Organic and Biological Chemistry

Conformational Analysis. LVII. The Calculation of the Conformational Structures of Hydrocarbons by the Westheimer–Hendrickson–Wiberg Method[1,2]

Norman L. Allinger, Mary Ann Miller, Frederic A. VanCatledge, and Jerry A. Hirsch

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received November 18, 1966*

Abstract: The basic method of Westheimer as modified by Hendrickson and Wiberg, which utilizes classical mechanics to calculate the structures and energies of molecules, has been further refined and applied to a series of hydrocarbons including methane, ethane, propane, *n*-butane, isobutane, neopentane, cyclohexane, methyl- and dimethylcyclohexanes (all isomers), ethyl- and isopropylcyclohexane, *cis*- and *trans*-decalin, and a few others. The bond lengths, angles, and the relative energies of different conformations (eclipsed, *gauche*, boats, etc.) were all calculated to within the accuracy of existing experimental data. Predictions have been made regarding the structure and energy of some novel systems, such as an axial *t*-butyl group on a cyclohexane ring.

There are a great many physical methods which are employed by chemists for the determination of the structures of molecules. Of these, only three have so far been widely used to give complete structural information about a molecule: microwave spectroscopy, electron diffraction, and X-ray diffraction. At the present time, each of these methods is well suited for the determination of certain types of structures, but none of them is completely general. The X-ray method is the most general, but at best it gives information only on that conformation which exists in the crystal, and it does not tell us the conformational situation in solution, which is usually of greater interest and may differ considerably from that in the crystal. Another very practical difficulty with the X-ray method is that the time required for a structure determination may be on the order of a year or more, unless the molecule contains a heavy atom.

If the physical properties of molecules were really adequately understood, it would be possible to calculate from first principles the exact structure of any molecule of interest. The method of calculation which should be used would be based on quantum mechanics, since this is the proper way to describe a molecular system. Up until now, hydrogen is the most complicated molecule on which really accurate quantum mechanical calculations have been carried out.[3] Recent studies on the ethane molecule,[4,5] while informative and exceedingly interesting, serve to show how far we are from being able to properly carry out a quantum mechanical calculation on even this rather simple system.

At the present time there appear to be two approaches which one might reasonably hope to employ to accurately determine molecular structure by theoretical calculation, and these are either (a) a simplified quantum mechanical treatment, such as the so-called extended Hückel method[6] (or better perhaps, a semiempirical method such as that of Pariser–Parr[7]); or (b) a method based on classical mechanics, rather than on quantum mechanics. Our own experience with quantum mechanical calculations has been such as to lead us to suspect that calculations of the type a would be extremely difficult to carry out to the desired degree of accuracy, and we have therefore turned our attention to the classical mechanical calculation (b).

The long-term objectives of the present work are to calculate the structures of ordinary molecules to the accuracy obtainable by experimental measurement under favorable conditions—0.01 A for bond lengths, 0.5° for bond angles, and 0.2 kcal/mole for relative energies. We have at the outset no guarantee that this high an accuracy will be attainable by a classical mechanical calculation, and the validity of such a calculation will ultimately have to come from the agreement between calculated and experimental quantities. We will therefore assume at this point that the structures of molecules can be calculated on the basis of a classical mechanical model, and having made that assumption, it is only necessary to evaluate the various types of interactions which will be found in the mechanical system representing the molecule.

Discussion and Results

This type of calculation was originally employed by Westheimer to calculate the racemization rates for

---

[1] Paper LVI: N. L. Allinger and C. D. Liang, *J. Org. Chem.*, **32**, 2391 (1967).

[2] This research was supported by Public Health Service Research Grant AM-5836 from the National Institute of Arthritis and Metabolic Diseases. It was first presented in a lecture at Princeton University, April 26, 1966.

[3] W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 219 (1960).

[4] R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963).

[5] W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2384 (1966).

[6] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers.

[7] (a) R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953); (b) N. L. Allinger, J. C. Tai, and T. W. Stuart, *Theoret. Chim. Acta*, in press, and references therein.

substituted diphenic acids,[8] and his success led others to utilize the method for the calculation of various items of structural interest.[9] Two significant developments in the calculation method were subsequently introduced. Hendrickson[10] employed this type of calculation for the determination of structure in some cyclic polymethylene compounds, and developed a method for utilizing an electronic computer to do the extensive arithmetic work. This development was a major advance, but the computational scheme employed by Hendrickson, while it was satisfactory for the cases he was dealing with, lacked generality, and was in fact excessively laborious to apply in other than relatively simple cases.

The second major advance in the development of the method was made by Wiberg,[11] who overcame both of the difficulties inherent in Hendrickson's computational scheme by utilizing an ordinary cartesian coordinate system for the molecule and by allowing the computer to adjust the conformation in order to obtain a minimum of energy, rather than doing this by hand. The computational scheme used in the present work does not differ in any fundamental way from that used by Wiberg.[12] The principles involved in making such a calculation are adequately described elsewhere, and the basic ideas behind the computational scheme have previously been published by Wiberg. To summarize briefly, a pair of atoms bound together is taken to have a natural bond length, and deviations from this bond length increase the energy of the molecule according to Hooke's law, the necessary force constants being obtained from spectroscopic data.[13] Similarly, bond angles between given atoms are taken to have natural values, and for small deviations (up to 5°) the increase in energy is taken as proportional to the square of the angular deformation,[14] the necessary force constants again being obtained from spectroscopic data.[13] Interaction force constants between bending and stretching deformations have been neglected. Atoms which are not bound to one another or to a common atom exert van der Waals forces upon one another. (The reasons for not considering van der Waals forces between atoms bound to a common atom were also arrived at independently by Wiberg, and have been discussed by him.[15]) As is well known, a calculation which includes only the above elements is insufficient to account for the observed torsional barriers which are found in molecules, and specifically the ethane type of barrier which is known to exist in saturated hydrocarbons. The van der Waals parameters we have used are such that the repulsion between hydrogens on different carbons will account for about 31% of the barrier in ethane, and the remainder is accounted for as a torsional quantity which is added in the usual way.[18] If the dihedral angle between two hydrogens attached to adjacent carbons is 60° or more the torsional interaction energy is considered zero, and this interaction increases sinusoidally in value to a maximum of 0.65 kcal/mole[19] when the hydrogens are eclipsed. In ethane itself, the three pairs of hydrogens yield a torsional energy of 1.95 kcal/mole when the methyls are eclipsed, and when added to the remaining energy terms, the barrier height is calculated to be 2.89 kcal/mole (see Table I).

The Wiberg energy minimization scheme moves atoms in 0.01-A increments in searching for energy minima. Errors in bond lengths of up to 0.005 A may therefore result from the *inaccuracy of minimiza-*

---

(8) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 523.

(9) (a) For a review, see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, p 433; (b) A. I. Kitaygorodsky, *Tetrahedron*, **14**, 230 (1961), and earlier papers, has also pioneered the method discussed by hand calculation.

(10) (a) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961); (b) *ibid.*, **84**, 3355 (1962); (c) *ibid.*, **86**, 4854 (1964).

(11) K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

(12) Work on our own computational scheme was carried out more or less concurrently with that of Professor Wiberg, as we were not aware of his work. Our computational program was still incomplete when we learned of Wiberg's work, and he kindly furnished us with a copy of his program. We therefore employed many sections of his program, particularly his elegant minimization procedure, in our own computational scheme. Much of our scheme differs from his in detail, but, in principle, the two schemes are the same.

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

(14) This type of force law is commonly used for small deviations; the question is what happens as the deviation becomes larger. If a carbon sp^3 orbital is held fixed in space and a hydrogen is placed at the bond distance, then moved through an arc at that distance, the overlap integral between the hydrogen 1s orbital and the carbon hybrid orbital decreases in a way that is very well approximated by the square of the deviation for an angular motion of up to 10°. However, as the deviation becomes larger than a few degrees, rehybridization and orbital following by the carbon orbital are expected to become more important, and as the deviation becomes still larger, the bond becomes so weak that the variation in energy becomes much smaller than the square of the angular deviation would indicate. While a theoretical study of this situation might be fruitful, we have not undertaken it. Instead, we have decided somewhat arbitrarily to use the usual relationship for deviations up to 5°, and beyond that to use a linear relationship: $E = (k/2)(5)(\theta)$. This relationship gives a reasonable bending energy for cyclobutane. It will not be satisfactory for cyclopropane or ethylene, but the bonding situations in these cases are such that one does not expect the same relationship to hold. (All energies in this paper are in kcal/mole, all distances in A, unless otherwise stated.)

(15) The fundamental idea is that when angular motion is considered and given a natural angle and a bending constant, as is done here, the van der Waals interaction between atoms attached to a common atom has been accounted for in a roundabout way, and to include it as a separate item would account for it twice. The other approach is possible, *i.e.*, to account for the van der Waals interaction as usual first, and then to use a bending constant and natural angle as a sort of correction factor to bring about agreement with experiment. The latter approach, which is essentially that of Bartell,[16] may be more fruitful in the long run, as it may allow the heat of formation of the molecule to be more accurately predicted. The empirical bond energy schemes (of which that given by Kalb, Chung, and Allen[17] is especially notable) always place a considerable importance on the type of interaction in question, but this may be done in the form of small correction terms. The reasons for choosing the present method were as follows. If one counts the van der Waals interactions between atoms bound to a common atom, the numerical values are enormous and tend to swamp the other interactions. This means that one must know very accurately the pertinent van der Waals data or the results may well be disastrous. It seems likely that the concept of spherical atoms may be too crude under these circumstances, and additional parameters may then be required. The present approach thus seems more practical, for the time being at least.

(16) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(17) A. J. Kalb, A. L. H. Chung, and T. L. Allen, *J. Am. Chem. Soc.*, **88**, 2938 (1966).

(18) In our view, the rotational barrier in ethane is best pictured physically as a van der Waals repulsion. We cannot accurately calculate it that way in the present scheme, although we could if the nuclei and electrons were treated separately. Such a separation would be equivalent to using nonspherical atoms, and it would give additional flexibility in the calculations, and better results, but it would require more parameters. We have decided to retain the more simple spherical atom approach for the present, until it is clearer just what the limitations of this approach are. Thus, we view the torsional energy as resulting from a defect in our van der Waals calculation, and we treat it appropriately.

(19) The value 0.65 kcal/mole was chosen to yield agreement between the calculated and experimental values (Table I). This value was chosen in conjunction with the van der Waals properties of the atoms (*vide infra*) and is dependent on those properties.

Table I. Barriers to Rotation

Compound	Barrier, kcal/mole Calcd	Barrier, kcal/mole Obsd	Ref
Ethane	2.89	2.8–3.1	*a, b*
Propane	3.46	3.4–3.6	*a, c*
Isobutane	...	3.6–3.9	*a, d*
Neopentane	4.17	4.2–4.8	*a*

[a] K. S. Pitzer, *Discussions Faraday Soc.*, **10**, 66 (1951). [b] D. R. Lide, Jr., *J. Chem. Phys.*, **29**, 1426 (1958). [c] L. H. Scharpen and V. W. Laurie, Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, 1965. [d] D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958).

tion. Rarely are bond lengths known more accurately than this anyway, so this in itself is not serious. We will record our calculated bond lengths here to 0.001 A, but they are not necessarily minimized to that degree of accuracy. There is a more serious problem with the energy minima calculated, as an error in a bond length of the order of 0.005 A can lead to an error in the energy of as much as 0.03 kcal/mole per bond. However, as long as one uses reasonable starting geometries, the difference in energy between two conformations of a molecule can be calculated from different initial geometries with a reproducibility of the order of 0.1–0.2 kcal/mole, for molecules of the size considered here. The only minimization operation the program does not do at all well is the changing of torsional angles. A basic difficulty is that the program moves one atom at a time, and while the rotation of, *e.g.*, a methyl group might improve the energy, moving one hydrogen may cost more in bending than is gained from torsional improvement. The torsional angles were therefore adjusted by hand if there was any doubt.

To fit the observed barrier in propane, the torsional energy of the hydrogen eclipsing carbon needs to be larger than that of hydrogens eclipsing hydrogens and 1.00 kcal/mole has been used. The correct rotational barrier for neopentane is also obtained from these numbers (Table I), as one would like.

For most simple hydrocarbons, since there is not very much stretching or bending deformation, the most important quantities for determining structure are the van der Waals interactions. Various sets of van der Waals functions have been used by earlier workers for different calculations.[8–11,20] For the most part, the functions used were adequate for the purpose for which they were intended. We have found, however that most of the functions used in the literature are totally inadequate for general types of calculations with hydrocarbons. It was therefore essential that we set as our first goal the determination of adequate van der Waals functions for covalently bound carbon and hydrogen atoms, which would be appropriate for calculations for hydrocarbons in general.

For hydrocarbons, the only van der Waals interactions are between carbons and hydrogens, and for most other organic compounds the bulk of the interactions are still between these atoms. These interactions are consequently the ones crucial to the success of the method. The present paper will deal only with hydrocarbons. We are presently extending this method to include atoms of other types, and from what we have found so far, other atoms present no special difficulty.

The reason for the profusion of van der Waals functions for covalently bound atoms in the literature stems from the fact that while it is possible to directly determine experimentally such functions between rare gas atoms, or between whole molecules, there is no direct way to measure these functions for different individual covalently bound atoms. Hill has shown that the van der Waals functions for the rare gas atoms, and for a number of simple molecules, can be adequately expressed in terms of a reduced function which involves only two parameters.[21] Since there does not appear to be any way to get at the van der Waals functions of covalently bound atoms directly, we accept Hill's function as being as good as is available, and this leaves us with two parameters to determine for each atom: one is the van der Waals radius of the atom, and the second (ϵ) is an energy parameter which measures the depth of the van der Waals minimum of energy. Our initial calculations utilized the van der Waals parameters for hydrogen determined by Hill, and parameters for carbon determined in a roundabout way based on Hill's method.[9] For hydrogen covalently bound to carbon, Hill gives $r^* = 1.2$ A, $\epsilon = 0.042$ kcal/mole; and for carbon the values are $r^* = 1.70$ A, $\epsilon = 0.107$ kcal/mole. To judge the suitability of these parameters, we carried out a number of calculations, of which the following cases willl serve to illustrate our conclusions.

The crystal structure of the paraffin hydrocarbons has been determined rather accurately by X-ray crystallography, and the heat of sublimation of a paraffin crystal can be calculated from available thermodynamic data. The lattice forces which determine the crystal spacings and energy are just the van der Waals forces about which information is desired. Using the van der Waals parameters mentioned above, and packing molecules together as parallel chains, as they are known to be in the crystal, we calculated what the separation between chains would be in the hexane crystal at the minimum of energy, and what the heat of sublimation of the hexane crystal would be for that crystal spacing.

Accurate crystallographic data are available for *n*-hexane,[22] and the *A* and *B* spacings between neighboring chains in the crystal are experimentally found to be 4.17 and 4.70 A (see Figure 1). It was found that considering a block of nine chains (3 × 3), the calculated *A* and *B* spacings of minimum energy were 3.85 and 4.35 A, in only fair agreement with experiment. (When the calculations were carried out on a 4 × 4 or 5 × 5 block of chains, these spacings were reduced by less than 0.01 A, showing the 3 × 3 crystal size is adequate for determining the spacing.) The nearest hydrogens on adjacent chains approach each other to within 2.1 A in this calculated crystal: to a distance which is much less than the sum of their van der Waals radii (2.4 A). Since the other atoms in the parallel chains are all attracting one another when the nearest hydrogens are separated by exactly the sum of their van der Waals radii, the chains will continue to approach each other until the increase in repulsion between the closest hydrogens which would result if the chains were to

---

(20) See ref 10a for a summary of many earlier ones.

(21) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

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

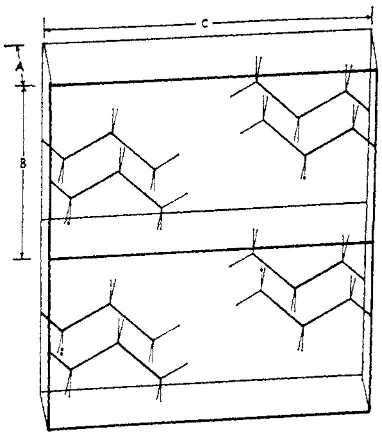


Figure 1. The hexane crystal.

approach still more closely outweighs the potential gain in the attraction between the remaining atoms. Consequently, the distance of closest approach in the crystal should always be appreciably smaller than the sum of the van der Waals radii of the atoms concerned. (Crystallographers often use distance of closest approach and van der Waals radius as synonymous, which clearly they are not.) To get the calculated crystal distances as large as those observed experimentally, it is necessary that the hydrogens either be bigger or harder (that is, they must have either a larger van der Waals radius or a larger value for ϵ).

From the interaction energy between two chains at various distances along the A, B, and C axes, the energy required to remove a single chain from an infinite block of chains was calculated, and this would be related to the heat of sublimation of our idealized crystal.[23] The value found directly from this calculation was 13.1 kcal/mole, but some further corrections are necessary to obtain a number that can be compared with experiment.

First, the actual heat of sublimation of the crystal measures the energy required to pull apart a mole of hexane chains, plus the amount of energy required to establish the conformational mixture which exists in the gas phase from the perfectly staggered arrangement which exists in the crystal. This latter conformational energy amounts to some 0.3 kcal/mole at the temperature of the melting point of *n*-hexane.[24] Thus our calculated heat of sublimation of the hexane crystal at −100° using the Hill parameters is 13.4 kcal/mole.

The experimental value of the heat of sublimation of the hexane crystal is equal to the heat of fusion of the crystal at the melting point plus the heat of vaporization of the liquid at the melting point. The latter is approximately equal to the heat of vaporization at the boiling point, and the sum of the heat of fusion at the freezing point plus the heat of vaporization at the boiling point is 10.0 kcal/mole.[25] The heat of sublimation of the calculated hexane crystal is therefore too large by 34%, and crystal spacings are too small by 8%. Thus these van der Waals functions gave only a fair approximation for properties of the hexane crystal. An improvement would appear to require a larger hydrogen van der Waals radius to increase the crystal spacing, and probably other adjustments to obtain a better heat of sublimation.

The conformational energy of a methyl group axial on a cyclohexane ring is one of the most accurately known of all conformational energies, so it was then calculated using the same parameters as above. This quantity has been measured repeatedly, and the experimental value is taken to be 1.9 kcal/mole,[26] with a probable error of about 0.2 kcal/mole.[27] The Hill parameters gave the calculated value for the conformational energy of the methyl as 0.0 kcal/mole. Obviously such results are not suitable for use in conformational analysis.[28] Since the net interactions of the axial methyl are not on the steeply repulsive part of the van der Waals curve, no adjustment of the ϵ values can bring the calculated and experimental values for the conformational energy of the methyl group into agreement. It is known that the conformational energies of cyano and ethynyl are very small compared to that of methyl,[29] and hence the repulsions must be mostly between hydrogens, and not involving carbons. A hydrogen radius appreciably larger than 1.2 A is clearly necessary, and there is no other alternative.

The commonly quoted value for the van der Waals radius of hydrogen (1.2 A) is in fact the distance of the closest approach between hydrogens in crystals and, as indicated above, this number is necessarily smaller than the actual van der Waals radius. Other values for the van der Waals radius of hydrogen have been used on occasion; notable is the value of 1.50 A advocated by Bartell,[16] in order to fit the observed angular deformations found in simple molecules. None of the values in the literature has any very sound basis, however, and since the quantity does not seem to be directly accessible by any known type of experiment, we feel free to treat the van der Waals radius of hydrogen as a parameter to be evaluated in the present work. The values used for the van der Waals radius of carbon in the literature have a similar dubious basis.

The literature values to be used for ϵ for carbon and hydrogen were also arrived at by indirect and uncertain methods. We are inclined to feel that the literature values for both the van der Waals radii and the ϵ values are probably good to within a factor of 2 or so, but there seems to be no compelling reason for using the exact literature values, and we feel free to treat all of

---

(23) A cubical block of 3375 chains was actually used, and the energy needed to pull out the middle chain was calculated. The change in the calculated energy which would result if an infinite block were used is estimated as less than 0.1 kcal/mole.

(24) This value was calculated from the partition function using 0.5 kcal/mole per *gauche* interaction (see S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press Inc., New York, N. Y., 1954, p 101).

(25) API Tables, Project 44, National Bureau of Standards.

(26) Reference 9, p 439.

(27) Unless otherwise specified, all energy differences in this paper are for the gas phase. Liquid-phase values are generally somewhat different (see ref 9, p 174), but can be corrected for.

(28) Hendrickson calculated the conformational energy of a methyl group on a cyclohexane ring to be 1.0 kcal/mole, using van der Waals functions similar to those mentioned above. He assumed the cyclohexane ring itself possessed tetrahedral angles however, and held them invariant in the calculation. It is now known that the CCC angle in the cyclohexane is considerably widened out from the tetrahedral value (to 111.55°; see below). This widening out of the CCC angle causes the axial methyl group to bend out away from the ring and reduces its energy considerably, so the 1.0 kcal/mole per mole value obtained by Hendrickson, while already too small, is much larger than it would have been if the correct geometry of the ring had been used in the calculation.

(29) N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, 27, 4601 (1962); B. Rickborn and F. R. Jensen, *ibid.*, 27, 4606 (1962); R. J. Ouellette, *J. Am. Chem. Soc.*, **86**, 3089 (1964).

these quantities as parameters. This gives us a series of four van der Waals parameters which must be evaluated before the type of calculation in which we are interested can be carried out. We wish to make quite clear the following point. If one is willing to accept the classical mechanical model upon which our calculations are based, then these van der Waals parameters are not arbitrary constants, but are actually physically significant quantities, which we do not happen to be able to measure at present by any direct experiment. If these quantities can be evaluated by considerations involving a few simple compounds, then to within the limits of accuracy of the model, they become physical quantities to be henceforth employed in calculations.

Thus, sets of van der Waals parameters were guessed and checked against the *n*-hexane crystal data, and sets which were inadequate were discarded. The adequate sets of van der Waals data were then applied to the small molecules indicated below, and the natural bond lengths and angles were chosen so the calculated and experimental geometries agreed. The resulting sets of numbers were then tried on the methylcyclohexane conformers. It was found that the van der Waals radius of hydrogen had to be in the range of approximately 1.4 to 1.6 A to fit all the above data. If the hydrogen radius was much smaller than 1.4 A, in order to fit the methylcyclohexane data the hydrogen ϵ had to be so large that the heat of sublimation calculated for the hexane crystal was too large. The latter could be corrected for within limits by making the carbon smaller and/or softer, but if the hydrogen radius went much below 1.4 A, the carbon disappeared altogether, and the results could not be brought to agreement.

The reason for choosing 1.60 A as an upper limit for the hydrogen radius is a little less direct. As the hydrogen radius is chosen larger, the ϵ required for carbon becomes larger. Now it is known[30] that carbons and hydrogens covalently bound have their polarizabilities (the attractive term in the van der Waals equation) in a ratio of 2.2:1. These numbers are evaluated indirectly, and the ratio that will give optimum results for the present type of calculation is not necessarily exactly 2.2, but it must be something on this order. This ratio increases as the hydrogen radius chosen increases, when the other restrictions are maintained, and reaches a value of about 100 for a hydrogen radius of 1.60 A, which seems definitely too large. We carried out a number of parallel calculations for hydrogen radii of 1.45 and 1.50 and found that, as long as the other parameters are adjusted appropriately, there was no significant difference in the results obtained. Thus it appeared that any hydrogen radius from 1.40 to 1.60 would be about as good as any other for the purposes we have so far studied, although a value near the middle of the range seemed a little more justifiable. We arbitrarily chose 1.50 A to carry through all of the following calculations.

Once the hydrogen van der Waals radius was decided upon, the hydrogen ϵ was fixed by the necessity of fitting the conformational energy of methylcyclohexane, and this in turn fixed the attractive part of the carbon van der Waals curve required to fit the heat of sublimation of hexane. Only the attractive part of the carbon curve was fixed, however, since none of the carbons are within the repulsive range of any of the atoms of other molecules in the crystal and there are various combinations of r^* and ϵ that will give the same attractive potential. A carbon radius of 1.70 A appeared to fit everything in which we were interested, but it was found that if a very small radius was used, most other things could be fit equally well, but in addition one could approximately account for the "branched chain effect," the increased stability of a branched chain compared to a normal paraffin.[31] The carbon radius finally settled on was 1.10 A.

The set of van der Waals constants chosen[32] gave hydrogen $r^* = 1.50$ A, $\epsilon = 0.049$; and carbon $r^* = 1.10$ A, $\epsilon = 0.650$. When applied to the hexane crystal, the predicted spacings for *A*, *B*, and *C* were 4.38, 4.85, and 10.19 A; the deviation of the first two from the experimental value averages 4%. The calculated heat of sublimation of the crystal is 10.1 kcal/mole, compared with experimental value of 10.0 kcal/mole. Thus the experimental and calculated crystal data are in good agreement.

Having now a set of van der Waals constants, it was next necessary to evaluate the "natural" bond lengths and angles from which deviations were to be measured. The C–H bond length in methane is 1.094 A and since all of the atoms in the molecule are either bound to each other, or to a common atom, there are no van der Waals interactions in the present type of treatment. The natural C–H bond length therefore must be 1.094 A. We have assumed that this number will carry over to other saturated hydrocarbons. Next, the C–C bond length in ethane (which is not well known, but which we had assumed is 1.526 A as it is in propane) is a resultant of the hydrogen atoms on opposite methyl groups pushing one another apart and the carbon–carbon bond trying to pull the two carbon atoms back toward the natural length. For the van der Waals parameters which we settled on ultimately, the natural C–C bond length is 1.520 A, and the pushing and pulling compromises at 1.526 A for the C–C bond length in the staggered form of ethane.

---

(30) J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., New York, N. Y., 1958, p 91.

(31) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 228.

(32) We wish to emphasize that any hydrogen radius from 1.4 to 1.6 and any carbon radius from 1.1 to 1.8 can, by appropriate adjustment of other quantities, yield substantially all the results given here, as illustrated by the comparative calculations given in Table X, and a decision as to the best values within these ranges will have to be made later, on the basis of additional experimental data, particularly heats of formation. The latter are not well calculated by the present scheme. Some reasons for this defect in the calculations are discernible from treatments which do work empirically, and it is also clear that the present scheme can be modified so that heats of formation can be calculated. The modifications necessary are not trivial ones, however, and this problem will be deferred to a subsequent paper.

Because of comments made by the referees, we want to state categorically that the results of this paper *do not suggest a 1.1-A value* for the van der Waals radius of carbon. There is, in our opinion, no basis for choosing any one value in the range 1.1 to 1.8 A over any other value, from the present work or elsewhere. Arguments concerning electron densities about *atoms* are invalid, because the appropriate orbital exponents for use in *molecules* are unknown. The rather wide spacing between graphite planes is also not applicable, since p electrons are, on the average, farther from the nucleus than s electrons, and bonding electrons are pulled into the region between the nuclei. Thus a carbon in graphite, to extend the present picture, would be an ellipsoid, which would have its major axis along the p orbital, and the value of the "van der Waals semimajor axis" would have to be about 2 A to yield the observed crystal spacing. This value tells us only that a tetracoordinated sp^3 carbon should have a smaller van der Waals radius than this.

Table II. Parameters Used in the Calculations

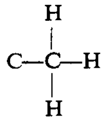
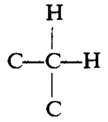
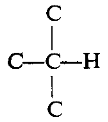
van der Waals parameters for use in Hill equation:		C: $r^* = 1.10$ A; $\epsilon = 0.650$ kcal/mole	
$d^* = 2r^*$		H: $r^* = 1.50$ A; $\epsilon = 0.049$ kcal/mole	
$E_v = -2.25\epsilon(d^*/r)^6 + 8.28(\epsilon)\exp(-r/0.0736d^*)$			
"Natural" Bond Lengths and Angles			
		θ_0(HCH)	
l_0(C–C)	1.510 A	CH_3	108.9°
l_0(C–H)	1.094 A	CH_2	107.3°
θ_0(C–C–C)			
neopentane	109.5°	ω_{H-H}	0.65 kcal/mole
isobutane	111.9°	ω_{H-C}	1.00 kcal/mole
propane	112.5°	ω_{C-C}	0.65 kcal/mole
θ_0(C–C–H)			
	110.1°		
	109.1°		
	107.1°		

Table III. Structures and Energies Calculated for Small Hydrocarbons

Compound	C–C length, A	C–C–C angle, deg	Total *E*	Conf *E*	Ref
Ethane staggered	1.526	110.7 CCH	0.72	0	*a*, *b*
Ethane eclipsed	1.538	111.1 CCH	3.61	2.89	
Propane stg, stg	1.526	112.4	0.16	0	*a*, *c*, *d*
Propane stg, ecl	1.526–1.529	112.4	3.46	3.46	
Butane ω_{C-C} 180°	1.526	112.4	−0.52	0	*e*
Butane ω_{C-C} 120°	1.526	112.4	3.08	3.60	
Butane ω_{C-C} 0°	1.533–1.544	114.3	4.38	4.90	*e*
Butane ω_{C-C} 60°, ω_{C-H} 8°	1.526–1.529	113.4	0.21	0.73	*f*
Butane ω_{C-C} 62.5°, ω_{C-H} 8°	1.526–1.528	112.5	0.24	0.76	*f*
Butane ω_{C-C} 65°, ω_{C-H} 6°	1.526–1.536	112.6	0.28	0.80	*f*
Butane ω_{C-C} 75°	1.526–1.531	112.6	0.63	1.15	
Isobutane	1.525	111.1	−1.72	. . .	*g*
n-Pentane	1.526	112.4	−1.21	. . .	*e*
Neopentane stg	1.528	109.5	−5.54	0	*a*
Neopentane ecl	1.528–1.530	109.5	−1.37	4.17	

[a] Footnote *a*, Table I. [b] Footnote *b*, Table I. [c] Footnote *c*, Table I. [d] D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960). [e] L. S. Bartell and D. A. Kohl, *ibid.*, **39**, 3097 (1963). [f] ω_{C-H} is the deviation in the dihedral angle of the methyl group from a perfectly staggered geometry, measured by the rotation of the hydrogen at C-1 about the C-1–C-2 bond away from the normal value of 60° from C-3. [g] Footnote *d*, Table I.

Having the bond lengths fixed for C–H and C–C bonds, the natural bond angles were adjusted so as to give the observed geometry for propane. These required, for example, that the natural C–C–C angle be taken to be 112.5°, and the natural H–C–H angle be taken as 107.3° on a secondary carbon or 108.9° on a methyl group. Similarly, for isobutane, the C–C–C angle was given a natural value of 111.9°, and the C–C–H angle for a tertiary hydrogen was given the value of 107.1°. In Table II are recorded all of the numerical data used in the calculation. With these numbers, plus the van der Waals parameters, the calculated structures for the simple hydrocarbons are all within experimental error of the experimental structures for all of the bond lengths and bond angles, the crystal structure of paraffins is adequately described, and the conformational energy of methylcyclohexane is properly calculated.

In Table III are given the calculated data for the small molecules. The geometries agree to within experimental error of those known in each case. We wanted to choose as accurately known standards as possible and hence have utilized microwave structures rather than other possibilities. Bond lengths determined from microwave spectra appear generally to be a little shorter than those determined by diffraction methods, because of the different method of averaging the atomic positions over the vibrational motions.[33] Consequently, if the results of the present calculation are to be compared with diffraction results, our bond lengths may be expected to be slightly smaller in general, although rarely will the difference be outside of experimental error in any case.

The data in Table III can now be discussed, and we will begin with ethane. The starting geometry chosen for the staggered conformation had the C–C bond length 1.526 A, the same as propane, and this did not change during the minimization calculation. The final C–C–H angle had a value of 110.7°, and the conformational energy was calculated to be 0.72 kcal/mole. In the eclipsed conformation there is more repulsion between the nearest pairs of vicinal hydrogens, and the C–C bond length stretched out to 1.538 A, the C–C–H angle opened out to 111.1°, and the C–H bond lengths also increased slightly (from 1.096 to 1.099 A), giving a conformational energy of 3.61 kcal/mole.

Behavior qualitatively similar to the above was noted with propane. The microwave geometry corresponds to the energy minimum and is characterized by a bond length of 1.526 A and a C–C–C angle of 112.4°. The eclipsed conformation has the eclipsed C–C bond lengthened to 1.529 A, and there are minor changes in the bond angles.

The *n*-butane molecule presents a more interesting

---

[33] D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1961).

situation.[34] Unfortunately, not all of the experimental data are as definitive as one would like for this key compound. The structure of the *anti* conformation is known from electron diffraction studies[37] to be just what one would predict from the data on propane. From the same studies, the structure of the *gauche* form shows no distortion from what would be anticipated to within the limits of experimental error. The relative energies of these forms have been determined experimentally in various ways, and the results are somewhat discordant. From the temperature variation of the Raman spectrum, the *gauche* form was found to have a higher enthalpy by 0.77 ± 0.07 kcal/mole in the liquid phase,[38] which is equivalent to 0.94 ± 0.13 kcal/mole in the gas phase.[27] The electron diffraction measurements gave a free energy difference of 0.63 ± 0.1 kcal/mole, but the temperature of the measurement was not determined. If it was indeed 287°K, as assumed, the enthalpy difference is calculated to be 0.99 kcal/mole, and this value would seem to be accurate to within perhaps 0.2 kcal/mole.

On the other hand, a variety of measurements and calculations indicate values from 0.4 to 0.8 kcal/mole for other *n*-alkanes.[39] All of the evidence is thus consistent with an enthalpy difference of 0.7 ± 0.3 kcal/mole for the butane conformations, but unfortunately the percentage uncertainty here is rather large. For this reason we have chosen methylcyclohexane as our standard compound, since the conformational energy difference here is 1.9 ± 0.2 kcal/mole (gas phase), and the percentage uncertainty is much smaller.

Returning now to *n*-butane, the calculated structure for the *anti* form is exactly as would be expected (Table III). Because our energy minimization program does not in general minimize dihedral angles, it was possible to vary the dihedral angle about the central C–C bond (ω_{C-C}) manually, and the program would then minimize the energy of the structure with that dihedral angle. Keeping the dihedral angles ω_{C-H} perfectly staggered and varying ω_{C-C}, the energies corresponding to a number of dihedral angles were obtained, and these furnish the profile shown in Figure 2. The *anti* form has the same bond lengths and angles as does propane, and an energy of −0.52 kcal/mole. The lower energy barriers (ω_{C-C} 120°) are similar in height to that found in propane (3.60 *vs.* 3.46 kcal/mole). The bond lengths and angles are as in the *anti* conformation. The higher energy barrier is only 4.90 kcal/mole above the *anti* form, and this relatively low energy is achieved by distortion of the bond angles and lengths in the molecule. In this conformation the central and end C–C bond lengths are 1.533 and 1.544 A, respectively, the C–C–C angles are opened out to 114.3°, and other small distortions occur.

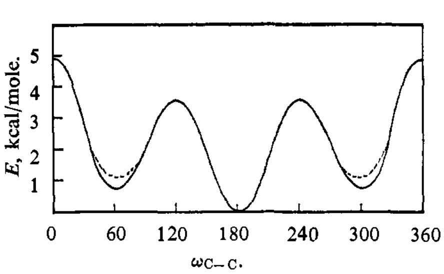


Figure 2. The relative energy of *n*-butane as a function of the dihedral angle (ω_{C-C}) about the 2,3 bond. The dotted line shows the energy when the dihedral angles involving the methyl group are kept staggered, and the solid line shows the energy when they are varied so as to minimize the total energy.

The *gauche* form of *n*-butane is of special interest. The potential well is fairly broad if the methyl groups are kept staggered, and the energy increases from 0.58 kcal/mole (1.10 kcal/mole above the *anti* form) at ω_{C-C} 60° to 0.78 kcal/mole at ω_{C-C} 75°. Again, the C–C bond lengths are stretched out and the C–C–C angles widened. The actual minimum of energy for the *gauche* conformation is found, however, when the methyl groups are allowed to rotate so as to separate the two hydrogens which are exhibiting the large van der Waals repulsion responsible for most of the unfavorable energy of the *gauche* conformer. As ω_{C-C} increases beyond 75°, this van der Waals repulsion becomes rather small compared to the unfavorable torsional quantities. Hence, the potential well is deepened substantially at the minimum by allowing for rotation of the methyl groups, and only slightly as ω_{C-C} gets 10° or more away from the minimum. When the energy is minimized with respect to this torsion for the different values of ω_{C-C} a new energy function is obtained, and it is also shown in Figure 2.

The values we find at the energy minimum differ from the perfectly staggered arrangements by approximately 1° about the 2,3 bond and by 7° about the 1,2 and 3,4 bonds. This is the same (to within experimental error) as the geometry obtained by electron diffraction. Our calculated enthalpy difference between the *anti* and *gauche* forms is 0.73 kcal/mole, which is in reasonable agreement with the experimental values.

A comparison of the *gauche* interaction energy here with the corresponding energy for methylcyclohexane is of interest. When the methyls in butane are not allowed to rotate, the *gauche* energy is more than half that in methylcyclohexane (1.10 *vs.* 1.81 kcal, respectively) but when the methyls are allowed to rotate it is less than half (0.73 *vs.* 1.81, respectively). Our interpretation of this situation is as follows. First, the dihedral angle corresponding to ω_{C-C} in butane is 71.4° in axial methylcyclohexane, which reduces appreciably the repulsion between the 1,4-hydrogens compared to what it would be at ω_{C-C} 60°. In butane itself the increase in torsional energy is unfavorable, and more than outweighs the decrease in this repulsion, but in methylcyclohexane the unfavorable torsion is present in the ring itself, and hence in the equatorial as well as the axial isomer, and thus only the decrease in repulsion is reflected in the $\Delta G°$ value. Compared to the 1.10

---

(34) Recently, theoretical studies of the conformational energies of butane and higher alkanes have been reported by two other groups.[35,36] They determined with some care the rotational energy profile on the assumption of constant bond lengths and angles. They evaluated the necessary van der Waals parameters from the paraffins themselves, and the values obtained are satisfactory for the paraffins, but not very adequate for conformational analysis in general. The rotational profiles obtained with rigid molecules differ somewhat from those obtained when molecular flexing is allowed for, especially the high-energy forms.

(35) P. J. Flory, A. Abe, and R. L. Jernigan, *J. Am. Chem. Soc.*, **88**, 631 (1966).

(36) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **44**, 3054 (1966).

(37) L. S. Bartell and D. A. Kohl, *ibid.*, **39**, 3097 (1963); K. Kuchitsu, *J. Chem. Soc. Japan*, **32**, 748 (1959).

(38) G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, **16**, 704 (1948).

(39) See ref 35 for further discussion and references.

Table IV. Calculated Structures and Energies for Cyclohexane and Methylcyclohexane[a]

Compound	C–C length, A	C–C–C angle, deg	Total *E*	Conf *E*
Cyclohexane, chair	1.528	111.55	−1.05	0
Cyclohexane, boat	1.526–1.528	111.7–112.1	5.38	6.43
Cyclohexane, twist	1.528	111.55	4.01	5.06
Cyclohexane, half-twist	1.521–1.547	111.6–119.3	10.95	12.00
Eq Me-cyclohexane	1.526–1.528	111.7–111.8	−3.24	0
Ax Me-cyclohexane	1.524–1.532	111.5–111.8	−1.43	1.81

[a] For references, see text.

kcal of the rigid butane, the *gauche* interaction in methylcyclohexane is only 0.90 kcal/mole. However, rotation of the methyl groups in butane can lower the value from 1.10 kcal/mole to 0.73 kcal/mole, while no such rotation is possible with the methylcyclohexanes. This situation is quite instructive, as it indicates the energy of a *gauche* interaction, while roughly applicable to various situations, actually varies from 0.73 kcal/mole in butane itself to 0.90 kcal/mole in methylcyclohexane, and it could well vary considerably more in either direction, depending on what other constraints are placed on the interaction by its environment.

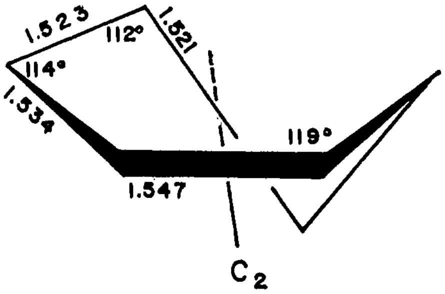


Figure 3. The calculated geometry for the transition state for the inversion of cyclohexane.

For isobutane, the interesting structural feature observed experimentally is the unusually long bond length of the tertiary hydrogen (1.108 ± 0.005 A), which is also found in the present calculation (1.104 A). The rest of the molecular geometry calculated is also within experimental error of that found. The total energy of isobutane is calculated to be less than that of *anti-n*-butane by 1.2 kcal/mole, which is in only fair agreement with experiment (1.8 kcal/mole, when the experimental value[25] is corrected by allowance for the *gauche* forms present). As mentioned earlier, heats of formation are not adequately dealt with by the present scheme.

As expected, *n*-pentane has an unexceptional *anti* conformation (Table III); other conformations were not studied. Neopentane has a lower calculated enthalpy than *anti-n*-pentane by 4.3 kcal/mole (the experimental quantity is 4.8 kcal/mole, which includes 1.0 kcal of zero-point energy). The rotational barrier of neopentane is correctly calculated from the same torsional quantities that were fit to the propane barrier. Isobutane, again, contains the same terms (different numbers of each), and it is clear that its calculated rotational barrier would similarly fit with experiment.

We next examined the cyclohexane molecule (Table IV). This molecule has previously been studied theoretically by Hendrickson, and his results were quite satisfactory. Since the present calculation scheme and the numerical values for the constants differ very much from Hendrickson's, there was no guarantee that our results would be as good as his, although it would be disappointing if they were not. Our results turn out to be quite good, if anything better than Hendrickson's. The geometry calculated for cyclohexane in the chair form agrees to within experimental error with that found by electron diffraction.[40] The conformational energy of the pseudo-rotating boat form is above that of the chair by an amount which is calculated to vary from 5.06 kcal/mole at $\theta = 90°$ to 6.43 kcal/mole at $\theta = 0°$. The experimental values[41] range from 4.8 to 5.9 for the physically existing species in various substituted cases, so these values are accurate to within experimental error. For the transition state (half-twist) leading from the chair to the boat form, assuming C_2 symmetry as proposed by Hendrickson, we calculate an energy of 12.00 kcal/mole relative to that of the chair. The reported values determined by nmr spectroscopy at low temperature vary over a range, but the value reported by Jensen of 11.0 kcal/mole appears to be the best.[42] The accuracy of the experimental value is somewhat uncertain, but it would appear that our calculated value may be slightly high.

The deformations which the half-twist form undergoes allow the molecule to lower its energy by 1.8 kcal/mole from that which it would have if it retained normal lengths and what might appear to be reasonable bond angles. The geometry of minimum energy is shown in Figure 3. The carbon–carbon bond lengths are rather variable; values from 1.521 to 1.547 are found. Relative to the normal chair, the compression energy from bond deformation has increased by 0.2 kcal, the bending energy by 2.0 kcal, the van der Waals energy by 4.4 kcal, and the torsional energy by 5.4 kcal/mole.

The methylcyclohexanes were next examined (Table IV). Equatorial methylcyclohexane is quite normal with respect to the bond lengths and angles. The axial conformer undergoes a number of deformations in an effort to minimize its energy. The methyl group might be expected to bend out away from the ring by enlarging slightly the C–C–C angles, but the angular enlargement is negligible. The hydrogens *syn*-axial to

---

(40) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

(41) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Am. Chem. Soc.*, **83**, 606 (1961); N. L. Allinger and L. A. Freiberg, *ibid.*, **82**, 2393 (1960); J. L. Margrave, M. A. Frisch, R. G. Bautista, R. L. Clarke, and W. S. Johnson, *ibid.*, **85**, 546 (1963).

(42) See F. R. Jensen and B. H. Beck, *Tetrahedron Letters*, **4523** (1966), for discussion and references.

Table V. Calculated Structures and Energies for the Dimethylcyclohexanes

Compound	C–C length, A	C–C–C angle, deg	Total energy	Conf energy Calcd	Conf energy Exptl[a] (±0.3)
1,1-Dimethyl	1.527–1.540	110.0–112.7	−4.21	...	...
cis-1,2-Dimethyl	1.523–1.535	111.1–113.1	−2.29	1.56	1.87
trans-1,2-Dimethyl	1.523–1.531	110.6–113.4	−3.85	0	...
cis-1,3-Dimethyl	1.523–1.527	111.6–112.1	−5.43	0	...
trans-1,3-Dimethyl	1.517–1.535	111.2–112.2	−3.37	2.06	1.96
cis-1,4-Dimethyl	1.521–1.530	111.5–112.0	−3.71	1.75	1.90
trans-1,4-Dimethyl	1.524–1.528	111.6–111.8	−5.46	0	...
cis-1,3,5-Trimethyl	1.519–1.528	111.4–112.2	−7.62	0	...
trans-1,3,5-Trimethyl	1.521–1.534	111.1–112.4	−5.48	2.14	2.05[b]

[a] See ref 25. [b] See ref 48.

the methyl do bend out away from the ring by some 0.5°, and the bond lengths of the interfering hydrogens are shortened slightly to 1.090 A (compared to 1.097 A for the equatorial conformer). The calculated energy of the axial form is 1.81 kcal/mole above that of the equatorial. An examination of the individual interactions shows that most of this energy is a result of the repulsion between the hydrogen on the methyl group which is over the ring and the other coaxial hydrogens. Thus one would predict that axial groups which lacked such hydrogens, such as cyano or ethynyl, would have only small conformational energies. This is in fact known to be true experimentally.[29]

Dimethylcyclohexanes were next considered. The conformational energy of methylcyclohexane itself is not accurately known,[43] but is inferred by studies on more complicated derivatives. Especially pertinent are the heats of combustion of the dimethylcyclohexanes, which are all known in the gas and liquid phases. High-temperature equilibration data have also furnished the enthalpy difference for the 1,3-dimethylcyclohexanes,[45] and recent measurements by Eliel[46] also have given accurate values for the conformational energy of a methyl group when there is a bulky group equatorial in the 3 or 4 position to the methyl.

The calculated data concerning the dimethylcyclohexanes are summarized in Table V. The following seem noteworthy. The conformational energy of a methyl in a 3 position to another equatorial group is greater than that when the arrangement is 1,4. The heat of combustion measurements are consistent with this difference, but the numbers do not differ by more than experimental error. Eliel's recent equilibration results[46] show very definitely that these numbers are in fact different, and there is a lot of indirect information (on the chromic acid oxidation of alcohols, for example) from which this same conclusion can be reached.[47] We will take up molecules containing oxygen in a subsequent paper and concentrate on the hydrocarbons here, but the principles are the same.

The calculated conformational energy of the methyl group in the gas phase which we obtained was 2.06 kcal/mole for the 1,3 isomer and 1.75 kcal/mole for the 1,4 isomer. Comparing these numbers (Table V) with the experimental values found by Eliel[46] (1.75 and 1.56 kcal/mole in the liquid phase), it is seen that the *difference* is quite similar and (to within experimental error) in agreement with the heats of combustion. Again, an examination of the detailed interactions between the various atoms in our calculation is instructive.

From the microwave studies, the C_1–C_2–H angle in propane is slightly larger than the corresponding angle in isobutane (109.5 *vs.* 107.7°, respectively). Similarly, in cyclohexane an axial hydrogen leans out away from the ring more than does the corresponding hydrogen on a carbon which bears an equatorial methyl group. In addition, the secondary axial hydrogen can bend outward rather easily, such bending being opposed mainly by the bending energy. On the other hand if the axial hydrogen is tertiary, bending it out toward the methyl group increases its van der Waals interaction with the hydrogens on the methyl group. Hence, a tertiary axial hydrogen tends to lean into the ring and interact with *syn*-axial substituents, and in addition is resistant to responding to pressure by outward bending away from the ring. The axial methyl in methylcyclohexane or in 1,4-*cis*-dimethylcyclohexane has its energy lowered significantly by the outward bending away from the ring of the *syn*-axial hydrogens. In 1,3-*trans*-dimethylcyclohexane, while one of the hydrogens bends outward easily, the other does not, and hence the conformational energy of the methyl is significantly larger. In 1,3,5-trimethylcyclohexane, the conformational energy of the axial methyl group would be predicted to be especially high, since neither of the hydrogens can respond by outward bending. Our calculated value is 2.14 kcal/mole and the experimental value[48] is 2.0–2.1 kcal/mole. It is clear that the phenomenon is a general one, and one would expect that a compound such as *trans*-3-*t*-butylcyclohexanol should oxidize a good deal faster in the chromic acid oxidation than does *cis*-4-*t*-butylcyclohexanol.[49] This is exactly what is found experimentally, and has been the subject of much controversy.[50] The original assumption made by Winstein and Holness[49] that a 4-*t*-butyl group would not introduce any steric effect into the cyclohexanol

---

[43] A free energy value is available[44] from ultrasonic measurements and is 1.83 ± 0.25 kcal/mole in the liquid phase. The entropy change should be zero. Measurements at different temperatures gave a nonzero entropy change and a corresponding unexpected enthalpy change. Our feeling is that the free energy change is much more reliable, and an assumed entropy change of zero is probably more accurate than the experimental value.

[44] J. E. Piercy and S. V. Subrahmanyam, *J. Chem. Phys.*, **42**, 4011 (1965).

[45] W. Szkrybalo, unpublished results quoted in ref 9.

[46] E. L. Eliel and T. J. Brett, *J. Am. Chem. Soc.*, **87**, 5039 (1965).

[47] E. L. Eliel, S. H. Schroeter, T. J. Brett, F. J. Biros, and J. C. Richer, *J. Am. Chem. Soc.*, **88**, 3327 (1966); E. L. Eliel and F. J. Biros, *ibid.*, **88**, 3334 (1966).

[48] C. J. Egan and W. C. Buss, *J. Phys. Chem.*, **63**, 1887 (1959).

[49] S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 77, 5562 (1955).

[50] H. Kwart and T. Takeshita, *ibid.*, **86**, 1161 (1964).

Table VI. The Calculated Structures and Energies of the Alkylcyclohexanes[a]

Compound	C–C length, A	C–C–C angle, deg	Total *E*	Conf *E*
Ax Et-cyclohexane	1.524–1.537	110.4–114.0	−0.07	1.95
Asymm-eq Et-cyclohexane	1.520–1.533	111.1–113.4	−2.02	0
Symm-eq Et-cyclohexane	1.525–1.540	111.2–114.8	−0.93	1.09
Ax *i*-Pr-cyclohexane	1.529–1.542	108.3–113.3	−0.10	2.04
Symm-eq *i*-Pr-cyclohexane	1.519–1.541	109.3–113.3	−2.14	0
Asymm-eq *i*-Pr-cyclohexane	1.518–1.539	109.3–114.2	−0.82	1.32
Eq *t*-Bu-cyclohexane	1.520–1.556	107.6–114.0	−2.13	0
Ax *t*-Bu-cyclohexane	1.525–1.547	105.2–117.3	10.14	12.27

[a] For references, see text.

ring appears to be a reasonably good one. If the *t*-butyl group (or other substituent) is in any other position, the assumption is not nearly as justifiable. Further discussion on this point will be deferred until a subsequent paper.

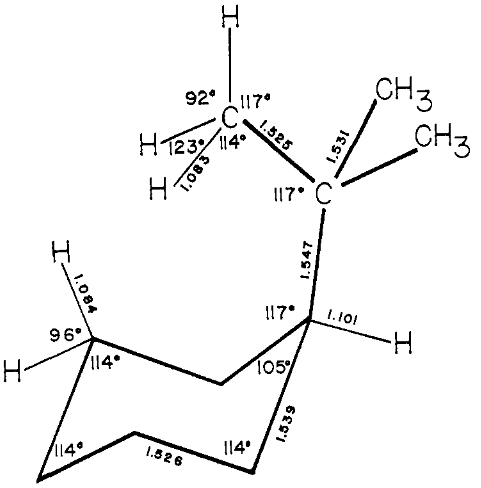


Figure 4. The calculated geometry of axial *t*-butylcyclohexane.

Since it appeared that we could deal quite adequately with the methylcyclohexanes, we next considered the other alkylcyclohexanes (Table VI). The enthalpies for the various conformations of ethyl, isopropyl, and *t*-butylcyclohexane were calculated. For axial ethylcyclohexane there are two mirror image conformations to consider (the third one, with the methyl back over the ring, has such a high enthalpy that it will not contribute to the physical state of the molecule under ordinary circumstances). The equatorial conformations, on the other hand, have three possible arrangements for the methyl group, all of which occur. A thermodynamic analysis was given earlier.[51] In the present work we calculated the relative enthalpies of each of these conformations, and they are summarized in Table VII. When the isomerization of an equatorial to an axial ethyl group is considered, taking into account the conformer populations and the entropies, a free energy change of 2.00 kcal/mole (at 298°K) is predicted. The conformational enthalpy of the isopropyl group was similarly calculated, and from the previous type of thermodynamic treatment,[52] it was concluded that the free energy of isomerization of an equatorial to an axial isopropyl would be 2.15 kcal/mole. These data are summarized in Table VII. The available (liquid phase) data show trends just as here calculated.[53]

Table VII. Calculated Equilibrium Data for the Reaction Equatorial $\rightleftharpoons$ Axial Alkylcyclohexane[a] (Temp, 298°K)

	R			
	Me	Et	*i*-Pr	*t*-Bu
$\Delta H°$	1.81	1.87	1.80	12.32
$\Delta S°$	0	−0.43	−1.19	0
$\Delta G°$	1.81	2.00	2.16	12.32

[a] For references, see text.

The conformational energy for the isomerization of an equatorial to an axial *t*-butyl group has not been previously available, as no molecule containing an axial *t*-butyl group on a cyclohexane ring is known. It is only known that the conformational enthalpy of the *t*-butyl in the axial position must be more than 5 kcal/mole because a cyclohexane ring assume up a boat form rather than adopt such a conformation. In the present work, following the same procedure described, the relative enthalpies of equatorial and axial *t*-butyl groups were calculated, and the latter was 12 kcal/mole higher. This is the first estimate of the conformational energy of the axial *t*-butyl group which has been made, and it awaits experimental verification.

If the axial *t*-butylcyclohexane molecule were to have normal bond lengths and angles, one of the hydrogens on the methyl back over the ring would be only 0.93 A from the *syn*-axial hydrogens, and the molecule would have a total energy of 972 kcal/mole. The molecule deforms in an effort to lower this energy, and in so doing is able to move the offending hydrogens 2.11 A apart, lowering the total energy to 10.1 kcal/mole. The bond lengths and angles which are finally obtained are most unusual (Figure 4). A diffraction study of a molecule with an axial *t*-butyl group would be very interesting. While it would appear that simple cyclohexane derivatives will not exist to any great extent in this conformation, it should be possible to prepare compounds containing this structural feature, such as a *t*-butyladamantane.

Finally, decalin and 9-methyldecalin were considered. The decalin system exists as *cis* and *trans* isomers. Each

---

(51) N. L. Allinger and S. Hu, *J. Am. Chem. Soc.*, **84**, 370 (1962); N. L. Allinger and S. Hu, *J. Org. Chem.*, **27**, 3417 (1962).

(52) N. L. Allinger, L. A. Freiberg, and S. Hu, *J. Am. Chem. Soc.*, **84**, 2836 (1962); Allinger and Hu, ref 51.

(53) For a summary of experimental data and references, see ref 46.

Table VIII. Calculated Structures and Energies for the Decalins

Compound	C–C length, A	C–C–C angle, deg	Total *E*	Conf *E*
trans-Decalin (double chair)	1.524–1.526	111.8–112.0	−6.48	0
cis-Decalin (double chair)	1.523–1.529	111.6–112.2	−3.61	2.87/0[a]
cis-Decalin (boat–chair A)	1.520–1.540	110.6–114.1	8.16	11.76
cis-Decalin (boat–chair B)	1.522–1.530	111.4–112.2	2.70	5.57
cis-Decalin (double boat, 0°)	1.522–1.532	110.3–111.8	4.53	8.14
cis-Decalin (double boat, 60°)	1.523–1.538	109.7–112.7	9.91	13.52
cis-Decalin (double twist)	1.518–1.527	110.1–111.7	3.73	7.34
cis-Decalin (twist–chair)	1.522–1.538	110.8–124.7	3.02	6.63
trans-9-Me-decalin	1.524–1.541	108.0–113.0	−4.16	0
cis-9-Me-decalin	1.522–1.541	106.8–113.9	−3.73	0.43

[a] The first value is relative to the *trans* isomer. The other *cis* forms are referred to this form, the relative energies being given calling the energy of this isomer zero.

of these is generally considered to exist in the chair form, although various other conformational possibilities have been suggested.[54] The only evidence for the existence of nonchair forms stems from calculations based on potential functions which have no experimental or theoretical validity. From the calculations given earlier in this paper, we feel that the functions used herein are well justified, and the predictions to which they lead for decalin are of interest.

Calculations on decalin have recently been reported by Gerig and Roberts.[55] The potential functions which they used, however, were similar to those shown to be inadequate (from the calculations on methylcyclohexane) in the earlier part of this paper.

The present results (Table VIII) show beyond a doubt that only the double chair forms need to be considered for this system. The enthalpy difference between the isomers calculated (2.87 kcal/mole) is in excellent agreement with that found experimentally (3.05 ± 0.25 when corrected to the gas phase).[56] The 9-methyldecalins were similarly found to be exclusively in the double-chair conformations, and the energy difference between isomers is in reasonable agreement with experiment.[57] (The experimental values are themselves rather divergent.)

The above calculations may be considered as samples of the general type which we feel will be useful for the prediction of the accurate structures and energies for hydrocarbon (and other) molecules. As the number of compounds and the number of types of physical properties examined increases, refinement of some of the parameters will be possible. It is especially desirable to fix more precisely the optimum values for the van der Waals radii of carbon and hydrogen. The extension to other atoms in the periodic table should be straightforward; some of these have been made already, and they will be discussed in subsequent papers.

A conclusion we would now draw, based upon the pioneering studies of Westheimer, Hendrickson, and Wiberg, as well as on the work described here, is that compared to the spectroscopic and diffraction methods for accurately determining molecular structure, we will now add a third method, the determination of structure by theoretical calculation. All of the molecular quantities calculated herein (bond lengths, angles, and conformational energy differences) are within the limits of error of the experimental values. Many of these quantities have not been measured experimentally at all, and many would be difficult, some perhaps impossible, to measure by existing techniques. The theoretical method has not yet received the intensive study and the years of refinement that the spectroscopic and diffraction methods have, yet we believe that it is already possible to determine the structures of many hydrocarbons theoretically with as much accuracy as is available by the experimental methods. The saving in time and effort thereby is so great that we feel the theoretical method may now really begin to supplant the experimental methods for the determination of both molecular structures and conformational energies, and it will also give us a way to study these properties for hypothetical molecules and transition states.

Acknowledgment. The authors are indebted to the Computing Center of Wayne State University for their generous allocation of computing time to the work described herein, and to Professor K. Wiberg for a copy ot his program.

Appendix

In Table IX are given the literature data used for comparison purposes. All of the bond angles and lengths obtained in the present work are within the limits of error of the experimental measurements of the microwave work (see ref 33). Table X gives an illustration of sample results.

All of the calculations described in this paper, except those involving the crystal structure, were carried out with the aid of a single computer program written for the purpose. Much of this program was adapted from that of Wiberg, and has previously been discussed by him. The present program is more general, and more flexible, than that described by Wiberg, and hence much longer. It was written in FORTRAN II for the IBM-7074 computer. This machine is considerably slower than machines of the 709 series (approximately a factor of 5) and has a much smaller storage (10 K). The program was written to handle a maximum of 31 atoms (which includes the hydrogens). For even a 31-atom system, the storage required greatly exceeded the 10 K available, and hence the program was seg-

---

(54) P. Geneste and G. Lamaty, *Bull. Soc. Chim. France*, 2439 (1964); *Tetrahedron Letters*, 3545 (1964).

(55) J. T. Gerig and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 2791 (1966).

(56) N. L. Allinger and J. L. Coke, *ibid.*, **81**, 4080 (1959); D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, **64**, 1723 (1960).

(57) N. L. Allinger and J. L. Coke, *J. Org. Chem.*, **26**, 2096 (1961); W. G. Dauben, O. Rohr, A. Labbauf, and F. D. Rossini, *J. Phys. Chem.*, **64**, 283 (1960).

Table IX. Experimental Bond Lengths and Angles

Compound	Bond lengths, A		Bond angles, deg	
Propane[a]	C–C	1.526 ± 0.002	C–C–C	112.4 ± 0.2
	C_1–H	1.091 ± 0.010	H–C_1–H	107.7 ± 1.0
	C_2–H	1.096 ± 0.002	H–C_2–H	106.1 ± 0.2
Isobutane[b]	C–C	1.525 ± 0.002	C–C–C	111.15 ± 0.2
	C_1–H	1.09–1.10	H–H–H	107.5–109.5
	C_2–H	1.108 ± 0.005		
Cyclohexane[c,d]	C–C	1.528	C–C–C	111.55
Butane[d,e]	C–C	1.533	C–C–C	112.7
Ethane[f]	C–C	1.534	C–C–H	109.8

[a] See footnote *d*, Table III. [b] See footnote *d*, Table I. [c] See ref 40. [d] From diffraction measurements. [e] See ref 37. [f] H. C. Allen, Jr., and K. E. Plyler, *J. Chem. Phys.*, **31**, 1062 (1959).

Table X. Sample Results Illustrating the Insensitivity of the Final Results to the van der Waals Radius Chosen for Carbon[a]

	Carbon radius, A		
	1.80	1.70	1.25
Ethane, stg			
l(C–C)	1.526	1.526	1.526
θ(CCH)	110.0	110.4	110.8
Ethane, ecl			
l(C–C)	1.526	1.526	1.532
θ(CCH)	111.1	110.9	111.2
Conf E	2.87	2.85	2.84
Propane, stg			
l(C–C)	1.526	1.526	1.526
θ(CCC)	112.4	112.4	112.4
Propane, ecl			
l(C–C)	...	1.525–1.534	1.526–1.528
θ(CCC)	...	112.4	112.4
Conf E	...	3.21	3.28
Butane, 180°			
l(C–C)	1.526	1.526	1.526
θ(CCC)	112.4	112.4	112.4
Butane, 60°			
l(C–C)	1.526–1.534	1.528–1.534	1.526–1.529
θ(CCC)	114.5	114.5	113.6
Conf E (from 180°)	1.05[b]	1.02[b]	1.14[b]
Isobutane			
l(C–C)	1.526	1.527	1.525
θ(CCC)	111.2	111.2	111.2
Cyclohexane, chair			
l(C–C)	1.528	1.525	1.528
θ(CCC)	111.6	111.5	111.6
Cyclohexane, twist-boat			
l(C–C)	1.528	1.528	...
θ(CCC)	111.6	111.6	...
Conf E	5.72	5.64	...
Cyclohexane			
l(C–C)	...	1.515–1.547	...
θ(CCC)	...	111.2–118.6	...
Conf E	11.44	11.58	...
Eq methylcyclohexane			
l(C–C)	1.525–1.527	1.526–1.528	1.524–1.528
θ(CCC)	111.6–111.8	111.6–111.8	111.4–111.7
Ax methylcyclohexane			
l(C–C)	1.522–1.532	1.522–1.533	1.525–1.532
θ(CCC)	111.8–112.2	111.2–112.2	111.5–111.7
Conf E	1.81	1.84	1.94
cis-1,4-Dimethylcyclohexane ΔE =	1.75	1.76	...
trans-1,3-Dimethylcyclohexane ΔE =	1.89	1.93	...

[a] The values for the various parameters requiring evaluation were chosen as described in detail in the text for the 1.10 carbon case, and they were in general different but similar in the different cases. [b] These values are for $\omega_{12} = 0$ and should be compared with the corresponding values (1.10 kcal) rather than the value given in Table III.

mented, and the segments are stored on disk and read into the core as required. The total storage used by the program is 35 K, of which 3 K are for data, and the rest is for the program itself. (The actual program would be somewhat smaller than this if it were not necessary to segment it, as there are redundancies caused by the fact that portions must be repeated in more than one segment.) The program contains 20,000 machine language instructions.

While the present paper is concerned with hydrocarbons only, the program is written in such a way as to deal with other atoms in addition. If a molecule contains more than one dipole, the net dipole of the molecule is also calculated, as are the interaction energies between dipoles. During the energy minimization, the changes in the dipole interaction energies are also included.

The running time required to treat a given molecule increases sharply with molecular size, decreases with symmetry, and decreases sharply with increasing accuracy of the initial structure. The positions of the carbon atoms in the molecule for the initial structure are calculated by hand, assuming standard bond angles and lengths. The coordinates for the hydrogens may also be inserted if known; otherwise the machine will position them in a standard optimum way from the known locations of the carbon atoms.

For small or symmetrical molecules, for which the starting geometry is a pretty good approximation to the final geometry, such as cyclohexane or *n*-butane, the running time is only a few minutes. For highly distorted molecules such as axial *t*-butylcyclohexane, or a conformation of decalin containing a boat for one ring and a chair for the other, and having no symmetry, the running time is of the order of 2–4 hr.

While in principle the present program could be expanded to deal with much larger molecules, the running times would become prohibitively long. While the time and space problems inherent in such calculations have been to some extent overcome, and can be more fully overcome by still more sophisticated programming, the availability of much larger and faster machines will very shortly minimize the importance of such sophisticated programs, and it would appear that it will be feasible to treat ordinary large organic molecules (with molecular sizes up to those of the common steroids and alkaloids) by this type of scheme within the next few years.

A separate series of programs was written for the calculations involving the hexane crystal. For these calculations, the molecular geometry of the hexane molecule was held invariant with bond lengths and angles as are experimentally known to exist. The van der Waals calculation was carried out as usual, inter- as well as intramolecularly. Initial crystal spacings (A, B, and C) were assumed, and the program determined the energy (E) and the slope ($\mathrm{d}E/\mathrm{d}A$) for different values of A in the vicinity until the value of A corresponding to $\mathrm{d}E/\mathrm{d}A = 0$ was located. Then holding A constant, the value of B corresponding to $\mathrm{d}E/\mathrm{d}B = 0$ was sought out. Then holding A and B constant, the energy was minimized with respect to C. Then the process was begun again, using as initial values for A, B, and C the values from the first iteration. The crystal studied contained 27 chains in a cubic array. Preliminary studies were carried out using a similar program which worked with only two chains, and it was found from the results with two chains, after some experience, that it was possible to fairly well predict the outcome of the 27 chain study. Other studies on larger blocks of chains showed that the crystal spacing obtained from 27 chains would vary by not more than 0.02 A along each axis from the distances that would be obtained from an infinite crystal. The heat of sublimation could not be obtained from such a small crystal, however. To obtain this quantity, a second program was developed which calculated the interaction energy for a central chain in an $n \times n \times n$ array. The heat of sublimation increased with increasing n, although the increase became very small as n became as large as 15. The heat of sublimation thus calculated is considered to be to well within 0.1 kcal of that which would be calculated for an infinite crystal.