

An Extended Hückel Theory. I. Hydrocarbons

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Citation: *J. Chem. Phys.* **39**, 1397 (1963); doi: 10.1063/1.1734456

View online: <http://dx.doi.org/10.1063/1.1734456>

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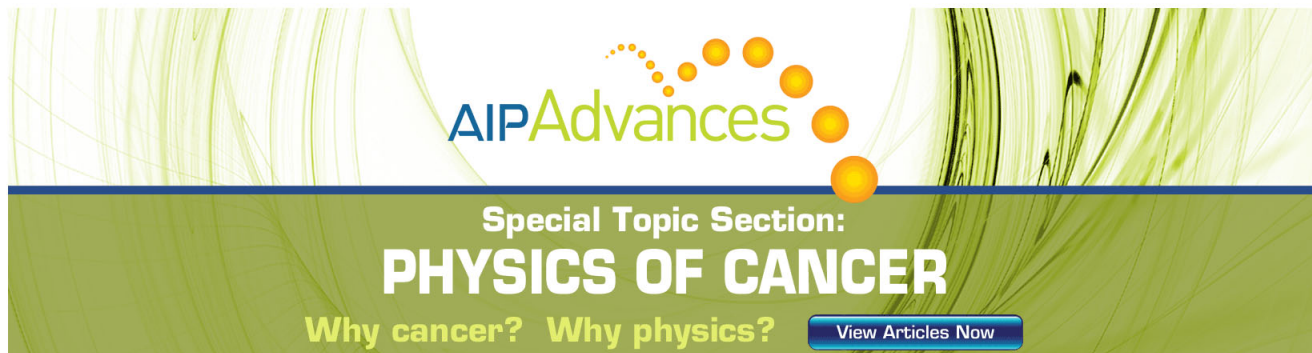
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sensation of the predictions of the more *a priori* theories. Both equations of state are improvements over those of the five-term virial series, the Born-Green integral equation, and the Kirkwood integral equation.

The integral equation of this approximation does not become singular even at densities much higher than that at which the molecular dynamics and Monte Carlo calculations exhibit phase transitions. There is, however, a marked tendency for a singularity to occur. This tendency is exhibited at a wavenumber k corresponding

to the smallest interparticle spacing for close-packed spheres. One might guess that this singularity would be exhibited in a higher-order approximation. We have associated this singularity with a gas-solid transition. This conclusion is based both on the location of the singularity in k space, and on the absence of the marked broadening of successive peaks in the radial distribution function such as are found in liquids.

Our results clearly justify an examination of the next approximation. Work on this is now under way.

An Extended Hückel Theory. I. Hydrocarbons

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(Received 10 April 1963)

The Hückel theory, with an extended basis set consisting of $2s$ and $2p$ carbon and $1s$ hydrogen orbitals, with inclusion of overlap and all interactions, yields a good qualitative solution of most hydrocarbon conformational problems. Calculations have been performed within the same parametrization for nearly all simple saturated and unsaturated compounds, testing a variety of geometries for each. Barriers to internal rotation, ring conformations, and geometrical isomerism are among the topics treated. Consistent σ and π charge distributions and overlap populations are obtained for aromatics and their relative roles discussed. For alkanes and alkenes charge distributions are also presented. Failures include overemphasis on steric factors, which leads to some incorrect isomerization energies; also the failure to predict strain energies. It is stressed that the geometry of a molecule appears to be its most predictable quality.

INTRODUCTION

THE Hückel theory has been widely exploited in chemistry, but a glance at any recent textbook will show that the emphasis has been rather one-sided.¹ The vast majority of calculations have been for planar conjugated and aromatic systems. Where hydrogens must be considered, they have been brought in by the artifice of a perturbation or a pseudoheteroatom. Where non-planarity plays a role, the effects of the violation of the sigma-pi separation have been generally ignored. The few calculations on aliphatics have been limited to the method of linear combinations of bond orbitals,² and the resultant parametrization is difficult to relate to

that used for aromatics. Indeed, the steady pursuit of correlations between theoretically computed π -electron properties and measurables has unfortunately cast a shadow of unreality on the σ framework.³

It is claimed here that the Hückel method, without the assumption of zero differential overlap, allows simply the calculation of the basic properties of all organic systems, aliphatic and aromatic, as well as inorganic structures, with one simple parametrization. The structure and relative importance of sigma and pi orbitals, where a separation exists, may be easily assessed. Conformational predictions, i.e., predictions of what three-dimensional shapes molecules take on in their ground states, are shown to be generally adequate. Indeed, the extended Hückel scheme succeeds, independent of the difficulties in choosing parameters, in just those areas, such as charge distributions, where the π -electron theory works; and performs as miserably in other areas, such as spectral predictions.

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¹ A. Streitwieser, *Molecular Orbital Theory* (John Wiley & Sons, Inc., New York, 1961). R. Daudel, R. Lefebvre, C. Moser, *Quantum Chemistry* (Interscience Publishers, Inc., New York, 1959). B. Pullman and A. Pullman, *Les théories électroniques de la chimie organique* (Masson et Cie., Paris, 1952).

² (a) G. G. Hall and J. Lennard-Jones, Proc. Roy. Soc. (London) **A202**, 336 (1950); **205**, 357, 541 (1951); (b) R. D. Brown, J. Chem. Soc. **1953**, 2615; (c) M. J. S. Dewar and R. Pettit, *ibid.* **1954**, 1625; (d) C. Sandorfy, Can. J. Chem. **33**, 1337 (1955); (e) K. Fukui, H. Kato, K. Morokuma, A. Imamura, and C. Nagata, Bull. Chem. Soc. Japan **35**, 38 (1962) and references therein.

³ A recent example of the consequences of this attitude may be seen in the work of O. Sovers and W. Kauzmann, J. Chem. Phys. **38**, 813 (1963).

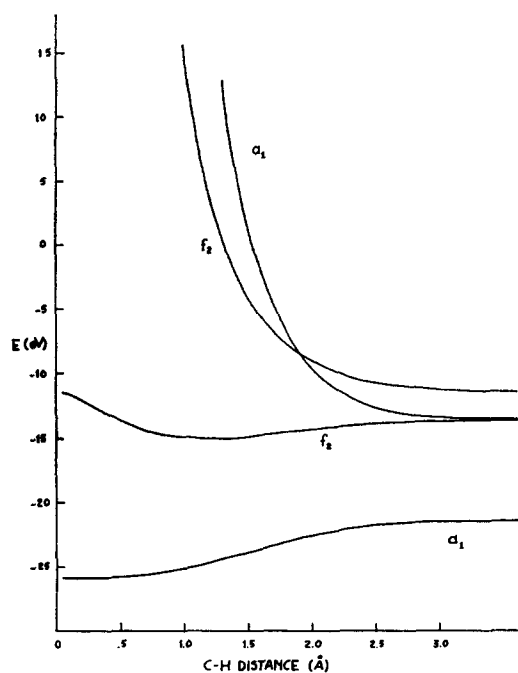


FIG. 1. Energy levels of methane as a function of C-H distance

METHOD OF CALCULATION

Expansion of a molecular orbital as a linear combination of atomic orbitals

$$\Psi_i = \sum_j c_{ij} \phi_j \quad (1)$$

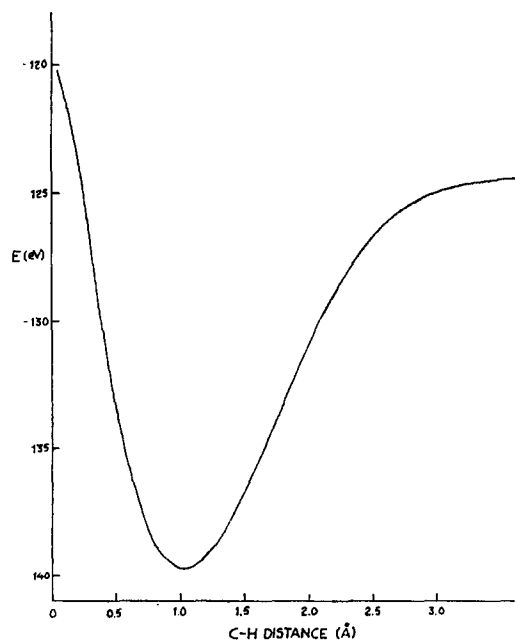


FIG. 2. Total energy of methane as a function of C-H distance.

yields, on minimizing the total energy, the set of Hückel equations

$$\sum_{i=1}^n [H_{ij} - ES_{ij}] c_{ij} = 0 \quad j=1, 2, \dots, n. \quad (2)$$

For a calculation of a molecule C_nH_m we use a basis set consisting of m hydrogen Slater orbitals, exponent 1.0; n $2s$ and $3n$ $2p$ carbon Slater orbitals, exponent 1.625. The order of the resulting secular determinant is $4n+m$. The complete secular determinant is treated, all interactions accounted for, and off-diagonal E 's retained. The critical choice is our manner of guessing the matrix elements H_{ij} . The H_{ii} are chosen as valence state ioniza-

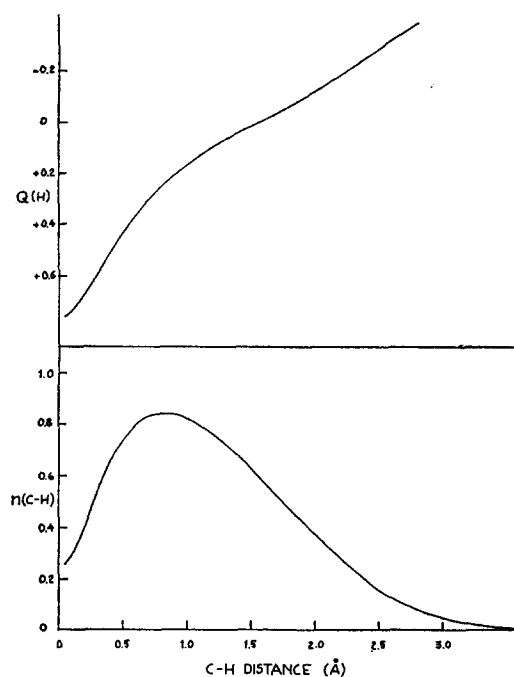


FIG. 3. Net charge on hydrogen (top) and C-H overlap population (bottom) in methane as a function of C-H distance.

tion potentials, and the particular values used are essentially those of Skinner and Pritchard⁴ for the carbon sp^3 valence state

$$H_{ii}(C2p) = -11.4 \text{ eV},$$

$$H_{ii}(C2s) = -21.4,$$

$$H_{ii}(H1s) = -13.6.$$

The H_{ij} are approximated as

$$H_{ij} = 0.5K(H_{ii} + H_{jj}) S_{ij}. \quad (3)$$

⁴H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.* **49**, 1254 (1953); H. O. Pritchard and H. A. Skinner, *Chem. Rev.* **55**, 745 (1955).

TABLE I. Calculated total energies of some hydrocarbons.

Molecule	ΣE_i (eV)	Molecule	ΣE_i (eV)		
C ₂ H ₆	ethane	-243.673	C ₂ H ₄	ethylene	-210.484
CH ₄	methane	-139.608	C ₄ H ₆	<i>trans</i> -butadiene	-386.094
C ₃ H ₈	propane	-347.889	C ₃ H ₆	propylene	-314.895
C ₄ H ₁₀	<i>n</i> -butane	-452.095	C ₃ H ₄	allene	-281.438
C ₄ H ₁₀	isobutane	-452.195	C ₄ H ₈	<i>cis</i> -butene-2	-419.074
C ₅ H ₁₂	<i>n</i> -pentane	-556.300	C ₄ H ₈	<i>trans</i> -butene-2	-419.219
C ₅ H ₁₂	isopentane	-556.133	C ₄ H ₈	isobutylene	-419.292
C ₅ H ₁₂	neopentane	-556.534	C ₄ H ₈	butene-1	-419.052
C ₆ H ₁₄	<i>n</i> -hexane	-660.504	C ₄ H ₆	methyl allene	-385.686
C ₆ H ₁₄	2,2-dimethylbutane	-660.200	C ₂ H ₂	acetylene	-178.028
C ₆ H ₁₄	2,3-dimethylbutane	-660.160	C ₂ H ₂	methyl acetylene	-282.300
C ₆ H ₁₄	2-methylpentane	-660.326	C ₄ H ₆	dimethyl acetylene	-386.447
C ₆ H ₁₄	3-methylpentane	-660.070			
C ₇ H ₁₆	<i>n</i> -heptane	-764.709			
C ₈ H ₁₈	<i>n</i> -octane	-868.914	C ₆ H ₆	benzene	-527.068
C ₉ H ₂₀	<i>n</i> -nonane	-973.118	C ₇ H ₈	toluene	-631.437
C ₆ H ₁₂	(chair) cyclohexane	-625.463	C ₈ H ₁₀	<i>ortho</i> -xylene	-735.699
C ₇ H ₁₄	methyl cyclohexane	-729.756	C ₈ H ₁₀	<i>meta</i> -xylene	-735.808
C ₈ H ₁₆	1,1-dimethylcyclohexane	-833.572	C ₈ H ₁₀	<i>para</i> -xylene	-735.784
C ₈ H ₁₆	1,2(<i>a-e</i>) dimethylcyclohexane	-833.247	C ₁₀ H ₈	naphthalene	-843.085
C ₈ H ₁₆	1,2(<i>e-e</i>) dimethylcyclohexane	-833.779	C ₁₀ H ₈	azulene	-841.681
C ₈ H ₁₆	1,3(<i>a-e</i>) dimethylcyclohexane	-833.511	C ₁₄ H ₁₀	anthracene	-1158.974
C ₈ H ₁₆	1,3(<i>e-e</i>) dimethylcyclohexane	-834.049	C ₁₄ H ₁₀	phenanthrene	-1158.790
C ₈ H ₁₆	1,4(<i>a-e</i>) dimethylcyclohexane	-833.520	C ₅ H ₅ ⁻	cyclopentadienyl anion	-449.624
C ₈ H ₁₆	1,4(<i>e-e</i>) dimethylcyclohexane	-834.049	C ₇ H ₇ ⁺	cycloheptatrienyl cation	-602.329
C ₁₀ H ₁₈	<i>trans</i> -decalin	-1007.396	C ₃ H ₃ ⁺	cyclopropenyl cation	-252.076
C ₁₀ H ₁₈	<i>cis</i> -decalin	-1006.592	C ₆ H ₆	fulvene	-525.960
C ₃ H ₆	cyclopropane	-314.019	C ₈ H ₈	pentalene	-665.576
C ₄ H ₈	cyclobutane (planar)	-417.013	C ₁₂ H ₁₀	biphenyl	-1019.095
C ₅ H ₁₀	cyclopentane ($\frac{1}{2}$ chair)	-520.892	C ₁₂ H ₈	biphenylene	-981.202
C ₄ H ₈	methylcyclopropane	-418.286			

This parametrization, first discussed by Mulliken⁵ and used in a molecular calculation by Wolfsberg and Helmholtz,⁶ is examined in the Appendix, along with the only remaining choice, that of K in Eq. (3), which in our calculations is taken as 1.75. The computer program which performs our calculations has been described earlier.⁷ Input to the program consists of precise atomic coordinates of the various atoms. The overlap matrix is internally computed, and the Hamiltonian matrix constructed from it by the recipe of Eq. (3). The complete set of Eq. (2) is solved with two matrix diagonalizations; for large molecules it is this step which determines the time consumed. The resultant wavefunction is subjected to a Mulliken population analysis,⁸ yielding overlap populations and gross atomic populations or effective charges. At present the program is limited to a maximum of 68 orbitals; anthracene (66) and decalin (58) thus about define the limits of present calculations. A complete run on the latter molecule takes about 9 min on an IBM 7090, and a run on one configuration of ethane about 10 sec. This speed allows computations at many different geometries; indeed the approach to stereochemical problems used here will be to perform

calculations at a variety of distances and orientations.

In Fig. 1 we show the energy levels of methane calculated by this method at a number of C-H distances, preserving tetrahedral symmetry. In Fig. 2 we plot the total Hückel energy, simply a sum of orbital energies of the eight valence electrons in the four filled orbitals of CH₄. Also shown in Fig. 3 are C-H overlap populations and the variation of the resultant charge on the hydrogens. A clear minimum in the potential curve is apparent at about 1.0 Å. The shape of the curve near the minimum is also more or less correct, as indicated by a rough calculated C-H stretching force constant of 5.5 mdyn/Å compared with the experimental value of 5.0.⁹

For almost all molecules, organic or inorganic, which we have considered, a Hückel calculation of this type, carried out as a function of internuclear distance, gives rise to a potential curve having a minimum not far from the correct experimentally determined geometry of the molecule.¹⁰

Of course this behavior has in theory been expected of all LCAO-MO functions and has been tested in non-empirical calculations on small molecules. It has been found that the correct internuclear distance has been obtained with wavefunctions which give a rather poor

⁹ G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand, Inc., New York, 1959), Vol. II.

¹⁰ The exceptions are some diatomics and triatomics for which this theory fails; for instance the obvious case of the ground state of the hydrogen molecule.

⁵ R. S. Mulliken, *J. Chim. Phys.* **46**, 497, 675 (1949).

⁶ M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.* **20**, 837 (1952).

⁷ R. Hoffmann and W. N. Lipscomb, (a) *J. Chem. Phys.* **36**, 2179, 3489 (1962); (b) *ibid.* **37**, 2872 (1962).

⁸ R. S. Mulliken, *J. Chem. Phys.* **23**, 1833, 1841, 2338, 2343 (1955).

TABLE II. Heats of formation at 0°K.*

Molecule		ΔH_f°	Molecule		ΔH_f°
CH ₄	methane	-15.987	C ₈ H ₁₆	1,trans 4 dimethylcyclohexane	-31.99
C ₂ H ₆	ethane	-16.517	C ₈ H ₁₀	cyclopentane	-10.68
C ₃ H ₈	propane	-19.482	C ₂ H ₂	acetylene	54.329
C ₄ H ₁₀	n-butane	-23.67	C ₃ H ₄	methyl acetylene	46.017
C ₅ H ₁₂	n-pentane	-27.23	C ₄ H ₆	dimethyl acetylene	38.09
C ₆ H ₁₄	n-hexane	-30.91	C ₂ H ₄	ethylene	14.522
C ₇ H ₁₆	n-heptane	-34.55	C ₃ H ₆	propylene	8.468
C ₈ H ₁₈	n-octane	-38.20	C ₄ H ₈	butene-1	4.96
C ₉ H ₂₀	n-nonane	-41.84	C ₄ H ₈	cis-butene-2	3.48
C ₄ H ₁₀	isobutane	-25.30	C ₄ H ₈	trans-butene-2	2.24
C ₅ H ₁₂	isopentane	-28.81	C ₄ H ₈	isobutylene	0.98
C ₅ H ₁₂	neopentane	-31.30	C ₃ H ₄	allene	47.70
C ₆ H ₁₄	2-methylpentane	-32.08	C ₄ H ₆	methyl allene	42.00
C ₆ H ₁₄	3-methylpentane	-31.97	C ₄ H ₆	butadiene	29.78
C ₆ H ₁₄	2,2-dimethylbutane	-34.65	C ₆ H ₆	benzene	24.000
C ₆ H ₁₄	2,3-dimethylbutane	-32.73	C ₇ H ₈	toluene	17.500
C ₆ H ₁₂	cyclohexane	-20.01	C ₈ H ₁₀	o-xylene	11.096
C ₇ H ₁₄	methylcyclohexane	-26.30	C ₈ H ₁₀	m-xylene	10.926
C ₈ H ₁₆	1,1 dimethylcyclohexane	-30.93	C ₈ H ₁₀	p-xylene	11.064
C ₈ H ₁₆	1,cis 2 dimethylcyclohexane	-28.95			
C ₈ H ₁₆	1,trans 2 dimethylcyclohexane	-30.91			
C ₈ H ₁₆	1,cis 3 dimethylcyclohexane	-32.02			
C ₈ H ₁₆	1,trans 3 dimethylcyclohexane	-30.06			
C ₈ H ₁₆	1,cis 4 dimethylcyclohexane	-30.08			

* As given by F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel in *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds* (Carnegie Press, Pittsburgh, 1953).

binding energy.¹¹ Unfortunately, the clear implication of these results, that geometries are more easily predictable than energies, was lost in the eagerness with which the deceptively useful resonance energies of early semiempirical theories were accepted. Some other factors which have prevented semiempirical calculations of geometries include a certain inertia against calculating overlap integrals between noncoplanar atoms, and the unavailability until recent times of computers efficient enough to solve the high-order secular equations.

Partial justification of using a simple sum of orbital energies is given in the Appendix. It should be emphasized here that a sound theoretical basis for our model is, however, not as yet available.

The determination of the most favorable arrangement of atoms in even such a small molecule as ethane involves very many calculations at a multitude of geometries. To a limited extent we have carried out this absolute minimization procedure for methane, acetylene, ethylene, and ethane. The results are

methane: tetrahedral, C-H, 1.02 Å;
 acetylene: linear; C-C, 0.85 Å; C-H, 1.0 Å;
 ethylene: D_{2h} planar; C-C, 1.47 Å; C-H, 0.95 Å;
 angle HCH 125°;
 ethane: (tetrahedral angles assumed) C-C 1.92 Å;
 C-H 1.0 Å, staggered.

¹¹ For H₂ the simplest LCAO and VB functions give a poor binding energy but an equilibrium separation within 10% of the correct value. Scaling, i.e., varying the Slater exponent, improves the energy somewhat and predicts the distance to 1% [see the review of H₂ calculations in A. D. McLean, A. Weiss, and M. Yoshimine, *Rev. Mod. Phys.* **32**, 211 (1960)]. For F₂ the best simple LCAO function gives the internuclear separation to 10%, but fails to predict binding [B. J. Ransil, *Rev. Mod. Phys.* **32**, 239, 245 (1960)].

All distances quoted are ± 0.05 Å. At the indicated distance for ethane, the difference in energy between the staggered and eclipsed form was 0.8 kcal. It will be noted that these minima come at C-C distances which are much too short for acetylene, much too long for ethane. We are faced with the following dilemma: Since the method is evidently useful for crude conformational analysis, should we run a separate absolute minimization for each molecule, or should we process all molecules of a similar chemical nature at some standard distance. Considering the labor involved in the first alternative, the latter choice is clearly indicated. The next problem was to choose the distance at which to perform calculations for a large number of molecules. Should, for instance, aliphatics be processed at a C-C distance giving the most stable ethane (1.92 Å), or should their properties be computed at a more realistic separation, taking the risk of anomalous effects arising from a calculation which we know is not at the equilibrium molecular distance for the given approximate method of computation. The latter choice was made, and, we believe, vindicated to some extent by the results obtained below.

A large variety of hydrocarbons was studied, in various idealized geometries, which in unstrained cases corresponded to tetrahedral angles at aliphatic carbons, 120° HCH angle in olefins; C-C, 1.54 Å; C=C, 1.34 Å; C≡C, 1.21 Å, C-C in aromatics 1.40 Å; C-H, 1.10 Å throughout. Aromatic hydrogens were placed radially out of the ring they were on. The total energies for the most stable conformations of the compounds calculated are given in Table I. In Table II we list some experimental heats of formation at 0°K which will be relevant in the discussion. Where conformational problems arise, several calculations at different orientations were per-

formed and these will be discussed separately. In Figs. 4-8 are shown the net charges and overlap populations for most molecules treated. For the more studied cases of ethane, ethylene, and benzene, the entire wavefunction will be given; for the other molecules these are available from the author.

Barrier to Internal Rotation in Ethane

At C-C, 1.54 Å; C-H, 1.10 Å; tetrahedral angles, the difference in energy between an eclipsed and a stag-

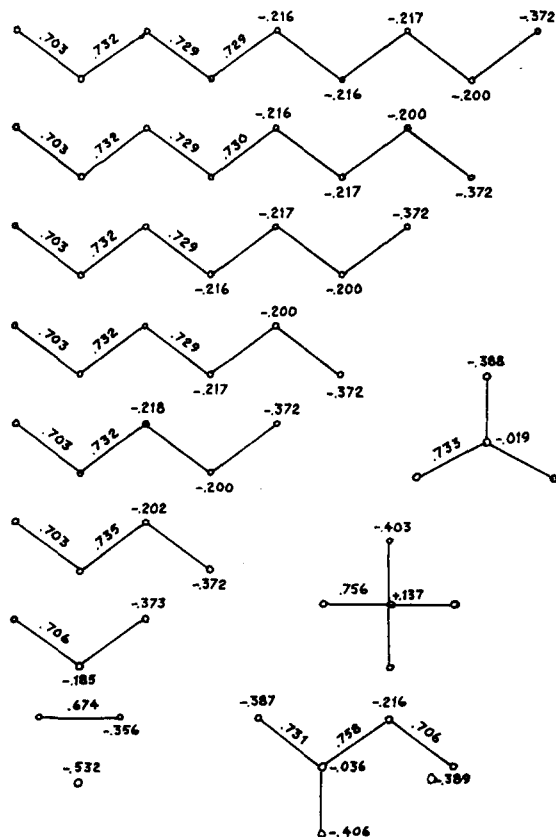


FIG. 4. Population analysis for alkane wavefunctions. Signed quantities are net charges, other numbers are C-C overlap populations.

gered conformation of CH_3CH_3 is computed to be 4.0 kcal/mole. The experimental value is 2.7-3.0 kcal/mole.

The aetiology of barriers is well developed.¹² It is our opinion that too much effort has gone into a search for a simple explanation to this phenomenon; in what follows we discuss only the symptoms accompanying ethane's torsional behavior.

The coordinates, energies, and AO coefficients for the seven filled orbitals in the staggered and eclipsed

¹² (a) W. G. Dauben and K. S. Pitzer in *Steric Effects in Organic Chemistry*, edited by M. S. Newman (John Wiley & Sons, Inc., New York, 1956), p. 1; (b) E. B. Wilson, Jr., *Advan. Chem. Phys.* **2**, 367 (1959); (c) D. J. Millen, *Progr. Stereochem.* **3**, 138 (1962).

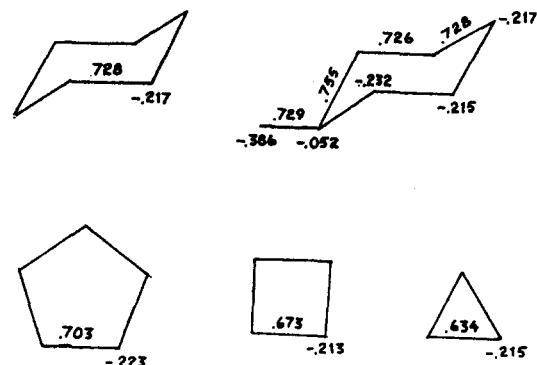


FIG. 5. Population analysis for some cycloalkane wavefunctions: chair cyclohexane, equatorial methyl cyclohexane, planar cyclopentane, planar cyclobutane, cyclopropane. Signed quantities are net charges, other numbers are C-C overlap populations.

conformations are listed in Tables III, IV. In Table V we give the gross atomic populations orbital by orbital, as well as certain subtotal overlap populations. Below we list $E_{\text{ecl}} - E_{\text{stag}}$ orbital by orbital (for degenerate e levels the energy difference is for one orbital of the pair)

e	0.101 eV,
a_1	-0.005,
e	-0.056,
a_2	0.002,
a_1	0.001.

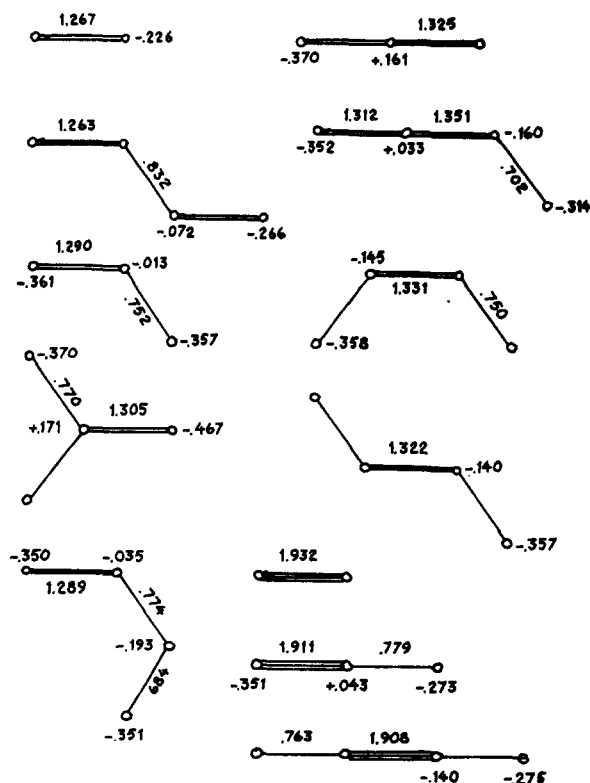


FIG. 6. Population analysis for some ethylenic and acetylenic hydrocarbons. The most stable conformation (see text) is chosen. Signed quantities are net charges, other numbers are C-C overlap populations.

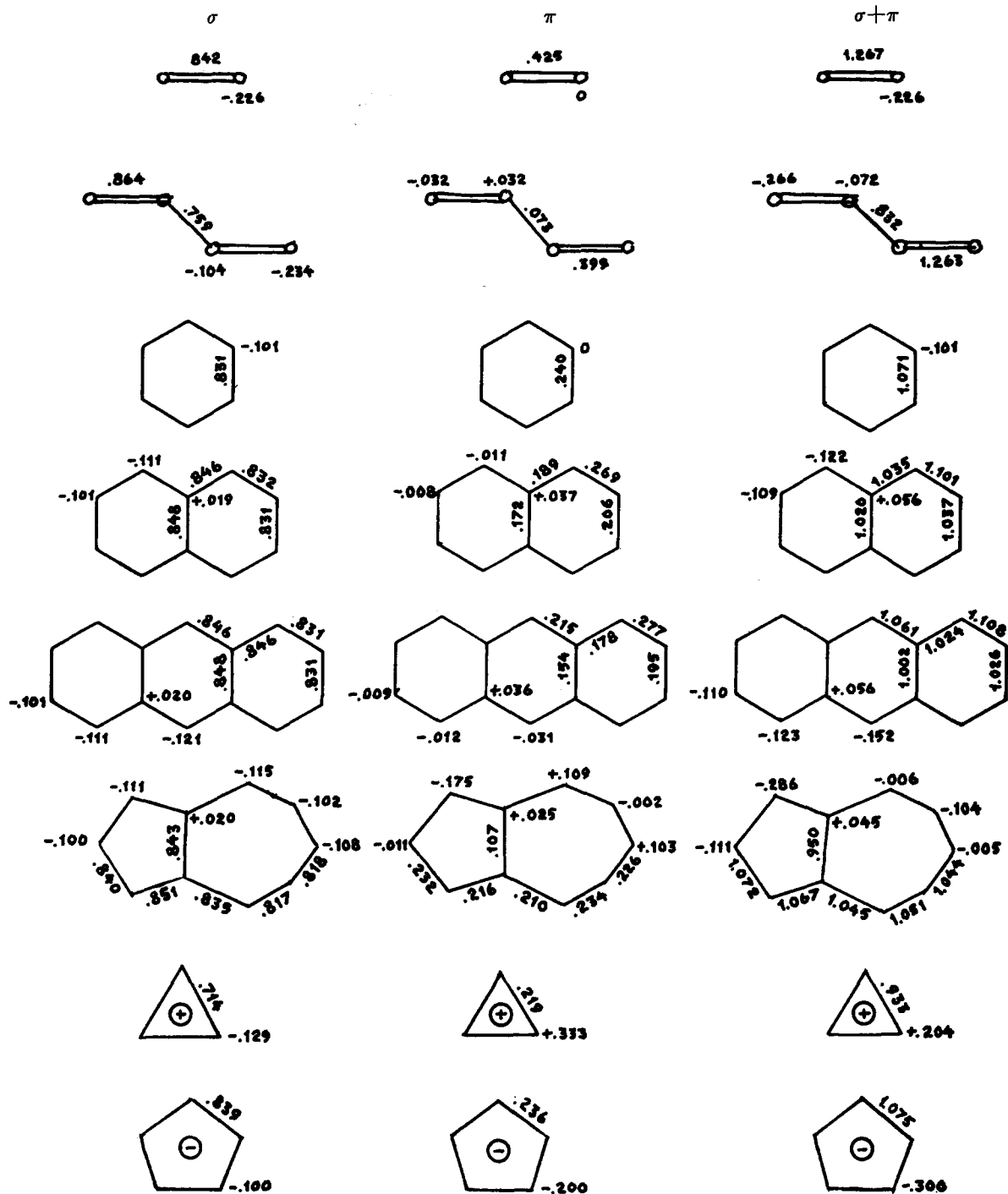


FIG. 7(a). Population analysis for aromatics and some other conjugated molecules. Net charges (signed numbers) and overlap populations (unsigned) are given separately for σ , π , $\sigma+\pi$ orbitals.

It can be noticed that the prevailing contribution to the barrier comes from the doubly degenerate orbitals; the top filled level determines the direction of the barrier. These orbitals are C-H orbitals composed of $1s$ H and $2p_x$, $2p_z$ carbon AO's ($2p_y$ lie along the C-C axis) and an examination of the electron distribution shows that in both cases transfer of electrons from carbons

to protons is associated with greater stability of the staggered form. The total C-C overlap population is less for the eclipsed form,¹³ while the C-H overlap population is very slightly greater. The charge on the

¹³ In the minimization procedure the staggered form stabilized at a slightly shorter C-C distance than the eclipsed.

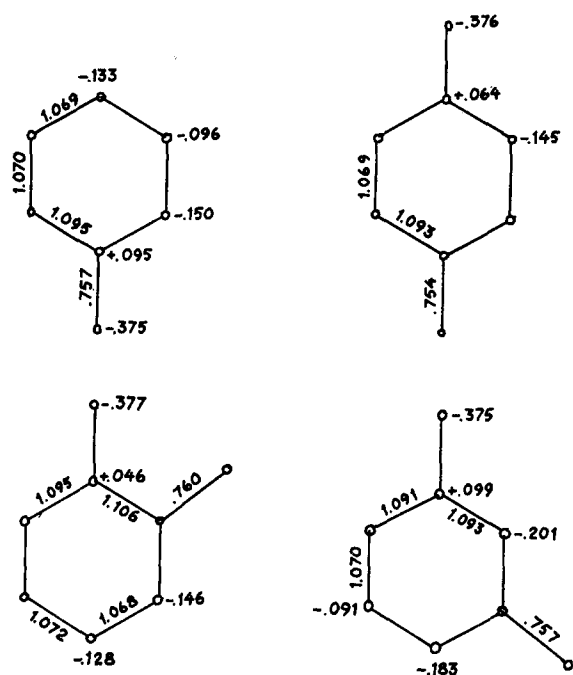


FIG. 8. Population analysis for toluene and the xylenes.

is followed with an absolute deviation of less than 1% over the entire range; the deviation is such that the actual curve is always wider than that given by a cosine form.

Normal and Branched Alkanes

The normal alkanes through *n*-nonane were considered in their completely staggered *trans* configurations. As expected the increment in total energy per CH₂ is constant, being 104.065 eV for methane-ethane, 104.216 for ethane-propane, 104.205±0.001 for all the higher members of the progression. The energy of the highest occupied orbital,

CH ₄ —14.977 eV,	C ₈ H ₁₄ —12.675,
C ₂ H ₆ —13.759,	C ₇ H ₁₆ —12.561,
C ₃ H ₈ —13.419,	C ₆ H ₁₈ —12.475,
C ₄ H ₁₀ —13.055,	C ₅ H ₂₀ —12.409,
C ₅ H ₁₂ —12.832,	

which is presumably related to the molecular ionization potential, decreased uniformly, but the absolute values are about 2 eV greater than the observed ionization potentials. In the population analysis (Fig. 4) note the remarkable uniformity as one progresses in the series. The terminal carbon in a chain carries a charge of -0.372, the penultimate is the most positive of the carbons, with a charge of -0.200, subsequent interior carbons stabilize at -0.216. The charges on the hydrogens and the carbon-hydrogen overlap populations are not shown in this figure, but representative values are

given in Tables VI, VII and are discussed separately below.

Three conformations were examined for propane, corresponding to staggered-staggered, eclipsed-staggered, eclipsed-eclipsed arrangements of the terminal hydrogens with respect to the interior atoms. The following energies were computed

stag-stag,	-347.889 eV,
stag-ecl,	-347.645,
ecl-ecl,	-347.351.

The equilibrium conformation predicted is thus the all staggered form, as was found by Lide in a microwave

TABLE III. Geometry of ethane: Cartesian coordinates of atoms.

staggered atom	x	y	z
C ₁	0.0	0.77	0.0
C ₂	0.0	-0.77	0.0
H ₁	1.037089	1.136666	0.0
H ₂	-0.518544	1.136666	-0.898146
H ₃	-0.518544	1.136666	0.898146
H ₄	0.518545	-1.136666	0.898146
H ₅	-1.037089	-1.136666	0.0
H ₆	0.518544	-1.136666	-0.898146

eclipsed	x	y	z
C ₁ , C ₂ , H ₁ , H ₂ , H ₃ same as staggered			
H ₄	1.037089	-1.136666	0.0
H ₅	-0.518544	-1.136666	0.898146
H ₆	-0.518544	-1.136666	-0.898146

TABLE IV. Molecular orbitals in ethane.^a

staggered	-13.759 e _g	-14.111 a _{1g}	-15.857 e _u	-21.823 a _{2u}	-26.671 a _{1g}
H(1)	-0.3711	0.0630	-0.1177	0.3132	-0.0215
H(2)	0.1310	-0.3529	-0.1177	-0.1379	0.2820
H(3)	0.2401	0.2899	-0.1177	-0.1753	-0.2605
H(4)	0.1310	-0.3529	-0.1177	0.1379	-0.2820
H(5)	-0.3711	0.0630	-0.1177	-0.3132	0.0215
H(6)	0.2401	0.2899	-0.1177	0.1753	0.2605
Cs(1)	-0.0000	0.0000	0.0788	0.0000	0.0000
Cs(2)	-0.0000	0.0000	0.0788	0.0000	-0.0000
Cx(1)	-0.4558	0.0774	0.0000	0.3979	-0.0274
Cx(2)	-0.4558	-0.0773	0.0000	0.3979	-0.0274
Cy(1)	0.0000	-0.0000	-0.5618	0.0000	-0.1036
Cy(2)	-0.0000	0.0000	0.5618	0.0000	-0.1036
Cz(1)	0.0773	0.4558	-0.0000	-0.0274	-0.3979
Cz(2)	-0.0774	-0.4558	0.0000	-0.0274	-0.3979

eclipsed	-13.658 e _{1'}	-14.116 a _{1'}	-15.913 e _{1'}	-21.821 a _{2'}	-26.670 a _{1'}
H(1)	-0.3711	0.0009	0.1179	-0.3176	0.0100
H(2)	0.1848	-0.3218	0.1179	0.1501	-0.2401
H(3)	0.1863	0.3209	-0.1179	0.1675	0.2700
H(4)	-0.3711	-0.0009	0.1179	-0.3176	0.0100
H(5)	-0.1863	-0.3209	0.1179	0.1675	0.2700
H(6)	-0.1848	0.3216	-0.1179	0.1501	-0.2401
Cs(1)	0.0000	0.0000	-0.0795	0.0000	-0.0000
Cs(2)	-0.0000	0.0000	-0.0795	0.0000	0.0000
Cx(1)	-0.4723	0.0011	-0.0000	-0.3925	0.0124
Cx(2)	0.4723	-0.0011	-0.0000	-0.3925	0.0124
Cy(1)	0.0000	-0.0000	0.5615	-0.0000	-0.0000
Cy(2)	0.0000	0.0000	-0.5615	0.0000	-0.0000
Cz(1)	0.0011	0.4723	0.0000	0.0124	0.3925
Cz(2)	-0.0011	-0.4723	-0.0000	0.0124	0.3925

^a p_x, p_y, p_z orbitals are directed along x, y, z axes. Atoms are located at positions given in Table III.

study.¹⁵ The barrier computed here, 0.244 eV, is much too large.

For *n*-butane 12 conformations were examined, three configurations of terminal hydrogens for each of four arrangements of carbons. In each geometry, the staggered-staggered arrangement of the terminal hydrogens was favored; the relative energies of the four carbon chain conformers are shown schematically in Fig. 9. Qualitatively again the picture conforms to what is known about *n*-butane—there being two potential minima, the more stable of which corresponds to the *trans* or *anti* form, the other to the *gauche* configuration.^{12c,16} Quantitatively all the energy differences are too big; the difference between the *anti* and *gauche* forms, the barrier to rotation about the central C-C bond, the barrier to rotation about a terminal carbon-carbon bond (computed in the *anti* form to be 0.475 eV). By now it will be realized that this feature will appear throughout our calculations—an apparent overemphasis of what colloquially would be termed steric factors.

Four conformations were considered for isobutane, the most stable being that with all atoms staggered, as found experimentally.¹⁷ The computed barrier to rotation was 0.300 eV. The isomerization energy of *n*-butane and isobutane is seen, from Table I, to be computed as 2.3 kcal/mole, compared to the experimental value of 1.6 kcal/mole.

For the various pentanes and hexanes, the hydrogen arrangements were assumed to be all staggered, and various carbon conformers were examined. In each case the most stable one was found to be that in which the longest possible chain was *anti* throughout. As may be

TABLE V. Ethane population analysis by orbitals.

Gross atomic populations (staggered)					
	e_g	a_{1g}	e_u	a_{2u}	a_{1g}
H	0.3117	0.0388	0.2844	0.1637	0.0825
C(<i>s</i>)	0	0.0090	0	0.4289	0.7446
C(<i>p_x</i>)	0.5324	0	0.5733	0	0
C(<i>p_y</i>)	0	0.8747	0	0.0799	0.0078
C(<i>p_z</i>)	0.5324	0	0.5733	0	0
$n(\text{C-H}) = 0.8135$		$n(\text{C-C}) = 0.6742$		$N(\text{H}) = 0.8812$	
Gross atomic populations (eclipsed)					
	e''	a_1'	e'	a_2''	a_1'
H	0.3008	0.0390	0.2926	0.1634	0.0826
C(<i>s</i>)	0	0.0091	0	0.4296	0.7446
C(<i>p_x</i>)	0.5488	0	0.5611	0	0
C(<i>p_y</i>)	0	0.8739	0	0.0802	0.0078
C(<i>p_z</i>)	0.5488	0	0.5611	0	0
$n(\text{C-H}) = 0.8149$		$n(\text{C-C}) = 0.6529$		$N(\text{H}) = 0.8784$	

¹⁵ D. R. Lide, J. Chem. Phys. **33**, 1514 (1960).

¹⁶ E. L. Eliel, *Stereochemistry of Carbon Compounds* (McGraw-Hill Book Company, Inc., New York, 1962).

¹⁷ D. R. Lide, J. Chem. Phys. **33**, 1519 (1960).

TABLE VI. Aliphatic carbons and hydrogens.

Molecule	$Q(\text{C})$	$Q(\text{H})$	$n(\text{C-H})$
methane	-0.532	+0.133	0.794
<i>primary</i>			
ethane	-0.356	+0.119	0.814
neopentane	-0.403	+0.123	0.809
<i>n</i> -nonane	-0.372	+0.120	0.812
isobutane	-0.388	+0.121	0.810
propylene	-0.357	+0.124 ^a	0.808
		+0.136	0.791
methyl allene	-0.314	+0.124 ^a	0.807
		+0.132	0.796
<i>trans</i> -butene-2	-0.357	+0.133	0.794
		+0.125 ^a	0.809
<i>cis</i> -butene-2	-0.358	+0.138 ^b	0.793
		+0.123	0.803
methyl acetylene	-0.273	+0.141	0.782
dimethyl acetylene	-0.275	+0.138	0.786
methyl cyclohexane	-0.386	+0.121	0.811
<i>secondary</i>			
cyclohexane	-0.217	+0.109 ^c	0.828
		+0.108	0.829
propane	-0.185	+0.105	0.832
<i>n</i> -nonane next to terminal	-0.200	+0.108	0.831
<i>n</i> -nonane inner	-0.216	+0.108	0.830
cyclopropane	-0.215	+0.107	0.821
cyclobutane	-0.213	+0.106	0.828
<i>tertiary</i>			
isobutane	-0.019	+0.092	0.852
isopentane	-0.036	+0.094	0.850
<i>quaternary</i>			
neopentane	+0.137		

^a Refers to single hydrogen eclipsing double bond, other entry to other two hydrogens.

^b Refers to the two hydrogens staggered with respect to double bond, other entry to remaining hydrogen.

^c Axial hydrogen, other entry refers to equatorial hydrogen.

gleaned from Tables I, II, the theory here fails to predict correctly the energetic relationships among the various isomers; thus while neopentane is computed to be more stable than *n*-pentane, isopentane is not. We attribute the failure here to the overemphasis of steric factors which we already noted in the extreme energy difference between *gauche* and *anti* *n*-butane. Since *gauche* conformations are unavoidable in the branched hexanes and isopentane, in our calculation they destabilize these so much as to make them less stable than the corresponding normal alkanes, in contrast to reality.

Cycloalkanes

The cyclohexane system has been subjected to considerable stereochemical scrutiny.^{12a,c,16} The ring

TABLE VII. Olefinic and acetylenic carbons and hydrogens.

Molecule	Q(C)	Q(H)	n(C-H)
primary			
ethylene	-0.226	+0.113	0.813
propylene	-0.361	+0.117 ^a	0.810
allene	-0.370	+0.145	0.777
methyl allene	-0.352	+0.139 ^a	0.781
butadiene	-0.266	+0.116 ^a	0.810
isobutylene	-0.467	+0.119	0.807
butene-1	-0.350	+0.116 ^a	0.810
secondary			
butadiene	-0.072	+0.107	0.822
<i>trans</i> -butene-2	-0.140	+0.106	0.822
<i>cis</i> -butene-2	-0.145	+0.105	0.826
butene-1	-0.035	+0.103	0.824
propylene	-0.013	+0.102	0.826
methyl allene	-0.160	+0.126	0.798
tertiary			
allene	+0.161		
methyl allene	+0.033		
isobutylene	+0.171		
acetylenic			
acetylene	-0.157	+0.157	0.789
methyl acetylene	-0.351	+0.158	0.788

^a Average of two nonequivalent hydrogens.

system proper we have calculated in the conformations

chair	-625.463,
boat (C_{2v})	-624.695,
planar	-623.254.

The chair form is preferred, but the boat-chair energy difference is greater than the observed 5.5 kcal/mole¹⁸ (this value should be really compared with the difference between a chair form and a twisted boat). The difference between axial and equatorial methyl cyclohexane is calculated as 0.529 eV in favor of the equatorially substituted conformer—this being much larger than the experimentally inferred value of about 1.8 kcal/mole.¹⁶ The barrier to rotation is here computed as 0.284 eV. The relative stabilities of the dimethyl cyclohexanes are predicted remarkably well. In each case we have in order of decreasing stability: equatorial-equatorial, equatorial-axial, axial-axial.¹⁶ The sterically hindered axial-axial 1, 3 dimethyl cyclohexane conformer has a particularly high energy. Finally *trans*-decalin is more stable than *cis*-decalin, with the computed difference again being much larger than the observed 2.7 kcal/mole.^{12a}

For cyclopentane three conformations were examined:

planar	-520.722,
1/2 chair	-520.892,
envelope	-520.819.

¹⁸ F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Am. Chem. Soc.* **84**, 386 (1962).

The half-chair and envelope geometries are those given by Brutcher and Bauer¹⁹ and are more puckered than the optimum forms described by Pitzer and Donath.²⁰ Both puckered forms are more stable than the planar arrangement, and for this degree of puckering, the half-chair is slightly preferred, as was also found by Brutcher and Bauer.

For cyclobutane the most stable conformation found was planar, but the potential curve was quite flat for bent forms with a dihedral angle up to 15°. Cyclopropane, as other cyclic and noncyclic paraffins, was studied with a C-C distance of 1.54 Å and tetrahedral exterior HCH angle. The resultant gap between filled and empty orbitals was smaller than in other saturated hydrocarbons. The barrier to internal rotation in methyl cyclopropane was computed as 0.137 eV. In subsequent work we hope to present contour plots of the electron density in these molecules. Some of the cycloalkane charge distributions are shown in Fig. 5.

Olefinic and Acetylenic Hydrocarbons

The coordinates and occupied molecular orbitals of ethylene are given in Tables VIII, IX. The highest filled and lowest empty orbitals are π type, as expected. The highest filled σ orbital, however, is not far below. Some recent work of Berry indicates that such an energy spectrum is not unreasonable.²¹ A calculation on the twisted D_{2d} geometry gives an energy 3.489 eV higher for its orbitally degenerate ground state.²² The geometry

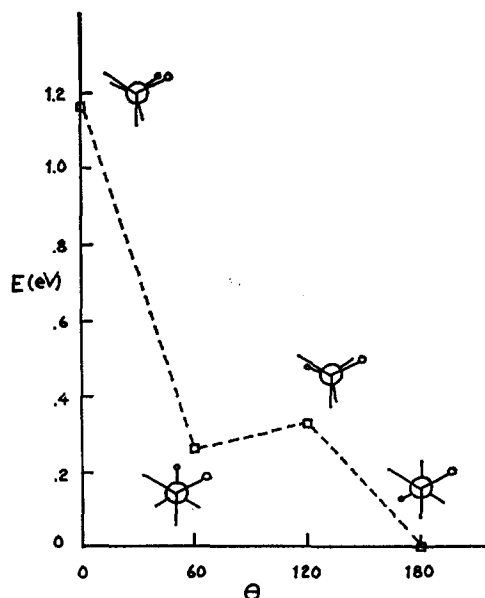


FIG. 9. Calculated energies of four conformations of *n*-butane, referred to the energy of the *trans* or *anti* form.

¹⁹ F. V. Brutcher, Jr., and W. Bauer, Jr., *J. Am. Chem. Soc.* **84**, 2233 (1962).

²⁰ K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.* **81**, 3213 (1959).

²¹ R. S. Berry, *J. Chem. Phys.* **38**, 1934 (1963).

²² R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.* **41**, 219 (1947).

is reversed in the first excited state. Allene (constructed with the same C-C distance as ethylene) is favored in the D_{2d} geometry by 1.264 eV over the planar structure. Again in the first excited state the favored geometry is the reverse. For propylene two conformations of the methyl group were examined and the form with a hydrogen eclipsing the double bond was favored over the staggered conformer by 1.1 kcal/mole. The absolute conformation is in agreement with a microwave determination.²³ Butadiene was examined in planar *cis* and *trans* geometries, and the *trans* form was favored by 7.6 kcal/mole.²⁴ The lowest filled π orbital was here found below a σ level. In methyl allene, as in propylene, the conformation with a hydrogen eclipsing the double bond was more stable by 1.3 kcal/mole. The calculated order of the propylene and methyl allene barriers is thus incorrect, the latter being 1.59 kcal/mole,²⁵ the former 1.98 kcal/mole.²⁶ However, from the previous section we have already learned that even fair absolute barriers are not to be expected from these calculations, while predictions of equilibrium conformations are satisfactory.

The next group of compounds examined includes butene-1, *cis* and *trans* butene-2, and isobutylene. For butene-1, eight conformations were studied and the one of lowest energy had a nonplanar carbon arrangement with one of the methylene hydrogens eclipsing the double bond and the terminal methyl group staggered with respect to the methylene hydrogens. For isobutylene three conformations were examined—the most stable one having both terminal methyl groups arranged as in propylene (calculated barrier here 0.8 kcal/mole). A similar arrangement, again with hydrogens eclipsing the double bond, was found in *trans*-butene-2, where the computed barrier is 1.1 kcal/mole. For *cis*-butene-2 the nonbonded steric factor dominates and the stable conformation comes out with both methyl groups staggered with respect to the double bond. The barrier here is calculated very large, 10.6 kcal/mole. Thermochemically the *cis*-butene-2 barrier is smaller than that of the *trans* isomer,^{12a} very clearly our method of calculation fails badly here.

The order of stabilities of the butenes is given correctly, though with some evidence of the steric problem in our model of *cis*-butene-2, as may be seen from the isomerization energies to the most stable isomer, isobutylene

	observed	calculated
<i>trans</i> -butene-2	1.26	1.68 kcal/mole,
<i>cis</i> -butene-2	2.50	5.03,
butene-1	3.98	5.54.

²³ D. R. Herschbach and L. C. Krisher, *J. Chem. Phys.* **28**, 728 (1958).

²⁴ R. G. Parr and R. S. Mulliken, *J. Chem. Phys.* **18**, 1338 (1950), obtained somewhat smaller estimates. See also O. Polansky, *Monatsh. Chem.* **94**, 23 (1963).

²⁵ D. R. Lide and D. E. Mann, *J. Chem. Phys.* **27**, 874 (1957).

²⁶ D. R. Lide and D. E. Mann, *J. Chem. Phys.* **27**, 868 (1957).

TABLE VIII. Ethylene atom positions.

atom	x	y	z
C ₁	0.0	0.67	0.0
C ₂	0.0	-0.67	0.0
H ₁	0.952629	1.22	0.0
H ₂	-0.952629	1.22	0.0
H ₃	0.952629	-1.22	0.0
H ₄	-0.952629	-1.22	0.0

TABLE IX. Molecular orbitals in ethylene.^a

	-13.218 b _{1u}	-13.776 b _{1g}	-14.448 a _g	-16.215 b _{2u}	-20.604 b _{2u}	-26.981 a _g
H(1)	0.	0.3436	0.1904	-0.2668	0.2396	0.0888
H(2)	0.	-0.3436	0.1904	0.2668	0.2396	0.0888
H(3)	-0.	-0.3436	0.1904	-0.2668	-0.2396	0.0888
H(4)	-0.	0.3436	0.1904	0.2668	-0.2396	0.0888
CS(1)	-0.	0.0000	-0.3741	-0.0000	0.3860	0.4870
CS(2)	0.	-0.0000	-0.3741	-0.0000	-0.3860	0.4870
CX(1)	0.	0.4428	-0.0000	-0.3821	0.0000	0.0000
CX(2)	-0.	-0.4428	0.0000	-0.3821	-0.0000	0.0000
CY(1)	0.	0.0000	0.5265	0.0000	0.1768	-0.0240
CY(2)	0.	-0.0000	-0.5265	-0.0000	0.1768	0.0240
CZ(1)	0.6275	0.	0.	-0.	-0.	0.
CZ(2)	0.6275	-0.	-0.	0.	0.	-0.

^a p_x , p_y , p_z orbitals are directed along x , y , z axes. Atoms are located at positions given in Table VIII.

Calculations were also performed for acetylene,²⁷ methyl acetylene, and dimethyl acetylene. For the latter the computed barrier is 0.01 kcal/mole in favor of the eclipsed form. Since this magnitude is near the estimated accuracy of our calculation, it is not clear if the number is significant. Methyl acetylene is correctly computed to be more stable than allene; the relative stability of butadiene and methyl allene is also given correctly, but not their relation to dimethyl acetylene.

Charges on Carbons and Hydrogens

The figures illustrating charge distributions in the hydrocarbons do not indicate hydrogen charges of C-H overlap populations. The inclusion of these quantities in the drawings would complicate the latter extensively. Moreover, these numbers show a regularity which may be appreciated from some typical and atypical cases given in Tables VI, VII. The over-all variation in hydrogen charge is small, while that of the carbon charges is considerable. The more carbons are bonded to a given carbon, the more positive it becomes; the associated hydrogens become slightly less positive and the C-H overlap populations rise. Those hydrogens which are sterically unhappy, i.e., which are forced into excessive proximity to other hydrogens, acquire a positive character roughly proportional to their discomfort—this already begins to be seen in the eclipsed ethane and the

²⁷ The acetylene wavefunction we obtain compares favorably with the SCF functions calculated by A. D. McLean, *J. Chem. Phys.* **32**, 1595 (1960) [see also A. D. McLean, B. J. Ransil, and R. S. Mulliken, *ibid.* **32**, 1873 (1960)], and L. Burnelle, *ibid.* **35**, 311 (1961). Our orbital energies, in eV, are $2\sigma_g$ -27.120, $2\sigma_u$ -19.642, $3\sigma_g$ -15.186, π_u -13.533. The total C-C overlap population is 1.93, of which 1.00 comes from the π orbitals. The charges and overlap population may be found in Table VII.

TABLE X. Atomic positions in benzene.

	x	y	z
C ₁	1.40	0.0	0.0
C ₂	-1.40	0.0	0.0
C ₃	0.70	1.212436	0.0
C ₄	0.70	-1.212436	0.0
C ₅	-0.70	-1.212436	0.0
C ₆	-0.70	1.212436	0.0
H ₁	2.50	0.0	0.0
H ₂	-2.50	0.0	0.0
H ₃	1.25	2.165064	0.0
H ₄	1.25	-2.165064	0.0
H ₅	-1.25	-2.165064	0.0
H ₆	-1.25	2.165064	0.0

axial hydrogens of cyclohexane, and was very apparent in some of the more sterically disfavored conformations which we examined. It is interesting to note that in the equilibrium conformations of molecules of the propylene type, there was a noticeable difference in the charges on the methyl hydrogens, the one eclipsing the double bond being more or less "normal," the other two more positive.

The carbon charge distributions are in themselves extremely interesting, particularly since we believe that these are the first estimates of these quantities. Though they are undoubtedly too drastic, we think they bear careful study in the interpretation of reactions—but such an undertaking is beyond the present scope of this work. We will only point to some of the more interesting results: the uniformity and charge alternation in the normal paraffin series; the charge distribution in methyl cyclohexanes (the charge alternation reminiscent of that

to be discussed below for toluene); the charge distributions in the allenes and butenes.

Aromatic Hydrocarbons

In Tables X, XI we give the coordinates and occupied molecular orbitals for benzene, calculated at C-C, 1.40 Å; C-H, 1.10 Å. The most interesting feature of this level scheme is that the lowest bonding π orbital is located below some of the σ levels. Indeed, such behavior was noted for all aromatics: the highest filled orbital was π type, as were the first few unoccupied levels, but lower bonding σ and π levels were interspersed. It is difficult to conceive of an experiment which could distinguish our arrangement of energy levels from the conventionally assumed one where all the occupied σ levels lie below the π 's²⁸; confirmation must await a complete SCF calculation on benzene.

In Fig. 7 we show charge distributions and overlap populations for a number of simple alternant and non-alternant conjugated systems. These are shown separately for the σ and π frameworks and for the composite, $\sigma+\pi$. Fukui *et al.*²⁹ have recently carried out calculations on σ frameworks in aromatics by taking linear combinations of H 1s and C sp^2 hybrid orbitals, with overlap and nonnearest-neighbor interactions neglected. The general features of the charge distributions obtained here agree with the above-quoted work, though there are discrepancies (e.g., order of charges of 1 and 2 positions in naphthalene is reversed). We believe that the great advantage of our calculation is that σ and π orbitals are obtained within one parametrization, while in Fukui's work the relative magnitudes of the Coulomb and resonance integrals used in σ and π calculations

TABLE XI. Molecular orbitals in benzene.*

	-12.797 e _{1g}	-12.879 e _{2g}	-14.297 b _{2u}	-14.510 a _{2u}	-14.637 e _{1u}	-16.576 a _{1g}	-16.601 b _{1u}	-19.933 e _{2g}	-25.785 e _{1u}	-29.567 a _{1g}				
H(1)	-0.0	0.1833	-0.1998	-0.0000	0.0	-0.2059	0.1588	-0.1803	0.2526	-0.1391	0.1787	0.0019	0.1081	-0.0151
H(2)	0.0	0.1833	-0.1998	0.0000	0.0	0.2059	-0.1588	-0.1803	-0.2526	-0.1391	0.1787	-0.0019	-0.1081	-0.0151
H(3)	0.0	-0.2647	-0.0589	-0.0000	0.0	0.0345	0.2577	-0.1803	-0.2526	0.2243	0.0311	0.0946	0.0524	-0.0151
H(4)	0.0	0.0814	0.2587	0.0000	0.0	-0.2404	-0.0989	-0.1803	-0.2526	-0.0852	-0.2098	-0.0927	0.0557	-0.0151
H(5)	-0.0	-0.2647	-0.0589	0.0000	0.0	-0.0345	-0.2577	-0.1803	0.2526	0.2243	0.0311	-0.0946	-0.0524	-0.0151
H(6)	-0.0	0.0814	0.2587	-0.0000	0.0	0.2404	0.0989	-0.1803	0.2526	-0.0852	-0.2098	0.0927	-0.0557	-0.0151
Cs(1)	0.0	-0.0209	0.0228	0.0000	0.0	0.0722	-0.0557	0.0199	0.1744	-0.1949	0.2504	0.0074	0.4150	-0.2810
Cs(2)	-0.0	-0.0209	0.0228	0.0000	0.0	-0.0722	0.0557	0.0199	-0.1744	-0.1949	0.2504	-0.0074	-0.4150	-0.2810
Cs(3)	-0.0	0.0301	0.0067	0.0000	0.0	-0.0121	-0.0904	0.0199	-0.1744	0.3143	0.0436	0.3631	0.2011	-0.2810
Cs(4)	-0.0	-0.0093	-0.0295	-0.0000	0.0	0.0843	0.0347	0.0199	-0.1744	-0.1194	-0.2940	-0.3557	0.2139	-0.2810
Cs(5)	0.0	0.0301	0.0067	-0.0000	0.0	0.0121	0.0904	0.0199	0.1744	0.3143	0.0436	-0.3631	-0.2011	-0.2810
Cs(6)	0.0	-0.0093	-0.0295	0.0000	0.0	-0.0843	-0.0347	0.0199	0.1744	-0.1194	-0.2940	0.3557	-0.2139	-0.2810
Cx(1)	-0.0	-0.1935	-0.2109	-0.0000	0.0	-0.3017	0.2326	-0.2263	0.1846	-0.0643	0.0826	-0.0003	-0.0148	-0.0045
Cx(2)	0.0	-0.1935	-0.2109	-0.0000	0.0	0.3017	-0.2326	0.2263	-0.1846	0.0643	-0.0826	0.0003	0.0148	0.0045
Cx(3)	0.0	-0.2102	0.2859	-0.2875	0.0	-0.1438	0.1729	-0.1131	-0.0923	0.0299	0.1649	-0.0297	0.0384	-0.0022
Cx(4)	0.0	-0.2668	0.2340	0.2875	0.0	-0.1307	-0.1830	-0.1131	-0.0923	-0.1672	0.0114	0.0311	-0.0373	-0.0022
Cx(5)	0.0	0.2102	-0.2859	-0.2875	0.0	0.1438	-0.1729	0.1131	0.0923	-0.0299	-0.1649	0.0297	-0.0384	0.0022
Cx(6)	0.0	0.2668	-0.2340	0.2875	0.0	-0.1307	0.1830	0.1131	0.0923	0.1672	-0.0114	0.0311	0.0373	0.0022
Cy(1)	0.0	-0.2763	0.2535	-0.3319	0.0	-0.0843	-0.1093	-0.0000	-0.0000	0.1451	0.1129	0.0554	-0.0300	0.0000
Cy(2)	0.0	-0.2763	0.2535	-0.3319	0.0	-0.0843	-0.1093	0.0000	0.0000	-0.1451	-0.1129	0.0554	-0.0300	0.0000
Cy(3)	0.0	-0.2013	-0.2368	0.1660	0.0	-0.0246	0.3362	-0.1960	-0.1599	0.1024	-0.0786	0.0022	-0.0304	-0.0039
Cy(4)	-0.0	-0.2533	-0.1802	0.1660	0.0	0.3314	0.0617	0.1960	0.1599	-0.0511	0.1185	0.0033	-0.0303	0.0039
Cy(5)	0.0	0.2013	0.2368	0.1660	0.0	-0.0246	0.3362	-0.1959	-0.1599	-0.1024	0.0786	0.0022	-0.0304	-0.0039
Cy(6)	-0.0	0.2533	0.1802	-0.1660	0.0	0.3314	0.0617	-0.1959	0.1599	0.0511	-0.1185	0.0033	0.0303	-0.0039
Cz(1)	-0.5101	0.1367	0.0	0.0	0.3257	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cz(2)	-0.5101	-0.1367	0.0	0.0	0.3257	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cz(3)	0.3734	-0.3734	0.0	0.0	0.3257	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cz(4)	0.1367	0.5101	0.0	0.0	0.3257	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cz(5)	-0.3734	0.3734	0.0	0.0	0.3257	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cz(6)	-0.1367	-0.5101	0.0	0.0	0.3257	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

* p_x , p_y , p_z orbitals are directed along x, y, z axes. Atoms are located at positions given in Table X.

²⁸ M. P. Gouterman has suggested that a careful search for transitions arising from $\sigma \rightarrow \pi^*$ excitations, and thus polarized perpendicular to the aromatic ring plane, would be useful in this respect. Our energy spectrum supports that given schematically by J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. 1, p. 234.

must be estimated *a posteriori*. The general features of our population analysis may be summarized as follows.

Charges

(1) π charges for alternant hydrocarbons generally small (in the simplest Hückel theory they all vanish) and fall into two groups depending on the number of nearest-neighbor carbons; slightly positive for carbons bonded to three others, slightly negative for carbons bonded to two others. The π charge distributions in naphthalene agree with those calculated by Ruedenberg²⁹ and McWeeny.³⁰

(2) π charges appreciable for nonalternant hydrocarbons.

(3) σ charges, independent of alternant character, fall into three classes depending on the number of nearest-neighbor carbons, and clustered around the following values: -0.23 single neighbor, -0.11 two neighbors, $+0.01$ three neighbors.

(4) Proton charges (not indicated in figures) are all close to $+0.10$ (± 0.01), except for the sterically unfavored hydrogens in phenanthrene and planar biphenyl, which are more positive.

(5) Within each σ and π class defined in (1) and (3) above, for alternant hydrocarbons the magnitude of charge variation over the molecule is small, and in the same direction in the σ and π frameworks, therefore in the entire molecule.

(6) For nonalternant hydrocarbons, σ and π variations are not necessarily in the same direction. The π charge variation dominates and is in agreement with calculations from the simple Hückel theory.¹

Overlap Populations

(1) Quite constant in the σ framework, independent of bond location (except for biphenylene, where the long bonds are clearly indicated even in the σ overlap population; biphenyl was computed with a C-C distance of 1.54 Å for the central bond and thus the small overlap population was built into the calculation).

(2) Quite varied in the π orbitals, and in excellent agreement with ordinary HMO bond orders and thus observed bond lengths. $\sigma + \pi$ dominated by π variation.

Conformations and isomerization energies calculated for the aromatics are generally fair. The sixfold barrier to internal rotation in toluene is computed to be negligible (less than 1 cal). A large barrier is encountered in *ortho*-xylene. This molecule is of particular interest because of the similarity of the barrier geometry to that in *cis*-butene-2; here the underlying rotational barrier should be nearly vanishing and only the nonbonded steric interaction remains, thus permitting an analysis of the relative roles of the two contributions. Unfortunately we have found no estimate of the *ortho*-xylene

TABLE XII. π -electron energies in the aromatics.

ethylene	-26.436 eV
cyclopropenyl cation	-28.414
butadiene	-52.964
cyclopentadienyl anion	-77.064
benzene	-80.208
cycloheptatrienyl cation	-82.002
fulvene	-78.928
pentalene	-105.328
naphthalene	-133.676
azulene	-132.934
biphenylene	-159.964
biphenyl	-160.436
phenanthrene	-187.286
anthracene	-187.020

barrier. The value computed by our method, no doubt too large again, is 0.419 eV with the most stable conformation, similar to that calculated for *cis*-butene-2, being that in which a hydrogen in both methyl groups eclipses the benzene ring plane away from the other methyl group.

Internal rotation about the central carbon-carbon bond in biphenyl has attracted much attention, theoretical as well as experimental. The molecule is planar in the crystal³¹ and twisted in the vapor.³² Theoretical computations indicate a small energy difference favoring a nonplanar form.³³ We have performed a calculation at only two conformations: rings coplanar and perpendicular. In both cases normal bond lengths were retained for the phenyl groups, but the bond joining the rings was taken as 1.54 Å. The perpendicular form comes out more stable by 0.449 eV—again we think over-biasing of nonbonded repulsions is involved.

The order of stabilities of the xylenes is in agreement with thermochemical data, though the quantitative differences are once again too large. Naphthalene emerges 32.3 kcal/mole more stable than azulene, in fortuitous agreement with the experimental value of 32.6 kcal/mole.³⁴ Fulvene is computed to be 25.6 kcal/mole less stable than benzene, the observed difference being about 27 kcal/mole.³⁵ Anthracene comes out 4.2 kcal/mole more stable than phenanthrene, while in actuality the latter isomer is more stable by 6.9 kcal/mole.³⁶ Again we think phenanthrene is discriminated against as a result of its two sterically unhappy hydrogens. This is borne out by the fact that the energy of the π orbitals only (Table XII) favors phenanthrene by 5.4 kcal/mole.

³¹ J. Trotter, *Acta Cryst.* **14**, 1135 (1961).

³² I. L. Karle and L. O. Brockway, *J. Am. Chem. Soc.* **66**, 1974 (1944); O. Bastiansen, *Acta Chem. Scand.* **3**, 408 (1949).

³³ C. A. Coulson, *Conference on Quantum Mechanical Methods in Valence Theory*, Shelter Island, New York, 1961, p. 42. F. J. Adrian, *J. Chem. Phys.* **28**, 608 (1958).

³⁴ E. Heilbronner in *Nonbenzenoid Aromatic Compounds*, edited by D. Ginsburg (Interscience Publishers, Inc., New York, 1959), p. 171.

³⁵ J. H. Day and C. Oestreich, *J. Org. Chem.* **22**, 214 (1956).

³⁶ A. Magnus, H. Hartmann, and F. Becker, *Z. Physik. Chem.* **197**, 75 (1951).

²⁹ K. Ruedenberg, *J. Chem. Phys.* **34**, 1878 (1961).

³⁰ R. McWeeny, *J. Chem. Phys.* **19**, 1614 (1951).

TABLE XIII. Highest occupied and lowest unoccupied energy levels in the aromatics and other compounds.

Molecule	Highest occupied level (eV)	Lowest unoccupied level (eV)	Gap (eV)
benzene	-12.797	-8.345	4.452
naphthalene	-12.073	-9.338	2.635
anthracene	-11.642	-9.839	1.803
phenanthrene	-12.023	-9.310	2.713
azulene	-11.730	-9.872	1.858
pentalene	-11.492	-10.809	0.683
fulvene	-11.991	-10.338	1.653
biphenylene	-11.555	-9.553	2.002
biphenyl (planar)	-12.284	-8.967	3.317
cyclopropenyl cation	-13.374	-8.636	4.738
cyclopentadienyl anion	-11.991	-6.464	5.527
cycloheptatrienyl cation	-12.922	-9.894	3.028
toluene	-12.502	-8.348	4.154
<i>p</i> -xylene	-12.246	-8.347	3.899
<i>m</i> -xylene	-12.397	-8.247	4.150
<i>o</i> -xylene	-12.382	-8.221	4.161
ethane	-13.759	3.131	16.890
ethylene	-13.218	-8.238	4.980
butadiene	-12.592	-9.031	3.561
acetylene	-13.533	-7.142	6.391

However, it may well be that phenanthrene is not precisely planar.³⁷

In Fig. 8 we see the population analysis results for toluene and the xylenes. These are of particular interest since the calculation is accomplished taking into account the hydrogen atoms directly, thus without any *ad hoc* assumptions about hyperconjugation. The toluene charge distribution is in agreement with its *o-p* directing character. It is interesting that the charge differentiation in the ring is accomplished with only a small charge transfer: the C₆H₅ group in benzene contains 29.101 electrons, in toluene 29.021. Incidentally, this is contrary to the accepted picture of a methyl group as an electron donor.³⁸

Energies of the top filled and lowest empty orbitals for aromatics and a few other compounds are shown in Table XIII. The absolute values of the gaps are too small if one relates them to the energy of the aromatic *p*-band transitions, but the variation is very similar to that computed by the simple Hückel theory. The calculated ionization potentials are similarly off, in this case being too large. The particularly small gap for pentalene can be relieved by formation of the -2 ion, which indeed was recently synthesized.³⁹

A calculation was performed on a number of possible geometries for cyclo-octatetraene. In agreement with recent experimental results,⁴⁰ the tub form was favored

³⁷ G. Ferguson and J. M. Robertson in *Advances in Physical Organic Chemistry*, edited by V. Gold (Academic Press Inc., New York, 1963), p. 203.

³⁸ See, however, W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron* **17**, 199 (1962).

³⁹ T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.* **84**, 865 (1962).

⁴⁰ H. L. Strauss and G. K. Fraenkel, *J. Chem. Phys.* **35**, 1738 (1961). T. J. Katz and H. L. Strauss, *ibid.* **32**, 1873 (1960).

in the neutral molecule, but the anion and dianion preferred the planar geometry.

Energetic Relationships

In our previous work on the boron hydrides we found that it was possible to make some absolute thermochemical sense from the computed total energies. If we calculate a binding energy for CH₄, i.e., subtract $\Sigma E = -139.608$ eV from ΣE of the atoms at infinity⁴¹ (C at infinity taken in *sp*³ valence state), we obtain a binding energy of 29.608 eV, roughly 1.8 times the correct atomization energy. This factor, not very different from *K*, approximately relates all of the calculated binding energies to the true dissociation energies.⁴²

In themselves the binding energies are not very interesting and are not tabulated here—they may easily be computed from the data in Table I. A question of interest is whether an over-all additive scheme of bond energies exists in our calculations. The prognosis must be poor since different atomic separations are used for different classes of compounds. For this purpose we can work with total energies, if we remember not to attribute any direct significance to the magnitudes manipulated. From *n*-octane and *n*-nonane we obtain the contribution to the total energy per bond: C-C, 34.4610 eV; C-H, 34.8715 eV. These reproduce the other normal paraffin energies very well but lead to disagreements already for methane and cyclohexane. Extended to other types of bonds, matters are sometimes good, sometimes bad. Another serious deficiency manifests itself in the energy per CH₂ in the cycloalkane series: C₃H₆, 104.673 eV; C₄H₈, 104.253; C₅H₁₀, 104.178; C₆H₁₂, 104.244. Thus no strain energies are apparent.

CONCLUSIONS

The most important accomplishment of this work is the demonstration that semiempirical molecular orbital theory need not limit itself to planar conjugated molecules. We have been able, with one and the same set of parameters, to gain insight into such diverse properties as the barrier to internal rotation and the relative role of σ and π frameworks in aromatics. In subsequent papers in this series we will show that indeed one need not confine oneself to organic compounds; that this parametrization makes it possible to make a good guess at the wavefunctions of inorganic compounds as well.

Let us review briefly the clear failures of the theory as it was applied with our choice of parameters. There exists a tendency to overemphasize steric repulsions, which finally leads to incorrect isomerization energies for the pentanes and hexanes. This behavior cannot be corrected by two obvious maneuvers: changing *K*, or

⁴¹ Note that as usual with LCAO-MO calculations, the wavefunction does not have the correct behavior at infinity.

⁴² It is interesting in this connection to note that in a calculation in which the Mulliken approximation was used for three- and four-center integrals, the binding energy was also overestimated. (L. Burnelle, Ref. 27).

increasing the hydrogen Slater exponent to a value more appropriate for molecules, about 1.2. These manipulations can reproduce the experimental barrier in ethane, but do not alleviate our difficulties with the hexanes. Using the alternate relation $H_{ij} = K'S_{ij}$ does help somewhat but if we are to deal later with a wide variety of heteroatoms we must reject this alternative (see Appendix). It is our feeling that the absolute minimization procedure carried out in detail for each molecule might lead to improved results, but this process seems much too complicated considering the degree of sophistication of the model. It should be stated that we are fortunate to obtain as good qualitative results as we have, having chosen to process our molecules at distances not corresponding to minima. The other major failure, the absence of strain energies in small rings, remains without an explanation.

As for the successes, they lie in the correct assignment of equilibrium conformations where these are known. Barriers are way off, and even qualitative behavior as one goes from molecule to molecule is sometimes incorrect. We have much greater faith in the charge distributions, since our experience with the simple Hückel theory tells us that these are quite insensitive to the choice of parameters. Indeed, we consider the calculation of charge distributions in aliphatics and the σ and π systems in aromatics as interesting a feature of this method as the fact that the Hückel theory can produce a barrier in ethane.

Finally, we want to issue a plea for a search for that semiempirical parametrization which will improve on these results. For it seems clear to us that a simple wavefunction with an atrocious energy can still nicely predict the geometry of a molecule, and thus answer the chemists prime question of molecular structure. Though the necessary integrals for a reasonable *a priori* calculation are now becoming available, a semiempirical procedure is still necessary, since the number and variety of these integrals increases astronomically with molecular size.

ACKNOWLEDGMENTS

I would like to express my indebtedness to L. L. Lohr, Jr., R. M. Pitzer, W. N. Lipscomb, E. B. Wilson, Jr., E. J. Corey, M. P. Gouterman, and H. Kobayashi for many discussions relating to the problems covered in this paper. Abundant computer time was made available by the Harvard and MIT Computation Centers. This work was supported in part by the National Institutes of Health.

APPENDIX

Choice of H_{ij}

Once one decides not to neglect the off-diagonal overlaps and Hamiltonian matrix elements in the secular determinant $|H_{ij} - ES_{ij}| = 0$, one is faced with the

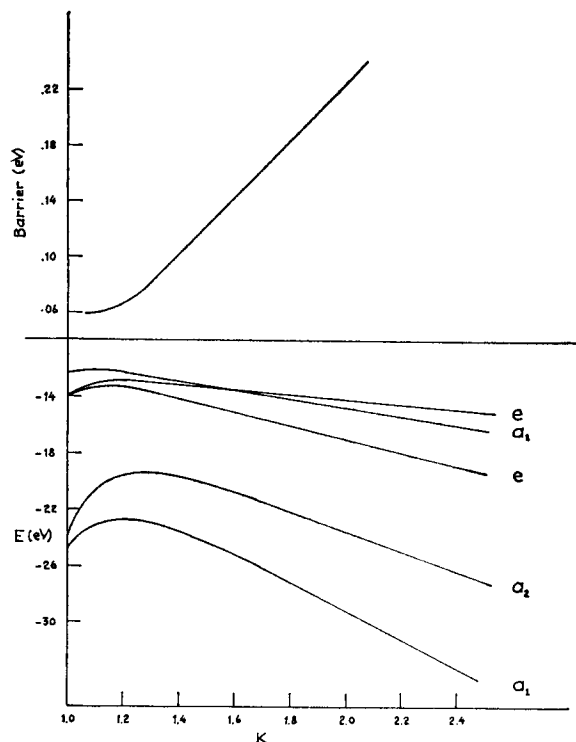


FIG. 10. Barrier to internal rotation (top) and individual bonding energy levels (bottom) for ethane as a function of K .

choice of the distance dependence of the H_{ij} . In our earlier work on the boron hydrides we used the relationship $H_{ij} = K'S_{ij}$, with a value of $K' = -21$ eV. However, if one is to consider a large variety of heteroatoms, one is forced to use an inordinately high magnitude of K' due to the requirement that K' be smaller than any diagonal matrix element, i.e., valence-state ionization potential. The difficulty may be appreciated from the following example. Suppose all $H_{ii} = \alpha$ and we chose K' also equal to α . Then our secular equation becomes $|(\alpha - E)S_{ij}| = 0$ which is satisfied by all $E = \alpha!$ For $K' > \alpha$ level inversion results, with generally absurd consequences. Thus K' must be strictly less than α .

A better approximation⁴³ is to take our Eq. (3), $H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$. If one makes use of the Mulliken approximation for the product of two charge distributions χ_i and χ_j

$$\chi_i\chi_j = 0.5S_{ij}(\chi_i\chi_i + \chi_j\chi_j),$$

one obtains $K = 1$. However, this again leads to absurd results for the homonuclear case. One is thus forced to

⁴³ L. L. Lohr, Jr., has used a similar expression $H_{ij} = K''S_{ij}(H_{ii}H_{jj})^{1/2}$ which differs from ours only in second order and has certain computational advantages. L. L. Lohr, Jr., and W. N. Lipscomb, J. Chem. Phys. **38**, 1607 (1963). T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, J. Am. Chem. Soc. **85**, 846 (1963). L. L. Lohr, Jr. and W. N. Lipscomb, *ibid.* p. 240. See also C. J. Ballhausen and H. B. Gray, Inorg. Chem. **1**, 111 (1962).

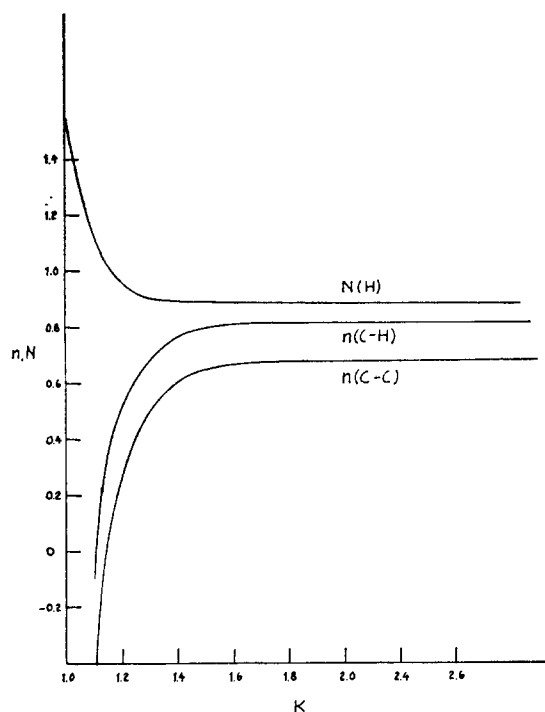


FIG. 11. Gross atomic population on hydrogen, C-H and C-C overlap populations in ethane as a function of K .

use K greater than 1.0. Various other authors have used $K = 1.87$ and 2.00 .^{6,43}

In Fig. 10 we show the variation of the energies of the occupied orbitals of ethane (staggered, C-C, 1.54 Å, C-H, 1.10 Å) with K . Above $K = 1.6$ a good linear proportionality holds. A different proportionality, however, holds for the energy levels of the eclipsed conformation, so that the barrier also varies with K (Fig. 10). In Fig. 11 we show the corresponding variation in the overlap populations and charges for the staggered geometry. Note the insensitivity of these quantities once K is again greater than about 1.6; the off-diagonal matrix elements begin to dominate and the wavefunction becomes independent of K .

We conclude that if we are interested in charge distributions in molecules, that these are insensitive to K over a large region. The binding energy, however, becomes proportional to $K - 1$ for large K and already exceeds the observed heat of atomization for any K greater than 1.0. The value 1.75 was chosen as a reasonable compromise between the desire to match the experimental barrier in ethane, and the necessity to work in a region where populations are stable.

Total Energy and Electronic Energy

It will be noted that the minimum in Fig. 2 arises when we plot the simple sum of one-electron energies vs internuclear separation. The complete Hamiltonian may be written as the sum of electron-electron, electron-nuclear, and nuclear-nuclear energies,

$$H = \sum_{ee'} H_{ee'} + \sum_{en} H_{en} + \sum_{nn'} H_{nn'}. \quad (4)$$

In the Hückel theory H is approximated by a sum of one-electron effective Hamiltonians, whose matrix elements we endeavor to guess in some systematic manner

$$H = \sum_e H_{eff}. \quad (5)$$

The term $H_{nn'}$ in Eq. (4) is a purely classical nuclear-nuclear repulsion, and one has the choice of taking it over to the left side of the expression before approximation by (5); or one can leave it where it is, and in effect include part of the nuclear repulsion in each effective one-electron Hamiltonian. If to the potential curve of Fig. 1 we add the nuclear repulsions of the protons and the carbon shielded by its $1s$ electrons, the minimum vanishes. This, and the behavior of the simple sum of one-electron energies at small internuclear distances leads us to conclude that our method of guessing H_{ij} simulates within the electronic energies the presence of nuclear repulsions at small distances, and this is what gives us our minimum.

To this operational argument we may add a theoretical one, due to an observation made by Slater.⁴⁴ The sum of the one-electron energies of a Hartree-Fock Hamiltonian is equal to the total energy minus the nuclear-nuclear repulsions, plus the electron-electron repulsions. The last two terms cancel, roughly (it is sufficient if their difference varies slowly with distance), and thus the simple sums of one-electron energies behave approximately as the true molecular energies. This parallelism and the accompanying overestimation of binding energies should be investigated further. The procedure of viewing simple sums of one-electron energies was advanced in our previous calculations on boron hydrides and carboranes,⁷ and by L. L. Lohr, Jr., in a number of calculations on transition metal ions, noble-gas halides, and sulfones.⁴³

⁴⁴ J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. I, p. 108.