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The Calculation of the Heats of Formation, Heats of Hydrogenation and Strain Energies in Nonconjugated Hydrocarbons by the Maximum Overlap Approximation

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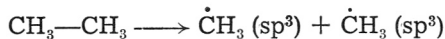
The heats of formation in nonconjugated hydrocarbons and the strain energies of small ring compounds were calculated within the (MOA) maximum overlap approximation. The agreement with experiment is fairly good. The results indicate that the overlap between the neighbouring bonding orbitals is responsible for the greatest part in the heats of formation and that the origin of the strain energies in small cyclic hydrocarbons is the bending of the Ψ_{CC} hybrids. The calculated heats of hydrogenation for some characteristic olefins are in good qualitative agreement with the experimental values.

INTRODUCTION

The variable sp^n hybridization model (where n is a noninteger) of chemical bonding in hydrocarbons, developed in this laboratory, proved very useful in correlating many physical and chemical properties associated with CC and CH electron pair bonds¹. The sp^n hybrids calculated by employing the maximum overlap criterion are related to $J(C-H)$ and $J(C-C)$ spin-spin coupling constants, proton chemical shifts, thermodynamic acidity and C—H stretching frequencies² in a semiquantitative fashion. In addition, the overlap integrals of the neighbouring bonding hybrid orbitals were successfully correlated with the CH^{2b} and CC^3 bond dissociation energies and the corresponding bond lengths⁴. In this paper we consider the calculation of the heats of formation in hydrocarbons. This endeavour has twofold purpose. Firstly, we would like to extend our local hybridization model to the problems of chemical reactions and consequently we have to examine the energetic properties of hybrids. Secondly, there is a controversy concerning capability of hybrid orbitals to reproduce the molecular energy. It was argued that the maximum overlap method can provide the approximate wave function but the same does not hold for the energy since this type of calculations is not based on the molecular hamiltonian⁵. On the other hand, it was shown that the overlap integrals are good indices of the bonding strengths and that they are linearly related to the C—C bond energies⁶. These results were substantiated by the more recent

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calculations of C—H dissociation energies^{2b} and C—C instantaneous bond dissociation energies (IBDE)³. The latter are defined as the energy of C—C bond breaking without the relaxation energy *i. e.*



where c_{ij} is a mixing parameter and $(2p)_{ij}$ is the 2p atomic orbital properly oriented in space. The subscripts *i* and *j* in the definition (1) denote that the hybrid Ψ_{ij} is placed on the atom *i* and directed toward the neighbouring atom *j*. It is assumed that the hybrids centered on the same atom are orthogonal yielding the relationship

$$c_{ij}c_{ik} + (1 - c_{ij}^2)^{1/2} (1 - c_{ik}^2)^{1/2} \cos \theta_{ij,ik} = 0 \quad (2)$$

where the angle between the symmetry axes of the hybrids is denoted by θ . The orthogonality condition (2) is of fundamental importance in the maximum overlap method and we shall discuss it in some more detail. In order to explain the tetravalency of the carbon atom we have to have four electrons with parallel spins. Since the spins are parallel the electrons tend to avoid each other as much as possible according to the Pauli principle. This is most easily accomplished by the orthogonality of the hybrid orbitals (2). It was shown in a recent semiempirical study of hybridization in hydrocarbons⁸ that the local hybrid orbitals extracted from the CNDO/2 and SCC (self-consistent charge) molecular orbitals overlap by an amount smaller than 0.1. Therefore, we can regard the orthogonality constraint (2) as fully justified. The relations (?) enable the theoretical prediction of bond angles in hydrocarbons since θ coincides with H—C—H and C—C—C angles in acyclic parts of a molecule. In small ring compounds the so called bent bonds necessarily appear⁹ and the interhybrid angle θ is related to the geometrical angle θ_g as follows

$$\theta_{g,ik} = \theta_g + \delta_{ij} + \delta_{ik}$$

where δ_{ij} and δ_{ik} are the deviation angles of the hybrids Ψ_{ij} and Ψ_{ik} placed on the carbon atom *g* from the straight lines passing through the corresponding nuclei. In these cases the p orbitals are decomposed into the parallel and the perpendicular to the bond components

$$p_{ij} = \cos \delta_{ij} (p_{ij}) + \sin \delta_{ij} (p_{\perp})$$

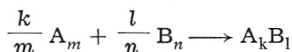
and one can distinguish between the sigma and pi type of overlap of the neighbouring p-orbitals. The hybridization parameters and the bond angles are determined by the maximum overlap criterion or in other words by maximising the weighted sum of all bond overlaps

$$S = k_{CC} \sum_{CC} S_{CC} + k_{CH} \sum_{CH} S_{CH} \quad (3)$$

where the weighting factors k_{CC} and k_{CH} take into account the difference in energy between the CC and CH bonds. They were determined in order to reproduce the average CC and CH bond energy in methane and ethane¹. If the Clementi double zeta functions¹⁰ and the hydrogenic orbital with $\zeta = 1.0$ are employed, then their numerical values are $k_{CC} = 121$ and $k_{CH} = 135$ kcal/mol. The maximum overlap calculations performed on molecules considered in this paper were based on experimental bond lengths.

RESULTS AND DISCUSSION

The standard heat of formation $\Delta_f H$ of a compound $A_k B_l$ is defined as the change in heat content for the synthesis of this molecule from its elements



where the process is carried out isothermally at room temperature* (25 °C) and the elements A_m and B_n as well as the final product $A_k B_l$ are assumed to be in their standard thermodynamic states¹¹. In the maximum overlap procedure we use the simple proportionality between the bond strength and bond overlap [eqn. (3)]. However, the calculations of the C—H and C—C bond dissociation energies^{2b,3} indicate that the more general linear relation

$$E_{AB}^b = k_{AB} S_{AB} + l_{AB} \quad (4)$$

should be employed in order to put the overlap integrals S_{AB} in line with the experimental bond energies. In the eqn. (4) the CC and CH bonds are denoted by AB while k_{AB} and l_{AB} are empirical parameters determined by the least squares fit method**. We have considered so far C—H and C—C bonds, the latter being essentially unstrained. Therefore, the use of only one constant of proportionality k_{AB} was plausible (AB stands for CC and CH bonds). Our study of the bond lengths in small cyclic and polycyclic hydrocarbons indicates that the use of the simple k_{CC} for a wide variety of C—C bonds is too severe a restriction¹². It was concluded that σ and π type of overlap in the strained CC bond should be parametrized separately.

Therefore we tried to fit the experimental heats of formation by the following expression

$$\Delta_f H = k_{CC}^\sigma \Sigma S_{CC}^\sigma + k_{CC}^\pi \Sigma S_{CC}^\pi + k_{CH} \Sigma S_{CH} + n_{CC} l_{CC} + n_{CH} l_{CH} \quad (5)$$

where n_{CC} and n_{CH} are the numbers of CC and CH bonds in a molecule in question, respectively and $k_{CC}^\pi S_{CC}^\pi$ denotes the pi-type interaction of the bent bond. The overlap integrals S_{CC}^π vanish, of course in strain-free molecules like methane and ethane. In the case of strained double bonds*** two more parameters $k_{C=C}^\sigma$ and $k_{C=C}^\pi$ are needed in order to describe its sigma- and pi-interactions. The overlap integrals obtained by the maximum overlap method are correlated with the experimental $\Delta_f H$ by using the relation (5) and the best parameters in the sense of the least squares fit method are as follows (in kcal/mol): $k_{C=C}^\sigma = -126.9$, $k_{C=C}^\pi = 685.4$, $k_{C=C}^\sigma = -49.8$, $k_{C=C}^\pi = -9.9$, $k_{CH} = -18.8$, $l_{CC} = 86.1$ and $l_{CH} = 9.4$. However, it should be mentioned that the correlated heats of formation for three-membered rings require a separate constant $k_{C-C}^\pi = 36.1$ i. e. the cyclopropyl ring is a special structural group

* It is tacitly assumed here that the heat capacities at constant pressure and the characteristic frequencies of the normal modes of vibrations do not vary too much from molecule to molecule.

** It should be mentioned here that the additive constants l_{AB} are not important in a search of the maximum value of the expression (3).

*** For a very good review article on the properties of the strained double bonds see: N. S. Zefirov and V. I. Sokolov, *Uspekhi Khimii* **36** (1967) 243.

which has to be parametrized separately. The correlated $\Delta_f H$, the experimental values and the available MINDO/1 results of Baird and Dewar¹³ are compared in Table I for a wide variety of hydrocarbons. The quality of our correlation is fairly good, the standard deviation being 3 kcal/mol.

TABLE I.

Comparison between the experimental correlated heats of formation as calculated by the MOA method and MINDO/1 for some characteristic hydrocarbons

Molecule	$\Delta_f H$ (corr.)	$\Delta_f H$ (exp.)	Diff.*	MINDO/1
	kcal mol ⁻¹	kcal mol ⁻¹	kcal mol ⁻¹	kcal mol ⁻¹
methane	-16.6	-17.9	1.3	-17.78
ethane	-20.7	-20.24	-0.5	-20.18
propane	-26.8	-24.82	-2.0	-24.91
isobutane	-30.3	-32.15	1.9	-31.82
neopentane	-35.2	-39.67	4.5	-40.63
ethylene	13.2	12.50	0.7	13.77
propene	5.8	4.88	0.9	5.21
2-methyl-propene	-1.9	-4.04	2.1	-5.92
2-butene (trans)	-1.8	-2.67	0.9	-3.04
trimethyl-ethylene	-9.6	—	—	—
tetramethyl-ethylene	-15.7	-16.68	1.0	—
1,3-butadiene	31.8	38.77	-7.0	—
n-butane	-30.6	-30.15	-0.5	-29.44
n-pentane	-35.5	-35.0	-0.5	-34.01
cyclobutane	2.1	6.38	-4.3	11.34
methylcyclobutane	1.7	0.60	2.3	4.51
cyclobutene	34.4	37.50	-3.1	40.88
1,2-dimethylcyclobutene	17.7	19.80	-2.1	19.62
cyclopentane	-23.4	-18.46	-4.9	-19.23
cyclohexane	-27.6	-29.43	1.8	-26.41
methylcyclopentane	-28.6	-25.50	-3.1	-26.19
1,1-dimethylcyclopentane	-33.9	-33.05	-0.8	—
cyclopentadiene	36.2	32.24	4.0	30.16
1,4-cyclohexadiene	24.6	26.30	-1.7	—
1,3-cyclohexadiene	24.0	26.00	-2.0	—
1,3,5-cycloheptatriene	48.2	44.50	3.7	—
cyclooctatetraene	69.8	71.30	-1.5	—
norbornane	-9.0	-12.42	3.4	—
norbornene	24.7	24.70	0	—
norbornadiene	60.50	59.70	0.8	—
1,3-dimethylene-cyclobutane	56.5	53.30	3.2	—
bicyclo(2.2.2)octane	-27.5	-24.09	-3.4	—
cubane	148.8	148.70	0.1	116.88
adamantane	32.8	32.94	-0.1	—
bicyclo(1.1.1)pentane	78.6	72.81**	5.8	—
cyclopropane	14.6	12.74	1.9	16.36
spiropentane	39.4	44.23	-4.8	42.23

* Diff. denotes the differences between the correlated and the experimental heats of formation.

** The force field calculation of N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.* **93** (1971) 1637.

Some trends in the changes of the heats of formation are qualitatively well reproduced. For instance, insertion of a CH₂ group in the aliphatic chain decreases $\Delta_f H$ by roughly 5 kcal/mol. Similarly, substitution(s) of the methyl group in ethylene decrease $\Delta_f H$ by approximately 8 kcal/mol. The discrepancies bet-

ween the calculated and experimental heats of formation found in neopentane and 1,3-butadiene indicate the limitations of the present form, of the MOA method *i. e.* the inability of this approach to take into account a large number of nonbonding repulsions* and π -electron delocalization. The errors in $\Delta_f H$ in cyclobutane and cyclopentane were also expected since the MOA method can not reproduce the experimental dihedral angle of cyclobutane or describe the pseudorotation in cyclopentane. According to the maximum overlap criterion the most stable conformation is planar in both molecules. It should be mentioned, however, that the overall overlap is very insensitive to the puckering of such molecules, and for example in cyclobutane, variations of 20° — 30° in the dihedral angle cause almost negligible change in overlap. In such cases the nonbonding repulsions might become decisive in determining the geometry of molecules and the hybrid orbitals calculated by the MOA method should be considered with due caution.

The calculated heats of formation exhibit larger deviations from the experimental values for molecules possessing cyclopropyl rings indicating that the maximum overlap hybrid orbitals provide less accurate description of these molecules. However, it has to be strongly emphasized that the calculation of the heats of formation is not at all an easy problem to tackle. The most successful approach in this respect is the semiempirical MINDO scheme, where the parameters were optimized in order to give the best heats of formation, and yet the MINDO/1 method (Table I) is in error for cyclopropane and cyclobutane by 3.6 and 5 kcal/mol, respectively. Furthermore, the deviations from the experimental values for molecules involving three and four-membered rings is proportional to the number of these small rings since the errors are additive. For example, the errors in bonding energies in dicyclopropyl and cubane are 8 and 32 kcal/mol respectively. The more refined MINDO/2 version gives $\Delta_f H$ with deviations which are as a rule less than 4 kcal/mol. It grossly overestimates, however, the stability of small rings¹⁴. The latest MINDO/3 variant yields the heats of formation with an average error of 5 kcal/mol¹⁵. Therefore we can say that, despite of the shortcomings discussed above, the MOA method gives a satisfactory agreement with experiment, particularly in view of the simplicity of the model employed.

The correlation between the bond overlaps and heats of formation can be used in a predictive manner for the calculation of $\Delta_f H$ in molecules where the experimental values are not available. We shall briefly discuss here the estimates of the heats of hydrogenation for some characteristic olefins by using the theoretical $\Delta_f H$ values of Table I. The heats of hydrogenation are obtained as a difference between the heats of formation of the resulting saturated molecule and the corresponding initial olefin. The comparison between the theoretical and experimental values is given in Table II. Both sets of data are in good qualitative agreement, but it seems that the present form of the MOA method is unable to reproduce finer quantitative details.

It is well known that molecules having very close nonbonded groups or those possessing distorted angles exhibit some strain. The concept of strain

* A portion of the effects like nonbonded repulsions and hyperconjugation is absorbed in the empirical parameters.

TABLE II.

Comparison between the experimental and calculated heats of hydrogenation for some characteristic olefins

Molecule	$\Delta_f H$ (exp.) kcal mol ⁻¹	$\Delta_f H$ (calcd.) kcal mol ⁻¹	Diff. kcal mol ⁻¹
ethylene	32.82	33.9	1.1
cyclobutene	31.1 ^a	32.3	1.2
propene	30.12	32.6	1.5
2-methylpropene	28.39	28.4	0
2-butene(trans)	27.62	28.8	1.2
1,3-butadiene	57.07	62.4	5.3
1,3-cyclohexadiene	55.37	51.6	-3.8
1,3-dimethylenecyclobutane	60.0 ± 1.0 ^b	55.5	-4.5
norbornene	31.1 ^c	33.7	-0.6
norbornadiene	68.1 ^d	69.5	1.4

* The experimental values are taken from J. R. Lacher, »Experimental Thermochemistry«, Vol. 2, ed. H. A. Skinner, John Wiley & Sons, New York 1962, p. 233, if not stated otherwise.

^a K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.* **90** (1968) 3395.

^b R. B. Turner, P. Goebel, B. J. Mallon, W. von Doering, J. F. Coburn Jr., and M. Pomerantz, *J. Amer. Chem. Soc.* **90** (1968) 4315.

^c P. von Schleyer, *J. Amer. Chem. Soc.* **80** (1958) 1700.

^d R. Turner, W. Meador, and R. Winkler, *J. Amer. Chem. Soc.* **79** (1957) 4116.

is not exact* and there is no absolutely strain-free molecule in nature but this ideal is probably most closely approached by acyclic alkanes in their completely staggered form and transoid zig-zag conformation¹⁷. We shall confine our discussion to the angular strain, *i. e.* the strain arising from the deviation of bond angles from the ideal tetrahedral or 120° values. In principle, one can obtain the strain energy of a molecule by taking a difference between $\Delta_f H$ of a molecule in question and its acyclic strain-free analog. This approach involves two calculations. Since our final correlations with experimental quantities are empirical in nature we shall correlate directly the CC bond overlaps with the estimated »experimental« strain energies taken from the paper of Schleyer *et al.*¹⁷. We take into account only the CC overlap because the angular strain is a consequence of the bending of Ψ_{CC} hybrids from the CC internuclear lines¹⁸. It is tacitly assumed that the increased strength of the C—H bonds attached to the strained carbon skeleton^{2b} compensates or at least is linearly related to the nonbonded H...H repulsions. We tried to fit the experimental strain energies by the following relationship:

$$E_s = K_{C-C}^\sigma \sum S_{C-C}^\sigma + K_{C-C}^\pi \sum S_{C-C}^\pi + K_{C=C}^\sigma \sum S_{C=C}^\sigma + K_{C=C}^\pi \sum S_{C=C}^\pi + L_{CC} n_{CC} \quad (6)$$

where n_{CC} is a number of CC bonds in a molecule and the other symbols have the same meaning as in the eqn. (5). The optimum parameters obtained by the least squares method are:

* The amount of strain depends on the choice of the reference molecules. (For a lucid discussion of the common errors in estimation of strain see: B. Nelander and S. Sunner, *J. Chem. Phys.* **44** (1966) 2476). In spite of that, the concept of strain proved very useful in chemistry. It provides a basis for various empirical force field methods¹⁶ and it is very helpful in discussing reactivity of a series of related molecules.

$K_{C-C}^{\sigma} = -18.9$, $K_{C-C}^{\pi} = 1110.1$, $K_{C=C}^{\sigma} = -11.7$, $K_{C=C}^{\pi} = 211.5$, and $L_{CC} = 13.2$ (in kcal/mol). Again, the cyclopropyl ring requires a separate empirical constant $K_{C-C}^{\pi} = 189.1$ in order to obtain a reasonable agreement with experiment. We notice that the largest positive contribution to the strain arises from the single CC bond bending. The comparison with the »experimental« values of Schleyer *et al.*¹⁷ (Table III) reveals good semiquantitative agreement between

TABLE III.

Comparison between the experimental and correlated strain energies for some cyclic and polycyclic alkanes and alkenes.

Molecule	E_s (corr.) kcal mol ⁻¹	E_s (exp.) kcal mol ⁻¹	Diff. kcal mol ⁻¹
cyclobutane	24.6	26.9	-2.3
methylcyclobutane	24.9	27.0	-2.1
cyclopentane	4.5	7.2	-2.7
cyclohexane	5.2	1.4	3.8
cyclobutene	29.6	30.6	-1.0
1,2-dimethylcyclobutene	29.6	29.6	0
cyclopentadiene	6.9	2.9	4.0
norbornane	17.1	17.6	-0.5
norbornene	20.7	27.2	-6.5
norbornadiene	35.0	34.7	0.3
1,4-cyclohexadiene	1.6	2.2	-0.6
1,3,5-cycloheptatriene	0.8	-2.0	2.8
cyclooctatetraene	0.7	2.5	-1.8
1,3-dimethylene-cyclobutane	28.9	30.4	-1.5
1,3-cyclohexadiene	1.3	1.9	-0.6
bicyclo(2.2.2)octane	7.7	11.0	-3.3
cubane	167.4	166.0	1.4
adamantane	11.9	6.5	5.4
methylcyclopentane	6.4	7.87	-1.5
1,1-dimethylcyclopentane	7.2	7.23	0.0
bicyclo(1.1.1)pentane	105.2	92.7*	12.5*
cyclopropane	31.0	28.0	3.0
spiropentane	62.8	65.1	-2.3
bicyclopropyl	62.5	55.8	6.7
bicyclo(1.1.0)butane	65.5	66.5	-1.0
1,3-dimethylbicyclo(1.1.0)butane	65.9	70.0	-4.1
tetrahydrane	105		

* The force field calculation of N. L. Allinger, M. T. Tribble, M. A. Miller, and A. H. Wertz, *J. Amer. Chem. Soc.* **93** (1971) 1637.

the two sets of data. The standard deviation of our correlation (6) is 3 kcal/mol. It is interesting to mention that our results are particularly good for the molecules possessing large H...H distances *e.g.* cubane, 1,3 and 1,4-cyclohexadiene and cyclooctatetraene. We obtained, however, much higher strain in adamantane than Schleyer *et al.*¹⁷. The fairly good agreement obtained for strain energies indicates that indeed the angular strain represents the predominant form of strain for molecules considered in this paper. This finding is in agreement with the current opinion, that the angular strain is dominant in small ring compounds and in the molecules composed of small rings while the non-bonding interactions prevail in medium-sized cycloalkanes. Tetra-

hedrane C_4H_4 is an interesting molecule which is expected to exhibit large strain. This molecule itself was not so far synthesized, although its tricarboxymethyl substituted derivative is known to be stable¹⁹. The earlier theoretical estimates of the strain energy in tetrahedrane gave widely different results. The PNDO (partial neglect of differential overlap) method predicts a strain energy of about 150 kcal/mol²⁰. On the basis of this result and the calculated difference in strain energies between tetrahedrane and bicyclo(1.1.0)butane of 83 kcal/mol it was concluded that the former molecule would immediately isomerize *via* the bicyclobutadiene diradical to cyclobutadiene²⁰. Therefore tetrahedrane would not be isolable at room temperature. The valence bond calculations, similar to that performed by Coulson and Moffitt²¹ on cyclopropane, were done by Weltner²² employing perfect pairing approximation. This estimate of the strain energy of tetrahedrane is about 90 kcal/mol. It should be mentioned that Baird and Dewar²⁰ and Weltner²² used in their calculations the idealized geometry *e. g.* the C—C bond lengths were taken to be 1.534 Å usually found in aliphatic chains. We calculated the geometry of tetrahedrane by the IMOA (iterative maximum overlap approximation) method¹² and obtained 1.491 Å and 1.065 Å for C—C and C—H bond lengths respectively. Our estimate of the strain energy in this molecule is 105 kcal/mol. The formula (6) may be employed for the prediction of strain energy in other molecules which are also not used in the derivation of this correlation. For example, we estimated the strain energy of biphenylene (77.7 kcal/mol) which can be favourably compared with the earlier calculation of 74 kcal/mol²¹. This result is only in qualitative agreement with the experimental value (60 kcal/mol)²³. However, in our MOA method we treat only sigma electrons explicitly and the pi electrons are regarded as perfectly localized. The delocalization energy, which undoubtedly exists in biphenylene, taken properly into account would stabilize the molecule thus lowering our estimated strain energy.

The question arises now why the simple model of variable hybridisation works so well for $\Delta_f H$ in nonconjugate hydrocarbons. The answer to this question is perhaps Dewar and Pettit's finding that the interaction between the localized two-center orbitals vanishes to a first approximation and that the second order effect can be to a large extent absorbed into the empirical bond energy scheme⁷. We shall discuss Dewar and Pettit's approach in greater detail since it is very instructive. This scheme is based on three essentially different types of interaction, namely the interaction within the fragments C—C—C, C—C—H, and H—C—H which will be denoted by *a*, *b*, and *c*, respectively. Then the heats of formation of alkanes can be calculated by simple addition of the bond energies E_{CH} and E_{CC} defined as

$$E_{CH} = E_{CH}^{\circ} + (1/4)(2b + 5c - a) \quad (7)$$

$$E_{CC} = E_{CC}^{\circ} + (3/2)(a + 2b - c)$$

where E_{CH}° and E_{CC}° stand for the standard C—C and C—H bonds which are constant for all bonds. They are estimated empirically as well as the interactions *a*, *b*, and *c*. It should be pointed out here that E_{CH}° and E_{CC}° represent the energies of the localized bonds formed by overlapping of hybrid orbitals with the hydrogenic orbital. The terms $(1/4)(2b + 5c - a)$ and $(3/2)(a + 2b - c)$ in eqns. (7) describe the interactions of the localized C—H and

C—C bonds with their immediate neighbourhood. The Dewar and Pettit's bond additivity scheme is quite successful for alkanes. However, there is still room for its improvement particularly if one tries to extend it to strained ring compounds where E_{CH}° and E_{CC}° »standard« bond energies may considerably vary from molecule to molecule. Here, the variable hybridization could be very useful in order to give reasonable estimates of E_{CH}° and E_{CC}° energies. Our results are supported also by Fischer and Kollmar's CNDO/2 study²⁴ of the heats of atomization in hydrocarbons. They found that the net contribution to molecular binding energy comes from the so called resonance energy $E_{\text{AB}}^{\text{r}} = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \beta_{\mu\nu} S_{\mu\nu}$ where A and B are the two directly bonded neighbouring atoms, $P_{\mu\nu}$ is the familiar element of the density matrix, $S_{\mu\nu}$ is the overlap integral between the atomic orbitals Φ_{μ} and Φ_{ν} and $\beta_{\mu\nu}$ is the appropriate empirical weighting factor. This very important conclusion is concomitant with our MOA results that the bonding overlap between the neighbouring hybrid orbitals is responsible for the largest amount of $\Delta_{\text{f}}H$ in nonconjugated hydrocarbons. It is also interesting to mention that the contribution of the nonbonding interactions to $\Delta_{\text{f}}H$ is negligible according to Fischer and Kollmar's analysis of CNDO/2 calculations²⁴.

In view of the present calculations and earlier results¹, we feel confident in saying that the model of the variable hybrid orbitals provides a very useful basis for discussing the physical and chemical properties of molecules. However, in most quantum chemical formulations the hybrids represent merely an arbitrary unitary transformation of the initial basis set functions and consequently they should have no effect on any observable. This is true if one uses a complete set of one-electron wave-functions in the Hartree-Fock theory. However, in practice we have to work with finite numbers of one-electron wave functions, or in other words, with incomplete sets of functions. In cases like that, the choice of the basis set becomes very important and the use of the hybrids instead of pure atomic s, p, d *etc.* orbitals should be advantageous. Firstly, the hybrid orbitals satisfy the local symmetry requirements, and consequently they are the first natural choice of the basis set functions. Secondly, the hybrid orbitals centered on the same atom avoid each other much more efficiently than the pure s, p *etc.* orbitals and therefore provide a better basis for a description of the electron correlation. Furthermore, the hybrid orbitals describing similar structural units in different molecules are transferable. One could expect that the matrix elements in the Hartree-Fock matrix would be also transferable if the hybrid basis set was used. Therefore, it is very likely that the hybridization represents the first step in solving one of the most important problems in quantum chemistry *i. e.* the quantum mechanical description of molecules by their fragments. The hybrids could be certainly useful for a construction of two-center localized orbitals called geminals^{25,26} which are actually the building blocks for most molecules. The additivity of bond energies, which is still not very well understood, could probably be rationalized by these two electron geminals.

Our results, obtained by the MOA method indicate that the hybrid orbitals frequently contain a large body of physical and chemical information. The present calculations show that the variable hybridization model gives fairly good account of the heats of formation in nonconjugated hydrocarbons. It

should be mentioned that in empirical force field methods the angle strain is usually estimated by the formula

$$E_a(s) = (k_b/2) (\alpha - \alpha_n)^2 \quad (8)$$

where α_n is the »normal« or unstrained value, α is the actual value of the CCC angle and k_b is the bending force constant. Since our method of calculating the angle strain, which employs a very simple physical model of Ψ_{CC} bending, works quite well, the success of formula (8) must be a consequence of the underlying very close relation between the bending of hybrids and the corresponding force constants. Therefore, the variable hybridization model provides a missing link between molecular mechanics and quantum mechanics.

Although the qualitative agreement with experiments for heats of formation, heats of hydrogenation, and strain energies is good, the quantitative agreement is still not quite satisfactory. Therefore, the model needs some refinements. The weak points of the present form of our approach are as follows. The nonbonding repulsions are completely neglected. This is not a significant failure for »normal« molecules but could be a serious shortcoming in the description of overcrowded systems. The neglect of nonbonded repulsion could be remedied by taking into account the negative overlap between the nonbonded groups weighted by a proper empirical factor²⁷. The use of the plain proportionality between the bond overlap and bond energy in eqn. (3) is not quite justified. It would be probably advantageous to develop the bond energy in a series of overlap integrals $E_b = A_0 + A_1S + A_2S^2$ where a significant contribution of the A_2S^2 term could be anticipated in view of the importance of the kinetic energy* in chemical bonding²⁸. The valence state energy of carbon be also included in the expression for the total energy by taking into account s^2p^2 , sp^3 and p^4 configurations as discussed by Jordan and Longuet-Higgins^{18a} and Offenhartz^{18b}. The delocalization of pi-electrons could be included, within the approximation of sigma-pi separability, by adoption of molecular maximum overlap (MOMO) orbitals²⁹ for these electrons. In fact, the MOMO orbitals are equivalent to Hückel molecular orbitals²⁹. Finally, the empirical constants which relate the overlap integrals to experimental heats of formation in eqn. (5) should be calculated in the following self-consistent manner: the calculated constants in this paper provide the results of the first iterative step. The next optimum hybrid parameters should be evaluated by minimizing the expression (5) for heats of formation and the next set of correlation constants is obtained by fitting the experimental data. This process is continued until self-consistency for all K_{CC} , K_{CH} etc. empirical parameters is achieved. The quality of the present results indicates that this type of approach is worth of effort.

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* The kinetic energy integrals are proportional to the square of the corresponding overlap integrals.

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SAŽETAK

Izračunavanje toplina stvaranja, toplina hidriranja i energija naprezanja kod nekih nekonjugiranih ugljikovodika metodom maksimalnog prekrivanja

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Primjenom metode maksimalnog prekrivanja izračunane su topline stvaranja nekih nekonjugiranih ugljikovodika kao i energije naprezanja malih prstenastih molekula. Postignuto je dobro slaganje s eksperimentalnim podacima. Dobiveni rezultati pokazuju da je prekrivanje susjednih hibridnih orbitala odgovorno za najveći dio toplina stvaranja molekula. Ustanovljeno je da energija naprezanja u prstenastim ugljikovodivima prouzrokuje izvijanje hibrida ψ_{CC} izvan geometrijske spojnice susjednih C-atoma. Izračunane topline hidriranja u dobrom su kvalitativnom slaganju s eksperimentom.

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