged with air, the rate of absorption of oxygen, and so on. Obviously such methods can give only the crudest of results. As a further complication we have the fact that the degree of dissociation of a given ethane varies considerably with temperature, with solvent, and with concentration, and frequently the determinations have not been made under comparable conditions. In spite of

⁸ K. Ziegler and L. Ewald, *Ann.* **473**, 179 (1932).

all these difficulties, however, we can say with some assurance that the tendency toward dissociation increases in the following order: any ethane with less than six aryl groups \ll diphenyldifluoryl \ll hexaphenylethane $<$ tetraphenyldi- β -naphthylethane $<$ tetraphenyldi- α -naphthylethane \cong diphenyltetra-*biphenylethane* $<$ hexa-*biphenylethane*. We have intentionally omitted tetraphenyldibiphenylethane from this list since we do not consider that its degree of dissociation has been measured with sufficient accuracy to warrant its inclusion. It has been studied neither photometrically nor cryoscopically, and so the estimate of 15 percent dissociation usually given in the literature is not to be taken very seriously. In most lists like the above it occupies a position between hexaphenylethane and tetraphenyldi- β -naphthylethane.

From such crude data as are to be found in the literature we can calculate approximate values of the equilibrium constants, and hence of the free energies of dissociation for the various hexaarylethanes. From our quantum-mechanical treatment, on the other hand, we obtain only the heats of dissociation, for which, except in the single case of hexaphenylethane, we have no experimental data. Thus, in order that we may compare our results with those of experiment, we must make the plausible assumption that the entropies of dissociation vary only slightly from ethane to ethane. Then at a given temperature the heats of dissociation run parallel to the free energies and can be used instead of the latter in predicting the relative degrees of dissociation of the different molecules.

In carrying out the calculations we use essentially the same procedure as in the case of benzene and naphthalene. As an additional simplification, however, we neglect entirely all the excited states of the molecule, since their contribution to the total energy is comparatively small, and since they would complicate the calculations tremendously if retained. Another slight modification of the procedure is necessitated by the fact that a free radical possesses an odd number of electrons, one of which must remain unpaired. This is taken care of formally by introducing a "phantom orbit" X with an accompanying "phantom electron" which is paired with the odd electron.⁴ In the subsequent

calculations it is necessary merely to remember that all exchange integrals which involve the phantom orbit vanish. The rules for setting up the matrix elements and the secular equations are otherwise unchanged.

We shall discuss in detail only one example, and for the sake of simplicity we shall take the (actually undissociated) sym. diphenylethane. Let us first consider what happens when the ethane dissociates. In the first step, the C-C bond breaks and there are formed two phenylmethyl radicals, which however can resonate between only the structures *A* and *B* of Fig. 3.

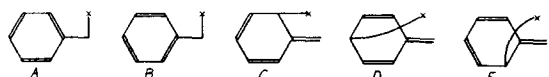


FIG. 3. The five unexcited canonical structures contributing to the normal state of the phenylmethyl radical.

ΔH for this reaction we take to be 3.65 v.e., the energy required to break a C-C bond in aliphatic compounds. The second step of the dissociation consists in a change in the structure of the radicals, involving a change in nuclear configuration from a tetrahedral arrangement of

bonds about the methyl carbon to a plane arrangement of all the nuclei, and in electronic structure through the removal of the restriction of the resonance to the structures *A* and *B*, all five of the canonical structures being now allowed. ΔH for this reaction is just twice the difference between the energies of a single radical after and before the removal of the restriction. The energy change for the over-all reaction is then the algebraic sum of the energy changes of the two steps.

To evaluate ΔH for the second step we must set up and solve the secular equations corresponding to the two different states of the radical. In the case where we consider only the structures *A* and *B* the secular equation is easily shown to be:

$$\begin{vmatrix} (Q-W')+\alpha & \frac{1}{4}(Q-W')+11\alpha/8 \\ \frac{1}{4}(Q-W')+11\alpha/8 & (Q-W')+\alpha \end{vmatrix} = 0.$$

On solving this we find for the energy $W' = Q + 1.9\alpha$, and for the wave function $\psi' = a(\psi_A + \psi_B)$ where a is a normalization factor.

When we consider resonance between all five structures we obtain a quintic secular equation:

$$\begin{vmatrix} (Q-W)+\alpha & \frac{1}{4}(Q-W)+11\alpha/8 & \frac{1}{8}(Q-W)+7\alpha/8 & \frac{1}{4}(Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 \\ \frac{1}{4}(Q-W)+11\alpha/8 & (Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & \frac{1}{4}(Q-W)+\alpha & \frac{1}{8}(Q-W)+7\alpha/8 \\ \frac{1}{8}(Q-W)+7\alpha/8 & \frac{1}{2}(Q-W)+5\alpha/4 & (Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & \frac{1}{4}(Q-W)+\alpha \\ \frac{1}{4}(Q-W)+\alpha & \frac{1}{4}(Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & (Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 \\ \frac{1}{2}(Q-W)+5\alpha/4 & \frac{1}{8}(Q-W)+7\alpha/8 & \frac{1}{4}(Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & (Q-W)+\alpha \end{vmatrix} = 0.$$

This can be simplified to a cubic equation since from considerations of symmetry it follows that the coefficients of ψ_A and of ψ_B must be the same in the complete function, and similarly for ψ_C

and ψ_E . We shall however, make a further simplification by assuming that ψ_D has the same coefficient as ψ_C and ψ_E , and thereby reduce the secular equation to a quadratic:

$$\begin{vmatrix} (5/2)(Q-W)+19\alpha/4 & (7/4)(Q-W)+25\alpha/4 \\ (7/4)(Q-W)+25\alpha/4 & (11/2)(Q-W)+10\alpha \end{vmatrix} = 0.$$

On solving this we find for the energy $W = Q + 2.4092\alpha$, and for the wave function $\psi = a(\psi_A + \psi_B) + b(\psi_C + \psi_D + \psi_E)$ where a and b are in the ratio $a : b = 1 : 1.0279$. The "free radical resonance energy" is thus $W - W' = 0.5092\alpha$, and ΔH

for the dissociation is equal to $3.65 \text{ v.e.} + 2 \times 0.5092\alpha = 3.65 \text{ v.e.} + 1.0184\alpha$. As we shall show later, the value of α is probably about -1.4 v.e. , and so the heat of dissociation of sym. diphenylethane is approximately 2.2 v.e. , a value in good

accord with the vanishingly small degree of dissociation. In view of the uncertainty connected with the values of α and of the C—C bond energy we shall as a rule not calculate the heats of dissociation of the remaining ethanes, but instead shall use as a criterion of the tendency of a given compound to dissociate simply the coefficient of

α in the expression for the free radical resonance energy. It will be noted that on account of the negative sign of α the dissociation increases as this coefficient increases.

The results obtained from this and from similar calculations for a number of other free radicals are summarized in Table III. In the first

TABLE III.

Radical	W'	W	$W - W'$
Phenylmethyl	$Q + 1.9000\alpha$	$Q + 2.4092\alpha$	0.5092α
Biphenylmethyl	$Q + 3.8000\alpha$	$Q + 4.3568\alpha$	0.5568α
β -Naphthylmethyl	$Q + 2.8703\alpha$	$Q + 3.5012\alpha$	0.6309α
α -Naphthylmethyl	$Q + 2.8703\alpha$	$Q + 3.6218\alpha$	0.7515α
Fluoryl	$Q + 3.3000\alpha$	$Q + 4.1004\alpha$	0.8004α
Diphenylmethyl	$Q + 3.8000\alpha$	$Q + 4.6409\alpha$	0.8409α
Phenylfluoryl	$Q + 5.2000\alpha$	$Q + 6.2764\alpha$	1.0164α
Triphenylmethyl	$Q + 5.7000\alpha$	$Q + 6.8078\alpha$	1.1078α
Biphenyldiphenylmethyl	$Q + 7.6000\alpha$	$Q + 8.7310\alpha$	1.1310α
Phenyldibiphenylmethyl	$Q + 9.5000\alpha$	$Q + 10.6545\alpha$	1.1545α
Tribiphenylmethyl	$Q + 11.4000\alpha$	$Q + 12.5773\alpha$	1.1773α
β -Naphthyldiphenylmethyl	$Q + 6.6636\alpha$	$Q + 7.8351\alpha$	1.1715α
α -Naphthyldiphenylmethyl	$Q + 6.6636\alpha$	$Q + 7.9033\alpha$	1.2398α

column we have listed the radical under consideration; in the second, the energy W' calculated for the radical with resonance restricted to the structures in which the unpaired electron is on the methyl carbon atom; in the third, the energy W calculated for the radical with resonance allowed among all possible states; and in the fourth, the free radical resonance energy $W - W'$.

Mention may be made of a special method developed for setting up the secular equation for free radicals. The direct calculation of matrix elements, even by the simple graphical method, would be extremely laborious for such a radical as tribiphenylmethyl, for example, for which 496 structures are taken into consideration. Let us consider three superposition patterns, each consisting of one of the substituent groups in the free radical plus the methyl carbon and the phantom orbit, the corresponding Coulomb and exchange coefficients being q_1, q_2, q_3 and a_1, a_2, a_3 , respectively. It is easily proved that the Coulomb coefficient q and the exchange coefficient a for the entire superposition pattern have the values

$$q = q_1 q_2 q_3$$

and

$$a = a_1 q_2 q_3 + q_1 a_2 q_3 + q_1 q_2 a_3.$$

For a set of superposition patterns obtained by combining a set for each of the three groups in all possible ways, the sums of the coefficients (for equal weights of the corresponding structures) are

$$\Sigma q = \Sigma q_1 \cdot \Sigma q_2 \cdot \Sigma q_3$$

and

$$\Sigma a = \Sigma a_1 \cdot \Sigma q_2 \cdot \Sigma q_3 + \Sigma q_1 \cdot \Sigma a_2 \cdot \Sigma q_3 + \Sigma q_1 \cdot \Sigma q_2 \cdot \Sigma a_3.$$

As an example we may use these equations to calculate the coefficients summed over the 64 matrix elements corresponding to the eight structures of triphenylmethyl with the unpaired electron on the methyl carbon. Reference to the secular equation for phenylmethyl shows that $\Sigma q_1 = \Sigma q_2 = \Sigma q_3 = 1 + 1 + \frac{1}{4} + \frac{1}{4} = 5/2$, and $\Sigma a_1 = \Sigma a_2 = \Sigma a_3 = 11/4$, leading to the values $\Sigma q = 125/8$ and $\Sigma a = 1425/16$.

The secular equations which must be solved for the values of W are frequently of very high degree, even after all of the simplifications arising from considerations of symmetry have been introduced. In such cases we have reduced the equations to cubics (sometimes to quadratics) by equating coefficients in a more or less arbitrary

manner. The calculated values for the free radical resonance energy are, therefore, uncertain to the extent to which they are affected by this not strictly legitimate simplification. We feel, however, that the errors introduced in this way are not very large, since we have found by actual calculation in two cases that the energies are not very sensitive to small changes in the coefficients. For example, the energy W of the triphenyl-

methyl radical is given in Table III as $Q + 6.8078\alpha$. This was obtained by solving rigorously the secular equation, which in this case could be reduced to a cubic. If, on the other hand, we equate all coefficients and make the equation linear, we obtain for W the value $Q + 6.8064\alpha$. In the case of the α -naphthyl-diphenylmethyl radical the value of $Q + 7.9033\alpha$ given for W in Table IV was derived from a cubic

TABLE IV.

Radical	Position of odd electron	Number of structures	Relative values of coefficients
Phenylmethyl	methyl carbon	2	1
	phenyl group	3	1.0279
Biphenylmethyl	methyl carbon	4	1
	biphenyl group	9	0.4526
β -Naphthylmethyl	methyl carbon ^a	1	1
	methyl carbon ^b	2	0.8789
	naphthyl group	6	0.5458
α -Naphthylmethyl	methyl carbon ^a	1	1
	methyl carbon ^b	2	0.8828
	naphthyl group	7	0.5916
Fluoryl	methyl carbon	4	1
	biphenylene group ^c	8	0.6768
	biphenylene group ^c	4	0.6056
Diphenylmethyl	methyl carbon	4	1
	phenyl group	12	0.7232
Phenylfluoryl	methyl carbon	8	1
	phenyl group	12	0.8983
	biphenylene group	24	0.8430
Triphenylmethyl	methyl carbon	8	1
	phenyl group (para)	12	0.8829
	phenyl group (ortho)	24	0.9896
Biphenyldiphenylmethyl	methyl carbon	16	1
	phenyl group	48	0.8546
	biphenyl group	36	0.6477
Phenyldibiphenylmethyl	methyl carbon	32	1
	phenyl group	48	0.7881
	biphenyl group	144	0.5969
Tribiphenylmethyl	methyl carbon	64	1
	biphenyl group	432	0.5535
β -Naphthyldiphenylmethyl	methyl carbon	12	1
	phenyl group	36	0.9085
	naphthyl group	24	0.8497
α -Naphthyldiphenylmethyl	methyl carbon	12	1
	phenyl group	36	0.9200
	naphthyl group	28	0.9121

^a With the naphthyl group symmetrical as in structure I, Fig. 2.

^b With the naphthyl group unsymmetrical as in structures II and III, Fig. 2.

^c The distinction between these two types of structure is described below in the discussion of the fluoryl radical.

equation, obtained by equating the coefficients of all structures in which the odd electron is (1) on the methyl carbon atom, (2) on the naphthyl group, and (3) on a phenyl group. If the equation is reduced further to a quadratic by equating the coefficients of all structures of the last two types the energy W is changed only in the fifth decimal. The effect of these errors which, though small, are sometimes quite appreciable will always be to make the value of W too large (that is, the coefficient of α too small). Since the secular equations for W' can be solved rigorously in all cases, this will cause the radicals to appear less stable relative to the ethanes than they should. This effect should be particularly pronounced in the cases of the α - and the β -naphthyldiphenylmethyl radicals because of the high degree of the secular equations. Furthermore, in these radicals we have had to give the structures in which the naphthyl group has the symmetrical form (as in structure I, Fig. 2) the same coefficient as the structures in which the naphthyl group has the unsymmetrical form (as in structures II and III, Fig. 2), and this simplification seems to be particularly unjustified. At any rate it is found to be pretty far off in the cases of the simple α and β -naphthylmethyl radicals where the calculations have been carried through somewhat more rigorously. This error has been partially corrected by making the same approximation in the calculations of W' ; that is, by putting all coefficients equal and solving linear instead of quadratic secular equations.

In order to make clear the manner in which we have simplified the treatment of the various radicals, we give in Table IV a statement of the value and significance of the coefficients occurring in the function ψ in the individual cases. It will not be necessary to give a similar table for the functions ψ' since, except in the cases of the α and the β -naphthyldiphenylmethyl radicals which have been discussed above, no simplifications were necessary for them, and the secular equations were solved rigorously.

Discussion of results

The principal source of inaccuracy in the treatment given the free radicals is the neglect of all excited structures. In the case of benzene the three excited structures contribute 0.2055α to the resonance energy, which is about 20 percent

of the total resonance energy of the molecule. The same error is introduced in W' for the phenylmethyl radical. The change in W produced by the inclusion of the nine excited structures as well as the five unexcited structures is not so large, so that $W - W'$ is decreased from 0.5092α to 0.4455α , a decrease of 0.06α or 12 percent of $W - W'$. Similar changes in the values of $W - W'$ would result from the consideration of excited structures for other radicals. In consequence, so long as excited structures are not included in the treatment the values of $W - W'$ cannot be considered to be accurate to 10 percent. This does not prevent us from making use of the values given in Table III, however, in certain cases. Thus for each of the radicals included in the table the value of $W - W'$ can be considered to give the extra resonance energy stabilizing the radical with an accuracy of 10–20 percent. Moreover, in some cases differences in the $W - W'$ values for different radicals can be trusted to the same extent; namely, when one radical differs from another only by the addition of a group, so that all of the structures considered for the first radical are retained for the second, as well as other structures. Thus the difference of the $W - W'$ values for biphenylmethyl and phenylmethyl should give with considerable accuracy the extra stability resulting from the substitution of biphenyl for phenyl, and a similar comparison should be reliable for α -naphthyl and β -naphthyl, α or β -naphthyl and phenyl, fluoryl and diphenyl, etc., but not for α -naphthyl and biphenyl, inasmuch as in these completely different groups the effect of neglect of excited structures may well mask the small differences under consideration. When this restriction in the interpretation of the $W - W'$ values is borne in mind, it is found that the agreement between the rather rough theoretical calculations and the existent empirical information is excellent, and provides sound evidence that resonance of the type considered is the primary factor in the stabilization of the hydrocarbon free radicals. A number of details in the comparison are treated in the following paragraphs.

(a) The calculation for triphenylmethyl leads to a value of $3.65 \text{ v.e.} + 2.2156\alpha$ for the heat of dissociation of hexaphenylethane. Equating this to the experimentally determined value of 0.5

v.e., we obtain as a result that $\alpha = -1.4$ v.e. This is in fair agreement with the value of -1.5 v.e. obtained from the calculation for benzene; the discrepancy may be due in part to the fact mentioned before that the evaluation of α from the benzene calculation is not strictly legitimate, and in part to the neglect of excited structures, which (from analogy with phenylmethyl) are expected to decrease the coefficient of α in $W - W'$, and so increase the absolute value of α .

(b) Except for comparisons of naphthyl and biphenyl, the amounts of dissociation indicated by the values of $W - W'$ for various radicals are in excellent qualitative agreement with experiment. It is undoubtedly significant that, as is demanded by experiment, the variations in the free radical resonance energies obtained by increasing the number of aryl groups is large compared with the variations obtained by changing the nature of the groups already present.

(c) In order to make a quantitative comparison of our results with experiment, let us calculate the ratio of the dissociation constants corresponding to a difference in the free radical resonance energies of 0.01α . If we let the subscript 1 refer to the more highly dissociated ethane and 2 to the less highly dissociated, we have the following relation:

$$RT \ln (K_2/K_1) = \Delta F_1 - \Delta F_2 \cong \Delta H_1 - \Delta H_2 = 0.02\alpha.$$

Since α is equal to -1.4 v.e. or $-32,000$ calories per mole, this equation becomes

$$RT \ln (K_1/K_2) = 640 \text{ cal./mole}$$

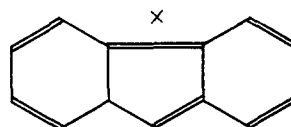
which at 20°C leads to

$$\ln (K_1/K_2) = 1.1 \quad \text{or} \quad K_1/K_2 = 3.0.$$

From Table III we see that the difference between the free radical resonance energies of triphenylmethyl and biphenylmethyl is 0.07α . Hence $K_1/K_2 = 3^7 = 2.2 \times 10^3$. Ziegler and Ewald⁸ found that at 20°C the value of the dissociation constant for hexaphenylethane in benzene solution is 4.1×10^{-4} and consequently we calculate for hexabiphenylethane a value of $K = 2.2 \times 10^3 \times 4.1 \times 10^{-4} = 0.90$. This value is probably too low as the compound is reported to be completely dissociated; the error may not be large, however, since a dissociation constant of 0.90 would lead to 91 percent dissociation in $0.05M$ solution.

The solutions actually worked with have usually been more dilute than this, and so our calculated value may be within the experimental error.

(d) The ability of the present method to distinguish between apparently small differences in structure is brought out forcibly by a comparison of the relative effectiveness of the α - and the β -naphthyl groups on the one hand, and of the fluoryl and the diphenylmethyl groups on the other. The greater dissociating power of α -naphthyl is qualitatively correlated with the fact that for it there are seven unexcited structures with the odd electron on a naphthyl carbon, whereas there are only six for β -naphthyl. The case of fluoryl is particularly striking. For the fluoryl radical it is possible to write six more unexcited structures than for the diphenylmethyl radical. These extra structures are all of the type



That is, they all have a double bond in the ortho linkage between the phenyl groups, and they all have the odd electron on one or the other of the phenyl groups. Hence it would seem that the radical should be stabilized by these extra possibilities of resonance, while the ethane should be left practically unaltered, and that consequently the dissociation should be increased. Actually, however, the opposite is the case. On putting in the phantom orbit and drawing all the bonds it is found that no matter where the phantom orbit is put with respect to the other orbits all the possible structures cannot be made canonical simultaneously. There will always be six non-canonical structures which must be represented as linear combinations of the canonical ones, and so the structures suggesting extra resonance are eliminated. Just which six structures are non-canonical will depend upon the position given the phantom orbit. If it be put in the symmetrical position indicated above, the non-canonical structures will be those in which there is a double bond between the two phenyl groups. Two of these structures turn out to be combinations of excited structures and so are neglected. The remaining four are combinations of one unexcited and one excited structure each.

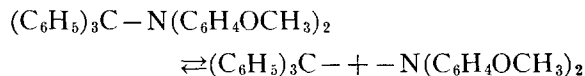
These excited structures are also neglected, and the four unexcited structures are distinguished from the remaining eight by being given a different coefficient. This is the reason for the fact noted in Table IV that for the fluoryl radical there are three instead of two coefficients. Since, however, the coefficients for the two different types of structures proved to be nearly the same here, they were put equal to each other in the calculation for the phenylfluoryl radical. This explains why the fluoryl group should not be more effective in promoting dissociation than the diphenylmethyl group, but to see why it is actually less effective we must turn our attention to the rules by which the matrix elements are calculated. Since we have shown that we can eliminate all the extra resonance structures of the fluoryl radical, the structures which we have left are exactly the same as those in the case of diphenylmethyl, except for the ortho bond between the two phenyl groups. Therefore the secular equation is the same except for the effect of the interchange integral between the atoms at either end of the bond, and this integral will always come into the matrix elements with a negative sign. Consequently the coefficient of α in any given matrix element for the fluoryl radical will be less than in the corresponding element for the diphenylmethyl radical. As a result of this, the coefficient of α will be decreased in both the energies W and W' , and since this decrease is greater in the former case than in the latter, the coefficient in the extra resonance energy $W - W'$ will also be decreased.

(e) Although the theory described in this paper is able to explain qualitatively and semi-quantitatively the dissociation of a considerable number of free radicals, it proves to be definitely inadequate in some cases. For example, di-tert.-butyl-tetraphenylethane has been found to be appreciably dissociated at room temperature, although our calculation would give exactly the same value of the free radical resonance energy as in the case of the undissociated tetraphenylethane, since the presence of the tert. butyl group does not affect the number of resonating

structures nor the values of the matrix elements. The same considerations also apply to decaphenylbutane, which has been found to be completely dissociated into pentaphenylethyl radicals. We consider that in these cases the steric effect may enter and be of dominating importance. There is no doubt that the tert. butyl and the triphenylmethyl groups are relatively large, and their presence in these compounds may tend to keep the radicals apart.

Furthermore, there are a number of interesting free radicals other than the hydrocarbons to which our treatment could be extended. In order to carry through similar calculations for compounds containing oxygen or nitrogen, however, we would have to introduce a number of additional parameters, corresponding to exchange integrals other than that to which we have given the value of α , which would make the calculations more difficult and the results less valuable.

Mention may be made of the interesting observation of Wieland that triphenylmethyldi-*p*-anisylamine does not dissociate appreciably except at temperatures above 140°



although the free radicals formed can exist to an appreciable extent in the monomeric form even at room temperature—a fact which has excited considerable comment. The explanation does not involve a difference in resonance in this compound and the corresponding ethane and hydrazine, but instead a difference in the energy of the carbon-nitrogen bond and the mean for the carbon-carbon and nitrogen-nitrogen bonds, resulting from additional ionic character of the unsymmetrical bond. This amounts to about 0.5 v.e.,⁹ and so is large enough to prevent dissociation.

On the other hand, the stability of positive and negative triarylmethyl ions is due to the same resonance effect as that of the neutral radicals discussed in this paper.

⁹ See the preceding and the following paper of this series.