# Organic and Biological Chemistry

## Conformational Analysis. LXIV. Calculation of the Structures and Energies of Unsaturated Hydrocarbons by the Westheimer Method[1,2]

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**Abstract:** From a study of the ethylene, propene, and isobutylene molecules, parameters required for the application of the Westheimer method to the calculation of the molecular structures of olefins have been deduced. The structures and energies of a number of simple olefins were then calculated, including the heights of rotational barriers and the positions of conformational equilibria. Such quantities as heats of hydrogenation, of *cis–trans* isomerization, and of positional isomerization have been calculated for a variety of molecules, including cyclopentene, cyclohexene, methylcyclohexenes, methylenecyclohexane, cycloheptene, cyclodecene, and the octalins. The agreement with the available experimental data is reasonably good, but it is not always perfect.

Previous papers[3,4] discussed the application of the Westheimer method[5,6] to saturated hydrocarbons, and showed that it was possible to use this theoretical method to obtain structures and energies for these compounds which were mostly comparable in accuracy to the values which can usually be obtained by experimental measurements. Because the amount of work required to determine a structure by calculation is often one or several orders of magnitude less than that required to obtain the same information from calorimetric studies, together with spectroscopic or diffraction investigations, there is at least one very real practical advantage to this approach to organic structural problems.

Chemists are most often concerned with problems involving molecules which are not saturated hydrocarbons, and an important step at this point is to extend the previous successes to molecules containing functional groups. This paper will be concerned only with the small step from saturated to unsaturated hydrocarbons. The inclusion of other elements poses additional problems. Such compounds have been studied in at least a preliminary way, and compounds containing nitrogen, oxygen, fluorine, sulfur, chlorine, or bromine will form the subject of the following paper.

### Method

The basis of the calculations is the same as that described in the previous paper.[4] A calculational model of a molecule was developed in which the molecule was formally considered as weights (atoms) joined together by means of springs (bonds). There are stretching and bending deformations which a molecule may undergo, which cost energy according to previously described functions. In addition, torsional energy is required to maintain a conformation which does not have an optimum torsional arrangement throughout, and van der Waals forces are included between each pair of atoms other than those bound together or to a common atom. For saturated hydrocarbons, it was

**Table I.** Parameters Needed for Calculation of Molecular Geometries[a]

| Bond[b] | | $l_0$[b] | $k$,[c] mdyn/Å$^2$ |
|---|---|---|---|
| $C_{sp^2}$—$C_{sp^3}$ | | 1.494 | 4.8 |
| $C_{sp^2}$=$C_{sp^2}$ | | 1.331 | 9.7 |
| $C_{sp^2}$—H | | 1.087 | 5.3 |
| **Angle** | **$N$[d]** | **$\theta_0$** | **$k$, mdyn/rad$^2$** |
| $C_{sp^3}$–$C_{sp^2}$–$C_{sp^2}$ | 0 | 122.35 | 1.1 |
| $C_{sp^3}$–$C_{sp^2}$–$C_{sp^2}$ | 1 | 122.8 | 1.1 |
| $C_{sp^3}$–$C_{sp^3}$–$C_{sp^2}$ | 0 | 109.47 | 1.1 |
| $C_{sp^3}$–$C_{sp^3}$–$C_{sp^2}$ | 1 | 111.00 | 1.1 |
| $C_{sp^3}$–$C_{sp^3}$–$C_{sp^2}$ | 2 | 109.80 | 1.1 |
| $C_{sp^3}$–$C_{sp^2}$–$C_{sp^3}$ | | 116.90 | 1.1 |
| $C_{sp^3}$–$C_{sp^2}$–H | | 117.80 | 0.66 |
| $C_{sp^2}$–$C_{sp^3}$–H | 0 | 108.00 | 0.66 |
| $C_{sp^2}$–$C_{sp^3}$–H | 1 | 108.60 | 0.66 |
| $C_{sp^2}$–$C_{sp^3}$–H | 2 | 107.20 | 0.66 |
| $C_{sp^2}$–$C_{sp^2}$–H | 0 | 119.4 | 0.66 |
| $C_{sp^2}$–$C_{sp^2}$–H | 1 | 118.8 | 0.66 |
| H–$C_{sp^2}$–H | | 122.40 | 0.55 |

[a] van der Waals parameters (for Hill equation)[4] $C_{sp^2}$ $r^* = 1.85$ Å; $\epsilon = 0.020$ kcal/mol. [b] The values for $\theta_0$ and $l_0$ were chosen so as to yield calculated values which agreed with experimental values for the simple model compounds propene and isobutylene. [c] The force constants are from Herzberg[7] or from R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **21**, 169 (1965). [d] Number of hydrogens (in addition to those specifically indicated) attached to the central atom.

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[1] Paper LXIII: N. L. Allinger and C. D. Liang, *J. Org. Chem.*, 33, 3319 (1968).

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

[3] N. L. Allinger, M. A. Miller, F. A. Van-Catledge, and J. A. Hirsch, *J. Amer. Chem. Soc.*, **89**, 4345 (1967).

[4] N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Am. Chem. Soc.*, **90**, 1199 (1968).

[5] 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.

[6] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965.

[7] G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., Inc., Princeton, N. J., 1945.

possible to fix all of the necessary parameters by studying four simple compounds.

Most of the parameters utilized in the present work, including the force laws, carry over from the last paper.[4] The additional numerical values which are now needed are the stretching, bending, and torsional constants specifically connected with the carbon–carbon double bond. They are all listed in Table I.

Torsional functions are required for olefins which are a little different from those for alkanes. In ethylene, the four substituents attached to the carbons are preferentially coplanar. Distortion of any bond angles in the molecule without the introduction of nonplanarity into the molecule (in-plane bending) is treated in the usual way. Out-of-plane bending, for any large motion, becomes serious as it will disrupt the $\pi$ bond. It is known that the energy of the ethylene molecule is increased by about 60 kcal/mol when one end is rotated 90° with respect to the other.[8] The present calculation has divided the angular distortions in ethylene into ordinary bending (deviation from normal bond angles), for which the in-plane bending constants have been used, and torsion, which will allow for any nonplanarity in a simple convenient way. The torsional funtion used was $E_t = V_1(1 - \cos|\omega_1|) + V_2(1 - \cos|\omega_2|)$ where $\omega_1$ and $\omega_2$ are the torsional angles between *cis* substituents, and $|\omega_1|, |\omega_2| \leq 90°$. To fit ethylene, the chosen torsional constants were $V_1 = V_2 = 30$ kcal/mol. If one or both of the substituents in the ethylene is other than hydrogen, different values could be used, but this has not been done for lack of data. In any case, these numbers are so large that torsion is effectively prevented in all the cases discussed here. It may be desirable to reconsider this matter when highly strained nonplanar olefins are dealt with.

In propene, besides the large torsional barrier about the $C_1$–$C_2$ bond, there is also an appreciable barrier about the $C_2$–$C_3$ bond. This barrier is threefold, with a height of 1.98 kcal, and a hydrogen attached to C-3 eclipses the $C_1$–$C_2$ bond in the ground state.[9]

There are a number of ways in which these values can be mathematically reproduced. We have chosen to examine the smallest dihedral angle ($\omega_1$) formed by hydrogen at C-2 on the double bond, with one hydrogen on the methyl. The smallest dihedral angle formed by the double bond itself and a hydrogen on methyl ($\omega_2$) was also examined. A threefold function has been used for each: $E_{\omega_1} = (V_1/2)(1 - \cos 3\omega_1)$, and $E_{\omega_2} = (V_2/2)(1 - \cos 3\omega_2)$, where $|\omega|$ is measured from 0 to 60° only in each case ($E_\omega = 0$ if $|\omega| \geq 60°$). The value of $V_2$ probably depends on the nature of the atom eclipsing the double bond, and it is probably different for carbon and hydrogen. For the time being, in the absence of other information we have set $V_2 = 0$, and hence $V_1$ was assigned the value 2.32 kcal/mol to fit the propene barrier. These torsional data are summarized in Table II.

We have kept the van der Waals parameters for all hydrogens the same, as previously described.[4] All atoms are taken to be spherical, and only pairwise interactions are considered as previously. There is no necessity to retain the same values for olefinic carbons as were used for tetrahedral carbon. Since we know that the crystal spacing in graphite[10] is 3.35 Å, a van der Waals radius of 1.85 Å for unsaturated carbon seems appropriate and has been used. The attractive part of the van der Waals curve has been retained, and the repulsion increased to give the desired radius, within the framework of the Hill potential discussed earlier.[4]

**Table II.**[a,b] Torsional Constants for Olefins

| Atom arrangement | $V$, kcal/mol |
|---|---|
| 1 2 3 4 | |
| A—$C_{sp^2}$—$C_{sp^3}$—A | $V_1$ 2.32 |
| A—$C_{sp^2}$—$C_{sp^3}$—A | $V_2$ 0.00 |
| A—$C_{sp^2}$=$C_{sp^2}$—A | 30.00 |
| A—$C_{sp^3}$—$C_{sp^3}$—$C_{sp^2}$ | 0.49 |

[a] These values were chosen to reproduce the rotational barriers in propene,[9] ethylene taken to be 60 kcal/mol.[8] [b] The four atoms are attached in the indicated sequence; A means hydrogen or $sp^3$ carbon.

The most objective way of trying to treat conformational or isomerization equilibria is in terms of the heats of formation of the species involved. Otherwise expressions like "strain energy" are not precisely defined. We therefore wish to be able to calculate heats of formation for molecules containing double bonds. One must be prepared at this point to accept the fact that, apart from the API data on saturated hydrocarbons,[11] very little accurate thermochemical data exist. In particular for olefins, one can count on his fingers the number of compounds for which accurate heats of formation (gas phase) have been reported. More data are available for hydrogenations in acetic acid. We have made the assumption that the heat of hydrogenation in acetic acid is the same as it is in the gas phase, not because the assumption is a good one, but because it is necessary if we are to utilize those few data which do exist. With saturated compounds the API data are generally good to 0.3 kcal/mol. If our calculations are equally good, agreement between calculation and experiment is acceptable for deviations up to 0.6 kcal/mol. For olefins, clearly a disagreement of 1 kcal/mol or so cannot be cause for alarm, but will only emphasize the need for more and better thermochemical data.

To understand equilibria one needs to know not only enthalpies, but entropies as well. There have been studies of equilibria involving olefins at different temperatures reported, but they are few indeed.

To calculate the heat of formation of an olefin, energy values for the various bonds of the molecule must be known. The minimum number of such values which we might reasonably hope to use would be, in addition to those already used for saturated hydrocarbons, one each for $C_{sp^2}$—H, $C_{sp^2}$=$C_{sp^2}$, $C_{sp^2}$—$C_{sp^3}$; and as previously discussed,[4] since van der Waals interactions between atoms bound to a common atom are not counted, we need also to differentiate an olefin of the type C—CH=C from the type >C=C (and it might also be desirable to further differentiate the type H—CH=C but we have not found the latter option necessary, possibly because of the paucity of exper-

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(8) J. E. Douglas, B. S. Rabinovitch, and S. F. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

(9) D. R. Lide, Jr., and D. Christensen, *ibid.*, **35**, 1374 (1961); D. R. Lide, Jr., and D. E. Mann, *ibid.*, 27, 868 (1957); D. R. Herschbach and L. C. Krisher, *ibid.*, **28**, 728 (1958); L. H. Scharpen and V. W. Laurie, *ibid.*, **39**, 1732 (1963).

(10) "Interatomic Distances," The Chemical Society, London, 1958.

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

imental data). These values are all included in Table III.

Table III. Bond Enthalpy Increments (kcal/mol) for Heat of Formation Calculations

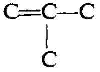
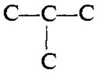
| | |
|---|---|
| $C_{sp^3}—C_{sp^3}$ | 2.89 |
| $C_{sp^3}—C_{sp^2}$ | 7.00 |
| $C_{sp^2}{=}C_{sp^2}$ | 0 |
| $C_{sp^2}—H$ | 2.99 |
| $C_{sp^3}—H$ | −3.995 |
|  $\mathrm{C{=}\underset{\displaystyle C}{\underset{\vert}{C}}{-}C}$ | −1.20 |
|  $\mathrm{C{-}\underset{\displaystyle C}{\underset{\vert}{C}}{-}C}$ | −1.70 |

Table IV. Calculated Heats of Formation and Other Data for Simple Olefins (kcal/mol)

| Compound | Bond energy contribn | Steric energy | $H_f°$ Calcd | $H_f°$ Exptl[a] | $\delta(-H_f°)$ calcd − exptl | Other | Ref |
|---|---|---|---|---|---|---|---|
| Ethylene | 11.96 | 0.55 | +12.51 | +12.50 | +0.01 | | *b* |
| Propene | −3.98 | 0.84 | + 4.83 | +4.88 | −0.05 | Barrier 1.95 kcal (exptl 1.98) | 9 |
| 1-Butene | −1.12 | | | | | Calcd 86.5% symm (exptl one-third symm) | *c* |
| *anti* | ... | 1.96 | +0.25 | −0.03 | +0.28 | | |
| *gauche* | ... | 1.27 | | | | | |
| *trans*-2-Butene | −3.99 | 0.98 | −3.01 | −2.67 | −0.34 | 1.62 kcal more stable than *cis* (exptl 1.2 kcal/mol) | *d, e* |
| *cis*-2-Butene | −3.99 | 2.60 | −1.39 | −1.67 | +0.28 | Barrier 0.98 kcal (exptl 0.75) | |
| Isobutylene | −5.19 | 0.81 | −4.38 | −4.04 | −0.34 | Barrier 1.89 kcal (exptl 2.21) | *f, g* |
| 2-Methyl-2-butene | −13.11 | 3.06 | −10.11 | −10.17 | +0.06 | Barrier 0.59 kcal | ... |
| 2,3-Dimethyl-2-butene | −22.34 | 6.83 | −15.51 | −15.91 | +0.40 | Barrier 0.77 kcal | ... |

[a] From ref 11. [b] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **31**, 400 (1959). [c] A. A. Bothner-By, C. Naar-Colin, and H. Günther, *J. Amer. Chem. Soc.*, **84**, 2748 (1962). [d] D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, **86**, 5416 (1964). [e] I. N. Sarachmann, as quoted by R. A. Beaudet, *J. Chem. Phys.*, **40**, 2705 (1964). [f] D. R. Lide, Jr., and D. Christensen, *ibid.*, **35**, 1374 (1961). [g] V. W. Laurie, *ibid.*, **34**, 1516 (1961); **39**, 1732 (1963).

To calculate the heat of formation of an olefin, then, one adds up the bond energies (or more precisely, the bond contributions to the heats of formation). To this one adds the total remaining molecular energy as is obtained from the Westheimer calculation (bending, stretch, van der Waals, and torsion) which we will call the steric energy. The resulting value is the calculated (gas phase) heat of formation at 25°, unless the molecule is a conformational mixture. In the latter case, the energy of each conformation must be calculated, and conformations must be mixed according to a Boltzmann distribution and the molar heat of formation subsequently arrived at by the usual thermodynamic methods.[12]

## Results

The heats of formation calculated for a number of olefins might be examined first, as a guide to what sorts of results might be anticipated with regard to energy calculations. In Table IV are given calculated and experimental values for all of the compounds for which we have been able to locate experimental structural data and/or heats of formation (gas phase).

The examination of Table IV will show the type of results that have been obtained. For each of these compounds the calculated bond lengths agree with the experimental ones to within 0.01 Å, and the angles to within 1° in all cases where experimental data are available.

Ethylene is found to have a calculated geometry which agrees with experiment.[13] Propene was used in the evaluation of the necessary natural bond angles and lengths, so the agreement is of course very good.[9] The results for 1-butene are satisfactory with regard to geometry, insofar as what one would expect (no actual experimental data being available), but it has been calculated that the *anti* form is less stable than the *gauche* form by 0.69 kcal/mol, while the only experimental measurements have indicated that there are roughly equal amounts of each of the three conformations.[14]

The calculations indicate that *trans*-2-butene should have a lower enthalpy than the *cis* isomer by 1.62 kcal/mol and the available experimental measurements[11,15] indicate a value of 1.2 kcal/mol. The rotational barrier calculated in propene is 1.95 kcal/mol (compared to 1.98 experimental), and a similar value would be expected for *trans*-2-butene. For *cis*-2-butene, on the other hand, we have calculated a much lower barrier of 0.98 kcal/mol, which is in reasonable agreement with the literature value of 0.75 kcal/mol.[16]

The structure of isobutylene was adequately calculated,[17,18] and its rotational barrier has a calculated value of 1.89 kcal/mol, a little lower than the experimental value of 2.21 kcal/mol. The structures of 2-methyl-2-butene and 2,3-dimethyl-2-butene which are calculated seem reasonable. The rotational barriers seem low, but similar to that observed for *cis*-2-butene. No experimental data are available for comparison.

Next, we wished to examine the cycloalkenes. Heat of formation data for these compounds are scarce,[11] but heats of hydrogenation are available, sometimes in the gas phase,[19] but often only in acetic acid solution.[20]

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(12) Reference 6, p 50.

(13) See Table IV, footnote *b*.

(14) See Table IV, footnote *c*.

(15) See Table IV, footnote *d*.

(16) See Table IV, footnote *e*.

(17) See Table IV, footnote *f*.

(18) See Table IV, footnote *g*.

(19) (a) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **59**, 831 (1937); (b) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, **58**, 137

The heat of solution of cyclohexene in acetic acid appears (from the difference in the heat of hydrogenation in the two phases) to be 1.5 kcal/mol greater than the heat of solution of cyclohexane, and the data for acetic acid solution are therefore only qualitatively useful. The calculated heats of hydrogenation for the cycloalkenes (the difference between the olefin and its reduction product, each in the lowest energy conformation) are given in Table V, along with the experimental data.

**Table V.** Heats of Hydrogenation (kcal) for the Cycloalkenes

| | $-\Delta H_{H_2}$(expt) (gas phase)[b] | $-\Delta H_{H_2}$ (calcd) | $\delta\Delta H_{H_2}$ |
|---|---|---|---|
| Cyclopentene | 26.92 | 25.81 | +1.11 |
| Cyclohexene | 28.59, 27.10[a] | 28.61 | −0.02 |
| Cycloheptene | 26.52, 25.85[a] | 26.82 | −0.30 |
| *cis*-Cyclooctene | 23.53, 22.98[a] | 23.25 | +0.28 |
| *trans*-Cyclooctene | 32.24[a] | 28.64 | +3.60 |
| *cis*-Cyclodecene | 20.67[a] | 22.82 | −2.15 |
| *trans*-Cyclodecene | 24.01[a] | 22.25 | +1.76 |

[a] These values are for acetic acid solution.[20] [b] See ref 19.

For cyclopentene, the heat evolved is smaller than for *cis*-2-butene (28.57 kcal/mol, experimental), because, although there is a relief of angular strain when the $sp^2$ carbons are converted to $sp^3$ (Brown's I strain[21]), the additional energy of eclipsing of ethane units more than outweighs the angular energy decrease. Our calculated cyclopentene is more stable than the experimental one[20] by 1.1 kcal/mol.

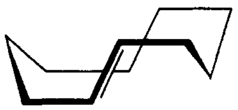
For cyclohexene, the calculated value for the heat of hydrogenation agrees well with experiment, and it shows that cyclohexene is an ordinary *cis* olefin. This compound will be discussed further below.

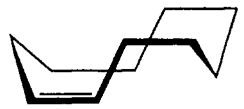
The calculations were carried out for both the boat and the chair forms of cycloheptene, and it was found that the boat form was of lower energy by 0.94 kcal/mol. No direct experimental information on this point is available, but from dipole moment measurements, it was concluded earlier[22] that 1,2-benzocyclohepten-5-one existed in the chair form to the extent of about 95%. These two results do not appear to be compatible, but that is not certain. The calculated heat of hydrogenation of cycloheptene is satisfactory. The value is smaller than for an ordinary *cis* olefin, because the unfavorable eclipsing and transannular hydrogen–hydrogen repulsions are worse in the saturated molecule than in the olefin (I strain[21]).

Our calculated heat of hydrogenation for *cis*-cyclooctene is in good agreement with experiment. The value is smaller than for the heat of hydrogenation of cycloheptene, because of the larger interactions of the same type. The conformation for the olefin was assumed to be of the general boat–chair class.


*cis*-cyclooctene


*trans*-cyclooctene


*trans*-cyclodecene


*cis*-cyclodecene

For *trans*-cyclooctene, the experimental heat of hydrogenation is very large (32.2 kcal/mol), even though the product is quite strained. Our calculated heat of hydrogenation is off by 3.6 kcal/mol of which 2.5 kcal/mol comes from the olefin calculation (the calculated cyclooctane energy is off by 1.1 kcal/mol). For *trans*-cyclodecene, the error in the heat of hydrogenation stems almost exclusively from the error in the energy of cyclodecane, so the source of the error in *trans*-cyclooctene is not clear.

For *cis*-cyclodecene, our calculated energy is quite a bit too high. It seems likely that the calculations have been carried out on a conformation other than the one of lowest energy. It is not apparent which conformation of the molecule has the lowest energy, and there are so many possible conformations that we have not pursued this problem.

The results of our calculations with the medium-ring olefins are not really satisfactory. While they could no doubt be improved, we have left that work at this stage so as to be able to first carry out a broad survey of olefins and ascertain more clearly where the calculational deficiencies lie.

Cyclohexene is a fundamental structural unit of a large number of more complicated systems, and a number of estimates have been made regarding the boat $\rightleftharpoons$ chair equilibrium in this molecule. The most recent and careful of these appears to be that of Bucourt,[23] who has concluded that the boat is about 7 kcal less stable than the chair, and in addition that they are not separated by an energy barrier but rather the boat is simply an extreme case of the pseudorotational motion of the chair form. Experimentally, nmr studies at low temperatures have indicated that there are two equivalent (chair) forms in equilibrium, which are separated by an energy barrier of 5.3 kcal/mol.[24] Our calculations indicate that the regular boat form ($C_s$ symmetry) is 4.33 kcal/mol higher in energy than is the chair form. From a study of models, it would seem that the energy barrier separating the boat from the chair form (if any) should probably occur when four atoms (2, 4, 5, and 6) of the ring are coplanar, and atoms 1 and 3 are above and below that plane, respectively. We therefore calculated the energy of such a structure, requiring only that the four atoms, 2, 4, 5, and 6, maintain coplanarity, and placing atoms 1 and 3, respectively, above and below the plane. The minimization therefore proceeded with respect to all of the other degrees of freedom in the molecule. The value obtained for the energy of this form was 5.93 kcal/mol. This is significantly greater than 4.33 kcal/mol calculated for the boat so we feel it does indicate the presence of a low barrier, 1.60 kcal/mol above the boat, between the boat and chair forms. Our calculated barrier height (5.93 kcal/mol) may be compared with Anet's value (5.3 kcal/mol). Our calculated potential

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(1936); (c) J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Amer. Chem. Soc.*, **61**, 1868 (1939).

(20) R. B. Turner and W. R. Meador, *ibid.*, **79**, 4133 (1957).

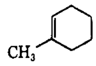
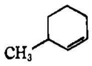
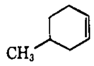
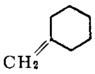
(21) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

(22) N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 4601 (1962).

(23) R. Bucourt and D. Hainaut, *Bull. Soc. Chim. Fr.*, 1366 (1965).

(24) F. A. L. Anet and M. Z. Haq, *J. Amer. Chem. Soc.*, **87**, 3147 (1965).

Table VI. The Thermodynamic Properties (kcal/mol and eu) of the Methylcyclohexene Isomers

| Compound | Σ bond energies | Steric energy | $\Delta H_i$ | $\Delta S_i$ | $\Delta H°$ | $\Delta S°$ | $\Delta G°_{298}$ | $\Delta G°_{523}$ | Equil % at 523°K Calcd | Equil % at 523°K Exptl[a] |
|---|---|---|---|---|---|---|---|---|---|---|
|  | −12.49 | 2.41 | 0.00 | 1.38 | 0.00 | 0.00 | 0.00 | 0.00 | 71.2 | 62.9 |
|  | −10.11 | ax 3.26<br>eq 2.50 | 3.23<br>2.47 | 1.38<br>1.38 | 2.66 | 1.10 | 2.33 | 2.07 | 9.8 | 16.5 |
|  | −10.11 | ax 3.06<br>eq 2.02 | 3.03<br>1.99 | 1.38<br>1.38 | 2.14 | 0.83 | 2.14 | 1.89 | 14.5 | 18.8 |
|  | −9.61 | 1.67 | 2.14 | 0 | 2.14 | −1.38 | 2.55 | 2.86 | 4.6 | 1.8 |

[a] See ref 28.

function for the pseudorotation of the molecule is shown in Figure 1.

Methylenecyclopentane and 1-methylcyclopentene are an interesting pair, because of the suggestion made some years ago by Brown[25] that double bonds tend to be exocyclic to five-membered rings to a greater extent than they do to six-membered rings. With respect to the hydrocarbon systems, Brown's suggestions were not borne out by subsequent experiments.[26-28] From gas-phase equilibrations at 523°K, Gil-Av finds[28] the methylcyclopentene predominates over the exocyclic compound by 100:1. Assuming the entropies of the two compounds are the same (which cannot be very far wrong), an experimental $\Delta H°$ of $-4.79$ kcal/mol is deduced. Direct measurements of $\Delta H°$ in acetic acid solution give the value $-3.87$ kcal/mol.[29] In the present work $\Delta H°$ is calculated to be $-5.66$ kcal/mol. The agreement is only fair, but it seems clear that there is a very strong preference for the double bond to be endocyclic. Part of this preference stems from the lower energy of a trisubstituted olefin, compared to a disubstituted one. An important consideration, however, is the poor torsional arrangement in the exocyclic case. We know from the barrier to the rotation of the methyl in propene that there is a strong tendency for the olefin to be eclipsed. In the cyclopentene derivative the ring is fairly flat and the methyl can position itself so that a very small torsional energy of the propene type results. Methylenecyclopentane cannot come close to such a torsional minimum with respect to the allyl hydrogens. The ring puckers somewhat in an attempt to improve the situation, but cannot approach the rotational potential minimum.

When the *exo–endo* equilibrium in the five-membered ring is compared with the six-membered analog, it is found that the cyclohexene is less flat than the cyclopentene, and the torsional energy about the olefin is less favorable. Methylenecyclohexane has very nearly a minimum energy torsional arrangement around the double bond where methylenecyclopentane is quite unfavorable. Thus calculations indicate that, compared to the five-membered case, the six-membered olefin tends to be exocyclic to a much greater degree, exactly opposite to the predictions of Brown, and in agreement with previously uninterpreted experiments.[26-28]

The equilibrium between the different isomers of the methylcyclohexenes was next studied. There are five isomers and a total of seven conformations. The enthalpy of each conformer was calculated by calculating the bond energy and adding to it the steric energy from our program. The enthalpy of each isomer was then calculated by mixing the conformers according to a Boltzmann distribution. These quantities, and the values of $\Delta H°$ for each isomer, are given in Table VI.

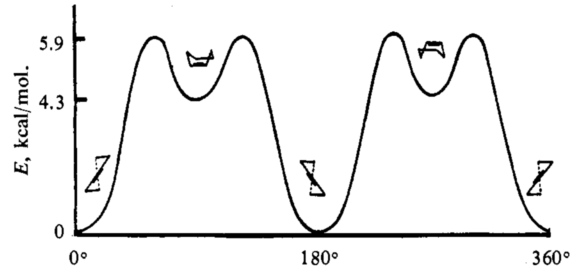


Figure 1. Pseudorotation of cyclohexane.

Next, the relative entropy of each isomer was calculated by considering whether it was *meso* or *dl* (the symmetry number is one in every case), and then adding any entropy of mixing whenever there were two conformers for the isomer. Having $\Delta H°$ and $\Delta S°$, it was then possible to calculate $\Delta G°$ and the corresponding equilibrium constants. These calculations were carried out for room temperature and for 523°K, as there are experimental data available for the latter temperature. The agreement with experiment is qualitatively correct and fairly good quantitatively (Table VI).

The compound with the trisubstituted double bond is the most stable, as this feature outweighs all other considerations. The last three entries in the table all have disubstituted double bonds. The endocyclic arrangement is preferred over the exocyclic, but most of the preference stems from entropy rather than from enthalpy considerations. The additional entropy results from symmetry differences and from mixing 3-methyl- and 4-methylcyclohexenes, each of which consists of a mixture of four chair conformations (two *dl* pairs, with axial and equatorial methyls), while the *exo*-methylene compound is a single conformation.

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(25) H. C. Brown, *J. Org. Chem.*, **22**, 439 (1957).

(26) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, *J. Amer. Chem. Soc.*, **81**, 3153 (1959).

(27) B. R. Fleck, *J. Org. Chem.*, 22, 439 (1957).

(28) E. Gil-Av and J. Shabtai, *Chem. Ind.* (London), 1630 (1959).

(29) R. B. Turner and R. H. Garner, *J. Amer. Chem. Soc.*, **80**, 1424 (1958).

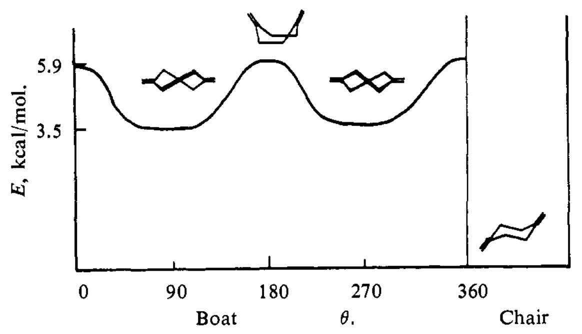

Figure 2. The conformational enthalpy calculated for 1,4-dimethylenecyclohexane.

An axial methyl is of higher energy than the corresponding equatorial by approximately 1 kcal/mol for both the 3- and 4-methylcyclohexenes. Perhaps the most interesting feature, in that it would not have been found from any simple first-order calculation, is that the 4-methyl compound is quite a bit more stable than the 3-methyl analog. Just why there is an energetic preference of the methyl for the 4 rather than the 3 position is not apparent. There are a great many small distortions in the molecule when the methyl is at either C-3 or at C-4. The sum of these distortions favors the latter, but no simple explanation of the situation is apparent to us. In any case, the calculations reproduce the experimental result reasonably well.

It has been suggested that 1,4-dimethylenecyclohexane exists predominantly in a boat or twist form on the basis of the coupling constants in the nmr spectrum.[30,31] We therefore undertook to study both methylenecyclohexane and the 1,4-dimethylene compound with respect to boat–chair equilibria. For methylenecyclohexane, the chair form was constrained to have $C_s$ symmetry, but otherwise allowed to minimize in all degrees of freedom. There are three extremes of the boat form of methylenecyclohexane which may be considered, and these are connected by a pseudorotational cycle. One of these extremes has the methylene group at the prow ($C_s$ symmetry), another has the methylene on the side of the boat ($C_1$), and the third extreme conformation of the molecule has the so-called twist structure, which has $C_2$ symmetry. These three forms correspond to $\theta = 0°, 60°, 90°$ on the graph, respectively. The energies calculated for these points can be used to sketch out the energy curve for pseudorotation, which is similar to that in Figure 2. The most favorable arrangement of the boat form is the twist-boat, which is calculated to have an energy 4.44 kcal/mol above that of the chair. This energy difference is slightly less than the corresponding one in the cyclohexane molecule.

If we now examine the 1,4-dimethylenecyclohexane system, we find a pseudorotational curve qualitatively similar to that calculated for methylenecyclohexane. In this case the energy of the most favorable arrangement, the twist-boat, is calculated to be 3.53 kcal/mol above that of the chair. The calculations therefore indicate that the presence of one or two methylene groups in the positions indicated on a cyclohexane ring leads to a modest stabilization of the boat form, relative to the chair, as compared with cyclohexane itself. The calculations clearly indicate, however, that the chair form has a distinctly lower enthalpy than does the boat in each of these molecules. The boat forms are, of course, relatively flexible, and so are expected to have higher entropies than do the chair forms. Just how large this entropy difference might be is not known, however, and the free energy difference is therefore not now calculable.

The octalin system was examined next. There are six isomers of octalin, and three of these have two diastereomeric conformations. Hence the conformational analysis of this system involves a study of nine conformations. Of these, one is *meso*, the others are *dl* pairs. The problem, then, is to calculate the amounts of the six isomers (structural and geometric) which will exist in equilibrium with one another as a function of temperature, as these quantities are directly measurable. Because of symmetry considerations, these equilibria are somewhat dependent on temperature. The enthalpy was calculated for each conformation of each of the isomers according to the methods described in the earlier part of this paper. The relative entropies were then calculated from the symmetries and mixing of conformations, and the results are summarized in Table VII. From the data in the table, plus the entropies of mixing conformations, the relative free energies of the isomers were calculated as functions of temperature, and the equilibrium composition was then calculated and is also given in Table VII. Experimental measurements of the equilibria are also given in Table VII.

The comparison of the experimental and calculated values in the table shows good general agreement, the free energies calculated usually being within about 0.2 kcal/mol of those measured experimentally. The temperature variation is also well reproduced.

It has been long recognized in the steroid field that the $5\alpha$-3-ketone compounds tend to enolize toward C-2, while the corresponding $5\beta$ compounds enolize toward C-4. Thus, for example, oxidation of a $5\alpha$-3-keto steroid gives the 2,3-seco diacid, while the $5\beta$ compound similarly oxidizes to the 3,4-seco diacid. An earlier interpretation of these facts was given by Bucourt.[23] Inspection of the data obtained in the present work indicates the following. The geometry of cyclohexane, with tertiary C–C–C bond angles, is such that the dihedral angle between the carbons is 55°, as indicated in the drawing. The corresponding Newman projections are given for both the 4,5 and the 3,4 linkages in cyclohexene. When we consider an octalin, we are putting the carbons of the cyclohexane as substituents on the cyclohexene ring. If these are placed in the 4,5-diequatorial positions, there is only a 5° torsional deviation from what is desired, while if they are placed in the 3,4-diequatorial positions, there is a 14° deviation. Obviously, the torsional situation will be more satisfactory in the former case. In the latter case, either one or the other ring will have to be torsionally rather unsatisfactory, or else bond angle deformation will have to occur to relieve this situation. In practice many small deviations occur. Clearly, however, the 4,5 fusion is preferable over the 3,4 fusion, if both substituents are equatorial. This is the most desirable arrangement, so that we see, in Table VII, the enthalpy

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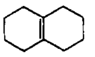
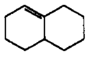
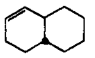
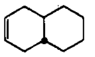
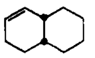
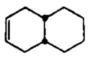
(30) J. B. Lambert, *J. Amer. Chem. Soc.*, **89**, 1836 (1967).

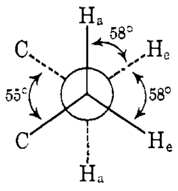
(31) F. Lautenschlaeger and G. F. Wright, *Can. J. Chem.*, **41**, 1972 (1963).

**Table VII.** Data for the Octalin System

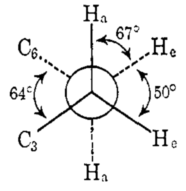
| Isomer | Calcd $H°$, kcal/mol | Symmetry number | *dl* or *meso* | Calcd $\Delta H°_{298}$, kcal/mol | Calcd $\Delta S°_{298}$, eu | % at 298° | | % at 373° | | % at 473° | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Calcd | Exptl[a] | Calcd | Exptl[a] | Calcd | Exptl[a] |
|  | 0.31<br>0.00 | 2<br>4 | *meso*<br>*dl* | 0.00 | 0.00 | 86.2 | 90.7 | 75.7 | 82.8 | 61.1 | 72.2 |
|  | 1.84 (eq)<br>... (ax) | 1<br>1 | *dl*<br>*dl* | 1.88 | 1.99 | 11.4 | 7.7 | 18.9 | 14.0 | 27.2 | 20.4 |
|  | 3.10 | 1 | *dl* | 3.14 | 1.45 | 0.86 | 0.6 | 2.0 | 1.4 | 4.5 | 3.7 |
|  | 2.57 | 2 | *dl* | 2.46 | 0.07 | 1.4 | 1.0 | 2.8 | 1.8 | 4.6 | 3.7 |
|  | (eq)<br>4.74 (ax) | 1<br>1 | *dl*<br>*dl* | 4.50 | 2.79 | 0.2 | | 0.5 | | 2.1 | |
|  | | | *dl* | 5.28 | 1.45 | 0.0 | | 0.1 | | 0.5 | |

[a] A. W. Weitkamp, private communication.

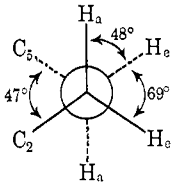
of the 2-octalin is lower than that of the 1-octalin by about 0.5 kcal/mol when the ring juncture is *trans*.



cyclohexane



cyclohexene
4, 5-torsion



cyclohexene
3, 4-torsion

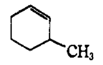
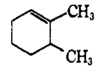
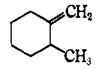
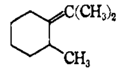
If we have a *cis* ring junction, the 1-octalin is preferred over the 2-octalin by about 0.8 kcal/mol. (With the octalins themselves, because of entropy effects, the results are not exactly analogous to the steroids. The free energies observed in the steroids should correspond more nearly to the enthalpies calculated for the octalins.)

The *cis* ring juncture is energetically inferior to the *trans* ring juncture in the octalins as in the decalins. The repulsions which are *gauche* interactions in the decalin (and the corresponding type of interactions in the octalin) are not greatly different energetically in the octalins from those in the decalins. Thus if we can compare *trans*-1-octalin with *cis*-1-octalin, the enthalpy difference is 1.4 kcal/mol. If we similarly compare the 2-octalins, the difference is 2.3 kcal/mol. In the former case the torsional energies tend to make the difference in total energies smaller, while in the latter case they tend to make it larger. The repulsion portion of the energy is similar in each case.

Next, we may examine the series of relationships which Johnson has recently studied and discussed in some detail.[32] Johnson has indicated that, although a methyl group at the 3 position on an unsubstituted cyclohexene ring prefers the equatorial position to the axial (by 0.76 kcal/mol according to the present work), this preference might be reduced or inverted if there was a substituent on the adjacent olefinic carbon.

We have examined 1,6-dimethylcyclohexene, and find that essentially no difference in the equilibrium is brought about by the presence of the extra methyl group (Table VIII). The reason for this state of affairs is that the dihedral angle which the axial hydrogen at C-3 in cyclohexene makes with the C-2 hydrogen is not much greater than that between the equatorial hydrogen at C-3 and the hydrogen at C-2. When the hydrogen at C-2 is replaced by methyl this methyl interacts almost equally with the hydrogens (or methyl groups) at C-3. Thus calculations do not bear out the suggestions of Johnson on this point.

**Table VIII.** Calculated Enthalpies (kcal/mol) for Conformational Equilibria: Equatorial- $\rightleftharpoons$ Axial-Methyl

| Compd | $\Delta H°$ |
|---|---|
|  | +0.76 |
|  | +0.84 |
|  | +0.50 |
|  | −2.62 |

Johnson has also suggested that for methylenecyclohexane an increase in the size of the substituents on the *exo* carbon would tend to shift the normal equatorial preference of a group at C-2 toward the axial position. Johnson has summarized available evidence to support this contention, and has made use of the phenomena in an elegant synthetic scheme designed to place an alkyl group at C-2 in a cyclohexanone ring into the otherwise difficultly accessible axial position. Here the present calculations fully bear out Johnsons conclusions and furnish in addition some numerical values (Table VIII).

Some related isomerizations have been studied theoretically and the results are given in Table IX. The diequatorial conformation of 3,4-dimethylcyclohexene is predicted to be of lower energy than the others, but the differences are notably small. Since the entropy is more favorable to the *cis* isomer, an actual equilibration

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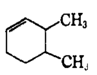
(32) F. S. Johnson and S. K. Malhotra, *J. Amer. Chem. Soc.*, **87**, 5492 (1965).

Table IX. Calculated Enthalpy Data (kcal/mol) for Dimethylcyclohexenes

| | | $\Delta H°$, kcal/mol |
|---|---|---|
|  | *trans*-Diequatorial | 0.00 |
| | *trans*-Diaxial | 0.71 |
| | *cis*-3-Axial,4-equatorial | 0.25 |
| | *cis*-3-Equatorial,4-axial | 0.46 |
|  | | 0.84 |

experiment might yield either isomer predominantly, depending on the temperature.

With the *gem*-dimethylcyclohexenes, the 4 isomer is predicted to be considerably better than the 3 isomer.

In summary, structures and energies and related data have been calculated for a wide variety of olefinic compounds. As with similar calculations on the alkanes, the bulk of the information obtained is in good agreement with the available experimental data. A few items are not, however, in satisfactory agreement, and these items suggest certain deficiencies in the calculations. In general, the calculations give rather accurate results for compounds which are not highly strained, as was also true with the alkanes. Refinement of the energy functions is now being studied and will be discussed in due course. However, for alkenes or alkanes which are not highly strained, it is believed that the structure–energy calculations described herein and in the previous paper are quite reliable, and insofar as experimental data are available, the calculations appear to give structures and energies within the combined limits of experimental and calculational error in every case.

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# A Perturbation Molecular Orbital Approach to the Interpretation of Organic Mass Spectra. The Relationship between Mass Spectrometric, Thermolytic, and Photolytic Fragmentation Reactions

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*Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210*

*Received April 25, 1968*

**Abstract:** Mass spectrometric reactions have been empirically divided into three classes based on metastable observations and the classification of reacting ions as odd- or even-electron ions. Class I reactions are presumed to occur from low-lying electronic states of the parent ion; simplified MO methods may be directly applied to these reactions. First-order perturbation theory (the PMO method)[1] has been expanded to deal with the aromaticity of radical cations. Procedures for applying this simple theory to the major classes of mass spectrometric reactions have been discussed. The electronic relationship between mass spectrometric, thermolytic, and photolytic fragmentation reactions has been reviewed.

Modern approaches to the interpretation of organic mass spectra have been highly successful in explaining the major fragmentation paths of complex molecules.[2] These same theories have also provided the basis for understanding the empirical relationship between mass spectrometric, thermolytic,[3] and photolytic[4] fragmentation reactions. Unfortunately, the present qualitative theory has not generally provided a sound basis for the prediction of relationships between electron impact, thermal, and photoprocesses. The statistical theory of mass spectra[5] (QET) has clearly accounted for the fragmentation of saturated hydrocarbons. The complexity of this theory has prohibited its adoption by organic chemists, and its utility in interpretation of organic mass spectra is very limited. This situation may be contrasted to the recent rapid development of theoretical organic chemistry, wherein simple procedures have been developed for accurately predicting both the course and stereochemistry of a large number of interesting reactions.[1,6]

There are two major factors which have limited the development of a semiquantitative electronic theory of mass spectral fragmentation reactions. (1) The reactive electronic states for ions that are produced by electron impact are not easily defined. The qualitative theory does not explicitly consider the electronic states of reacting ions;[2] however, most reactions are interpreted

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(1) M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).

(2) (a) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966; (b) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Ions," Holden-Day, Inc., San Francisco, Calif., 1967; (c) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) (a) D. C. DeJongh, R. Y. VanFossen, and C. F. Bourgeois, *Tetrahedron Lett.*, 271 (1967); (b) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 2836 (1966), and papers cited therein.

(4) (a) A. L. Burlingame, C. Feneslau, W. J. Richter, W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *ibid.*, **89**, 3346 (1967); (b) N. J. Turro, D. S. Weiss, W. F. Haddon, and F. W. McLafferty, *ibid.*, **89**, 3370 (1967), and papers cited therein.

(5) H. M. Rosenstock, M. B. Wallenstein, A. L. Warhaftig, and H. Eyering, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952).

(6) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).