An Empirical Model for Nonbonded H–H Repulsion Energies in Hydrocarbons

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A suggestion of Mulliken for estimating nonbonded H–H repulsion energies has been applied in cases of interest in organic chemistry. The energy expression, derived from LCAO theory, generates in effect a potential function which is only dependent on 1s–1s overlap integrals. This simple model has qualitative value in predicting rotation barriers, conformational enthalpies, and thermodynamic stabilities of hydrocarbons which are relatively free of angle strain. A scheme has been devised based on Dreiding models, an "Ångstrom ruler," and a plot of repulsion energy vs. distance that allows rapid estimation of LCAO repulsion energies and should be a useful adjunct to the use of molecular models.

Introduction

Intramolecular nonbonded repulsive interactions make important contributions to the general phenomenon of steric effects and so influence kinetic, thermodynamic, conformational, and spectral properties of organic molecules. These interactions are not fully understood theroretically, and their relationship to experimental observations has aroused much controversy. Notwithstanding this incomplete picture, organic chemists have found the concept of nonbonded repulsive interactions to be useful,[1] and several empirical and theoretical potential functions have been derived for their calculation.

The purpose of this paper is to consider a semiempirical scheme, based on a suggestion of Mulliken,[2] for the estimation of nonbonded hydrogen–hydrogen repulsions in some selected hydrocarbons. At the outset it must be emphasized that no sound theoretical foundation can be offered for the resulting simple model of hydrocarbons. This treatment of these weak interactions may be useful to the chemist in the same spirit as many other modern empirical concepts.

A Semiempirical Model.—Recently Hoffmann[3] has shown that LCAO theory (using a basis set of 2s and 2p carbon and 1s hydrogen AO's) predicts a rotation barrier in ethane. When his treatment was adjusted to agree with the experimental barrier, subsequent calculations of the LCAO binding energy as a function of conformation showed that the gross geometry of several hydrocarbons was correctly predicted. This model, for example, correctly finds that the energy of the chair form of cyclohexane is lower than that of any boat form. It is not generally possible to relate a Hückel calculation (with its unspecified Hamiltonian) to the set of specific physical effects currently believed responsible for the determination of molecular geometry.[4] However, it has been suggested by Mulliken[2] that one of these effects, nonbonded H–H repulsions,

can be simulated by considering four electrons in two isolated carbon–hydrogen bonds and treating this system by either MO or VB theory. In this manner, Mulliken concluded that this repulsion energy was simply proportional to the square of the overlap integral of two 1s hydrogen distributions. Although this theory is too naive to represent the physical problem, it seems reasonable to us that nonbonded H–H repulsions will be reflected in a qualitative sense by the overlap integral.

Spectroscopic studies are not fully in agreement as to the magnitude of nonbonded H–H repulsions, particularly those of geminal hydrogens[5]; however the steric effect of hydrogen atoms has been used fruitfully to explain many observations in organic thermochemistry.[6,7] It is in this latter light that we will employ the term nonbonded H–H repulsion. Hendrickson[8] has studied the conformational energies of the C_5–C_7 cycloalkanes and concluded that their geometry is determined largely by the nonbonded H–H interactions. Attempts have also been made to treat nonbonded effects in hydrocarbons by considering principally carbon–hydrogen interactions.[9]

The Hoffmann[3] and Mulliken[2] views have a common origin, and we might expect that results obtained from the simple Mulliken theory will embody those from the lengthier solution of a secular equation. Our purpose is to explore the use of the Mulliken relation (1)[2]

$$E_{HH} = AIS^2/2(1 - S^2) \qquad (1)$$

where A is a constant, S is the overlap integral for two 1s hydrogen distributions, and I is the valence state ionization potential of hydrogen. In this way we seek to treat nonbonded H–H repulsions in a purely additive fashion. Since eq. 1 is to be used solely as a semiempirical relation, nonbonded attractions will not be taken explicitly into account although it is recognized that this is a serious simplification. Mulliken showed[2] that eq. 1 was able to reproduce remarkably well the van der Waals

(1) See articles by W. G. Dauben and K. S. Pitzer and by F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

(2) (a) R. S. Mulliken, J. Am. Chem. Soc., **72**, 4493 (1950); (b) R. S. Mulliken, Record Chem. Progr. (Kresge-Hooker Sci. Lib.), **13**, 67 (1952).

(3) R. Hoffmann, J. Chem. Phys., **39**, 1995 (1963).

(4) (a) K. S. Pitzer, Discussions Faraday Soc., **10**, 66, 124 (1951); (b) C. A. Coulson, "Valence," Oxford Press, London, 1952, pp. 314–317; (c) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954; (d) L. J. Oosterhoff, Discussions Faraday Soc., **10**, 79, 87 (1951); (e) K. S. Pitzer, J. Chem. Phys., **8**, 711 (1940).

(5) (a) T. Simanouti, ibid., **17**, 245, 734, 848 (1949); (b) D. F. Heath and J. N. Linnett, ibid., **18**, 147 (1950); (c) L. S. Bartell and K. Kuchitsu, ibid., **37**, 691 (1962).

(6) E. A. Mason and M. M. Kreevoy, J. Am. Chem. Soc., **77**, 5808 (1955).

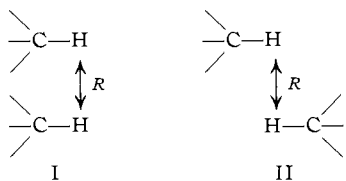(7) See the important series beginning J. Allinger and N. L. Allinger, Tetrahedron, **2**, 64 (1958), and later papers in J. Am. Chem. Soc.

(8) J. B. Hendrickson, ibid., **83**, 4537 (1961); ibid., **84**, 3355 (1962).

(9) A. I. Kitaygorodsky, Tetrahedron, **14**, 230 (1961).

repulsion energy between two helium atoms as computed by direct theoretical procedures in the range 1–3 Å. when $A = 0.65$. Our studies of hydrocarbons show that a value of $A_{HH} = 0.95$ gives the best agreement with experiment in several problems. This empirical adjustment enhances the magnitude of H–H repulsions beyond the range currently believed reasonable,[5c,10] so that in effect the overlap function is forced to compensate for the neglect of other significant effects. At short distances (<2 Å.) eq. 1 will overestimate repulsions because of the inherent hardness of the overlap function, while at large distances the neglect of dispersion forces suggests that the net nonbonded interaction will again be overestimated.

We assume that the hydrogens in carbon–hydrogen bonds in hydrocarbons can be treated as spherical 1s atomic distributions. No mention of the associated bond is made, and two hydrogen atoms in different environments, e.g., I and II, will contribute equally to the total repulsion energy as long as their internuclear separation R is the same.

$$\begin{array}{ccc}
\diagdown & & \diagdown \\
-C-H & & -C-H \\
\diagup \quad \updownarrow R & & \diagup \quad \updownarrow R \\
\diagdown & & \qquad \diagup \\
-C-H & & H-C- \\
\diagup & & \diagdown \\
I & & II
\end{array}$$

The total nonbonded H–H repulsion energy E_{HH} is expressed by eq. 2, where the sum is over all hydrogen atoms in the molecule numbered serially. The over-

$$E_{HH} = (A_{HH}I_H/2) \sum_{i>j} S_{ij}^2/(1 - S_{ij}^2) \qquad (2)$$

lap integral for 1s hydrogen orbitals (χ_H^{1s}) can be expressed as[11]

$$S(\chi_i, \chi_j : R_{ij}) = \int \chi_i^* \chi_j dv =$$
$$e^{-p}[1 + p + (1/3)p^2] \qquad (3)$$

where $p = R_{ij}/a_0$ is the internuclear separation expressed in Bohr units ($a_0 = 0.52917$ when R_{ij} is in Å.). The valence state ionization potential is 13.60 e.v. for hydrogen. An effective nuclear charge of unity is implicit in eq. 3, although a referee has pointed out that a value of 1.2 might be more realistic. Since we propose to treat primarily nonpolar hydrocarbons and seek a semiempirical relationship, we have retained the Slater value whose use appears partially justified by the results.

When two structures, isomers, conformers, etc. (A and B), are compared, the difference in nonbonded H–H repulsion energy $\Delta E_{HH}^{A,B} = E_{HH}^A - E_{HH}^B$ is given simply by eq. 4

$$\Delta E_{HH}^{A,B} = A_{HH}I_H/2 \left[\sum_{i<j} {}^A S_{ij}^2/(1 - S_{ij}^2) - \right.$$
$$\left. \sum_{m<n} {}^B S_{mn}^2/(1 - S_{mn}^2)\right] \qquad (4)$$

where i,j are hydrogens in A and m,n are hydrogens in B. Since the S_{ij} are dimensionless, $\Delta E_{HH}^{A,B}$ is given in kcal./mole when $A_{HH}I_H/2 = 149.05$ kcal./mole.

Applications.—Use of the Mulliken expression for the empirical estimation of nonbonded interactions has

several advantages: (1) the interactions are attributed to the most "exposed" atoms, the hydrogens; (2) the energy (eq. 2) is simply expressed, the "effective potential function" it simulates being hidden in the overlap integrals; (3) overlap integrals can be computed exactly for hydrogen atoms and are tabulated in the literature[11]; and (4) the overlap integral and its simple functional dependence are easily visualized by the organic chemist.

We have used eq. 4 in two ways: (I) E_{HH} was computed after determining the molecular geometry exactly, e.g., by the convenient procedure of Corey and Sneen[12]; (II) E_{HH} was estimated by constructing Dreiding models, measuring H–H distances with an "Ångstrom ruler," and reading repulsion energies directly from a plot (Table IV lists machine computed values used to prepare a large plot). An Ångstrom ruler was made of stiff cardboard and ruled in scale with the Dreiding models. This technique when applied to the few closest H–H interactions of two structures gives a rapid, crude estimate of $\Delta E_{HH}^{A,B}$.

A. Rotation Barriers.—When eq. 4 is applied to ethane with A = eclipsed and B = staggered form, $\Delta E_{HH}^{A,B}$ can be identified with the rotation barrier. Using $R_{CC} = 1.544$ Å. and $R_{CH} = 1.102$ Å., the following interactions were considered. In A there are three type-1 and six type-2, and in B, six type-3. Geminal

A   B
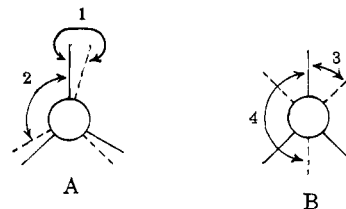
interactions need not be counted since they cancel. It has been found in several examples that pure *trans* interactions, such as type-4 in B, must be *consistently* neglected to obtain best agreement with experiment. In the context of the assumed model, the hydrogen atoms do not "see" each other through bonds. This reduction in magnitude of quantum mechanical integrals (occurring in energy expressions) over atomic orbitals between whose density distributions there are intervening atoms or bonds has precedent.[13] Evaluation of eq. 4 by method I gave $\Delta E_{HH}^{A,B} = +2.85$ kcal./mole[14] in good agreement with experiment (2.875 ± 0.125 kcal./mole).[4a] The model employed by Hendrickson[8] gives 0.14 kcal./mole.

Several rotation barriers were calculated in this way, and the results are given in Table I. The effects of heteroatoms and their lone pairs were neglected, and preliminary attempts to include them gave poorer agreement. The ability of this simple model to reflect experiment is evident.

B. Conformational Energies.—From the barrier to rotation, Pitzer[4e] has estimated that the energy of the *trans* form of n-butane is 0.8 kcal./mole lower than the *gauche*. The application of eq. 4 (method II) gives 1.9 kcal./mole for this difference, where again only pure *trans* interactions were neglected. The agreement is gratifying for such a crude model, and the over-

(10) J. T. Vanderslice and E. A. Mason, *Tetrahedron*, **16**, 399 (1960).
(11) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *ibid.*, **17**, 1248 (1949).

(12) E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **77**, 2505 (1955).
(13) *Cf.* R. B. Hermann, *J. Org. Chem.*, **27**, 441 (1962).
(14) The neglected B-4 interactions contribute 0.42 kcal./mole.

TABLE I

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES
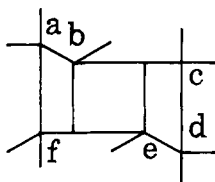OF $\Delta E_{HH}{}^{A,B}$ (EQ. 4)

Compound[a]	Calcd., kcal./mole	Exptl., kcal./mole	Ref.
CH_3CH_3	2.85	2.875 ± 0.125	b
CH_3SiH_3	1.00	1.314 ± 0.229	c
SiH_3SiH_3	0.20	"Appreciable"	d
$CH_3C{\equiv}CCH_3$	0.00	0	e
CH_3OH	1.45	1.07	f
CH_3NH_2	1.70	1.80	g
		1.90	h
NH_2NH_2	2.50	2.80	i
$CH_3CH_2CH_3$[j]	3.38	3.30	k
		3.40	l

[a] Bond angles and distances listed in Table I of ref. 6. [b] K. S. Pitzer, *Discussions Faraday Soc.*, **10**, 66 (1951). [c] D. R. Lide and D. K. Coles, *Phys. Rev.*, **80**, 911 (1950). [d] H. S. Gutowsky and E. O. Stejskal, *J. Chem. Phys.*, **22**, 939 (1954). [e] I. M. Mills and H. W. Thompson, *Proc. Roy. Soc.* (London), **A226**, 306 (1954). [f] E. V. Ivash and D. M. Dennison, *J. Chem. Phys.*, **22**, 1804 (1953). [g] D. R. Lide, *ibid.*, **22**, 1613 (1954). [h] J. G. Aston and F. L. Gittler, *ibid.*, **23**, 211 (1955). [i] D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard, and H. M. Huffman, *J. Am. Chem. Soc.*, **71**, 2293 (1949). [j] Minimum opposed minus minimum staggered, see ref. 6. [k] G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **8**, 610 (1940). [l] K. S. Pitzer, *ibid.*, **12**, 310 (1944).

estimation results from the simulated potential which is inherently hard at small separations.

Method I was applied to determine the conformational energies of cyclohexane. All angles were assumed to be tetrahedral and $R_{CC} = 1.544$ Å., $R_{CH} = 1.102$ Å. The types of interactions for the chair form are given in Table II,[15] where the bookkeeping is tabulated to emphasize the partitioning of the terms. The bracketed terms, $a(a)-b(a)$ and $b(e)-d(e)$, are *trans* interactions and were omitted from ΣE_{HH} which then equals 49.38 kcal./mole.

TABLE II

NONBONDED H-H REPULSIONS IN CHAIR CYCLOHEXANE

Type[a]	Number (n)	R_{HH}, Å.	nE_{HH}, kcal./mole[b]
a(a)-b(e)	12	2.504	24.47
a(a)-c(a)	6	2.521	11.70
a(a)-d(e)	6	4.143	0.12
a(a)-b(a)	6	3.084	[2.57]
a(a)-c(e)	12	3.759	0.75
a(a)-d(a)	3	3.984	0.09
b(e)-d(e)	6	4.321	[0.08]
b(e)-c(e)	6	2.504	12.24
b(e)-e(e)	3	4.994	0.01
		$\Sigma E_{HH} =$	49.38

[a] The notation a(a)-b(e) signifies the interaction of the axial (a) hydrogen on a with the equatorial (e) hydrogen on b, etc. [b] The bracketed terms were omitted from sum, see text.
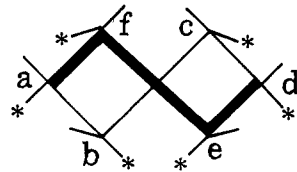
A similar calculation was carried out for the full-boat and twist-boat[16] conformations, and the details

(15) Geminal interactions were omitted since they cancel.
(16) See N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5727 (1959), and ref. 8 for excellent discussions of the conformational properties of medium ring compounds.

of the latter are given in Table III. In the flexible twist-boat conformer, there are no pure *trans* interactions; there are, however, four distant interactions (0.6 kcal./mole) in which a bond similarly intervenes between hydrogens. These (a-e, a-e*, b-e*, and b-f*) were omitted from the sum on the same grounds as *trans* interactions, so that $\Sigma E_{HH} = 54.96$ kcal./mole. The value of ΣE_{HH} for the full boat is 59.24 kcal./mole.

TABLE III

NONBONDED H-H REPULSIONS IN TWIST-BOAT CYCLOHEXANE

Type[a]	Number (n)	R_{HH}, Å.	nE_{HH}, kcal./mole[b]
a-b	8	2.354	24.22
a-c	4	2.755	4.19
a-d	2	4.389	0.02
a-e	4	4.298	[0.05]
a-b*	4	3.046	1.90
a-c*	4	3.875	0.18
a-d*	2	4.666	0.01
a-e*	4	3.736	[0.27]
a-f*	4	2.689	5.00
b-c	4	2.576	6.75
b-e	2	4.884	0.01
b-f	4	3.754	0.26
b-c*	2	2.438	4.85
b-e*	4	3.793	[0.23]
b-f*	2	4.295	[0.03]
c-f	2	2.315	6.67
c-e*	2	3.693	0.15
b*-c	2	3.078	0.86
		$\Sigma E_{HH} =$	54.96

[a] The notation a-b signifies the interaction of the unstarred hydrogen on a with the unstarred hydrogen on b, etc. [b] The bracketed terms were omitted from sum, see text.

If we identify differences of nonbonded H-H repulsions between conformers with enthalpy differences, ΔE_{HH} (twist-boat-chair) = 5.58 kcal./mole, ΔE_{HH} (full-boat-chair) = 9.86 kcal./mole. The first result is in good agreement with the experimental (thermochemical) values of 5.5[17] and 5.9 ± 0.6.[18]

Recently Jensen, Noyce, Sederholm, and Berlin[19] concluded (n.m.r.) that the interconversion of two chair forms proceeds with $\Delta H^* = 11.1$ kcal./mole *via* the twist-boat form as a stable intermediate, placing this conformer at 5.5 kcal./mole above the chair. Hendrickson[8] computed the geometry and energy of this transition state and found it to be 12.66

chair   [TS] $\rightleftharpoons$ twist-boat $\rightleftharpoons$ [TS] $\rightleftharpoons$ chair
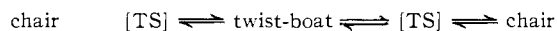
kcal./mole above the chair when only H-H repulsions and torsion and angle strain were taken into account. Equation 2 gives 57.41 kcal./mole for this quantity, but in this case angle strain cannot be properly neglected. The treatment of Westheimer[1] gives a value of 3.64 kcal./mole for this quantity, so that the final

(17) W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Am. Chem. Soc.*, **82**, 1256 (1960); **83**, 606 (1961).
(18) N. L. Allinger and L. A. Freiberg, *ibid.*, **82**, 2393 (1960).
(19) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *ibid.*, **84**, 386 (1962).

transition state energy is 61.05 kcal./mole, corresponding to $\Delta H^* = 11.67$ kcal./mole.

Equation 4 has also been applied to the cyclobutane ring. Although there is good evidence that the minimum energy conformation of various substituted cyclobutanes is folded,[20] the structure of cyclobutane itself is still unsettled. The energies of the planar and folded (20° dihedral angle[20b]) forms, using the bond distances (C–C) = 1.548 Å., (C–H) = 1.092 Å., $\angle$ HCH $\approx$ 111.5°,[21] were calculated. When one opposite pair of C–C–C angles is held at 90°, it was found that E_{HH} increased continuously from the planar model to that with 20° dihedral angle. At this point of considerable folding, the other pair of angles is required to have descreased only to 88° 16′. The energy difference $\Delta E_{HH}^{A,B} = +0.47$ kcal./mole is small, indicating that the ring may indeed be rather flexible.

C. Summary of Method.—The procedure outlined above has proved valuable over a period of time for estimating the steric effect of hydrogen atoms in a variety of organic problems. It is important, however, to note the following shortcomings. The idea of an additive overlap function as a measure of hydrogen steric repulsions is plausible but cannot be theoretically justified. The neglect of other recognized effects (particularly dispersion) is a gross simplification.

Further, the neglect of repulsions between masked hydrogens has no sound basis in quantum mechanics. In some cases, such as *trans* interactions, masking is clear. Generally, it is necessary to construct a model, and we have followed the rule of neglecting those interactions *where one hydrogen nucleus is clearly masked from another by a Dreiding bond*. Fortunately, these questionable interactions are usually at distances where their magnitudes are small.

The behavior of the overlap function cannot be expected to reflect repulsions accurately at small (<2 Å.) distances, so that predictions based on eq. 4 are dubious when steric crowding is severe. E_{HH} can be calculated from an approximate formula derived by curve-fitting (numerical values in Table IV), i.e.

$$E_{HH} = (907.7560 + 220.2723R) \exp(-2.1127R)$$

where R is in Å. and E_{HH} in kcal./mole. The deviation is 0.05% at 1.50 Å. and 3.8% at 3.50 Å.

Perhaps the most gratifying result is the ability of the model to predict correctly the ethane barrier and the enthalpy difference of the cyclohexane conformers employing one semiempirical parameter. Previously, other schemes have been less successful in the concurrent treatment of these two problems.[1,3,6,8]

LCAO Repulsion Energies.—In the event that LCAO repulsion energies reflect nonbonded H–H repulsions, the following observations can be made. It is reasonable to suppose that empirical bond and strain energies will depend on the magnitude of E_{HH}. Empirical bond energies are the sum of the (theoretical) binding energy of the orbitals involved plus all of the effects

(20) (a) W. D. Phillips in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillip, Ed., Academic Press, New York, N. Y., 1962, p. 453; (b) J. Dunnitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

(21) O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962); A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961).

TABLE IV

E_{HH} vs. DISTANCE

R_{HH}, Å.	E_{HH}, kcal./mole	R_{HH}, Å.	E_{HH}, kcal./mole
1.50	25.552	3.05	0.468
1.55	22.594	3.10	0.409
1.60	19.980	3.15	0.355
1.65	17.669	3.20	0.309
1.70	15.624	3.25	0.269
1.75	13.813	3.30	0.234
1.80	12.209	3.35	0.202
1.85	10.789	3.40	0.176
1.90	9.529	3.45	0.153
1.95	8.414	3.50	0.132
2.00	7.426	3.55	0.115
2.05	6.550	3.60	0.099
2.10	5.775	3.65	0.086
2.15	5.088	3.70	0.074
2.20	4.481	3.75	0.065
2.25	3.943	3.80	0.055
2.30	3.468	3.85	0.048
2.35	3.050	3.90	0.042
2.40	2.678	3.95	0.036
2.45	2.351	4.00	0.031
2.50	2.062	4.05	0.027
2.55	1.809	4.10	0.023
2.60	1.585	4.15	0.020
2.65	1.388	4.20	0.017
2.70	1.214	4.25	0.014
2.75	1.056	4.30	0.012
2.80	0.928	4.35	0.010
2.85	0.810	4.40	0.009
2.90	0.708	4.45	0.008
2.95	0.618	4.50	0.007
3.00	0.538		

of their environment including nonbonded H–H repulsions. The concept of strain energy arises when we compare two related structures. The considerations that led to eq. 2 predict (with similar reservations) that binding energies are proportional to the appropriate overlap integral.[2a,b] The energy of bond ij is given by

$$E_{ij} = -A_{ij}(I_i I_j)^{1/2} S_{ij}/(1 + S_{ij}) \qquad (5)$$

where the symbols have the previous meanings.

Since eq. 2 and 5 are similarly derived, we can first test the idea that empirical bond energies in strain-free molecules are significantly affected by nonbonded H–H repulsions by considering staggered ethane and chair cyclohexane. By eq. 5, $E_{CH} = -114.03$ and $E_{CC} = -101.74$, so that the total energy of ethane is $6E_{CH} + E_{CC} + E_{HH} = -773.68$ kcal./mole, and similarly of cyclohexane, -1929.37 kcal./mole. If we call $-\epsilon_{CH}$ and $-\epsilon_{CC}$ "theoretical" empirical bond energies, then

$$-\epsilon_{CC} - 6\epsilon_{CH} = -773.68$$

$$-6\epsilon_{CC} - 12\epsilon_{CH} = -1929.37$$

whence, $\epsilon_{CH} = 113.03$ and $\epsilon_{CC} = 95.50$ kcal./mole. These values cannot be compared directly with thermochemical bond energies, but their relative values should be the same. The agreement with the thermochemical ratio is very good $[(\epsilon_{CH}/\epsilon_{CC}) = 1.183; (D_{CH}/D_{CC})^{22} = 98.75/83.6 = 1.181]$ and omission of nonbonded repulsions gives a poorer value of 1.121.

(22) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 117.

A. Cycloalkanes.—A simple model for strained hydrocarbon rings was considered as follows. Assuming chair cyclohexane is essentially strain-free, the bond energies of the bent bonds in cyclopropane, cyclobutane, and cyclopentane were computed and compared with the corresponding relative H–H repulsion energies. The overlap integrals are taken from Coulson and Goodwin,[23] the geometries of the rings from ref. 21, and the results are shown in Table V. Geminal repulsion must be now included, and because the effect of hybridization changes on molecular energetics is poorly understood and difficult to assess quantitatively, bent-bond models were assumed. The quantity $n(E_{CC}^n - E_{CC}^6)$ measures the decrease in binding energy due to poorer orbital overlap in the smaller rings.

TABLE V

ENERGY TERMS OF THE CYCLOALKANES

| Cyclo-C_nH_{2n}	S_{CC}^a	E_{CC}^n, kcal./mole[b]	$n(E_{CC}^n - E_{CC}^6)$, kcal./mole	E_{HH}^n, kcal./mole	$\bar{E}_{HH}^n$
C_6H_{12}	0.6730	−101.74	0	+126.49	1.92
C_5H_{10}	0.6726	−101.70	+0.20	+109.58	2.44
C_4H_8	0.6630	−100.82	+3.68	+76.22	2.72
C_3H_6	0.6228	−97.06	+14.04	+49.34	3.29

[a] Values in part were extracted from data in ref. 23. [b] Calculated from eq. 5 with $A_{ij} = 0.95$, $I = 11.54$ e.v.

A molecule containing $2n$ hydrogen atoms will experience $n(2n - 1)$ distinct H–H interactions, so that the energy per interaction is $\bar{E}_{HH}^n = E_{HH}^n / n(2n - 1)$. $\bar{E}_{HH}^n$ is highly characteristic of molecular structure, and values for molecules of arbitrary structures are not simply related. The relative values of this quantity can be more meaningfully compared in a series of rigid molecules whose geometries are analytically related. If an empirical carbon–carbon bond energy is largely determined by the environment provided by the four attached hydrogen atoms and by strain due to imperfect orbital overlap, our model will be the unit (–CH₂–CH₂–) in which there are six distinct H–H interactions. A strain-free carbon–carbon bond in cyclohexane will then experience $6\bar{E}_{HH}^6 = 11.52$ kcal./mole of internal H–H repulsion. The other cycloalkanes give the following results.

	$6(\bar{E}_{HH}^n - \bar{E}_{HH}^6) +$ $(E_{CC}^n - E_{CC}^6)$, kcal./mole	Calcd. $D(CC)$, kcal./mole	Exptl. $D(CC)$, kcal./mole[22]
C_6H_{12}	+0	−83.6	−83.6
C_5H_{10}	+3.16	−80.4	−80.2
C_4H_8	+5.76	−77.8	−78.9
C_3H_6	+13.14	−70.5	−75.4

The values relative to cyclohexane represent corrections to the empirical strain-free bond energy. A comparison of the experimental and theoretical values shows rather good agreement for this quantity except for cyclopropane. This shows that the simple model fails when bond bending becomes important; however, in this case too, concurrent use of eq. 2 and 5 gives reasonable results over a considerable range.

B. Aromatic Monocycles.—It is similarly instructive to compare the aromatic monocycles from this viewpoint. Stability depends on π-delocalization, σ-frame-

(23) C. A. Coulson and T. H. Goodwin, J. Chem. Soc., 2851 (1962).
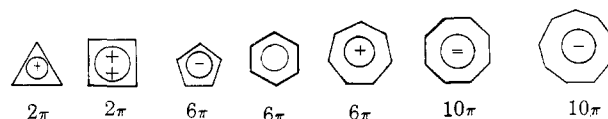
work, and nonbonded H–H repulsion energies among other factors. In this series, only the bond length of benzene is accurately known, and this value (1.397 Å.) has been assumed for the other members. It was also assumed that the framework orbitals are trigonal hybrids which make an angle ω with the line of centers of adjacent ring atoms.[24] For a ring of D_{nh} symmetry, $\omega = (180 - 30n)/n$ (degrees), and the overlap integral of two positively directed trigonal hybrids can be expressed as

$$S(tr,tr) = \tfrac{1}{3}S(s,s) + 2\sqrt{3}/3 \cos \omega\, S(s,\sigma) +$$
$$\tfrac{2}{3} \cos^2 \omega\, S(\sigma,\sigma) + \tfrac{2}{3} \sin^2 \omega\, S(\pi,\pi)$$

Energy terms for the aromatic monocycles are given in kcal./mole in Table VI. With trigonal hybrids, LCAO theory almost certainly underestimates the effect of bond bending (E_{CC}^n); however, the monotonic increase in E_{HH}^n suggests that this factor will be important in destabilizing rings larger than benzene.

TABLE VI

ENERGY TERMS FOR AROMATIC MONOCYCLES

C_n	ω	$S(tr,tr)$	E_{HH}^n	E_{CC}^n
3	+30°	0.757	0.37	−108.9
4	+15°	.815	0.81	−113.5
5	+6°	.832	1.33	−114.8
6	0	.835	2.17	−115.1
7	−4° 17′	.833	3.14	−114.9
8	−7° 30′	.830	4.20	−114.7
9	−10°	.826	5.23	−114.4

Hückel delocalization energies for these ions are given in Table VII. Although the estimates of the σ-framework energies cannot be compared directly with the π-electron energies, their behavior as a function of ring size is clear. With benzene as standard, deviations in framework energy can be espressed as n-$(E_{HH}^n - E_{HH}^6 + E_{CC}^n - E_{CC}^6)$. This model predicts cyclopentadienide ion is particularly favored with respect to angle strain and hydrogen repulsions. The larger rings are destabilized by these factors, but it is anticipated that rings with more than nine members may still be capable of existence, since the differential increase in E_{HH} becomes very small.

TABLE VII

HÜCKEL DELOCALIZATION ENERGIES

C_nH_n	$n(E_{HH}^n - E_{HH}^6) +$ $n(E_{CC}^n - E_{CC}^6)$, kcal./mole	DE_π, β^{-1}	$DE_\pi^n - DE_\pi^6$, kcal./mole
$C_3H_3^+$	+12.99	2	0
$C_4H_4^{+2}$	+0.68	2	0
$C_5H_5^-$	−3.00	2.47	7.52
C_6H_6	0	2	0
$C_7H_7^+$	+7.70	2.99	15.84
$C_8H_8^{-2}$	+19.28	3.66	26.56
$C_9H_9^-$	+33.66	3.52	24.32

(24) No attempt was made to minimize total overlap as in ref. 23.