triplets of the complex, which are in a favorable energetic position and are known[13] to be unreactive toward redox decomposition.

The comparison between the results obtained with biphenyl and with biacetyl suggests that the triplet charge-transfer state of the hexaamminecobalt(III) complex ion is too high in energy to be reached from the triplet state of biacetyl (which is placed at about 19,000 cm^{-1} in aqueous solution) but low enough to accept energy transfer from the biphenyl triplet (which has an energy of about 23,000 cm^{-1}).

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Conformational Structure, Energy, and Inversion Rates of Cyclohexane and Some Related Oxanes[1a]

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Abstract: The conformations of cyclohexane, *s*-trioxane, *p*-dioxane, *m*-dioxane, and tetrahydropyran are defined in terms of a new coordinate system which allows the structure and energy of all the significant conformations to be specified by only two coordinates. Using a potential derived from vibrational and geometrical data, detailed maps of conformational energy are constructed. These maps show that the more symmetric molecules are almost freely pseudorotating in the transition state between the chair and boat–twist forms. From calculated structural and potential data, the kinetic parameters for chair inversion are determined. A detailed picture of the chair–chair inversion process is given and the calculated rates are compared to experiment. As a result of the pseudorotation, values of $\Delta S^{\ddagger}$ are found which are positive and large.

The conformations of cyclohexane and of related six-membered rings have been of active interest since at least 1890.[2] Since then a large number of methods have been used to attempt to calculate the geometry and relative energy of the various conformations.[3] There have been a number of continuing difficulties with these attempts.[4] The exact structures have been difficult to determine or even to enumerate accurately, although most workers have had at least a qualitative understanding of the chair and boat conformers. The conformations that are in some sense intermediate between the boat and the chair structures have been especially elusive. Another major difficulty has been the lack of experimental information on any but the most stable forms of the molecules. For most of the simple ring compounds this, of course, means that the only direct evidence concerns the chair form. Derivatives of the simple saturated ring systems have been found to have a variety of the possible conformations, but this has led to quantitative understanding of the conformational possibilities only indirectly.[5] Only a relatively few properties of the simple ring systems are sensitive to the various possible conformations. The geometry and vibrational properties of the chair form give some information concerning the forces which hold it in its conformation.[6] The thermodynamic properties especially at high temperature are sensitive to the existence of the boat form.[7] Finally, the rate of inversion of the rings—a property that has been carefully and repeatedly measured in recent years—is sensitive to the nature of the transition state.[8] Unfortunately, the last two characteristics depend on thermal averages over the dynamical coordinates of the conformations and this makes it difficult to work backward from the experimental measurements to precise statements about the nature of the conformations.

In this paper we present a relatively complete conformational analysis of cyclohexane, *s*-trioxane, *p*-dioxane, *m*-dioxane, and tetrahydropyran. We first present a new set of internal coordinates which makes it easy to define the various conformations precisely and we then evaluate the energies of all the significant conformations using a potential function we have previously derived from vibrational and geometrical data.[6] Finally, we consider the chair–chair inversion process in detail and derive values for its rate. Many aspects of our system of coordinates and our consideration of symmetry are immediately extendable to the conformational properties of all the medium rings, but in this paper we will confine ourselves to six-membered ring systems and leave the larger rings for a later paper.

The Out-of-Plane Coordinates

We start by considering the coordinates which describe the out-of-plane motion of a planar six-membered

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(1) (a) Supported in part by the National Science Foundation; (b) National Science Foundation Predoctoral Fellow; (c) Alfred P. Sloan Foundation Fellow; address correspondence to this author.

(2) H. Sachse, *Ber.*, **23**, 1363 (1890).

(3) An elementary discussion is in J. B. Lambert, *Sci. Amer.*, **222** (1), 58 (1970). See ref 4 for more extensive references.

(4) J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968). This reference gives a summary of minimization algorithms.

(5) For example, calorimetric studies of carefully selected model compounds: J. C. Margrave, M. A. Frisch, R. G. Bautista, R. L. Clarke, and W. S. Johnson, *J. Amer. Chem. Soc.*, **85**, 546 (1963).

(6) H. M. Pickett and H. L. Strauss, *J. Chem. Phys.*, **53**, 376 (1970).

(7) C. W. Beckett, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2488 (1947).

(8) A critical survey of the nmr methods is J. Jonas and H. S. Gutowsky, *Annu. Rev. Phys. Chem.*, **19**, 447 (1968).

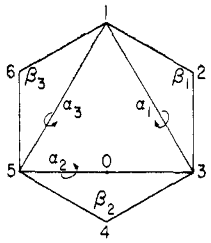

Figure 1. Numbering of the ring atoms and definition of the six ring-bending coordinates, α_1, α_2, α_3 and β_1, β_2, β_3. "0" is a convenient origin with which to write the geometry in terms of the α's and β's.

ring. The planar conformation of cyclohexane and similar rings is, of course, one of very high energy, and therefore this planar ring does *not* represent a favorable conformation of any of the rings we will study. However, the coordinates are particularly easy to visualize for the planar case. A planar six-membered ring can bend out of plane in three independent ways. The out-of-plane displacement of each ring atom, Z_i, in cyclohexane can be given by

$$\begin{aligned} Z_i &= \xi \cos (2\pi/3)i \\ Z_i &= \eta \sin (2\pi/3)i \qquad (1) \\ Z_i &= \zeta \cos \pi i = \zeta(-1)^i \end{aligned}$$

where $i = 1$–6. The form of these coordinates follows from the symmetry of the ring and they are similar to the coordinates defined by Pitzer and coworkers in their early discussions on pseudorotation of five-membered rings.[9] Note that the ζ coordinate carries the planar ring into a chair-like form, the ξ coordinates carries it into a boat-like form, and the η coordinate carries it into a twist-like form. For infinitesimal values of ξ, η, and ζ the out-of-plane motion of the ring is accompanied by very little change in the values of the various other coordinates of the molecule. Therefore the conformations of the molecule can be completely characterized by the values of ξ, η, and ζ. These three coordinates are not, however, the most convenient. The ξ and η coordinates belong to a degenerate representation of the symmetry group of the planar molecule. This means that the conformations with small values of ξ must have the same energy as those with the same values of η. We can use this fact to consider the properties of the configuration defined by the new coordinates

$$\begin{aligned} \rho &= \sqrt{\xi^2 + \eta^2} \\ \tan \phi &= \xi/\eta \end{aligned}$$

or

$$Z_i = \rho \cos (2\pi i/3 + \phi) \qquad (2)$$

We expect the energy to change rapidly as a function of ρ and very slowly or not at all with a change in ϕ. Note that successive values of the ϕ coordinate carry the molecule from a boat-like conformation to a twist-like conformation, then to another boat, then another twist, and so on through all six of the possible boat and the six possible twist conformations. Since there must be 12 positions of equal energy for an increase of ϕ by 2π, the lowest order term in the expression of the energy in terms of ϕ must be proportional to cos 6ϕ. The proportionality constant is expected to be very small.

We may bring ζ into our new system of coordinates by defining

$$\begin{aligned} r &= \sqrt{\xi^2 + \eta^2 + a^2\zeta^2} \\ \cos \theta &= a\zeta/r \qquad (3) \\ \tan \phi &= \xi/\eta \end{aligned}$$

or

$$Z_i = r[a(-1)^i \cos \theta + \cos (2\pi i/3 + \phi) \sin \theta]$$

In eq 3, a is a parameter which is not determined by symmetry considerations. We shall find it convenient to take $a = {}^1/_2$ so that

$$Z_i = r\{{}^1/_2(-1)^i \cos \theta + [\cos (2\pi i/3 + \phi)] \sin \theta\} \qquad (4)$$

The boat-like and twist-like conformations are now characterized by $\theta = \pi/2$, the one chair-like form is characterized by $\theta = 0$, and the inverted chair is characterized by $\theta = \pi$. *All* the other possible conformations of cyclohexane (for infinitesimal r) are intermediate between these conformations, and can be described *completely* by specifying the values of r, θ, and ϕ. For example, the half-chair form which is thought to be close to the shape of the transition state for the chair-to-boat transition is characterized by $\theta = \pi/4$ and $\phi = 0$.

The conformations of cyclohexane and of the other ring molecules are, of course, very far from being planar, and this necessitates some changes in the coordinates used to describe the conformations. The most important change lies in the fact that the three coordinates discussed for the hypothetical near-planar case are no longer sufficient to describe the various conformations in a reasonable approximation. The various in-plane coordinates of the ring in-plane bending and stretching modes can be expected to vary just as much as do the out-of-plane coordinates. We have, however, found a set of coordinates which very nearly give an ideal description of the chair–boat–twist changes, and we now proceed to describe these. We use the internal coordinates given in Figure 1 and define new coordinates, r, θ, and ϕ, in analogy with those of eq 4

$$\alpha_i = r\{\cos \theta + 2[\cos (4\pi i/3 - 2\pi/3 + \phi)] \sin \theta\} \qquad (5)$$

where $i = 1$–3. The transformation from the set r,θ,ϕ defined by eq 4 to that defined by eq 5 is rather complex and is not linear. This introduces some additional complications into the various properties of the molecules when expressed in the coordinates of eq 5, in particular the symmetry of the potential energy as a function of the coordinates of eq 5 is a bit lower than it would be if we could write eq 5 in terms of a set of six equivalent angles. The symmetry of the molecule and

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[9] (a) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2483 (1947). Their ϕ is defined as twice ours and it has a periodicity of π instead of 2π. Later papers on pseudorotation have used our definition of ϕ: J. A. Greenhouse and H. L. Strauss, *J. Chem. Phys.*, 50, 124 (1969); D. O. Harris, G. G. Engerholm, C. A. Tolman, A. C. Luntz, R. A. Keller, H. Kim, and W. D. Gwinn, *ibid.*, 50, 2438 (1968); G. G. Engerholm, A. C. Luntz, W. D. Gwinn, and D. O. Harris, *ibid.*, 50, 2446 (1968). (b) We consider the hydrogen atoms to be rigidly attached to the appropriate ring carbon atom. We assume the hydrogen atoms to move so that they are always situated in a plane perpendicular to the local plane of the ring formed by the carbon atom to which they are attached and the two other ring atoms to which the carbon atom is attached. The HCH angle is taken as the tetrahedral angle and the hydrogen atoms are placed symmetrically above and below the local ring plane.

of the entire Hamiltonian (kinetic energy plus potential energy) does not change with our choice of coordinates, of course.

Equation 3 contains the arbitrary parameter a which we picked equal to $^1/_2$ for the infinitesimal displacement case. We have found by calculation that this factor also gives a value of r for minimum energy which is about the same for both the chair and the boat conformations, and so we keep $a = {}^1/_2$ in eq 5.

The Potential Functions

In a recent paper[6] we reviewed the vibrational spectra of the molecules we are considering and examined the nature of the normal coordinates for these molecules. We were able to show that the ring-bending motions separate from all the other possible modes of motion to a great degree. These six separable modes are the ones that can be represented by varying the α_i and β_i coordinates shown in Figure 1. We then derived the following potential function for just these six bending modes.

$$2V = \sum_{i=1}^{6} H_i(\psi_i - \psi_i^0)^2 + 2F_i(\psi_i - \psi_i^0) \times (\psi_{i+1} - \psi_{i+1}^0) + T_i \cos 3\tau_i + U_i \cos \tau_i \quad (6)$$

In these equations the six ψ_i are the values of the instantaneous ring-bending angles and the ψ_i^0's are their equilibrium values. The six τ_i are the values of the torsional angles. The angles ψ are the angles between two adjacent ring bonds. To define the torsion angle consider four adjacent ring atoms 1, 2, 3, and 4. The torsional angle is then the dihedral angle between the two planes defined by atoms 1, 2, and 3 and by atoms 2, 3, and 4. The angles β are just three of the six possible ψ angles. The H_i, F_i, and T_i are the usual force and torsional constants. The term in U_i was found to be necessary to fit the observed geometry of cyclohexane. The values arrived at for all of these parameters are given in Table I. In comparing this potential function to others that have been used for conformational analysis, it is important to note that this function has been derived using the six-ring-bending-mode model and that the hydrogen nonbonded forces contribute to the various constants, especially ψ^0 and U, in a manner which is hard to separate from other effects.

Table I. The Parameters of Eq 6

	Bending[a]	
H_{CCC}	0.862	±0.054
H_{CCO}	1.152	±0.046
H_{OCO}	1.661	±0.064
H_{COC}	1.018	±0.053
F_{CC}	−0.070	±0.041
F_{CO}	0.096	±0.026
	Torsion[b]	
T_{CCCC}	1764	±197
T_{CCCO}	1699	±248
T_{OCCO}	1206	±191
T_{COCC}	708	±123
T_{COCO}	1294	±140
U_{CCCC}[c]	−1150	
U_{CCCO}[c]	−1150	

Equilibrium angles: $\psi_{CCC}^0 = \psi_{COC}^0 = 112.6°$
All other $\psi^0 = 109.47°$

[a] In (mdyn Å)/rad^2. [b] In cm^{-1}. [c] U is taken to be zero for the other cases; cm^{-1}.

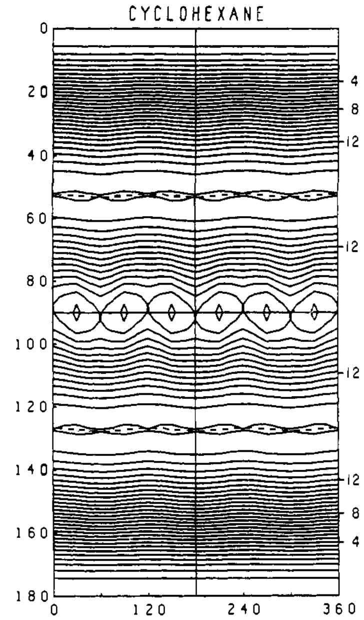

Figure 2. Conformation map of cyclohexane. The abscissa is ϕ and the ordinate is θ. The contour lines are spaced at 0.5-kcal/mol intervals and are labeled on the right. The dashed lines are at maximum energy and represent the dividing surface for the transition state. Closed contours near $\theta = 90°$ are local minima. The chair conformations are at $\theta = 0$ and 180°. The boat–twist form is close to $\theta = 90°$ (see Table V).

We are interested in the energy and geometry of the chair, boat, and twist conformations and of all relatively low-energy intermediate conformations. As we have shown in the last section the relative chair, boat, and twist character of each possible configuration can be specified in terms of r, θ, and ϕ.

Using the potential function of eq 6 we have carried out a series of calculations in which we have specified values for θ and ϕ and then minimized the energy with respect to r, and with respect to the three ring angles β_1, β_2, and β_3. The computer program calculated the values of the various ψ_i and τ_i from given values of θ, ϕ, r, β_1, β_2, and β_3. From these it calculated the energy by eq 6. The values of r, β_1, β_2, and β_3 were then varied and the energy was recalculated until a minimum value was found. These four coordinates are almost independent, and we encountered none of the difficulties that appear in some of the complex minimization schemes that have been used for conformational analysis.[3] The minimization was carried out to 0.1 cm^{-1} for a grid of points every 2.5° in θ and every 15° in ϕ. In Figures 2–6 we present the results as a series of energy contour lines plotted as a function of θ and ϕ. The contour lines are spaced at intervals of 0.5 kcal/mol. The energy increases from $\theta = 0°$ up to the dotted lines, then decreases to about $\theta = 90°$, the boat–twist conformation, increases again to the dotted line, and decreases to the inverted chair form at $\theta = 180°$. The closed contours near 90° represent local minimal (valleys) and the closed contours near 50° are local maxima (hills). We have used spherical coordinates for our diagrams and therefore the figures are but maps of contour lines on a sphere.[10] Figures 2–6 represent

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[10] A qualitative picture of a conformational sphere was drawn in J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7047 (1967).

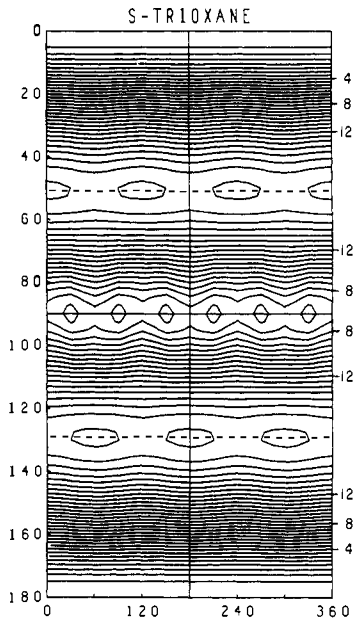

Figure 3. Conformation map of *s*-trioxane.

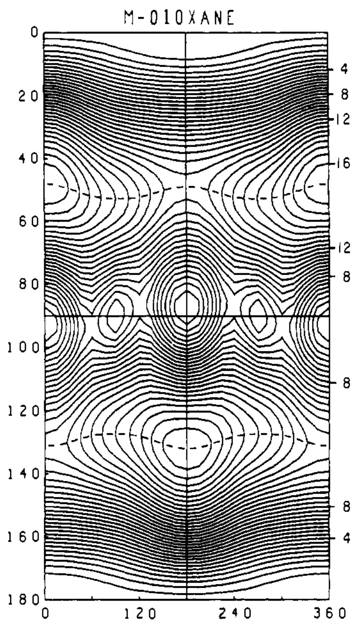

Figure 5. Conformation map of *m*-dioxane.

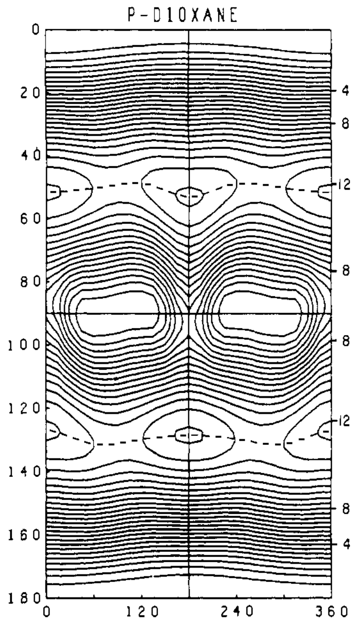

Figure 4. Conformation map of *p*-dioxane.

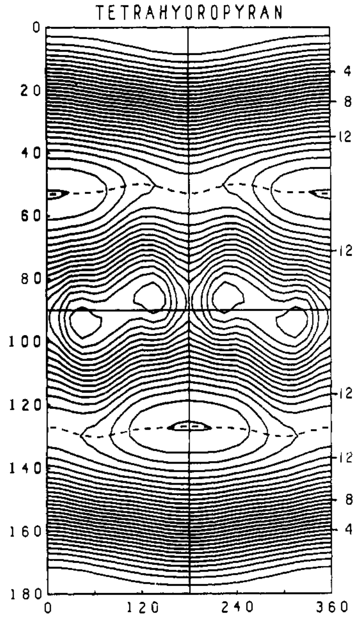

Figure 6. Conformation map of tetrahydropyran.

a simple cylindrical or *plate carrée* projection of the sphere. In Figure 7 we present the results for cyclohexane in an equidistant polar projection.[11] The true spherical nature of the plots can be visualized by comparing Figures 2 and 7. Finally, in Figure 8 we present the energies as a function of θ taken with ϕ fixed at 180°.

Details of the Conformation Maps

The various conformation maps of Figures 2–6 display the symmetry of the molecule as translated into our coordinates. To show how the translation is done, we consider the group of a hypothetical planar cyclohexane, D_{6h}, since all the groups in which we are interested are subgroups of this one. We wish to consider the symmetry operations on the conformation sphere and we consider the ξ, η, and ζ of eq 1 as the Cartesian axes of the sphere. The symmetry operations of the potential function drawn on the sphere form a group which is isomorphous to the molecular point group. We can identify the operations on the sphere by considering the effect of the molecular operations on ξ, η, and ζ. For example the operation σ_h on the molecule changes ξ, η, and ζ to $-\xi$, $-\eta$, and $-\zeta$ and it thus corresponds to the inversion operation, *i*, on the sphere. The results are summarized in Table II (also see ref 12).

As we have mentioned above, the coordinates defined by eq 5 have lower symmetry than the molecules and therefore the conformational maps will have corre-

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(11) C. H. Cotter, "The Astronomical and Mathematical Foundations of Geography," American Elsevier, New York, N. Y., 1966.

(12) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

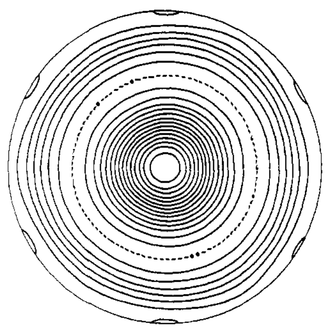

Figure 7. Conformation map of cyclohexane in an equidistant polar projection. Compare to Figure 2 which is a simple cylindrical projection. The chair conformation is at the pole (center of the diagram) and the boat–twist is at the equator (edge of the diagram). The transition state is again represented by the dotted line.

spondingly lower symmetry. The various symmetries are summarized in Table III. (Again we emphasize that the full Hamiltonian has the full symmetry, even if our plot does not.) In Table IV the symmetry of the conformation maps is translated into sets of coordinates which represent conformations of identical structure and energy. In Table V we display the coordinates of the "ideal" chair, boat, and twist conformations (the ideal conformations are defined by setting all the ϕ_i = 109.47°; the true structures differ from this slightly). Note the reduction of symmetry using the coordinates of eq 5 in the value of θ for the boat form. We would have liked to use coordinates that made this value of θ = 90° but at least our coordinates do not deviate from this value very much.

Table II. Molecule and Conformation Map Symmetry—D_{6h}

Operations[a]	Representations
Molecule Map	Molecule Map
$E \rightarrow E$	$A_{1g} \rightarrow A_{1g}$
$C_6 \rightarrow S_3$	$A_{2g} \rightarrow A_{2g}$
$C_3 \rightarrow C_3$	$B_{1g} \rightarrow A_{1u}$
$C_2 \rightarrow \sigma_h$	$B_{2g}(\zeta) \rightarrow A_{2u}$
$C_2' \rightarrow C_2''$	$E_{1g} \rightarrow E_{2u}$
$C_2'' \rightarrow \sigma_d$	$E_{2g} \rightarrow E_{2g}$
$i \rightarrow C_2$	$A_{1u} \rightarrow B_{2u}$
$S_3 \rightarrow S_6$	$A_{2u}(z) \rightarrow B_{1u}$
$S_6 \rightarrow C_6$	$B_{2u} \rightarrow B_{1g}$
$\sigma_h \rightarrow i$	$E_{1u}(x,y) \rightarrow E_{1g}$
$\sigma_d \rightarrow C_2'$	$E_{2u}(\xi,\eta) \rightarrow E_{1u}$
$\sigma_v \rightarrow \sigma_v$	

[a] Notation of ref 12. C_2' is taken through the atoms in the molecule and through ξ in the sphere; σ_d is perpendicular to C_2'; the C_6 axis is through the z axis of the molecule and the ζ axis of the sphere.

Table III. The Symmetries

	Molecule		Conformation map, planar form[a]	
	Planar form	Chair form	Coordinates of eq 4	Coordinates of eq 5
Cyclohexane	D_{6h}	D_{3d}	D_{6h}	D_{3d}
s-Trioxane	D_{3h}	C_{3v}	D_{3d}	D_{3d}
p-Dioxane	D_{2h}	C_{2h}	D_{2h}	C_{2h}
m-Dioxane	C_{2v}	C_s	C_{2h}	C_{2h}
Tetrahydropyran	C_{2v}	C_s	C_{2h}	C_{2h}

[a] The conformation map as a whole has the same symmetry as that of the planar form of the molecule in the appropriate coordinates.

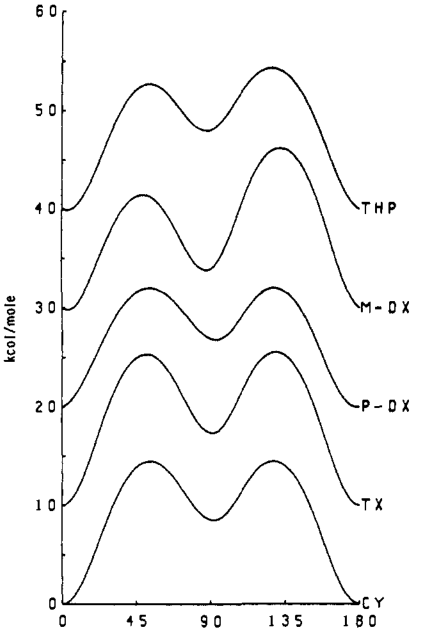

Figure 8. Variation of the energy (ordinate) with θ (abscissa) at ϕ = 180°. The boat–twist form is at about θ = 90°. The maxima in the curves represent the energy of the transition states. (For the unsymmetrical cases, M-DX and THP, the curves would have the two maxima interchanged for ϕ = 0°.)

In our maps we have plotted the energy as a function of only θ and ϕ. The out-of-plane nature of the configuration is also determined by r, and Table VI shows

Table IV. Equivalent Symmetry Positions

Spherical coordinates of eq 5
Both D_{3d} and C_{2h}, All Molecules
r, θ, ϕ
$r, \pi - \theta, \pi - \phi$
$r, \pi - \theta, \pi + \phi$
$r, \theta, -\phi$
D_{3d}, Cyclohexane and *s*-Trioxane Only
$r, \theta, \phi + 2\pi/3$
$r, \theta, \phi - 2\pi/3$
$r, \theta, 2\pi/3 - \phi$
$r, \theta, -2\pi/3 - \phi$
$r, \pi - \theta, \pi/3 - \phi$
$r, \pi - \theta, -\pi/3 - \phi$
$r, \pi - \theta, \phi + \pi/3$
$r, \pi - \theta, \phi - \pi/3$

Table V. Coordinates of the Ideal Chair, Boat, and Twist Conformations[a]

For all	$\psi_i = \beta_i = 109.47$	
Chair	$\alpha_1 = 35.36$	$r = 35.26$
	$\alpha_2 = 35.26$	$\theta = 0$
	$\alpha_3 = 35.26$	All ϕ
Also at	$\theta = 180$	All ϕ
Boat	$\alpha_1 = -35.26$	$r = 36.51$
	$\alpha_2 = 74.21$	$\theta = 88.06$
	$\alpha_3 = -35.26$	$\phi = 0$
Also at	$\theta = 88.06$	$\phi = 120, 240$
	$\theta = 91.94$	$\phi = 60, 180, 300$
Twist	$\alpha_1 = 63.29$	$r = 36.54$
	$\alpha_2 = 0$	$\theta = 90$
	$\alpha_3 = -63.29$	$\phi = 90$
Also at	$\phi = 30, 150, 210, 270, 330$	

[a] Coordinates in degrees.

Table VI. Parameters for Cyclohexane at $\phi = 0°$

θ	r	$^1/_3(\beta_1 + \beta_2 + \beta_3)$
0 (chair form)	32.05	111.47
10	31.64	111.64
20	30.15	112.26
30	27.82	113.22
40	26.13	113.88
50	25.89	113.94
60	27.33	113.30
70	30.06	112.11
80	32.13	111.41
90	32.66	111.75
Boat form	32.65	111.59

Table VII. Parameters of the Transition State

	ν_1,[a] cm^{-1}	ν_2,[a] cm^{-1}	ν_3,[a] cm^{-1}	$\lvert I^{\ddagger}\rvert/\lvert I\rvert$	V_0, cm^{-1}	V_1, cm^{-1}	V_2, cm^{-1}	V_3, cm^{-1}	$\mathcal{B}$, cm^{-1}	E_0, kcal/mol
Cyclohexane	293 (384)	430 (427)	458 (427)	1.0496	5078	0	0	0	2.274	14.08
a-Cyclohexane-d_{11}	238 (309)	394 (390)	426 (329)	1.0581	5078	0	0	0	1.507	14.15
e-Cyclohexane-d_{11}	238 (309)	394 (391)	426 (398)	1.0434	5078	0	0	0	1.505	14.15
s-Trioxane	379 (467)	538 (524)	542 (524)	1.0534	5417	0	0	42	2.857	14.93
p-Dioxane	330 (420)	463 (433)	493 (485)	1.0586	4095	0	128	0	2.535	10.96
m-Dioxane	378 (435)	480 (453)	534 (488)	1.0508	4881	766	39	72	2.503	11.40
Tetrahydropyran	342 (402)	433 (432)	490 (455)	1.0282	4792	324	4	−37	2.339	12.52

[a] Frequencies in parentheses are the frequencies of the chair form from ref 6.

that r is relatively constant over the whole map for cyclohexane. This means that all the low-energy conformations have about the same total deviation from planarity. Since r does remain relatively constant, it is proper to characterize a conformation by just the values of θ and ϕ as we have done in the maps. Table VI also shows that the sum of the ring angles remains practically constant, a result that might be expected.

The Inversion Process

Much of the recent evidence for the nature of the conformations of six-membered rings has come from nmr measurements.[13,14] For the molecules we are discussing, these measurements depend on the difference in chemical shift or other spin property between the axial and equatorial hydrogens of the compounds in their chair forms. The rates can be measured in a number of different ways and give a relatively consistent set of numbers for a large variety of compounds. The temperature dependence of the rate is much more difficult to measure, however,[8] and there has been appreciable disagreement about even the sign of the entropy of reaction in cyclohexane. A number of reaction mechanisms have been proposed, but we do not quite agree with any of them. We will first explain our picture of the reaction process and then compare it to those of others.

The chair conformations of the rings are at the poles of our spherical maps. The nmr process measures the rate for the molecule at one pole getting to the other pole. The number of molecules not in a chair conformation at a given time is very small and the time spent in any nonchair conformation is also small. Therefore, the only process that contributes to the measured rate is the transfer of a molecule from one pole to the other by any path. The process is best visualized using Figure 7. A molecule starts at the pole and eventually reaches the "transition state," the dividing surface of which is indicated in each figure by the dashed lines.[15] The molecule then proceeds downhill in energy to the boat–twist conformations at about $\theta = 90°$. The molecule leaves the boat–twist conformation with equal probability of going to either pole and so the overall rate is one-half the rate of the chair to boat–twist reaction. In all of the diagrams, θ is very nearly the reaction coordinate, but the molecule can travel from pole to pole at a large number of values of ϕ. For the molecules of high symmetry such as cyclohexane, there is very little energy dependence on ϕ and the molecule must be considered to be pseudorotating freely in the transition state. In order to calculate the rate of reaction we must first calculate the vibrational parameters of the transition state. We take the Hamiltonian for the pseudorotating coordinate as

$$H = \mathcal{B}P_{\phi}^2 + V_{\phi} \tag{7}$$

and expand V as

$$V = V_0 + V_1 \cos \phi' + V_2 \cos 2\phi' + V_3 \cos 3\phi' \tag{8}$$

$$\phi \cong \phi'$$

The various pseudorotation parameters were calculated by the method described in the Appendix, and the results are listed in Table VII. This table also lists the ratio of the determinant of the moment of inertia tensor for the transition state to that for the chair configuration. This factor does not vary much. We also calculated the vibrational frequencies for the three lowest vibrational modes (other than the ones which involve θ and ϕ), since these might be expected to change the most on changing conformation. The rates calculated from these data are given in Table VIII, and a comparison with measured quantities[16–18] is made in Table IX. We see that the measured values of $\Delta S^{\ddagger}$ and therefore of $\Delta H^{\ddagger}$ are in doubt. Our calculations definitely predict a substantial positive $\Delta S^{\ddagger}$, a prediction which is not sensitive to the exact nature of our potential function but depends on the existence of the pseudorotation path in the ϕ coordinate (see also below). The major contributions to the calculated $\Delta S^{\ddagger}$ are the absence of the θ vibration in the transition

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(13) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Amer. Chem. Soc.*, **82**, 1256 (1960).

(14) F. A. L. Anet and A. J. R. Bourn, *ibid.*, **89**, 760 (1967), and references therein.

(15) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966, contains excellent definitions of these terms.

(16) B. Pederson and J. Schaug, *Acta Chem. Scand.*, **22**, 1705 (1968).

(17) F. R. Jensen and R. Neese, preliminary work on *p*-dioxane derivatives.

(18) G. Gatti, A. L. Segre, and C. Morandi, *J. Chem. Soc. B*, 1203 (1967).

Table VIII. Calculated Rate Constants of the Chair-to-Boat–Twist Reaction

Temp, °K	Rate, sec^{-1}	$\Delta F^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Temp, °K	Rate, sec^{-1}	$\Delta F^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
	Cyclohexane					*p*-Dioxane			
75	4.15×10^{-28}	13.58	13.96	5.10	75	1.47×10^{-19}	10.65	10.92	3.64
100	8.22×10^{-18}	13.46	13.96	5.05	100	1.81×10^{-11}	10.55	10.95	3.93
125	1.29×10^{-11}	13.33	13.94	4.84	125	1.38×10^{-6}	10.45	10.95	3.96
150	1.75×10^{-7}	13.21	13.90	4.56	150	2.56×10^{-3}	10.36	10.93	3.85
175	1.58×10^{-4}	13.10	13.85	4.27	175	5.59×10^{-1}	10.26	10.90	3.67
200	2.60×10^{-2}	13.00	13.80	3.98	200	3.20×10	10.17	10.86	3.46
225	1.37	12.90	13.74	3.70	225	7.45×10^{2}	10.09	10.82	3.24
250	3.27×10	12.82	13.67	3.44	250	9.25×10^{3}	10.01	10.76	3.02
275	4.37×10^{2}	12.73	13.61	3.19	275	7.26×10^{4}	9.94	10.71	2.80
300	3.78×10^{3}	12.66	13.54	2.96	300	4.04×10^{5}	9.87	10.65	2.60
	e-Cyclohexane-d_{11}					*m*-Dioxane			
75	2.40×10^{-28}	13.66	14.06	5.30	75	3.16×10^{-21}	11.22	11.32	1.33
100	5.54×10^{-18}	13.53	14.04	5.09	100	7.56×10^{-13}	11.18	11.34	1.56
125	9.35×10^{-12}	13.41	14.00	4.77	125	8.58×10^{-8}	11.14	11.34	1.60
150	1.33×10^{-7}	13.30	13.96	4.41	150	2.08×10^{-4}	11.10	11.34	1.54
175	1.23×10^{-4}	13.19	13.90	4.06	175	5.52×10^{-2}	11.07	11.32	1.43
200	2.06×10^{-2}	13.09	13.84	3.74	200	3.67	11.03	11.29	1.30
225	1.10	13.00	13.78	3.43	225	9.66×10	11.00	11.26	1.16
250	2.65×10	12.92	13.71	3.15	250	1.33×10^{3}	10.98	11.23	1.04
275	3.56×10^{2}	12.84	13.64	2.89	275	1.14×10^{4}	10.95	11.20	0.91
300	3.09×10^{3}	12.78	13.57	2.65	300	6.84×10^{4}	10.93	11.17	0.80
	a-Cyclohexane-d_{11}					Tetrahydropyran			
75	2.26×10^{-28}	13.67	14.07	5.31	75	3.91×10^{-24}	12.22	12.44	3.01
100	5.30×10^{-18}	13.54	14.05	5.10	100	6.12×10^{-15}	12.14	12.46	3.15
125	9.03×10^{-12}	13.42	14.02	4.77	125	2.12×10^{-9}	12.06	12.45	3.10
150	1.29×10^{-7}	13.30	13.97	4.41	150	1.08×10^{-5}	11.99	12.43	2.97
175	1.20×10^{-4}	13.20	13.91	4.06	175	4.83×10^{-3}	11.91	12.41	2.82
200	2.02×10^{-2}	13.10	13.85	3.73	200	4.75×10^{-1}	11.84	12.38	2.65
225	1.08	13.01	13.78	3.42	225	1.69×10	11.78	12.34	2.49
250	2.60×10	12.93	13.72	3.14	250	2.96×10^{2}	11.72	12.30	2.33
275	3.49×10^{2}	12.85	13.65	2.88	275	3.08×10^{3}	11.66	12.26	2.17
300	3.04×10^{3}	12.78	13.58	2.64	300	2.17×10^{4}	11.61	12.22	2.02
	s-Trioxane								
75	9.79×10^{-31}	14.48	14.84	4.73					
100	8.52×10^{-20}	14.36	14.85	4.88					
125	3.29×10^{-13}	14.24	14.84	4.82					
150	8.30×10^{-9}	14.12	14.82	4.65					
175	1.17×10^{-5}	14.01	14.78	4.42					
200	2.69×10^{-3}	13.90	14.74	4.18					
225	1.85×10^{-1}	13.80	14.68	3.92					
250	5.45	13.70	14.63	3.68					
275	8.66×10	13.62	14.56	3.45					
300	8.67×10^{2}	13.53	14.50	3.22					

Table IX. Comparison of Experimental and Theoretical Parameters for the Chair-to-Twist–Boat Reaction at ~200°K

Molecule	Exptl $\Delta F^{\ddagger}$	Exptl $\Delta H^{\ddagger}$	Exptl $\Delta S^{\ddagger}$	Theor $\Delta F^{\ddagger}$	Theor $\Delta H^{\ddagger}$	Theor $\Delta S^{\ddagger}$	Exptl ref
Cyclohexane	10.3	9.1–11.5	−6–+5	13.0	13.8	4.0	14
Cyclohexane-d_{11}	10.3	10.8 ± 1	2.8 ± 0.5	13.1	13.8	3.7	14
s-Trioxane	10.9 ± 0.2	8.8 ± 1.2	−10.0 ± 6	13.9	14.7	4.2	16
p-Dioxane	~9.7			10.1	10.9	3.5	17
m-Dioxane	9.9 ± 0.2	9.5 ± 0.5	−2 ± 3	11.0	11.3	1.3	16
Tetrahydropyran	9.9 ± 0.4	10.1 ± 1.2	1.0 ± 6	11.8	12.4	2.7	18

state, which contributes about −1 eu, and the existence of the pseudorotation motion, which gives a large positive contribution. Note that the contribution is large even for *m*-dioxane which has low symmetry and a substantial barrier to free pseudorotation. The calculations show that the inversion process is very similar in the various oxanes.

Comparison with Other Calculations

Our maps of the conformations agree qualitative with calculations which have been made by others in all respects except one. Our calculations predict the existence of relatively free pseudorotation paths. Much of the literature suggests that the inversion process proceeds by a number of *distinct* paths and then tries to calculate a transition state along each path. This we claim is incorrect, especially for the molecules of high symmetry. The distinct path picture brings up the problem of either counting reaction paths or calculating symmetry number (which amounts to the same thing). Instead of this we do all our calculations using the full symmetry of the potential function and then

Table X. Comparison of Cyclohexane Energies

Boat, kcal/mol	Twist, kcal/mol	Transition state		Ref
		$\phi = 0°$	$\phi = 30°$	
8.5	7.9	14.5	14.5	This work
7.0	5.8	9.9	9.9	20
6.4	5.6	11.3	11.0	10

Table XI. Torsional Contribution to the Conformations[a]

	A_1[b]	A_2[b]	A_3[b]	A_4[b]	A_5[b]	A_6[b]
Chair	3.465	−1.998	−5.773	−4.670	0.380	5.108
Boat	4.341	0.741	−1.810	−1.203	2.041	5.216
Twist	4.284	0.613	−2.136	−2.605	−2.004	−2.223
Chair–boat transition state, $\phi = 0$	4.695	1.959	0.113	0.280	1.354	1.355
Chair–twist transition state, $\phi = 30°$	4.693	1.951	0.108	0.363	1.848	2.843

[a] This table gives the *relative* contribution of a term of the form A_n to the various conformations. This contribution can vary from −6 to 6 for each n. [b] $A_n = \Sigma_{i=1}^{6} \cos (n\tau_i)$.

count all equivalent forms explicitly. The problem is very similar to the classical example of determining the symmetry number of ammonia.[19]

In Table X we compare some of the parameters derived from our calculation of cyclohexane with those of other calculations. Hoffmann's calculations were done using extended Hückel theory[20] and our values for the geometrical coordinates. In Hendrickson's calculations both the geometrical coordinates and the energies were determined.[10] Hendrickson's geometries agree well with ours and all three calculations place the transition state at about the same place. Hoffmann's calculations and ours predict the pseudorotation of the transition state and a calculation using Hendrickson's potential function undoubtedly would predict the same. The absolute energies derived by the different calculations differ. Our energies for the transition state, the boat, and the twist form are higher than those generally accepted, but our boat–twist energy difference is about the same or a bit lower than that given by others. The higher energy for the transition state is not too surprising. Our model does not include the stretching coordinates and constrains the hydrogen atoms to move as discussed in footnote 9. This should not make much difference in the chair conformation, which is unstrained, but should make an appreciable difference in the transition and boat–twist conformations, which are considerably strained. Furthermore, we have done calculations of the conformational energies using slightly different sets of constants than those of Table I. These showed that the experimental error in our force constants could lead to an error of 3–4 kcal/mol in the transition-state energies (however, the flatness of our pseudorotation paths is not sensitive to this uncertainty in our force constants).[21] Finally, we point out that there is very little experimental evidence on the exact energy difference between boat and twist forms and that this energy difference depends critically on the nature of the assumed potential, as shown in Table XI, which shows the relative contributions to the energy of torsional potential terms of different forms. Of particular interest is the effect of a five- or sixfold term in the potential on the relative energies of the boat and twist forms. The exact value of such terms is exceedingly hard to determine either experimentally[22] or theoretically.

Summary

A new coordinate system of internal coordinates has been defined for six-membered ring compounds similar to cyclohexane. With these coordinates, the chair, boat, and twist conformers are easily defined and the low-energy paths linking them can be mapped in two dimensions on the surface of the sphere. The coordinate system has considerable advantages over other coordinate systems, in which the significant conformations can only be displayed in the total space of the six independent ring-bending coordinates or, worse, in spaces of even higher dimension. Since our coordinate system is directly related to the geometry, we have been able to systematically explore the nature of the potential function relating relevant conformers.

Using potential functions previously derived from vibrational and geometrical data for the molecules cyclohexane, *s*-trioxane, *p*-dioxane, *m*-dioxane, and tetrahydropyran, maps of conformational energy in these compounds have been prepared. These maps show that the more symmetrical molecules are almost freely pseudorotating in the transition state for the reaction of chair conformers to boat or twist conformers. By variation of the potential parameters, we have found that the qualitative nature of the surface is very insensitive to the value of the potential function parameters. This conclusion is substantiated by the observed agreement of structures in the transition state and in the boat and twist forms of cyclohexane with those of other calculations using quite different potential functions. The absolute values of the energies for these forms do, however, differ significantly.

The potential and structural information on the transition state available from these calculations was used to determine the kinetic parameters for the chair-to-boat–twist reaction. The rate of this reaction, in condensed media, is always twice that for chair–chair inversion. While experiments yield $\Delta F^{\ddagger}$ in the liquid state with good precision, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$

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[19] J. E. Mayer and M. G. Mayer, "Statistical Mechanics," Wiley, New York, N. Y., 1940, Chapter 8.

[20] R. Hoffmann, using methods described in R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), but with a change in the H(1s) exponent to 1.3.

[21] One should also take solvent effects into account. A 2-kcal/mol difference in $\Delta F^{\ddagger}$ for liquid and gas-phase values was found for *N*,*N*-dimethylnitrosamine: R. K. Harris and R. A. Spragg, *Chem. Commun.*, 362 (1967).

[22] The immense difficulty of determining the value of the sixfold term in methanol is discussed in R. M. Lees and J. G. Baker, *J. Chem. Phys.*, 48, 5299 (1968).

are in doubt. Our calculation of $\Delta F^{\ddagger}$ and $\Delta H^{\ddagger}$ for isolated molecules is quite sensitive to the nature of the potential. The corresponding value of $\Delta S^{\ddagger}$, however, depends mainly on the pseudorotational nature of the transition state and not on the exact values of the energy of the transition state. The methods developed thus allow us to determine the value of $\Delta S^{\ddagger}$ with some confidence, as well as to gain new semiquantitative insights into the nature of the conformational energies in these molecules.

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Appendix. Calculation of the Pseudorotation Parameters

In order to calculate the parameters of the transition states we first must calculate the quantities given in Table VII. We wish to find the parameters for the equation

$$H = \mathcal{B}P_{\phi}^{2} + V_{\phi} \tag{7}$$

and then solve for its energy levels and finally compute the transition state partition function. In this Appendix we will outline the steps in this calculation. We also describe a way to satisfy the Eckart conditions[12,23] for a situation requiring large displacements of the coordinates.

The $\mathcal{B}$ of eq 7 is just the appropriate kinetic energy matrix. We wish to evaluate it at intervals of ϕ of 60° and this involves large displacements of coordinates—a situation which makes it difficult to satisfy the Eckart conditions. We used the following procedure.

1. Find the Cartesian coordinates of the atoms for values of ϕ at intervals of 60° along the transition state.
2. Rotate the Cartesian coordinates such that they obey the Eckart axis conditions.
3. Find the derivatives of the Cartesian positions with respect to ϕ by expanding the positions as a function of ϕ in a Fourier series.
4. Evaluate $\mathcal{B}^{-1}$ at intervals of 60° using

$$\mathcal{B}^{-1} = \sum_{k} m_k \frac{\partial x_k}{\partial \phi}\frac{\partial x_k}{\partial \phi} \tag{A-1}$$

where the x_k's are the Cartesian coordinates for the geometry of interest.

Eckart gives a prescription for finding the rotation needed to satisfy the axis condition.[23] One constructs a matrix A such that

$$A_{ij} = \sum_{k} m_k (a_k)_i (x_k)_j \tag{A-2}$$

where a_k is a vector of Cartesian coordinates for the reference geometry. If A is symmetric, the Eckart axis conditions are satisfied. If A is not symmetric, then an orthogonal rotation matrix, T, must be found which will transform x_k to an axis system where the conditions are met. The matrix equation that can be solved to find T is

$$AT = S \tag{A-3}$$

where S is a symmetric matrix. One can then multiply (A-3) by its transpose to give

$$A\tilde{A} = S^2 \tag{A-4}$$

The matrix $A\tilde{A}$ can be diagonalized with an orthogonal transformation to give a matrix D

$$\tilde{U}A\tilde{A}U = D = \tilde{U}S^2U \tag{A-5}$$

and

$$S = U\sqrt{D}\tilde{U} \tag{A-6}$$

Finally

$$T = A^{-1}S \tag{A-7}$$

and

$$x_k' = \tilde{T}x_k \tag{A-8}$$

where x_k' satisfies the Eckart conditions.

One problem with this scheme is that A can have a determinant equal to 0 (*e.g.*, when all atoms lie in a plane for either a_k or x_k), which leads to an indeterminate solution in eq A-7. A second problem comes in eq A-7, since there is an ambiguity of sign for each of the three diagonal elements of $\sqrt{D}$. As a result there will be eight different S matrices and eight different T matrices. By matrix algebra, it can be easily established that all the solutions of T are orthogonal, although only four will represent proper rotations, in the sense that the determinant of T is unity. If one examines the problem similar to this in two dimensions, where

$$T_{11} = \cos\theta$$

$$T_{12} = -\sin\theta$$

$$T_{21} = \sin\theta$$

$$T_{22} = \cos\theta$$

then

$$\tan\theta = \frac{A_{12} - A_{21}}{A_{11} + A_{22}} \tag{A-9}$$

Equation A-9 has two roots between 0 and 2π and these are the expected double solutions. The four solutions for T in three dimensions that represent proper rotations have a similar origin. Only two of the three Eulerian angles are defined over a full circle, and expressions like (A-9) produce double solutions only for these two angles, to give four solutions for T.

An alternate method for finding T can be used

$$\tilde{U}AR = \sqrt{D} \tag{A-10}$$

where

$$T = R\tilde{U}$$

and where U and R are different orthogonal matrices. This method will work only if a way can be found to diagonalize (A-10). (It will be noted that $\sqrt{D}$ does not contain the eigenvalues of A since the operation used to diagonalize A is not a similarity transform.)

If A were a 2 × 2 matrix, we could write

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[23] C. Ekhart, *Phys. Rev.*, 47, 552 (1935); see also A. Sayvetz, *J. Chem. Phys.*, 7, 383 (1939). We are not calculating the myriad remaining terms that couple pseudorotation and overall rotation (see ref 9a); however, they should have only a small effect on the calculated $\Delta S^{\ddagger}$.

$$U_{11} = \cos \theta_1 \qquad R_{11} = \cos \theta_2$$
$$U_{12} = -\sin \theta_1 \qquad R_{12} = -\sin \theta_2$$
$$U_{21} = \sin \theta_1 \qquad R_{21} = \sin \theta_2$$
$$U_{22} = \cos \theta_1 \qquad R_{22} = \cos \theta_2$$

The conditions for diagonalization are

$$\tan (\theta_1 + \theta_2) = \frac{A_{12} + A_{21}}{A_{11} + A_{22}} \qquad \text{(A-11)}$$

$$\tan (\theta_2 - \theta_1) = \frac{A_{12} - A_{21}}{A_{11} + A_{22}} \qquad \text{(A-12)}$$

For the three-dimensional case, we can apply successive two-dimensional rotations of the form above. It can be shown that the sum of the squares of the off-diagonal elements not being rotated to zero is a constant for a given rotation, just as it is in the Jacobi method for diagonalization of symmetric matrices.[24] Thus, the complete sum of the squares of the off-diagonal elements is diminished with each rotation, and convergence is assured. A single solution for T is found which involves a minimum of rotation by selection of the roots of (A-11) and (A-12) such that $|\theta_1|$ and $|\theta_2| \leq 90°$. Most important, a solution for T can be found whether A is singular or not.

With this important hurdle past, the rest of the calculation of $\mathcal{B}$ is straightforward, and yields values of $\mathcal{B}$ that change significantly with ϕ. When $\mathcal{B}$ is not constant, the kinetic energy part of the quantum mechanical Hamiltonian can become quite complicated. It would be easier if we could define a new ϕ' such that it retained all the symmetry properties of ϕ but had a constant $\mathcal{B}$. The transformation from old to new is

$$\mathcal{B}' = \mathcal{B}\left(\frac{d\phi}{d\phi'}\right)^2 \qquad \text{(A-13)}$$

We can solve for $d\phi'/d\phi$ and expand in a Fourier series in ϕ.

$$\frac{d\phi'}{d\phi} = \sqrt{\mathcal{B}/\mathcal{B}'} = 1 + C_1 \cos \phi + C_2 \cos 2\phi + C_3 \cos 3\phi \qquad \text{(A-14)}$$

Integrating (A-14)

$$\phi' = \phi + C_1 \sin \phi + {}^1/_2 C_2 \sin 2\phi + {}^1/_3 C_3 \sin 3\phi \qquad \text{(A-15)}$$

Equation A-15 has a form which allows ϕ' to have the same value as ϕ at 0 and π (and multiples of π). The resulting corrections to ϕ' were less than a degree for all values of ϕ in all the transition states studied. Values of $\mathcal{B}'$ are given in Table VII.

In the same program, the potential was expanded in a cosine series in ϕ'

$$V = V_0 + V_1 \cos \phi' + V_2 \cos 2\phi' + V_3 \cos \phi' \qquad \text{(A-16)}$$

The coefficients of the expansion are given in Table VII. In addition, the determinant of the moment of inertia matrix, $|I|^{\ddagger}$, was evaluated at values of ϕ in increments of 60°. It was found in all cases to be constant in ϕ to less than 2%. Accordingly, the value was determined at the lowest point in the potential energy surface for the cases where the energy profile in ϕ varied by greater than 150 cm^{-1}. The average value was used for the low-barrier cases. As can be seen from Table VII, $|I^{\ddagger}|/|I|$ is virtually the same for all the compounds, and will contribute only about 0.05 eu to the entropy of activation.

The energy levels for the ϕ vibrational Hamiltonian were determined by matrix methods using the first 200 functions of a sin $m\phi$, cos $m\phi$ basis set. All 200 energy levels were used in the calculation of thermodynamic functions, since the basis functions become better and better representations of the wave function as the energy increases. A basis set of 200 is large enough so that, even for the highest barrier, the 200th energy level has an energy which is 15 times greater than the barrier height. These calculated energy levels should be quite accurate, especially for the determination of the kinetic parameters.

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(24) J. Todd, Ed., "Survey of Numerical Analysis," McGraw-Hill, New York, N. Y., 1962, p 248.