148.9, 114.7, and 129.2, respectively, so the agreement is good, fair, and poor, respectively. The MM3 values are 148.2, 129.3, and 154.9, which is some improvement.

The MM3 force field gives 1.5431 Å for the bond length in diamond (calculated with our usual model of fused adamantane rings[7]). The MM2 value is 1.5417, and the experimental value is 1.5445. The latter cannot contain rigid body motion and should be approximately an r_α value. Thus, the discrepancy may be slightly more serious than it appears.

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Supplementary Material Available: Molecular mechanics details for pentamethylethane, di-*tert*-butylmethane, tri-*tert*-butylmethane, 2,2,4,4,5,5,7,7-octamethyloctane, 5,6-di-*n*-butyl-5,6-diphenylethane, cycloheptane, cyclododecane, 1,2-dimethylcyclohexane, 1,1,3,5-tetramethylcyclohexane, decalin, perhydrophenanthracenes, pentacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecane, and various derivatives, [4.4.4]propellane, (*i*,*o*)-bicyclo[6.2.2]dodec-11-ene 2,3-anhydride, 2,3-diadamantyl-2,3-dimethylbutane, ditriptycyl ether, and 1,4,7-cyclononatriene including structures in Figures 1, 3, 4, and 6 and Tables III, VII, and VIII of relative enthalpies of perhydrophenanthrenes, strainless heats of formation, and ab initio heat of formation of dodecahedrane, respectively (15 pages). Ordering information is given on any current masthead page.

Molecular Mechanics. The MM3 Force Field for Hydrocarbons. 2. Vibrational Frequencies and Thermodynamics[‡]

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Abstract: In the development of the MM3 force field, vibrational frequencies were considered for a set of eight relatively simple hydrocarbons. The 213 observed experimental frequencies over this set were fit to within a root-mean-square error of 35 cm^{-1}, of which the largest errors occur in the C–C–H bending frequencies. The torsional frequencies are generally calculated to a much higher accuracy, which allows the calculation of entropies near room temperature for a variety of alkanes and cycloalkanes with errors of less than 1%. A number of rotational barriers in hindered compounds were also calculated. The values of $\Delta S^{\ddagger}$ are usually more negative than −4 eu in congested molecules, and consequently the entropy contribution to rotational barriers can be appreciable. The largest and average discrepancies between the calculated and found values for $\Delta G^{\ddagger}$ are 2.46 and 1.02 kcal/mol, for seven examples.

Force fields can be constructed to reproduce different kinds of data. The MM2 force field was specifically constructed to fit structures and energies of organic molecules.[1-3] A few other properties were also fit, but we frankly omitted fitting vibrational spectroscopic data, because we could not see how to fit those data, and fit the other above-mentioned data at the same time, with the same parameter set. Various other force fields have been constructed along similar lines in some cases, and to fit other data, such as spectroscopic data, as well.[3,4] Such force fields have fit more things, but they have fit less well to structures and energies.[4]

With the experience now available in the design and construction of force fields, it is possible to fit both structures and energies better, overall, than was done with MM2. The previous paper[5] described the development of MM3, which does exactly that. This paper will be concerned with the fitting of some of the other kinds of data which went into the development of MM3, namely, vibrational spectra and other properties that depend on the vibrational levels (entropies, thermodynamic functions). The following paper will describe the results obtained with crystallographic data. All of this work was carried out at the same time and employs the same force field and parameter set. As discussed long ago,[6] if one can correctly calculate the unit cell constants and heat of sublimation of a crystal, one has an indication that the van der Waals' properties of the molecules are, on the whole, reasonable. Because there are many more variables in the van der Waals' parameters than there are cell constants, good fits to crystal data are required if one is to have a good van der Waals' parameter set, but such data alone do not guarantee that the van der Waals' parameter set is, in fact, accurate.

Besides the structural, energy, and crystal data mentioned above, we also wanted to fit vibrational spectroscopic data insofar as possible. Vibrational spectra have been studied in great detail

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[‡] Abstracted mainly from the Ph.D. dissertation submitted by J.-H. Lii to the University of Georgia, 1987.

(1) The MM2 force field for hydrocarbons was first described in ref 2. Extensions to functionalized molecules and other sorts of special problems have been described in subsequent papers, which are summarized in ref 3. The original version of the program (MM2(77)) is available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405, Program 395. The latest version of the MM2 program, which is referred to as MM2(87), is available to academic users from the Quantum Chemistry Program Exchange, and to commercial users from Molecular Design Limited, 2132 Farallon Dr., San Leandro, CA 94577. The MM3 program is still under development, but it is intended to make it available shortly from Technical Utilization Corp., Inc., 235 Glen Village Ct, Powell, OH 43065, and from MDL.

(2) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(3) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, D.C., 1982.

(4) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Altona, C. L.; Faber, D. H. *Top. Curr. Chem.* **1974**, *45*, 1. (c) Dunitz, J. D.; Burgi, H. B. *MTP International Reviews of Science, Series Two: Chemical Crystallography*; Robertson, J. M. R., Ed.; Butterworths: London, 1975; p 81. (d) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. (e) Ermer, O. *Struct. Bonding (Berlin)* **1976**, *27*, 161. (f) Bartell, L. S. *J. Am. Chem. Soc.* **1977**, *99*, 3279. (g) Niketic, S. R.; Rasmussen, K. *The Consistent Force Field*; Springer Verlag: Berlin, 1977. (h) Warshel, A. In *Modern Theoretical Chemistry*; Segal, G., Ed.; Plenum: New York, 1978; Vol 7, p 133. (i) White, D. N. J. In *Molecular Structure by Diffraction Methods*; The Chemical Society: London, 1978; Vol. 6, p 38. (j) Osawa, E.; Musso, H. *Top. Stereochem.* **1982**, *13*, 117.

(5) Allinger, N. L.; Lii, J.-H.; Yuh, Y. H. *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) Allinger, N. L.; Miller, M. A.; Van-Catledge, F. A.; Hirsch, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4345.

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over many years, and there is a vast literature on the subject. Historically, vibrational spectra have been determined in various ways. Either infrared or Raman spectra may be determined for most molecules, and ordinarily some vibrations will be forbidden in one or the other or sometimes both of the spectra. In other cases, one observes not only the fundamental transitions desired, but also combination tones, overtones, and perhaps other complications. Accordingly, the assignment of observed frequencies to specified vibrational modes is not always straightforward. Additionally, we want to study spectra for isolated molecules, which is also the way we do the calculations, in most cases. But often the literature spectra were determined in solvents, as liquids, etc. More errors thus were introduced into the comparison.

More recently, it has become practicable to determine vibrational force constants from ab initio calculations.[7] Because Hartree–Fock calculations do not permit bonds to dissociate to the proper limits, there are systematic errors in such calculated vibrational spectra; namely, the frequencies are calculated to be about 10% too great. There errors can be approximately corrected for, and then the force constants for the vibrational motion can be determined so as to give an accuracy to the calculated frequencies of about ±30 cm^{-1}. While many molecules can have their vibrational frequencies determined experimentally with an accuracy of ±2 cm^{-1} or so, experimental problems often limit the accuracy of the measurement to something larger than this. Thus we might think that the calculation of vibrational frequencies by molecular mechanics methods to an accuracy of something like ±30 cm^{-1} would be desirable and useful. It would be of practical use to experimental chemists to have calculated spectroscopic values that were reliable to this kind of accuracy for studies in complicated molecular systems. Such accuracy has been reported from previous molecular mechanics force fields, but only over very limited sets of compounds.[8] Our objective here was to obtain vibrational frequencies with a moderate accuracy that was very reproducible and reliable, but with a reasonably simple force field. At the outset, it was not clear what kind of accuracy could be expected or how complicated a force field might be required.

For a molecular mechanics force field to give useful reliable results, it is necessary that the force parameters be completely transferable from one molecule to another. That is, the C–C stretching force parameter k_s in ethane must be the same as in propane, or in cyclohexane, or in aliphatic hydrocarbons in general. Or, it could also be that the parameters for bonds between, let us say, primary carbons and between secondary carbons have slightly different values, but those values must be transferable and clearly specified. Spectroscopists have long known that force constants in general are not very transferable. That is, one may be able to transfer the C–C stretching constant from hexane to heptane with reasonable accuracy, but if one tries to transfer the same number to a congested molecule such as hexamethylethane, the vibrational frequencies calculated with such force constants will not be adequate. There are really two separate problems here. First, the spectroscopist is frequently interested in an accuracy on the order of 3 cm^{-1}. In terms of energy, such a small difference is quite negligible for most nonspectroscopic purposes. (It is equal to only 0.009 kcal/mol.) Hence, for other aspects of molecular mechanics, one does not need spectroscopic accuracy, but what we might call "chemical accuracy", which would seem to us to be something of the order of 30 cm^{-1} (0.09 kcal/mol).

The other problem with the transferability of force constants comes from the fact that molecular mechanics force fields explicitly include van der Waals' interactions, whereas spectroscopic force fields do not. Therefore, in a molecular mechanics force field we have something that looks like a force constant and is described by a similar equation, but which we will call a force *parameter*. The actual force constant (the element in the Hessian matrix) is determined by not only stretching, if that is the degree of freedom under examination, but also by the changes in van der Waals' interactions which occur upon stretching. And we therefore expect, and find, that the force field *parameters* are transferable to a high degree, whereas force *constants* are much less transferable.[3]

The vibrational frequencies are useful in determining the accuracy of a force field, because if they are well fit, then the force field for that particular molecule is likely to be quite good. If the frequencies can be well calculated in general, we should have a force field that is quite good, in general. So a necessary (but not sufficient) condition for a really good, general force field is that vibrational frequencies be adequately calculated.

Other quantities can be calculated if the vibrational frequencies are known.[9] For our purposes, probably the most important one is the entropy. Chemical equilibria, in which we are usually most interested, are determined by free energies, not just by enthalpies, and so one wants not only to be able to calculate enthalpies, which MM2 in fact did pretty well, but one also wants to be able to calculate entropies, which MM2 did poorly.

Parameters. The structural parameters were all taken to be the same as used in the regular MM3 program. It was, however, found that changes in parameters needed be made to obtain good heats of formation when the full statistical mechanical calculation was carried out. Of course, the parameters in general are quite different, because the zero point and thermal energies are explicitly added, rather than being included implicitly in the other parameters. But there were two other notable differences in addition. First, the parameter called TORS in the heat of formation calculation was increased from 0.42 to 0.75 kcal/mol. This parameter is used in the nonvibrational formulation of the heat of formation calculation to explicitly account for the fact that the low frequencies of certain torsional modes leads to a large fraction of the molecules being in excited torsional states, which increases the thermal energy. But in the vibrational calculation, the thermal energy is explicitly calculated and added, and so TORS should have the value zero here. But such a value gives unacceptably poor results. We, therefore, use the value indicated for this parameter, but the physical reason for its requirement is unknown. Also, a ring parameter (times the number of rings in the molecules excluding three-, four-, and five-membered rings) was added for the heat of formation calculation.

Results and Discussion

In the development of MM3, we fit the crystal data and the structural data for molecules, as we did with our early force fields.[3,6,10] However, we have a lot more data now, and generally speaking it is more accurate. Hence, we are able to do a better job in that respect. Additionally, by introducing a few more parameters, we made an effort to fit the vibrational data at the same time. We did not explicitly fit entropies, but rather after the vibrational data were fit as well as we wished to fit then, we used a few molecules with known entropies as a test, to see how well we could calculate these.

When MM1 was developed, we studied the available methods for geometry optimization and decided that a block-diagonal Newton–Raphson method was the most advantageous.[10] Other methods in common usage at the time[3] involved the full matrix Newton–Raphson, which we decided not to use, because it ran more slowly and required much more memory than the block-diagonal method, the steepest descent method, with various kinds of modifications, which we had used, but which was very slow. Other available methods involved estimation of second derivatives by numerical methods, and, again, these seemed slow and cumbersome relative to the method chosen. The block-diagonal Newton–Raphson method, the method that was fastest and most free of hangups available at the time, did suffer certain defects. One defect is that one never calculates the full force constant matrix, and hence this method cannot be used for the calculation

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(7) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(8) (a) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121. (b) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574.

(9) Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; D. Van Nostrand: New York, 1947.

(10) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579.

of vibrational spectra. The second major disadvantage is that the method does not find transition states well, if at all. Nonetheless, we retain it in MM3 as our default method, because of its speed and minimal storage requirements. However, if one does wish to calculate a vibrational spectrum, then it is necessary to use some method which will generate the full force constant matrix, and we have incorporated the full matrix Newton–Raphson method in MM3 for that purpose. This calculation is straightforward although complicated, and has been previously described in the literature.[3] In our version, all of the first and second derivatives are calculated by analytical methods. Our standard MM3 (VAX) program is currently limited to 700 atoms, which is adequate for most purposes. The full matrix version is, however, currently limited to 80 atoms, because of memory requirements and long running times.

If we write our force constant matrix in terms of internal coordinates (MM2 and MM3 work in Cartesian coordinates, but we may think more conveniently in internal coordinates), we will have as diagonal elements the stretching, bending, and torsion modes, and as the off-diagonal elements the interactions between these. We wish to have a force field which is close to being diagonal. The reasons for this are several. First, it is known that in all ordinary force fields most of the off-diagonal elements are small, often zero. These off-diagonal elements break down into many different groups, and the determination of numerical values for all of these, which are general and transferable (not just for hydrocarbons, for all molecules!), does not appear to be an easy job. We do not, in fact, at this point know to what extent it is possible. Hence the amount of labor that would be needed to determine a full general valence force field would be very large, and the results for other than spectroscopic purposes might not be noticeably better than one can obtain with an almost-diagonal force field. Additionally, for every term added to the force field, more computation time will be required for each molecular calculation carried out. It is not clear at this point that the additional computational time would be wisely spent at present, even if the program for carrying out such computations were available. It is equally clear that this is something that needs to be explored in the future.

There are a few interaction terms which are sufficiently important that we need to include them in the force field for purposes of accurate calculation of structures, apart from spectroscopic considerations. In MM2 we had a stretch–bend interaction, which was given one of a few generic numerical values, depending on the nature of the three atoms bound together. This interaction applied only when the stretching and the bending involved a common central atom. All other off-diagonal terms were set to zero. We have done something similar for MM3, although we have more finely subdivided the stretch–bend interaction classes. Additionally, we have included in MM3 a torsion–stretch interaction, which is necessary in order to obtain accurate bond lengths when the torsional structure is far from the minimum energy conformation. Again, the values of the constants here were established from structural considerations, not from spectroscopy.

We then set out to choose values for the parameters so as to optimize the force field for a group of small hydrocarbons using only the diagonal elements, together with a few off-diagonal elements with specified numerical values as above. Our test set of compounds consisted of the following: ethane, propane, butane, isobutane, neopentane, 2,2,3-trimethylhexane, cyclohexane, and *trans*-decalin. Over this set of compounds, MM2 would give a set of calculated vibrational frequencies[11] that differ from experiment with a root-mean-square (rms) value of[13] about 80 cm^{-1}. The stretching and torsional modes would be better than this, and the bending modes somewhat worse. For MM3, the preliminary overall rms error for these compounds with the limitations described was about 45 cm^{-1}. The largest errors seemed to come from the neglect of a bend–bend interaction term, where the two angles undergoing bending were centered on the same atom. The next most serious error seemed to be introduced by neglect of a bend–bend interaction where the two bendings were centered on adjacent atoms. Stretch–stretch interactions involving bonds to a common atom were also important. We decided that we would include the first of these, but not the latter two, in the calculation. This led to a noticeable improvement in the agreement between calculated and experimental frequencies, from an error of about 45 cm^{-1} when this term was omitted, to about 35 cm^{-1} when this term was included. There is no doubt that inclusion of a few more terms could reduce this error considerably for this set of compounds. However, it is not certain that significant error reductions would result for compounds in general.

In any event, we decided to stop with the calculation of these off-diagonal elements at this point. The bend–bend interaction leads to no structural differences which we regard as significant. It seems likely that most of the other interactions would likewise not lead to much that was of structural significance. We do note that torsion–bend and stretch–stretch interactions may under certain circumstances be of marginal structural importance, but we have decided to limit the force field as described to this point.

In Table I are given the MM3 calculated and experimental spectra for the molecules in our test set. It can be seen that the largest errors occur with bending motions which involve hydrogens. The largest absolute error (126 cm^{-1}) is found in ethane. We could lower somewhat these errors by increasing the values of the bending constant parameters for angles that involve hydrogens, but such increases would involve adverse effects on the structural calculations. As we did with MM2, and for the same reasons, we choose to take the errors in the spectroscopic frequencies and keep the structural and energy fit as good as we can make it.

The compounds in Table I show that we can get vibrational frequencies that are more or less of chemical accuracy, although certainly not of spectroscopic accuracy, and we can get them with a relatively simple force field. Additionally, we can get really good structures and energies, by current standards, with the same force field.[5]

Vibrational Frequencies

The vibrational frequency data base used in the optimization of the force constants in this work consists of 213 experimental frequencies of eight alkanes, namely, ethane, propane, *n*-butane, isobutane, 2,2,3-trimethylbutane, neopentane, cyclohexane, and *trans*-decalin. The observed frequencies for the alkanes are based on the vibrational assignments in ref 14–16. The calculated vibrational frequencies, compared to the observed values, are generally satisfactory. In Table I we have listed, together with the observed and calculated frequencies, the symmetries of the vibrations. The results show a good transferability of the force field parameters among the saturated hydrocarbons.

C–H Stretching Modes. Our calculations indicated that asymmetric CH_3, symmetric CH_3, asymmetric CH_2, and symmetric CH_2 stretching frequencies for the saturated hydrocarbons have average values of 2966, 2874, 2945, and 2894 cm^{-1}, respectively: those are found to be close to the observed values. The C–H stretching frequencies are calculated to be about right for the primary hydrogens, but about 0.7% too high for the secondary hydrogens and 0.5% too low for the tertiary hydrogens. Our overall C–H frequency fit is very good although it could undoubtedly be improved by the inclusion of stretching interaction constants. For comparison, the averaged C–H stretching frequencies for the different hydrogen classes are listed in the Table II.

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(11) The calculated frequencies referred to throughout this paper are harmonic, and they were calculated via the diagonalized mass-weighted force constant matrix following the method of Wilson, Decius, and Cross (ref 12).

(12) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; Dover Publications: New York, 1980.

(13) Since the full force constant matrix is never calculated by MM2, this value is an estimate.

(14) Schachtschneider, J. H.; Snyder, R. G. *Spectrochim. Acta* **1963**, *19*, 117.

(15) Snyder, R. G.; Schachtschneider, J. H. *Spectrochim. Acta* **1965**, *21*, 169.

(16) Lifson, S.; Warshel, A. *J. Chem. Phys.* **1968**, *49*, 5116.

It was noted that the methyl symmetric and asymmetric C–H stretching bands, especially the latter since they are comparatively free of overlapping neighbors, offer themselves as a basis for estimating methyl content in alkanes since, unlike methyl bending and rocking modes, they are virtually pure methyl vibrations. In our calculations, we used the same force parameters for the different classes of hydrogens, but the results show that the vibrational frequencies are significantly changed by the environment, and the observed values are reasonably well reproduced. There is a very good transferability among the alkanes. Table II also shows that the vibrational frequencies vary in a manner consistent with the bond dissociation energies; this implies that one may be able to predict the reactivities of hydrogens by examining the calculated vibrational frequencies. This may be especially useful when observed spectra are not available or are uninterpretable.

C–C **Stretching Modes.** The C–C stretching is not as simple as the C–H stretching. Since the energies of the C–C stretchings (near 1000 cm^{-1}) are close to those of the CCH and HCH bendings, the C–C stretchings are coupled with those two bending interactions. According to our calculations, the C–C stretching frequencies are spread out over a wide range (from 700 to 1100 cm^{-1}), depending upon the structures. There is a relatively pure C–C stretching mode in the case of ethane. The observed value for ethane was found to be 995 cm^{-1}; it was calculated to be 960 cm^{-1}.

HCCH and CCCC Torsion Modes. The frequencies of the torsional motions around the C–C bond are about 280 cm^{-1} or less. Since the energies of the torsional motions are relatively low and far away from those of other motions, they are usually more simple than the others.[18] Unfortunately, because of the usual low intensities of the torsional motion absorptions, they have been observed only rarely. The force constant for the HCCH torsion was chosen to fit the observed torsional frequency of ethane in our calculations, and the CCCC and CCCH torsional force constants were determined by fitting available data, such as rotational barriers and heats of formation. The torsional frequency of ethane was calculated to be 283 cm^{-1}, just slightly higher than the observed value 279 cm^{-1}.

CCC **Bending Modes.** The frequencies of the CCC bending modes are in the range of 300–500 cm^{-1}. This motion may couple with the C–C stretch or with torsion around the C–C bond, but the coupling is usually small, so the motion, compared to the CCH and HCH bendings, is relatively more simple. The average of the calculated values is 386 cm^{-1}, about the same as the observed value of 384 cm^{-1}.

HCH and CCH Bending Modes. The HCH and CCH bendings are more complicated than others. They not only couple with each other, but also with other interactions, such as C–C stretching especially, and also CCC bending or torsion around the C–C bond, although the latter two are less significant. In general, the frequencies which are due to the CH_3 deformation or CH_2 scissoring are about right on the average, but the frequencies due to the CH_2 twisting, CH_2 wagging, or CH_3 rocking were calculated to be too low. These motions appear to be strongly correlated with the CCH bendings as well as the bend–bend interactions between two angles on adjacent carbons. After carefully examining these kinds of motions, we concluded that it would require a bigger CCH bending constant, or more cross-term interactions, in order to get a better fit of the vibrational frequencies.[19] Unfortunately, we have to make a compromise between geometries and vibrational frequencies, and the set of force parameters reported here is the set we decided to accept.

In summary, the standard deviation between our calculated values and observed frequencies for the compounds listed in the Table I is about 35 cm^{-1}. The results are generally satisfactory, considering the wide range of requirements imposed on our MM3 force field.

Heats of Formation

Traditionally, heats of formation have been calculated by the increment addition (bond energy) method.[20–24] In molecular mechanics the increments are considered to consist of contributions from the formation of bonds (bond energies), the effects of strain energy represented by steric energy, and contributions from statistical thermodynamics caused by population of vibrational levels, conformational mixing, and perhaps other terms. Because of the difficulty of calculating vibrational levels, the most extensive and accurate previous studies of heats of formation have always used some simplication, the most usual one of which is to evaluate the bond energies at room temperature, and thereby to include the vibrational contribution directly in the bond increment terms. It is not obvious that this can be done with acceptable accuracy. This approximation has been made, in MM2, and in MM3 for example, and it seems to work remarkably well.[3,5] However, since the vibrational energies are real and in absolute terms quite large, and since the vibrational levels are available from our calculation, we have also utilized the more proper method for calculation of heats of formation, based on the full statistical mechanical treatment, and we will describe this method here. This kind of method was used earlier in molecular mechanics by Lifson and Warshel[25] and Boyd,[8b,26] and Wertz and Allinger.[27] In our calculation of heats of formation, it was assumed that they are a function of (a) the number and type of bonds in the molecule, (b) the steric energy, (c) the vibrational heat content (including zero-point energy and statistical thermal energies), (d) the number and kinds of structural features (such as primary, tertiary, and quaternary carbon centers and ring structures), and (e) the other statistical mechanical energy corrections (such as POP and TORS) ordinarily used.[3]

All of the terms in the heat of formation equation are self-explanatory, and all have been discussed previously,[3,5] except the term called "Ring". We found that when heats of formation are calculated by the present scheme, it is necessary to have an extra term which counts the number of rings (other than small rings, which are accounted for separately) in the molecule. (For this usage, the number of rings is defined as equal to the minimum number of bonds that must be broken to given an open-chain skeleton, excluding rings of five or fewer members, which are dealt with separately.) It is not clear why this term is needed. In fact, the alkanes and cycloalkanes, since the number of carbons and hydrogens also determines the number of rings, it would seem that this parameter is redundant. It is not, however, and it is needed in order to obtain a good fit of the calculated values to experiment. (This parameter was also examined in the conventional MM3 bond energy approach,[5] but the improvement there is not really significant.) The parameters needed in the heat of formation calculations are shown in Table III. The steric energy and statistical mechanical terms associated with the minimum energy conformation were calculated directly from the force field, while the numerical values of the bond energies and structural increments were derived for use in the heat of formation equation, by a least-squares optimization of the fit to the experimental heats of formation at 25 °C for the compounds listed in Table IV.

It was noted that the averaged bond energies (equilibrium energies) for the $C(sp^3)$–$C(sp^3)$ and $C(sp^3)$–H type bonds were

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(17) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon, Inc.: Boston, 2nd ed., p 46.

(18) From perturbation theory, the interaction of two states of different energies is proportional to the reciprocal of their energy difference.

(19) The same conclusions were reached earlier by other authors (ref 14). They found that it was necessary to introduce CCH bend interaction constants as far down the normal paraffin chain as second-nearest neighbor carbons to obtain spectroscopic accuracy.

(20) Benson, S. V. In *Thermochemical Kinetics*; John Wiley: New York, 1968.

(21) Gasteiger, J. *Comput. Chem.* **1978**, *2*, 85.

(22) Gasteiger, J. *Tetrahedron* **1979**, *35*, 1419.

(23) Gasteiger, J.; Jacob, P.; Strauss, U. *Tetrahedron* **1979**, *35*, 139.

(24) The procedure was used in MM2, and the reported calculations were very good (see ref 3).

(25) Lifson, S.; Warshel, A. *J. Chem. Phys.* **1968**, *49*, 5116.

(26) Chang, S.; McNally, D.; Shary-Tehrany, S.; Hickey, J. M.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109.

(27) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1979**, *35*, 3.

(28) Cox, J. D.; Pilcher, G. In *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

Table I. Vibrational Frequencies of Selected Alkanes

no.	symmetry	calcd	obsd	assignment	no.	symmetry	calcd	obsd	assignment
					Ethane (D_{3d})[a]				
1	Eu	2967.8	2974	CH_3 asym stretch	13	Eg	1063.6	1190	CH_3 sym rocking
2	Eu	2967.8			14	Eg	1063.6		
3	Eg	2963.4	2950		15	A1g	960.2	995	CC str
4	Eg	2963.4			16	Eu	908.3	822	CH_3 asym rocking
5	A1g	2881.6	2915	CH_3 sym str	17	Eu	908.3		
6	A2u	2863.7	2915		18	A2u	283.3	279	CH_3–CH_3 torsion
7	Eu	1455.4	1460	CH_3 deformation					
8	Eu	1455.4							
9	Eg	1443.9	1469						
10	Eg	1443.9							
11	A1g	1436.6	1388						
12	A2u	1360.0	1370						
					Propane (C_{2v})[a]				
1	B2	2967.5	2965	CH_3 asym str	15	A1	1394.4	1385	CH_2 sci + CH_3 def
2	A2	2966.7	-		16	B1	1354.5	1332	CH_2 wag + CH_3 def
3	A1	2966.2	2965		17	A2	1219.1	1278	CH_2 twist
4	B1	2964.4	2965		18	B2	1065.9	1187	CH_2 rock + CH_3 def
5	B2	2942.5	2915	CH_2 asym str	19	A1	1060.9	1157	CH_3 rock + CCC bend
6	A1	2895.3	2875	CH_2 sym str	20	B1	1036.7	1049	CH_3 rock + CH_2 wag + (CC str)
7	B1	2873.6	2875	CH_3 sym str	21	A2	960.8	899	CH_2 twist + CH_3 def
8	A1	2869.0	-		22	B1	938.0	921	CH_3 rock + asym CC str/str
9	B1	1471.4	1464	CH_3 def + CH_2 wag	23	A1	850.2	868	CH_3 rock + sym CC str/str
10	B2	1459.8	1459	CH_3 def	24	B2	802.7	748	CH_2 rock + CH_3 def
11	A1	1458.3	1473	CH_2 sci + CH_3 def	25	A1	379.3	375	CCC bend
12	A2	1452.8	-	CH_3 def	26	B2	250.6	265	CH_3–CH_2 torsion[bk]
13	B1	1449.2	1370		27	A2	208.1	217	
14	A1	1438.5	1449	CH_2 sci + CH_3 sci					
					Butane (C_{2h})[a]				
1	Au	2967.3	2966	CH_3 asym str	20	Bu	1334.7	1293	CH_2 wag + CH_3 def
2	Bg	2967.1	2965		21	Au	1238.8	1257	CH_2 twist
3	Bu	2965.3	2966		22	Bg	1220.9	1300	
4	Ag	2965.2	2965		23	Ag	1075.0	1148	(cen) CC str + CH_3 rock
5	Au	2946.0	2920	CH_2 asym str	24	Bg	1052.9	-	CH_2 rock + CH_3 def
6	Bg	2942.0	2912		25	Au	996.8	944	CH_2 twist + CH_3 def
7	Ag	2898.1	2872	CH_2 sym str	26	Bu	995.2	1010	CH_3 rock + (CC str)
8	Bu	2890.5	2875		27	Ag	991.3	1053	(side) CC str + CH_3 rock
9	Ag	2871.5	2853	CH_3 sym str	28	Bu	976.1	965	
10	Bu	2870.7	2861		29	Bg	857.2	-	CH_2 rock + (CH_3 def)
11	Ag	1507.8	1462	CH_3 def + (CH_2 wag + CC str)	30	Ag	844.2	835	(cen) CC str + CH_3 rock
12	Bg	1457.9	1460	CH_3 def	31	Au	778.1	733	CH_2 rock + (CH_3 def)
13	Au	1457.0	1455	CH_3 def	32	Ag	393.6	427	sym CCC bend + CCC bend
14	Bu	1454.8	1468	CH_2 sci + (CH_3 sci)	33	Bu	286.8	-	asym CCC bend + CCC bend
15	Ag	1453.8	1455		34	Bg	244.7	266	CH_3–CH_2 torsion[bj]
16	Bu	1441.4	1459	CH_2 sci + (CH_3 sci)	35	Au	215.7	-	
17	Ag	1438.5	-		36	Au	121.8	121	CH_2–CH_2 torsion[bk]
18	Bu	1410.9	1375	CH_2 sci + CH_3 def					
19	Ag	1382.3	-						
					Isobutane (C_{3v})[a]				
1	A1	2968.8	2962	CH_3 asym str	22	E	1111.3	1166	CH_3 rock + (CC str)
2	E	2967.9	2962		23	E	1111.3		
3	E	2967.9			24	A1	1092.2	1177	CH_3 rock + CCC bend
4	E	2966.9	2962		25	E	966.4	966	CH_3 rocking
5	E	2966.9			26	E	966.4		
6	A2	2964.6	2958	CH_3 asym str	27	A2	965.0	-	
7	A1	2890.2	2904	CH stretch	28	E	911.5	918	
8	E	2874.6	2894	CH_3 sym str	29	E	911.5		
9	E	2874.6			30	A1	778.6	797	CC str + (CH_3 rock)
10	A1	2870.5	2880		31	A1	445.0	433	CCC bend + (CH_3 rock)
11	A1	1470.2	1477	CH_3 def	32	E	367.2	367	CCC bend
12	E	1466.4	1477		33	E	367.2		
13	E	1466.4			34	E	240.8	-	CH_3–CH torsion
14	E	1459.1	1475		35	E	240.8		
15	E	1459.1			36	A2	210.8	-	
16	A2	1449.6	1450						
17	E	1437.7	1371						
18	E	1437.7							
19	A1	1405.0	1394						
20	E	1345.6	1330						
21	E	1345.6							

Table I (Continued)

no.	symmetry	calcd	obsd	assignment	no.	symmetry	calcd	obsd	assignment
Noepentane (Td)[a]									
1	E	2969.4	-	CH_3 asym str	25	T2	1231.3	1249	CH_3 rock + (CC str + CCC bend)
2	E	2969.4			26	T2	1231.3		
3	T1]	2969.3	-		27	T2	1231.3		
4	T1	2969.3			28	E	981.3	-	CH_3 rock + (CC str)
5	T1	2969.3			29	E	981.3		
6	T2	2966.5	2955		30	T1	965.9	-	CH_3 rocking
7	T2	2966.5			31	T1	965.9		
8	T2	2966.5			32	T1	965.9		
9	T2	2875.9	2876	CH_3 sym str	33	T2	896.3	921	
10	T2	2875.9			34	T2	896.3		
11	T2	2875.9			35	T2	896.3		
12	A1	2875.6	2909		36	A1	703.1	733	CC str + (CH_3 rock)
13	T2	1476.2	1475	CH_3 def	37	T2	414.2	414	CCC bend + (CH_3 rock)
14	T2	1476.2			38	T2	414.2		
15	T2	1476.2			39	T2	414.2		
16	E	1458.2	1451		40	E	336.7	335	
17	E	1458.2			41	E	336.7		
18	T1	1458.0	-		42	T2	254.2	-	CH_3–C torsion
19	T1	1458.0			43	T2	254.2	-	CH_3–C torsion
20	T1	1458.0			44	T2	254.2	-	
21	T2	1423.5	1372		45	A2	214.6	-	
22	T2	1423.5							
23	T2	1423.5							
24	A1	1411.7	-						
2,2,3-Trimethylbutane (C_s)[b]									
1	A′	2986.3	-	CH_3 asym str	34	A′	1241.7	1318	CR_2–CR str + CH_3 rock
2	A″	2985.4	-		35	A″	1194.7	1223	CH_3–C str + CH_3 rock
3	A″	2983.3	-		36	A′	1179.5	1210	CC str + CH_3 rock
4	A′	2979.1	-		37	A′	1077.4	1165	
5	A″	2976.7	-		38	A″	1075.9	1107	CH_3–C str + CH_3 rock
6	A′	2972.5	-		39	A′	1042.0	1082	CH_3 rock
7	A′	2970.7	-		40	A′	979.1	-	
8	A″	2969.7	-		41	A″	977.9	-	
9	A′	2967.9	-		42	A″	967.3	993	
10	A″	2967.0	-		42	A″	962.6	961	CH_3 rock + CC str
11	A′	2888.6	-	CH_3 sym str	44	A″	931.3	-	
12	A′	2885.4	-		45	A′	912.6	-	
13	A″	2885.3	-		46	A′	910.4	914	
14	A′	2880.5	-		47	A″	906.6	-	
15	A″	2880.4	-		48	A′	825.0	832	CC str + CH_3 rock
16	A′	2872.2	-	CH str	49	A′	659.3	689	
17	A′	1511.1	-	CH_3 def	50	A′	500.3	520	CCC bend + CH_3 rock
18	A″	1498.1	-		51	A′	443.1	436	
19	A″	1491.3	-		52	A″	423.7	454	CCC bend
20	A′	1486.9	-		53	A′	389.2	385	
21	A′	1476.4	-		54	A′	365.3	-	
22	A″	1474.0	-		55	A″	349.9	359	
23	A″	1464.3	-		56	A″	307.4	-	CCC bend + CH_3–C tors
24	A′	1460.8	-		57	A′	300.9	-	
25	A′	1457.5	-		58	A″	270.7	-	CH_3–C torsion
26	A″	1455.9	-		59	A′	254.4	-	
27	A′	1450.5	-	CH_3 def	60	A″	242.5	-	
28	A″	1435.7	-		61	A′	233.4	-	
29	A′	1432.0	-		62	A″	204.7	-	
30	A″	1425.9	-		63	A″	56.9	-	CR_3–CR_2 torsion
31	A′	1422.2	-						
32	A′	1402.9	-						
33	A″	1361.4	-						
Cyclohexane (D_{3d})[a]									
1	A2u	2949.2	2934	CH_2 asym str	16	Eu	1460.1	1454	CH_2 sci + CH_2 wag
2	Eg	2946.0	2932		17	Eu	1460.1		
3	Eg	2946.0			18	A1g	1459.8	1451	CH_2 sci (sym)
4	A1g	2944.8	2938		19	A2u	1437.2	1454	CH_2 sci (asym)
5	Eu	2943.6	2932		20	Eg	1416.0	1348	CH_2 sci + CH_2 wag
6	Eu	2943.6			21	Eg	1416.0		
7	A1g	2904.9	2853	CH_2 sym str	22	Eu	1373.4	1350	CH_2 wag
8	Eu	2899.2	2863		23	Eu	1373.4		
9	Eu	2899.2			24	A2g	1340.4	-	6 CH_2 sym wag
10	Eg	2887.7	2885		25	Eu	1232.2	1259	4 CH_2 asym twist
11	Eg	2887.7			26	Eu	1232.2		
12	A2u	2881.8	2855		27	Eg	1212.2	1267	4 CH_4 sym twist
13	Eg	1468.3	1444	CH_2 sci + CH_2 wag	28	Eg	1212.2		
14	Eg	1468.3			29	A1u	1201.0	-	6 CH_2 asym twist
15	A1u	1461.0	-	6 CH_2 asym wag	30	A2g	1191.9	-	6 CH_2 sym twist

Table I (Continued)

no.	symmetry	calcd	obsd	assignment	no.	symmetry	calcd	obsd	assignment
31	Alu	1046.3	-	6 CC asym str	40	Eg	785.8	785	CH_2 rock
32	Alg	1042.1	1157	CH_2 rock	41	Eg	785.8		
33	Eg	1036.2	1029	4 CC str	42	Alg	771.6	802	6 CC sym str
34	Eg	1036.2			43	A2u	560.0	524	CCC bend
35	Eu	916.0	905	CH_2 rock	44	Eg	415.9	425	
36	Eu	916.0			45	Eg	415.9		
37	A2u	869.0	862	CH_2 rock + CCC bend	46	Alg	373.2	383	ring puckering
38	Eu	855.8	862	4 CC str	47	Eu	232.1	248	ring twisting
39	Eu	855.8			48	Eu	232.1		
				trans-Decalin (C_{2h})[b]					
1	Bu	2949.2	-	CH_2 asym str	39	Ag	1262.3	1254	CH_2 twisting
2	Bg	2948.7	-		40	Bu	1233.0	1253	
3	Ag	2947.6	-		41	Au	1219.7	1227	
4	Au	2947.0	-		42	Bg	1218.4	-	
5	Bu	2945.3	-		43	Bu	1212.7	1136	
6	Bg	2944.9	-		44	Ag	1210.4	1230	
7	Ag	2944.4	-		45	Au	1199.1	1153	
8	Au	2944.4	-		46	Bg	1195.3	-	
9	Ag	2904.1	-	CH sym str	47	Ag	1082.0	1160	CR_2–CR_2 str + CH_2 rock
10	Au	2903.1	-	CH_2 sym str	48	Bg	1060.5	-	CR_2–CR str CH_2 rock
11	Bu	2900.0	-	CH asym str	49	Ag	1052.4	-	CC stretching
12	Bg	2897.5	-	CH_2 sym str	50	Au	1047.3	1085	CR–CR str + CH_2 wag
13	Ag	2894.8	-		51	Bu	1045.8	1049	CC strecthing
14	Au	2890.4	-		52	Ag	1036.4	1057	CH_2 rocking
15	Bu	2889.5	-		53	Au	1010.9	1029	CR_2–CR str + CH_2 rock
16	Ag	2888.0	-		54	Au	975.0	-	CH_2 rocking
17	Bg	2884.3	-		55	Bu	952.6	-	CC str + CCC bend
18	Bu	2883.8	-		56	Bg	941.8	990	CR–CR str + CH_2 wag
19	Bng	1510.6	-	CH_2 scissoring	57	Bu	919.4	918	CH_2 rocking
20	Au	1487.4	-		58	Ag	883.7	-	
21	Ag	1467.0	-		59	Bg	877.8	-	
22	Bu	1465.4	-		60	Ag	848.0	846	CH_2 rock + CCC bend
23	Au	1463.9	-		61	Bg	834.2	873	
24	Ag	1462.0	-		62	Au	828.6	842	CH_2 rocking
25	Au	1456.1	-	CH_2 scissoring	63	Bu	805.0	825	CH_2 rock + CCC bend
26	Bg	1454.5	-		64	Au	803.0	805	
27	Ag	1445.7	-	CCH sym bend (bridge head)	65	Ag	737.5	751	CH_2 rocking
28	Bu	1441.4	-	CH_2 scissoring	66	Bg	572.8	563	CCC bend + CH_2 rock
29	Bg	1436.0	-		67	Bu	517.7	-	CCC bend + CH_2 rock
30	Ag	1431.3	-		68	Ag	473.0	492	CCC bend + CC str
31	Bu	1412.8	-	CH_2 wagging	69	Au	451.2	-	CCC bend
32	Au	1410.9	1342		70	Bu	374.1	-	
33	Ag	1385.5	-		71	Bg	372.0	-	
34	Bg	1373.2	-		72	Ag	359.4	405	
35	Bu	1356.1	1331		73	Au	343.1	-	
36	Bu	1326.7	1306	CCH asym bend (bridge head)	74	Ag	294.4	300	rings puckering
37	Au	1321.8	1297	CH_2 wagging	75	Bu	292.2	-	rings twisting
38	Bg	1321.0	-		76	Bg	228.7	-	
					77	Bu	147.4	-	
					78	Au	134.6	-	

[a] Observed values from ref 14. [b] Observed values from ref 15. [c] Observed values from ref 16.

Table II. Averaged C–H Stretching Fequencies (cm^{-1})[a]

class	obsd	calcd	bond energy[17] (kcal/mol)
$-CH_3$	2962/2885	2966/2874	-97
$-CH_2$	2927/2870	2945/2894	-94
$-CH$	2904	2890	-91

[a] The values are taken from the average of ethane, propane, butane, isobutane, neopentane, and cyclohexane.

Table III. Heat of Formation Parameters (kcal/mol)

bond	value	group	value
C–C	-90.101	methyl	-0.141
C–H	-105.552	iso	-1.297
		neo	-3.313
		5-ring	1.504
		ring[a]	6.200
		TORS[b]	0.75/bond

[a] This increment is added for each ring present that contains six or more ring members. [b] This value is larger than the experimental value and suggests that it is also being used to reduce some other (unrecognized) systematic error.

calculated to be about −90 and −106 kcal/mol, respectively. These values have a more direct physical meaning than those calculated by the ordinary MM3 method,[29] and they are also very close to the literature values.[30] Calculations of heats of formation based on the full statistical mechanical treatment are often poor, because of the lack of accuracy of the vibrational levels; however, they have an advantage in that they can be used to calculate the heats of formation as a function of temperature. The standard deviation between the calculated and the observed heats of formation[28] for the compounds listed in Table IV is 0.41 kcal/mol, essentially the same as that obtained from the MM3 bond energy scheme.

There are several items in Table IV which require comment. First, note that there is no systematic trend in the error from ethane to nonane, the largest straight-chain alkane listed. This would seem to be a requirement of any heat of formation calculation, since these numbers are fundamental and accurately known.

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(29) The values for C–C and C–H bond energies are 2.447 and −4.590 kcal/mol, respectively, in the current MM3 (ref 5). Those are the bond energies plus the vibrational contributions, relative to the elements.

(30) Pitzer, K. S. In *Quantum Chemistry*; Prentice Hall; Englewood Cliffs, NJ, 1953; p 170.

Table IV. Heats of Formation of Alkanes, Gas Phase, 25 °C (kcal/mol)

compound	wt	calc	obs[28]	dev[a]
methane	0	−17.89	−17.89	0.00
ethane	6	−19.86	−20.24	0.38
propane	9	−24.13	−24.82	−0.31
butane	8	−30.09	−30.15	0.06
pentane	7	−35.02	−35.00	−0.02
hexane	6	−39.95	−39.96	0.01
heptane	5	−44.89	−44.89	0.00
octane	4	−49.82	−49.82	0.00
nonane	3	−54.76	−54.75	−0.01
isobutane	9	−32.35	−32.15	−0.20
isopentane	7	−36.59	−36.92	0.33
neopentane	9	−40.97	−40.27	−0.70
2,3-dimethylbutane	6	−42.08	−42.49	0.41
2,2,3-trimethylbutane	6	−48.27	−48.95	0.68
2,4-dimethylpentane	6	−47.97	−48.21	0.24
2,5-dimethylhexane	5	−52.68	−53.18	0.50
2,2,3,3-tetramethylbutane	5	−53.97	−53.92	−0.05
2,2,3,3-tetramethylpentane	5	−56.16	−56.64	0.48
di-*tert*-butylmethane	5	−57.62	−57.80	0.18
tetraethylmethane	5	−55.69	−55.67	−0.02
cyclopentane	9	−18.94	−18.74	−0.20
cyclohexane	8	−29.69	−29.43	−0.26
cycloheptane	7	−27.44	−28.22	0.78
cyclooctane	5	−29.01	−29.73	0.72
cyclononane	4	−31.40	−31.73	0.33
cyclodecane	4	−36.15	−36.88	0.73
cyclododecane	2	−54.39	−54.59	0.20
1,1-dimethylcyclopentane	5	−33.42	−33.04	−0.38
methylcyclopentane	0	−26.36	−26.31	−0.05
ethylcyclopentane	5	−30.80	−30.34	−0.46
eq-methylcyclohexane	9	−37.18	−36.99	−0.19
1,1-dimethylcyclohexane	6	−43.67	−43.26	−0.41
1-*ax*-2-*q*-dimethylcyclohexane	6	−41.54	−41.13	−0.41
1-*eq*-2-*eq*-dimethylcyclohexane	6	−43.50	−42.99	−0.51
bicyclo[3.3.1]nonane	5	−29.86	−30.50	0.64
bicyclo[2.2.2]octane	3	−23.17	−23.65	0.48
cis-bicyclo[3.3.0]octane	3	−22.00	−22.07	0.07
trans-bicyclo[3.3.0]octane	3	−15.91	−15.86	−0.05
trans-decalin	6	−43.86	−43.54	−0.32
cis-decalin	6	−40.75	−40.45	−0.30
trans-hydrindane	4	−32.12	−31.45	−0.67
cis-hydrindane	4	−31.08	−30.41	−0.67
trans-syn-trans-perhydroanthracene	0	−58.12	−58.12	−0.00
trans-anti-trans-perhydroanthracene	0	−51.24	−52.73	1.49
norbornane	7	−12.25	−12.42	0.17
1,4-dimethylnorborane	5	−30.02	−30.58	0.56
adamantane	2	−31.78	−31.76	−0.02
1,3,5,7-tetramethyladamantane	2	−67.28	−67.15	−0.13
protoadamantane	5	−19.70	−20.54	0.84
congressane	3	−34.71	−34.61	−0.10
			std dev	0.41

[a] Dev (deviation) is the calculated minus the observed value.

This fit could only be achieved here by using the large value for TORS previously discussed.

Based on the earlier treatment and discussion regarding the heat of formation of *tat*-perhydroanthracene,[5] it seems certain that the reason for the calculated positive 1.53 kcal/mol value here is largely experimental error.

The positive value for cyclodecane is of interest. Note that it is considerably more positive than the value for cyclododecane, whereas the reverse was true in the standard bond energy scheme calculation.[5]. This scheme works well in ordinary cases, but there are some things that are not accounted for by it. These include interactions between hydrogens across the ring in cyclodecane, not in terms of the van der Waals' interactions (which are accounted for) but rather in terms of the fact that the experimental frequencies of these vibrations are raised some 50 wavenumbers because of the transannular repulsions. Since there are four C–H stretching frequencies that are thus raised, and four more that are raised somewhat, there is a significant contribution to the zero-point energy from this source. This is clearly not an ordinary van der Waals' effect, because it is directional. The hydrogens across the ring are hitting head on, which increases their energy as they approach each other and has the effect of narrowing the van der Waals' energy wells in which they are vibrating, thus raising the frequencies. If their orientations were different, they could hit in such a way as to leave the shape of the well unchanged, or even to make it more shallow, and hence the values of these frequencies could in principle go in any direction. Thus, highly strained compounds need individual consideration with respect to this problem. Here we might expect the calculated heat of formation of cyclodecane would be somewhat higher when the vibrational levels were used as in the present case than when a simple bond energy scheme was used; this is indeed found to be the case. However, since these frequencies are calculated too high by about 50 wavenumbers, the calculated zero-point energy and heat of formation are also too high. In cyclododecane, this extra contribution to the vibrational energy is small; hence there is little error in the heat of formation calculated by the vibrational method for this compound. If we examine the calculated vibrational frequencies for C–H stretching vibrations where the hydrogens are pressed up against other hydrogens, such as in cyclodecane, binorbornane, or Weinstein's birdcage compound, we note that while the experimental frequencies are unusually high, as anticipated, the calculated frequencies are even higher (Table V). In both cases the shorter the distance between the opposing hydrogens, the greater the force between them, and the higher the frequency. The reason for the calculated frequencies being systematically higher than observed may stem from different possible causes which cannot be untangled here.

Table V. Calculated and Observed C–H Stretching Frequencies for Congested Hydrogens (cm^{-1})

compound	H/H dist.	calcd	obsd
cyclohexane		2949	2934
cyclododecane	2.105	2997	2941
cyclodecane	1.916	3046	2991
I[a]	1.754	3113	3031
II[a]	1.630	3127	3048

[a] **I** is *exo,exo*-tetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodecane, and **II** is the pentachlorohydroxy derivative of pentacyclo[6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$]dodecane.

It is also perhaps of note that bicyclo[2.2.2]octane, the heat of formation of which has been quite troublesome to fit in both MM2 and MM3, is in fact well fit here. For some reason, the heat of formation calculated by the vibrational method here is about 0.5 kcal less than that calculated by the MM3 bond energy scheme,[5] removing the problem. It is interesting to note that the torsional frequency in this compound is quite low (57 cm^{-1}), and perhaps 200 cm^{-1} below the lowest frequency in most other ring compounds. This low frequency tends to lower the enthalpy (and raise the entropy) of this molecule noticeably, compared with other molecules that seem similar. It is noted that in earlier work, including MM2, this compound did not have D_{3h} symmetry, but only D_3, it was twisted about the axis that runs through the bridgeheads. However, in MM3 the compound does have D_{3h} symmetry, although there is a broad flat well (corresponding to the 57 cm^{-1} frequency). Ab initio calculations[31] (6-31G*//3-21G) indicate that the D_{3h} structure is 1 cal/mol above the D_3 structure, and experimentally[32] the D_{3h} structure is 75 ±100 cal higher.

Table IV clearly shows that the overall heat of formation calculation, when done by the full statistical method, using the MM3 force field, is quite acceptable. One conclusion to be drawn is that the vibrational levels, particularly the higher ones, which add very much to the zero-point energy, are well calculated, on the average. The main calculational errors in the vibrational levels are in the splittings, rather than in the average group frequencies, with the result that collective properties, such as zero-point energy, can be better calculated than the individual levels themselves can

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Table VI. Entropies (eu) of Selected Alkanes in the Gas Phase (1 atm)

compound	σ	temp, K	obsd	calcd	dev, %
methane[33a]	12	298.16	44.47	44.58	0.24
ethane[33b]	6	184.10	49.49	49.44	-0.11
propane[33c]	2	231.09	60.49	60.47	-0.04
butane[33d,34]	2	272.65	72.20	71.81	-0.54
isobutane[33e]	3	261.43	67.66	67.48	-0.27
pentane[33a,34]	2	298.16	83.68	83.20	-0.57
neopentane[33f]	12	282.61	71.25	71.86	0.86
hexane[33a,34]	2	298.16	93.00	93.03	+0.03
2,2,3-trimethylbutane[33g]	1	298.16	91.61	91.80	+0.21
cyclopropane[36]	6	240.30	54.17	54.09	-0.15
cyclobutane[37]	4	485.67	62.72	62.71	-0.02
cyclopentane[38,39]		298.16	70.70	70.34	-0.51
cyclohexane[42]	6	298.16	71.25	71.29	0.06
cycloheptane[43]	2	298.16	81.82	82.05	0.28
cyclooctane[43]	1	298.16	87.66	87.94	0.32
trans-decalin[33g]	2	298.16	89.52	89.45	-0.08
cis-decalin[33g]	1	298.16	90.28	90.03	-0.27
				std dev	0.35
				av	-0.03

be. As will be shown in the following discussion of entropies, the same also holds true for the low-frequency vibrations. The entropies, which are affected collectively by the low frequencies, are better calculated than are the individual frequencies themselves, and for reasons similar to those described above.

Entropies

The next question is, how well can these be calculated? Entropies depend (at room temperature) only on the very low frequencies, the torsional modes in most cases. We can usually fit these very well. It is the CCH bending modes, which are generally around 1000 cm^{-1}, where we have the largest errors, and these do not contribute significantly to the entropy at room temperature. Hence, we expect (and find) that we can calculate good entropies. We should likewise be able to calculate quantities like heat capacity, which depend only on the lower frequencies. (Of course, if one goes to sufficiently high temperatures, the higher frequencies become more important, and the force field may do less well.)

The MM3 calculated and experimental (thermochemical) entropies for a series of representative alkanes and cycloalkanes are given in Table VI. It can be seen that the agreement is quite good, with an overall standard deviation of 0.35%.

One of the significant flaws in MM2, which has been referred to several times in the literature, concerns the claim that for congested hydrocarbons, hexamethylethane, for example, the barriers to rotation calculated are 40% lower than those determined experimentally.[44] It must, however, be noted here that the calculated values refer to $\Delta H^\ddagger$, while the experimental values, determined by low-temperature NMR, are $\Delta G^\ddagger$ values.

In a congested system, the vibrational amplitudes of the motions of the congested atoms will ordinarily be restricted by the congestion. The result is that the potential wells in which the atoms lie have steeper walls than in the case where there is less congestion. As the walls become steeper, the vibrational levels are spread upward. Hence, the vibrational entropies for such atoms will decrease, because in the limit all of the atoms are at the lowest level, rather than being spread out over several levels. If we think about a molecule like 2,3,3-trimethylbutane, for example, what that means is as follows. In the ground state, the methyl groups are undergoing torsional oscillations at relatively low frequencies (205–271 cm^{-1}; see Table I), and the entropy of the molecule receives some contributions from these low-frequency torsion modes. When the molecule goes over a torsion barrier, some of these methyls become even more congested than they were in the ground state; their torsional frequencies increase to 243–315 cm^{-1}, and entropy is consequently lost. Since the entropy of the torsional motions of these methyls is a significant component of the total entropy, what should in principle happen is that the restriction of the rotational motion should lead to a *substantial* negative value for $\Delta S^\ddagger$. Just how big is *substantial*? In Table VII we have given rotational data for a number of molecules, beginning with 2,3-dimethylbutane and going to much more congested systems. We have calculated the vibrational modes both in the ground state and at the rotational transition state, and we have calculated the entropies from these modes. For 2,2,3-trimethylbutane, $\Delta S^\ddagger$ is −4.00 eu. The entropy differences for other molecules are listed in Table VII. Note that whenever the molecule has methyl groups which can become congested at the transition state, there is a significantly negative value for $\Delta S^\ddagger$. This value also contains symmetry contributions, but can be seen to vary from −0.86 in the relatively unhindered 2,3-dimethylbutane up to −8.57 in the much more hindered 2,2,3,3-tetramethylbutane. A typical value might be −5 eu; this would correspond to about 1.5 kcal/mol added to the barrier at room temperature. Note that the exception in Table VII is cyclohexane. There are no methyls here to have their rotation hindered; in addition, we go from a molecule with a high symmetry number to one which has a much lower symmetry number, and the transition state is a *dl* mixture besides.

When rotational barriers are measured by NMR methods, there are coalescence temperatures where the thermodynamic parameters apply. As the compounds becomes more congested, the rotational barriers get bigger, and the coalescence temperatures also become higher. Hence, the $T\Delta S$ term makes an increasingly important contribution in more congested molecule, because both T and ΔS increase in magnitude. Note the sizes of the $T\Delta S^\ddagger$ terms in Table VII by comparing $\Delta H^\ddagger$ with $\Delta G^\ddagger$ and the errors introduced by assuming that these are equal. With MM2, the values for $\Delta H^\ddagger$ are generally too low, but this has the effect of broadening the potential wells and hence increasing the values of $\Delta S^\ddagger$. The comparison of $\Delta H^\ddagger$ calculated by MM2 with $\Delta G^\ddagger$ measured experimentally is thus a particularly poor approximation.

These $T\Delta S$ terms are listed in Table VII, together with the free energies of activation calculated by MM3. It can be seen that the entropies contribute significantly to the barriers of the congested molecules; looking back, one can, in fact, conclude that the MM2 barriers were not low by 40%, as claimed, but rather by about 20%. (The MM2 values for $\Delta H^\ddagger$ were too low by about 25%, but the MM2 entropies would have, therefore, been too large (in absolute value), compensating the errors in the $\Delta H^\ddagger$ values in part. Thus a proper comparison of the experimental $\Delta G^\ddagger$ values

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Table VII. Rotational Barriers of Selected Alkanes[a]

		MM2	this work (MM3)				
compound	T	$\Delta H^{\ddagger}$[b]	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$[c]	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger}_{\text{obs.}}$[d]	dev,[e] %
2,3-dimethylbutane	98.16	3.07	4.18	−0.86	4.26	4.30	−0.8[45]
2,2,3-trimethylbutane	143.56	4.11	5.92	−4.00	6.49	6.97	−6.9[46]
2,2,3,3-tetramethylbutane	176.16	5.24	7.77	−8.57	9.28	(9.60)	...[f]
3,3,4,4-tetramethylhexane	209.00	6.95	8.46	−5.04	9.51	10.60	−10.3[47]
2,2,4,4,5,5,7,7-octamethyloctane	254.50	9.23	10.95	−4.70	12.15	13.80	−12.0[47]
cyclohexane	206.00	10.53	10.28	3.63	9.53	10.22	−6.7[48]
hexamethylcyclohexane	333.00	11.61	14.19	−2.88	15.14	17.60	−15.0[49]
						std dev	6.4

[a] Units: temperature T, Kelvin; entropy S, cal/mol·deg; enthalpy H, kcal/mol; free energy G, kcal/mol. [b] Since entropies are not available for the MM2 calculation, only enthalpies are given. [c] For the pseudorotation frequency in the transition state, a special treatment was used in the entropy calculation (see ref 40). [d] All observed values are determined by the equilibrium (NMR) method; thus they are free energy values. [e] The deviation is the calculated minus the observed value. [f] An estimated value (see ref 3).

Table VIII. Thermodynamic Functions of Selected Alkanes[a]

compounds	$C_p°$	$S°$	$H_f°$	$G_f°$	log K_p
ethane	12.25	54.59	−19.86	−7.02	5.15
	(12.58)	(54.85)	(−20.24)	(−7.87)	(5.68)
propane	17.05	64.42	−25.13	−5.56	4.08
	(17.57)	(64.51)	(−24.82)	(−5.61)	(4.12)
butane	22.25	73.80	−30.09	−3.55	2.60
	(23.29)	(74.12)	(−30.15)	(−4.10)	(3.00)
isobutane	22.56	70.30	−32.35	−4.86	3.56
	(23.14)	(70.42)	(−32.15)	(−4.99)	(3.66)
neopentane	28.55	73.36	−40.97	−4.71	3.45
	(29.07)	(73.23)	(−40.27)	(−4.24)	(3.11)
2,2,3-trimethylbutane	39.19	91.80	−48.27	1.97	−1.44
	(39.33)	(91.61)	(−48.95)	(1.02)	(−0.75)
cyclopentane	20.54	70.34	−18.94	8.97	−6.58
	(19.84)	(70.00)	(−18.74)	(8.95)	(−6.56)
cyclohexane	25.40	71.29	−29.69	7.58	−5.56
	(25.40)	(71.28)	(−29.43)	(7.59)	(−5.56)
cycloheptane	30.87	82.05	−27.44	16.41	−12.03
	(29.42)	(81.82)	(−28.52)	(15.06)	(−11.04)
cyclooctane	35.51	87.94	−29.01	22.69	−16.63
	(33.45)	(87.66)	(−30.06)	(21.49)	(−15.76)
trans-decalin	40.56	89.45	−43.86	17.49	−12.82
		(89.52)	(−43.57)	(17.55)	(−12.86)
cis-decalin	40.36	90.03	−40.75	20.42	−14.97
		(90.28)	(−40.38)	(20.51)	(−15.03)
methylcyclohexane	31.11	81.85	−37.18	6.64	−4.87
	(32.27)	(82.06)	(−36.99)	(6.52)	(−4.78)
1,1-dimethylcyclohexane	37.10	86.94	−43.67	8.33	−6.11
	(36.90)	(87.24)	(−43.26)	(8.42)	(−6.17)

[a] Gas phase, temp 298.16 K, pressure 1 atm. All observed values are adapted from ref 33 and are given in parentheses. Heat capacity C_p and entropy S are in units of cal/mol·deg; formation enthalpy and free energy are in kcal/mol. All conformational mixtures were taken into account. The correction terms needed to convert the harmonic oscillator values to the restricted internal rotation values around the RC–CR bond have been added to the entropies, heat capacities, and enthalpy (see ref 34). No attempt was made to explicitly correct for the restricted internal rotation of the terminal methyl group as such a correction is implicitly included in the methyl heat parameter.

with MM2 $\Delta G^{\ddagger}$ values would have shown the latter to be too low by about 20%.)

The rotational barriers in Table VII show that the values calculated by MM3 are still on the low side. The largest error in $\Delta G^{\ddagger}$ is 2.46 kcal/mol (15.0%), and the average error is 1.02 kcal/mol (7.9%). We could, of course, increase these barriers to any desired value by appropriate changes in the torsional constants. Higher barriers here would be at the expense of poorer heats of formation in the medium rings and elsewhere, however, and all of the values chosen for all of the parameters in MM3 represent our assessment of the best fit to all of the data available to us at this time.

Thermodynamic Functions

It will be evident to the reader at this point that we now have sufficient information that we may calculate the thermodynamic functions for compounds of the type studied herein. In Table VIII are given the thermodynamic functions for a group of selected alkanes under standard conditions, together with the experimental values. The agreement seems quite acceptable, remembering that the calculation at this point is totally a priori.

Of course, we can also calculate these functions at various temperatures, although the approximations involved are expected to be somewhat worse as the temperature increases. In Table IX (Supplementary Material) are given the thermodynamic functions for the same group of compounds at room temperature, 400 K, and 500 K. Again, the agreement seems reasonable.

Conclusions

Based on Tables I–IX, previous and future papers,[5,51–53] we find that the MM3 program will permit us to calculate vibrational frequencies for the representative sample of eight simple hydrocarbons with an rms accuracy of about 35 cm^{-1}. (It is indicated how this value may be further reduced when it becomes desireable to do so.) We can also calculate absolute entropies, and entropies of activation for internal rotations, from these frequencies which are of approximately of "chemical accuracy". These quantities can all be determined without any sacrifice in the accuracy of the structures and energies calculated for hydrocarbon molecules, which in fact is now noticeably improved over the MM2 equivalents for highly strained molecules. The MM3 force field thus represents a definite advance relative to MM2. Of course, chemistry consists of much more than hydrocarbons, and the still more important question is how well will MM3 apply to functionalized molecules? It has been applied in a preliminary way, using methods similar to those described in this paper and in the previous ones, to a variety of molecules containing several different functional groups.[53] The overall conclusions, which will be reported in detail in subsequent papers, are that the things which can be calculated for functionalized molecules, and the overall accuracy obtained, are similar to what has been demonstrated here for hydrocarbons. The hydrocarbon force field is completely transferable to these functionalized molecules with little or no loss in accuracy.

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Supplementary Material Available: Table IX, thermodynamic functions of selected alkanes at room temperature, 400 K, and 500 K (5 pages). Ordering information is given on any current masthead page.

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