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THE CALCULATION OF STRAIN ENERGY BY MOLECULAR ORBITAL THEORIES

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Abstract—Strain energies are calculated for a series of polycyclic alkanes containing small-membered rings by the MINDO molecular orbital theory. Comparison of experimental and theoretical strain energies indicates that while the MINDO method accounts for the total strain semiquantitatively, it fails to predict correctly the nonadditivity of strain in bicyclic and spirocyclic systems. Significant strain energies are also predicted for cyclopropane and cyclobutane by the Extended Huckel Method, although these effects are swamped by errors introduced in the handling of nonbonded interactions by the method.

INTRODUCTION

Beginning in 1963 with the introduction of the Extended Huckel Theory by Hoffmann,[1] several semiempirical MO methods, which consider explicity all valence electrons in molecules, have been devised.[2–5] Extensive application of these theories has been made to the calculation of charge and spin densities, dipole moments, bond angles, conformational effects, electronic excitation energies, etc. In contrast, the calculation of accurate bonding energies for the ground states of organic molecules has received relatively little attention. This is perhaps not surprising, since empirical techniques are available by which heats of formation (ΔH_f's) of most compounds can be deduced.[6]

There remains one class of organic molecules, however, to which the empirical schemes cannot be applied as yet and for which little thermochemical data is available: strained, polycyclic hydrocarbons. Since the thermal properties of such compounds is required in order to evaluate their physical and chemical stabilities, Dewar *et al.* have attempted to devise LCAO-MO theories which can be used to calculate accurately strain energies.[3, 4] The MINDO method appears particularly promising in this respect, since the calculations successfully reproduce the ΔH_f's of acyclic hydrocarbons to ± 1 kcal/mole and ΔH_f's of several strained cyclic and bicyclic systems to ± 5 kcal/mole.[4] In contrast, the Extended Huckel Method is completely "blind" to the strain in small-membered rings.[1]

The present study was undertaken to test thoroughly the ability of the MINDO method to predict the strain energy characteristics of polycyclic hydrocarbons. In particular, it is important to determine whether the theory is successful in calculating the *deviations from additivity* in the total strain for hydrocarbons containing fused rings. The theoretical reasons behind the inability of the Extended Huckel Method to account for strain are also explored.

THEORY

In the Modified Intermediate Neglect of Differential Overlap (MINDO) method, the molecular orbitals ψ_i for valence electrons are expanded as linear combinations of the valence-shell atomic orbitals:

$$\psi_i = \sum_u C_{iu} \varnothing_u \qquad (1)$$

The basis set for hydrocarbons consists of 1s orbitals of hydrogen, and 2s and 2p orbitals of carbon. The Roothaan SCF-LCAO-MO equations for molecules are simplified by neglecting 2-, 3-, and 4-centre integrals which involve differential overlap between different atomic orbitals. The one-center energy integrals are evaluated empirically using experimental data for the isolated atoms, whereas the remaining 2-center integrals are calculated using semi-empirical formulae.[4]

The resonance integrals β^{AB}_{uv} between atomic orbitals ϕ_u and ϕ_v (centered on atoms A and B respectively) are evaluated according to the equation

$$\beta^{AB}_{uv} = S_{uv}(I^A_u + I^B_v)\,(\beta^I_{AB} + [\beta^{II}_{AB}/R^2_{AB}]). \qquad (2)$$

Here S_{uv} is the overlap integral between the orbitals, I^A_u and I^B_v represent valence-state ionization potentials, and R_{AB} is the distance between the atoms. The values used for the empirical parameters β^I and β^{II} for the H—H, C—H, and C—C interactions in the hydrocarbons considered herein are identical to those previously employed.[4]

The same basis set and orbital exponents (1·0 for H, 1·625 for C) are used in the original Extended Huckel Method.[1] In the EHT scheme, however, overlap integrals S_{uv} between different orbitals are retained in the secular equations. The diagonal elements F_{uv} of the Roothaan equations are assigned characteristic values corresponding to valence-state ionization potentials, and the off-diagonal terms are calculated as

$$F^{AB}_{uv} = KS_{uv}\,(F^{AB}_{uu} + F^{BB}_{vv})/2 \qquad (3)$$

The empirical parameter K is taken as 1·75, and consequently is independent of the nature of the atoms A and B.[1]

In summary, both EHT and MINDO are semiempirical LCAO-MO methods, the former being a *one-electron* theory which includes overlap integrals and the latter a *two-electron* theory which neglects differential overlap.

RESULTS

Molecular orbital calculations by the MINDO method are reported in Table 1 for a series of cyclic alkanes. C—C distances of 1·514Å, 1·555Å, and 1·534Å are used for the bonds in 3-, 4- and 5-membered rings, respectively,[4] arithmetic averages of these values are employed for bonds common to two rings. The bond length in methane of 1·093Å is used for all C—H linkages.[4]

The HCH bond angles at methylenic C atoms in 3-, 4-, and 5-membered rings are taken as 120°, 114°, and 109·5° respectively.[3, 4] The assumed angle between the planes of the two rings in the bicyclic alkanes IV–VIII is 120°, and similarly for XI. The remaining geometric variables for the molecules are defined by employing the structure of greatest symmetry, and using CCH bond angles of 120° at bridgehead carbons.

The strain energies of the alkanes are computed using Benson's group equivalent values[6] and the calculated and experimental heats of formation (ΔH_f) at 25°. The calculated deviations from additivity in the strain energies for polycyclic systems are

TABLE 1. MINDO STRAIN ENERGIES IN HYDROCARBONS (kcal/mole)

Hydrocarbon	ΔH_f[a]		Total Strain[e]		Deviation from Additivity	
	Calcd[b]	Exptl[c]	Calcd	Exptl	Calcd	Exptl
Cyclopropane (I)	+16·4	+12·73	31·2	27·6	—	—
Cyclobutane (II)	+11·3	+6·35	31·1	26·2	—	—
Cyclopentane (III)	−19·2	−18·46	5·5	6·3	—	—
Bicyclo[1.1.0]butane (IV)	+52·3	+51·9	66·0	65·6	+3·6	+10·4
Bicyclo[2.1.0]pentane (V)	+43·3	+36·7[d]	62·0	55·4	−0·3	+1·6
Bicyclo[3.1.0]hexane (VI)	+15·8	+9·1[d]	39·4	32·7	+2·7	−1·2
Bicyclo[2.2.0]hexane (VII)	+35·6	—	59·2	—	−3·0	—
Bicyclo[3.2.0]heptane (VIII)	+7·3	—	35·9	—	−1·0	—
Spiropentane (IX)	+42·2	+44·23	61·5	63·5	−0·9	+8·3
Spirohexane (X)	+37·3	—	61·6	—	−0·7	—
Bicyclo[1.1.1]pentane (XI)	+49·9	—	68·6	—	−24·7	—
Tetrahedrane (XII)	+135·2	—	142·8	—	+18·0	—
Cubane (XIII)	+116·9	+148·7	132·1	163·9	−54·5	+6·7

[a] At 25°

[b] Several of these values have been reported previously; see ref. 4

[c] From the compilation in ref. 4 unless otherwise indicated

[d] R. H. Boyd, to be published

[e] Calculated via the group equivalent values in ref. 6

computed using as a standard the sum of the strain energies summed over all the faces of the hydrocarbons.

All Extended Huckel calculations use the bond lengths and parameters recommended by Hoffmann.[1]

DISCUSSION

A comparison of the calculated strain energies with the experimental values in the eight cases (I–VI, IX, XIII) for which the latter is available indicates that the MINDO method accounts for the total strain energy to within ±20% in alkanes (Table 1). Thus the MINDO method is at least an order of magnitude more accurate than other existing molecular orbital theories in handling ring strain.

However, organic chemists are usually more interested in accurate values for the *deviations from additivity* in the strain for polycyclic hydrocarbons than in an approximate value for the total effect. For example, the strain energy in bicyclobutane (IV) is *expected* to be roughly twice that of cyclopropane (I) since there are two 3-membered rings in the former. The quantity of real interest is then the degree to which the bicyclobutane strain *exceeds* (or is less than) the value calculated by additivity.

Thus the real test of the utility of the MINDO method for thermochemical applications rests in its ability to account for the departures from additivity in the strain of polycyclic compounds. The deviations from additivity of strain computed from both the theoretical and experimental strains are listed in Table 1; the theoretical values are evaluated using the theoretical strain energies in I, II, and III.

The only substantial deviation from strain additivity in the bicyclo [n.m.o.] alkanes occurs for bicyclobutane (IV). The MINDO strain for this compound is 3·6 kcal/mole greater than twice the calculated strain for cyclopropane, compared to the + 10·4 kcal/mole difference observed experimentally (Table 1). For bicyclopentane (V) and bicyclo [3.1.0] hexane (VI), the calculated and observed deviations are very small, but in both cases MINDO predicts the sign incorrectly. Since the experimental deviations for bicyclo [m.1·0] alkanes progressively decrease as m is increased whereas the theoretical values do not, the calculated deviations for VII and VIII may be in error by several kilocalories. Thus, at best, the MINDO theory accounts only *qualitatively* for the nonadditivity of strain in bicyclic alkanes.

Calculations are reported in Table 1 for two spiroalkanes—spiropentane IX and spirohexane (X). A substantial increase over additivity is observed experimentally for IX, whereas MINDO predicts that the deviations should be small and negative for both IX and X. Thus the MINDO method is completely blind to "spiro strain"!

The situation is even worse for cubane (XIII). The experimental strain energy is just slightly *greater* than six times that for cyclobutane, whereas MINDO predicts it should be some 54·5 kcal/mole *smaller*. A large negative deviation from additivity is also predicted for bicyclo [1.1.1] pentane (XI), compared to the substantial positive deviation predicted for tetrahedrane (XII).

In summary, the MINDO method generally *underestimates* the additional strain energy, over and above that estimated by simple additivity rules, in most polycyclic alkanes. The reasons for this failure of the theory are not entirely clear. It is possible that more accurate results can be obtained if the actual bond distances and angles in particular hydrocarbons are used in place of the averages assumed. Since, in its present form, MINDO does not successfully predict C—C or C—H bond lengths, however, this would restrict the use of the method to compounds whose structures have been accurately determined.

Even more striking than the failures discussed above for MINDO method is the fact that the Extended Huckel Method is "blind" to ring strain even in cyclopropane and in cyclobutane.[1] The theoretical reasons for this discrepancy can be seen clearly by an analysis of the "bond energy" terms predicted by the Extended Huckel Method.

In one-electron molecular orbital theories (such as EHT), the total molecular energy E is given by

$$E = \sum_{u} \sum_{v} P_{uv} F_{uv} \tag{4}$$

where P_{uv} is the Coulson bond-order index

$$P_{uv} = 2 \sum_{i}^{\text{occ.}} C_{iu} C_{iv} \tag{5}$$

and where the summation runs over all doubly-occupied molecular orbitals. It is possible to split E into a series of energy terms for each atom A,B,...... as

$$E_A = \sum_{u}^{(A)} \sum_{v}^{(A)} P_{uv} F_{uv} \tag{6}$$

and a series of contributions from each pair of atoms A-B, A-C, ...

$$E_{AB} = 2 \sum_{u}^{(A)} \sum_{v}^{(B)} + P_{uv} F_{uv} \tag{7}$$

such that

$$E = \sum_{A} E_A + \sum_{A<B} \sum E_{AB} \tag{8}$$

We have performed the above analysis on EHT results for C_2H_6, C_3H_8, n-C_4H_{10}, cyclopropane, and cyclobutane, and the results can be summarized as follows:

(1) The atom energies for carbon are remarkably constant at $-40{\cdot}8 \pm 0{\cdot}2$ ev in both the acyclic and cyclic alkanes, and similarly for the hydrogen atom energies of $-8{\cdot}2 \pm 0{\cdot}2$ ev.*

(2) As expected, large negative energies are found for each C—H and C—C bond in the acyclic series. Although the C—C bond energies in the latter follow empirical trends, the corresponding terms in cyclopropane and in cyclobutane are much smaller (by 18% and 9% respectively) than that calculated for acyclic $—CH_2—CH_2—$ linkages. *Thus the effects of strain are present in the bonded interactions calculated by the Extended Huckel Method.*

(3) Unexpectedly large positive (and hence antibonding) interaction energies of $+1{\cdot}8 \pm 0{\cdot}2$ ev are predicted for each pair of atoms (H—H, C—H, and C—C) which form bonds to a common C atom in both the acyclic and cyclic alkanes.† All other nonbonded interactions are very small in comparison.

As a whole, both the nearest-neighbour and second-nearest neighbour interactions are overestimated by EHT, the former being too negative and the latter too positive. The two errors of opposite sign tend to compensate each other in the n-alkanes and the medium and large cyclo-alkanes; Hoffmann established that the energy increment per $—CH_2$-group added in these compounds followed the empirical trends.[1]

Unfortunately, this compensation cannot occur in cyclopropane and cyclobutane, since the total number of α,γ nonbonded interactions per $—CH_2$-group in these systems is less than that for the acyclics and larger rings. Addition of one methylenic unit into an n-alkane increases the number of C—C and C—H bonds by 1 and 2 respectively, and the number of α—γ H—H, C—H, and C—C nonbonded interactions by 1, 4, and 1 respectively. Thus the number of C—C nonbonded interactions "expected" for cyclopropane is three, compared to zero actually present. Thus the compensation of errors is not complete in cyclopropane (or in cyclobutane), with the result that the *total* energy shows no *apparent* strain effects, even though the C—C bonded interactions are in fact reduced.

The origin of the overestimation of nonbonded interactions by EHT probably lies in the evaluation of the off-diagonal F_{uv} matrix elements (equation 2). According to simplified SCF theories,[5]

$$F_{uv} = \beta_{uv} - \tfrac{1}{2} P_{uv} \gamma_{uv} \tag{9}$$

where β_{uv} and γ_{uv} have opposite signs. For *bonded* interactions (where P_{uv} has the same sign as β_{uv}) both β_{uv} and $-\frac{1}{2}P_{uv}\gamma_{uv}$ are of like sign, and one can assume that F_{uv} is roughly proportional to β_{uv} alone. For *nonbonded* interactions however, the two terms in F_{uv} are of *opposite* sign and cancel each other to a large extent so that the total F_{uv}

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* These atom energies are significantly smaller than those in the free atoms, since much of the electron density is delocalized as overlap density in the molecules rather than localized on the individual atoms.

† The only nonbonded interaction of this type which falls outside the range quoted occurs in cyclobutane, where $E(C_1—C_3) = +3{\cdot}2$ ev.

is small. This compensation cannot be made using an equation for F_{uv} which does not involve P_{uv}. Thus the Extended Huckel Method has difficulties in handling nonbonded effects at small internuclear separations since the same parametric relationship (Equ 3) is employed for both bonded and nonbonded interactions. Presumably this difficulty could be overcome by iterative EHT schemes in which F_{uv} is dependent explicitly upon P_{uv}.

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