Tetrahedron Letters No. 2, pp 101 - 104, 1975. Pergamon Press. Printed in Great Britain.

THE CALCULATION OF STRAIN ENERGIES IN CYCLIC AND POLYCYCLIC HYDROCARBONS BY THE MAXIMUM OVERLAP APPROXIMATION

Z.B.Maksić*, K.Kovačević and M.Eckert-Maksić

Institute "Ruđer Bošković", 41001 Zagreb, Croatia, Yugoslavia and Department of Physical Chemistry, The University of Zagreb, 41000 Zagreb, Croatia, Yugoslavia

(Received in UK 6 November 1974; accepted for publication 26 November 1974)

Although the molecular strain energy can not be rigorously defined because its numerical values depend on the choice of the reference strain-free molecule(s)[1], or on the more or less arbitrary choice of the nonbonded potential functions[2], the concept of strain proved very useful in chemistry. It provides a basis for various empirical force field methods and it is useful in discussing the reactivity of a series of related molecules. The aim of this paper is to show that the angular or Baeyer strain arises due to the bending of the local hybrid orbitals. The details of the variable hybridization method based on the maximum overlap criterion are published elsewhere[3]. Briefly, the local hybrid orbital placed on the atom A is of the form:

$$\Psi_{A_i} = a_{Ai}(2s) + (1-a_{Ai}^2)^{1/2}(2p)_{Ai} \qquad (1)$$

where i refers to the direction in space of the $(2p)_{Ai}$ orbital. It was shown by the numerous semiempirical SCF-MO calculations that the local hybrid orbitals are very nearly orthogonal[4]. Therefore the hybrids (1) are constrained in the maximum overlap approach to be orthonormal which yields a set of conditions:

$$a_{Ai}\, a_{Aj} + (1-a_{Ai}^2)^{1/2}(1-a_{Aj}^2)^{1/2} \cos\theta_{ij} = \delta_{ij} \qquad (2)$$

where θ_{ij} denotes the angle between the symmetry axes of the hybrids Ψ_{Ai} and Ψ_{Aj}. The relationship (2) enables the theoretical determination of bond angles. The hybridization parameters a_{Ai} are calculated by maximizing the sum of the weighted bond overlaps:

$$E_b = k_{CC}\sum_{C-C} S_{CC} + k_{CH}\sum_{C-H} S_{CH} \qquad (3)$$

where $S_{AB} = \int \Psi_A \Psi_B \, dv$ is the overlap integral. The proportionality constants k_{CC} and k_{CH} take into account the difference in energy of CC and CH bonds. Their numerical values are $k_{CC} = 121.2$ and $k_{CH} = 135.9$ (in kcal/mole). It is well known that the hybrid orbitals subject to the orthogonality conditions (2) can not follow the molecular angles in small ring compounds, i.e. the so called bent bond appear[6]. The overlap of the bent hybrids is relatively poor causing thus increase in molecular energy. This is the main reason behind the angular strain and its empirical potential function $V = (k_{\alpha}/2)(\alpha - \alpha_0)^2$ where k_{α} is the bending force constant and $\alpha - \alpha_0$ is the angular deformation from the standard strain-free α_0 value. We correlated the CC bond overlaps with "experimental" strain energies for twenty characteristic cyclic and polycyclic hydrocarbons. Since in the case of bent bonds there are two types of interaction, σ and π, which should be parametrized separately, the correlation formula was of the form

$$E_s = k^{\sigma}_{C-C} \sum S^{\sigma}_{C-C} + k^{\pi}_{C-C} \sum S^{\pi}_{C-C} + l_{CC}\, n_{CC} \qquad (4)$$

where S^{σ}_{C-C} and S^{π}_{C-C} are the σ and π components of the total overlap of the bent bond and n_{CC} is the number of CC bonds. The empirical constants k_{CC}, k_{CC} and l_{CC} were optimized in the sense of the least squares method. If the double C=C bonds were present in a molecule then two additional constants $k^{\sigma}_{C=C}$ and $k^{\pi}_{C=C}$ were necessary in order to describe their σ and π interactions. The experimental estimates of strain energies were taken from Schleyer et al[1]. It was tacitly assumed in our calculations that the enhanced strength of C-H bonds attached to strained carbon rings at least partially cancels the nonbonded repulsions. The least square fit method gave the following optimum parameters: $k^{\sigma}_{C-C}=-18.9$, $k^{\pi}_{C-C}=1110.1$, $k^{\sigma}_{C=C} = -11.7$, $k^{\pi}_{C=C}=211.5$ and $l_{CC}=13.2$ (in kcal/mole). We notice that the angular strain is a consequence of the bending of Ψ_{CC} hybrids since the constants k^{π}_{C-C} and $k^{\pi}_{C=C}$ are large and positive. The additive constant l_{CC} actually cancels the stabilizing effect of σ-bonding. This is most easily seen in ethane. If one substitutes $n_{CC}=1$, $k^{\sigma}_{C-C}=-18.9$, $l_{CC}=13.2$, $S^{\pi}_{C-C}=0$ in the eqn. (4) and takes into account that the S^{σ}_{C-C} overlaps is roughly 0.7 it turns out that the (angular) strain is zero as it should be. The calculated and "experimental" strain energies are presented in the Table I. Since the correlation coefficient is 0.996 the probability that the calculated strain energies are uncorrelated is less than 0.01%. The correlated values are in fairly good agreement with the experimental ones the standard deviation being 2.8 kcal/mole. Our results are particularly good for molecules possesing large H...H nonbonded distances e.g. cubane, 1,3 and 1,4-cyclohexadiene and cyclooctatetraene. The present correlation indicates that the angular strain is a predominant factor in determining the strain energy in small cyclic and polycyclic hydrocarbons and that other types of molecular

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

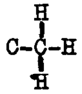
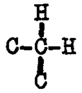
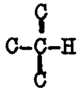
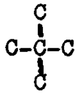
Molecule	E_s (corr.)	E_s (exp.)[a]	Diff.
cyclobutane	24.6	26.9	-2.3
methylcyclobutane	24.9	27.0	-2.1
cyclopentane	4.5	7.2	-2.7
cyclohexane	5.2	1.4	3.8
cyclobutene	29.6	30.6	-1.0
1,2-dimethylcyclobutene	29.6	29.6	0
cyclopentadiene	6.9	2.9	4.0
norbornane	17.1	17.6	-0.5
norbornene	20.7	27.2	-6.5
norbornadiene	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[b]	12.5

[a] the "experimental" estimate of strain energies were taken from the ref.(6)

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

deformation energy and nonbonded repulsions could be successfully adsorbed in the empirical parameters. The angular strain is a consequence of the hybrids' bending. Therefore, the variable hybridization model provides a simple quantum mechanical rationalization of the empirical force field methods. This conclusion is substantiated by a comparison between the natural (or strain-free) bond angles employed in various force field methods and bond angles calculated by the maximum overlap approximation (MOA) shown in the Table II. There is a high degree of similarity between the

Table II. Comparison between the natural bond angles employed in various force field methods and bond angles calculated by the maximum overlap approximation (MOA).

Functional group	Allinger et al.[a]	Schleyer et al.[b]	MOA
 $\mathrm{C{-}\overset{H}{\underset{H}{C}}{-}H}$	α_0(C-C-H)=107.8° α_0(H-C-H)=111.2°	109.5° 109.2°	109.04° 109.90°
 $\mathrm{C{-}\overset{H}{\underset{C}{C}}{-}H}$	α_0(C-C-H)=112.8° α_0(H-C-H)=108.5° α_0(C-C-C)=110.2°	109.0° 109.1° 110.4°	109.5° 108.5° 110.5°
 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}H}$	α_0(C-C-H)=108.4° α_0(C-C-C)=110.6°	109.2° 110.1°	109.4° 109.5°
 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$	α_0(C-C-C)=109.47°	109.47°	109.47°

[a] ref. (7); [b] ref. (2)

natural and MOA bond angles. Thus we can say that the maximum overlap local hybrid orbitals provide a link between the molecular mechanics and rigorous quantum mechanics.

Acknowledgement: We thank to Proffessor C.F. Wilcox, Jr. for inspiring discussions and to the referee for a useful comments.

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