———., *Fluidization Engineering*, p. 94, 180, 242, Wiley (1969).
Lewis, W. K., E. R. Gilliland, and W. Glass, "Solid-catalyzed Reaction in a Fluidized Bed," *AIChE J.*, **5**, 419 (1959).
Miyauchi, T., "Rate Processes and the Two Phase Model for a Fluid Bed," 30th Annual Meeting, Soc. Chem. Engrs., Japan, No. 6110 (1965).
———., *J. Chem. Eng. Japan*, paper submitted (1973).
———., and S. Morooka, "Mass Transfer Rate between Bubble and Emulsion Phase in Fluid Bed," *Kagaku Kogaku*, **33**, 880 (1969).
———., "Circulating Flow and its Effects on Chemical Reaction in Fluid Bed Contactor," *ibid.*, 369.
Miyauchi, T., H. Kaji, and K. Saito, "Fluid and Particle Dispersion in Fluid-bed Reactors," *J. Chem. Eng. Japan*, **1**, 72 (1968).
Mori, S., and I. Muchi, "Mathematical Model for Catalytic Reaction in Fluidized Bed," *Kagaku Kogaku*, **34**, 510 (1970).
Morooka, S., and T. Miyauchi, "Mean Residence Time of Adsorptive Tracer Gases in Solid-Fluid Contactors", *ibid.*, **33**, 569 (1969).
Murray, J., "On the Mathematics of Fluidization," *J. Fluid Mech.*, **22**, 57 (1965).
Rowe, P. N., and B. A. Partridge, "An X-ray Study of Bubbles in Fluidized Beds," *Trans. Inst. Chem. Engrs.*, **43**, T157 (1965).
———., and E. Lyall, "Cloud formation around bubbles in gas fluidized beds," *Chem. Eng. Sci.*, **19**, 973 (1964).
Shichi, R., S. Mori, and I. Muchi, "Interaction between Two Bubbles in Gaseous Fluidization," *Kagaku Kogaku*, **32**, 343 (1968).
Toei, R., R. Matsuno, K. Nishitani, H. Hayashi, and T. Iwamoto, "Gas Interchange between Bubble Phase and Continuous Phase in Gas-Solid Fluidized Bed at Coalescence," *ibid.*, **33**, 668 (1969).

Manuscript received January 17, 1973; revision received April 13 and accepted April 17, 1973.

Application of Conformational Analysis Techniques to the Prediction of Heats of Formation and Gas-Phase Thermodynamic Functions

Conformational energy calculations based on describing the deformation of chemical bonds by energy functions allow the prediction of molecular geometries, heats of formation, vibrational frequencies, and gas-phase thermodynamic functions of compounds which contain bonds or groups of bonds whose properties are transferable from molecule to molecule.

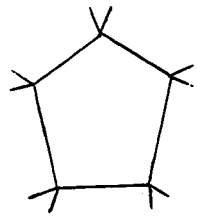
R. H. BOYD
S. M. BREITLING
and
M. MANSFIELD

Department of Chemical Engineering
University of Utah
Salt Lake City, Utah 84112

SCOPE

In quest of predicting or estimating the properties of molecules and compounds, chemists and chemical engineers have for many years taken advantage of the fact that the properties of chemical bonds or groups of chemical bonds are often independent of the particular kind of molecule in which they reside. Highly successful empirical schemes for property prediction have been based on this principle. An outstanding example is the development of bond energy or group contribution schemes which allow the heats of formation of appropriate compounds to be calculated within the accuracy of measurement. Other examples are bond moments for molecular dipole moment calculation, transferable spectroscopic force constants for the stretching, bending, and twisting of bonds that allow vibrational frequency prediction, and natural bond lengths and angles for geometry estimation. Although there are many examples of molecules where electronic effects (often called resonance,

delocalization, conjugation, hyperconjugation, etc.) alter significantly the properties of bonds, many molecules, particularly in organic chemistry, can be thought of as built from blocks of bonds or groups of bonds. However, a serious complication that has limited the application of the building block or group approach to property predictions is that many molecules cannot be assembled without sterically distorting in some way the component bonds. For example, cyclopentane,



cannot be assembled from bonds of fixed length with the C—C bond angles near tetrahedral values and the C—C—C—C twist angles near the preferred 60°, 180°, or 300° values. The angles are thus distorted from the natural or relaxed values. This manifests itself in the heat of formation as strain energy, the molecule is ~ 6 kcal/mole less stable than bond energies would predict. An attractive hypothesis for handling situations like this is to propose that the strain energy can be described by the same empirical energy functions as used in vibrational spectroscopy to describe bond distortion. To calculate the strain energy, one would simply add up the distortion energies

$$\frac{1}{2} k^{\theta}_{ijk} (\theta_{ijk} - \Theta_0)^2$$

for each C_i—C_j—C_k bond angle where θ_{ijk} is the actual bond angle and θ^0_{ijk} the natural or relaxed bond angle and k^{θ}_{ijk} is the spectroscopic force constant for angle bending. Similar terms would be added for bond stretching and twisting. For several reasons, early applications of this method were not very successful. Pitzer and coworkers in their monumental studies on hydrocarbon structure attempted it but concluded (Kirkpatrick et al., 1947):

> Initially we had hoped that it would be possible to correlate a number of quantities which depend on bond twisting and bending forces in the cyclanes. These include the heats of formation per CH_2 group of cyclopentane, cyclohexane and cyclooctane, the energy difference of chair and boat forms of cyclohexane and the detailed nature of the puckering of cyclopentane. While the use of the ethane potential for twisting gives rough agreement, some of these relationships indicate a lower value while others indicate a higher value of this twisting potential. Numerous plausible assumptions are involved in these relationships at least one of which apparently must be in error but we are not prepared to say which it is.

However, Westheimer (1946, 1947) achieved success in representing the effects of steric hindrance on internal rotation in substituted biphenyls as it affects their rates of racemization by the use of energy functions.

A further complication is the fact that in most molecules the actual structure is not known so that the bond lengths, bond angles, and twist angles are not available for comparison with the relaxed ones. This problem can be handled in principle by seeking the geometry (or conformation) which minimizes the strain energy. The formidable mathematical difficulties involved has prevented this from being explored until fairly recently. Henrickson (1961, 1962) used a computer to assist investigation of various geometries of cycloalkanes. Wiberg (1965) made a major advance when he developed a computer routine based on steepest-descent which, from a starting guess of the coordinates, would converge on the geometry of minimum energy and used it to investigate geometries of cycloalkanes. Several workers showed that this appeared to be a promising method for studying molecular structure (Scott and Scheraga, 1966; Bixson and Lifson, 1967; Allinger et al., 1967, 1968). A disadvantage was that the method converged rather slowly in medium-sized molecules. In a further development, Boyd (1966, 1968) showed that a Newton-Raphson method is a faster minimization procedure and after convergence also serves as the starting point for a calculation of the vibrational frequencies of the molecule (Jacob et al. (1967) used the Newton-Raphson method without the frequency calculation). Furthermore, of course, the vibrational frequencies and calculated geometry can be used to compute the gas-phase thermodynamic functions (heat capacity, entropy, free energy, enthalpy) from standard statistical mechanical formulae.

The possibility of calculation of vibrational frequencies in the above manner is particularly important since although there may be some transferable frequencies there is no appropriate bond or group method for prediction of all of the frequencies of even unstrained molecules. Quoting from Davidson (1962):

> The usefulness of these empirical bond frequencies for statistical calculations is seriously limited, however, by the following consideration: It is usually possible to make reasonable guesses as to the high-frequency stretching vibrations for a molecule. For a complicated, "floppy" molecule, there are a large number of low-frequency skeletal, torsional, and bending vibrations. There are no well-developed empirical schemes for the estimation of these frequencies. However, it is the low frequencies which are most effectively excited at any temperature and which contribute most to the thermodynamic properties.

Rather than estimation of frequencies directly, the use of transferable force constants in a vibrational analysis calculation of the frequencies has been demonstrated to be highly successful for a number of hydrocarbons (Snyder and Schachtschneider, 1965). The requirement that the geometry be known and the molecule be unstrained, however, remains in these vibrational analyses. Thus the conformational energy minimization approach presents the possibility that a whole body of molecular information—heats of formation, geometry, vibrational frequencies, and thermodynamic functions—that previously was estimated in separate calculations and limited to sterically relaxed molecules can be calculated in a unified manner in a single strategy. Experimental data of all of the above types can be compared with calculated values to develop and adjust the energy functions used to describe the bond or group properties. Lifson and Warshel (Lifson and Warshel, 1968; Warshel and Lifson, 1970) have incorporated the feature of least-squares adjustment of energy parameters to give a best fit to a selected data base. In general the method promises to be

highly successful (Boyd et al., 1971; Chang et al., 1970; Shieh et al., 1969; Boyd, 1970). This work reports the development of a computer-based system that will allow its convenient application to calculation of heats of formation and gas-phase thermodynamic functions of appropriate molecules by the generally interested person.

CONCLUSIONS AND SIGNIFICANCE

A computer-based system that accomplishes the convenient calculation of heats of formation and thermodynamic functions as described above has been developed. The basic method, as used by a number of workers, shows promise of becoming a molecular structure tool in its own right in competition with X-ray and electron diffraction, IR vibrational analysis, etc. It must be used, however, within the applicability of the building block assumption, and the necessary energy parameters must be derived from experiment. The success of the approach for hydrocarbons in terms of the accuracy and reliability of the calculated results has been discussed in several recent publications but is reviewed here. The early difficulties encountered by Pitzer have been largely resolved. The use of nonbonded potentials to partially represent the bond twisting energetics and the taking into account of the effects of temperature and zero-point energy on strain energy were important in accomplishing this.

Another important feature of the computerized system is that it provides a convenient source of geometries for the display and illustration of molecular structure by computer graphic techniques. These displays have an advantage over traditional hardware molecular models in that steric effects such as strain are incorporated properly, and they are inherently in a form suitable for reproduction.

STRATEGY AND METHODS

The computational strategy (Figure 1) which we call molecule builder consists of two phases and is implemented by two main Fortran IV computer programs. The first phase is the generation of a trial molecular structure and the assembly of the necessary energy functions. This is accomplished by the program MOLGEN (a neumonic for molecule generator). The second phase is the energy minimization and subsequent calculation of properties. This main program is called MOLBD3 (a neumonic for molecule builder 3). Two earlier versions MOLBD1 and MOLBD2, have previously been made available on a request basis and MOLBD2 has been published (Boyd, 1973).

The various parts of the strategy are discussed separately below. As the energy minimization scheme is the heart of the method, it will be discussed first.

ENERGY MINIMIZATION (BOYD, 1966, 1968)

The total molecular energy (energy of atomization) in a hypothetical motionless state (with respect to vibration, rotation, and translation) is written as the sum of individual bond (or groups) energies, plus energies of bond stretching, bending and twisting, plus the energies of nonbonded interactions. The quadratic approximation is usually used for the bond stretching and bending terms, a periodic cosine potential for bond twisting and any of a number of specialized functions for the nonbonded interaction. Thus,

$$E_a^* = \sum_{(ij)} E_{ij}^B + \sum_{(ij)} \frac{1}{2} k_{ij}^R (r_{ij} - R_{ij}^0)^2 + \sum_{(ijk)} \frac{1}{2} k^\theta_{ijk} (\theta_{ijk} - \Theta^0_{ijk})^2 + \sum_{(ijkl)} \frac{V_{ijkl}}{2} (1 + \cos 3\phi_{ijkl}) + \sum_{(ij)} V_{ij}^{NB} (r_{ij}). \quad (1)$$

The sums are considered to be taken over each type of interaction present in the molecule, each bond for the bond energy and bond stretching, each bond angle, each bond twisting situation and each nonbonded interaction. Another angular coordinate δ is necessary for out-of-plane bending (in benzene rings) but is left out here for brevity. The geometry of minimum energy can not be found by differentiation of Equation (1) with respect to the valence coordinates r_{ij}, θ_{ijk}, ϕ_{ijkl}, etc. because they are highly redundant. There are many more such valence coordinates than the $3N$-6 internal degrees of freedom in a typical molecule of N atoms. The easiest way to proceed is to transform Equation (1) to Cartesian coordinates which are inherently nonredundant. This is accomplished in two steps. First, Equation (1) is expanded in a Taylor's series to quadratic terms about a trial geometry with valence coordinates r_{ij}^0, θ^0_{ijk}, ϕ^0_{ijkl}. The deviations from the trial geometry Δr_{ij}, $\Delta\theta_{ijk}$, $\Delta\phi_{ijkl}$ are each transformed to Cartesian deviations $\Delta X_i^{(1)}$, $\Delta X_i^{(2)}$, $\Delta X_i^{(3)}$ by a Taylor's series expansion through quadratic terms. The result is that the energy in Equation (1) is now approximated by a quadratic function of the Cartesian displacements,

$$E_a^* = \sum_{(ij)} E_{ij}^B + \sum_{i,\alpha} A_i^\alpha \Delta X_i^\alpha + \frac{1}{2} \sum_{(i,j,\alpha,\beta)} C_{ij}^{\alpha\beta} \Delta X_i^\alpha \Delta X_j^\beta. \quad (2)$$

Application of the necessary condition for a minimum in E_a^*,

$$\partial E_a^*/\partial X_i^\alpha = 0 \quad (\alpha = 1, 2, 3; \quad i = 1 \ldots N), \quad (3)$$

to Equation (2) leads to a set of linear algebraic equations for the ΔX_i^α which may be solved by standard methods

$$-A_i^\alpha = \sum_{j=1}^{N} \sum_{\beta=1}^{N} C_{ij}^{\alpha\beta} \Delta X_j^\beta, \quad (4)$$

where each A_j^α is the sum of all the coefficients of ΔX_i^α in the linear terms and each $C_{ij}^{\alpha\beta}$ is the sum of all the coefficients of ΔX_i^α in the quadratic terms resulting from the quadratic expansion of Equation (1) and the transformation to Cartesian coordinates. The ΔX_i^α values determined lead to a new conformation, which minimizes (or maximizes) E_a^* in Equation (2). This will not, in general, minimize E_a^* in Equation (1), since the expansion of the potential and the expansions in the transformations are approximate. However, the ΔX_i^α values may be used to calculate a new set of trial coordinates

$$X_i^{0(\alpha)}\,(\text{new}) = X_i^{0(\alpha)}\,(\text{old}) + \Delta X_i^\alpha; \qquad (5)$$

and the minimization is repeated. When, after repeated iteration, the ΔX_i^α are zero to within prescribed limits, the iteration can be terminated and the geometrical factors of interest calculated from the final set of trial coordinates. Notice that to start the iterative process an initial guess in the form of a starting set of Cartesian coordinates is required.

INPUT OF TRIAL STRUCTURE

The most troublesome aspect of using the molecule builder system is furnishing the trial structure for the first iteration. This problem has two parts. The first is deciding what the approximate geometry or conformation is likely to be. The minimization is surprisingly effective in adjusting a fairly bad approximation to that of minimum energy. However, many molecules have more than one minimum energy geometry or conformation (each stable with respect to small atomic coordinate displacements). These conformers may differ in absolute energy by a small or large amount. An example of a small difference would be the trans and gauche conformers of *n*-butane (0.6 kcal/mole difference) and a larger difference would be found in chair and boat cyclohexane (10 kcal/mole). The minimization settles on one of the stable conformers and usually the one the starting structure most resembles. In order to obtain an accurate heat of formation and accurate thermodynamic functions, all of the conformers of reasonable energy should be located (see the section on heat of formation and thermodynamic functions below). Because there is no rigorous or systematic way of finding all of the conformers, some judgement is required. Our experience has been that constructing and manipulating Fieser type plastic spaghetti molecular models (Frame Work Molecular Models by Prentice-Hall) is a good way of investigating likely conformers. Once these have been decided on, the second problem of communicating these in the form of Cartesian coordinates to the main program remains. Direct measurements (with a ruler or other device) on the hardware model or photographs of it can be made. However, this is very cumbersome. For hydrocarbons we have found the most convenient procedure to be a visual estimate of one of the sets of the minimum number of twist angles (ϕ's), bond angles (θ's), and bond lengths (r's) required to specify the geometry. The bond angles and especially the bond lengths are often near the relaxed values so that the estimation requires just a few ϕ angles along with perhaps one or two slightly distorted θ's. The MOLGEN program combines these with the remaining fixed θ's and r's required to specify the conformation. Then MOLGEN calculates a set of initial Cartesian coordinates from this set of estimated valence coordinates.

Several workers are developing methods based on a priori notions of what types of conformers should exist

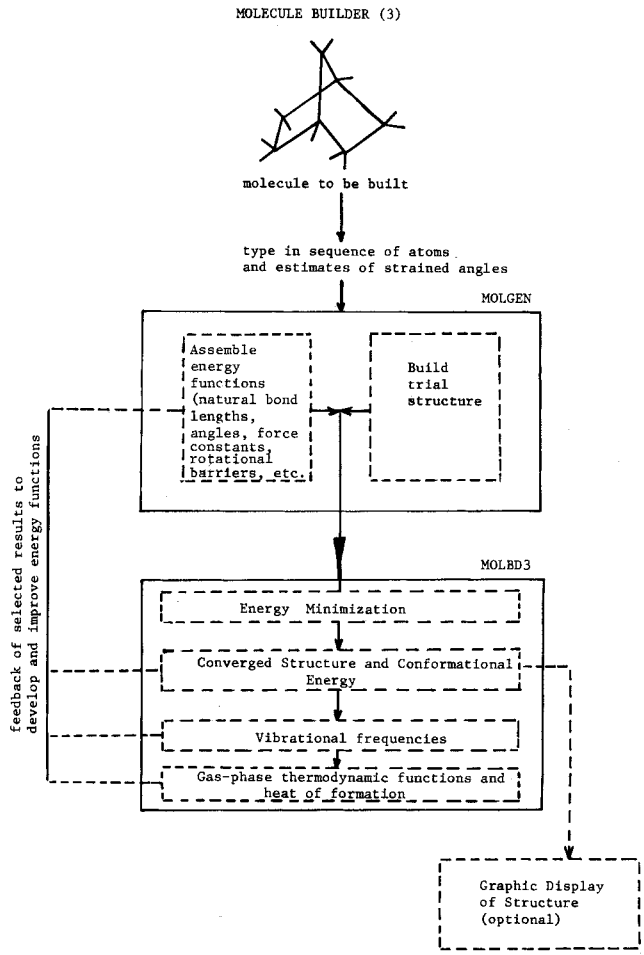


Fig. 1. The molecule builder system comprises two main computer programs, one (MOLGEN) sets up a trial structure and furnishes the information necessary for the conformational energy minimization to MOLBD3.

that attempt to generate automatically the starting structures for all of the conformers. While these methods will prove very convenient in many cases, they do run the risk of overlooking conformations, especially in some of the more interesting situations in which notions of likely types of conformations are not well developed. Therefore, we prefer to require specification of each likely conformer but to have a convenient method for doing so.

ENERGY FUNCTIONS

The force constants, natural bond lengths, bond angles and twist angles, and barrier heights in Equation (1) have to be determined by adjustment to give agreement between calculated and experimental properties. Given this determination, it is still a formidable task to assemble for a given molecule the necessary energy functions for each bond stretching, bending, twisting and nonbonded interaction. For example, cyclohexane, a rather small molecule, requires 159 interactions. Over a thousand interactions have been used in larger molecules. MOLGEN constructs and supplies the list of required interactions and energy functions from the information originally furnished to it for generating the trial structure.

VIBRATIONAL FREQUENCIES AND GAS-PHASE THERMODYNAMIC FUNCTIONS (BOYD, 1966, 1968)

Referring back to the section on energy minimization we see that in the final iteration, each A_i^α is zero (very

nearly); and only $C_{ij}^{\alpha\beta}$ terms remain. This final energy

$$E_a^* = E_a^* (\ldots X_i^{0(\alpha)} \ldots) + \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\alpha,\beta=1}^{3} C_{ij}^{\alpha\beta} \Delta X_i^{\alpha} \Delta X_j^{\beta} \quad (6)$$

may then be used to calculate the vibrational frequencies of the molecule by standard methods; that is, solution of the determinant (where m_i is the mass of the ith atom),

$$|C_{ij}^{\alpha\beta} - m_i \delta_{ij} \omega^2| = 0, \quad (7)$$

yields the vibrational frequencies, $\nu_i = \omega_i/2\pi$. The vibrational frequencies, together with the moments of inertia calculated from the final coordinates, can be used to calculate the rotational and vibrational contributions to the thermodynamic functions. The vibrational eigenvectors may also be calculated if desired.

A subroutine for carrying out their calculation is included in MOLBD3.

HEATS OF FORMATION (CHANG ET AL., 1970; SHIEH ET AL., 1969)

The heat of formation at T°K of a compound $A_nB_m \ldots$ is related to the enthalpy of atomization at T°K as

$$\Delta H_f^0 (A_nB_m \ldots, T°K) = -\Delta H_a^0 + n \Delta H_f^0 (A, T°K) + m\Delta H_f^0 (B, T°K) + \ldots \quad (8)$$

Since

$$\Delta H_a^0 (T°K) = E_a^* - (H_T^0 - H_0^0) - ZPE + \frac{5}{2}(n + m + \ldots)RT \quad (9)$$

the heat of formation is related to the molecular energy of Equation (1) as

$$\Delta H_f^0 (A_nB_n \ldots, T°K) = -E_a^* + (H_T^0 - H_0^0) + ZPE - \frac{5}{2}(n + m + \ldots)RT + n\Delta H_f^0 (A, T°K) + m\Delta H_f^0 (B, T°K) + \ldots \quad (10)$$

The conformational energy minimization furnishes values of the valence coordinates for use in Equation (1) to determine E_a^*. This value substituted in Equation (10) then gives a calculated value for ΔH_f^0 when combined with calculated values of the enthalpy function and zero point energy from the vibrational calculation and experimental values of the atomic heats of formation.

If more than one stable conformation is found, each conformation (a conformer) is treated as a distinct molecule and the thermodynamic properties are calculated for the equilibrium mixture of conformers. This calculation is carried out as follows. The most stable conformer at 0°K (as judged from the calculated E_a^* values) is labeled as 1. A free energy function for the ith conformer is defined as

$$\mathcal{G}_i/T = (\Delta H_f^0 (i, T_0) - (H_{T_0} - H_0^0)_i)/T + (G_T^0 - G_0^0)i/T - (\Delta H_f^0 (1, T_0) - (H_{T_0} - H_0^0)_1)/T - (G_T^0 - G_0^0)_1/T. \quad (11)$$

This function has the property that the standard free energy change for the reaction to form the ith conformer from conformer 1,

$$C_1 \rightarrow C_i \quad (12)$$

is

$$\Delta G_{i,1}^0 = \mathcal{G}_i \quad (13)$$

The equilibrium composition is given by

$$X_i = e^{-G_i/RT} \Big/ \sum_i e^{-G_i/RT} \quad (14)$$

The entropy of the equilibrium ideal gas mixture is defined by the process

$$C_1 (0°K) \rightarrow X_1 C_1 (T°K) + X_2 C_2 (T°K) + X_3 C_3 (T°K) + \ldots \quad (15)$$

and is given in terms of the entropies of the conformers as

$$S_T^0 = \Sigma X_i S_{T,i}^0 - R\Sigma X_i \ln X_i. \quad (16)$$

The enthalpy can be defined by the two-step process

$$C_1 (0°K) \rightarrow C_1 (T°K)$$

$$C_1 (T°K) \rightarrow X_1 C_1 (T°K) + X_2 C_2 (T°K) + X_3 C_3 (T°K) + \ldots \quad (18)$$

and is given by

$$H_T^0 - H_0^0 = (H_T^0 - H_0^0)_1 + \Delta H_T \quad (19)$$

where

$$\Delta H_T = \Sigma X_i \mathcal{H}_i \quad (20)$$

and

$$\mathcal{H}_i = \Delta H_f^0 (T_0, i) - \Delta H_f^0 (T_0, 1) + (H_T^0 - H_0^0)_i - (H_T^0 - H_0^0)_1 - ((H_{T_0}^0 - H_0^0)_i - (H_{T_0}^0 - H_0^0)_1) \quad (21)$$

Notice that

$$\frac{\partial \mathcal{G}_i/T}{\partial T} = -\mathcal{H}_i/T^2 \quad (22)$$

The heat capacity is defined by

$$C_p^0 = \frac{\partial}{\partial T}(H_T^0 - H_0^0) = \Sigma X_i C_{p,i}^0 + \Sigma \mathcal{H}_i \frac{\partial X_i}{\partial T} \quad (23)$$

Since

$$\ln X_i = -\mathcal{G}_i/RT - \ln \Sigma e^{-G_i/RT}, \quad (24)$$

then

$$\frac{\partial X_i}{\partial T} = X_i \left[-\frac{\partial \mathcal{G}_i/RT}{\partial T} + \frac{\Sigma \frac{\partial \mathcal{G}_i/RT}{\partial T} e^{-G_i/RT}}{\Sigma e^{-G_i/RT}} \right] = X_i \mathcal{H}_i/RT^2 - X_i \Sigma X_i \mathcal{H}_i/RT^2 \quad (25)$$

and

$$C_p^0 = \Sigma X_i C_{p,i}^0 + \Sigma X_i \mathcal{H}_i^2/RT^2 - (\Sigma X_i \mathcal{H}_i)^2/RT^2 \quad (26)$$

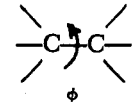
The heat of formation is given by

$$\Delta H_f^0 = \Sigma X_i \Delta H_f^0 (i) \quad (27)$$

APPLICATION TO HYDROCARBONS

Model

In applying Equation (1) several further assumptions concerning the rotational barrier term involving the ϕ coordinate must be made. Here we have assumed that there is an inherent barrier that arises for rotation about the C—C bond,



but does not depend on the substituents attached to the carbons. The effects of different substituents (that is, C versus H) are represented by nonbonded potentials, the same nonbonded potentials as used between atoms more distant than the four center interaction of bond rotation. The nonbonded interactions were adapted from those determined by Williams (1967) from fitting crystal structures and heats of sublimation. The other force constants were adjusted from those of Snyder and Schachtschneider (1965) to take into account the effects of nonbonded interactions which the latter did not include in their force field. The final parameters derived are listed by Chang et al. (1970) and Boyd et al. (1971).

Results

A large number of heats of formation and thermodynamic functions of hydrocarbons have been calculated with the above energy parameters. A few of these results taken from our recent publications (Tables 1 and 2) are compared with experimental values. Also listed in Table

Table 2. Calculated Thermodynamic Functions of Hydrocarbons[a]

T	$(G^0 - H_0^0)/T$	$(H^0 - H_0^0)/T$	S^0	C_p^0
		n-butane[b,c]		
298.15	58.68 (58.54)	15.22 (15.58)	73.90 (74.12)	22.76 (23.29)
400.00	63.52 (63.51)	17.93 (18.35)	81.46 (81.86)	29.06 (29.60)
500.00	67.83 (67.91)	20.79 (21.19)	88.63 (89.10)	35.17 (35.34)
		n-pentane[b,c]		
298.15	64.29 (64.52)	18.63 (18.88)	82.93 (83.40)	28.07 (28.73)
400.00	70.23 (70.57)	22.01 (22.38)	92.25 (92.95)	35.84 (36.53)
500.00	75.53 (75.94)	25.56 (25.94)	101.09 (101.88)	43.38 (43.58)
		cyclopentane[d], pseudorotator, D_{5h}, $\sigma = 10$		
298.15	57.81 (57.93)	12.41 (12.07)	70.22 (70.00)	20.11 (19.82)
400.00	61.87 (61.88)	15.41 (15.12)	77.24 (77.00)	28.25 (28.24)
500.00	65.67 (65.62)	18.76 (18.52)	84.43 (84.14)	35.78 (35.86)
		cyclohexane[e], D_{3d}, $\sigma = 6$		
298.15	57.24 (57.07)	14.36 (14.21)	71.60 (71.28)	25.67 (25.40)
400.00	62.03 (61.80)	18.52 (18.38)	80.55 (80.18)	35.64 (35.82)
500.00	66.63 (66.39)	22.89 (22.85)	89.52 (89.24)	44.72 (45.47)
		cis-decalin, cis 4·4·0 bicyclodecane[f], C_2, $\sigma = 2$, d, 1 pair		
298.15	68.75 (68.77)	21.26 (20.75)	89.95 (90.28)	40.48 (39.48)
400.00	76.30 (76.68)	27.82 (27.64)	104.12 (104.32)	56.64 (56.64)
500.00	83.29 (83.70)	35.10 (35.02)	118.39 (118.71)	71.21 (71.64)
		trans-decalin, trans 4·4·0 bicyclodecane[f], C_{2h}, $\sigma = 2$		
298.15	68.75 (68.77)	21.26 (20.75)	90.01 (89.52)	40.91 (40.04)
400.00	75.96 (75.78)	28.31 (27.84)	104.28 (103.62)	56.90 (56.78)
500.00	83.06 (82.83)	35.53 (35.17)	118.60 (118.01)	71.40 (71.14)
		benzene[c], D_{6h}, $\sigma = 12$		
298.15	53.05 (52.95)	11.64 (11.41)	64.68 (64.34)	19.89 (19.52)
400.00	56.87 (56.69)	14.57 (14.41)	71.44 (71.10)	26.44 (26.74)
500.00	60.44 (60.24)	17.54 (17.50)	77.98 (77.74)	32.17 (32.80)
		toluene[c], C_{2v}, $\sigma = 2 \times 3 = 6$		
298.15	62.20 (61.98)	14.48 (14.44)	76.68 (76.42)	24.50 (24.80)
400.00	66.96 (66.74)	18.96 (18.17)	85.02 (84.91)	32.48 (33.25)
500.00	71.38 (71.20)	21.67 (21.94)	93.05 (93.13)	39.42 (40.54)

[a] Units are °K and cal mol^{-1} K^{-1}.
[b] Calculated for the equilibrium mixture of conformers using Equations (16, 19, 26) of the text.
[c] Values in parentheses from F. D. Rossini, et al., *Selected Values of Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, Pa. (1953).
[d] Values in parentheses are from J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, 69, 2483 (1947). A q_0 value of 0.39A from our calculated structure was used (compare q_0 − 0.47A), K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, 81, 3213 (1959).
[e] Values in parentheses are from C. W. Beckett, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, 69, 2488 (1947).
[f] Values in parentheses are from T. Miyazawa and K. S. Pitzer, *J. Am. Chem. Soc.*, 80, 60 (1958).

1 are heats of formation calculated from a simple group contribution scheme similar to Franklin's (1949). The latter are listed to demonstrate the inadequacy of simple group additivity for strained compounds and the improvement gained by the conformationally calculated bond deformation energies. Figure 2 shows calculated heat capacities of several gases plotted versus temperature and compared with tabulated literature values. Figure 3 illustrates the input of data to the computer program. Table 3 shows the output resulting from the sample input.

There are several limitations to the general application

Table 1. Calculated Heats of Formation Compared with Experimental (kcal/mole)

Compound	$\Delta H_f°$ (25°C) calc	$\Delta H_f°$ (25°C) exp	$\Delta H_f°$ (25°C) simple group
cyclopentane[a]	−18.4	−18.46	−25.5
cyclohexane[a]	−29.7	−29.43	−30.4
cycloheptane[a]	−28.7	−28.41	−35.6
cyclooctane[a]	−29.3	−29.90	−40.6
cis-decalin[a]	−39.7	−40.40	−44.5
trans-decalin[a]	−43.8	−43.50	−44.6
norbornane[b]	−11.7	−12.40	−29.2
bicyclo [2·2·2][b] octane	−22.9	−23.80	−34.3
tetrahydro-dicyclopentadiene[b]	−12.2	−14.40	−37.2

[a] S. J. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *J. Am. Chem. Soc.*, 92, 3109 (1970).
[b] R. H. Boyd, S. N. Sanwal, S. Shary-Tehrany, and D. McNally, *J. Phys. Chem.*, 75, 1264 (1971).

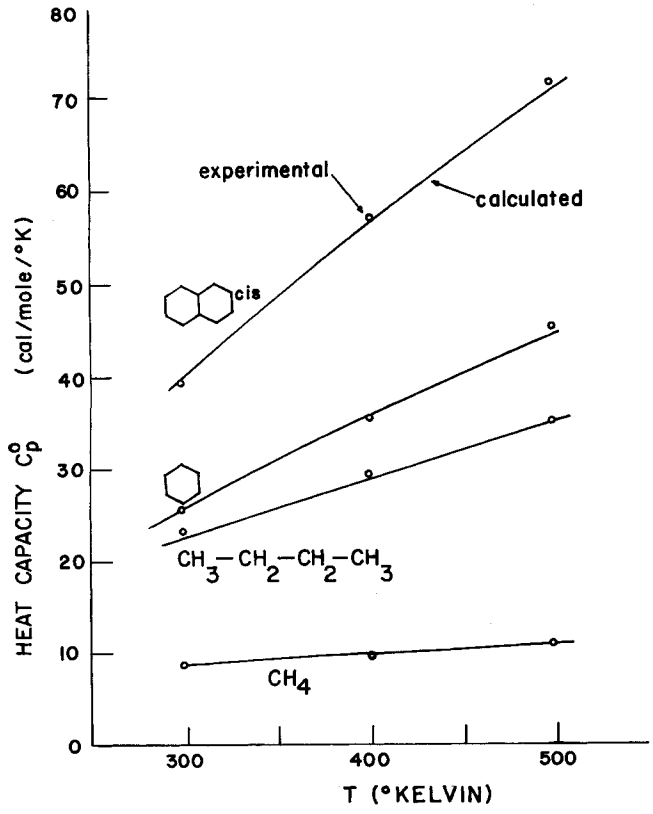
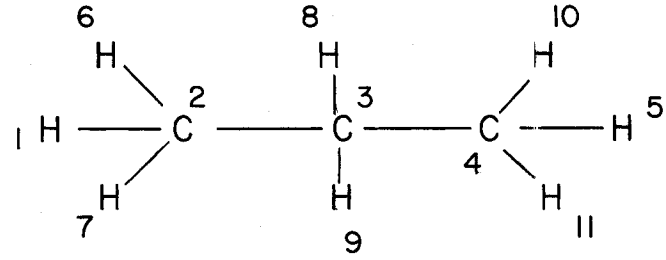


Fig. 2. The calculated heat capacities of several hydrocarbons (methane, n-butane, cyclohexane and cis-decalin) plotted vs. temperature (solid curves) and compared with literature values (open circles).



PROPANE

```
HM.
C.
C.
C.P180.
HM.

1,2,3
2,3,4
3,4,5

END
```

BUILDS SKELETON, ATOMS 1-5

EXTRA HYDROGENS ATOMS 6-11

Fig. 3. The teletypewriter input to MOLGEN for a simple example (propane). The sequence of atoms HM. (=atom 1, methyl hydrogen); C. (=atom 2, carbon); C. (=atom 3, carbon); C. P180. (=atom 4, twist angle = 180°); HM. (=atom 5, methyl hydrogen (twist angle defaults to the previous value) specifies the skeleton. The sequences 1, 2, 3; 2, 3, 4 and 3, 4, 5 place the extra hydrogens (atoms 6, 7, 8, 9, 10, 11). MOLGEN then calculates the trial structure shown (in this case it will be very close to the final one since propane is unstrained). MOLGEN also assembles the list of bond stretching, bond bending, and bond twisting interactions to be used.

of the system described here. One is that not all molecules fall within the scope of the transferable bond property or building block assumption. Benzene, for example, is a resonating or delocalized system whose bonding seriously departs from the classical alternating double bond structure. This is well recognized, however, and the benzene ring can be considered a transferable group of bonds and used in other structures. Indeed we have developed the appropriate parameters for benzene rings. The number of such resonate systems in hydrocarbons is limited enough that the scheme is not seriously impaired. Another limitation is that energy function parameters have been developed to date only for hydrocarbons. However, we see no fundamental reason why such parameters can not be developed for organic compounds containing other atoms. We must keep in mind though that more atoms increase the number of bonding systems that could depart from the building block hypothesis (nitrogen heterocycles, for example) that one is likely to encounter. Another difficulty is that the vibrational frequencies are determined in the harmonic approximation. At higher temperatures the thermodynamic functions can be in error for this reason. Of course, traditional spectroscopic analyses also can suffer from this deficiency. Some molecules exhibit such serious anharmonicity that it affects the thermodynamic functions at all temperatures. A classic example is cyclopentane which possesses an essentially zero vibrational frequency for an out-of-plane ring puckering motion. This results from the ring puckering being able to almost freely adjust its phase around the ring.

TABLE 3. OUTPUT STRUCTURE AND GEOMETRICAL PARAMETERS FOUND BY MINIMIZING THE CONFORMATIONAL ENERGY FOR THE OUTPUT OF MOLGEN (FIGURE 3). THE VIBRATIONAL FREQUENCIES THERMODYNAMIC FUNCTIONS, AND HEAT OF FORMATION ARE ALSO LISTED

Final structure

I	X	Y	Z	Mass	Charge
1	−1.60433	1.45193	0.00000	1.00790	0.00000
2	−0.51349	1.45193	0.00000	12.00000	0.00000
3	0.02367	0.01251	0.00000	12.00000	0.00000
4	1.55959	−0.02529	0.00001	12.00000	0.00000
5	1.91572	−1.05636	0.00002	1.00790	0.00000
6	−0.17164	1.99031	0.88491	1.00790	0.00000
7	−0.17164	1.99031	−0.88491	1.00790	0.00000
8	−0.35276	−0.51577	−0.87832	1.00800	0.00000
9	−0.35277	−0.51577	0.87832	1.00800	0.00000
10	1.95686	0.47361	0.88491	1.00790	0.00000
11	1.95687	0.47359	−0.88490	1.00790	0.00000

I = 1	J = 2	RIJ =	1.09084	SE =	.00	
I = 2	J = 3	RIJ =	1.53639	SE =	.01	
I = 3	J = 4	RIJ =	1.53639	SE =	.01	
I = 4	J = 5	RIJ =	1.09084	SE =	.00	Bond lengths
I = 2	J = 6	RIJ =	1.09077	SE =	.00	
I = 2	J = 7	RIJ =	1.09077	SE =	.00	
I = 3	J = 8	RIJ =	1.09189	SE =	.00	
I = 3	J = 9	RIJ =	1.09189	SE =	.00	
I = 4	J = 10	RIJ =	1.09077	SE =	.00	
I = 4	J = 11	RIJ =	1.09077	SE =	.00	Twist angles
I = 1	J = 2	K = 3	L = 4	PHI = −179.990	SE = .0000	SE Driver
I = 2	J = 3	K = 4	L = 5	PHI = −179.986	SE = .0000	SE Driver

Total Strain Energy = 1.13295770

Frequency (CM-1) (1) = 2974	Frequency (CM-1) (15) = 1404
Frequency (CM-1) (2) = 2973	Frequency (CM-1) (16) = 1370
Frequency (CM-1) (3) = 2973	Frequency (CM-1) (17) = 1199
Frequency (CM-1) (4) = 2971	Frequency (CM-1) (18) = 1064
Frequency (CM-1) (5) = 2925	Frequency (CM-1) (19) = 1053
Frequency (CM-1) (6) = 2872	Frequency (CM-1) (20) = 1000
Frequency (CM-1) (7) = 2865	Frequency (CM-1) (21) = 967
Frequency (CM-1) (8) = 2855	Frequency (CM-1) (22) = 929
Frequency (CM-1) (9) = 1561	Frequency (CM-1) (23) = 851
Frequency (CM-1) (10) = 1493	Frequency (CM-1) (24) = 773
Frequency (CM-1) (11) = 1440	Frequency (CM-1) (25) = 388
Frequency (CM-1) (12) = 1436	Frequency (CM-1) (26) = 244
Frequency (CM-1) (13) = 1421	Frequency (CM-1) (27) = 197
Frequency (CM-1) (14) = 1412	

Thermodynamic functions

T	$-(F(0)-H(0,0))/T$	$(H(0)-H(0,0))/T$	$S(0)$	$CP(0))$
200.00	48.533	10.066	58.599	13.086
298.15	52.849	11.704	64.533	17.158
400.00	56.564	13.702	70.284	22.104
500.00	59.858	15.888	75.745	26.849
600.00	62.948	18.069	81.016	31.002
800.00	68.720	22.185	90.905	37.753

Zero Point Energy = 62.365
Symm Number = 2
Heat of Formation (Gas, T) = −25.52 T = 298.15

The calculated thermodynamic functions in Table 2 for cyclopentane include an ad hoc pseudo-rotator calculation of the thermodynamic function for this degree of freedom. The lesson here is that special features of particular molecules must be watched for. On balance, however, we are of the opinion that the methods described here will provide convenient predictions of heat of formation and thermodynamic function that are more reliable and are of wider applicability than those estimated by current methods.

The Fortran V programs MOLGEN and MOLBD3 are available on request to R. H. Boyd.

ACKNOWLEDGMENTS

The authors are indebted to the U. S. Air Force Office of Scientific Research through a project THEMIS contract and to the U. S. Army Research Office (Durham) for financial support of this work.

NOTATION

A_i^α = the sum of all the coefficients of ΔX_i^α in the linear terms
$C_{ij}^{\alpha\beta}$ = the sum of all the coefficients of ΔX_i^α in quadratic terms
C_p^0 = constant pressure heat capacity
E_a^* = energy of atomization in the hypothetical motionless state
E_{ij}^B = bond (or group) energies between atoms (or groups) i and j
$G_T^0 - G_0^0$ = Gibbs free energy relative to 0°K
$H_T^0 - H_0^0$ = enthalpy relative to 0°K
ΔH_a^0 (T°K) = enthalpy of atomization for compound $A_nB_m \ldots$ at T degrees Kelvin
ΔH_f^0 (A, T°K) = enthalpy of formation for atom A at T degrees Kelvin
ΔH_f^0 (B, T°K) = enthalpy of formation for atom B at T degrees Kelvin
ΔH_f^0 ($A_nB_m \ldots$, T°K) = heat of formation of compound $A_nB_m \ldots$ at T degrees Kelvin
k^θ_{ijk} = force constant for angle bending between atoms i, j, and k
k_{ij}^R = force constant for bond stretching between atoms i and j
m = number of atoms of B
n = number of atoms of A
r_{ij} = distance between atom i and j
Δr_{ij} = distance deviation of valence coordinate r_{ij} from r_{ij}^0
RT = gas constant multiplied by the absolute temperature
R_{ij}^0 = equilibrium distance between atoms i and j
S^0 = absolute entropy
T = absolute temperature
$V_{ij}^{NB}(r_{ij})$ = nonbonded potential function for atoms i and j
V_{ijkl} = barrier height for bond twisting between atoms i, j, k, and l
X_i = mole fraction of ith conformer
$X_i^{0\alpha}$ = Cartesian coordinates for atom i
ΔX_i^α = Cartesian coordinate deviations for atom i
ΔX_j^β = Cartesian coordinate deviations for atom j
ZPE = zero point energy

Greek Letters

δ = angular coordinate for out-of-plane bending
δ_{ij} = Kronecker delta
θ_{ijk} = angle between atoms i, j, and k
Θ^0_{ijk} = equilibrium angle between atoms i, j, and k
$\Delta\theta_{ijk}$ = angle deviation of valence coordinate θ_{ijk} from θ^0_{ijk}
ν = vibrational frequency
ϕ_{ijkl} = bond twist angle formed by atoms i, j, k, and l
ω = angular frequency

A superscript 0 on X_i, r_{ij}, θ_{ijk} and ϕ_{ijkl} indicates the values of these coordinates for the trial structure the potential energy is being expanded about. In general, the values of r_{ij}^0 and θ^0_{ijk} do not coincide with the equilibrium or relaxed values of the bond lengths (R_{ij}^0) and angles (Θ^0_{ijk}) which appear as constants in the potential functions.

LITERATURE CITED

Allinger, N. L., M. A. Miller, F. A. Van Catledge, and J. A. Hirsch, "Conformational Analysis. LVII. The Calculation of the Conformational Structures of Hydrocarbons by the Westheimer-Hendrickson-Weinberg Method," *J. Am. Chem. Soc.*, **89**, 4345 (1967).

Allinger, N. L., J. A. Hirsch, M. A. Miller, I. Tyminski, and F. A. Van Catledge, "Conformational Analysis. LX. Improved Calculations of the Structures and Energies of Hydrocarbons by the Westheimer Method," *ibid.*, **90**, 1199 (1968).

Bixson, M., and S. Lifson, "Potential Functions and Conformations in Cycloalkanes," *Tetrahedron*, **23**, 769 (1967).

Boyd, R. H., "A Method for Calculation of the Configurational Potential Energy and Thermodynamic Functions of Molecules from Empirical Valence Force Potentials," Div of Phys. Chem. Abstracts, 152nd National Meeting, Am. Chem. Soc., New York (1966).

———., "Method for Calculation of the Conformation of Minimum Potential Energy and Thermodynamic Functions of Molecules from Empirical Valence-Force Potentials—Application to the Cyclophanes," *J. Chem. Phys.*, **49**, 2574 (1968).

———., "The Prediction of the Thermodynamic Functions of Ideal Gases of Complex Molecules," Fifth Symp. Thermophys. Properties, *Am. Soc. Mech. Eng.*, (1970).

———., *MOLBD2*, in "Computer Programs for Chemistry," Vol. V, K. B. Wiberg (ed.), Academic Press, in press (1973).

———., S. N. Sanwal, S. Shary-Tehrany, and D. McNally, "The Thermochemistry, Thermodynamic Functions and Molecular Structures of Some Cyclic Hydrocarbons," *J. Phys. Chem.*, **75**, 1264 (1971).

Chang, S. J., D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, "The Heats of Combustion and Strain Energies of Bicyclo [n.m.o.] Alkanes," *J. Am. Chem. Soc.*, **92**, 3109 (1970).

Davidson, N., *Statistical Mechanics*, McGraw-Hill, New York (1962).

Franklin, J. L., "Predictions of Heat and Free Energies of Organic Compounds," *Ind. Eng. Chem.*, **41**, 1070 (1949).

Hendrickson, J. B., "Molecular Geometry. I. Machine Computation of the Common Rings," *J. Am. Chem. Soc.*, **83**, 4537 (1961); "Molecular Geometry. II. Methyl-cyclohexanes and Cycloheptanes," *J. Am. Chem. Soc.*, **84**, 3355 (1962).

Jacob, E. J., H. Thompson, and L. S. Bartell, "Influence of Nonbonded Interactions on Molecular Geometry and Energy: Calculations for Hydrocarbons Based on Urey-Bradley Field," *J. Chem. Phys.*, **47**, 3736 (1967).

Kilpatrick, J. E., K. S. Pitzer, and R. Spitzer, "The Thermodynamics and Molecular Structure of Cyclopentane," *J. Am. Chem. Soc.*, **69**, 2483 (1947).

Lifson, S., and A. Warshel, "Consistent Force Field for Calculations of Conformations, Vibrational Spectra, and Enthalpies of Cycloalkane and n-Alkane Molecules," *J. Chem. Phys.*, **49**, 5116 (1968).

Scott, R. A., and H. A. Scheraga, "Conformational Analysis of Macromolecules. II. The Rotational Isomeric States of the Normal Hydrocarbons," *ibid.*, **44**, 3054 (1966).

Shieh, C. F., D. McNally, and R. H. Boyd, "The Heats of Combustion and Strain Energies of Some Cyclophanes," *Tetrahedron*, **25**, 3653 (1969).

Snyder, R. G., and J. H. Schachtschneider, "A Valence Force Field for Saturated Hydrocarbons," *Spectrochim. Acta*, **21**, 169 (1965).

Warshel, A., and S. Lifson, "Consistent Force Field Calculations. II. Crystal Structures, Sublimation Energies, Molecular and Lattice Vibrations, Molecular Conformations, and Enthalpies of Alkanes," *J. Chem. Phys.*, **53**, 582 (1971).

Westheimer, F. H., "A Calculation of the Energy of Activation for the Racemization of 2,2'-Dibromo-4,4'-Dicarbozydiphenyl," *ibid.*, **15**, 252 (1947).

———., and J. E. Mayer, "The Theory of the Racemization of Optically Active Derivatives of Diphenyl," *ibid.*, **14**, 733 (1946).

Wiberg, K. B., "A Scheme for Strain Energy Minimization. Application to the Cycloalkanes," *J. Am. Chem. Soc.*, **87**, 1070 (1965).

Williams, D. E., "Nonbonded Potential Parameters Derived from Crystalline Hydrocarbons," *J. Chem. Phys.*, **47**, 4680 (1967).

Manuscript received November 27, 1972; revision received May 4 and accepted May 7, 1973.