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CONFORMATIONAL ANALYSIS—129

HEATS OF FORMATION AND THERMODYNAMIC PARAMETERS FOR HYDROCARBONS, CALCULATED BY THE MOLECULAR MECHANICS METHOD INCLUDING THE EFFECTS OF MOLECULAR VIBRATIONS[1,2]

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Abstract—A force field is presented in which the zero point energies and the effects of vibrational thermal excitation are included in the heat of formation calculations. The standard deviation of the difference between the calculated and experimental heats of formation of a diverse set of 44 hydrocarbons is 0.38 kcal/mole, which is the same as the average experimental error for this set of compounds. This standard deviation is substantially lower than in previous similar force fields which did not include vibrational effects, and it is argued that much of this improvement is due to the inclusion of vibrational terms in the heat of formation. This force field also reproduces the experimental structures of compounds well.

Thermodynamics is one of the most powerful tools available to the chemist. However, the number of experimentally determined thermodynamic quantities are limited, and yearly additions to the list are few indeed, especially when compared with the number of new compounds synthesized each year. The need for accurate and inexpensive ways to estimate thermodynamic quantities is obvious.

In principle, quantum mechanics can be used to calculate the energies and structures of molecules, but in practice the cost of doing such calculations for even small molecules is great when accuracy comparable to experiment is desired. Worse, the cost of doing a single quantum mechanical calculation usually greatly underestimates the true cost of using this method, because the geometries of most molecules are not accurately known, which requires that one do a large number of calculations to find the geometry of lowest energy.

Molecular mechanics calculations, in contrast to the quantum mechanics calculations, are quite inexpensive. When sufficient experimental data are available to properly develop the force field, the method can yield results, the accuracy of which is comparable with that obtainable by experimental measurement. In molecular mechanics calculations the energy of the molecule is described by a set of classical equations of motion which are functions of the atomic positions. The atomic positions are varied from an initial approximate geometry chosen by the chemist until a geometry of minimum energy is found. One can also use the equations of motion to calculate the vibrational frequencies of the molecule. The set of equations used for such calculations is called the *force field*. A variety of force fields have been published and reviews are available.[3,4]

Development of the force field

In 1971 we published a force field for the calculation of the energies and structures of hydrocarbons.[5] Despite the fairly good results obtained with this 1971 force field, work was started on a new force field in the hope that the agreement between the calculated and experimental energies could be improved.

A variety of modifications were tested in an attempt to find a better force field. While the details of the successes and failures of the different force fields varied, all of these force fields had one problem in common with the 1971 force field and with Schleyer's 1973 force field.[6] Namely that as one went from ethane to n-hexane the calculated heat of formation went from too positive for ethane to much too negative for n-hexane. This problem was relatively insensitive to the changes in the force fields which were tried, and a solution had to be found elsewhere.

Our model is aimed at reproducing structures and energies of molecules. We did not wish to explicitly consider any more detail than necessary to reach those objectives. Accordingly, we assumed that the structure of the molecule was fixed at the thermally averaged values of the bond lengths and angles. An actual molecule, is, of course, undergoing vibrational motions, and more or less of the molecules will be in ground or excited vibrational states, depending on circumstances. A more thorough treatment of the problem would calculate the vibrational potential functions, the corresponding vibrational levels, and then have these levels occupied according to the Boltzmann distribution function and the temperature. Lifson[7] and Boyd[8] have used these statistical mechanical terms as part of their calculated energies, but since their calculated energies did not seem to be any better than those obtained with our 1971 force field (which omitted such calculations), we initially believed that the statistical mechanical energy terms could be implicitly included as part of the group and bond energy terms, and did not have to be explicitly included. However, the intractabililty of the n-alkane problem caused us to reexamine this question.

Pitzer, in a classic paper,[9] calculated the statistical mechanical functions of a hindered rotor. The tables in Pitzer's paper show that the thermal excitation of rotation about the C–C bond of an n-alkane would contribute about 0.3 kcal/mole to the energy of the compound at 25°. The manner in which the statistical mechanical energy terms were lumped into the group energy terms in our calculations appeared to be the main reason why the calculated (1971) heat of formation of ethane was too high.

If we compare a group of molecules which contain some n-alkanes and some rigid compounds (cyclic or bicyclic rings systems, for example) there will generally be discrepancies between the two sets of compounds. In the first set, there are bonds about which these hindered rotations can occur, and in the second set there are not. If the bond energy terms are picked to fit the rigid set, for example, then the torsional increments must be explicitly included in the calculations involving open chains, if the agreement between the calculated and experimental energies of the open chain set is to be good. This will be taken care of automatically if the statistical mechanics calculations using these frequencies are carried out. Alternatively, the following approximation was used in our 1973 force field. Since our bond energy scheme has an increment for a methyl group, rotations of the methyl attached to some other group (in methylcyclohexane, for example) are already accounted for in that increment. But in butane, for example, it is necessary to add about 0.3 kcal/mole for this torsional effect to take care of the central bond. For the larger alkanes it is necessary to add about 0.3 kcal/mole for each CH_2–CH_2 bond. Ethane is a special problem, because it contains two Me groups, but only one bond about which rotation is occurring. Since each of the Me increments includes the Me torsional term, about 0.3 kcal/mole must be subtracted in the case of ethane. Thus, when our 1973 force field[4,10] was being developed, the heat of formation calculation was modified to include the torsional increments as mentioned above. In addition, statistical mechanical energy terms amounting to 3RT per molecule for the external degrees of freedom, and RT for the pressure-volume work were also included. This permitted the 1973 force field (MMI program) to give a reasonable overall a fit to the heats of formation of hydrocarbons. For large selected list of 38 compounds, the standard deviation for the difference between the experimental and calculated heats of formation was 0.61 kcal/mole, where the average experimental error was 0.40 kcal/mole. (The deviation was 0.69 kcal/mole for a similar list with the 1971 force field.) For a slightly different list, Schleyer's 1973 force field gave a standard deviation of 0.83 kcal/mole. It should be noted that different investigators have chosen different sets of data to fit their force fields to, and consequently the goodness of fit to an overall set, such as above, cannot be used to conclude that one force field is superior to another. Both our 1973 force field and Schleyer's 1973 force field contain inaccuracies, and each does better than the other on certain types of compounds. Overall, the two force fields seem to do about equally as well in predicting structures and energies.

Having found that it was desirable to explicitly include the effects of thermal excitation in the calculation of the heats of formation of the n-alkane, we decided to examine the possibility that other vibrations had frequencies low enough so that the effects of excitation also needed to be explicitly included. Schachtschneider and Snyder, in their paper on the normal mode vibrations of the n-alkanes,[11] showed that the vibrations composed largely of C–C–C bending modes were often lower in energy than the vibrations associated with torsional modes. This implied that the effects of exciting C–C–C vibrational modes might contribute as much to the heat of formation as the torsional vibrations did. Like the torsional modes, one would expect some of the frequencies of C–C–C vibrational modes in acyclic compounds to be considerably lower than the frequencies of such vibrations in more rigid compounds, where bond angle bendings are partly coupled with bond stretchings or other angle bendings.

These considerations suggested that one might be able to obtain more accurate heats of formation if all of the statistical mechanical energy terms were accurately accounted for. The objective of this present work was to determine whether or not any real significant improvement in heat of formation results would in fact be obtainable in this way.

In order to calculate the statistical mechanical energy terms, one must first calculate the vibrational frequencies of the molecule. The method chosen for calculation of these frequencies was standard.[12] Boyd[8] and Lifson[7] earlier carried out such calculations for a few molecules, but no systematic study of heats of formation at this level has previously been reported. Since a knowledge of the vibrational frequencies makes it easy to calculate the zero point energy of a molecule, these terms were also included in the calculated heats of formation.

Since writing a general program to calculate the vibrational frequencies of molecules, without using excessive amounts of computer time, and working in Cartesian coordinates (which is essential if the program is to be generally useful for cyclic compounds), required a great deal of programming effort, the 1973 force field was developed for use while work on a force field using vibrational frequencies could be developed and assessed.

Results of the force field using vibrational frequencies

The force field described herein includes in full the effects of the vibrational frequencies in the heat of formation calculations (Table 1). The functional form of this force field differs from the 1973 force field in the following ways: (1) The effects of thermal excitation of vibrations and the zero point energies are explicitly included in calculating the heats of formation. These are calculated from the vibrational frequencies using standard statistical mechanical functions.[13] An R^{-12} term is used in the van der Waals function in place of the exponential term. (2) No torsion-bend function is used.

The reasons for these changes are as follows. The Urey–Bradley function was used in place of the stretch-bend function because it was believed that it would give the same qualitative effects, and yet be easier to program in the vibrational frequency calculations. The torsion-bend function was not included in this force field because it would be an especially difficult function to program into the vibrational frequency calculations. Since the major reason for having a torsion-bend function earlier was to give the observed degree of nonplanarity to cyclobutane, it was felt that including this function in the calculations could be deferred until the effects of using vibrational frequencies could be assessed. It could then be added if it seemed worthwhile. Four-membered rings were consequently not treated in the present work. The R^{-12} term was used because less computer time is required to evaluate this function than is required to evaluate the exponential function as is used in the 1971 and 1973 force fields. The functions are essentially indistinguishable in the region of interest. The full force field is given in Table 1.

The force field parameters were optimized in part using a least squares computer program designed for the purpose. While it is possible to have a completely automated program of this kind,[7] in fact a lot of human intervention is practical. The problem is that one wants to simultaneously optimize a lot of quantities which are not related by a simple criterion. For example, bond lengths, angles, and molecular energies, although related, are measured in different units and measured by different

Table 1. Force field with zero point energies and statistical mechanical terms

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Heat of Formation = Steric Energy + Zero Point Energy + Thermal Energy + Group Energy Terms

Steric Energy = Bond Stretching + Angle Bending + Urey–Bradley + Torsion + van der Waals.

Bond Stretching

$$E_b = 71.94\, K_b\, (l - l^{\circ})^2$$

Bond	l° (A)	K_b (ergs / $A^{\circ 2}$)
C–C	1.516	4.5
C–H	1.096	4.6

Angle Bending

$$E_a = 71.94\, K_a\, ((\theta - \theta)^2 \pi^2 / 180^2)$$

Angle	θ (degrees)	K_a (erg / rad²)
C–C–C	110.0	0.33
C–C–H	109.0	0.30
H–C–H	109.0	0.40

Urey - Bradley

$$E_{ub} = K_{ub}\, (l_{13} - l^{\circ}_{13})^2$$

Atoms Types	K_{ub} (kcal)	l°_{13} (A)
C. . . C	14.0	2.60
C. . . H	0.0	——
H. . .H	0.0	——

Torsion

$$E_{\omega} = 0.05\left[1 - \cos(3\theta)\right]$$

(For all torsional angles)

van der Waals

$$E_{vdw} = \epsilon\left((R^{\circ}/R)^{12} + A(R^{\circ}/R)^{6}\right)$$

$$A = -1.75$$

Atoms Types	ε (kcal)	R (A)
C. . .C	0.058	3.45
C. . .H	0.075	3.05
H. . .H	0.140	2.74

For van der Waals calculations, hydrogen atoms are placed 0.9 of the distance out along the C–H bond.

$$\text{Zero point energy} = \frac{1}{2}\sum_{i=1}^{3n-6} \nu_i A$$

$A = 1.4296$ cal when ν_i is in cm^{-1}

Statistical Mechanical Energy = Thermal excitation of vibrations + Excitation of translation and rotations + PV work

$$\text{Thermal excitation of vibrations} = \sum_{i=1}^{3n-6} \frac{\Theta}{e^{\Theta} - 1} \qquad \Theta = h\nu/kT$$

$$\text{Translational excitation} = \tfrac{3}{2}RT$$

$$\text{Rotational excitation} = \tfrac{3}{2}RT$$

$$\text{PV work} = RT$$

Table 1. (*Contd*)

If a molecule contains conformations of different energies, the heat content of the lowest must be corrected by admixture of the higher energy conformations (Boltzmann distribution). (Reference 4, Page 42).

Group Energy Terms (kcal / mole)

Group	Energy contribution
C-H bond	-7.619
C-C bond	-6.906
Methyl group	-6.535
Iso group	5.313
Neo group	10.041

experimental techniques to different levels of accuracy. There is consequently no rigorous way to equate these quantities so as to be able to carry out a least squares minimization of errors. However, the least squares method in fact requires that they are equated. Just how this is done depends on the error in the experimental quantities, but it also depends in a more subjective way on the relative importance of the different quantities with respect to the number and kinds of compounds under study, and the relative importance for each kind, as a representative of a class of molecules. In practice, it is expedient to basically make these decisions by hand, using the computer to help when the arithmetic becomes too cumbersome.

The results obtained from this force field are presented in a series of Tables 2–4. The experimental and calculated structural parameters are compared in Table 2. In common with most recent force fields, the agreement be-

Table 2. Experimental and calculated structural parameters

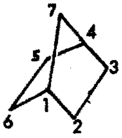
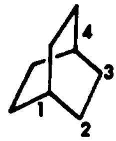
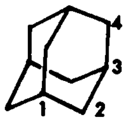
Alkane	Parameter	Experimental[a,b]	Calculated
propane	r(CC)	1.526[c] , 1.532[d]	1.533
	Θ (CCC)	112.4 , 112.0	112.2
isobutane	r(CC)	1.535[e]	1.535
	Θ (CCC)	110.8	111.0
cyclopentane	r(CC)	1.539[g] 1.546[f]	1.540
cyclohexane	r(CC)	1.536[h]	1.535
	ω(CCCC)	54.9	55.6
methylcyclohexane	r(CC)av	1.52[i]	1.535
	Θ(CCC)ring	111.3	111.3
	Θ(CCC)methyl	110.1	111.7
	ω(CCCC)av, ring	55.3	55.4
norbornane 	r(C_1C_2)	1.539[j] 1.534[k], 1.556[l]	1.545
	r(C_2C_3)	1.557, 1.578, 1.551	1.547
	r(C_1C_7)	1.560 1.535, 1.559	1.541
	Θ($C_1C_7C_4$)	93.1 , 93.2 95.3, 96.0	93.3
bicyclo-[2.2.2.]-octane	r(C_1C_2)	1.538[m]	1.541

Table 2. (*Contd*)

 	$r(C_2C_3)$	1.552	1.542
	$\theta(C_1C_2C_3)$	109.7	109.5
	$d(C_1{-}{-}C_4)$	2.592	2.594
adamantane	$r(CC)av$	1.540^n	1.539
 	$\theta(C_1C_2C_3)$	109.8	109.6
	$\theta(C_2C_3C_4)$	108.8	109.4
Neopentane	$r(C{-}C)$	1.539^o	1.538
diamond	$r(C{-}C)$	1.544^q	1.542^p
n-Hexane crystal	A spacing	4.17^s	4.14^r

(a) Distances are in Angstroms and angles in degrees.

(b) When microwave data are used C–C bond lengths have been corrected to electron diffraction values by adding 0.007A° to the microwave valves. For a discusion of this correction see: Dr. R. Lide, Jr., Tetrahedron, 17, 125 (1962).

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(m) A. Yokozeki, K. Kuchitsu and Y. Morino, Bull. Chem. Soc. Japan, 43, 2017 (1970).

(n) I. Hargittai and K. Hedberg, Chem. Comm., 1499 (1971).

(o) B. Beagley, D. P. Brown and J. J. Monaghan, J. Mol. Struct., 4, 233 (1969).

(p) Calculated using as a model for the diamond lattice ethane in which each hydrogen has been replaced by carbon (C_8). It appears that this model understates the C-C bond length obtained from a more complete model of the diamond lattice by 0.003A°.

(q) "Tables of Interatomic Distances and Configurations In Molecules and Ions, Supplement 1956–59," special publication No. 18, the Chemical Society(London).

(r) Calculated using a n-hexane dimer as a model for the crystal. See the text for a discusion of the errors in using this model.

(s) N. Norman and H. Mathisen, Acta Chem. Scand., 15, 1755 (1961).

tween the calculated and experimental structural parameters is excellent. This force field does significantly better on one structural quantity for which our earlier force fields did poorly. This is the C–C bond length in diamond. In our 1973 field the calculated diamond C–C bond length was about 0.02 A too short.

In this work the n-hexane crystal A spacing was calculated using two n-hexane molecules as a model for the crystal. This crystal spacing is important in establishing the correctness of long-range van der Waals forces.[14] Using this model for the crystal ignores two effects important in determining the actual interchain spacing: the long range crystal packing forces which decrease the interchain distance and thermal expansion which causes the interchain distance to increase. We know from calculations performed using previous force fields[10,14] that the long range packing forces (observed when a larger crystal model is used) cause a relatively small decrease in the interchain distance (about 0.04 A) while Lifson[15] found that the effects of thermal expansion caused the interchain distance to increase on the order of 0.1 A. We believe that the Lifson result overestimates the degree of thermal expansion, but it is still likely that the effects of thermal expansion are greater than the shrinkage effects of the longer range crystal packing forces, and that the n-hexane dimer understates the true distance between the chains in the crystal at the temperature the X-ray structure was determined. We therefore believe that having the calculated interchain distance 0.04 A too short is better than having this distance identical to the experimental distance.

The only compound in Table 3 for which the difference

Table 3. Calculated and experimental heats of formation (ΔH_f^0) in kcal/mole at 25°C

Compound	Steric Energy	Zero Point Energy	Heat Content	Calculated ΔH_f^0	Experimental ΔH_f^0 error	Ref.	Exp-Calc
Ethane	0.601	41.880	2.949	-20.26	-20.24 ± 0.12	a	0.02
Propane	0.641	58.172	3.725	-25.29	-24.83 ± 0.14	a	0.46
Butane	0.563	74.302	4.613	-30.23	-30.19 ± 0.16	b	+0.04
Butane-gauche	1.077	74.652	4.541	-29.70			
Iso-Butane	0.123	74.139	4.590	-32.35	-32.41 ± 0.13	a	-0.06
2-MeButane	0.571	90.524	5.461	-36.68	-36.85 ± 0.15	b	-0.17
2,3-DiMe-Butane	1.048	107.023	6.235	-42.40	-42.61 ± 0.24	a	-0.21
2,2,3-TriMe-Butane	1.953	123.263	6.514	-48.92	-48.87 ± 0.33	a	0.06
2,2,3,3-Tetra-MeButane	2.733	140.033	7.429	-54.41	-53.95 ± 0.29	c	0.46
Pentane	0.474	90.393	5.536	-35.23	-35.10 ± 0.15	b	0.13
Neopentane	-0.838	89.803	5.467	-40.72	-40.27 ± 0.25	a	0.45
2-MePentane	0.492	106.596	6.411	-41.68	-41.77 ± 0.25	b	-0.09
3-MePentane	1.276	106.877	6.417	-40.71	-41.13 ± 0.24	b	0.42
3,3-DiMe-Pentane	1.280	123.356	7.030	-47.76	-48.08 ± 0.29	a	-0.32
3,3-DiEt-Pentane	4.126	157.074	8.655	-53.87	-55.41 ± 0.44	a	-1.54
2,2,4-Tri-MePentane	1.973	139.284	7.887	-53.66	-.53.54 ± 0.37	a	0.12
Hexane	0.378	106.468	6.480	-40.05	-39.92 ± 0.18	b	0.07
2,2,5,5-TetraMeHexane	-0.151	170.847	9.388	-68.81			
Cyclopentane	8.671	79.722	3.771	-18.56	-18.44 ± 0.20	a	-0.24
Cyclohexane	2.146	96.532	4.756	-29.42	29.50 ± 0.15	a	-0.08
Cycloheptane	7.240	114.163	5.510	-28.09	-28.21 ± 0.18	a	-0.12
Cyclooctane	10.874	131.101	6.212	-28.96	-29.73 ± 0.28	a	-0.77
Cyclononane	12.506	147.955	6.805	-32.02	-31.73 ± 0.40	a	0.29
Cyclodecane	12.265	164.047	7.648	-37.31	-36.88 ± 0.40	b	0.43
MeCyclopentane	7.878	95.668	5.106	-25.43	-25.27 ± 0.18	a	0.16
MeCyclohexane	1.355	112.266	5.751	-36.85	-36.98 ± 0.25	a	-0.13
1,1-DiMeCyclohexane	1.719	128.558	6.559	-43.33	-43.23 ± 0.47	a	-0.10
trans-1,2-Di-MeCyclohexane	1.289	128.364	6.695	-43.24	-42.99 ± 0.47	a	0.25
cis-1,2-DiMe-Cyclohexane	2.401	129.132	6.544	-41.51	-41.13 ± 0.44	a	0.38
cis - 1,3,-DiMe-Cyclohexane	0.550	127.986	6.774	-44.28	-44.13 ± 0.42	a	0.15
trans-1,3-Di-MeCyclohexane	1.799	128.719	6.649	-42.42	-42.18 ± 0.41	a	0.24
trans-1,4-Di MeCyclohexane	0.551	127.981	6.774	-44.28	-44.10 ± 0.42	a	0.18
cis-1,4-DiMe-Cyclohexane	1.748	128.725	6.641	-42.48	-42.20 ± 0.42	a	0.28
trans-Bicyclo (3.3.0) octane	19.978	116.514	5.873	-15.82	-15.9 ± 0.6	d	-0.08
cis- Bicyclo (3.3.0) octane	13.562	116.842	5.833	-21.95	-22.3 ± 0.5	d	-0.35
Bicyclo (2.2.2) octane	10.144	118.085	5.512	-24.45	-23.75 ± 0.30	f	0.70
trans-Bicyclo (4.3.0) nonane	9.253	133.164	6.549	-31.36	-31.42 ± 0.52	a	-0.06

Table 3. (*Contd*)

Compound	Steric Energy	Zero Point Energy	Heat Content	Calculated ΔH_f^o	Experimental ΔH_f^o error	Ref.	Exp–Calc
cis-Bicyclo (4.3.0) nonane	9.401	133.977	6.459	-30.49	-30.38 ± 0.48	a	0.11
trans-Bicyclo (4.4.0) decane	1.722	149.849	7.150	-43.75	-43.52 ± 0.56	a	0.23
cis-Bicyclo (4.4.0) decane	3.674	150.988	6.956	-40.85	-40.43 ± 0.56	a	0.42
Norbornane	18.798	100.179	4.803	-12.26	-12.42 ± 0.70	f	-0.16
trans-2,3-Di MeNorbornane	18.490	132.422	6.703	-25.15	-25.71 ± 0.54	g	-0.56
cis-endo-2,3-DiMeNorbornane	20.992	133.353	6.585	-21.84			
cis-exo-2,3-DiMeNorbornane	19.172	132.868	6.563	-24.17			
1,4-DiMeNorbornane	15.146	131.078	6.999	-30.73	-30.63 ± 0.38	g	0.10
Bicyclo (3.2.1) octane	11.132	117.793	5.396	-23.86			
Bicyclo (3.3.1) nonane	8.803	135.686	6.172	-29.67			
cis-*trans*-Perhydroanthracene	3.119	204.204	9.454	-55.31			
trans-syn-trans-Perhydroanthracene	1.222	203.086	9.652	-58.12	-58.12 ± 0.93	a	0.00
trans-anti-trans-Perhydroanthracene	6.271	203.810	9.722	-52.29	-52.73 ± 0.98	a	-0.44
trans-syn-trans-Perhydro-phenanthrene	9.333	204.734	9.100	-48.92			
trans-anti-trans-Perhydro-phenanthrene	2.492	203.554	9.643	-56.40			
Adamantane	4.936	139.120	5.923	-30.64	-30.79 ± 0.9	e	-0.01
Standard deviation (| exp–calc |) of heats of formation					0.38		
Standard deviation of experimental error					0.42		
Average deviation (| exp–calc |) of heats of formation					0.26		
Average deviation of experimental error					0.38		

(a) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York (1970).

(b) Calculated Heats of Formation are adjusted for the increase due to the presence of *gauche* conformations which have energies higher than the anti conformation. The amount of the adjustment is: butane, +0.27; 2-methylbutane, +0.10; Pentane, +0.49; 2-methylpentane, +0.30; 3-methylpentane, +0.20; hexane, +0.88; and cyclodecane, +0.16. The experimental heats of formation were taken from the reference in footnote (a).

(c) W. D. Good, *J. Chem. Thermodyn.*, **4**, 709 (1972).

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between the calculated and experimental heats of formation differ by more than 1 kcal/mole is 3,3-diethylpentane. This one compound is responsible for about 20% of the standard deviation for the compounds in Table 3. Because the "experimental" heat of formation of this compound contains an *estimated* heat of vaporization, we initially thought the discrepancy between the calculated and experimental heats of formation might be due to errors in the heat of vaporization. In the 3 years since the work on this force field was completed, it has become apparent that at least part of the problem with 3,3-diethylpentane is not with the heat of vaporization but with the calculated heat of formation, and that the latter is too high because the hydrogens in this force field are too hard.[18–20] The hard hydrogens were used because they gave better results overall than softer hydrogens. We now believe that these hard hydrogens helped to compensate for deficiencies in the way the repulsion between the terminal bonds of torsional angles is treated.

Two different ways to better account for these interactions between the terminal bonds of torsional angles have been recently introduced. The first is the EPEN force field of Scheraga in which the bonding electrons are an explicit part of the molecule and electron centered, as well as atom centered, electron-electron repulsion terms are used.[21] This force field has not been extensively tested on hydrocarbons but it reproduces both the hexane crystal spacings and heats of vaporization as well as the *anti*- to *gauche*-butane energy difference. It also reproduces the ethane torsional barrier without a torsional function. The other approach is to use a more complete torsional function.[18,22] The rational here is that the 3-fold torsional term used in this force field is really only one term in the Fourier series necessary to reproduce the change in the energy with change in torsional angle. The C_3 symmetry axis of ethane causes all terms in the Fourier series which are not multiples of 3 to cancel. However, in a molecule like butane that does not have C_3 symmetry, these other terms in the Fourier series do not necessarily cancel, and can become an important part of the net energy. This approach improves considerably the agreement between the experimental and calculated heats of formation.[18]

Assessment of the benefits of using vibrational frequencies in heat of formation calculations

We believe that our present results (Tables 3 and 4) can be characterized as quite good. The *standard deviation* of the experimental error in the heats of formation for compounds in Table 3 is slightly larger than the standard deviation of the difference between the experimental and calculated heats of formation, and the average experimental error is substantially larger than the average difference between the calculated and experimental heats of formation.

Direct assessment of the benefits of using the zero-point energies and statistical mechanical energies calculated from the vibrational frequencies is difficult. It is certainly true that these terms are very important in an absolute sense. The zero point energies are many times larger than the steric energies of the molecules; the contributions of the thermally excited vibrations to the heat contents of the molecules, while much smaller than the zero point energies, are still larger for most molecules in Table 3 than are the steric energies of the molecules. It is also true that changes in the zero-point energies are in general responsible for about 30% of the calculated differences in the conformational energies. However, these facts do not answer the important question of how good would the agreement between the calculated and experimental heats of formation be if the force field were reparameterized to fit the data without including the effects of the vibrations explicitly.

Without actually reparameterizing the force field there is no way to answer this question conclusively. However, we believe that the 1973 force field is quite similar to what this force field would be like if it were to be reparameterized without including vibrational effects. For example, the change in the gauche H-H interaction in going from *anti*- to *gauche*-butane is almost the same per cent of the change in the total steric energy in this force field as it is in the 1973 force field.[4,10]

If one makes the assumption that the 1973 force field is very similar to what this force field would be like if it were reparameterized without frequency effects, then a comparison of the standard deviations of this force field with those of the earlier force fields should answer the question of how much the inclusion of the vibrational frequency terms improves the force field. The standard deviations of the difference between the calculated and experimental heats of formation of the compounds in Table 3 which were also examined using the 1971 and 1973 force fields, and are 0.37 kcal/mole for this force field, 0.62 kcal/mole for the 1973 force field and 0.68 kcal/mole for the 1971 force field. The average claimed experimental error for this set of compounds is 0.39 kcal/mole. The standard deviation in the heats of formation of the set of compounds in Table 3 which were also examined by Schleyer[6] is 0.36 for this force field and

Table 4. Selected calculated and experimental energy differences and barriers

Compound	Steric Energy	Zero Point Energy	Heat Content	Calculated	Experimental	Ref.
Eclipsed Ethane	2.065	0.41	−0.01	2.48	2.9	a
Cyclohexane-inversion transition state	8.79	1.03	0.04	9.86	10.71	b
ax-eq-Dimethylcyclohexane difference	1.20	0.74	−0.13	1.81	1.90	c
cis,trans-bicyclo(4.3.0)nonane difference	0.15	0.81	−0.13	0.79	1.00	c

a S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968).

b F. A. L. Anet and R. Anet, in Dynamic Nuclear Magnetic Resonance Spectroscopy, L. M. Jackman, ed., Academic Press, New York, 1975, p. 579.

c Table 3.

0.72 for Schleyer's force field. (Average experimental error for this set is 0.37 kcal/mole.) It thus appears that the inclusion of the vibrational frequency effects reduces the standard deviation relative to the 1973 force field (which already contained easily calculated statistical mechanical terms) by 0.25 kcal/mole.

It might be claimed that much of the improvement of the standard deviation of this force field is due to the fact that 4-membered rings were not included. 4-Membered ring compounds were omitted because a torsion-bend function (or its equivalent) is needed if the ring puckering of cyclobutane is to be reproduced. At this stage it was not considered that the (considerable) effort required to program the torsion-bend function was worthwhile. If a torsion-bend function were to be included in the force field, there is no reason to believe that including 4-membered rings in the parameterization would significantly affect the other results.

CONCLUSIONS

The principal objective of this work was to determine if heats of formation could be calculated more accurately for a broad selection of hydrocarbons by specifically including the vibrational effects in the calculations. Our conclusion is that the results can indeed be much improved in this manner. Despite the fact that Table 3 shows that the standard deviation of the difference between the calculated and experimental heats of formation is the same as the average experimental error, we believe that this force field can be further improved in two ways. First, subsequent to the completion of this work it was learned that the inclusion of low-order torsional terms enables one to correct a great many problems involving van der Waals functions[18,22] in this, and in earlier force fields as well. Second, the purpose of this study was to determine if the inclusion of vibrational effects (zero point energies and heat contents) improved the accuracy of the calculated heats of formation. We made no attempt to make the individual calculated vibrational frequencies agree with the experimental values as it is already known that can be done.[7,8] As a result, the agreement between the individual calculated and experimental vibrational frequencies is not very good. This leads to inaccurate calculated heat contents. Now that the inclusion of vibrational frequency effects has been shown to significantly improve calculated heats of formation, it would be best if the zero-point energies, vibrational frequencies, heats of formation, structural and equilibrium data, together with such derived quantities as entropies and heat contents as functions of temperature were all simultaneously optimized in the parameterization process. (This has been previously suggested in part, and some limited calculations along these lines have been reported.[7,8])

Since the average standard deviation shown in Table 3 (0.38 kcal/mole) is the same as the average claimed experimental error one might be inclined to say that further improved agreement between the calculated and experimental heats of formation is limited by the experimental error, but this is probably not true. The reported experimental errors are *twice the standard deviation* of the difference between the average and the individual experimental values. Thus an "experimental error limited" force field should in principle have a standard deviation of the difference between the calculated and experimental heats of formation of one half the average reported experimental error. This ideal situation ignores two facts. (1) Most of the heats of formation in Table 3 are based on the API tables,[23] in which the various experimental results for each compound were averaged and the heats of formation "smoothed". This procedure is believed to give results that are more accurate than implied by the experimental errors. (2) Only random errors are reflected in the claimed experimental errors. If the experimental results contain systematic errors, this would limit the agreement. It seems probable that the systematic errors in the experimental heats of formation of some of the compounds in Table 3 are as large as or larger than the claimed experimental errors,[24] but we suspect that the average systematic experimental errors in Table 3 are actually much smaller than claimed.

The idea that an experimental error limited force field would have a standard deviation near one-half the claimed experimental error is supported by the fact that if the five compounds[25] in Table 2 which we believe are adversely affected by the hard van der Waals function used in this force field are removed, and the heat of formation parameters are redetermined, then the standard deviation for the compounds in Table 3 drops from 0.38 to 0.24 kcal/mole.[26]

It would not surprise us if an "experimental error limited" force field would have a standard deviation that was close to one half the claimed experimental error. Given the results obtained here with use of statistical mechanics in the calculation of the heats of formation; together with the results that can be obtained when 1–4 interactions are properly handled,[18,22] it seems reasonable that such an "experimental error limited" force field can be developed in the near future.

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[24] Adamantane furnishes a pertinent example. There are now available five independent experimental values: −32.96 ± 0.19 (M. Mansson, N. Rapport and E. F. Westrum, Jr., *J. Am. Chem. Soc.* **92**, 7296 (1970)); −30.65 ± 0.98 (ref. f, Table 3); −31.76 ± 0.32 (ref. 16); and −32.84 ± 0.36 and −32.74 ± 0.78 (W. D. Steele and I. Watt, *J. Chem. Thermodynam.* **9**, 843 (1977)).

[25] The five compounds are cyclooctane, cyclononane, cylodecane and 3,3-diethylpentane, which contain unusually severe H–H repulsions, and bicyclo[2.2.2]octane, which contains an unusually severe C–C repulsion.

[26] A referee has asked about the expense of running this program (with the vibrational calculations) as opposed to other similar programs (without). In most cases, the bulk of the computing time is required to minimize the energy with respect to the geometry. The vibrational frequencies do not enter the calculation until after that is done, and consequently they add very little to the overall time required.