California at Los Angeles) for the determinations of the nuclear Overhauser effects and to Dr. R. O. Hutchins and Sr. M. Knoeber for several stimulating discussions. The A-60A nmr instruments used in this investigation were acquired under National Science Foundation equipment Grant GP-6875.

# Ground States of $\sigma$-Bonded Molecules. IX.[1] The MINDO/2 Method[2]

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**Abstract:** A computer program has been written for automatically optimizing the parameters in MO treatments. Using this, and using parametric functions for the core resonance integrals and core–core repulsions similar to those used in the PNDO approximation, we have been able to develop a version (MINDO/2) of the MINDO method which gives good estimates of bond lengths, heats of formation, and force constants simultaneously for a wide variety of hydrocarbons, thus satisfying the minimum requirements for a procedure to be used convincingly for calculating potential surfaces. Potential surfaces are calculated for the torsional isomerization of ethylene and cumulenes, for hydrogen abstraction reactions of methyl, and for the dimerization of ethylene. The results are encouraging. The method also gives good estimates of first ionization potentials.

The present theory of organic chemistry is very largely based on simple qualitative versions of MO theory; there is, however, a growing need for some more quantitative approach which would allow the mechanisms and rates of chemical reactions to be predicted. If an approach of this kind is to be of practical value to organic chemists in their study of reactions, on a basis analogous, say, to kinetic studies or nmr spectroscopy, it must be generally applicable, and the calculations involved in it must be feasible for quite large systems without unreasonable expense.

In order to predict chemical reactivity and reaction mechanisms, we must be able to calculate complete potential surfaces for assemblies of atoms as a function of their coordinates in space. The minima in the corresponding many-dimensional potential surface for a given assembly correspond to possible stable species, and the cols separating them to transition states for their interconversion. If our predictions are to be reliable, the potential surface must be calculated with an accuracy of the order of ±1 kcal/mol.

Such accuracy cannot of course be attained by direct or approximate integration of the Schrödinger equation, except for the very simplest systems. In the case even of simple organic molecules, the energies given by the best methods at present available are in error by chemically speaking huge amounts. If therefore the results of such calculations are to be usefully correlated with chemical phenomena, the correlations can be established only on an empirical basis.

It would of course be entirely possible for the errors to be the same for a given assembly of atoms regardless of their geometry; this could apply to exact SCF calculations if the correlation energy were constant. In that case heats of formation would be correctly predicted and the errors in the absolute energies would be chemically unimportant. This unfortunately is not the case. The most reliable SCF calculations for diatomic molecules lead to heats of atomization that can be in error by ±100% and similar huge errors appear in the results of more approximate calculations for polyatomic molecules. Even errors of this kind might be tolerable in certain connections if the errors in the calculated heats of atomization were the same for different sets of molecules formed from the same set of atoms; in this case one could at least predict heats of reaction. Even here, however, the errors are not constant.[4] This kind of approach cannot therefore be applied with any assurance to chemical problems. It would be necessary first to carry out very extensive calculations for a wide variety of molecules and try to devise empirical corrections to the calculated heats of formation to bring them into line with experiment;[5] even if an approach of this kind were feasible, it would be of very little practical value to organic chemists because the computations for molecules of even quite moderate size would take too much time and so cost too much.

An alternative procedure is to try to improve the practical results of quantum mechanical calculations by treating some of the integrals appearing in them as parameters. This type of approach has of course often been used in chemistry in cases when exact mathematical solutions of chemical problems were not available (*e.g.*, the theory of strong electrolytes) and the HMO method represents an early application of this kind to quantum theory.

Insofar as quantum chemistry claims to be a branch of chemistry, its sole criterion must be its usefulness to chemists. Which of these two equally empirical approaches is the better must be decided on this basis. The main requirements are that the procedure should

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[1] Part VIII: N. Bodor and Michael J. S. Dewar, *Tetrahedron*, in press.

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[3] Robert A. Welch Postdoctoral Fellow.

[4] L. C. Snyder, *J. Chem. Phys.*, 46, 3602 (1967).

[5] An approach of this kind has been applied to the CNDO/2 method by K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1968).

give reliable predictions of sufficient accuracy, and that the necessary calculations should be feasible using existing computers and should not involve excessive cost. This point needs to be emphasized, for there has recently been a tendency for protagonists of "*ab initio*" methods to imply that they are more rigorous and more valid than "semiempirical" ones. So far as chemistry is concerned, the *only* criterion is practical success; whether parameters are introduced openly into the quantum mechanical treatment, or tacitly into correlations of results of inherently inaccurate *ab initio* calculations with observation, is of no practical significance. The situation would of course be different if exact solutions of the Schrödinger equation were available, but they are not.

In establishing the validity of a calculated potential surface, the only experimental data available to us concern the potential minima, *i.e.*, the possible stable species. The quantities available are the geometries of the stable species and their energies, which define the positions of the minima, and the frequencies of molecular vibrations, which define the curvatures of the potential surfaces at the minima. It is easily seen that *all* these quantities must be correctly estimated if the intervening parts of the potential surface are to be predicted with any reliability. This is best illustrated by the one-dimensional case in Figure 1. Here A represents a stable species that can be converted to B or C *via* transition states X and Y, respectively. The full line indicates the "true" solution, the favored reaction being A → C. The other lines show the effect of miscalculating (a) the geometry of B (· · ·), corresponding to a horizontal displacement of the minimum; (b) the energy of B (---), corresponding to a vertical displacement; and (c) the vibration frequencies of B (- · · --), corresponding to an error in the curvature at the minimum. In each case, the result is a wrong prediction that A → B should be favored over A → C.

None of the methods so far proposed satisfies these criteria. *Ab initio* methods, or semiempirical methods in which the parameters are chosen to mimic them,[6] give adequate estimates of molecular geometries but unsatisfactory energies; these procedures also seem to give poor estimates of force constants in the few cases where calculations have been reported.[7] The extended Hückel method[8] is even worse, giving unacceptable errors in both geometries and energies.

The most hopeful indication seemed to be the success of a semiempirical SCF-MO treatment of conjugated compounds using the Hückel $\sigma,\pi$ approximation;[9] this gave remarkably good estimates of geometries, heats of formation, and even force constants for a wide variety of conjugated molecules derived from carbon, hydrogen, nitrogen, and oxygen. While the limitation to conjugated systems is far too restrictive for general chemical purposes, it seemed likely that an analogous treatment including all the valence electrons, but differing from those of Pople, *et al.*,[6] in that the parameters are chosen to fit experiment rather than to match the results of *ab initio* calculations, might prove successful.

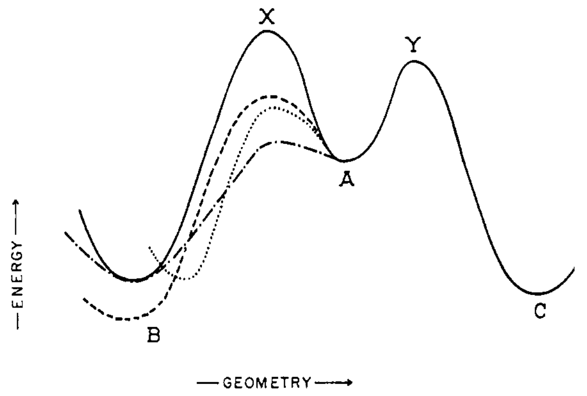

Figure 1.

Preliminary studies along these lines indeed led to two semiempirical SCF-MO treatments (PNDO[10] and MINDO[11]) which gave surprisingly good estimates (to within a few kcal/mol) of the heats of formation of a wide range of organic compounds. Unfortunately neither procedure gave satisfactory molecular geometries and our efforts to improve them failed. It now appears, however, that the trouble lay in the choice of parameters rather than in the general approach. The choice of parameters in fact presents a very difficult problem, since they are all so interrelated that it seems impossible to deduce by intuition what the effect of a given change in a given parameter will be. After fruitless trials, we finally wrote a computer program to optimize parameters automatically; using this we have been able to devise a version (MINDO/2) of the MINDO approximation, which gives good estimates of geometries, and reasonable estimates of energies and force constants, for a wide variety of hydrocarbons. The present paper describes this approach and its application to several specific chemical problems.

## Theoretical Approach

The procedure used here is the INDO approximation of Pople, *et al.*,[6b] parametrized to give good estimates of ground-state properties rather than to match the results of *ab initio* calculations. The one-center integrals, and two-center repulsion integrals, were estimated as in the original MINDO method[11] (henceforth termed MINDO/1) and core-electron attractions were likewise set equal to *minus* the corresponding electron–electron repulsions. The one-electron resonance integrals $\beta_{ij}{}^{c}$ and the core–core repulsions $CR_{mn}$ are represented by functions of internuclear distance that conform to the physical requirements and contain parameters that can be adjusted to give the best fit to experiment. To avoid proliferation of parameters, we have limited ourselves to two per atom pair. Thus in hydrocarbons there will be two parameters for CC interactions, two for CH interactions, and two for HH interactions.

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[6] *E.g.*, the CNDO/2 and INDO methods of Pople and his collaborators: (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys., Suppl.*, **43**, 5129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, 5136 (1965); *J. Chem. Phys.*, **44**, 3289 (1966); (b) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967).

[7] See, *e.g.*, G. E. Segal, *ibid.*, **47**, 1876 (1967).

[8] R. Hoffmann, *ibid.*, **39**, 1397 (1963).

[9] See M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969); and M. J. S. Dewar and T. Morita, *ibid.*, **91**, 796 (1969), and papers cited therein.

[10] M. J. S. Dewar and G. Klopman, *ibid.*, **89**, 3089 (1967); N. C. Baird and M. J. S. Dewar, *ibid.*, **89**, 3966 (1967); *Theor. Chim. Acta*, **9**, 1 (1967).

[11] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262, 1275 (1969); *J. Amer. Chem. Soc.*, **91**, 352 (1969).

The restrictions on the forms of these functions were stated previously.[10,11] As pointed out by Mulliken[12] $\beta_{ij}^c$ should be more or less proportional to the overlap integral $S_{ij}$, and to a mean of the valence-state ionization potentials ($I_i$ and $I_j$) of the orbitals in question. Setting $\beta_{ij}$ proportional to $S_{ij}$ also ensures that the results of the calculation are invariant to rotation of the coordinate axes.[6] We have therefore used functions of the type

$$\beta_{ij}^c = BS_{ij}(I_i + I_j)_1 f(r_{ij}) \tag{1}$$

where $r_{rj}$ is the internuclear distance and $B$ a parameter.

The core repulsion between atoms m and n, *i.e.*, $CR_{mn}$, must be equal to the electron–electron repulsion between neutral atoms ($ER_{mn}$) when $r_{mn}$ is large, in order that there should be no long range coulomb interactions between neutral atoms. In MINDO/1, $CR_{mn}$ was set equal to $ER_{mn}$ at all distances, as in the $\pi$ approximation;[9] this, however, inevitably leads to bond lengths which are too short. We have therefore used various parametric expressions for $CR_{mn}$ which tend to $ER_{mn}$ as $r_{mn} \rightarrow 0$ and become larger than $ER_{mn}$ at shorter distances; physical intuition suggests that as $r_{mn} \rightarrow 0$, $CR_{mn}$ should tend to the point-charge potential $Z_m Z_n e^2/r_{mn}$ when $Z_m$ and $Z_n$ are the formal charges on the cores of the two atoms. A suitable expression for $CR_{mn}$ is then

$$CR_{mn} = ER_{mn} + (Z_m Z_n e^2/r_{mn} - ER_{mn})f_2(r_{mn}) \tag{2}$$

where

$$\begin{aligned} f_2(r_{mn}) &\rightarrow 0 \text{ as } r_{mn} \rightarrow \infty \\ &\rightarrow 1 \text{ as } r_{mn} \rightarrow 0 \end{aligned} \tag{3}$$

and where the function $f_2$ contains a parameter ($\alpha$) that determines the internuclear distance at which $CR_{mn}$ begins to deviate from $ER_{mn}$.

## Parametrization Procedure

The parametrization procedure depends on a least-squares fit to the heats of formation of a set of standard molecules, and to the length of one bond in each of them. The molecules are of course ones for which accurate experimental data are available and the number of molecules must be considerably greater than the number of parameters to be determined. The input consists of the data required for MINDO calculations for the molecules, the input geometries being those experimentally determined, together with an initial set of values for the parameters. Using a Taylor expansion, the total variation $\delta E^m$ in the MINDO energy $E^m$ for molecule m for variations $\delta B_r$, $\delta\alpha_s$ in the parameters $B_r$ and $\alpha_s$ can be written approximately as

$$\delta E^m = \sum_r \frac{\partial E^m}{\partial B_r}\delta B_r + \sum_s \frac{\partial E^m}{\partial \alpha_s}\delta\alpha_s \tag{4}$$

If the experimental value for the energy is $E_0{}^m$, the changes in the $B$'s and $\alpha$'s necessary to make the MINDO value agree with it must then obey the equation

$$\sum_r \frac{\partial E^m}{\partial B_r}\delta B_r + \sum_s \frac{\partial E^m}{\partial \alpha_s}\delta\alpha_s = E_0{}^m - E^m \tag{5}$$

There will be $n$ such equations ($n$ being the total number of standard molecules) which can be written in the form

$$\sum_{r=1}^{2k} C_{mr}{}^E x_r = E_0{}^m - E^m = A_m{}^E \; (m = 1, 2, \ldots, n) \tag{6}$$

where

$$C_{mr}{}^E(r \leq k) = \frac{\partial E^m}{\partial B_r};\; C_{mr}{}^E(r > k) = \frac{\partial E^m}{\partial \alpha_{(r-k)}}$$

$$x_r(r \leq k) = \partial B_r;\; x_r(r < k) = \delta\alpha_{(r-k)} \tag{7}$$

and $k$ is the total number of different types of atom pairs (three in the case of hydrocarbons; *viz.* CC, CH, HH).

Since $n > 2k$ the problem is overdetermined; the optimum (least-squares) solution is given[13] by constructing the square matrix $[Q_{ij}{}^E]$, and the vector $[D_k{}^E]$ defined by

$$Q_{ij}{}^E = \sum_m C_{mi}{}^E C_{mj}{}^E;\; D_k{}^E = \sum_m C_{mk}{}^E A_m{}^E \tag{8}$$

and solving the set of $2k$ simultaneous equations for the $x_r$

$$[Q_{ij}{}^E][x_j] = [D_k] \tag{9}$$

The differential coefficients $\partial E^m/\partial B_r$ are found by calculating $E^m$ for two values of $B_r$, $B_r$ and $(B_r + \epsilon)$, $\epsilon$ being small, and equating the differential to $\delta E^m/\epsilon$.[14] Since the parameters $\alpha$ normally appear only in the expression for the core repulsion (eq 2), the differential coefficients $\partial E^m/\partial\alpha_s$ can be found by direct differentiation.

Since this treatment depends on the validity of a first-order Taylor expansion, it depends on the $E^m$ being essentially linear functions of the parameters $B_r$ and $\alpha_s$. This condition seems to be satisfied by the $B$ parameters, but not always by the $\alpha$ ones. Now we can write

$$E^m = E_1{}^m(B_r) + E_2{}^m(\alpha_s) \tag{10}$$

where $E_1{}^m$ is a function only at the parameters $B_r$ (it is in fact the total electronic energy) while the total core repulsion $E_2{}^m$ is a function only of the $\alpha_s$. It is therefore a simple matter to recalculate the $E^m$, replacing each $\alpha_s$ by $(\alpha_s + \delta\alpha_s)$, where $\delta\alpha_s$ is the correction to $\alpha_s$ found by solving eq 9; the parametrization procedure is then repeated, and the cycle continued until solution of eq 9 gives essentially zero values for the corrections $\delta\alpha_s$. This procedure allows for nonlinearity in the dependence of $E^m$ on the $\alpha$'s.

So far of course we have considered only the energies of the molecules; the parameters found in this way will give good heats of formation but poor estimates of bond lengths. We can set up an alternative set of equations to choose parameters that will optimize the bond lengths instead of total energies, as follows. Our object is to fit the length of one bond in each molecule; let the length of that bond in molecule m be $R_m$. We now repeat the MINDO calculations for the molecules with $R_m$ replaced by $R_m \pm \epsilon$, $\epsilon$ being small. Denote the corre-

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[12] For a detailed discussion see M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1969.

[13] G. E. Forsythe and C. B. Moler, "Computer Solution of Linear Algebraic Systems," Prentice-Hall Inc., Englewood Cliffs, N. J., 1967, pp 13, 16.

[14] In a recent improved version of this program, written by Dr. A. Brown, the differential coefficients are calculated from the bond-order matrix, using the perturbation method of Coulson and Longuet-Higgins.[15]

[15] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A191**, 39 (1947); **A192**, 16 (1947); **A193**, 447, 456 (1948); **A195**, 188 (1948).

sponding energies by $E^{m\pm}$; if the equilibrium length given by the MINDO method is in fact $R_m$, then

$$E^{m+} = E^{m-} \tag{11}$$

since if $\epsilon$ is small, the potential function of the bond can be regarded as parabolic. If this relation does not hold, then we must modify the $B_r$ and $\alpha_s$ so that it does. As before

$$\delta E^{m+} = \sum_r \frac{\partial E^{m+}}{\partial B_r}\,\delta B_r + \sum_s \frac{\partial E^{m+}}{\partial \alpha_s}\,\delta\alpha_s \tag{12}$$

$$\delta E^{m-} = \sum_r \frac{\partial E^{m-}}{\partial B_r}\,\delta B_r + \sum_s \frac{\partial E^{m-}}{\partial \alpha_r}\,\delta\alpha_s \tag{13}$$

Hence the quantities $\delta B_r$, $\delta\alpha_s$ must obey the equation

$$\sum_r\left\{\frac{\partial E^{m+}}{\partial B_r} - \frac{\partial E^{m-}}{\partial B_r}\right\}\delta B_r + \sum_s\left\{\frac{\partial E^{m+}}{\partial \alpha_s} - \frac{\partial E^{m-}}{\partial \alpha_s}\right\}\delta\alpha_s = E^{m+} - E^{m-} \tag{14}$$

This set of $m$ equations may be written (*cf.* eq 6)

$$\sum_{r=1}^{2k} C_{mr}{}^{R}x_r = E^{m+} - E^{m-} = A_m{}^{R} \qquad (m = 1, 2, \ldots, n) \tag{15}$$

where the quantities $C_{mr}{}^{R}$ are defined in terms of the coefficients in eq 14 by obvious analogy with eq 7. We now construct a square matrix $[Q_{ij}{}^{R}]$ and a vector $[D_k{}^{R}]$ defined by

$$Q_{ij}{}^{R} = \sum_m C_{mi}{}^{R}C_{mj}{}^{R};\; D_k{}^{R} = \sum_m C_{mk}{}^{R}A_m{}^{R} \tag{16}$$

Solution of the set of simultaneous equations

$$[Q_{ij}{}^{R}][x_j] = [D_k{}^{R}] \tag{17}$$

then gives us a set of parameters that optimize bond lengths at the expense of energies.

In order to optimize both energies and bond lengths simultaneously, we construct a new matrix $[Q_{ij}]$ and vector $[D_k]$ defined by

$$[Q_{ij}] = [Q_{ij}{}^{E}] + a[Q_{ij}{}^{R}];\; [D_k] = [D_k{}^{E}] + a[D_k{}^{R}] \tag{18}$$

where $a$ is a weighting factor that determines the relative importance attached to errors in bond lengths and to errors in bond energies. Solution of the set of equations

$$[Q_{ij}][x_j] = [D_k] \tag{19}$$

then gives us our final set of corrections $\delta B_r$ and $\delta\alpha_s$.

The success of this procedure depends of course on the initial choice of parameters, since the Taylor expansions are valid only if the corrections $\delta B_r$ and $\delta\alpha_s$ are small; if this condition is not met, the calculation is repeated with a new set of initial values, chosen on the basis of the results of the previous calculation or calculations.

Finally the equilibrium bond lengths $r_m$ and energies $E_m$ are calculated by quadratic interpolation from the values $E^m$ and $E^{m\pm}$, these being the energies for bond lengths $r_m$ and $(r_m \pm \epsilon)$. The whole calculation is carried out for various values of the statistical weighting factor $a$ and the optimum set of resulting equilibrium bond lengths and energies chosen by inspection.

## Results and Discussion

**A. Parametrization.** Calculations of this kind were carried out for the twenty hydrocarbon systems listed below (Table I). Note that several of the hydrocarbons appear twice, a different bond being considered in each case. Experimental values were used for the remaining bond lengths and for the bond angles. All together one hundred and fifty different combinations of possible functions $f_1$ and $f_2$ in eq 1 and 2 were tried, with varying degrees of success. However one feature seemed common to all the otherwise more successful procedures; any set of parameters which led to acceptable heats of formation, and CC bond lengths, invariably gave CH bond lengths that were systematically too long. Since the parametrization procedure suffers from obvious problems if there are such systematic deviations, and since a systematic error in CH bond lengths is not chemically important (because it does not affect the over-all molecular geometry, hydrogen being univalent[16]), the parameters were fitted to structures with the CH bond lengths all increased by 0.1 Å.

The best choice of functions $f_1$ and $f_2$ corresponded closely to the original choice[10] made on the basis of physical intuition, a rather pleasing result; *i.e.*,

$$f_1 = 1;\; f_2 = \exp(-\alpha r_{mn}) \tag{20}$$

where $\alpha$ is the core repulsion parameter. The choice of parameters in these expressions turned out to be ambiguous, however, several different sets giving comparable results. The set used in the calculations reported below was as follows

$$B_{CC},\ 0.36862;\; B_{CH},\ 0.34104;\; B_{HH}, 0.48328$$
$$\alpha_{CC},\ 1.6343\ \text{Å}^{-1};\; \alpha_{CH},\ 1.1843\ \text{Å}^{-1};\; \alpha_{HH},\ 0.6653\ \text{Å}^{-1} \tag{21}$$

Note that the constants $B$ are dimensionless, while the $\alpha$'s have the dimension of reciprocal length.

Table I compares the calculated and observed heats of formation and selected bond lengths for the standard compounds; the "assumed" values for CH bonds are, as indicated, greater than those observed by 0.1 Å. Even if allowance is not made for this offset, the agreement between the calculated and observed bond lengths is at least as good as that given by other methods[6,17] while the errors in the calculated heats of formation are less by two or three orders of magnitude, being mostly less than ±4 kcal/mol. Note in particular the good fit for acetylene; in the PNDO[10] and MINDO/1[11] methods it was found impossible to fit the heats of formation of ethane, ethylene, and acetylene simultaneously. The calculated CC bond lengths are also in remarkable agreement with experiment along the series. The heats of formation and geometries of butadiene and benzene are also well reproduced, suggesting that the approach used here also works well for conjugated and aromatic hydrocarbons. Indeed, the only deviation significantly

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(16) It should perhaps be pointed out that excessive stress tends to be placed by theoreticians on the calculation of bond lengths, probably because these can be estimated much more easily than other quantities such as energies. From a chemical standpoint, the exact lengths of bonds are not often in themselves of much importance, particularly the lengths of peripheral bonds which do not influence the geometry of the molecule as a whole.

(17) See, *e.g.*, M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968); H. A. Pohl and L. M. Raff, *Intern. J. Quant. Chem.*, **1**, 577 (1967).

Table I. Heats of Formation, Bond Lengths, Force Constants, and Ionization Potentials of Hydrocarbons

| Compound and bond[a] | Heat of formation, kcal/mol | | Bond length, Å | | | Force constant, dyne/cm × $10^5$ | | | Ionization potential, eV | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Obsd[b] | Calcd | Assumed[c] | Calcd | CNDO/2[d] | Obsd[e] | Calcd | CNDO/2[d] | Obsd[f] | Calcd[g] |
| Methane, CH | −17.9 | −11.9 | 1.194 | 1.196 | | 5.0 | 5.7 | | 12.98 | 12.69 |
| Ethane, CC | −20.2 | −21.2 | 1.534 | 1.524 | 1.476 | 4.5 | 5.4 | 33.9 | 11.51 | 10.89 |
| Ethane, CH | −20.2 | −21.8 | 1.193 | 1.209 | 1.110 | 4.8 | 5.6 | 12.7 | 11.51 | 10.89 |
| Ethylene, CC | +12.5 | +16.7 | 1.337 | 1.335 | 1.320 | 9.6 | 10.1 | 23.9 | 10.50 | 10.59 |
| Ethylene, CH | +12.5 | +16.2 | 1.183 | 1.201 | 1.110 | 5.1 | 5.8 | 12.8 | 10.50 | 10.59 |
| Acetylene, CC | +54.3 | +53.5 | 1.205 | 1.200 | 1.198 | 15.8 | 15.9 | 35.5 | 11.36 | 11.00 |
| Acetylene, CH | +54.3 | +53.5 | 1.159 | 1.170 | 1.093 | 5.9 | 6.3 | 12.3 | 11.36 | 11.00 |
| Propane, CC | −24.8 | −24.9 | 1.534 | 1.534 | | | 5.6 | | 11.06 | 10.56 |
| *n*-Butane, CC | −30.2 | −28.4 | 1.534 | 1.540 | | | 5.5 | | 10.67 | 10.13 |
| Ethane (ecl),[f] CC | −17.3 | −19.8 | 1.534 | 1.536 | | | 5.5 | | | |
| *t*-Butadiene, C═C | +26.3 | +29.5 | 1.337 | 1.345 | | | 10.1 | | 9.07 | 9.40 |
| *t*-Butadiene, C—C | +26.3 | +29.6 | 1.483 | 1.473 | | | 5.6 | | 9.07 | 9.40 |
| *t*-2-Butene, C═C | −2.7 | −8.7 | 1.337 | 1.350 | | | 9.9 | | 9.12 | 9.34 |
| 1-Butene, C═C | 0.0 | +1.3 | 1.337 | 1.346 | | | 10.1 | | 9.59 | 9.74 |
| Cyclopropane, CC | +12.7 | +3.8 | 1.514 | 1.519 | | | 5.6 | | 10.06 | 10.21 |
| Cyclopentane, CC | −18.5 | −22.4 | 1.534 | 1.549 | | | 6.3 | | 10.49 | 9.76 |
| Cyclohexane (chair), CC | −29.4 | −26.6 | 1.534 | 1.549 | | | 6.2 | | 9.81 | 9.65 |
| Cyclohexane (boat), CC | −24.1 | −22.0 | 1.534 | 1.551 | | | | | | |
| Benzene, CC | +19.8 | +20.2 | 1.397 | 1.407 | | 7.6[h] | 9.4 | | 9.24 | 9.61 |
| Toluene, CMe | +11.9 | +11.1 | 1.520 | 1.509 | | | 5.3 | | 8.82 | 9.18 |

[a] Bond or bonds used in determining parameters. [b] See ref 11. [c] CC bond lengths from ref 11; CH bond lengths greater than those of ref 11 by 0.1 Å. [d] G. E. Segal, *J. Chem. Phys.*, **47**, 1876 (1967). [e] G. Herzberg, "Infrared and Raman Spectra," Van Nostrand Co., Inc., New York, N. Y., 1945. [f] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969). [g] Values calculated using assumed bond lengths. [h] B. L. Crawford, Jr., and F. A. Miller, *J. Chem. Phys.*, **17**, 249 (1949).

greater than the mean is in the calculated heat of formation of cyclopropane (−8.9 kcal/mol); this could indicate that the present procedure underestimates strain energies, unlike PNDO[10] or MINDO/1.[11]

The equilibrium bond lengths and heats of formation are found by parabolic interpolation from the calculated values $E^{m}$ and $E^{m\pm}$; if a parabolic potential function is assumed, the force constant of the bond can of course be calculated from the same data. Values found in this way are also compared with experiment in Table I; the agreement is remarkably good. Very few attempts have been reported to calculate force constants by other methods; some CNDO/2 values are listed in Table I. It will be seen that they are uniformly too great by a factor of more than two.

A final confrontation with experiment is shown in the last two columns of Table I, where the energies ($E^{max}$) of the highest occupied MOs are compared with the first ionization potentials ($I_1$) measured by photoelectron spectroscopy (and therefore reliable to *ca.* 0.01 eV, unlike electron impact values). From Koopmans' theorem, $E^{max}$ should be approximately equal to $-I_1$; it will be seen that this relation holds remarkably well over the whole range of compounds studied. The agreement is far better than that for orbital energies calculated by other methods, where the differences between $I_1$ and $E^{max}$ commonly amount to >1 eV.[6,17,18]

These last two checks are particularly gratifying since force constants, and the energies of the highest occupied MO's, bear no direct relation to the properties (heats of formation and bond lengths) used to fit the parameters in our treatment. The correlation of $E^{max}$ and $I_1$ in particular seems to suggest that our use of parameters can bring about a very fundamental improvement in our simple MO treatment, rather than a minor patching in the areas concerned with the specific properties used to fix the parameters.

**B. Detailed Calculations for Hydrocarbons.** We next carried out more detailed calculations for a number of hydrocarbons, minimizing the energy with respect to variation in the lengths of all the bonds. We also carried out calculations for some larger molecules where a complete empirical minimization by varying the bond lengths would have been too laborious and expensive;[19] here some of the bonds were assumed to have standard lengths. The results are shown in Table II, the bonds listed there being the ones whose lengths were optimized; the calculated lengths of the CH bonds have been corrected for the 0.1-Å offset.

Here again the results are mostly in remarkably good agreement with experiment; note in particular the striking success for diacetylene, allene, and azulene. The results for cyclopropane and cyclobutane seem, however, to confirm the impression from Table I that MINDO/2 underestimates strain energies in small rings; however the calculations do reproduce the short CC bond lengths in cyclopropane and long ones in cyclobutane. Conformational effects are also reproduced fairly satisfactorily. Thus the difference in energy between the chair and boat forms of cyclohexane (Table I) is quite well predicted (4.6 kcal/mol; obsd 5.2 kcal/mol), and the stable form of ethane is correctly predicted to be staggered, although the predicted rotational barrier is too low (1.5 kcal/mol; obsd 2.9 kcal/mol). The predicted first ionization potentials ($I_1$) are again in remarkable agreement with experiment considering that they were derived from Koopmans' theorem. Note in particular the way the orbital energies reproduce changes in $I_1$ along the series acetylene–allene–diacetylene, and ethylene–1-butene–2-butene.

Calculations for radicals and other open-shell systems present problems in a semiempirical LCAO–MO approach of the kind developed here. A single determinant description of a radical should logically be

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(18) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2367 (1966); W. E. Palke and W. N. Lipscomb, *ibid.*, **88**, 2384 (1966).

(19) We are developing programs for carrying out such minimizations automatically.

**Table II.** Heats of Formation, Bond Lengths, and Ionization Potentials of Hydrocarbons

| Compound | Heat of formation, kcal/mol Obsd[a] | Heat of formation, kcal/mol Calcd | Ionization potential, eV Obsd[b] | Ionization potential, eV Calcd | Bond lengths, Å, calcd[c] (obsd)[d] |
|---|---|---|---|---|---|
| Ethane | −20.2 | −21.7 | 11.51 | 10.87 | C–C, 1.524 (1.534); C–H, 1.103 (1.093) |
| Ethane (ecl) | −17.3 | −20.2 | | | C–C, 1.524 ( ); C–H, 1.103 ( ) |
| Ethylene | +12.5 | +16.4 | 10.50 | 10.60 | C=C, 1.337 (1.338); C–H, 1.093 (1.083) |
| Acetylene | +54.3[e] | +53.4 | 11.40[f] | 11.02 | C≡C, 1.206 (1.206); C–H, 1.069 (1.059) |
| *t*-Butadiene | +26.3 | +29.6 | 9.07 | 9.40 | C=C, 1.347 (1.343);[i] C–C, 1.473 (1.467)[i] |
| Isobutane | −32.2 | −23.8 | 10.78 | 10.63 | C–C, 1.534 (1.540) |
| Isobutylene | +5.9 | +0.4 | 9.17 | 9.36 | C=C, 1.347 ( ); C–C, 1.51 (1.54) |
| *t*-2-Butene | −2.7 | −6.2 | 9.12 | 9.23 | C=C, 1.347 (1.339); C–C, 1.50 (1.52) |
| *c*-2-Butene | −1.7 | −2.2 | 9.12 | 9.32 | C=C, 1.347 ( ); C–C, 1.50 ( ) |
| Cyclopropane | +12.7 | +2.5 | 10.06 | 10.27 | C–C, 1.514 (1.51, 1.524); C–H, 1.103 (1.089) |
| Cyclobutane | +6.4 | −2.2 | | 9.80 | C–C, 1.550 (1.548, 1.567); C–H, 1.103 (1.092) |
| Diacetylene | +111.8[e] | +101.8 | 10.17[f] | 9.80 | C=C, 1.205 (1.205); C–C, 1.386 (1.376); C–H, 1.069 (1.046) |
| Allene | +45.9[e] | +40.0 | 9.83 | 9.74 | C=C, 1.309 (1.308, 1.311); C–H, 1.093 (1.06, 1.081) |
| Azulene | +68.9 | +67.4 | 7.43 | 7.95 | $C_9$–$C_{10}$, 1.486[g] (1.483[h]) |

[a] See ref 11. [b] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50,** 654 (1969). [c] For standard bond angles, and applying a correction of −0.1 Å to all calculated CH bond lengths. Where no CH bond length is quoted, the length was assumed to be the standard value[11] plus 0.1 Å. [d] L. E. Sutton, "Table of Interatomic Distances," The Chemical Society, London, 1958 and 1965. [e] See ref 10. [f] C. Baker and D. W. Turner, *Chem. Commun.*, 797 (1967). [g] Parabolic interpolation; other CC bond lengths assumed to be 1.397 Å. [h] J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Crystallogr.*, **15,** 1 (1962). [i] W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20,** 1726 (1966).

based on the open-shell SCF treatment in which different orbitals are used for electrons of different spin; however parameters appropriate to a closed-shell treatment of normal molecules are not satisfactory for a corresponding open-shell treatment of radicals. This point was discussed in detail in a paper describing the treatment of radicals in the π approximation[20] and an appropriate closed-shell description of radicals was developed ("half-electron" method) which circumvented this difficulty. This procedure was successfully applied to radicals in the MINDO/1 approximation; Table III shows the results of corresponding calculations by a "half-electron" version of MINDO/2.

**Table III.** Calculated Heats of Formation and Geometries of Radicals

| Radical | $\Delta H_f$ (calcd), kcal/mol | $\Delta H_f$ (obsd) kcal/mol | Geometry[a] |
|---|---|---|---|
| Methyl | 30.2 | 34.0[c] | Planar; C–H; 1.092[b] |
| Allyl | 35.2 | 37.0[d] | C–C, 1.382 |
| Phenyl | 71.7 | 71.0,[c] 80.0[e] | C–C, 1.395 |
| Benzyl | 48.6 | 45.0[c] | C–$CH_2$, 1.421 |
| $CH_4^+$ | 272.4 | 282.6[d] | C–H, 1.092[b] |
| $C_6H_6^+$ | 243.9 | 233.3[d] | C–C, 1.398 |

[a] Standard values[11] assumed for all other bonds, and for bond angles. Length (Å) of indicated bond found by quadratic interpolation. [b] Corrected for 0.1-Å offset. [c] J. A. Kerr, *Chem. Rev.*, **66,** 465 (1966). [d] Calculated from the heats of formation and ionization potentials of neutral hydrocarbons.[11] [e] A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **89,** 4578 (1967).

The calculated heats of formation are again in satisfactory agreement with experiment, given the uncertainty in some of the experimental values. There are of course no reliable experimental estimates of geometries, apart from the demonstration that carbon radicals are planar; our calculations correctly predict a planar geometry and the calculated bond lengths seem reasonable on this basis. Thus the CH bond length in methyl is predicted to be close to that of ethylene (1.083 Å; note that we have again corrected the calculated CH bond lengths for the 0.1-Å offset) and the CC bond lengths in allyl and benzyl are short, due to mesomerism, with that in allyl being, as one would expect, the shorter.

**C. Cumulenes; Rotation about the C=C Bond.** As was pointed out above, there is little point in trying to calculate potential surfaces for reactions by any treatment that does not give reasonably good estimates simultaneously for the heats of formation and geometries of molecules and for the force constants of the bonds in them. Since the results reported above seemed to suggest that MINDO/2 meets these criteria reasonably well for hydrocarbons of all types, we decided to try it out on some simple reactions. An obvious first choice was the barrier to rotation about the C=C bond in ethylene.

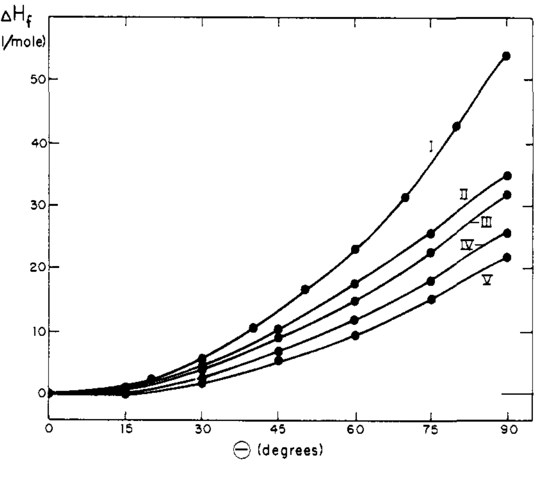

Figure 2. Plot of relative heats of formation ($\Delta\Delta H_f$) *vs.* the angle of rotation ($\theta$) about the carbon axis for ethylene (I), allene (II), butatriene (III), pentatetraene (IV), and hexapentaene (V).

Figure 2 shows the calculated energy of ethylene as a function of angle ($\theta$) of twist about the C=C bond, the geometry for each value of $\theta$ being chosen to minimize the total energy. The calculated barrier height (54.1

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(20) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, **90,** 1953 (1968).

Table IV. Calculated Ground-State Properties and Barriers to Rotation for Cumulenes

| | Ground state | | | | | Transition state | | Rotational barrier, kcal/mol | | Torsional frequency, $cm^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta H_f$, kcal/mol | | IP, eV | | | $\Delta H_f$, kcal/mol | Bond lengths, Å[b] | | | | |
| Compd | Calcd | Obsd[a] | Calcd | Obsd[a] | Bond lengths, Å[b] | | | Calcd | Obsd | Calcd | Obsd |
| I | 16.4 | 12.5 | 10.60 | 10.50 | C–C, 1.337 (1.337)[c] | 70.5 | C–C, 1.367 | 54.1 | 65.0[d] | 1094 | 1027[e] |
| II | 42.7 | 45.9 | 9.74 | 9.83 | C–C, 1.309 (1.308)[c] | 77.9 | C–C, 1.316 | 35.2 | | 929 | 865[f] |
| III | 72.4 | | 8.98 | | $C_1$–$C_2$, 1.311 (1.318)[g] | 107.4 | $C_1$–$C_2$, 1.319 | | | | |
| | | | | | $C_2$–$C_3$, 1.288 (1.283)[g] | | $C_2$–$C_3$, 1.293 | 32.3 | 30[h] | 841 | 736[i] |
| IV | 99.0 | | 8.62 | | $C_1$–$C_2$, 1.310 | 125.1 | $C_1$–$C_2$, 1.311 | 26.1 | | 747 | |
| | | | | | $C_2$–$C_3$, 1.288 | | $C_2$–$C_3$, 1.288 | | | | |
| V | 127.6 | | 7.25 | | $C_1$–$C_2$, 1.312 | 150.3 | $C_1$–$C_2$, 1.315 | 22.7 | 20[h] | 703 | |
| | | | | | $C_2$–$C_3$, 1.287 | | $C_2$–$C_3$, 1.290 | | | | |
| | | | | | $C_3$–$C_4$, 1.289 | | $C_3$–$C_4$, 1.293 | | | | |

[a] See Table II. [b] C–H assumed 1.183 Å, angle HCH = 120°; quadratic interpolation used to determine minima. [c] L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Chemical Society Special Publications, No. 11 and 18, The Chemical Society, London, 1958 and 1965. [d] R. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 2439 (1955). [e] R. L. Arnett and B. L. Crawford, *ibid.*, **18**, 118 (1950). [f] R. C. Lord and P. Venkatesvarlu, *ibid.*, **20**, 1237 (1952). [g] Unpublished work by A. Almenningen, O. Bastiansen, and M. Traetteberg, quoted by O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962). [h] R. Kuhn, B. Schulz, and J. C. Joachims, *Angew. Chem.*, **78**, 449 (1966); estimated from rates of *cis–trans* isomerization of tetrasubstituted derivatives. [i] F. A. Miller and I. Matsubaru, *Spectrochim. Acta*, **22**, 173 (1966).

kcal/mol) is in quite good agreement with experiment (65 kcal/mol for *cis*-ethylene-$d_2$[21]). It is interesting that the calculated and observed barrier heights are considerably greater than the estimated $\pi$-bond energy in ethylene, although, as Mulliken and Roothaan[22] have pointed out, one would expect the transition state (*i.e.*, the perpendicular form with $\theta = 90°$) to be significantly stabilized by hyperconjugation. Indeed, our results suggest that such stabilization is very significant in the perpendicular form, the calculated CC bond length (1.367 Å) being only 0.03 Å greater than the value (1.337 Å) calculated and observed for ethylene itself (see Table IV).

It has commonly been assumed in the past that the potential function for twisting in ethylene has the form of a sine function; it will be seen from Figure 1 that the present calculations lead to a barrier of very different shape, being much flatter for small angles of twist. Ganis and Dunitz[23] have concluded from crystallographic studies of olefins that the torsional barrier about the C=C bond must be of this form. Moreover our torsional function leads to an estimate (1094 $cm^{-1}$) for the frequency of the torsional vibration in ethylene in reasonable agreement with experiment[24] (1027 $cm^{-1}$) and much less than the values calculated for a sine function (1235 and 1354 $cm^{-1}$ for barrier heights of 54.1 and 65 kcal/mol, respectively[25]).

Table IV shows the results of analogous calculations for the cumulenes up to $C_6H_4$; heats of formation and bond lengths are listed for the planar and perpendicular forms together with the derived rotational barriers, torsional vibration frequencies, and ground-state ionization potentials estimated by using Koopmans' theorem. Experimental values are included where these are available.

Here again the heats of formation, bond lengths, and ionization potentials for the parent hydrocarbons are in good agreement with the limited experimental data available, and the calculated torsional frequencies also agree well with those observed. Indeed, the differences between the calculated and observed frequencies may be due largely to our assumption that the HCH angles are 120°; the moment of inertia of methylene about the carbon axis, and so the torsional frequency, depends critically on this angle. The calculated barrier heights for butatriene and hexapentaene also agree remarkably well with recent experimental values (Table IV).

**D. Reactions of Methyl.** We next considered a simple bimolecular reaction, *i.e.* the abstraction of hydrogen from methane by methyl. The potential surface was calculated in some detail for variation of the whole geometry. It was established that the optimum reaction path involves approach of methyl along the axis of one CH bond of methane, that there are no minima along the reaction path (corresponding to stable intermediates), and that the transition state has the symmetrical structure shown in Figure 3, in which both carbon atoms are essentially tetrahedral. The calculated barrier to rotation about the C–H–C axis in the transition state is essentially zero. Note that the bond lengths in eq 23 are not corrected for the 0.1-Å offset; they are to be compared with the corresponding uncorrected value, 1.196 Å, for methane. The calculated activation energy (11.6 kcal/mol) agrees quite well with experiment (14.65 ± 0.3 kcal/mol[29]) and the calculated geometry for the transition state seems very reasonable. The lengths of the bonds to the central hydrogen atom are 13% greater than those of the other bonds, or of the bonds in methane.

$$H_3C\cdot\ H\text{—}CH_3 \longrightarrow H_3C\text{—}H\ \cdot CH_3 \qquad (22)$$

We also carried out calculations of the potential surface in the vicinity of the transition state for the corresponding reaction of methyl radicals with benzene assuming the geometry of the phenyl moiety to be the

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(21) R. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 2439 (1955).

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

(23) P. Ganis and J. D. Dunitz, *Helv. Chim. Acta*, **50**, 2379 (1967).

(24) R. L. Arnett and B. L. Crawford, *J. Chem. Phys.* **18**, 118 (1950).

(25) While, for reasons indicated above, we do not consider calculations of potential surfaces significant unless carried out by methods which meet the criteria indicated in the introduction, it may be noted that *ab initio* calculations of the ethylene barrier, using gaussians, gave a value of 82.1 kcal/mol,[26] while two independent calculations by the extended Hückel method gave values of 63[27] and 101.7[28] kcal/mol.

(26) R. J. Buenker, *J. Chem. Phys.*, **48**, 1368 (1968).

(27) R. Hoffmann, *Tetrahedron*, 22, 521 (1966).

(28) E. B. Moore, Jr., *Theor. Chim. Acta*, **7**, 144 (1967).

(29) F. S. Dainton, K. J. Ivin, and F. Wilkinson, *Trans. Faraday Soc.*, **55**, 929 (1959).

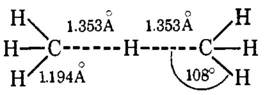


Figure 3. Calculated transition state for the methyl–methane reaction.

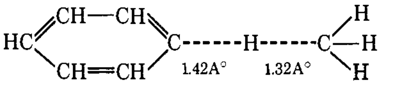


Figure 4. Calculated transition state for the methyl–benzene reaction.

same as in benzene (Table I) and that of methyl to be as

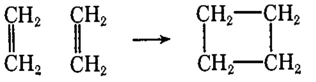
$$H_3C\cdot\ H{-}C_6H_5 \longrightarrow H_3C{-}H\ \cdot C_6H_5 \qquad (23)$$

in Figure 3. The reaction is again predicted to take place in one step *via* the transition state shown in Figure 4. The central bond lengths were calculated only to ±0.01 Å, but the results clearly indicate that the transition state should be not quite symmetrical. The calculated activation energy (10.8 kcal/mol) is less than that calculated for the corresponding methane reaction and agrees well with the values reported (9.2,[30a] 9.3[30b] kcal/mol). The experimental values were, however, derived from measurements of the rate at which methane is formed from methyl radicals and benzene; recently it has been suggested[31] that it might in fact have been formed by the two-step process

$$C_6H_6 + \cdot CH_3 \longrightarrow (C_6H_6CH_3) \xrightarrow{\cdot CH_3} C_6H_5CH_3 + CH_4 \qquad (24)$$

rather than by the one-step process of eq 23. Our calculation seems to support the latter mechanism (*i.e.*, eq 23).

**E. Dimerization of Ethylene.** As a final test, we calculated part of the potential surface for the dimerization of ethylene (I). Although this reaction has not been observed experimentally, the converse dissociation of cyclobutane (II) into ethylene is well known.



$$\begin{matrix} CH_2 & CH_2 \\ \| & \| \\ CH_2 & CH_2 \end{matrix} \longrightarrow \begin{matrix} CH_2{-}CH_2 \\ |\qquad\quad| \\ CH_2{-}CH_2 \end{matrix} \qquad (25)$$

I II

Considerations of orbital symmetry[32] and the fact that the transition state for a one-step reaction would be antiaromatic [12,33] make it very unlikely that the reaction can take place in a single step *via* a symmetrical rectangular transition state. Symmetry arguments do not, however, rule out a one-step reaction involving an unsymmetrical transition state, whereas the arguments concerning antiaromaticity of such a structure seem inconsistent with any mechanism not involving in effect a genuine biradical intermediate.

Figure 5 shows the calculated reaction path for the one-step reaction *via* a symmetrical rectangular transition state, the geometry at each point along the path (defined by the distance between the two ethylenic $C_2$ units as the reaction coordinate) being chosen to minimize the energy. It will be obvious that this path is very unfavorable, involving a very large activation energy (58 kcal/mol); the calculated activation energy for the converse process (dissociation of cyclobutane) is correspondingly much greater (113.3 kcal/mol) than that observed (62.5 kcal/mol[34]).

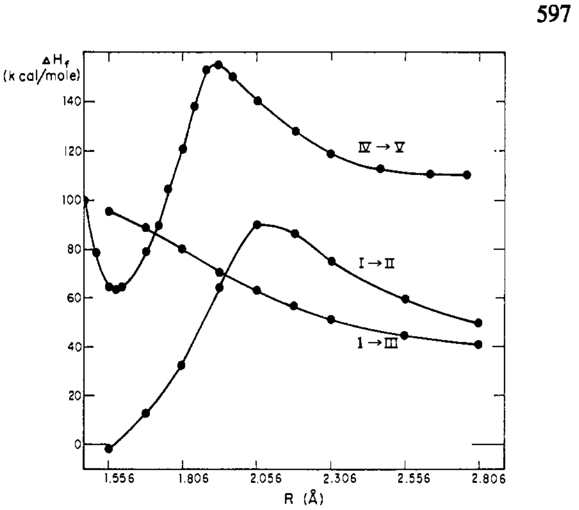
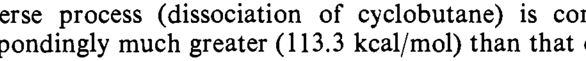


Figure 5. Calculated reaction paths for dimerization of ethylene to cyclobutane (—) and the 1,4-butadiyl diradical (· · · ·), and for dimerization of acetylene to cyclobutadiene (– – –).

We also calculated the reaction path for dimerization of ethylene to the *cis* conformation of the 1,4-butadiyl diradical III



$$CH_2{=}CH_2\quad CH_2{=}CH_2 \longrightarrow \dot{C}H_2{-}CH_2{-}CH_2{-}\dot{C}H_2 \qquad (26)$$

III

It will be seen (Figure 5) that the calculated heat of formation (93 kcal/mol) of III is much too large. An estimate of this can be obtained by adding twice the difference between the heats of formation of ethyl (25.7 kcal/mol[35]) and ethane (−20.24 kcal/mol; Table I) to the heat of formation of *n*-butane (−30.19 kcal/mol; Table I); the resulting value (28 kcal/mol) is less than that calculated by 65 kcal/mol.

The reason for this discrepancy can be easily seen. III is a genuine biradical in which there must be very little coupling between the unpaired electrons; the dissociation of II into III is therefore formally analogous to the dissociation of $H_2$ into 2H. As is well known, the latter process cannot be described in terms of single determinant wave functions, since in such a description the system (2H) has an energy greater than that of two isolated atoms by $^1/_2\gamma_H$, $\gamma_H$ being the repulsion between two electrons occupying the same 1s hydrogen AO.[36]

This argument will of course apply equally to any MO description of any process involving bond dissociation; to treat such processes it will be necessary to introduce configuration interaction, at any rate between the ground state and the lowest doubly excited state.[37]

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(30) (a) A. F. Trotman-Dickinson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); (b) M. Krech and S. J. W. Price, *Can. J. Chem.*, **45**, 157 (1967).

(31) A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **89**, 4578 (1967).

(32) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2048 (1965).

(33) M. J. S. Dewar, *Tetrahedron, Suppl.*, **8**, 75 (1966).

(34) R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, **67**, 1370 (1963).

(35) J. A. Kerr, *Chem. Rev.*, **66**, 469 (1966).

(36) This can be seen very clearly from the pictorial representation of the half-electron method.[20] In the MO description of (H + H), each hydrogen atom is in effect pictured as having two half-electrons of opposite spin, instead of one whole electron; the term $^1/_2\gamma$ represents the mutual repulsions between the half-electrons.

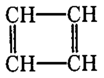
(37) In an SCF treatment, the ground state does not mix with singly

This argument suggests that similar though smaller discrepancies might also occur in the case of transition states for "normal" reactions in which bonds are stretched, even if they are not completely dissociated. However if our argument was applied literally, we would expect the calculated heat of formation of III to be too high by $^1/_2\gamma_C$ ($\gamma_C$ being the repulsion between two electrons in a given carbon 2p AO), *i.e.* 5.58 eV or 130 kcal/mol. The actual discrepancy, even in this extreme case where the radical centers are about 2.5 Å apart and separated by two saturated carbon atoms, is only half this. It therefore seems likely that in normal transition states, where the bonds are stretched only by 10–20% (*cf.* Figures 3 and 4), the effect should be relatively unimportant. Indeed, the calculated activation energy for *cis–trans* isomerization of ethylene (Figure 2) was too *low*, not too high.

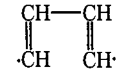
Figure 5 also shows the calculated reaction path for dimerization of acetylene (IV) to cyclobutadiene (V) *via* a symmetrical rectangular transition state; here again the calculated activation energy (43 kcal/mol) is extremely high, much greater than the estimated difference in energy (17 kcal/mol) between I and the biradical VI.[38]

$CH\equiv CH$

IV



V



VI

These calculations leave open the possibility that I might dimerize to II, and IV to V, by one-step processes involving unsymmetrical transition states. Such processes were too complicated to be followed by the blunderbuss approach used here, in which the reaction path was deduced by inspection from a large number of calculated points (over 2000 in Figure 4); we are developing a program for following the reaction path step by step so as to reduce the amount of computation to manageable proportions. It should be pointed out that these are extremely simple reactions, chemically speaking; in order to carry out calculations in cases where the results could be chemically useful, one must be prepared to deal with potential surfaces in at least twenty dimensions, corresponding to bond lengths and bond angles that vary, or may vary, during the reaction.

## Summary and Conclusions

These preliminary investigations show that the present form of the MINDO/2 method comes near to satisfying the requirements listed in the introduction to this paper and the preliminary applications to simple reactions are certainly encouraging. The present procedure does, however, suffer from obvious shortcomings. It certainly underestimates strain energies in small rings, the errors becoming serious in highly strained systems, and it overestimates the attractions between nonbonded hydrogen atoms. The latter effect is seen in the low value for the rotational barrier in ethane, and in the tendency of calculated HCH angles to be too small (*e.g*, 106° in ethylene).[39] The errors in the predicted heats of formation, while very much less than those given by other methods, are still a bit too large for chemical purposes. A final difficulty is a purely theoretical one which does not show itself in the case of hydrocarbons. The neglect of one-center overlap in the MINDO method means that it in effect neglects electrostatic effects due to the polarity of lone pairs of electrons occupying hybrid AO's. This seems likely to cause trouble when the method is extended to elements such as nitrogen or oxygen, particularly when two such atoms are close together so that lone pair dipole–dipole interactions are important.

For these reasons we consider the main value of the present investigation to lie in its demonstration that this kind of approach can give quite unexpectedly good estimates of ground-state properties. It seems very likely that even the treatment of hydrocarbons within the MINDO/2 framework can be improved over that reported here, for owing to the degeneracy of solutions from the parametrization procedure, it is by no means certain that the parameters we used were the best and the choice of functions $f_1$ and $f_2$ in eq 1 and 2 might also be improved. It is perhaps significant that MINDO/1 gave good estimates of strain energies, even in highly strained systems, whereas the present procedure gives values that are too low. And finally, one could without excessive complication change to a more sophisticated version of the Pople method, *e.g.*, PNDO or NDDO. Thus the possibilities for further improvement of this kind of approach seem ample, although even in its present form it seems likely to be of practical value in the study of hydrocarbon reactions.

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excited states. Interaction with the lowest doubly excited state introduces the type of electron correlation corresponding to "localization" of two unpaired electrons at the radical centers.

(38) The heat of formation of VI was estimated by adding twice the difference between the heats of formation of vinyl radical (64 kcal/mol[36]) and ethylene (12.5 kcal/mol; Table I) to the heat of formation of 1,3-butadiene (26.3 kcal/mol; Table I).

(39) For this reason the calculations reported here were carried out with assumed values for bond angles.