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Robert Serber

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The Energies of Hydrocarbon Molecules¹

ROBERT SERBER,* *University of California, Berkeley*

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The energies of a number of hydrocarbon molecules have been calculated by the Heitler-London-Pauling-Slater method with two objects in view, first, to see if this simple theory leads to the correct energies of formation, and second, to determine what significance can be attached to the empirical additivity rule for bond energies. Our equations involve three parameters, which roughly speaking, determine the gross energies of a C-H bond, a C-C bond, and a C=C bond. These have been evaluated from the ob-

served energies of methane, ethane and ethylene. The energies calculated for other hydrocarbons then agree surprisingly well with the observed values. Nevertheless, the validity of an empirical bond additivity rule seems to be purely fortuitous. The calculations further indicate that the theoretical significance ordinarily ascribed to the so-called "observed resonance energies" is a very questionable one.

VAN VLECK,^{2, 3, 4, 5} Penney^{6, 7, 8} and their collaborators have applied the Heitler-London-Pauling-Slater theory with considerable success in explaining the structure of polyatomic molecules. While the theory has thus shown its adequacy for such semiquantitative considerations, it would indeed be optimistic to expect of it an equally good account of the total energies, that is, the energies liberated in forming molecules from widely separated atoms in their normal states. Our calculation of the total energies of a number of hydrocarbon molecules thus affords a much more severe test of the approximations involved in the H-L-P-S procedure. The calculation is additionally interesting since through it one may hope to obtain a theoretical explanation of the empirical bond additivity rule.

Let us suppose that a hydrogen orbit, α , is paired to a carbon orbit, a . The total interaction energy between the hydrogen and carbon atoms is then

$$W_{HC} = 3/2 J_{\alpha a} + S_{HC}, \quad (1)$$

where $S_{HC} = Q_{HC} - 1/2 \sum_{i=s, \sigma, \pi, \pi'} J_{\alpha i}$.

Here the J 's are the ordinary exchange integrals,

and Q_{HC} is the Coulomb energy. The steric term, S_{HC} , is a function only of the internuclear distance and is quite independent of the choice of carbon orbits,⁹ i.e., of the angles between the bonds. Advantage has been taken of this invariance to write S_{HC} in terms of unhybridized orbits. The individual J 's, on the other hand, do depend on the bond angles. If the hydrogen orbit is not paired to any orbit on the carbon atom the first term in (1) drops out and only the steric term is left. In a similar way, the interaction between two carbon atoms is

$$W_{CC'} = 3/2 \sum_{\text{pairs}} J_{ii'} + S_{CC'}, \quad (2)$$

where $S_{CC'} = Q_{CC'} - 1/2 \sum_{i, i'=s, \sigma, \pi, \pi'} J_{ii'}$.

To the approximation of pure electron pair bonding, the total energy of the molecule is

$$W = \sum_{ij} W_{H_i C_j} + \sum_{i < j} W_{C_i C_j} + \sum_i W_v(C_i) + \sum_{i < j} M(H_i H_j). \quad (3)$$

The last sum in (3) represents the hydrogen-hydrogen repulsions. $W_v(C_i)$ is the energy of the valence state of the i th carbon atom, the normal state of the carbon atom being taken as the zero of energy. Because of the influence of the $L-S$ structure of the carbon atom $W_v(C_i)$ is not necessarily the same for all carbon atoms in the molecule, but depends on the angles

¹ A preliminary account was given at the Ann Arbor Meeting of the American Physical Society, June, 1934. (Phys. Rev. **46**, 335A (1934)).

* National Research Fellow.

² J. H. Van Vleck, J. Chem. Phys. **1**, 177 (1933).

³ J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933).

⁴ J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

⁵ J. H. Van Vleck, J. Chem. Phys. **2**, 297 (1934).

⁶ W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934).

⁷ W. G. Penney, Proc. Roy. Soc. **A146**, 223 (1934).

⁸ W. G. Penney, Proc. Phys. Soc. (London) **46**, 333 (1934).

⁹ This is a simple consequence of the unitary character of the transformation from one set of orbits to another. A proof is given by Penney, reference 7.

between the bonds made by the atom in question. In the cases we will consider, $W_s(C_i)$ lies between 7 v and 7.5 v. For any particular molecular model, the third and fourth sums of (3) can readily be evaluated by means of formulas given by Van Vleck.¹⁰ The first and second sums of (3) contain terms of two types: interactions between adjacent atoms, i.e., between atoms which are bonded to each other, and steric interactions between distant, unbonded atoms. It will be seen from (1) and (2) that the steric terms consist of sums of terms of opposite sign which largely annul each other. The steric terms, W_{HC} and $W_{CC'}$, between distant atoms are certainly small, and we shall provisionally suppose that they are so small that they may be neglected. If we obtain good agreement between the calculated and observed energies, we can regard this supposition as substantiated. The terms W_{HC} between adjacent atoms can be calculated by using Van Vleck's⁴ values of the exchange integrals N_{ss} , $N_{ss'}$, $N_{ss''}$, and by determining S_{HC} from the observed energy of methane. We shall neglect the small differences in internuclear distances in different molecules. The $W_{CC'}$ terms between adjacent carbon atoms appear at first glance much more troublesome, since they involve numerous exchange integrals, $C_{\alpha\beta\gamma\delta}$ in Penney's notation,⁶ whose values are not reliably known. The problem is greatly simplified, however, by the following considerations, which we shall illustrate by reference to Penney's model of the ethylene molecule.⁶ In this model W_{HC} is the same for all four hydrogen atoms, and is a function of the angle ω (see insert in Fig. 1. Of course for ethylene the lower C atom is also bonded to two H atoms in the same manner as the upper one). $W_{CC'}$ can be written

$$W_{CC'} = W_{C-C'} + 3/2\alpha, \quad (4)$$

where α is the exchange integral $J_{\pi\pi}$ in the notation of (2), or $-C_{\pi\pi\pi\pi}$ in Penney's notation. The first term in (4) is the bonding energy of the principal carbon-carbon bond (the one directed along the C—C line), the second term represents the energy of the second carbon bond (the $\pi-\pi$ bond), which is independent of ω and

¹⁰ Reference 4. Note corrections given in reference 5.

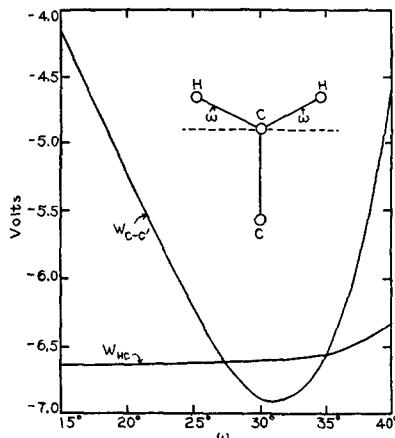


FIG. 1. In computing $W_{C-C'}$ it has been supposed that the hybridization ratios of the two orbits in the C—C bond are equal, an obvious condition in order that $W_{C-C'}$ be a minimum.

of no interest for our present purposes. In Fig. 1 we have plotted W_{HC} as a function of ω . It will be seen that the curve is very flat over a wide range of values of ω . Hence if we suppose that $W_{C-C'}$ has a sharp minimum in this range, the carbon-hydrogen interaction plays very little part in determining the form of the molecule: the hydrogen bonds simply arrange themselves in directions which bring the carbon single bond energy to its minimum. The stability of the benzene ring immediately suggests that the minimum of $W_{C-C'}$ should fall at $\omega = 30^\circ$; we shall assume this to be so in our further calculations. One may test this assumption by using the values of the various exchange integrals, $C_{\alpha\beta\gamma\delta}$, suggested by Penney.¹¹ The variation of $W_{C-C'}$ with ω found in this way is shown in Fig. 1. We see that with this choice of exchange integrals, $W_{C-C'}$ does indeed have a sharp minimum at 30° .

For Van Vleck's θ type bonds¹² the curves obtained for W_{HC} and $W_{C-C'}$ are again very

¹¹ Reference 7. The set of values labeled (2) has been employed since Dr. Penney informs the writer that these are probably the best estimate.

¹² See Fig. 2 and Eq. (33), reference 3. In this case the C atom is bonded to three H atoms and another C atom. If the C—C line is taken as the polar direction, the azimuths of the three H atoms are 0° , 120° , 240° , respectively, rather than 0° , 180° , as shown in Fig. 1, and θ is the angle CCH.

similar in appearance to those shown in Fig. 1. It thus appears that for all molecular models involving bonds of the ω and θ types, maximum stability is attained when the various bonding angles are such that $W_{C-C'}$, for each carbon-carbon bond, takes on its minimum value.¹³ In order to find the energy of the principal carbon-carbon bond we accordingly need not know the values of the individual carbon-carbon exchange integrals, $C_{\alpha\beta\gamma\delta}$ but only that of the particular linear combination of them involved in $W_{C-C'}$ at its minimum. Hereafter, $W_{C-C'}$ is to be understood as representing the minimum value of this quantity, unless otherwise stated. We shall determine $W_{C-C'}$ from the observed energy of ethane. The only other carbon-carbon exchange integral which plays an important role in our calculations is α , which, as (4) shows, fixes the energy of the second bond in a carbon-carbon double bond. α will be evaluated from the observed difference between the energies of ethane and ethylene.

Before we proceed to the explicit calculations, one troublesome point must be examined. The observed molecular energy is the sum of the "electronic" energy and the energy of nuclear motion. Our calculations should refer only to the electronic part of the energy. However, it is not usually possible to actually compute the nuclear energy. This can be done approximately in a few cases. Zahn¹⁴ estimates that the nuclear energy of methane is 1.25 v, that of ethane is 1.97 v, and each additional CH_2 group increases the nuclear energy by about 0.7 v. In a similar way, using the data of Mecke¹⁵ and of Eucken and Parts¹⁶ and Sutherland,¹⁷ one finds the value 1.4 v for ethylene and 0.7 v for acetylene. It will be seen that these figures can be represented fairly well by a rule of the bond additivity type which assigns a nuclear energy of about 0.3 v to each C-H bond, and an energy of about 0.1 v

to each carbon-carbon bond. We must suppose that this representation of the nuclear energies is sufficiently accurate for our purposes. The nuclear energies then need not be taken into account explicitly: their only effect will be to increase the "observed" value of S_{HC} by 0.3 v, and of $S_{\text{CC'}}$ by 0.1 v.

From the observed energy of methane, $W(\text{CH}_4) = -16.3$ v, we find, by a calculation similar to that given by Van Vleck,⁴ that W_{HC} for methane is -6.47 v. Once this value is determined it is a simple matter to compute W_{HC} for any other arrangement of carbon orbits.

For ethane we shall use the model proposed by Penney.⁶ In order to make $W_{C-C'}$ a minimum we must take $\theta = 112^\circ$, this being the value of θ which gives the same hybridization ratio in the C-C bond orbits as does $\omega = 30^\circ$. The energy of ethane is then

$$W(\text{C}_2\text{H}_6) = 6W_{\text{HC}}(\theta = 112^\circ) + W_{C-C'} + 2W_v(\text{C}) + \sum_{i < j} M(\text{H}_i\text{H}_j). \quad (5)$$

The values of the various terms are: $W_{\text{HC}}(\theta = 112^\circ) = -6.42$ v, $W_v(\text{C}) = 7.06$ v, $\sum M(\text{H}_i\text{H}_j) = 3.72$ v. In computing $\sum M(\text{H}_i\text{H}_j)$ we have taken the carbon-hydrogen internuclear distance to be 1.08A, and the carbon-carbon distance to be 1.37A. From the observed energy, $W(\text{C}_2\text{H}_6) = -27.57$ v, we find $W_{C-C'} = -6.89$ v.

The difference in energy between ethane and ethylene is

$$W(\text{C}_2\text{H}_6) - W(\text{C}_2\text{H}_4) = 6W_{\text{HC}}(\theta = 112^\circ) - 4W_{\text{HC}}(\omega = 30^\circ) - 3/2\alpha + 2[W_v(\text{C}) - W_v(\text{C}')] + \sum M(\text{H}_i\text{H}_j) - [\sum M(\text{H}_i\text{H}_j)]'.$$

The primed terms here refer to ethylene. Using $W_{\text{HC}}(\omega = 30^\circ) = -6.59$ v, $W_v(\text{C}') = 7.20$ v, $[\sum M(\text{H}_i\text{H}_j)]' = 1.09$ v, $W(\text{C}_2\text{H}_6) - W(\text{C}_2\text{H}_4) = -5.73$ v, we find $\alpha = -2.72$ v. It should be noted that this value of α is entirely compatible with Penney's calculation of the twisting frequency of ethylene,⁸ since his calculation determines not α , but $\alpha - \alpha'$, where $\alpha' = -C_{\pi\pi'\pi''\pi'''} (\alpha' = J_{\pi\pi'}$ in the notation of (2)). Pauling and Wheland¹⁸ give $\alpha = -1.5$ v, but, as we shall see,

¹³ If, with ω type bonding, the carbon atom is bonded to two other carbons and one hydrogen, rather than to two hydrogens and one carbon, the influence of the H-C interaction is considerably more important than indicated by Fig. 1. Fortunately, in this case the H-C interaction, as well as the C-C interaction, favors the 30° configuration. See reference 7.

¹⁴ C. T. Zahn, J. Chem. Phys. 2, 671 (1934).

¹⁵ R. Mecke, Zeits. f. physik. Chemie B17, 1 (1932).

¹⁶ Eucken and Parts, Zeits. f. physik. Chemie B20, 184 (1933).

¹⁷ Quoted by Penney, reference 8.

¹⁸ L. Pauling and G. W. Wheland, J. Chem. Phys. 1, 362 (1933).

the argument which leads to their value is a very dubious one.

It is now a simple matter to compute the energies of hydrocarbons for which simple electron pair bonding is a reasonable approximation, i.e., which do not involve resonance effects. In our models of molecules of the ethane and ethylene series, the carbon atoms are arranged in a staggered chain. The staggering is of course necessary to preserve the 120° angles between the carbon-carbon bonds. For example, for propane, the bonding of the two end carbon atoms is of the θ type, with $\theta = 112^\circ$, while the bonding of the center carbon atom is of Van Vleck's class (a) type,¹⁹ with $(180^\circ - 2\omega)$, the angle between the carbon-carbon bonds, equal to 120° . The energy of propane is thus²⁰

$$W(\text{C}_3\text{H}_8) = 6W_{\text{HC}}(\theta = 112^\circ) + 2W_{\text{HC}}(\omega = 39.3^\circ) \\ + 2W_{\text{C-C}} + 2W_v(\text{C}_1) + W_v(\text{C}_2) + \sum M(\text{H}_i\text{H}_j),$$

with

$$W_{\text{HC}}(\omega = 39.3^\circ) = -6.37v, \quad W_v(\text{C}_2) = 7.10v,$$

$$\sum M(\text{H}_i\text{H}_j) = 4.90v,$$

and the remaining terms as given in (5). This gives $W(\text{C}_3\text{H}_8) = -38.92v$. The observed value is $-38.9v$. The results of the calculations for a number of molecules are given in Table I.

The approximation of simple electron pair bonding is inadequate for molecules such as acetylene and benzene which involve multiple π - π bonds. Here more accurate methods must be employed. For acetylene, we use a linear model. If the axis of figure be the z axis, each carbon atom has a π orbit directed along the x and y axes. The interaction between these four orbits must be considered as a four-electron problem, rather than as two electron pairs with a small interaction term. The energy can be written $W(\text{C}_2\text{H}_2) = W_0 + W_1$, where $W_0 = 2W_{\text{HC}} + W_{\text{C-C}} + 2W_v(\text{C}) + M(\text{H}_1\text{H}_2)$, and W_1 is the energy due to the four π orbits. For this model $W_{\text{HC}} = -6.61v$, $W_v(\text{C}) = 7.51v$ and $M(\text{H}_1\text{H}_2)$ is negligible. Unlike the other cases we consider, for acetylene $W_{\text{C-C}}$ does not have its minimum value. In order to estimate its deviation from

the minimum we have used Penney's values of the carbon-carbon exchange integrals. The deviation is found to be $0.33v$, thus $W_{\text{C-C}} = -6.56v$. The familiar four-electron formula²¹ gives

$$W_1 = -\{2[(\alpha - \alpha')^2 + (\alpha - K_{\pi\pi'})^2 \\ + (\alpha' - K_{\pi\pi'})^2]\}^{1/2} + \alpha + \alpha' + K_{\pi\pi'}, \quad (6)$$

where $\alpha' = -C_{\pi\pi'}\pi' = J_{\pi\pi'}$, and $K_{\pi\pi'}$ is the intra-atomic exchange integral between the π orbits. The ordinary four-electron formula comprises only the term under the radical sign in (6); the necessity of adding the remaining terms can be seen as follows. The term under the radical sign represents the complete contribution to the energy from the four π orbits, hence W_0 should contain no contribution from these orbits. However, if we examine W_0 in detail we see from (2) that S_{CC} contains, for each choice of a pair of π orbits, one on each carbon atom, either the term $-\frac{1}{2}\alpha$ or the term $-\frac{1}{2}\alpha'$, depending on the relative orientation of the orbits. The total contribution to S_{CC} of our four π orbits is thus $-\alpha - \alpha'$. Similarly, from Van Vleck's formula for $W_v(\text{C})$, we see that the contribution of our π orbits to $W_v(\text{C})$ is $-\frac{1}{2}K_{\pi\pi'}$. The term $\alpha + \alpha' + K_{\pi\pi'}$ must thus be added to the radical in (6) in order to correct for these steric terms which appear in W_0 . A simpler example of the same point is afforded by noting from (2) or (4) that the difference in energy between a carbon single bond and a carbon double bond is $\frac{3}{2}\alpha$, not α as one might at first suppose. The energy of the π - π bond is indeed α , but it must be remembered that if this bond were lacking, the interaction of the two π orbits would contribute a term $-\frac{1}{2}\alpha$ to the energy, and this no matter what the choice of carbon orbits. The difference in energy due to the presence of the π - π bond is thus $\frac{3}{2}\alpha$. A similar interpretation holds for the added terms in (6).

According to Van Vleck,⁵ $K_{\pi\pi'} = 0.56v$. The exchange integral α' can be obtained from the difference $\alpha - \alpha' = -0.72v$ deduced by Penney from the observed twisting frequency of ethylene. Using these values we find $W(\text{C}_2\text{H}_2) = -14.9v$, compared to the observed value, $-15.2v$. Since most of the stability is due to W_1 , W_0 amounting

¹⁹ See Fig. 1 and Eqs. (32) and (34), reference 3.

²⁰ The value $\omega = 39.3^\circ$ is determined from the constraint between the angles given by Eq. (32), reference 3.

²¹ F. London, *Zeits. f. Electrochemie* **35**, 552 (1929); J. C. Slater, *Phys. Rev.* **38**, 1109 (1931).

to only -4.76 v, the agreement between the calculated and observed values is a very nice confirmation of the value we have found for α .

The interaction of the π orbits in benzene must be treated as a six electron problem. The energy is $W = W_0 + W_1$, with

$$W_0 = 6W_{\text{HC}}(\omega = 30^\circ) + 6W_{\text{C-C}'} + 6W_v(\text{C}) \\ + \sum M(\text{H}_i\text{H}_j),$$

and²²

$$W_1 = 2\alpha + 5\gamma/2 - [9(\alpha - \beta)^2 + 4(\alpha - \gamma)^2]^{\frac{1}{2}}. \quad (7)$$

Here β and γ are the values of $-C_{\pi\pi\pi\pi}$ at internuclear distances corresponding to the distance between alternate carbon atoms, and the distance between diagonally opposite atoms, respectively. The steric correction term $3\alpha + 3\beta + 3\gamma/2$ is included in W_1 . An estimate of the magnitude of β and γ can be obtained from Bartlett's²³ theoretical calculation of $C_{\pi\pi\pi\pi}$. While the absolute magnitude of $C_{\pi\pi\pi\pi}$ is not given correctly by this calculation, it is not unreasonable to suppose that the ratios of the values of $C_{\pi\pi\pi\pi}$ at different internuclear distances are fairly well represented. Using Slater's²⁴ value of the screening constant for the π orbits, one concludes that β and γ are quite small and we have accordingly neglected them in computing the value of $W(\text{C}_6\text{H}_6)$ given in Table I. It should be emphasized that in computing the energies of molecules

such as benzene it is not sufficient to consider merely the interaction between π orbits. It is imperative also to include the forces in the plane of the benzene ring, as we have done. The importance of bond forces in the plane of the ring has been shown by Penney;⁷ the importance of the steric terms which appear in W_0 has been discussed above in connection with acetylene. The errors which attach to incomplete treatments which consider only π orbits will be illustrated in the discussion of results.

On taking account of the interaction of the four π orbits in 1,2 dihydrobenzol, we find $W_1 = 3.23\alpha$. For naphthalene we have used Sherman's²⁵ result for the resonance energy. This gives $W_1 = 9.54\alpha$.

DISCUSSION OF RESULTS

The agreement between the calculated and observed energies is remarkably good, much better than one has any right to expect from so crude a theory. It should be pointed out that inclusion, in the H-L-P-S treatment, of non-orthogonality and higher order permutation integrals generally seems to spoil the results of the simple theory.²⁷ Any agreement obtained by use of the simple theory must consequently be regarded as rather accidental.

It is not at all clear why molecules for which (3) is a good approximation should so nearly obey a bond additivity law. The variation in W_{HC} from molecule to molecule is over $\frac{1}{4}$ v, while $W_v(\text{C})$ varies by almost $\frac{1}{2}$ v. In addition, the hydrogen-hydrogen repulsion energy is often quite large, and it by no means obeys an additivity rule. The situation is not clarified by considering net, rather than gross, bonding energies. For example, the net C-H bonding energy in ethylene is 4.45 v, in ethane 4.04 v, and in cyclohexane 3.95 v. In computing these net bonding energies, the energy of the hydrogen-hydrogen repulsions has been divided equally among the C-H bonds. The energy of the C-C bond in ethane is 3.36 v, and that of the C=C bond in ethylene is 3.77 v. The empirical bonding energies given by Pauling and Sherman²⁸ are

		Calc.	Obs.
Methane	CH_4	(16.3)v	16.3v
Ethane	C_2H_6	(27.6)	27.6
Propane	C_3H_8	38.9	38.9
Butane	C_4H_{10}	50.2	50.2
Ethylene	C_2H_4	(21.8)	21.8
Propylene	C_3H_6	33.1	33.1
1,2,3,4 tetrahydrobenzol	C_6H_{10}	61.9	61.8
Cyclohexane	C_6H_{12}	67.4	67.1
Acetylene	C_2H_2	14.9	15.2
Benzene	C_6H_6	52.2	52.2
1,2 dihydrobenzol	C_6H_8	56.3	56.7
Naphthalene	C_{10}H_8	81.4	82.5

²² F. Seitz and A. Sherman, J. Chem. Phys. 2, 11 (1934); R. Serber, J. Chem. Phys. 2, 697 (1934).

²³ J. H. Bartlett, Jr., Phys. Rev. 37, 507 (1931).

²⁴ J. C. Slater, Phys. Rev. 36, 57 (1930).

²⁵ The experimental values have been taken from the following sources: F. D. Rossini, Bur. Standards J. Research 13, 21 (1934); L. Pauling, J. Am. Chem. Soc. 54, 3570 (1932); and references 14, 28, 30.

²⁶ J. Sherman, J. Chem. Phys. 2, 488 (1934).

²⁷ H. M. James, J. Chem. Phys. 2, 794 (1934); A. S. Coolidge and H. M. James, ibid. 2, 811 (1934).

²⁸ L. Pauling and J. Sherman, J. Chem. Phys. 1, 606 (1933).

(C-H)=4.07 v, (C-C)=3.15 v, (C=C)=5.56 v. The wide divergences between these values force one to the conclusion that the validity of an empirical bond additivity law is purely fortuitous. The bond additivity rule does, in fact, overstabilize cyclohexane and 1,2,3,4 tetrahydrobenzol by $\frac{2}{3}$ v and $\frac{1}{4}$ v, respectively. The H-L-P-S method thus gives a somewhat better account of the energies of these molecules than the additivity rule, although, of course, the accuracy of our treatment is hardly sufficient to justify the comparison.

Although no general bond additivity rule should be expected to hold for molecules whose energies are given by (3), the theory does predict an additivity relation between the energies of the higher members of the paraffin series, C_nH_{2n+2} . This follows from the fact that the bonding of each added CH_2 group is of the same type, namely Van Vleck's class (a) type, while for $n > 6$ the repulsions between the two added H atoms and the H atoms on the two end C atoms become negligible. This agrees qualitatively with the results of Rossini,²⁶ who finds an additivity relation for the paraffins when $n > 5$, but slight deviations for the lower members of the series.

Before discussing benzene, a few words regarding Pauling, Wheland and Sherman's²⁹ theoretical formulas for resonance energies may not be amiss, since the precise significance of their method of calculation is by no means clear. Thus Hückel³⁰ has argued that if benzene were considered to have three single carbon-carbon bonds and three double bonds the energy would be $W' = W_0 + 3\alpha$, whereas solution of the six electron problem would give $W = W_0 + 2.605\alpha$. The resonance energy $W - W'$ is consequently asserted to be -0.395α , and not 1.105α , as stated by Pauling and Wheland. But this argument is evidently not correct. In fact, we see from (2) or (4) that $W' = W_0 + 4\frac{1}{2}\alpha$, while (7)

gives, on putting $\beta = \gamma = 0$, $W = W_0 + 5.605\alpha$. The difference $W - W'$ has just the value found by Pauling and Wheland. One can readily show that their method will always give the correct resonance energy. The fallacy in the argument to the contrary arises from the fact that it does not properly take into account the steric terms which appear in W_0 .

One must carefully distinguish between the theoretical resonance energy and the so-called "observed resonance energy" used by Hückel and by Pauling, Wheland and Sherman. The former is the difference between the theoretical energy obtained by treating the interaction of the π orbits as an n electron problem, and the energy calculated under the assumption of simple electron pair bonding. The latter is taken to be the difference between the observed energy and the energy computed from the empirical bond additivity law: the name "resonance energy" has been applied to this quantity under the supposition that it is equal to the theoretical resonance energy. However, the theory as we have developed it indicates a serious breakdown of the bond additivity law as used for molecules such as benzene. For benzene, we find, under the assumption of simple electron pairing, $W' = -49.2$ v, while the bond additivity law gives $W' = -50.6$ v. For 1,2 dihydrobenzol the corresponding figures are -51.6 v and -56.3 v, and for naphthalene -75.9 v and -79.2 v. This failure of the bond additivity law results from the very low value of the theoretical C=C bonding energy for such molecules, 3.77 v, compared to the empirical value, 5.56 v. The theoretical resonance energies for the three molecules are -3.0 v, -4.7 v, -5.5 v, respectively, while the "observed resonance energies" are -1.6 v, -0.4 v,³¹ -3.2 v. The "observed resonance energies" appear to have no theoretical significance whatsoever. It consequently seems very difficult to attach any meaning to calculations, such as those of Pauling, Wheland and Sherman, which refer to these quantities.

²⁹ Pauling and Wheland, reference 18; Pauling and Sherman, J. Chem. Phys. 1, 679 (1933); Sherman, reference 25.

³⁰ E. Hückel, *Aromatic and Unsaturated Molecules*, International Conference on Physics, London, October, 1934.

³¹ It should be noted that the Pauling-Wheland-Sherman procedure predicts a resonance energy, -2.6 v, in definite disagreement with this value.