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Conformations of Cycloheptane[1]

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Abstract: A relatively complete calculation of the low-energy conformations of cycloheptane is presented. The various paths for pseudorotation and the various transition states are rigorously characterized. It is shown that the pseudorotation paths of cycloheptane can be visualized as occurring on a helical track wound around a torus. Our results for the equilibrium conformations of cycloheptane are compared to the results of other calculations and found to agree qualitatively. Our calculated results give the best agreement with the available rotational constants, but final determination of the details of the potential functions and of the detailed properties of the conformations of cycloheptane will have to await the results of future experiments.

I. Introduction

The conformations of the cycloalkanes have been of great concern to chemists ever since recognition of the tetrahedral nature of the bonds of a saturated carbon atom.[2] The understanding of the conformations of cyclohexane, for example, has played a crucial role in the understanding of the conformation of large numbers of other compounds. The smallest ring, cyclopropane, has, of course, only one possible conformation. The next, cyclobutane, is puckered with a small barrier to flattening. With cyclopentane, the next largest ring, the situation becomes dramatically more complex, and it was recognized in 1947 that cyclopentane could exist in a large number of conformations of essentially equal energy.[3] The molecule moves among these conformations in a motion known as pseudorotation. For cyclohexane, the possible conformations are well-known. Understanding of the existence and relative stability of the chair form of cyclohexane has made possible much of "conformational analysis." However, the nature of the pathway between the two possible chair forms and the role of the boat and twist conformations was cleared up only recently.[4] The next more complex ring is cycloheptane.[2,5] The basic conformations were identified by Hendrickson as the chair, twist-chair, boat, and twist-boat (Figures 1-4). The chair and twist-chair conformations are connected by a pseudorotation pathway as are the boat and twist-boat conformations. The paths between these sets of conformations have proved to be difficult to define and relevant experimental observations exceedingly hard to come by. In this paper, we first present a model with which to visualize the conformations of cycloheptane, its pseudorotation, and the interconnections among the various conformations. We then present detailed calculations of the entire conformational energy surface and compare the results to the results of other calculations. Finally, we discuss the limited experimental information available and the possibilities for resolving a number of the remaining unanswered questions.

II. Outline of the Model

The conformations of the cycloalkanes can be specified by giving the z or out-of-plane coordinates of all the ring atoms. These coordinates can be thought of as the out-of-plane displacements for each ring atom from its position in a planar ring. The z displacements naturally come in sets determined by symmetry, and the number of such independent sets is $N - 3$ where N is the number of ring atoms. These coordinates have been described in detail for cyclopentane,[3] cyclohexane[4,6] and for rings in general.[7] For cycloheptane there are four independent sets of z displacements and they may be written

$$z_j = \xi_2 \cos(2\pi 2j/7) + \eta_2 \sin(2\pi 2j/7) + \xi_3 \cos(2\pi 3j/7) + \eta_3 \sin(2\pi 3j/7) \quad (1)$$

$$j = 1, 2, \ldots, 7$$

Here the index, j, labels the number of the carbon atom and ξ_2, η_2, ξ_3, and η_3 are coordinates corresponding to sets of z displacements which take a planar ring into conformations which are like the boat, twist-boat, chair, and twist-chair conformations, respectively (Figure 5). The actual boat and chair conformations are more complex than those of Figure 5 but the characterization as boat-like, etc., will prove useful. Equation 1 may be written in a number of alternate forms

$$z_j = \rho_2 \cos(2\pi 2j/7 + \phi_2) + \rho_3 \cos(2\pi 3j/7 + \phi_3) \quad (2)$$

with

$$\rho_2 = \sqrt{\xi_2^2 + \eta_2^2}, \quad \tan \phi_2 = \eta_2/\xi_2$$
$$\rho_3 = \sqrt{\xi_3^2 + \eta_3^2}, \quad \tan \phi_3 = \eta_3/\xi_3 \quad (3)$$

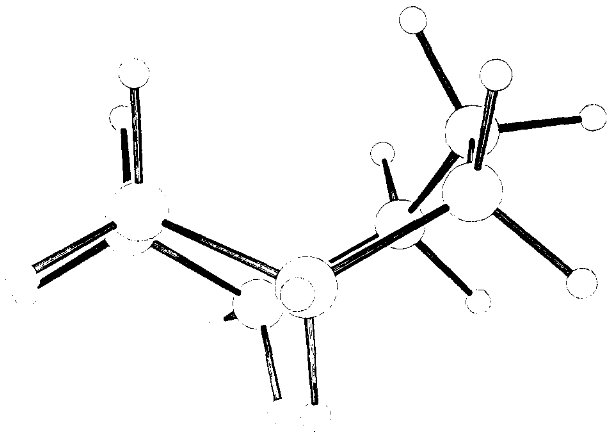

Figure 1. Computer projection of the boat conformation. Note especially the eclipsed hydrogens at the "stern" (left side of the projection) of the boat.

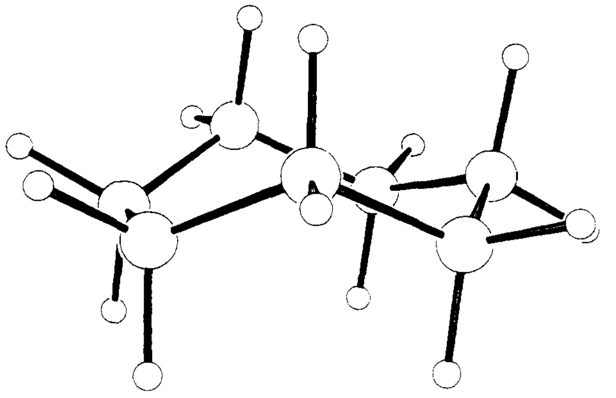

Figure 2. Computer projection of the chair conformation. Again note the eclipsed hydrogens on the left side of the projection.

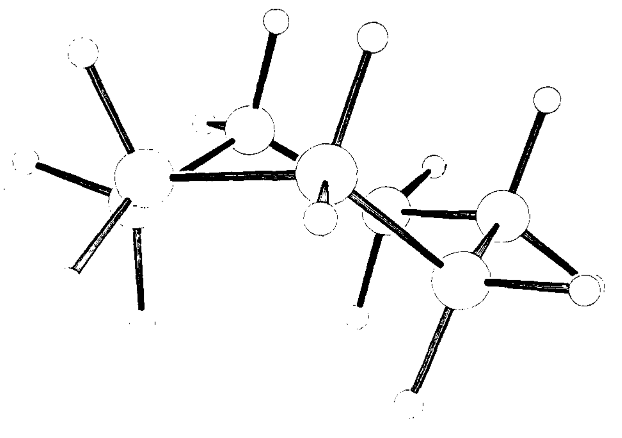

Figure 3. Computer projection of the twist-chair conformation. Comparison with Figure 2 shows that the previously eclipsed hydrogens on the left side of the projection are now staggered.

or

$$z_j = \rho[\cos\theta\cos(2\pi 2j/7 + \phi_2) + \sin\theta\cos(2\pi 3j/7 + \phi_3)] \quad (4)$$

with

$$\rho = \sqrt{\rho_2^2 + \rho_3^2},\ \tan\theta = \rho_3/\rho_2,\ 0 \leq \theta \leq \pi/2 \quad (5)$$

This last set of coordinates, eq 4 and 5, will prove to be the most useful. The energy of a conformation can be written in these coordinates and the sevenfold symmetry of the ring requires that the conformations specified by various sets of values of the ϕ's be identical. Equivalent sets of values of the ϕ's are listed in Table I which is derived from ref 7.[8] In eq 4, ρ specifies the amount by which a conformation differs from planar, θ specifies the relative contributions of the boat-like and chair-like conformations of Figure 5, and the two ϕ's specify one of the many possible identical conformations and also specify the relative contributions of the twisted and bent forms.

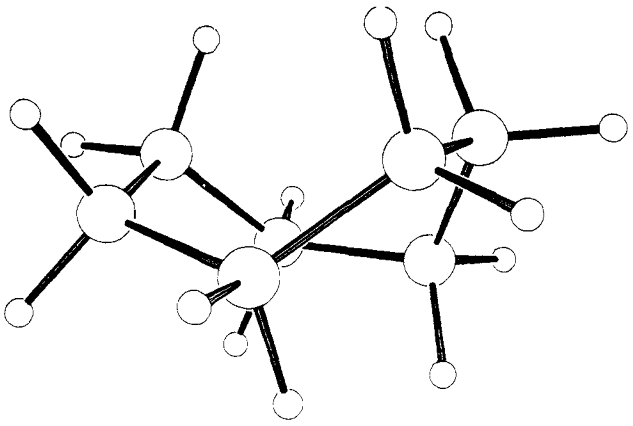

Figure 4. Computer projection of the twist-boat conformation. The "bow" of the boat is the atom second from the left in the projection and the "stern," which is slightly staggered, is formed by the atom on the extreme right and its nearest neighbor.

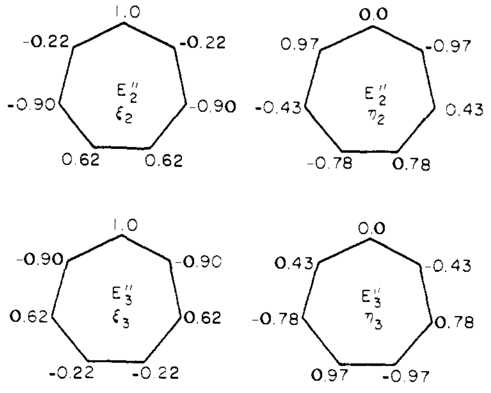

Figure 5. Displacements corresponding to the four coordinates of eq 1. The diagrams are labeled with the name of the coordinate and with the name of the representation of D_{7h} to which they belong.

Our goal is to picture the potential energy surface as a function of all four of these coordinates with particular emphasis on the low-energy areas of the surface. The energy has a very sharp minimum with respect to a variation in ρ, that is, nearly all the interesting low-energy conformations occur at a given value of ρ, and we need not consider the variation of ρ further in this section. The energy as a function of θ shows a number of distinct minima, and we discuss these below. At a fixed value of ρ and θ, variation of either ϕ alone leads to a periodic variation of the energy. The periodicity is different for each of the ϕ's with a change of π required in ϕ_2 and of $\pi/3$ required in ϕ_3 to complete a period. A geometrical figure that is periodic in two angular coordinates simultaneously is a torus, Figures 6 and 7. We can define a set of tori so that if we draw the potential energy as contour lines on the surface of the tori, the various equivalent conformations will be properly related as given by eq 4 and 5 and Table I. A torus is generated by revolving a circle of radius b about an exterior line in its plane at a distant a from its center.[9] We take the radius a to equal $c\rho\cos\theta$ and $b = \rho\sin\theta$. Then ϕ_2 and ϕ_3 are as indicated in Figure 6. This representation of the coordinate space defined by eq 4 has its difficulties. For example, the torus is reenterant for

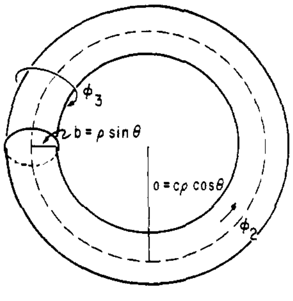

Figure 6. Section of the torus defined by the coordinates of eq 4. The constant c can be chosen to give the torus a convenient shape.

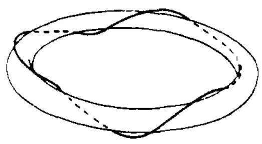

Figure 7. Drawing of the torus with the dimensions defined in Figure 6. The helix wound around the torus represents the pseudorotation path for the chair-twist-chair form of cycloheptane.

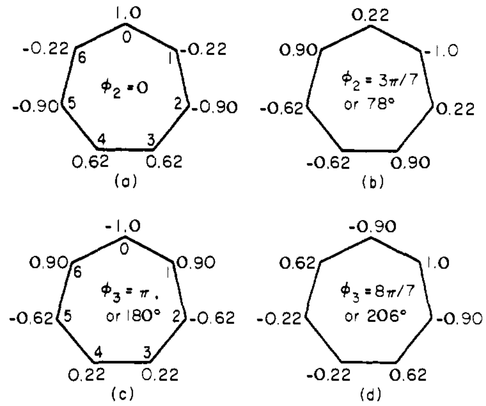

Figure 8. The relationship of the symmetry components of the displacements of the chair conformation of cycloheptane. One chair form consists of a superposition of the displacements of (a) and those of (c) weighted by cos θ and sin θ, respectively. The chair form next on the pseudorotation path is made up of (b) and (d). The appropriate value of ϕ for each form is given.

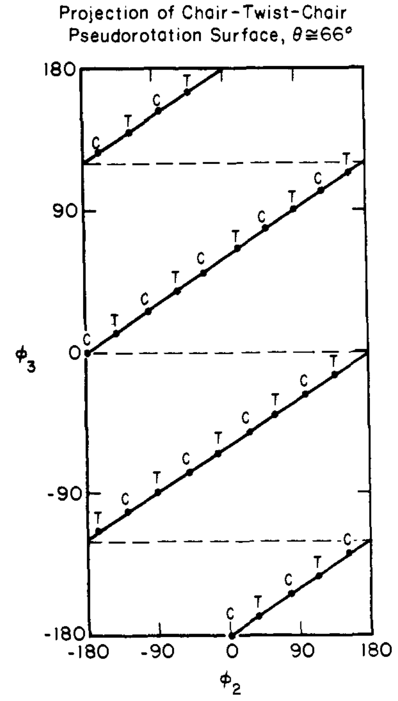

Figure 9. Schematic pseudorotation map for the chair-twist-chair form of cycloheptane. The map is a projection of the torus of Figure 7 with a constant c chosen as one. The 14 equivalent chair positions are marked C. The 14 equivalent twist-chair positions are marked T. The pseudorotation path is the line connecting the C and T and is the helix of Figure 7.

tan $\theta > c$, but the torus does achieve a reasonable three-dimensional representation of a four-dimensional coordinate system.[10] The constant c is arbitrary, and we chose it large enough to be able to illustrate large values of θ without considering reenterant systems. A value $c = 5$ will be convenient.

Now consider an arbitrary conformation specified by the fixed values ρ_0, θ_0, $\phi_2{}^\circ$, and $\phi_3{}^\circ$. Application of the symmetry rules of Table I will, in general, generate 27 more equivalent conformations for a total of 28. These conformations can all be represented by points on the surface of the torus with the fixed radii $c\rho_0 \cos\theta_0$ and $\rho_0 \sin\theta_0$. Note that the symmetry operations change ϕ_2 and ϕ_3 simultaneously. The lowest energy path between the equivalent conformations will be the one that connects these conformations through other conformations that involve a minimum of atomic displacements. Such paths are helices which wind around the torus so as to pass through all 28 of the equivalent conformations.[10]

The calculations to be described below show that the chair conformation of cycloheptane is characterized by $\theta_0 \simeq 66°$, $\phi_2{}^\circ = 0$, and $\phi_3{}^\circ = \pi$. This is a conformation with a plane of symmetry so that the symmetry operations of Table I generate only 14 equivalent forms.[7] The values of $\phi_2{}^\circ$ and $\phi_3{}^\circ$ indicate that this reference chair conformation is made up of contributions from the displacements ξ_2 and ξ_3 only (Figure 5). The chair conformation contains considerably more contribution from the ξ_3 displacements than from the ξ_2 displacements. The energy will therefore have a greater dependence on ϕ_3 than on ϕ_2. The lowest energy pass away from the reference chair conformation should lead to the equivalent chair conformation which is as close as possible to the reference conformation in its ϕ_3 coordinate. This leads to the choice $\phi_3{}' = \phi_3{}^\circ + (\pi/7)$ for the next conformation and examination of Figure 8 shows that this is indeed the conformation that can be reached by the least possible motion of the carbon atoms. Figure 8 also shows that $\phi_2{}'$ must equal $\phi_2{}^\circ + (3\pi/7)$ in order to arrive at a conformation equivalent to the reference conformation. Now consider the path defined by $\phi_2 = \phi_2{}^\circ + 3\phi$, $\phi_3 = \phi_3{}^\circ + \phi$ with ϕ varying from 0 to 2π. The variable ϕ defines a helix on the surface of the torus[10] and is illustrated in Figure 7. It passes through all the equivalent chair conformations in turn. The twist-chair conformations are found just half-way between the chairs, that is the first twist-chair is given by $\phi_2{}^{\mathrm{T}} = \phi_2{}^\circ + (3\pi/14)$, $\phi_3{}^{\mathrm{T}} = \phi_3{}^\circ + (\pi/14)$. We can map the variation of energy as a function of ϕ_2 and ϕ_3 only, if we project a torus of fixed radii onto a rectangle (or alternatively imagine the surface of the torus cut and flattened out to form the rectangle[10]). Such a map is shown schematically in Figure 9 and the detailed results of our calculations are plotted as contour lines in Figure 10. The variable ϕ does indeed define a long continuous valley and we take this to be the pseudorotation pathway for the chair-twist-chair form of cycloheptane.

For the special cases $\theta = 0$, $\pi/2$, the torus degenerates into a circle. The boat and boat-twist conformations have $\theta = 0$ and so the energy is just a function of ϕ_2 and this defines the pseudorotation path. The energy along this path is just a curve that can be represented as $E = 15.32 + 0.10 \cos 14\phi_2$.

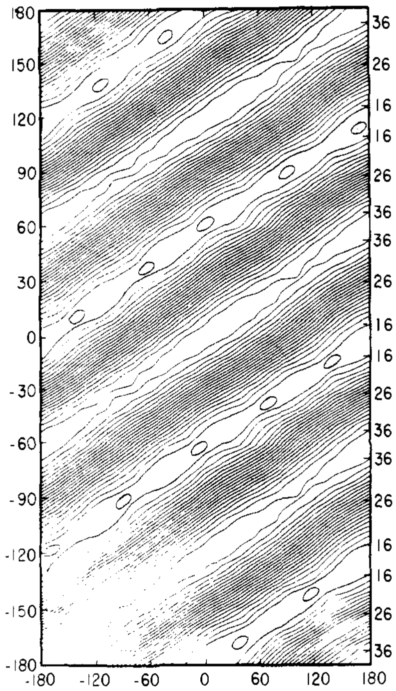

Figure 10. Contour map of the chair-twist-chair pseudorotation pathway of cycloheptane. The energy contours are plotted at 1-kcal intervals and are labeled on the right, the ordinate is ϕ_3 labeled on the left and the abscissa is ϕ_2. The map is shown schematically in Figure 9. Comparison with Figure 9 shows that the 14 equivalent twist-chairs are located within the ellipses along the diagonal pseudorotation pathway and that the 14 equivalent chairs are located midway between the twist-chair positions. Note that the pseudorotation valleys are separated by a high energy ridge approximately 20 kcal above the valleys.

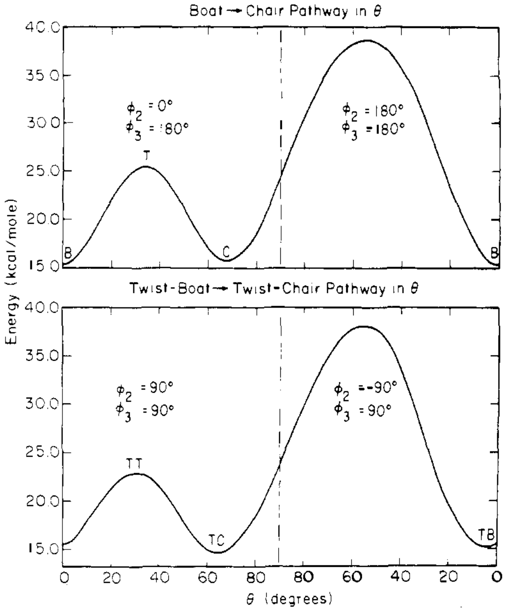

Figure 11. Boat to chair pathway for cycloheptane (top) and twist-boat to twist-chair pathway (bottom). The boat is marked by B, the chair by C, and the bent transition state by T. The twist-boat, twist-chair, and twisted transition state are marked TB, TC, and TT, respectively. The close similarity between the two graphs shows that all the conformations represented have rather low barriers to pseudorotation. The energy is plotted as a function of θ at constant ϕ_2 and ϕ_3 except ϕ_2 switches at $\theta = 90°$ where $\rho_2 = 0$ and near TB, ϕ_3 changes in the manner discussed in the text. The TB conformation is actually found at a small value of θ rather than the "ideal" value of $\theta = 0$.

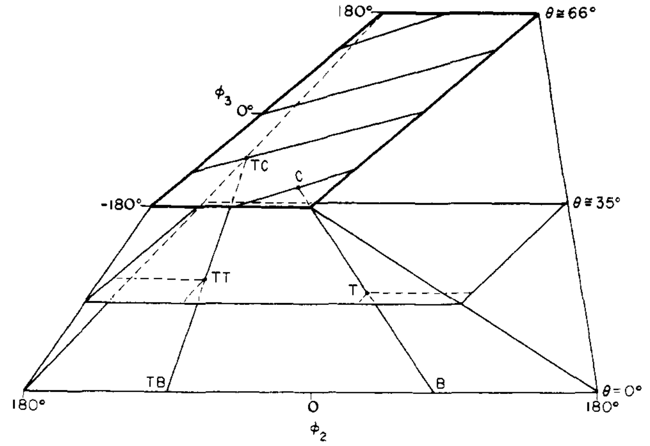

Figure 12. A drawing showing the relationship among the various pseudorotation surfaces. The top rectangle is a representation of the chair-twist-chair pseudorotation map of Figure 9. The bottom line is the pseudorotation map for the boat-twist-boat form (Figure 11). The lower rectangle is the pseudorotation map for the transition state. The lines indicate the paths shown on the left-hand sides of Figures 12a and 12b. The constant c is one for this diagram.

There exist a large number of paths between conformations on the boat-twist-boat pseudorotation path and those on the chair-twist-chair path. Imagine the boat-twist-boat torus (just a circle) inside of the chair-twist-chair torus. A different value of the parameter c can be chosen for two tori so that one can be buried in the other. The simplest paths between the two sets of pseudorotating forms are then straight lines running from points on the chair torus to points on the boat torus (circle). Such paths are ones in which only θ varies and a number of plots of the energy as a function of θ at different places along the tori are given in Figure 11. We can illustrate the paths between the chair forms and the boat forms in another way. If the various tori are unfolded into rectangles as in Figures 9 and 10, the various rectangles can be considered as lying on top of one another. The paths between the boat and chair forms are then lines connecting points on the chair rectangle with points on the boat rectangle (line). This is illustrated in Figure 12. In Figure 12 the rectangles are shown with the relative dimensions they would have if $c = 1$ for all of them. Note that all the possible conformations between the chair and the boat forms also lie on tori or rectangles and for every such conformation there are in general 28 equivalent conformations.

The exact energy and some of the detailed properties of the conformations of cycloheptane depend on the exact nature of the potential function used in the calculations and these details are discussed in the next sections. However, the general features of the conformations can be calculated from any reasonable potential function. Indeed, we have assumed these general features in most of our discussion so far and we conclude this section with a summary of them. The chair, boat, twist-chair, and twist-boat conformations all have about the same energy with the twist-boat and the twist-chair some hundreds of calories below the boat and chair forms, respectively. The variation of the energy along the pseudorotation paths defined above is monotonic between the twisted and bent forms.

For the chair forms other simple paths between equivalent paths exist but these paths are of very high energy. For example, we can define a path by $\phi_2 = \phi_2{}^\circ - \phi$, $\phi_3 = \phi_3{}^\circ + 3\phi$. This path is perpendicular to the pseudorotation path and Figure 10 shows that it goes over a barrier of about 20 kcal. There are also many possibilities for going from the chair conformations to the boat conformations. The lowest energy paths are characterized by a variation in θ alone. The transition state for this path can also pseudorotate. Its twisted form is lower than its bent form by about 2 kcal and the twisted form is about 8 kcal above the energy of the

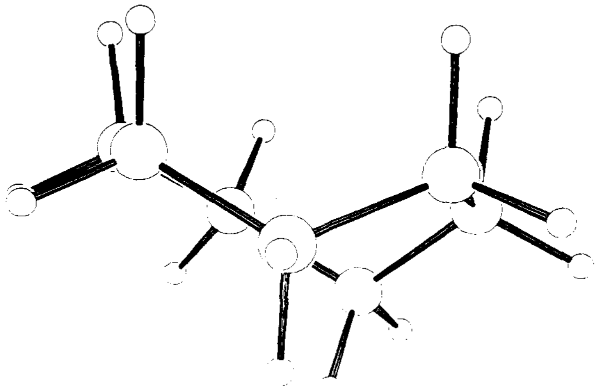

Figure 13. Computer projection of the bent transition state. Note the five coplanar atoms as the "bow" methylene group of the boat (left side of the projection) moves toward the position it will have in the chair conformation.

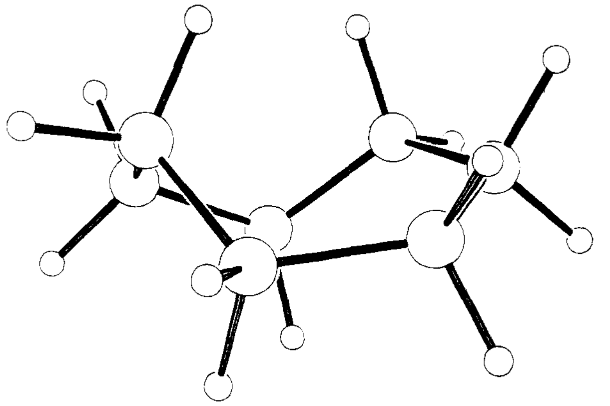

Figure 14. Computer projection of the twisted transition state. Comparison with Figure 13 shows that the previously eclipsed hydrogens at the "stern" of the boat (here on the left side of the projection) are now staggered and that there is a slight deviation from coplanarity in the set of atoms formed by the "bow" methylene group and its four nearest neighbors.

boat and chair forms. We call this set of conformations "the transition state" for cycloheptane and Figures 13 and 14 show its bent and twisted forms, respectively.

III. Details of the Model and the Potential Functions

A. The Coordinates. The coordinates of eq 1-5 must be expressed in terms of geometrical parameters of a seven-sided polygon. If we assume that the bond lengths or sides of the polygon remain constant, we require four in-plane and four out-of-plane coordinates to characterize the conformations of the figure. The coordinates we use are shown in Figure 15. The four angles α_1, α_2, α_3, and δ define the out-of-plane coordinates and the four quantities β_1, β_2, β_3, and r_{15} define the in-plane coordinates. From these eight coordinates, three sets of geometrical parameters are calculated: the Cartesian coordinate positions of all the atoms, the valence coordinates in which the potential functions are expressed, and the symmetry coordinates of eq 1-5. The values of ξ_2 and η_2 are scaled relative to ξ_3 and η_3 so that the ρ's calculated for the boat and chair forms are approximately equal. The process of generating these coordinates using projection operators[11] is described in detail in the supplementary material.[8]

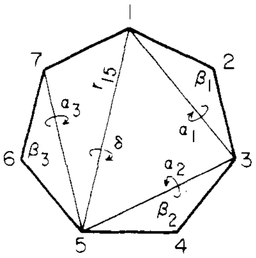

Figure 15. Definition of the four out-of-plane coordinates α_1, α_2, α_3, and δ and the four in-plane coordinates β_1, β_2, β_3, and r_{15}.

The ξ and η are defined in eq 1 by the z displacements of each atom or by the angular displacements of each atom as measured from the center of the ring. Unfortunately, the ξ and η defined this way are rather nonlinear functions of the α and δ for anything greater than infinitesimal displacements. In principle, the situation is exactly the same as it was in our representation of cyclohexane,[4] but for the cyclohexane case we were able to pick a set of α which kept at least three-fold symmetry in contrast to the situation of coordinates of Figure 15 for which the coordinates are not related by symmetry at all. Because of this nonlinearity, symmetry related conformations were found by actually applying the appropriate permutations to the Cartesian coordinates and then calculating the new set of ξ and η rather than by applying the symmetry operations to the ξ and η directly as indicated in Table I (see microfilm). The nonlinearity also makes Figure 10 look a little less symmetric than it would otherwise. It should be emphasized that the ξ and η are of actual help in computation as well as providing a basis for the idealized description of section II. Much of the effort and computational time is expanded in exploring the potential energy surface as a function of the four out-of-plane coordinates. The description of the surface in terms of the ξ and η provides an extrapolation of the entire surface from calculations which cover only a relatively small range of parameters. Even though this extrapolation is not exact and must be supplemented by detailed calculations at each point of interest, the practical realization of the ξ and η in terms of the α and δ is good enough to reduce the computational time used by an order-of-magnitude.

B. The Potential Functions and Detailed Calculations. We have used a potential function of the form

$$V = \sum_{i=1}^{7} \Big[H(\psi_i - \psi_i{}^0)^2 + 2F(\psi_i - \psi_i{}^0)(\psi_i - \psi_j{}^0) + T \cos 3\tau_i + U \cos \tau_i + \sum_{\substack{j=i+3 \\ \mathrm{mod}\ 7}}^{\substack{i+4 \\ \mathrm{mod}\ 7}} \sum_{m=1}^{4} \left(A e^{-r_{ijm}/r_0} - \frac{B}{r_{ijm}{}^6} \right) \Big] \tag{6}$$

In this equation, the seven ψ_i are the values of the seven C-C-C angles and the $\psi_i{}^0$ are the equilibrium values they would have if the ring were opened. The τ_i are the torsional angles defined in ref 4. The r_{ijm} are the distances between the *hydrogen* atoms attached to the carbon atoms indexed i and j. The index m labels the four distances between the hydrogens on these atoms.

The hydrogen atom positions are calculated assuming that these atoms are located in the plane perpendicular to the local plane of the ring formed by the carbon atom to which the hydrogen atoms are attached and the two other carbon atoms to which the carbon atom is attached. The H-C-H angle is taken to be 107° and the hydrogen atoms are placed symmetrically above and below the plane. The carbon-carbon bond lengths are 1.532 Å and the carbon-hydrogen bond lengths are 1.110 Å. The parameters H, F, T, and U were obtained by fitting the frequencies of the low-frequency motions of cyclohexane and a number of oxacyclohexanes[12] with the potential that has proved successful in calculating the conformational energy surface of cyclohexane. Since the potential parameters were obtained from fitting the low-frequency vibrations (the ring motions) only, they are effective potential constants which contain the effects that in other potential functions would be modeled by a large series of hydrogen–hydrogen, hydrogen–carbon, and carbon–carbon interactions.

However, for rings larger than cyclohexane, it is clear that more terms must be added to the potential function. The cyclohexane ring is small enough so that the potential terms in *H*, *F*, *T*, and *U* alone determine the positions of all the atoms. Conversely, it is unlikely that additional terms could be accurately determined from ring bending modes of six-membered rings alone. For cyclooctane, the situation is dramatically different. Calculations[13] show that a potential function with just *H*, *F*, *T*, and *U* terms leads to untenable conformations with unreasonably small 1,5-hydrogen–hydrogen distances. A repulsion term between 1,5-hydrogens must therefore be added to the potential function. The *H*, *F*, *T*, and *U* terms should correlate the positions of the 1,2 and 1,3-hydrogen atoms and so the 1,5-hydrogen–hydrogen terms are not applied to these. The situation with respect to 1,4-hydrogen interactions and consequently the applicability of these terms to cycloheptane was unclear *a priori*, but calculations show that these terms do have a small but none-the-less significant effect. The possible range of the parameters A and $1/r_0$ is very large and we have investigated the effect of three sets of parameters found in the literature. For all these the value of B is set at approximately the value estimated for long range van der Waals interactions. The values of all the potential parameters are listed in Table II.

Preliminary calculations were performed by specifying the values of the four ξ and η or alternatively of the α and δ, and then minimizing the energy with respect to the four in-plane coordinates β_1, β_2, β_3, and r_{15}. These calculations determined preliminary values of ρ for the boat and chair forms, and this allowed the scaling of the symmetry coordinates ξ_2 and η_2 by the factor of 1.88 discussed above.[8] The scaling made the ρ defined with the new ξ_2, η_2, ξ_3, and η_3 approximately equal in the boat and chair forms. Thereafter only θ, ϕ_2, and ϕ_3 were specified and the energy was minimized with respect to variations in β_1, β_2, β_3, r_{15}, and ρ. The minimizations were carried out to the nearest 0.0005 kcal, and no difficulties were encountered in finding the minima. The detailed results of the calculations using eq 8 and the Abe, *et al.*,[14] values of A and $1/r_0$ are shown in the figures and the tables. Table III shows the coordinates found for various conformations. Most of the general features of these coordinates have already been discussed. Many conformations can be considered as transition states between other conformations. What we shall call "the transition state" is the lowest maximum connecting boat-twist-boat with the chair-twist-chair surface and represented by the maxima to the left in Figure 11. The twist-boat conformations differ a bit from the idealized picture we have presented so far. The coordinate θ is about 6° rather than 0°. This represents a rather small contribution of ρ_3 to the twist form as $\tan \theta = 0.1$. The convergence criterion of 0.0005 kcal defines the geometrical parameters of a given conformation over a small range. This is illustrated in Table IV (see microfilm) for one of the twist-chair conformations and one of the twist-boats. The table shows that the ϕ_2 and ϕ_3 angles are determined to a few tenths of a degree for the twist-chair. The value of ρ is also shown; this value is determined for fixed θ, ϕ_2, and ϕ_3 by minimizing the energy and it varies by a few hundredths of a degree. The various in-plane coordinates also vary, but these are not listed in the table. The usual valence coordinates are shown in Table V (see microfilm) and the contributions to the energy in Table VI. The entries for the twist-chair are keyed to Table IV (microfilm) and show that the bond angles are determined to one-tenth of a degree while the torsional angles are determined to about half a degree. The contributions to the energy are remarkably stable, but this undoubtedly is due to using the energy as the criterion for convergence. At first glance, the situation looks much worse for the twist-boat. The angle ϕ_2 is determined to about a half a degree and the ϕ_3 is determined to within a few degrees. The values of ϕ_3 vary from those suggested by our simple symmetry considerations by tens of degrees. For the twist-boat conformation shown in Table IV the expected values of ϕ_2 are $\pi/2 + \pi/7 = 115.7°$ and of $\phi_3 = -\pi/2 + 5\pi/7 = 39°$. However, Tables V and VI show that, in fact, the calculations for the twist-boat have converged to the same accuracy as those for the twist-chair in both the valence angles and the energy. The large variations of ϕ_3 from the values expected are due to the effect of the nonlinearity of the ρ, θ, ϕ_2, ϕ_3 coordinates in determining a value of ϕ_3 which has only a small effect on the geometry and the energy. The boat-twist-boat energy surface should therefore be pictured as the surface of a very "thin" torus with a small and variable value of the radius b (Figure 6). The torus is nearly a circle as described in section II and the simpler description suffices for almost all parts of this discussion. We have described the lowest energy paths between the boat-twist-boat and the chair-twist-chair surface as being paths in which θ varies as ϕ_2 and ϕ_3 are held constant. This is not quite correct and the lowest single path, that from the twist-chair to the twist-boat, actually has a hook shape near the twist-boat end in which ϕ_3 varies as well as θ. We have not indicated this in Figure 12, and in Figure 11 only the variation with θ is plotted.

Using the geometrical parameters we have just described, projections of the three-dimensional conformations of the various forms of cycloheptane were generated by the standard computer program ORTEP[17] and are shown in Figures 1-4, 13, and 14.

The values for the energy and the geometrical parameters are, of course, sensitive to the details of the potential function. In Table VII (see microfilm), we list the rotational parameters for the various conformations.[18] These rotational parameters provide a simple method of characterizing small changes in geometry and can be determined experimentally (see section III). The parameters listed are the moments of inertia, *I*, the rotational constants, *A*, *B*, *C*, and Ray's asymmetry parameter, κ,[18] which describes the deviation of a molecule from a symmetric top.

In choosing the potential function of eq 6, we have had to choose parameters for the hydrogen–hydrogen repulsive potential on an *ad hoc* basis. The effect of varying the parameters in this part of the potential is shown in Table VIII which gives both relative energies and the rotational constants. Examination of Table VI shows that the hydrogen–hydrogen terms make a repulsive contribution to the boat-

Table II. Parameters Used in Equation 6

H, kcal/(mol deg^2)	F, kcal/(mol deg^2)	T, kcal/mol	U, kcal/mol	ψ^0, deg	Ref
62.05	−5.04	2.52	−1.6429	112.60	12

	A, kcal/mol	$1/r_0$, Å^{-1}	B, (kcal Å^6)/mol	Ref
V_1	9950	4.55	45.2	14
V_2	6191	4.084	49.2	15
V_3	2300	3.6	49.2	16

Table III. Coordinates of the Cycloheptane Conformations

Conformation	Coordinate[a] θ	ϕ_2	ϕ_3	ρ
Boat	0.0	0.0	b	35.5
		$0.0 + (n^d/7)\ 180$		
Twist-boat	5.8	90.0	-95.4^c	36.3
		$90.0 + (n/7)\ 180$	$\sim -90 + (5n/7)\ 180$	
Chair	68.0	0.0	180.0	35.2
		$0.0 + (3n/7)\ 180$	$180.0 + (n/7)\ 180$	
Twist-chair	64.0	90.0	90.0	36.3
		$90.0 + (3n/7)\ 180$	$90.0 + (n/7)\ 180$	
Bent transition state	31.0	0.0	180.0	31.5
		$0.0 + (3n/7)\ 180$	$180.0 + (n/7)\ 180$	
Twist transition state	34.0	90.0	90.0	34.3
		$90.0 + (3n/7)\ 180$	$90.0 + (n/7)\ 180$	

[a] All values in degrees. [b] For $\theta = 0$, the value of ϕ_3 has no meaning. [c] These values vary erratically among the equivalent conformation; see text. [d] $n = 0, 1, \ldots, 13$.

Table VI. Energies for Cycloheptane Conformations[a]

Conformation[b]	E_H	E_F	E_U	E_T	ΣE_{Bond}	E_{H-H}	ΣE	ΔE
Twist-chair^6	2.646	−0.343	6.066	6.558	14.928	−0.301	14.627	0.0
Twist-chair^2	2.642	−0.342	6.067	6.561	14.928	−0.301	14.627	0.0
Twist-boat^9	1.050	−0.160	4.157	9.918	14.964	0.260	15.224	0.597
Twist-boat^{11}	1.051	−0.160	4.156	9.918	14.964	0.260	15.224	0.597
Boat	1.025	−0.158	4.143	10.240	15.249	0.171	15.420	0.793
Chair	3.507	−0.535	5.899	7.080	15.952	−0.247	15.705	1.078
Twisted transition state	4.003	−0.489	4.309	15.353	23.176	−0.351	22.825	8.198
Bent transition state	6.396	−0.935	3.824	16.003	25.289	0.200	25.489	10.862

[a] The energy values in kilocalories. The contributions to the energy contributed by each term of eq 6 are listed separately. [b] The numbers refer to Table IV (microfilm), see text.

Table VIII. Effect of Hydrogen–Hydrogen Repulsion Term on Conformational Energies

Conformation	V_1[a] ΔE[b]	$(A + B)/2$[c]	V_2[a] ΔE[b]	$(A + B)/2$[c]	V_3[a] ΔE[b]	$(A + B)/2$[c]
Twist-chair	0.0	0.09909	0.0	0.09899	0.0	0.09837
Twist-boat	0.597	0.10065	1.541	0.10013	1.448	0.10032
Boat	0.793	0.10062	1.657	0.10014	1.582	0.10032
Chair	1.078	0.09847	1.076	0.09837	1.056	0.09836
Twisted transition state	8.198	0.09991	8.449	0.09957	8.501	0.09957
Bent transition state	10.862	0.09808	11.351	0.09778	11.213	0.09793

[a] V_1, V_2, and V_3 are identified in Table II. [b] In kilocalories. [c] Rotational constants in wave numbers.

twist-boat energies, but not to the chair-twist-chair. The Bartell[15] and Hendrickson[16] potentials are both steeper or harder than the Abe, *et al.*,[14] potential. Consequently they raise the energy of the boat-twist-boat compared to that of the chair-twist-chair. Indeed, changing the hydrogen-hydrogen potential has almost no effect on the chair forms at all. It affects the energy of the boat forms but has a relatively small effect on the rotational constants. The effect of the hydrogen-hydrogen potential is also sensitive to the details of the geometry, in particular to the value of the H-C-H angle. With the usual assumption that the bond angles are defined by the directions of atomic orbital maxima and the assumption that there is local C_{2v} symmetry about a carbon atom, symmetry arguments require that a small increase in the C-C-C angle from tetrahedral be accompanied by a corresponding decrease in the H-C-H angle.[19] The value for the equilibrium C-C-C angle of 112.6° (Table II) then leads to a H-C-H angle of about 107°. This value is used to calculate Table VIII. Table IX (see microfilm) gives corresponding values of the relative energies and rotational constants for an H-C-H angle of 110°.[16] From the tables, it can be seen that decreasing the H-C-H angle has about the same effect as softening the hydrogen-hydrogen potential. This is obviously correct for cycloheptane for which the H-C-H group always points outward from the center of the ring. The calculated values of the rotational constants are relatively insensitive to the H-C-H angle. For example, varying the H-C-H angle from our usual value of 107° to 110° varies the thermally averaged value of $(A + B)/2$ from 0.09929 to 0.09934 cm^{-1} for the V_1 potential.

The energy differences between the boat forms and the chair forms are small and consequently the relative amount of these forms actually found in the molecule at equilibrium depends appreciably on the entropy as well as the energy terms. An estimate of the difference in entropy between the different forms can be made by treating the pseudorotation motion as a hindered rotor using the simple Hamiltonian originally suggested for cyclopentane.[3] The free energy can be found from standard tables[20] and is a function of the

Table X. Partial Thermodynamic Parameters at 300°K

Conformation	ΔE,[a] kcal	Pseudorotation barrier,[b] kcal	$\Delta G°_{300}$, Pseudorotation, kcal	$\Delta G°_{300} + \Delta E$, kcal
Chair-twist-chair	0.0	1.0	0.0	0
Boat-twist-boat	0.6	0.2	−0.5	0.1
Transition state	8.2	2.7	−0.1	8.1

[a] Difference between the energy of the minimum on each pseudorotation surface. [b] Difference between the maximum and minimum along the pseudorotation path.

barrier heights listed in Table VIII and of the reduced mass for the motion. This reduced mass is

$$M_r = m_0 q_0^2 \tag{7}$$

We have used a value of 28.1 amu Å^2 for the effective mass, m_0, of a methylene group and estimated q_0 from our calculated geometries. The results are shown in Table X. The contribution of the pseudorotation is appreciable and makes up for the difference between the energies of the chair-twist-chair and boat-twist-boat forms, if we use the values calculated for the Abe, *et al.*, potential. Note that these values are only part of the free energy function; the remainder could be calculated in detail as we have previously done for cyclohexane,[4] but at the moment too little experimental information exists to make this worthwhile.

IV. Comparison with Experiment and with Other Calculations

Our calculations show that cycloheptane exists in two sets of pseudorotating conformations, the chair-twist-chair and the boat-twist-boat. These two sets of conformations have approximately equal populations. They are separated by a transition state which is about 8 kcal higher in energy. The existence of two similar nonrigid forms for the molecule makes the experimental determination of the structural parameters of cycloheptane exceedingly difficult. Many groups have tried to observe the freezing out of some mode of motion of cycloheptane using nuclear magnetic resonance as a monitor. Attempts have been made by Meiboom,[21] Anet,[22] and also by ourselves using the proton-enhanced-nuclear-induction techniques of Pines at liquid nitrogen temperature.[23] These attempts have been unsuccessful, in agreement with the calculations, but not of much help. We have taken extensive vibrational spectra of both cycloheptane and of some of the oxacycloheptanes. As might be expected from the calculations these spectra are complex and difficult to interpret. The low-frequency bands of oxacycloheptane (oxepane) show a complex structure which suggests two or more conformations, at least one of which is somewhat nonrigid, but detailed interpretation has not yet been possible. We have made a thorough search for evidence of free pseudorotation in both cycloheptane and in oxygen-substituted seven-membered rings. We have found no evidence of very low-lying bands (nothing <100 cm^{-1}) which is in accord with our calculations.

A more quantitative result has been obtained by Kainndy and Weber[24] who have obtained good rotational Raman spectra of cycloheptane. Their experiments show a symmetric top-like spectrum and their data come from states with high rotational quantum number, *J*. Their results are

$$B_0 = 0.099395 \pm 0.00002 \text{ cm}^{-1}$$

$$D_J = (4.34 \pm 0.07) \times 10^{-8} \text{ cm}^{-1}$$

The effective rotational constant B_0 is approximately equal to $(A + B)/2$ and we have listed calculated values for this in our tables. We have not attempted to calculate a value of the effective centrifugal distortion constant, D_J. The effective rotational constant is not only an average over the two different moments of inertia and over a myriad of angular momentum coupling terms, but is is also an average over the different populated conformations. We have carried out this average over different conformations in two different ways. In the first, we average the rotational constants of the four distinct low-energy conformations, the chair, boat, twist-chair, and twist-boat, weighted by the appropriate Boltzmann factors. Using the Abe, *et al.*, potential and a H-C-H bond angle of 107°, this gives $B_0 = 0.0993$. In the second, we first average the chair and twist-chair values and the boat and twist-boat values and then average these two weighted by the free-energy difference of Table X. This gives $B_0 = 0.0996$. Both of these are in excellent agreement with the experimental value of 0.0994 cm^{-1}.[24,25] The rotational constant is not as sensitive to variation of the potential function as one might hope. We have calculated the rotational constants for the geometries determined by Hendrickson[16] and by Bixon and Lifson[26] and these are listed in Table XI together with the relative energies. Table XII (see microfilm) lists the differences between the experimental rotational constant and the various calculated values.[8] We see that our calculation yields good agreement with experiment with the Abe, *et al.*, potential, V_1, and either choice of bond angle. Our calculations with the harder potentials of Bartell, V_2, and Hendrickson, V_3, give values a bit too low. On the other hand Hendrickson's[16] and Bixon and Lifson's[26] results are distinctly too high.

Table XI also compares our results for the relative energies with those of Hendrickson[16] and of Bixon and Lifson.[26] Only the relative energies are meaningful since we have defined the absolute difference of energy differently. Our geometries are closer to Hendrickson's than to Bixon and Lifson's as reflected by the rotational constants. The energy differences differ among the calculations. In particular both

Table XI. Comparison of Conformational Energies

Conformation	This work		Ref 16			Ref 26		
	E	ΔE	E	ΔE	$(A + B)/2$[a]	E	ΔE	$(A + B)/2$[b]
Twist-chair	14.63	0.00	7.10	0.00	0.10082	5.55	0.00	0.10136
Twist-boat	15.22	0.59	9.50	2.40	0.10104	8.19	2.64	0.10276
Boat	15.42	0.79	9.74	2.64	0.10080	7.95	2.40	0.10229
Chair	15.71	1.08	8.52	1.42	0.10023	6.22	0.67	0.10105
Twist transition state	22.83	8.20	15.20	8.10				
Bent transition state	25.49	10.86						

[a] Calculated from the geometries of ref 16. [b] Calculated from the geometries of ref 26.

of the other calculations put the boat-twist-boat much higher than ours does. Our pseudorotation barriers and values for the transition state barriers are, however, remarkably similar to those of Hendrickson.

In summary, we have presented a complete calculation of the low-energy parts of the cycloheptane conformational energy surface. We have defined the various possible pseudorotation pathways and calculated the properties of a number of the possible "transition states." Our calculations agree qualitatively with those of others at the low-energy conformations for which the other calculations have been done.

Our calculated values of the rotational constant agree with the experimental value considerably better than do the values calculated from the geometries published heretofore. In this sense our structures and potential functions are more accurate, but the comparison with the rotational constant cannot be considered definitive. The vibrational spectra probably show the existence of more than one set of low-energy conformations and we hope to be able to provide definitive data by analyzing these data. Microwave data on simple seven-membered ring systems would be most helpful since they should show both different conformations and the presence of relatively low-frequency vibrations. Cyclooctane and larger rings have conformations more sensitive to some aspects of the intramolecular potential than does cycloheptane and comparison of calculations of these conformations with the available definitive experimental information should provide more critical tests for the potential functions.

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Supplementary Material Available. The description of the coordinate transformations and Tables I, IV, V, VII, IX, and XII will appear following these pages in the microfilm edition of this journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm., 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-687.

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