Structure of Transition States in Organic Reactions. II. MINDO/2 Study of the Cyclohexane Inversion

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Abstract: The inversion of cyclohexane has been studied using a potential-energy surface obtained from the semiempirical MINDO/2 molecular-orbital method. Six stationary points were found on this surface and the force constants for each calculated. On this basis, two of the structures, the D_{3d} chair and the D_2 boat, are minima. The C_{2v} boat is a barrier to the pseudorotation. Two other structures, of C_2 and C_s symmetries, are transition states for the conversion of chair to boat. In contrast to previous studies, the C_s structure is found to be the lower energy barrier. The sixth structure, of D_{6h} symmetry, is neither a minimum nor a transition state since the force-constant matrix has three negative eigenvalues. Zero-point corrections and entropies of activation are calculated from the force constants of chair cyclohexane and the two transition states, and comparisons with experimental results are made.

The cyclohexane system has long been a popular model in conformational studies.[2,3] Although there was much initial controversy concerning the energies and geometries of the stable conformers, and their modes of interconversion, the following facts now seem to be fairly well established experimentally. Cyclohexane assumes a slightly flattened D_{3d} chair structure as the most stable conformer.[4] Although never isolated, there is evidence from related systems that a boat form exists at an energy of about 5 kcal higher than that of the chair.[5] It is generally agreed that a "twist" (D_2 symmetry) form of the boat is more stable than the traditionally accepted C_{2v} structure.[6] Nmr studies indicate that chair cyclohexane inverts,[7,8] while theoretical considerations strongly suggest that this inversion takes place *via* the boat as an intermediate.

What remains as controversy, or not completely understood about this system, falls chiefly into the category of structural and energetic details. Is the twist boat, for example, a fairly rigid structure or does the boat interconvert between equivalent structures *via* a pseudorotational mode? In order words, are the two boat forms nearly equal in energy? Previous theoretical calculations indicate a difference of about 1.5 kcal between the two structures.[9] Is the entropy of activation for the chair to the boat conversion positive or negative? Here experimental values range from −6.5 to +4.9 eu. Finally, what is the detailed structure of the transition state for the interconversion and what is its energy, and is there only one distinct barrier or are there competing processes? There have been a number of computational studies, pioneered by Hendrickson,[10] on this problem. Hendrickson postulated a structure of C_2 symmetry, in which four carbon atoms were coplanar (similar to half-chair cyclohexene) as a likely transition state. A similarly postulated C_s structure, in which five carbon atoms were coplanar, was dismissed on the basis that its energy, as calculated by a valence force field method, was 1.5 kcal above that of the C_2 structure.

In the last few years there have been a number of other attempts to calculate both the structure of cyclohexane and the transition state for its interconversion using valence force field or molecular orbital methods.[11-16] All of these studies of the transition state, however, were based on assumed geometries, either those postulated by Hendrickson or related structures obtained by optimizing these structures under the constraint that either four or five carbon atoms be coplanar. In the light of a need for a more complete quantum-mechanical study of this system we have calculated the geometries of the stable forms of cyclohexane and the transition states for its interconversion using the MINDO/2 molecular orbital method[17] and previously developed methods for rapidly locating these stationary points.[18] The results for the structure of these transition states differ somewhat from those previously assumed.

There have been no previous *a priori* attempts to calculate the entropy of activation for this process. In an effort to resolve the experimental discrepancies mentioned above we have calculated all of the force

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constants and have used them to construct the vibrational partition functions and thereby estimate the entropy of activation.

Method of Calculation

The valence electron semiempirical molecular orbital methods, as originally developed by Pople[19] and more recently by Dewar,[17] show much promise as a tool for approximately accessing the potential-energy surfaces of polyatomic systems. The MINDO/2 method represents the latest published stage in this development.[20] This method has been shown to yield reasonable geometries and stretching-force constants of a number of hydrocarbons and in many cases to account for their differences in stability. Its deficiencies and limitations are also becoming increasingly well established. Some of these, such as the excessive stability ascribed to ring systems, relative to their open chain analogs, are also present in other zero-differential overlap methods.[21] Others, such as the excessively long C–H bonds and small H–C–H angles may be due to the current parameterization.[17] We have also found that MINDO/2 gives bending frequencies in hydrocarbons which are about 10–15% too small.[22] Since a cyclic system is preserved in the transformations of cyclohexane, we would expect at least a partial cancellation of errors in the relative energies.

All equilibrium geometries and transition states are stationary points on the many dimensional potential-energy surface. Moreover, any stationary point within a given symmetry is also stationary with respect to all degrees of freedom. This because the potential-energy gradient is totally symmetric.[18] It is therefore convenient to characterize stationary points on the basis of their symmetry and, whenever possible, to utilize symmetry in the location of these stationary points. Further characterization of the stationary points as equilibrium geometries or transition states requires additional computation. The six structures studied herein will be designated by their symmetries: D_{3d} for chair cyclohexane, C_{2v} for the boat, D_2 for the twist boat, D_{6h} for the planar carbon skeleton structure, C_s for the structure resembling Hendrickson's five coplanar carbon transition state, and C_2 for the structure resembling cyclohexene.

Two distinct methods were used to locate the stationary points. Both methods have been described previously and both utilize the gradient of the potential energy.[18] If the desired structure was believed to be an energy minimum, or a minimum within a given symmetry, the variable metric minimization method was used.[23] This was the case for the D_{3d}, C_{2v}, D_{6h}, and D_2 structures. The remaining structures were located by using a least-squares technique to minimize the sum of the squares of the components of the gradient.[24] The variable metric method automatically preserves symmetry, whereas in the least-squares method symmetry adapted coordinates were used. The structures used as initial guesses for the two methods were those studied by Hendrickson.[10] In all cases the geometries were optimized until the magnitude of the largest component of the gradient was less than 10^{-4} hartree bohr^{-1}.

Force constants are required to further characterize the stationary points as equilibrium geometries or transition states, to construct the vibrational-partition functions used to calculate entropies, and finally to calculate the zero-point energies. For transition states, the symmetry of the eigenvector corresponding to the single negative eigenvalue of the force-constant matrix allows us to further identify these structures.[25] The force constants were calculated by the finite difference method described in Appendix B of ref 26. On the basis of asymmetry of the force-constant matrix, and the extent to which the zero-frequency translations and rotations are reproduced, the errors in the force constants were judged in all cases to be less than 10^{-6} hartree bohr^{-2}. The vibrational frequencies were obtained from the eigenvalues of the mass-weighted force-constant matrix.[27] As a final check of the transition states, the structures were distorted along the direction of most negative curvature toward reactant and product and then the energy minimized. This helped ensure that the transition state is indeed the highest point on a continuous (but somewhat arbitrary) path connecting reactants and products.

Results and Discussion

D_{3d} Chair. The calculated geometrical parameters for this form of cyclohexane are given in Table I along with the experimental values obtained in two different electron-diffraction studies.[28,29] The calculated values can be seen to be in reasonable accord with experiment, as has been previously noted by Dewar and coworkers.[16] The notable exceptions are the overestimated flattening

Table I. Experimental and Calculated Geometrical Parameters of Cyclohexane D_{3d} Symmetry

	Calcd	Exptl
Bond, Å		
C_1–C_2	1.512	1.528,[a] 1.528[b]
C_1–H_1	1.223	1.104,[a] 1.119[b]
Angles, deg		
C_1–C_2–C_3	112.8	111.55, 111.05
C_1–C_2–H_2	110.2	108.8
C_1–C_2–H'_2	111.4	
H_1–C_1–H'_1	100.1	110.0
Dihedral angle, deg		
C_1–C_2–C_3–C_4	50.8	54.5, 55.9
C_1–C_2–C_6–C_5	134.4	

[a] Reference 28. [b] Reference 29.

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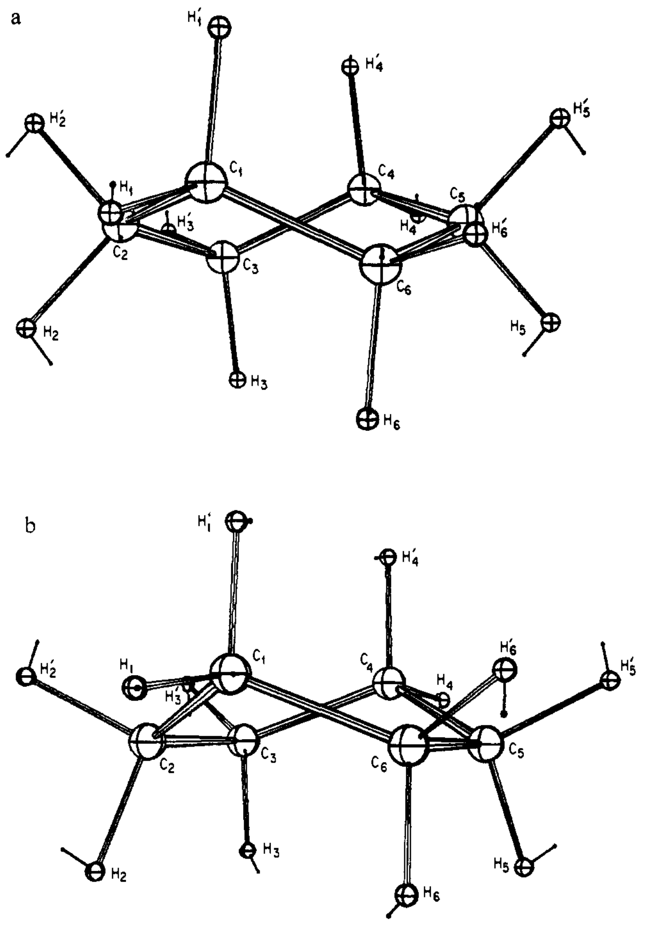

Figure 1. An ORTEP-II plot of the D_2 (a) and C_{2v} (b) symmetry structures of cyclohexane. The arrows (the arrowheads are represented as small spheres) correspond to the interconverting pseudorotational mode. In the D_2 structure this is the lowest vibrational mode, in the C_{2v} structure this is the negative curvature direction.

Table II. Calculated Geometrical Parameters of Cyclohexane in D_2 and C_{2v} Symmetry

	D_2	C_{2v}
Bond, Å		
C_1–C_2	1.517	1.512
C_2–C_3	1.517	1.521
C_3–C_4	1.509	1.512
C–H (av)	1.22	1.22
Angle, deg		
C_1–C_2–C_3	113.3	113.9
C_2–C_3–C_4	113.9	113.9
C_3–C_4–C_5	113.3	113.4
H_1–C_1–H'_1	99.6	99.5
H_1–C_1–C_2	110.8	110.4
H'_1–C_1–C_2	111.1	111.1
Dihedral angle, deg		
C_1–C_2–C_3–C_4	27.3	0.0
C_1–C_2–C_6–C_5		137.5
C_2–C_3–C_4–C_5	56.3	47.6

Table III. Calculated Thermodynamic Quantities for Five of the Stationary Points of Cyclohexane[a]

	D_{3d}	D_2	C_{2v}	C_s	C_2
Relative energy	0.0	4.8	5.0	6.9	7.1
Zero-point energy	96.1	95.8	95.7	95.5	95.5
Energy with zero-point correction	0.0	4.5	4.6	6.3	6.4
Entropy of activation				5.98	6.84
$R \ln (Q^{\ddagger}/Q)$ (vibrational)				2.41	3.27

[a] Energies are in kilocalories, entropies in eu.

of the ring as measured by the low value of the torsional angle, the H–C–H angles which are typically too small by several degrees, and the C–H bond lengths which again are typically too long by 0.1 Å. The fact that the force-constant matrix had no negative eigenvalues confirms this structure to be an energy minimum. The zero-point energy is calculated to be 96.14 kcal and the vibrational contribution to the entropy is 12.2 eu compared with the experimental value of 9.3.[5]

D_2 **and** C_{2v} **Boat.** The calculated geometries of these two structures are given in Table II. Experimental values are not given since the structures have not been isolated, although the existence of the boat, in either configuration, has been recognized and in fact shown necessary to explain the calorimetric data.[5] Both calculated structures are quite similar to the D_{3d} chair in that there is very little difference in the C–C bond lengths as well as in the H–C–H angles. Also like D_{3d}, both structures are "flattened" in that the C–C–C angle has increased to 113.9 relative to the ideal tetrahedral value of 109.5. Correspondingly the two torsional angles in D_2 have decreased from the idealized values (based on tetrahedral carbons) of 33.2 and 70.6 to 27.3 and 56.3°, respectively.

The energies of these structures relative to D_{3d} chair are given in Table III along with other calculated thermodynamic data. The value of 4.8 kcal for the difference in enthalpies between the D_{3d} and D_2 structures is within the range of 4.8 to 6.0 kcal, reported in previous experimental[6] and theoretical[9,10,15] studies. It is interesting to note that the enthalpy difference between the two boat structures is only 0.2 kcal. This difference decreases to less than 0.1 kcal when zero-point corrections are included.[30] This small difference implies nearly free pseudorotation in the boat. The possibility of pseudodorotation was confirmed by examining the calculated force constants of both D_2 and C_{2v} boat. The C_{2v} boat had a single negative eigenvalue of the force-constant matrix with a corresponding eigenvector of A_2 symmetry, the required species if C_{2v} is to serve as the transition state for the D_2 to D_2 pseudorotation.[25] As seen in Figure 1, a displacement along this mode does correspond to the pseudorotation. Similarly, the lowest frequency vibrational mode in D_2 boat belongs to the B_1 representation, the symmetry required if D_2 were the transition state and C_{2v} the minimum in the pseudorotation. From Figure 1 it is evident that this mode also corresponds to the pseudorotation. The two vibrational frequencies are quite small: 47i cm^{-1} (the imaginary frequency implies that the energy is a maximum for this mode) for the C_{2v} and 58 cm^{-1} for D_2.

D_{6h}. Although objections have been raised,[31] the

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(30) The MINDO/2 method was originally parameterized to heats of atomization at 298°K.[17] Although this casts some doubt on our use of zero-point corrections, etc., we have simply ignored this problem and have treated the MINDO/2 method as a means of obtaining a potential energy function only. Note, from Table III, that the calculated zero-point energies are all within about half a kilocalorie of one another. This suggests that the zero-point energy surface lies parallel to the potential-energy surface in the vicinity of these stationary points.

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planar carbon skeleton D_{6h} structure has generally been excluded from consideration as the transition state for the inversion, primarily because its energy, as estimated from force field calculations, is substantially higher than nonplanar structures leading to the boat as an intermediate.[10] The MINDO/2 results support these findings in two ways. In the first place, the calculated difference in enthalpy from the D_{3d} chair is 15.5 kcal, considerably higher than the experimental estimates for the transition state which range from 9.0 to 11.5 kcal.[32] Since MINDO/2 tends to underestimate bending-force constants and strain energies, we would expect the barrier to be underestimated rather than overestimated. Secondly, the calculated force-constant matrix for the D_{6h} structure had three negative eigenvalues which in itself implies that a lower energy barrier exists.[26,33] The eigenvector corresponding to the most negative eigenvalue was of B_{1g} symmetry, the species necessary if this were the transition state for the chair–chair inversion.[25] The remaining two eigenvalues had eigenvectors belonging to the degenerate E_{2u} representation. The geometrical parameters obtained for this structure are R_{C-C} = 1.52 Å, R_{C-H} = 1.22 Å, and the H-C-H angle 100.2°.

***C_2* and *C_s*.** The geometrical parameters for these two structures are given in Table IV, while the thermodynamic data is shown in Table III. ORTEP-II[34] plots of these structures are shown in Figure 2 which also indicates the numbering of the atoms. Although these structures resemble those originally proposed by Hendrickson and calculated by others, there are significant differences. In the C_2 structure, for example, the four carbon atoms (C_2-C_3-C_4-C_5 in Figure 2), which were assumed to be coplanar in previous studies, form a torsional angle of 12.4°. The "flap" angle (the C_4-C_3-C_5-C_6 dihedral angle in Figure 2) in the C_s structure is calculated to be 171.6° rather than the 180.0° previously assumed. It is also interesting to note that despite the large conformational differences among the various calculated structures, the carbon–carbon and carbon–hydrogen bond lengths as well as the H-C-H bond angles remain virtually unchanged. Although primarily of academic interest, it is noteworthy that the 129.0° C_1-C_2-C_6-C_5 dihedral angle in the C_s structure does not lie intermediate between its values for the chair (134.4°) and boat (137.5°). The significance of this is that in a search for a transition state using other methods one might consider only values of internal coordinates which are intermediate between those of reactant and product. Clearly such a bias would fail to locate this transition state.

Table IV. Calculated Geometrical Parameters of Cyclohexane in C_2 and C_s Symmetry

	C_2	C_s
Bond, Å		
C_1-C_2	1.509	1.507
C_2-C_3	1.521	1.515
C_3-C_4	1.523	1.523
C_4-C_5	1.521	1.523
C_5-C_6	1.509	1.515
C_1-C_6	1.506	1.507
Angle, deg		
C_1-C_2-C_3	115.5	113.6
C_2-C_3-C_4	118.7	117.1
C_3-C_4-C_5	118.7	119.2
C_5-C_6-C_1	111.5	113.6
H_1-C_1-H'_1	99.8	99.8
H_2-C_2-H'_2	99.7	99.9
H_3-C_3-H'_3	99.1	99.4
H_4-C_4-H'_4	99.1	99.0
Dihedral angle, deg		
C_1-C_2-C_3-C_4	6.6	24.2
C_2-C_3-C_4-C_5	12.4	
C_4-C_5-C_6-C_1	43.9	24.2
C_5-C_6-C_1-C_2	63.4	57.9
C_4-C_3-C_5-C_6		171.6
C_1-C_2-C_5-C_6		129.0

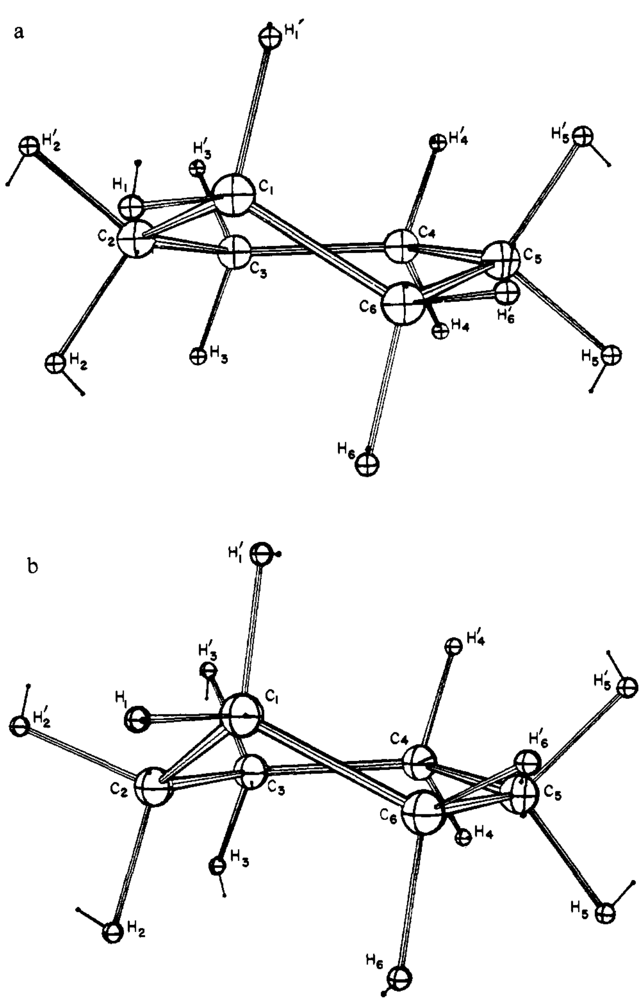

Figure 2. An ORTEP-II plot of the C_2 (a) and C_s (b) symmetry structures of cyclohexane, the calculated transition states in the chair to boat interconversion. The arrows (the arrowheads are represented as small spheres) correspond to the pseudorotational mode. In both structures this is the lowest vibrational mode.

From Figure 2 it is evident that both the C_2 and C_s structures more closely resemble boat cyclohexane rather than the chair. This is in accord with the Hammond postulate[35,36] since the conversion of chair to boat is endothermic.

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The calculated energies of the C_s and C_2 structures relative to chair are nearly equal, the C_s structure being slightly more stable than the C_2 structure in marked contrast to some previous studies.[10,15] When zero-point corrections are included, the difference between these two energies shrinks to less than 0.1 kcal. The force field calculations of Bucourt and Hainaut, on partially optimized structures resembling the original C_2 and C_s structures of Hendrickson also predict their energies to be virtually identical.[36] The MINDO/2 calculated enthalpies of activation for the C_2 and C_s structure are less than the experimental values by 4.5 kcal. This result is not surprising in view of MINDO/2's tendency to underestimate bending-force constants. Thus barriers to internal rotation are also underestimated as evidenced by ethane (calculated[37] 1.9 kcal *vs.* experimental[38] 2.9 kcal) and propene (calculated[37] 1.3 *vs.* 1.95 kcal experimental[39]). In contrast, valence force field calculations generally overestimate the barrier to cyclohexane inversion by about 1.0 kcal.[9,10]

The calculated force-constant matrices for these two structures each possessed a single negative eigenvalue with a corresponding eigenvector that was totally symmetric, as required by symmetry if these structures are to serve as transition states for the chair to boat conversion.[25] Furthermore, a displacement of each structure along the direction of negative curvature, toward reactant and product, followed by geometry optimization confirmed that each structure was the highest point on a path linking reactant, transition state, and product. This feature is also necessary to ensure that the structures are indeed transition states for this reaction.[26] In the present case, the two paths can be chosen such that each point on them has C_2 or C_s symmetry. One such point in the C_2 case has four carbon atoms coplanar and in the C_s case has five carbon atoms coplanar. The energies of these two points must be lower than that of the transition states in each symmetry. If the energy in each symmetry were minimized subject to the constraint that four (in the C_2 case) or five (in C_s) carbons be coplanar, the resulting structures must also have lower energies than the transition states. There is no reason to expect that the nonplanarity of four (C_2) or five (C_s) carbon atoms should be peculiar to the MINDO/2 surface. Since previously published studies, either valence force field or molecular orbital, have all employed the coplanarity constraint, their structures must be ones which have been displaced along the transition vector. Therefore, the structures obtained in previous studies give lower bounds on the enthalpies of activation on their respective surfaces.

In addition to the direction of negative curvature in each case, there was a very low-frequency (15 cm^{-1} for the C_2 structure and 25 cm^{-1} for the C_s structure) vibrational mode with a corresponding asymmetric eigenvector. The arrows in Figure 2 indicate the displacements along these directions. By comparing Figures 1 and 2 it is evident that these modes closely correspond to the pseudorotation mode in the boat. By this analogy we would expect that the two lowest frequency modes would serve to interconvert the C_2 and C_s structures. Furthermore, any structure lying along the pseudorotational coordinate would have an energy comparable with either the C_2 or C_s structure and would effectively act as a transition state. Thus the MINDO/2 calculations suggest that the barrier of the chair to boat interconversion is that of a very wide ridge rather than a narrow saddle. Commensurate with this view, we would expect a large positive vibrational contribution to the entropy of activation.

The calculated force constants were also used to construct the zero-point energies and the vibrational contributions to the partition functions, which were simply taken as the product over all real frequencies at 298°K. As seen in Table III, the effect of zero-point corrections is small, the barriers being effectively lowered by only 0.5 kcal. In contrast, the vibrational contributions to the entropies of activation are positive and significant, as we would expect from naive considerations, *i.e.*, the boat is more flexible than the chair and the transition states resemble the boat. In estimating the total entropy of activation we make the usual assumptions, namely that aside from statistical factors[40] there are no contributions from rotational and translational entropies of activation. For both the C_2 and C_s structures the statistical factor is 6. This gives rise to a contribution of 3.57 eu to the entropies of activation. From the vibrational-partition functions we calculate a contribution of 3.27 and 2.41 eu to the entropy of activation of the C_2 and C_s structures, respectively at 298°K. The most recent experimental estimate of the entropy of activation is that of Anet and Bourn[32] for the C_6HD_{11} system, their value being 2.8 ± 0.5 eu. If we subtract the contributions due to statistical factors from this number, the result is that for either the C_2 or C_s structure, the vibrational contribution to the entropy of activation is negative.

There appear to be several possible reasons for this discrepancy. (1) MINDO/2 has incorrectly predicted the entropies of the chair to boat transition states. (2) Neither calculated structure resembles the true transition state. (3) The experimental values are in error. (4) The transition-state theory is inadequate for this system.

Although MINDO/2 does underestimate bending-force constants, which are certainly relevant here, it is difficult to imagine that this could be a larger effect in the transition states than in the chair, at least not large enough to reverse the sign of the vibrational entropy difference. On the other hand, the experimental vibrational contribution of −0.8 eu (obtained by subtracting the statistical factor contribution of $R \ln 6$ from the experimental activation entropy) is more consistent with a transition state which is not pseudorotating. In this respect, our results are in agreement with those of Pickett and Strauss[41] who, using a two-dimensional valence force field model, find an entropy of activation of 4.0 eu and a transition state exhibiting psuedorotation. Their calculated barrier height of 13.8 kcal, however, is 4 kcal *higher* than the experimental activation enthalpy. It is interesting to

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note that the D_{6h} structure, if it were a proper transition state, would likely have a negative activation entropy (the statistical factor is unity, therefore the only contribution to the entropy of activation would come from the vibrational-partition functions). Both MINDO/2 and valence force field methods dismiss this possibility on energetic grounds, and MINDO/2 eliminates this structure on the basis of its force constants as well. Anet and Bourn give an extensive discussion of the errors in their experiment. However, the fact that two independent nmr techniques were used to give rate constants over nearly a 100° temperature range indicates that their value of 2.8 is probably reliable.

Conclusion

We have located and characterized six of the stationary points in the cyclohexane system with the MINDO/2 semiempirical molecular orbital method. A comparison of the calculated structures with those found previously, either experimentally or theoretically, shows good overall agreement. The surprising result that the C_s structure is predicted to be slightly more stable than the C_2 structure, as well as the consistently low-activation barriers, could be an artifact of the MINDO/2 method and awaits further verification by studies on a more accurate potential-energy surface. Based on the results of the force-constant calculations, and the nearly equal energies of the C_2 and C_s structures, we have suggested, as have Pickett and Strauss,[41] that there is effectively only one transition state. This transition state can be envisioned as encompassing a rather wide ridge on the many dimensional potential-energy surface, which would include all points along a pseudorotational coordinate connecting the C_2 and C_s structures. Furthermore, we have shown that previous calculations for the inversion have necessarily provided lower bounds to the enthalpies of activation on their respective surfaces. Finally the calculated entropy of activation, although positive, is in disagreement with presently accepted experimental values. Further work aimed at understanding the applicability and limitations of these methods in the elucidation of structures of organic transition states is in progress.

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Electronic Structure of Iron Trifluoride[1]

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Abstract: *Ab initio* quantum mechanical electronic structure calculations have been carried out on the neutral molecule FeF_3. An essentially "double ζ" basis set of contracted gaussian functions was used. Calculations were carried out for three different F–Fe–F angles, 120, 109.471, and 90°. The high-spin $^6A_1'$ state is predicted to be the ground state and have a planar or nearly planar equilibrium geometry. For planar geometry, the low-spin $^2A_1'$ state is predicted to lie 7.66 eV above the high-spin state. A Walsh-like analysis is used to discuss the possible geometries of other transition-metal trifluorides. The electronic structure is further discussed on the basis of Mulliken populations, and a variety of molecular properties are reported.

For a variety of transition-metal complexes,[4–14] *ab initio* electronic structure calculations are now becoming feasible. These calculations have already considerably furthered our fundamental understanding of the electronic structure of these interesting molecules, and the future appears very bright for this area of research. The most serious criticism which can be raised of these calculations[4–14] concerns the choice of basis set. In most of the calculations, either a minimum basis set (one function per occupied atomic orbital of the separated atoms) or a slightly better than minimum basis was used. The deficiencies of such small basis

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