Conformational Analysis. LX. Improved Calculations of the Structures and Energies of Hydrocarbons by the Westheimer Method[1,2]

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Abstract: The basic method of Westheimer (which utilizes classical mechanics to calculate the exact structures and conformational energies of molecules) has been further refined so that for a series of hydrocarbons, calculated energies may be used as a basis for the calculation of heats of formation without loss of correlation with the other experimental results. Previous predictions regarding the structures and energies of certain systems are revised, and additional systems are considered. The calculations predicted that *trans*-1,3-di-*t*-butylcyclohexane would exist as a conformational mixture of chair and boat forms, and variable-temperature infrared spectra showed two conformations differing in enthalpy by 0.4 kcal/mol.

One of the major problems in organic chemistry has always been the determination of the structures of organic molecules. While in earlier times a knowledge of the gross structural features of a molecule was adequate to satisfy the majority of the wants of organic chemists, the present day desire to interpret a variety of physical data, of which coupling constants in nmr spectra and amplitudes of circular dichroism curves might be mentioned as illustrative examples, requires a rather accurate knowledge of molecular geometry. Unfortunately, existing methods for the determination of complete accurate molecular geometries are cumbersome at best.

Conformational analysis can profitably utilize a more thorough knowledge of the relationship between conformational structure and energy. With such relationships, and a better knowledge of molecular structures, the more accurate prediction of the physical and chemical properties of organic molecules would be possible.

Our previous paper[3] discussed a general method for determining the conformations and the corresponding energies for a large number of saturated hydrocarbons. The method is basically that introduced by Westheimer, as subsequently modified by Hendrickson and Wiberg, and widely used by others.[4-12] We refer to the basis of the method as classical mechanics, because, although it contains certain semiempirical quantum mechanical features, we wish to distinguish it from the more legitimate type of quantum mechanical calculation now being done at varying levels of sophistication.[13-15] It should be noted that our calculations are for the gas phase. Corrections to the liquid phase are small, but can sometimes be made if desired.[3] Such a classical calculation does not allow for zero-point energy. The calculations could be done for 0°K, but then applications to systems for which experimental zero-point energy data are unavailable (which include most compounds of interest) would contain this uncertainty at 298°K. We have instead done the calculations for 298°K, for each different conformation, and considered conformational mixtures by standard thermodynamic methods. Thus it is necessary to assume that the other contributions to zero-point energy will be proportional to the number of bonds present for each type, and proportional for each branch in the chain, and hence will cancel out in the present treatment. This seems like the most useful way of reproducing the results of a quantum calculation by a classical one.

While our earlier calculations were shown to predict accurate geometries and satisfactory conformational energies for a wide variety of structures, and hence to be quite general, they really represented just a first approximation. It was felt that an important conclusion reached concerned the van der Waals radius of hydrogen needed for successful application of the method. The radius necessary was larger than commonly used in

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(1) Paper LIX: N. L. Allinger, W. Szkrybalo, and F. A. Van-Catledge, *J. Org. Chem.*, **33**, 784 (1968).

(2) This research was supported by Grant AM-5836 from the U. S. Public Health Service, National Institutes of Health.

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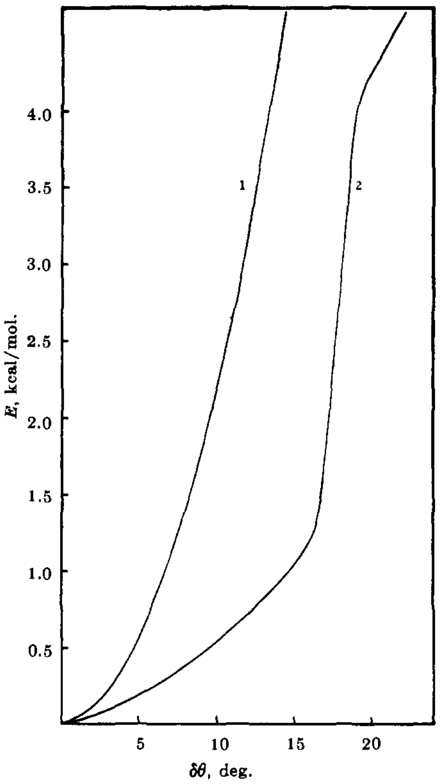

Figure 1. Bending functions: Hooke's law (1) and empirical (2).

calculations of this type; values in the range of 1.4–1.6 Å seemed suitable. We were not able to recommend a value for the radius of a tetrahedral carbon, however, as none of the calculated values of the properties or molecules studied were significantly affected by the value used for this quantity.

While the results of the previous paper gave encouragement regarding the approach to the problem, it suffered from one major deficiency in that heats of formation were not adequately calculated. The present work is primarily concerned with refining the method of calculation so that accurate heats of formation may be obtained, in addition to the other quantities previously discussed. As it turns out, the heats of formation of the group of hydrocarbons considered in our previous paper (normal and branched-chain alkanes, cyclohexane, and its mono- and dimethyl derivatives) can be well calculated by picking the appropriate value for the carbon radius. The value for the carbon radius required to give correct heats of formation varies inversely with the value used for the hydrogen radius. When 1.50 Å was used for the hydrogen radius, a carbon radius of 1.55 Å was found to be suitable. When a hydrogen radius 1.45 Å was used, a carbon radius of 1.65 Å gave good results. The latter combination was used for the work to be described herein, but the former set was also used for a substantial representative sample of compounds, and gave essentially the same results.

Now to be really useful for the calculation of heats of formation, the method must work not only for acyclic hydrocarbons and six-membered rings (which has been accomplished previously),[16] but it must also be satisfactory for at least moderately strained compounds, such as cyclopentanes and cycloheptanes. The first observation made was that these molecules, and other smaller and larger rings also, gave calculated heats of formation that were much too high. For cyclopentane, to bring its heat of formation into line, one can in principle either reduce the torsional energy or the bending energy. There is no satisfactory way to reduce the torsional energy, however, because then other experimental facts would not be adequately calculated. For example, reducing the torsional energy of hydrogen eclipsing hydrogen will lower the energy of cyclopentane, but it will also lower the ethane barrier, which is not desired. Lowering the torsional energy for carbon eclipsing carbon will likewise lower the energy of cyclopentane, but will also cause the calculated energy of the boat form of cyclohexane to be too low. Hence we must in fact reduce the bending energy of cyclopentane if we are to fit the heat of formation. We chose to change the form of bending function to one which does not increase as rapidly with angular deformation as the square term used earlier, and which is illustrated in Figure 1. Wiberg[17] has independently made the same type of change to fit cyclobutane. Alternatively, one might reduce the numerical values of the bending constants, and this approach has recently been used by Bixon and Lifson.[12] Having the part of the curve for energy *vs.* bending in the region of modest bending, and also having cyclobutane data to fit to, we placed a sigmoid curve through these points, and, in fact, the resulting curve looks like the curve Wiberg also arrived at independently.

One important improvement in the computer program which is utilized for the calculations was also made (see Appendix), which allows the energy minimum and corresponding geometry for a molecule to be located with much greater accuracy than did the earlier version.

We also made a further study of the hexane crystal by the methods described earlier. Whereas at that time we adjusted the ϵ value for carbon so as to give a heat of sublimation of 10 kcal/mol for the crystal, we subsequently decided that the best experimental value for this quantity is in fact 12–13 kcal/mol. The 10 kcal/mol is the heat of fusion of the crystal plus the heat of vaporization of the liquid at the boiling point (corrected for the presence of *gauche* conformations). Actually, to this number should be added the energy required to expand the liquid from its volume at the melting point to its volume at the boiling point (again correcting for *gauche* conformations). The latter quantity was calculated to be 3.0 kcal/mol from our crystal studies, or 2.0 kcal/mol from the equation of Watson.[18] Hence we feel the correct (experimental) value for the heat of sublimation of the hexane crystal is 12–13 kcal/mol at the melting point, and the calculations have been adjusted to give a value in that range. The hydrogen ϵ also had to be increased to keep the methylcyclohexane energy as large as desired.

The *A* and *B* spacings calculated for the hexane crystal were 4.39 and 4.86 Å, compared with the experimental values[19] of 4.17 and 4.70 Å.

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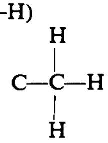
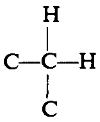
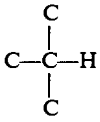
Table I. Parameters Used in the Calculations

van der Waals parameters for use in the Hill equation
C: r^* 1.65 Å; ϵ 0.040 kcal/mol
H: r^* 1.45 Å; ϵ 0.100 kcal/mol
Natural bond lengths
l_0(C–C) 1.513 Å (for primary and secondary)
1.509 Å (for tertiary and quaternery on either end)
l_0(C–H) 1.094 Å
Natural bond angles
θ_0(C–C–C) (neopentane) 109.5°
(isobutane) 111.0°
(propane) 109.8°
θ_0(C–C–H)


107.2°


108.6°


108.0°

θ_0(H–C–H) (–CH_3) 111.8°; (–CH_2–) 111.0°
Torsional parameters
$\omega_{H/H}$ 0.55; $\omega_{H/C}$ 0.98; $\omega_{C/C}$ 0.49

Table II. Structures and Energies for Model Hydrocarbons[a]

Compound	C–C length, Å	C–C–C angle, deg	Total E	Conf E(calcd)	Conf E(exptl)
Ethane staggered	1.527	110.1(CCH)	1.06	0	
Ethane eclipsed	1.533	112.1(CCH)	3.92	2.86	2.8–3.1
Propane staggered,staggered	1.526	112.4	1.02	0	
Propane staggered,eclipsed	1.527–1.533	113.4	4.39	3.37	3.4–3.6
Butane $\omega_{C/C}$ 180°	1.526–1.527	112.4	0.98	0	
Butane $\omega_{C/C}$ 120°	1.527–1.532	114.0	4.71	3.73	4.1 ± 0.4[b]
Butane $\omega_{C/C}$ 60°	1.527–1.530	115.1	1.65	0.67	
Butane $\omega_{C/C}$ 0°	1.528–1.538	116.7	5.30	4.32	
Isobutane	1.525	111.15	0.66		
Isopentane sym	1.525–1.530	111.0–117.5	1.98	0.44	0.1[c]
Isopentane asym	1.525–1.529	110.6–116.7	1.54	0	
Neopentane staggered	1.528	109.5	−0.10	0	
Neopentane eclipsed	1.528–1.534	109.1–109.8	4.54	4.64	4.2–4.8
2,3-Dimethylbutane sym	1.526–1.534	109.0–113.6	2.72	0	
2,3-Dimethylbutane asym	1.526–1.537	110.8–115.3	2.80	0.08	0[c]
Cyclohexane chair	1.526	111.3	1.06	0	
Cyclohexane boat	1.525–1.532	110.1–113.0	7.65	6.59	
Cyclohexane twist	1.523–1.529	110.4–112.3	5.92	4.86	4.8–5.9
Cyclohexane (≠)	1.519–1.542	109.8–118.7	12.10	11.04	10.8[d]
Equatorial methylcyclohexane	1.523–1.527	110.8–111.8	0.62	0	
Axial methylcyclohexane	1.524–1.527	110.2–112.9	2.39	1.77	1.9
Cyclobutane nonplanar[e]	1.521	89.1	26.93	0	
Cyclobutane planar	1.523	90.0	27.85	0.92	1.0[e]
Cyclopentane (half-chair)	1.522–1.527	103.0–106.3	7.35		
Cyclodecane (X-ray)[f]	1.527–1.534	117.3–121.8	16.29		

[a] Insofar as experimental data are available, all the calculated bond lengths and angles for this table are within 0.01 Å and 1.0° of the experimental (microwave) values, with the exception of cyclobutane and cyclodecane (see text), and allowing for the fact that C–C bond lengths are found to be 0.005–0.010 Å longer by diffraction measurements than by microwave determinations. For experimental results see references contained in ref 3, except as noted. [b] Butane rotational barrier: J. E. Piercy and M. G. S. Rao, *J. Chem. Phys.*, **46**, 3951 (1967). [c] G. J. Szasz and N. Sheppard, *ibid.*, **17**, 93 (1949). [d] Cyclohexane inversion barrier (≠); F. A. L. Anet and A. J. B. Bourn, *J. Amer. Chem. Soc.*, **89**, 760 (1967). [e] Cyclobutane: G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *ibid.*, **75**, 5634 (1953); A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961). [f] Cyclodecane: E. Huber-Buser, and J. D. Dunitz, *Helv. Chem. Acta*, **43**, 760 (1960); **44**, 2027 (1961); J. D. Dunitz, and K. Verkatesan, *ibid.*, **44**, 2033 (1961); J. D. Dunitz and H. P. Weber, *ibid.*, **47**, 951 (1964); M. H. Mladeck and W. Nowacki, *ibid.*, **47**, 1280 (1964); E. Huber-Buser and J. D. Dunitz, *ibid.*, **49**, 1821 (1966); M. Bixon, H. Dekker, J. D. Dunitz, H. Eser, S. Lifson, C. Mosselman, J. Sicher, and M. Svoboda, *Chem. Commun.*, 360 (1967).

The new values of all the parameters used in the present work are given in Table I.

The structures and conformational energies calculated for a variety of relatively simple molecules are given in Table II. For all but 2,3-dimethylbutane and the last four entries, calculations were reported in our earlier paper. For these compounds, the more recent modifications lead to no significant changes. Generally the agreement with the experimental values is within 0.2 kcal/mol for conformational energies, 0.01 Å for bond lengths, and 1° for bond angles where these quantities are known, with the exception of cyclobutane and cyclodecane. For the latter the calculated C–C–C angles are about 3° too large. For the former the calculated bond lengths are 0.02 Å too short. The poor calculated geometry of cyclodecane may be in part due to the fact that the experimental studies were carried out on substituted compounds in crystals. It seems that the error is sufficiently large and consistent to be real, however. For cyclobutane, since we do not count van der Waals repulsions between atoms bound to a common atom, there is no repulsion between the carbons of the molecule in the present treatment. While this approximation appears to be adequate for molecules in which the C–C–C angles are tetrahedral or larger, and is even good enough for cyclopentane (the repulsion energy being included as part of the angular deformation energy), it is not satisfactory for cyclobutane, because here the repulsion is large enough that the bonds actually stretch. Thus we can fit the energy adequately (by the adjustment of the bending function) but we cannot obtain good bond lengths with the present scheme. We are reluctant to add further empirical modifications here at this time, however, and will instead accept the errors noted. It should be pointed out that the energy of cyclobutane and its barrier to inversion agree with experimental values because the bending function was chosen in such a way as to yield agreement. We believe that the calculational behavior of cyclobutane thus chosen will be useful for predicting the behavior of substituted cyclobutanes. It may also be pointed out here that the present scheme is not adequate for the calculation of energies of cyclopropane or ethylene derivatives. The latter require different torsional functions, etc., while the former do not fit within the scheme because of the way in which bending is treated. The value of our bending function when the bond angle is 60° includes the effects of van der Waals repulsion; *i.e.*, it is appropriate for a propane molecule distorted to this geometry. It is not appropriate for cyclopropane, in which the atoms are now bound together. Thus olefins and cyclopropanes are not in principle amenable to treatment by the present scheme (as it now stands).

Heats of Formation

Considerable effort has been expended in the investigation of techniques which permit the calculation of heats of formation[16] which would correlate well with the values obtained from experimental calorimetric measurements.[20] The scheme to be utilized here may be considered as a bond energy scheme modified by group interactions, both bonded and nonbonded. In essence, constant empirical bond energies are assigned to C–C and C–H bonds, and these have the same energies in all molecules. However, additional enthalpy terms are added to (or subtracted from) the enthalpy resulting from the summation of the bond energy terms. These additional enthalpy terms are of three types. First of all, the enthalpy of the minimum energy structures resulting from the mechanical computation described above is added as a measure of the various interactions resulting from stretching, bending, torsion, and van der Waals forces. Secondly, enthalpy terms based on the types of branching within the given structure are added. These terms are empirically deduced from the heat of formation calculations for isobutane and neopentane. Physically, they would arise from at least two causes. First, the "bond energy" of a C–C bond may not really be a constant. The difference in electronegativity between carbon and hydrogen and the possibility that hybridization differences exist between primary, secondary, tertiary, and quaternary carbons may lead to bond energies which vary with substitution. In addition, the van der Waals interactions between atoms bound to a common atom doubtlessly depend on the atoms involved, and again should be different for primary, secondary, tertiary, or quaternary carbons. These numbers are large, although the differences between different atom combinations should be small (but probably not zero). A central force field treatment should be able to account for these van der Waals differences, but the valence force field as we use it can not. We take some arrangement of natural angles to have an energy of zero, and we can account for the energy change with deviations from those angles but our zero will be different in isobutane, say, from what it is in *n*-butane. Since the number of unknowns far exceeds the amount of available data, we have chosen to lump together these quantities (and perhaps others) as a single empirical amount to be added. No correction is needed for primary and secondary carbons, a term $H°_{\text{neo}}$ is added for each quaternary carbon present, and another term $H°_{\text{iso}}$ for each tertiary carbon.

Finally, the heat of formation which we calculate is for a single conformation. Experimental heats of formation (at 25°) often correspond to conformational mixtures, and in general the different conformations have different energies. The value of the heat of formation calculated for the stable conformation is therefore corrected to 25° by adding an amount of enthalpy $H°_{\text{conf}}$ (found by the usual methods of thermodynamics as required by the conformational situation). Thus

$$\Delta H_f° = \Sigma \text{ bond energies} + \Delta H°_{\text{calcd}} + \Sigma\Delta H°_{\text{neo}} + \Sigma\Delta H°_{\text{iso}} + \Delta H°_{\text{conf}} \quad (1)$$

The bond energies for C–C and C–H single bonds were arrived at by calculations involving the series of *n*-alkanes: *n*-pentane, *n*-hexane, and *n*-heptane (see Appendix). The enthalpies for each iso or neo grouping were assigned by inspection of the difference for representative compounds. A comparison of calculated and experimental heats of formation is shown in Table III, along with the various enthalpy terms involved in the summations.

Inspection of Table III shows the excellent correlation between calculation and experiment in almost all of the compounds studied. Only those cases wherein the difference between the calculated and experimental heats of formation is greater than 0.5 kcal/mol need be considered as significant problems, and there are only six compounds in this category. (Experimental values are lacking for a few of the compounds tabulated, and for these the calculated values are put forth as predictions.) The larger cycloalkanes (C_7, C_8, C_{10}) are the group for which the calculated and experimental values are consistently most seriously lacking in agreement. The inclusion of conformational corrections in these systems, if warranted, would only increase the errors which appear. Some trial calculations were made in which the bond lengths were allowed to be a little longer (by 0.002 Å for propane and isobutane). This change could be used to improve the heats of formation of 1,1-dimethylcyclohexane and cyclodecane by 0.3 and 0.2 kcal/mol, respectively without introducing any other errors. It was not, however, deemed worthwhile to repeat the calculations for the whole group of compounds for this small over-all improvement. There is currently no really satisfactory solution to the problem posed by the medium-ring systems, since the geometries as well as the energies seem to be inaccurate. Part of the problem could well be in the heats of vaporization used. These have to be estimated in some cases, as experimental values are lacking.

The pentalanes (or bicyclo[3.3.0]octanes) appear to represent the most serious disagreement between calculation and experiment in Table III. It is conceivable that *cis*-pentalane has been minimized to a conformation other than that of minimum energy (see below), but this would not explain the results with the *trans* compound as our calculations suggest a conformation for which the heat of formation is more negative than the experimental value. The experimental difference in the heats of formation between the *cis* and *trans* isomers of 6.0 kcal/mol rests on rather old heat of combustion data, however, and we feel that the experimental

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(20) API Tables, Project 44, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C.

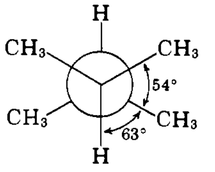
values are inaccurate. An experimental investigation of this point is currently in progress.

It is especially encouraging that moderately strained compounds such as cyclopentane, hydrindans, and cycloheptane have their heats of formation rather well calculated. Even the highly strained norbornane and cubane have their values accurately reproduced. The error in the case of adamantane seems more likely to be in the experimental value (especially from the heat of sublimation).

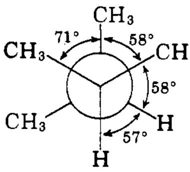
The average deviation of the calculated values from the experimental ones for all the compounds listed in Table III is 0.29 kcal/mol, and this may be compared with the 0.3 kcal/mol probable errors ordinarily expected in the experimental quantities under favorable conditions.[20]

Conformational Results

For those acyclic and cyclohexyl compounds listed in Table III, most of the calculated results other than heats of formation are similar to those reported in our earlier work.[3] Only one additional acyclic system will be considered at this time, and that is 2,3-dimethylbutane, which may exist in *anti* (Ia) and *gauche* (Ib) forms, with respect to the two methylene hydrogens. Our calculations indicate similar enthalpies for these two conformations (within 0.1 kcal/mol), a result which is contrary to usual (first-order) conformational thinking.[21,22] Because of the entropy factor, Ib is predicted to predominate in the equilibrium at room temperature.



Ia



Ib

The reason for the relative enthalpy values of Ia and Ib is quite instructive, and illustrates some of the limitations of the usual method of estimating stability by just counting up *gauche* interactions. The C–C–C bond angle at a tertiary center is considerably wider than tetrahedral. In the present case, this means that in Ia the dihedral angles between methyl groups are less than 60°—the methyls are forced closer to one another than they want to be. In Ib, the methyls are pushed apart, and the *gauche* hydrogens are forced together. The dihedral angles which are calculated to result at the energy minima are shown in the structures. While there are three *gauche* interactions in Ib, each of these is less severe than either of the two *gauche* interactions in Ia. The same type of phenomenon is predicted to play an important part in determining the conformational energies in many systems, in isopropylcyclohexane (see below) and cyclohexylamine, for example.

Examination of polymethylcyclohexane systems (Table IV) indicates many of the results are roughly in agreement with those reported earlier, and these will not be discussed. Some additional items have now been calculated. The enthalpy difference between diaxial and diequatorial 1,3-dimethylcyclohexane, for example, for which there is no direct experimental measurement, but for which a value of 5.5 kcal/mol has been deduced from other measurements,[23] is here calculated to be 5.41 kcal/mol. The enthalpy difference between *cis*-1-axial-1,3,5-triequatorial tetramethylcyclohexane and the *trans*-1,3-diaxial isomer is calculated to be 4.07 kcal/mol, while the experimental value[23] is 3.7 ± 0.2 (in the liquid phase).

A check was made to see if by any chance 1,1,3,3-tetramethylcyclohexane might prefer to go into a boat form to relieve the *syn*-axial methyl–methyl repulsion, but it was found that the chair form was still preferred by a comfortable margin (4.78 kcal/mol).

Conformational analysis of the ethylcyclohexane and isopropylcyclohexane systems was repeated as before,[3] and the data are presented in Tables IV and V. As indicated above, the three conformers of equatorial isopropylcyclohexane are roughly similar with respect to enthalpy, by analogy with the 2,3-dimethylbutane system and in contradiction to assumptions made in earlier thermodynamic analyses.[3,24] Because of the more refined minimization scheme used in the present work, these values are considered to be markedly superior to the earlier ones.

It was interesting to note that the magnitude of the enthalpy change as we go along the series methyl, ethyl, isopropyl goes down, but it is more than compensated for by an opposing entropy change. The $\Delta G°$ values for the groups which are calculated therefore go up and are in good agreement with the experimental values. The predictions made here regarding the enthalpy changes cannot be verified on the basis of existing experimental data, which are either not sufficiently accurate or else are only available on such complicated systems that much mathematical manipulation (and uncertainty) is required to deduce the desired quantities.

The conformational energy of the axial *t*-butyl group is now revised downward from our earlier estimate.[3] While the cyclohexane ring would still prefer to adopt a twist-boat conformation (4.86 kcal/mol) rather than exist in a chair form with the *t*-butyl group axial (5.41 kcal/mol), the two enthalpies are now of sufficiently similar magnitude that chair conformations may contribute significantly to the equilibrium mixture in simple axial *t*-butylcyclohexane systems, and additional substitution or strain might produce a predominantly chair conformation in some more complicated systems. The fact that the conformational enthalpy calculated for the axial *t*-butylcyclohexane (chair) is only 0.5 kcal above that of the cyclohexane twist-boat suggested that *trans*-1,3-di-*t*-butylcyclohexane should exist as a mixture of twist-boat (diequatorial) and chair (axial,equatorial) forms. The infrared spectrum of the compound[25] was therefore measured at +25 and at −125°. The compound was observed to set to a glass rather than to crystallize at the latter temperature. The spectrum was clearly that of a conformational mixture, as one group of bands increased in intensity at the expense of the other group as the temperature was lowered. The

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(21) 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 5; see, however, the discussion on tetrabromoethane on p 18.

(22) C. A. Kingsbury and D. C. Best, *J. Org. Chem.*, **32**, 6 (1967); C. A. Kingsbury and W. B. Thornton, *ibid.*, **31**, 1000 (1966); E. I. Snyder, *J. Amer. Chem. Soc.*, **88**, 1165 (1966).

(23) N. L. Allinger and M. A. Miller, *ibid.*, **83**, 2145 (1961).

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

(25) N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, **82**, 2393 (1960).

Table III. Heats of Formation[a]

Compound	CC	CH	Σ bond energies	$\Delta H°_{\mathrm{calcd}}$	$\Delta H°_{\mathrm{iso}}$	$\Delta H°_{\mathrm{neo}}$	$\Delta H°_{\mathrm{conf}}$	Calcd $\Delta H°$	Exptl $\Delta H°$	Calcd − exptl	Ref
Ethane	1	6	−21.08	+1.06	0	0	0	−20.02	−20.24	+0.22	
Propane	2	8	−26.18	+1.02	0	0	0	−25.16	−24.82	−0.34	
n-Butane	3	10	−31.28	+0.98	0	0	+0.28	−30.02	−30.15	+0.13	
n-Pentane	4	12	−36.38	+0.91	0	0	+0.46	−35.01	−35.00	−0.01	
n-Hexane	5	14	−41.48	+0.85	0	0	+0.67	−39.96	−39.96	0.00	
n-Heptane	6	16	−46.58	+0.77	0	0	+0.88	−44.93	−44.89	−0.04	
n-Octane	7	18	−51.68	+0.75	0	0	+1.05	−49.88	−49.82	−0.06	
Isobutane	3	10	−31.28	+0.66	−1.70	0	0	−32.32	−32.15	−0.17	
Isopentane	4	12	−36.38	+1.54	−1.70	0	+0.1	−36.44	−36.92	+0.48	
Neopentane	4	12	−36.38	−0.10		0	0	−40.08	−39.67	−0.41	
2,3-Dimethylbutane	5	14	−41.48	+2.72	−3.40	0	0	−42.16	−42.49	+0.33	
Cyclobutane	4	8	−20.40	+26.94	0	0	0	+6.54	+6.38	+0.16	*b,c*
Cyclopentane	5	10	−25.50	+7.35	0	0	0	−18.15	−18.46	+0.31	
Cyclohexane	6	12	−30.60	+1.06	0	0	0	−29.54	−29.43	−0.11	
Cycloheptane	7	14	−35.70	+7.87	0	0	0	−27.83	−28.34	+0.51	*c,e,f*
Cyclooctane	8	16	−40.80	+11.84	0	0	0	−28.96	−30.06	+1.10	*c,e,f*
Cyclodecane	10	20	−51.00	+16.29	0	0	0	−34.71	−36.29	+1.58	*g*
Methylcyclobutane	5	10	−25.50	−22.27	−1.70	0	+0.23	−4.70			
cis-1,3-Dimethylcyclobutane	6	12	−30.60	+22.40	−3.40	0	+0.25	−11.35			
trans-1,3-Dimethylcyclobutane	6	12	−30.60	+22.98	−3.40	0	0	−11.02			
Methylcyclopentane	6	12	−30.60	+6.88	−1.70	0	+0.32	−25.10	−25.50	+0.40	
cis-1,3-Dimethylcyclopentane	7	14	−35.70	+6.89	−3.40	0	+0.1	−32.11	−32.47	+0.36	
trans-1,3-Dimethylcyclopentane	7	14	−35.70	+7.07	−3.40	0	+0.1	−31.93	−31.93	+0.00	
Methylcyclohexane	7	14	−35.70	+0.62	−1.70	0	+0.1	−36.68	−36.99	+0.31	
1,1-Dimethylcyclohexane	8	16	−40.80	+2.04	0	−3.60	0	−42.36	−43.26	+0.90	
cis-1,2-Dimethylcyclohexane	8	16	−40.80	+2.69	−3.40	0	0	−41.51	−41.15	−0.36	
trans-1,2-Dimethylcyclohexane	8	16	−40.80	+1.21	−3.40	0	0	−43.09	−43.02	−0.07	
cis-1,3-Dimethylcyclohexane	8	16	−40.80	+0.17	−3.40	0	0	−44.03	−44.16	+0.13	
trans-1,3-Dimethylcyclohexane	8	16	−40.80	+1.98	−3.40	0	0	−42.22	−42.20	−0.02	
cis-1,4-Dimethylcyclohexane	8	16	−40.80	+1.87	−3.40	0	0	−42.33	−42.22	−0.11	
trans-1,4-Dimethylcyclohexane	8	16	−40.80	+0.16	−3.40	0	0	−44.04	−44.12	+0.08	
cis-1,3,5-Trimethylcyclohexane	9	18	−45.90	−0.28	−5.10	0	0	−51.28			
1,1,3,3-Tetramethylcyclohexane	10	20	−51.00	+5.72	0	−7.20	0	−52.48			
Ethylcyclohexane	8	16	−40.80	+1.59	−1.70	0	+0.13	−40.78	−41.05	+0.27	
Isopropylcyclohexane	9	18	−45.90	+3.14	−3.40	0	+0.17	−45.99			
t-Butylcyclohexane	10	20	−51.00	+4.81	−1.70	−3.60	0	−51.49			*d*
cis-Pentalane	9	14	−29.92	+14.50	−3.40	0	0	−18.82	−22.3	+3.5	*l*
trans-Pentalane	9	14	−29.92	+15.77	−3.40	0	0	−17.55	−16.3	−1.25	*l*
cis-Hydrindan	10	16	−35.02	+8.43	−3.40	0	0	−29.99	−30.41	+0.42	*k*
trans-Hydrindan	10	16	−35.02	+6.77	−3.40	0	0	−31.65	−31.45	−0.20	*k*
cis-8-Methylhydrindan	11	18	−40.12	+9.00	−1.70	−3.60	0	−36.42			
trans-8-Methylhydrindan	11	18	−40.12	+9.66	−1.70	−3.60	0	−35.76			
cis-Decalin	11	18	−40.12	+2.75	−3.40	0	0	−40.77	−40.45	−0.32	*j*
trans-Decalin	11	18	−40.12	+0.02	−3.40	0	0	−43.50	−43.54	+0.04	*j*
cis-9-Methyldecalin	12	20	−45.22	+5.10	−1.70	−3.60	0	−45.42	−58.31	*m*	*m*

Table III (*Continued*)

trans-9-Methyldecalin	12	20	−45.22	+4.53	−1.70	−3.60	0	−45.99	−59.70	*m*	*m*
Cubane	12	8	+2.72	+159.72	−13.70	0	0	+148.7	+148.7	0.00	*h*
Norbornane	8	12	−24.82	+12.01	−3.40	0	0	−16.2	−15.8	−0.4	*i*
Adamantane	12	16	−29.24	+1.42	−6.80	0	0	−34.62	−33.0	−1.62	*n*
Bicyclo[2.2.2]octane	9	14	−29.92	+15.77	−3.40	0	0	−17.55			
Bicyclo[3.3.1]nonane	10	16	−35.02	+7.40	−3.40	0	0	−31.02			

[a] Parameters: C–C = +2.89; C–H = −3.995; iso = −1.70, neo = −3.60 (kcal/mol). Unless otherwise specified, experimental enthalpies are from ref 20. All values (in kcal/mol) are for the gas phase at 25°. [b] G. W. Rathjens, Jr., and W. D. Gwinn, *J. Amer. Chem. Soc.*, **75**, 5629 (1953). [c] S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, **71**, 261 (1952). [d] A liquid-phase heat of combustion is reported by L. I. Belenyessy, B. J. Gudzinowicz, R. C. Reid, and J. O. Smith, *J. Chem. Eng. Data*, **7**, 66 (1962). [e] R. Spitzer and H. M. Huffman, *J. Amer. Chem. Soc.*, **69**, 211 (1947). [f] H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, and G. Waddington, *ibid.*, **78**, 5469 (1956). [g] Heat of combustion (liquid phase) from J. Coops, H. van Kamp, W. A. Lambregts, B. J. Visser, and H. Dekker, *Rec. Trav. Chim.*, **79**, 1226 (1960). Heat of vaporization at 25° estimated from ref *c* and O. N. Kachinskaya, *Russ. J. Phys. Chem.*, **34**, 654 (1960); *Chem. Abstr.*, **56**, 12376*i* (1962). [h] B. D. Kybett, S. Carrol, P. Natalis, D. W. Bonnell, J. L. Margrave, and J. L. Franklin, *J. Amer. Chem. Soc.*, **88**, 626 (1966). [i] Crystalline heat of formation at 25° from A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963). Heat of fusion assumed to be 4.0 kcal/mol and heat of vaporization calculated as 2.2 kcal/mol from Trouton's rule. Involves serious approximations. [j] D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, **64**, 1723 (1960). [k] C. C. Browne and F. D. Rossini, *ibid.*, **64**, 927 (1960). [l] Calculated from a gas-phase heat of combustion (at an unspecified temperature) determined by J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936). [m] Liquid-phase heat of formation reported by W. G. Dauben, O. Rohr, A. Labbauf, and F. D. Rossini, *J. Phys. Chem.*, **64**, 283 (1960), listed as the experimental value for $\Delta H_f°$. No attempt to estimate heat of vaporization. [n] W. K. Bratton, I. Szilard, and C. A. Cupas, *J. Org. Chem.*, **32**, 2019 (1967).

Table IV. Calculated Structures and Energies of Alkylcyclohexanes[a]

Compound	C–C length, Å	C–C–C angle, deg	Total *E*, kcal/mol	Conf *E*(calcd), kcal/mol
1,1-Dimethyl	1.525–1.530	108.5–114.4	2.04	
cis-1,2-Dimethyl	1.523–1.529	110.6–115.4	2.64	1.43
trans-1,2-Diequatorial dimethyl	1.523–1.530	110.5–114.1	1.21	0
trans-1,2-Diaxial dimethyl	1.525–1.529	111.1–113.9	3.90	2.69
cis-1,3-Diequatorial dimethyl	1.523–1.526	110.8–112.3	0.17	0
cis-1,3-Diaxial dimethyl	1.525–1.527	110.2–116.1	5.58	5.41
trans-1,3-Dimethyl	1.522–1.529	110.2–113.3	1.99	1.82
cis-1,4-Dimethyl	1.522–1.526	110.3–112.8	1.87	1.71
trans-1,4-Dimethyl	1.522–1.527	110.8–111.8	0.16	0
cis-1,3,5-Triequatorial trimethyl	1.522–1.527	110.9–111.9	−0.28	0
trans-1,3,5-Diequatorial trimethyl	1.522–1.529	110.1–113.4	1.61	1.89
1,1,3,3-Tetramethyl chair	1.526–1.532	108.3–120.9	5.72	0
1,1,3,3-Tetramethyl twist-boat	1.523–1.536	106.2–119.8	10.50	4.78
1-Axial-1,3,5-triequatorial tetramethyl	1.523–1.531	106.6–115.1	1.43	0
1,3-Diaxial-3,5-diequatorial tetramethyl	1.523–1.532	105.2–118.9	5.50	4.07
Equatorial sym-ethyl	1.523–1.531	110.1–118.6	2.26	0.67
Equatorial asym-ethyl	1.523–1.530	110.3–116.6	1.59	0
Axial ethyl	1.524–1.531	109.2–117.0	3.37	1.78
Equatorial sym-isopropyl	1.523–1.537	108.6–114.4	3.14	0
Equatorial asym-isopropyl	1.524–1.537	109.8–115.3	3.33	0.19
Axial isopropyl	1.526–1.535	106.7–115.9	4.66	1.52
Equatorial *t*-butyl	1.522–1.544	106.2–115.7	4.81	0
Axial *t*-butyl	1.524–1.548	105.8–120.6	10.22	5.41

[a] For pertinent references see ref 3. All calculated values are for the gas phase at 25°.

Table V. Calculated Equilibrium Data for the Reaction Equatorial–Axial Alkylcyclohexane[a] (T = 298°K)

	R =			
	Me	Et	*i*-Pr	*t*-Bu
$\Delta H°$	1.77	1.69	1.40	5.41
$\Delta S°$	0	−0.61	−2.18	0
$\Delta G°$	1.77	1.87	2.05	5.41

[a] For pertinent references see ref 3. All compounds are in the gas phase at 25°.

enthalpy difference between the conformations was calculated from the band areas in the usual way.[26] There were three separate pairs of bands which were suitable for the purpose, and the mean enthalpy difference obtained was 0.37 ± 0.20 kcal/mol, in remarkable agreement with the predictions. Since there is no definite information as to which set of bands belongs to which conformation, only the absolute value of the experimental enthalpy is known; however, from the entropy of isomerization to the *cis* isomer, the boat must be the predominant form.[25]

The remainder of this paper will be devoted primarily to hydrocarbon systems not previously considered in our work,[3] particularly cyclobutanes, cyclopentanes, medium-ring cycloalkanes, and various fused and bridged systems. As indicated in Tables II and III, our calculations suggest that a nonplanar cyclobutane ring with a 20° puckering (14° C–C–C dihedral angle) is 0.92

(26) Reference 21, p 147.

Table VI. Calculated Structures and Energies of Cyclobutanes and Cyclopentanes[a]

Compound		C–C length, Å	C–C–C angle, deg	Total *E*, kcal/mol	Conf *E*, kcalmol
Equatorial methylcyclobutane	A[b]	1.518–1.523	84.8–119.9	22.43	0.16
Equatorial methylcyclobutane	B[b]	1.515–1.527	84.2–118.2	22.27	0
Axial methylcyclobutane	A	1.519–1.522	85.2–114.0	22.83	0.56
Axial methylcyclobutane	B	1.516–1.527	85.2–114.1	23.21	0.94
cis-1,3-Diequatorial dimethylcyclobutane	A	1.518–1.520	85.2–120.1	22.87	0.47
cis-1,3-Diequatorial dimethylcyclobutane	B	1.520–1.521	83.9–118.0	22.40	0
cis-1,3-Diaxial dimethylcyclobutane	A	1.520–1.522	85.4–115.5	24.20	1.80
cis-1,3-Diaxial dimethyl	B	1.519–1.523	84.5–114.7	24.27	1.87
trans-1,3-Dimethylcyclobutane	A	1.516–1.522	84.3–119.9	22.98	0
trans-1,3-Dimethyl	B	1.518–1.524	83.3–118.0	22.98	0
Cyclopentane half-chair		1.522–1.527	103.0–106.3	7.35	0
Cyclopentane envelope		1.521–1.528	102.5–106.1	7.39	0.04
Cyclopentane planar		1.528	108.0	13.71	6.36
1-Methylcyclopentane	C[c,d]	1.521–1.525	102.6–113.3	7.73	0.85
2-Equatorial methylcyclopentane	C	1.520–1.526	102.8–113.6	7.35	0.47
2-Axial methylcyclopentane	C	1.521–1.528	101.82–113.1	8.48	1.60
3-Equatorial methylcyclopentane	C	1.517–1.527	103.2–114.9	7.01	0.13
3-Axial methylcyclopentane	C	1.521–1.528	101.4–112.9	7.92	1.04
1-Equatorial methylcyclopentane	E[c,d]	1.518–1.529	103.1–114.5	6.88	0
cis-2,5-Diequatorial dimethylcyclopentane	E[d]	1.518–1.527	103.8–114.4	8.74	1.85
cis-1,3-Equatorial dimethylcyclopentane	C[d]	1.517–1.526	102.8–115.5	7.11	0.22
cis-2,4-Diequatorial dimethylcyclopentane	C	1.517–1.527	103.2–115.1	6.89	0
cis-2,5-Equatorial,axial dimethylcyclopentane	C	1.520–1.527	102.2–104.9	8.34	1.45
trans-1,3-Equatorial dimethylcyclopentane	C	1.517–1.525	102.6–115.4	7.07	0
trans-2,5-Diequatorial dimethylcyclopentane	C	1.520–1.523	102.8–114.5	7.17	0.10
trans-2,5-Dimethylcyclopentane	E	1.518–1.527	102.2–115.9	8.40	1.33
trans-2,4-Dimethylcyclopentane	C	1.519–1.527	101.4–115.5	8.00	0.93

[a] See text for pertinent references. All compounds in gas phase at 25°. [b] See text for explanation of A and B. [c] C = half-chair, E = envelope. [d] Numbered as in structures II and III.

kcal/mol more stable than the planar form.[18,27,28] While a planar cyclobutane ring has been observed in crystal studies[29] (because of packing?) all gas- and liquid-phase determinations[27] seem to indicate nonplanarity with a puckering of 20–35°. The exact angle of puckering in cyclobutane itself must still be considered to be open to some question, since substitution *per se* would most likely change this quantity to some extent. We have also investigated methylcyclobutane and the *cis*- and *trans*-1,3-dimethylcyclobutanes (Table VI). Because of puckering, the methyl group can occupy an axial or an equatorial position, and the *cis*-1,3-dimethyl derivative can exist in distinct diequatorial and diaxial conformations analogous to cyclohexane derivatives.[30]

According to our calculations, while cyclobutane itself is what we might call a puckered square, substituted cyclobutanes tend to be of a puckered diamond shape, with two of the diagonally opposite interior ring angles enlarged at the expense of the other two. The substituents may then be located on a ring corner with a smaller ring angle (case A) or a larger ring angle (case B). Each of these possibilities has been considered, (Table VI), although not exhaustively. The results indicate that there is a preference for the equatorial position, but it only amounts to about 0.5 kcal/mol. The energy difference between equatorial conformations A and B is negligible. That the axial methyl would be less favorable than the equatorial by a small amount was predicted and rationalized earlier.[30] The greater stability for the *cis*-1,3-diequatorial dimethylcyclobutane, the isomer with the least nonbonded interactions, is also as anticipated. There is earlier experimental evidence which has led to the same conclusion.[30]

Turning next to cyclopentane and its methyl derivatives, Table VI indicates the close similarity in the energies of the half-chair (II) and envelope (III) forms of cyclopentane itself, as suggested by Pitzer,[31] established

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(27) See footnote on cyclobutane in Table III, and also J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3884, 3891 (1965), and references therein.

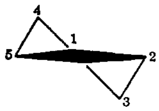
(28) W. G. Rothschild and B. P. Dailey, *J. Chem. Phys.*, **36**, 2931 (1962); A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961).

(29) I. L. Karle, J. Karle, and K. Britts, *J. Amer. Chem. Soc.*, **88**, 2918 (1966); T. N. Margulis, *Acta Cryst.*, **19**, 857 (1965); J. N. Margulis and M. S. Fischer, *J. Amer. Chem. Soc.*, **89**, 233 (1967).

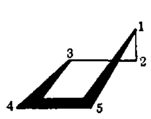
(30) N. L. Allinger and L. A. Tushaus, *J. Org. Chem.*, **30**, 1945 (1965).

(31) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2483 (1947); K. S. Pitzer and W. E. Donath, *ibid.*, **81**, 3213 (1959).

by McCullough,[32] and calculated previously by Hendrickson.[6] For the methylcyclopentane conformations (numbered as shown in II and III where the two substituents on C-1 of the half-chair II are identical in energy), the present calculations indicate that the lowest energy form is that of the envelope with the methyl group at the "tip of the flap" as was suggested earlier.[31,33] It was also suggested[31,33] that the most stable conformation of the *cis*-1,3-dimethylcyclopentane would be the envelope with the methyls in the 2,5-diequatorial positions of III, but our calculations do not bear this out (Table VI).



II



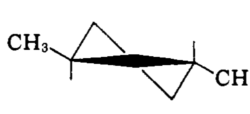
III

Considering the methylcyclopentane conformations in which the ring is roughly a half-chair, on carbons 2 and 3 there are equatorial positions roughly in the plane of the ring and corresponding to low energies, and axial positions of higher energy. The isoclinal positions at C-1 are identical with one another and with intermediate energy. These values are summarized in Table VII.

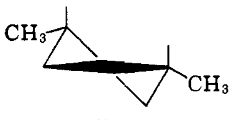
Table VII. The Relative Energies of Methyl Substitution in the Half-Chair Form of Cyclopentane

Position of methyl	Rel energy, kcal/mol
1	0.72
2 equatorial	0.34
3 equatorial	0.00
2 axial	1.47
3 axial	0.91

From these values it is clear that the 3 equatorial is the most favorable, and a 1,3-equatorial conformation will be a good one for either a *cis* or a *trans* isomer, with a total relative energy of 0.72 kcal/mol (assuming additivity). The *trans* isomer cannot do much better than this, a 2,5-diequatorial conformation with an energy of 0.68 being the best one available to it. For the *cis* isomer, a 2,4-diequatorial conformation is available, with a calculated energy of only 0.34 kcal/mol. Thus a first-order treatment of the type commonly used in cyclohexane indicates the *cis* isomer should be some 0.3 kcal/mol lower in enthalpy than the *trans*, in satisfactory agreement with experiment. A complete calculation indicates that, as predicted from the methylcyclopentane calculations (Table VII), the *cis*-2,4-diequatorial conformation is the most favorable. The best *trans* conformation proves to be 1,3 equatorial, but this is only 0.1 kcal better than the 2,5 diequatorial. The *cis* isomer is calculated to be of lower enthalpy than the *trans*, although the calculated difference is smaller than the experimental difference by 0.36 kcal/mol. The entropies of the two isomers should be essentially the same, because they each have the same number of conformations with similar energy differences. Although the *trans* isomer is *dl* and the *cis* is *meso*, the instantaneous conformations of the *cis* are *dl*, and hence no difference in the entropy of mixing is expected from this source (analogous to the 1,2-dimethylcyclohexanes). Thus the agreement with experiment is quite satisfactory, and shows in addition that a first-order treatment as used in cyclohexane should also be applicable to cyclopentane systems—at least as long as the substituents are small and nonpolar.



trans-2, 5-diequatorial



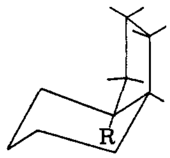
cis-2, 4-diequatorial

Our studies of medium-ring cycloalkanes are not as exhaustive as those of other workers.[6,7,12] As indicated in Tables III and VIII, the twist-chair structure of cycloheptane is in reasonable agreement with the heat of formation of this compound, although we have not examined other conformations. Similarly, the chair-boat form of cyclooctane is the most favorable of those we have thus far considered (Table III)[34] as was previously predicted by both Wiberg and Hendrickson. The crown structures are, according to our calculations, all very similar in energy, and some 2 kcal/mol above the boat-chair.

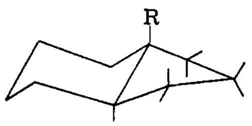
In the case of cyclodecane[6,7,12,35] the conformation known to exist in crystalline derivatives from X-ray studies[36] was the only one considered. The minimum energy geometry we obtained was appreciably distorted from that known, and the energy was too high by 1.6 kcal/mol. Further studies on these medium-ring cycloalkanes are clearly needed, but have been postponed for the present so as to allow investigation of a wider range of systems.

Decalin has been the subject of previous calculations,[3,10] and the results obtained here are comparable with both earlier calculations and with experiment. Likewise the results for 9-methyldecalin are good.

For hydrindan there are various conformations possible in principle for the five-membered ring. No experimental structural data are available. We have not examined these exhaustively, but find that the *cis* and *trans* isomers have conformations of minimum energy as indicated by structures IVa and Va. The *trans* isomer has a twofold axis of symmetry and the cyclopentane ring has a half-chair conformation. The compound has a calculated heat of formation 0.2 kcal too low, and the structure probably represents an absolute minimum. The *cis* isomer has a calculated energy



IVa, R = H
b, R = Me



Va, R = H
b, R = Me

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[32] J. P. McCullough, *J. Chem. Phys.*, **29**, 966 (1958); J. P. McCullough, R. E. Pennington, J. C. Smith, I. A. Hossenlopp, and G. Waddington, *J. Amer. Chem. Soc.*, **81**, 5880 (1959).

[33] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Section 9-1.

[34] J. D. Dunitz and A. Mugnoli, *Chem. Commun.*, 166 (1966); A. Almenningen, O. Bastiansen, A. Haaland, and H. M. Seip, *Angew. Chem. Intern. Ed. Engl.*, **4**, 819 (1965); F. A. L. Anet and M. St. Jacques, *J. Amer. Chem. Soc.*, **88**, 2585, 2586 (1966); A. Almenningen, O. Bastiansen, and H. Jensen, *Acta Chem. Scand.*, **20**, 2689 (1966); F. A. L. Anet, Twentieth National Organic Chemistry Symposium, Burlington, Vermont, June 1967.

[35] M. Saunders, *Tetrahedron*, **23**, 2105 (1967).

[36] See footnote on cyclodecane in Table II.

Table VIII. Calculated Structures and Energies of Medium-Ring Cycloalkanes and Bridged and Fused Cyclic Hydrocarbons[a]

Compound	C–C length, Å	C–C–C angle, deg	Total *E*, kcal/mol	Conf *E*, kcalmol
Cycloheptane twist-crown	1.527–1.528	114.8–116.1	7.87	
Cyclooctane chair-boat	1.526–1.530	116.8–119.5	11.84	0
Cyclooctane regular-crown	1.529	119.5	13.93	2.09
Cyclooctane twist-crown	1.527–1.529	119.0–119.2	14.04	2.20
Cyclooctane stretched-crown	1.527–1.529	118.1–119.9	14.09	2.25
Cyclodecane (X-ray)	1.527–1.534	117.3–121.8	16.29	
cis-Decalin	1.523–1.526	110.3–113.9	2.75	2.73
trans-Decalin	1.523–1.526	111.0–112.0	0.02	0
cis-9-Methyldecalin	1.524–1.533	106.7–116.7	5.10	0.57
trans-9-Methyldecalin	1.523–1.530	108.2–114.4	4.53	0
cis-Hydrindan	1.518–1.527	101.4–119.3	8.43	1.66
trans-Hydrindan	1.515–1.529	102.1–118.7	6.77	0
cis-8-Methylhydrindan	1.519–1.528	101.0–117.7	9.00	0
trans-8-Methylhydrindan	1.516–1.530	99.4–120.1	9.66	0.66
cis-Pentalane	1.514–1.527	102.9–115.7	14.50	0
trans-Pentalane	1.514–1.532	100.7–126.1	15.77	1.27
Norbornane	1.513–1.526	93.7–110.4	12.01	
Bicyclo[2.2.2]octane	1.522–1.529	109.1–110.1	8.92	
Bicyclo[3.3.1]nonane chair	1.519–1.528	107.4–115.9	7.40	0
Bicyclo[3.3.1]nonane chair-boat	1.520–1.529	107.8–114.5	10.13	2.73
Adamantane	1.521	107.8–110.8	1.42	

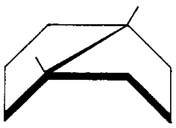
[a] See text and ref 3 for references to the experimental work. All data for 25° and gas phase.

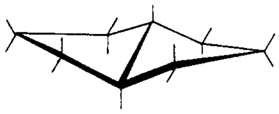
which is 0.4 kcal too high, and the conformation found has the cyclopentane ring in an envelope conformation. A conformation of slightly lower energy may exist, and the calculated geometry may correspond to a local minimum. The calculations predict the *trans* isomer is of lower enthalpy than the *cis* by 1.66 kcal, while the experimental value is 1.04 ± 0.52 kcal/mol from heat of combustion[37] and 1.07 ± 0.09 kcal/mol from liquid-phase isomerization studies (at 552°K).[38]

The energetics of the 8-methylhydrindan systems have not been studied directly, but some roundabout conclusions suggest that here the *cis* isomer is the more stable,[39] and in the present work the *cis* isomer is in fact calculated to be more stable by 0.66 kcal/mol.

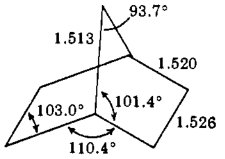
According to our calculations, the cyclopentane ring in the 8-methylhydrindans has qualitatively the same shape as it does in the parent hydrindans: an envelope for the *cis* isomer IVb, and a half-chair for the *trans* Vb. Some substituted *trans*-8-methylhydrindan structures have been determined by X-ray crystallography on steroidal compounds.[40] Three different kinds of conformations have been found; the type which occurs depends on the exact system. No experimental data exist regarding the systems we have studied, and we are not now able to do calculations for any of the systems for which data do exist, because our computer is too small and too slow. Hence, while our results concerning these systems seem reasonable, no comparison with experiment is possible at present.

The conformation calculated for *cis*-pentalane (VI) has both rings in envelope forms, and there is a C_2 axis perpendicular to the general plane of the rings. The *trans*-pentalane (VII) has both rings in the half-chair conformation, and it has a C_2 axis in the general plane of the rings.

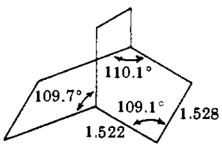

VI


VII

Finally, a series of bicyclic hydrocarbons has been studied. Norbornane (VIII) is of special interest because of extensive physical[41] and chemical[42] studies of derivatives and many earlier calculations at various levels of sophistication.[5,10,43] While an electron diffraction study has been carried out on the parent hydrocarbon,[44] these results have never been directly published in detail. Allowing for the fact that our bond lengths correspond to microwave values and are shorter, the agreement between our calculation and experiment is not completely satisfactory, but it is not certain to what extent (if any) the disagreement is due to calculational deficiencies.



VIII



IX

No detailed structural determinations exist for either bicyclo[2.2.2]octane (IX) or bicyclo[3.3.1]nonane (X), although both species have been the subject of calculations.[11] The results of our calculations on a bicyclo-

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(37) C. C. Browne and F. D. Rossini, *J. Phys. Chem.*, **64**, 927 (1960).

(38) N. L. Allinger and J. L. Coke, *J. Amer. Chem. Soc.*, **82**, 2553 (1960).

(39) For a discussion and references see N. L. Allinger, *J. Org. Chem.*, **21**, 915 (1966); N. L. Allinger and J. L. Coke, *J. Amer. Chem. Soc.*, **82**, 2553 (1960).

(40) F. V. Brutcher, Jr., and E. J. Leopold, *ibid.*, **88**, 3156 (1966), and earlier papers; H. J. Geise and C. Romers, *Acta Cryst.*, **20**, 257 (1966), and earlier papers.

(41) G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 1976 (1961); D. A. Bruechner, T. A. Hamer, J. M. Robertson, and G. A. Sim, *ibid.*, 799 (1962); A. F. Cesur and D. F. Grant, *Acta Cryst.*, **18**, 55 (1965); A. C. MacDonald and J. Trotter, *ibid.*, **18**, 243 (1965); **19**, 456 (1965).

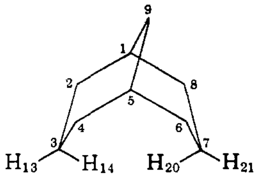
(42) For a review, see G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

(43) H. Krieger, *Suomen Kemistilehti*, **B31**, 348 (1958); **B32**, 109 (1959); C. F. Wilcox, Jr., *J. Amer. Chem. Soc.*, **82**, 414 (1960).

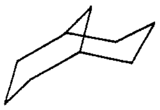
(44) Footnote 59 of ref 10 (V. Schoemaker and W. C. Hamilton); W. C. Hamilton, Ph.D. Thesis, California Institute of Technology, 1954.

[2.2.2]octane structure containing D_{3h} symmetry[45] are shown in structure IX.

Because of the extreme strain in the chair form of bicyclo[3.3.1]nonane (Xa),[21] both the double-chair and chair-boat (Xb) structures have been investigated. As indicated in Table VIII, conformation Xa, the double-chair, is distinctly more favorable (2.7 kcal/mol).[46] Most interesting are the deformations the double-chair undergoes to relieve the repulsion between the two close hydrogens on the underside. The distance C_3–C_7 increased from what would have been its normal value of 2.56 to 3.18 Å. By compressing the angle $H_{13}C_3H_{14}$ to 95.2°, the H_{14}–H_2 distance was finally increased from 0.81 to 2.25 Å.



Xa



Xb

Conclusions

The results presented herein reinforce our earlier conclusions[3] that the method of theoretical calculation is truly competitive with spectroscopic and diffraction methods for the accurate determination of molecular structure. To this we now add that classical mechanical techniques also permit the accurate prediction of both absolute and relative thermodynamic properties in spite of the many approximations involved in the approach as it now stands (spherical atoms, empirical bending function, one basic van der Waals function for all interactions, etc.).

The physical model used is clearly a very good, but not perfect, one for the prediction of the structures and thermodynamic properties of hydrocarbons. As indicated earlier, we believe the parameters could be refined slightly to give a small improvement, but it does not appear that any real significant improvement is possible without more fundamental changes. Hence, the problem divides in two at this point. One path is to improve still further the results described herein, and this appears to require one or more rather fundamental changes in method, and this aspect of the problem is now being pursued along various lines. The second point of attack now is to extend the existing (very good but not perfect) approach to compounds other than hydrocarbons, and such an extension is also in progress.

Appendix

The computational scheme used in the present work is similar to that described by Wiberg,[7] and the basic ideas and principles have been thoroughly discussed previously.[3,7] Briefly, atoms bound together are assigned a natural bond length which corresponds to the energy minimum on a Hooke's law relationship. Bond angles between given atoms are taken to have natural values which are dependent on the environment about the central atom in each angle,[47] and changes from this natural value are converted to energies by use of spectroscopic force constants and an empirical function (see below). Interaction force constants between bending and stretching deformations are neglected, and van der Waals forces are considered only for those atoms which are not bound to one another or to a common atom. Spherical atoms are assumed, and Hill's function[49] is used for the nonbonded interactions. The van der Waals parameters provide a portion of the torsional barriers, and the remainder of this barrier is added as a torsional quantity which depends on the types of atoms involved in the dihedral angle under consideration. The total energy, E_T, is then calculated for each molecule by an energy minimization scheme involving all of the energy components in the summation in eq 2. Only those changes made since our previous

$$E_T = E_{\text{stretch}} + E_{\text{bend}} + E_{\text{VDW}} + E_{\text{torsion}} \quad (2)$$

paper[3] will be discussed herein.

The major deficiency in the program described earlier was that energies were not minimized with a sufficiently high degree of accuracy. It was found that the original Wiberg program, which moves atoms in 0.01-Å increments in seeking energy minima, led to different geometries, depending on what starting geometry was chosen. Errors of up to 0.005 Å in each coordinate of each atom resulted, which lead to errors as much as 0.6 kcal/mol for a molecule like *n*-pentane. In addition, the original version of the method continued the calculation until the energy improvement fell below 0.02 kcal/mol per iteration. The program did not deal adequately with torsional motions because of the rather large increments and the necessity of a sizeable energy improvement at each iteration. The minimization program was therefore changed to use increments of 0.002 Å and a minimum energy improvement of 0.002 kcal/mol. These changes appear to have eliminated the obvious torsional problems, and the program now yields very similar calculated results from any starting geometry, as the atomic coordinates are now located to within 0.001 Å of the minimum energy position, and the final energies are reproducible to within about 0.1 kcal/mol. Further, the program now deals adequately with torsion in a molecule like *gauche* butane, slowly rotating the methyl groups in small increments to the positions of minimum energy.[50]

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(45) J. J. Macfarlane and I. G. Ross, *J. Chem. Soc.*, 4169 (1960); A. H. Nethercot and A. Javan, *J. Chem. Phys.*, **21**, 363 (1953); however, see P. Bruesch and H. H. Gunthard, *Spectrochim. Acta*, **22**, 877 (1966), and R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957).

(46) For structural studies of related molecules, see W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965); M. Doblen and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); G. Eglinton, J. Martin, and W. Parker, *J. Chem. Soc.*, 1243 (1965); I. Laszlo, *Rec. Trav. Chim.*, **84**, 251 (1965); M. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 206 (1965); R. A. Appleton and S. H. Graham, *ibid.*, 297 (1965); but see R. Lygo, J. McKenna, and I. O. Sutherland, *ibid.*, 356 (1965); C. Y. Chen and R. J. W. LeFevre, *Tetrahedron Letters*, 737 (1965); W. D. K. Macrosson, J. Martin, and W. Parker, *ibid.*, 2589 (1965).

(47) While the natural values of the various angles at a given center were manipulated in an empirical fashion, the resulting natural angles at a given center do not differ significantly from those which would result from the correlation of orbital hybridizations and bond angles at each given center.[48]

(48) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

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

(50) It should be emphasized that with calculations of this type, the structure under study will go toward and remain in local energy minima even if other lower energy structures do exist. While this creates a disadvantage in terms of the number of structures that must be calculated for many molecules, and in requiring a careful analysis of the results in more complicated compounds, the easy calculation of higher energy structures, such as transition states, is possible by adding symmetry constraints to the atomic motions in the minimization scheme.

With the more accurate results of the new program, it became necessary to add a few refinements in the parameters to fully utilize the increased accuracy. The first change required was the introduction of different C–C natural bond lengths (but not in the C–H natural bond lengths). One natural bond length was defined for bonds between primary and secondary carbons, and a second (shorter) bond length was defined for C–C bonds where one (or both) end carbons were tertiary or quaternary.

The second change was the treatment of the "bending function" as a parameter, changing the function from one proportional to the square of the angular deformations at deviations below 5°, to a many-sectioned function. The function finally chosen for an angle was

$$E_{\text{bend}} = 0.021914k_b(A\Delta\theta^2 + B\Delta\theta + C) \tag{3}$$

θ is the angle in degrees, $\theta°$ is the natural angle in degrees where $\Delta\theta = (\theta - \theta°)$, k_b is the spectroscopic bending force constant in millidynes/radian^2 and A, B, and C are constants given in Table IX. The function is pictured in Figure 1. It is single valued and continuous and has a continuous derivative. The tabular form seems especially peculiar, in part due to the way it is formulated. As indicated earlier, an ordinary Hooke's law function is satisfactory for small bendings and will give the same ultimate results as the present function for unstrained or slightly strained compounds. For more strained compounds, such as cyclopentane or cyclodecane, a softer function such as this (or other means of reducing the bending energy) is required if one is to obtain useful results. For bending in excess of 20°, the form of the function was chosen to fit the available data on cyclobutane with a continuous function. Any way of connecting these two portions requires a sigmoid function, which was arbitrarily chosen. There are essentially no data available for the 15.8–19.4° range, and we do not wish to make any strong case for the function in this region. We do not attach any physical significance to the over-all function, other than the empirical one; it enables us to calculate molecular properties insofar as the function has been tested. We suspect that the neglect of interaction force constants (bend–stretch, etc.) in our treatment leads to deficiencies which are being more or less compensated for in some average way by the arbitrary function used. The neglect of these interaction terms would, of course, become more serious in strained systems. This problem is under investigation and will be reported on later. Meanwhile, we will only note that the function gives satisfactory results up to about 15° (where it has been tested) and becomes quite uncertain for still larger bendings.

Table IX. Bending Function (eq 3)

Range of $\Delta\theta$, deg	A	B	C
0–0.5	1.0	0	0
0.5–15.8	0.15	0.85	−0.2125
15.8–18.0	8.466240	−261.9432	2075.854
18.0–18.97	23.07755	−787.9502	6809.917
18.97–19.4	−91.25210	3549.708	−34332.69
>19.4	0.0	9.1266	10.95162

Heats of Formation

The experimental heats of formation of *n*-pentane and *n*-hexane, corrected by their respective conformational enthalpy values, $\Delta H°_{\text{conf}}$ (to reduce the experimental values to the lowest single conformations), and their respective calculated enthalpy terms (from the program), were compared to produce a value for the total contribution to the heat of formation of a methylene group (equivalent to one C–C and two C–H bonds), $E_{\text{C–C}}$ from eq 4 was then substituted for the bond energy of a C–C

$$E_{\text{C–C}} + 2E_{\text{C–H}} = -5.10 \tag{4}$$

bond in eq 1, and the latter was then solved for *n*-hexane, using its experimental heat of formation (corrected as previously), and yielded a value for the C–H bond energy. Substitution of this C–H bond energy back into eq 4 yielded the desired C–C bond energy. Those values assigned to iso and neo structures were empirically assigned by inspection of Table III.