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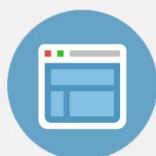J. Chem. Phys. **3**, 230 (1935); 10.1063/1.1749641

The Quantum Mechanics of Unsaturated and Aromatic Molecules: A Comparison of Two Methods of Treatment

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A comparison is made of two quantum-mechanical methods of treatment of unsaturated and aromatic organic molecules. The HLSP treatment, which is based upon the use of Slater valence-bond eigenfunctions, seems to give results in somewhat better general agreement with experiment than the HMH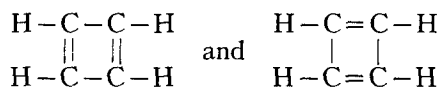, which is based upon the use of molecular orbitals of the Hund-Mulliken type. The latter, however, can be extended to a wider variety of problems. The problems considered include the energy relations among hydrocarbons, the dissociation of aryl substituted ethanes, the electron-affinity of free radicals and the acid strength of hydrocarbons.

FOR the quantum-mechanical treatment of the problems connected with molecular structure, there have been devised two methods of attack which differ somewhat in the nature of the approximations introduced. In a number of cases for which calculations have been made, these have been found to lead to results which agree quite well with each other in a general sort of way but which disagree, nevertheless, in some rather important particulars. Slater[1] has treated this question in some detail, with special reference to the metals and to the hydrogen molecule and Van Vleck[2] has done the same for methane. In this paper I wish to extend the discussion to several types of unsaturated and aromatic organic molecules.

The Heitler-London-Slater-Pauling (HLSP) Method

This method, which was developed originally by Slater[3] as a generalization of Heitler and London's[4] treatment of the hydrogen molecule, was first applied to aromatic compounds by E. Hückel[5] but has since been greatly simplified and extended by Pauling and his co-workers.[6] As

an illustration we shall take the simple case of cyclobutadiene, C_4H_4. (The extension to more complicated systems will be obvious. For a detailed discussion of the method, the reader is referred to the original articles.) Each carbon atom will be considered to have one $2s$ and three $2p$ orbital functions, occupied by one electron each. Of these, the $2s$ and two of the $2p$ functions are used up in forming single bonds to the two adjacent carbon atoms and to the attached hydrogen atom. The remaining $2p$ function, which projects at right angles to the plane of the ring, is then free to combine with the corresponding functions on the other carbon atoms. Only these last interactions need be considered, since the neglect of the others affects merely the position of the arbitrarily chosen zero point of the calculation. Thus the problem becomes one of four electrons only. For the molecule there are then the two "canonical" structures

$$
\begin{array}{ccc}
\text{H}-\text{C}-\text{C}-\text{H} & & \text{H}-\text{C}=\text{C}-\text{H} \\
\quad \| \quad \| & \text{and} & \quad | \quad | \\
\text{H}-\text{C}-\text{C}-\text{H} & & \text{H}-\text{C}=\text{C}-\text{H}
\end{array}
$$

for which the corresponding Slater valence-bond eigenfunctions can be set up in the usual way. The secular equation is

$$
\begin{vmatrix}
Q+\alpha-W & \tfrac{1}{2}Q+2\alpha-\tfrac{1}{2}W \\
\tfrac{1}{2}Q+2\alpha-\tfrac{1}{2}W & Q+\alpha-W
\end{vmatrix} = 0,
$$

as is easily shown, either by the procedure given by Pauling[6] for calculating the matrix elements,

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[1] J. C. Slater, Phys. Rev. **35**, 509 (1930).

[2] J. H. Van Vleck, J. Chem. Phys. **1**, 177, 219 (1933); **2**, 20 (1934).

[3] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[4] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[5] E. Hückel, Zeits. f. Physik **70**, 204 (1931).

[6] L. Pauling, J. Chem. Phys. **1**, 280 (1933); L. Pauling and G. W. Wheland, ibid. **1**, 362 (1933); L. Pauling and J. Sherman, ibid. **1**, 679 (1933).

or by the one given by Eyring and Kimball.[7] In this equation Q is the coulomb integral $(\psi_1\psi_2\psi_3\psi_4 | H | \psi_1\psi_2\psi_3\psi_4)$, α is the single exchange integral between adjacent carbon atoms $(\psi_1\psi_2\psi_3\psi_4 | H | \psi_2\psi_1\psi_3\psi_4)$, and ψ_i is the $2p$ function on the ith carbon atom. Here the single interchange integrals of the energy between non-adjacent atoms, all multiple interchange integrals, and all interchange integrals of unity have been neglected. The solutions of the secular equation are $W = Q + 2\alpha$, $Q - 2\alpha$, of which the former represents the ground state, since α is presumably negative. It will be convenient to eliminate Q from the problem by considering not the total energy $Q + 2\alpha$, but merely the resonance energy, which is the difference between this quantity and the energy of a single one of the two equivalent "Kekulé-like" structures with alternating single and double bonds. This gives: Resonance energy $= Q + 2\alpha - (Q + \alpha) = \alpha$.

THE HUND-MULLIKEN-HÜCKEL (HMH) METHOD

This method, which has been used with considerable success by Hund,[8] Mulliken,[9] Lennard-Jones,[10] Herzberg,[11] Dunkel,[12] Bloch[13] and others in treating a wide variety of problems, has also been extended to the unsaturated and aromatic compounds by Hückel.[5, 14] The following discussion follows his treatment quite closely, except for a slight modification in the nomenclature. Again let us use cyclobutadiene as an example. As before, the problem is limited to a consideration of the interactions of the $2p$ functions (one for each carbon atom) projecting at right angles to the plane of the ring. Instead of setting up valence-bond eigenfunctions, however,

we shall consider each electron moving alone in a Hartree self-consistent field, which is produced by the nuclei and by all the electrons other than itself and which possesses the symmetry of the nuclei. The eigenfunction for a single electron can then be represented by a linear combination of the functions $\psi_1 \cdots \psi_4$ and the corresponding secular equation is

$$\begin{vmatrix} q-W & \beta & 0 & \beta \\ \beta & q-W & \beta & 0 \\ 0 & \beta & q-W & \beta \\ \beta & 0 & \beta & q-W \end{vmatrix} = 0,$$

where q is the coulomb integral $(\psi_i | H' | \psi_i)$, β is the resonance integral $(\psi_i | H' | \psi_{i\pm 1})$, with $i = 1$, 2, 3, 4 and H' is the Hamiltonian operator corresponding to the self-consistent field. The resonance integrals between non-adjacent carbon atoms and all resonance integrals of unity have been neglected. The solutions of the equation are:

$$W = q + 2\beta \cos (2\pi j/4) \qquad (j = 0, 1, 2, 3)$$
$$= q + 2\beta, q, q - 2\beta, q.$$

Of these roots, $q + 2\beta$ is the lowest, since β is presumably negative, and consequently two of the electrons are assigned to the corresponding eigenfunction, one with positive and one with negative spin. The other two electrons are then assigned to the eigenfunction corresponding to the next lowest root, q. On account of the degeneracy of this root, however, the assignment can be made in various ways, and hence the ground state of the molecule is degenerate; there are in fact one triplet and three singlet terms, all with energy $2(q + 2\beta) + 2q = 4q + 4\beta$. In this treatment the interactions between the electrons have been neglected, except insofar as they are taken care of by the self-consistent field.

It is again convenient to eliminate the integral q from the problem by subtracting from the total energy, $4q + 4\beta$, the energy of a single "Kekulé-like" structure, which can readily be shown to be $4q + 4\beta$. Thus according to this treatment, cyclobutadiene has zero resonance energy—a result in poor agreement with the value, α, found by the HLSP method.

[7] H. Eyring and G. E. Kimball, J. Chem. Phys. 1, 239 (1933).

[8] F. Hund, Zeits. f. Physik 73, 1 (1931); 73, 565 (1932).

[9] R. S. Mulliken, J. Chem. Phys. 1, 492 (1933) and further references given there.

[10] J. E. Lennard-Jones, Trans. Faraday Soc. 25, 668 (1929).

[11] G. Herzberg, Zeits. f. Physik 57, 601 (1929).

[12] M. Dunkel, Zeits. f. physik. Chemie B7, 81; 10, 434 (1930).

[13] F. Bloch, Zeits. f. Physik 52, 555 (1928).

[14] E. Hückel, Zeits. f. Physik 72, 310 (1931); 76, 628 (1932); 83, 632 (1933); Trans. Faraday Soc. 30, 40 (1934).

General Comparison of the Two Methods

It is readily seen that the HMH procedure is the less rigorous of the two, since it does not take proper account of the Pauli exclusion principle. As Van Vleck[2] has pointed out, this results in an extreme piling up of electrical charges in the molecule. In fact, for an appreciable part of the time all the electrons are located on the same carbon atom. This shows that the self-consistent field has not properly accounted for the interactions between the electrons and throws some doubt upon the validity of the procedure. It seems likely that this error will increase in importance with the size of the molecule. A more rigorous procedure would be to set up an antisymmetric linear combination, Φ, of functions which involve the molecular orbitals that result from the solution of the secular equation, and then to calculate the energy from the relation $W = (\Phi|H|\Phi)/(\Phi\Phi)$, where H is now the correct Hamiltonian operator for the actual system under consideration. This refinement would be very difficult to carry out, however, since it would introduce a number of additional integrals which could not be readily evaluated. Consequently, we shall continue to use the simpler, but less rigorous procedure originally described. As a matter of fact, the HMH treatment, even with the refinement indicated, would probably still be somewhat inferior to the HLSP. The reason for this is that then the two methods become equivalent, except for the fact that in the former each bond is considered to be half ionic and half covalent, while in the latter each bond is considered to be completely covalent. The truth undoubtedly lies somewhere between the two extremes but somewhat nearer the latter. In the analogous case of the hydrogen molecule, calculation shows that the HLSP treatment gives a better answer than the corrected HMH treatment by approximately 6 kcal.[15] Furthermore, Weinbaum[16] has found that the ratio of the ionic to the covalent terms in H_2 is approximately 1 : 4, in better agreement with the HLSP treatment than with the HMH.

From this discussion we are led to expect that the HLSP procedure will in general give results in better agreement with experiment than the HMH. Since, however, both methods are so extremely crude, it seems advisable to consider as large a number of specific examples as possible before coming to any definite conclusion.

Hydrocarbons

In Table I are collected the results of calculations for a number of unsaturated and aromatic hydrocarbons. The agreement with experiment is indicated by the constancy of the values of α and of β in the fifth and sixth columns, respectively. It will be seen that the agreement is fairly good. From the heats of hydrogenation of benzene, Hückel has derived a further estimate of $\beta = -15$ kcal. $= -0.65$ e.v., which is considerably higher than most of the values in the table, but agrees well with that found for graphite. (This last calculation was made on the assumption that the interactions between the different planes could be neglected.[17]) This variation in the values of β may result from experimental error or may indicate a defect in the method of calculation. The mutual consistency of the results obtained by the two methods is indicated by the constancy of the ratio β/α given in the last column. It will be seen that, if cyclobutadiene and cyclooctatetraene are left out of account, the extreme variation is only from 0.477 to 0.555, which is no larger than might be expected in view of the different nature of the approximations made in the two cases.

The discrepancies in the cases of cyclobutadiene and cyclooctatetraene need to be considered in some detail. Hückel considered that the HMH treatment was the more reliable since it seemed to account more definitely for the instability of the four and eight membered rings, as compared with benzene but it is doubtful if his conclusion is justified. If the interactions between the electrons were properly considered, the calculated energies would be considerably altered. A careful investigation of this point, which is too involved to be given here, shows that the effect is in the proper direction and perhaps of the correct order of magnitude to bring the results of the HMH treatment into

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[15] L. Pauling, private communication.

[16] S. Weinbaum, J. Chem. Phys. 1, 593 (1933).

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[17] Cf. J. E. Lennard-Jones, Trans. Faraday Soc. 30, 58 (1934). Each bond is a double bond one-third of the time, instead of two-thirds, as stated by Lennard-Jones.

TABLE I. *Resonance energies (R.E.) of hydrocarbons.*

Compound	R.E. Empirical	R.E. HLSP	R.E. HMH	α	β	α/β
Cyclobutadiene		$1.000\alpha^e$	$0.00\beta^d$			∞
Benzene	-1.7^a e.v.	$1.106\alpha^{e,\ e}$	$2.00\beta^d$	-1.5 e.v.	-0.85 e.v.	0.553
Cycloöctatetraene		$1.290\alpha^h$	$1.66\beta^d$			0.777
Biphenyl	-3.77^a	$2.37\alpha^b$	$4.38\beta^d$	-1.6	-0.86	0.541
Naphthalene	-3.24^a	$2.04\alpha^{e,\ f}$	$3.68\beta^d$	-1.6	-0.88	0.555
Anthracene	-4.54^a		$5.32\beta^d$		-0.85	
Phenanthrene	-4.78^a		$5.45\beta^h$		-0.88	
Phenylethylene	-2.00^a	$1.31\alpha^b$	$2.42\beta^h$	-1.5	-0.83	0.541
Stilbene	-4.09^a	$2.59\alpha^b$	$4.88\beta^h$	-1.6	-0.84	0.531
Isostilbene	-3.87^a	$2.55\alpha^b$	$4.81\beta^h$	-1.5	-0.80	0.530
1,3,5 Triphenylbenzene	-7.9^b	$4.77\alpha^b$	$9.15\beta^h$	-1.66	-0.86	0.521
Butadiene		$0.232\alpha^b$	$0.47\beta^d$			0.494
Hexatriene		$0.482\alpha^b$	$0.99\beta^d$			0.487
Octatetraene		$0.725\alpha^b$	$1.52\beta^d$			0.477
Graphite	-0.37^g		$0.58\beta^h$		-0.64	

[a] L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606 (1933).

[b] L. Pauling and J. Sherman, J. Chem. Phys. **1**, 679 (1933).

[c] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

[d] E. Hückel, Zeits. f. Physik **76**, 636 (1932).

[e] E. Hückel, Zeits. f. Physik **70**, 253 (1931).

[f] Corrected value obtained by rigorous solution of the secular equation, J. Sherman, J. Chem. Phys. **2**, 488 (1934).

[g] J. Sherman, private communication. The figure gives the resonance energy per carbon atom.

[h] New calculations by present author.

agreement with those of the HLSP. Hückel argued further that the ground states of cyclobutadiene and of cycloöctatetraene are degenerate in the HMH treatment as long as the electronic interactions are neglected, while that of benzene is single, and hence that the instability of the former may be partly due to the ease with which they can be raised to higher and more reactive levels. If, however, the electronic interactions are included, the degenerate ground states are split into levels with separations of at least the same order of magnitude as that between the two lowest states of benzene.[18] It seems more likely that the correct explanation of the instability of cyclobutadiene and of cycloöctatetraene is to be found in the steric factors involved, which neither method can take into account; in the former the strain is considerable, while in the latter the large ring probably does not lie in one plane. Hence the apparent superiority of the HMH treatment in these two cases is apparently to be explained as the result of a quite fortuitous cancellation of errors.

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[18] Cf. the term-diagrams given by Hückel in his first paper, reference 5, pp. 249–251.

Free radicals

Pauling and Wheland[6] have applied the HLSP and Hückel[14] the HMH procedure to the problem of the dissociation of aryl substituted ethanes into free radicals. The two treatments agree in ascribing the stability of the radicals to the fact that an increase in the resonance energy of the system after dissociation partially compensates for the energy required to break the ethane bond in the original molecule. Obviously, the degree of dissociation will be expected to increase with this extra "free radical resonance energy." In Table II are collected the results of a number of calculations for various radicals. The consistency of the results obtained by the two methods is again indicated by the constancy of the ratio of β/α given in the last column. It will be observed that the ratio is not so constant as before, varying from 0.587 to 0.927 and that it is uniformly higher than was found for the hydrocarbons (cyclobutadiene and cycloöctatetraene excepted). This discrepancy can be explained partially, although apparently not completely, on the assumption that the free radical resonance energies calculated by the HLSP method are too high, in consequence of the neglect of excited structures. It is only to

TABLE II. *Free radical resonance energies of substituted methyls.*

Radical	HLSP[a]	HMH[b]	β/α
Phenylmethyl	0.509α	0.720β	0.707
β-naphthylmethyl	0.631α	$0.743\beta^c$	0.849
Biphenylmethyl	0.647α	$0.756\beta^{c,\ d}$	0.856
α-naphthylmethyl	0.752α	$0.811\beta^c$	0.927
Fluoryl	0.800α	$1.343\beta^c$	0.596
Diphenylmethyl	0.841α	1.300β	0.647
Phenylfluoryl	1.076α	$1.835\beta^c$	0.587
Triphenylmethyl	1.108α	1.794β	0.617
β-naphthyldiphenylmethyl	1.172α		
Biphenyldiphenylmethyl	1.174α	1.819β	0.645
Dibiphenylphenylmethyl	1.235α	1.841β	0.671
α-naphthyldiphenylmethyl	1.240α	$1.856\beta^c$	0.668
Tribiphenylmethyl	1.291α	1.859β	0.694

[a] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 370 (1933). Note the corrections in a number of the values which are listed at the end of this paper.

[b] E. Hückel, Zeits. f. Physik **83**, 632 (1933).

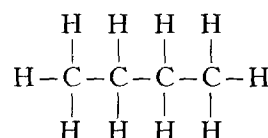[c] New calculations by present author.

[d] For this radical Hückel gives the value of 0.897β but his calculations are apparently in error.

be expected, however, that the values of β/α, obtained from systems of different types, may not agree perfectly. The comparison of the calculations with experiment is rather difficult here since the experimental data are both meager and inaccurate. It is fairly certain, however, that the qualitative order of increasing dissociation is: any ethane with less than six aryl groups ≪diphenyldifluoryl≪hexaphenylethane < tetraphenyldi-β-naphthylethane < tetraphenyldi-α-naphthylethane ≦diphenyltetrabiphenylethane < hexabiphenylethane. Tetraphenyldibiphenylethane has not been included in this list since its degree of dissociation has never been measured, even approximately. It is usually estimated to lie between hexaphenylethane and tetraphenyldi-β-naphthylethane, but the present calculations indicate that this may not be correct. With this one possible exception, the HLSP treatment leads to qualitatively correct predictions in regard to all the hexa-aryl substituted ethanes, while the HMH treatment, on the other hand, is in error in the case of diphenyldifluoryl. Thus the former seems here to be definitely the more reliable, in confirmation of the considerations of a preceding paragraph. The calculations by the two methods disagree further in the comparison of tetra-
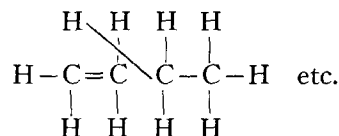
phenylethane with difluoryl, but in this case no experimental data are available.

The quantitative comparison of the calculations with experiment is much less conclusive on account of lack of accurate data. The agreement seems to be somewhat better, in general, for the HMH treatment than for the HLSP (except in the case noted in the preceding paragraph) but it is doubtful if any very great significance can really be attached to the quantitative aspects of such extremely crude calculations. (Cf. the further discussion of this point in the section entitled "Errata" at the end of this paper.)

Aliphatic as well as aryl substituents have been found to increase the dissociation of an ethane. Pauling and Wheland suggested that this effect was due to steric factors connected with the large size of the groups concerned but the explanation was not very satisfactory since it was rather inconsistent with the rest of the theory. Consequently, it is of interest to observe that by a slight extension of the HLSP method of treatment these cases can be taken care of without the necessity of introducing further hypotheses. As an illustration let us consider the molecule *n*-butane, or sym-dimethylethane. This can resonate between the unexcited structure
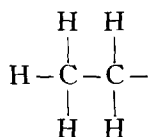
$$
\begin{array}{cccc}
H & H & H & H \\
| & | & | & | \\
H-C-C-C-C-H \\
| & | & | & | \\
H & H & H & H
\end{array}
$$

and several excited ones, such as

$$
\begin{array}{cccc}
H & H & H & H \\
\diagdown & | & | \\
H-C=C\diagdown C-C-H \quad \text{etc.} \\
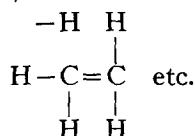| & | & | & | \\
H & H & H & H
\end{array}
$$

These latter, however, are very much less stable than the former since in them two single bonds have been broken in order to change a third into a double bond. Hence, such structures contribute only very slightly to the normal state of the molecule and the resonance energy is small. (It perhaps should be mentioned here that these considerations do not lead to the conclusion that the molecule should dissociate spontaneously into ethane and ethylene in the manner

indicated (except at elevated temperatures) nor are they inconsistent with the principle of the constancy of bond energies, since this type of resonance, being always present, can be considered to make a constant contribution to the energies of the bonds concerned.) The dissociated ethyl radical can also resonate in a similar way between the normal structure

$$\begin{array}{cc} H & H \\ | & | \\ H-C-C- \\ | & | \\ H & H \end{array}$$

and excited ones, such as

$$\begin{array}{cc} -H & H \\ & | \\ H-C=C & \text{etc.} \\ | & | \\ H & H \end{array}$$

It is easily seen that the resonance is much more effective here than with the undissociated molecule since the excited structures lie relatively much lower than there. This follows from the fact that in the radical only *one* single bond must be broken to change a second into a double bond. Consequently the resonance energy of the radical is materially greater than half that of the ethane and the dissociation of the molecule is correspondingly promoted. In the case of ethane itself these considerations do not apply since resonance of the type described cannot occur. Hence we conclude that butane should be more highly dissociated than ethane or, in other words, that a methyl group is a more effective substituent than a hydrogen atom in promoting the dissociation of an ethane into free radicals. It would be rather difficult to put these purely qualitative arguments upon a satisfactory quantitative basis since the values of a number of additional integrals would be required. A rough calculation, which is not given here on account of its extreme crudity, indicates, however, that the calculated effects are probably of the correct order of magnitude to account for the observed differences between primary, secondary and tertiary alkyl groups.[19] Hückel[20] has proposed a similar explanation of these effects upon the basis of the HMH treatment.

[19] J. B. Conant, J. Chem. Phys. **1**, 427 (1933).

[20] E. Hückel, personal communication to Professor Pauling.

Electron affinity of free radicals

This problem can be easily treated by a slight extension of the HMH method. In the case of triphenylmethyl, for example, we consider the reaction

$$(C_6H_5)_3C+E^-\rightarrow(C_6H_5)_3C^-.$$
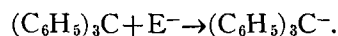
The energies of the radical and of the ion can be calculated in the usual manner. Since the secular equations are identical, the only difference between the two systems is that the latter contains one additional electron. This must be assigned to the most stable available orbit, which is seen from Hückel's calculation for the radical to have the energy q. This quantity, however, is simply the required electron-affinity and can be set equal to the experimentally determined value of -59 kcal.[21] or -2.7 e.v. This figure seems reasonable, but unfortunately cannot be checked by an independent calculation. In general, the electron-affinity of a free radical will be of the form $q+c\beta$, where c is a small constant which must be evaluated for each case individually from the secular equation. Since, however, β is also small compared with q, the second term in the expression is of minor importance and so, to a first approximation, the electron-affinity has a constant value q for all radicals. This result seems to be in satisfactory agreement with the experimental data.

It has not been found possible as yet to extend the HLSP treatment to problems of this type.

Acid strength of hydrocarbons

This problem is quite similar to the previous one, and can also be easily treated by the HMH method. Let us take triphenylmethane as an example. ΔE for the reaction

$$(C_6H_5)_3CH\rightarrow(C_6H_5)_3C^-+H^+$$
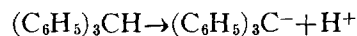
is clearly the difference between the resonance energy of the negative ion and that of the hydrocarbon, plus some additional terms connected with the energy of separating the ions, the heats of solvation, etc. If the sum of all these additional terms is called k, then we find (using the results of Hückel's calculations) $\Delta E=1.794\beta+k$. Since the value of k is completely unknown and

[21] H. E. Bent, J. Am. Chem. Soc. **52**, 1498 (1930); **53**, 1786 (1931); H. E. Bent and M. Dorfman, **54**, 1393 (1932).

since, moreover, the relation between ΔE and the dissociation constant is uncertain, this does not give a definite solution of the problem. The results of the calculation can be used for purposes of comparison, however, if two further assumptions are made; first, that k is constant for all the hydrocarbon acids under consideration and second, that the difference between the ΔE values for two compounds can be set equal to the difference between the corresponding ΔF values. Both assumptions are quite reasonable and are essentially the same as those made by Pauling and Wheland and by Hückel in their treatments of the free radicals. The ratio of the dissociation constants of two acids can now be calculated from the relation

$$\Delta E_1 - \Delta E_2 \cong \Delta F_1 - \Delta F_2 = RT \ln (K_2/K_1).$$

The results of the calculations for several hydrocarbons are given in Table III. It will be seen

TABLE III. *Ionization of hydrocarbons.*

| Hydrocarbon	ΔE	$K/K_{(C_6H_5)_3CH}$ calc.[a]	obs.[b]
Cyclopentadiene	$2.00\beta + k$	1.2×10^3	definitely acidic
Cycloheptatriene	$1.11\beta + k$	1.1×10^{-10}	not acidic
Phenylmethane	$0.72\beta + k$	2.0×10^{-16}	$\ll 10^{-2}$
Diphenylmethane	$1.30\beta + k$	6.6×10^{-8}	$\ll 10^{-1}$
Triphenylmethane	$1.79\beta + k$	1	1
Fluorene	$1.52\beta + k$	1.1×10^{-4}	$\gg 2.5 \times 10^4$
Phenylfluorene	$1.98\beta + k$	5.7×10^2	$\gg 2.5 \times 10^6$

[a] Calculated for 20°C, with $\beta = -0.86$ e.v. (-19.8 kcal.).
[b] Numerical values from J. B. Conant and G. W. Wheland, J. Am. Chem. Soc. **54**, 1212 (1932).

that if fluorene and phenylfluorene are left out of account, the agreement with experiment is excellent qualitatively and perhaps satisfactory quantitatively. The error in the case of these two, however, is too large to be the result of the special assumptions used in this calculation; it must rather be attributed to the method itself. This is apparently a further case in which the neglect of the interactions between the electrons invalidates the conclusions reached by the HMH procedure.

The HLSP treatment is not so easily extended to these systems, since, in the calculations for the negative ions orbital as well as spin degeneracy has to be taken into account. This results in the introduction of several further integrals which cannot be readily evaluated. The following dis-

cussion of cyclopentadiene will illustrate the procedure that must be employed and will show the sort of results that can be obtained. The problem will be simplified by the neglect of all excited structures of the type
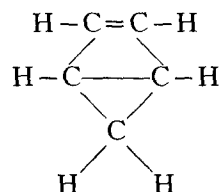
in which fewer than the maximum number of double bonds are formed between adjacent carbon atoms. This step is not absolutely necessary but it greatly facilitates the calculation and has the partial justification that, since the excited structures contribute more or less equally to the energies of both the hydrocarbon and the ion, their effect cancels out to some extent. With this approximation, then, the resonance energy of the hydrocarbon is seen to be zero, since only one structure is to be considered. In the ion, on the other hand, there is resonance among the five equivalent structures
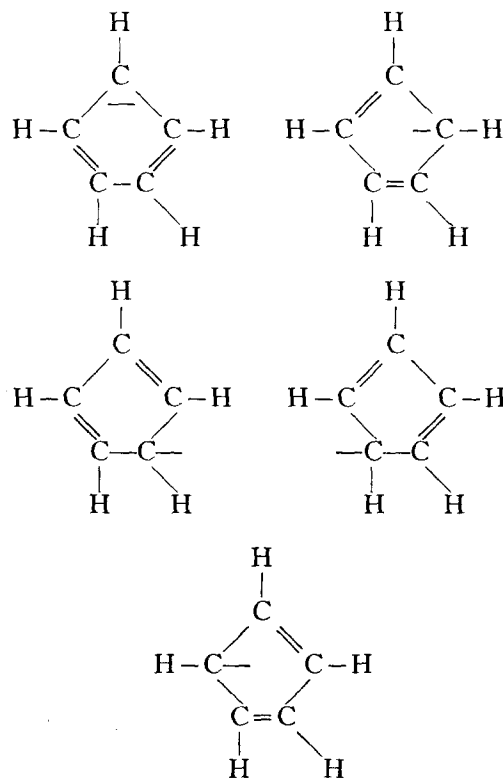
The secular equation is found to be

$$
\begin{vmatrix}
Q-\tfrac{1}{2}\alpha-W & \tfrac{1}{2}\rho & 2\sigma & 2\sigma & \tfrac{1}{2}\rho \\
\tfrac{1}{2}\rho & Q-\tfrac{1}{2}\alpha-W & \tfrac{1}{2}\rho & 2\sigma & 2\sigma \\
2\sigma & \tfrac{1}{2}\rho & Q-\tfrac{1}{2}\alpha-W & \tfrac{1}{2}\rho & 2\sigma \\
2\sigma & 2\sigma & \tfrac{1}{2}\rho & Q-\tfrac{1}{2}\alpha-W & \tfrac{1}{2}\rho \\
\tfrac{1}{2}\rho & 2\sigma & 2\sigma & \tfrac{1}{2}\rho & Q-\tfrac{1}{2}\alpha-W
\end{vmatrix} = 0,
$$

where Q and α have their usual significance, ρ and σ indicate the integrals

$$\rho = (\psi_1\psi_1\psi_2\psi_3\psi_4\psi_5 \,|\, H \,|\, \psi_1\psi_2\psi_2\psi_3\psi_4\psi_5)$$

and

$$\sigma = (\psi_1\psi_1\psi_2\psi_3\psi_4\psi_5 \,|\, H \,|\, \psi_1\psi_2\psi_3\psi_3\psi_4\psi_5),$$

and all further integrals have been neglected. The solutions are

$$W = Q - \tfrac{1}{2}\alpha + \rho \cos 2\pi j/5 + 4\sigma \cos 4\pi j/5$$
$$(j = 0, 1, 2, 3, 4).$$

Since ρ and σ are presumably negative, the lowest of the roots is that with $j=0$ and the resonance energy becomes $\rho+4\sigma$. ΔE of ionization is thus $\rho+4\sigma+k$. By the same procedure, ΔE of ionization for cycloheptatriene is found to be $0.455\rho+2.492\sigma+k$ and accordingly the calculation agrees with experiment in predicting that cyclopentadiene should be the stronger acid. Unfortunately, it has not been found possible to extend this treatment to more complicated systems of this type.

Basicity of aryl carbinols

The basic strength of triphenylcarbinol and similar compounds can be treated in a manner completely analogous to the above. Since, how-ever, suitable experimental data are not available for purposes of comparison, we shall not go into the problem here.

CONCLUSION

Two methods have been described for the quantum-mechanical treatment of unsaturated and aromatic organic molecules. In general these lead to very similar results but occasionally definite discrepancies do occur. In such cases, a comparison with experiment shows that the HLSP treatment is somewhat more reliable than the HMH, a result which can be anticipated on the basis of the greater rigor of the former. The HMH procedure, on the other hand, has shown itself superior to the HLSP in its ability to treat a wider variety of problems (although not always successfully, as, for example, the acid strengths of fluorene and phenylfluorene). This is a consequence of its simpler mathematical form. In general it would seem wise to carry through the calculation by both methods wherever possible and to check each against the other.