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A Theoretical Study of 1–2, 1–3, and 1–4 Hydride Shifts in the Cyclohexyl Cation

J. J. Dannenberg,* C. Abrams, C. Decoret,[1] and J. C. Rayez[2]

Department of Chemistry, City University of New York—Hunter College, New York, New York 10021

F. Metras

Institut Universitaire de Recherche Scientifique, Département de Chimie, B.P. 523, Pau-Université, France

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The energies of the chair and boat conformations of the cyclohexyl cation were calculated by using the MINDO/3 approximation of molecular orbital theory with complete geometrical optimization, as were the transition states for 1–2, 1–3, and 1–4 hydride shifts. The "transition state" for the 1–2 hydride shift (the H-bridged carbonium ion) was the lowest energy species, closely followed by the chair and boat cations, which were almost identical in energy. The boat cation had one β hydrogen that was more positive and more closely associated with the cationic center than the other three. The transition state for the 1–3 shift was significantly lower in energy than that for the 1–4 shift. The transition state for the 1–3 shift resembled a protonated cyclopropane in that the C–C distance between the two carbons bound to migrating hydrogen is short (1.81 °A), and the charge distribution resembles that of protonated cyclopropane. The transiton state for the 1–4 shift was more similar to what one would expect for migration of a hydride between two unassociated carbons. The results of this study are discussed in the context of recent results in solvolyses of cyclohexyl derivatives. Similar calculations using the MNDO method were less successful.

Recent studies of the solvolyses of cyclohexyl tosylates under different reaction conditions have suggested that several different cationic cyclohexyl intermediates may be involved. In particular, 1–2 and 1–3 hydride shifts were often observed, but 1–4 hydride shifts were never observed in the solvolyses.[3] In the context of these experimental observations, it was of interest to determine the energies of the various possible cyclohexyl cations: chair, **1**, boat, **2**, or a hydrogen-bridged species, **3**. Although hydrogen-bridged structures for simple alkyl cations have not been widely accepted until recently, there is a growing body of evidence in their favor. Recent NMR studies involving isotopic perturbation[4] have confirmed earlier product and kinetic[5] studies that suggested a hydrogen-bridged structure for the 2-butyl cation. Other experimental studies on the solvolyses of cyclohexyl derivatives have variously reported evidence for a complex pattern of 1–2 and 1–3 hydride shifts in the products that are very dependent upon the medium.[3] NMR studies have been used to measure the rates of 1–2, 1–3, and 1–4 shifts in 1,2-, 1,3-, and 1,4-dimethylcyclohexyl cation[6] and 1–2 and 1–3 shifts in norbornyl cation,[7] which can be considered a substituted cyclohexyl cation constrained to a boat-like conformation.

Several groups have reported that unstabilized cyclohexyl cation rearranges to methylcyclopentyl cation so rapidly that the existence of free cyclohexyl cation was seriously questioned in both the gas phase[8] and superacid solution.[9] A recent report, however, presents evidence for a lifetime of at least 10^{-7} s in the gas phase for this species.[10]

Table I. Heats of Formation and Relative Energies of the Various $C_6H_{11}^+$ Species[a]

	heat of formation		relative energy	
species	MINDO/3	MNDO	MINDO/3	MNDO
1	168.8	186.9	2.0	0
2	169.2	187.1	2.4	0.2
3	166.8	205.4	0	18.5
4	181.1	222.7	14.3	35.8
5	195.4	222.5	28.6	35.6

[a] All energies in kcal/mol.

In this paper, we address the questions raised by the earlier reports using theoretical chemistry in the spirit described by one of us previously.[11]

Methods

We have performed molecular orbital calculations using both the MINDO/3[12] and MNDO[13] approximations, with complete geometrical optimization of all independent coordinates (except where constraints were necessary, as noted). We chose these methods as they are much less costly than ab initio methods, thereby allowing us to perform extensive geometrical optimization. In addition, our confidence in the ability of small basis set ab initio calculations to accurately predict activation energies is not any higher than that for the better semiempirical methods;[14] large basis set calculations are precluded by cost. In

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[1] NATO Postdoctoral Fellow, 1975–76. Permanent address: Faculté des Sciences, Université de Bordeaux, Talence, France.

[2] NATO Postdoctoral Fellow, 1977–78. Permanent address: Université Claude Bernard, Villeurbanne, France.

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Table II. Calculated Activation Energies for Various Hydride Shifts in Cyclohexyl Cation[a]

H-shift	activation energy MINDO/3	activation energy MNDO
1–2	−2.0	18.5
1–3	12.3	35.8
1–4	26.4	35.6

[a] All energies in kcal/mol.

our experience, MINDO/3 has reproduced the experimental relative gas-phase protonation energies of various molecules used in other studies.[15] We have had success with the MNDO method in the study of the thermal decomposition of azoalkanes,[16a] and the benzyl cation/tetrafluoroborate ion pair,[16b] but it is not so successful in predicting protonation energies as is MINDO/3. Small basis set ab initio methods have led to erroneous predictions of the structure of simple alkyl cations, such as the ethyl cation.[17,18b] MINDO/3, on the other hand, predicts structures and relative energies that are in accord with more sophisticated ab initio calculations using correlated wave functions (CEPA) and experimental results.[18]

Geometrical optimization was performed, using all 45 independent internal coordinates for the optimizations of the cations. The only exception was the constraint of keeping the C–H bond lengths on each pair of β-carbons equal, which was necessary to obtain the open cations as the more stable 1–2 bridged was otherwise spontaneously formed. This reduced the geometrical search to 43 variables. The activation energies for the hydride shifts were calculated by choosing the distance between the migrating hydride and the carbon to which it is to migrate as a reaction path. The other 44 variables were independently optimized for each of several fixed values of this reaction coordinate.

Results

The three possible conformations of the cation are all quite similar both in energy and structure, as can be seen from Table I and illustrations **1**, **2**, and **3**. A previously reported value of 169 kcal/mol for cyclohexyl cation (no conformation specified) agrees well with our results.[19] As the side of the ring containing the cationic center is virtually planar in **1**, the direction of pucker of the opposite side has little effect upon the overall energy.

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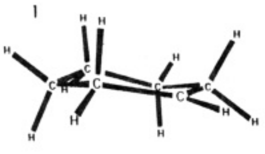

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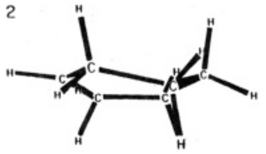

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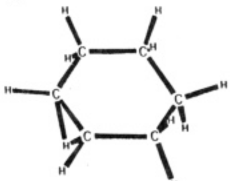

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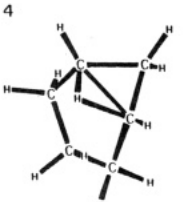

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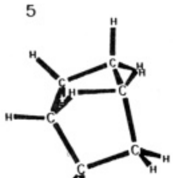

Table III. Energies of Protonation of Bicyclohexanes and Cyclopropane (MINDO/3)[a]

species	relative energies of protonation
[3.1.0]bicyclohexane	0
[2.2.0]bicyclohexane	4.5
cyclopropane	6.8

[a] Given in kcal/mol.

Table IV. Significant Properties of the $C_6H_{11}^+$ Species and Edge-Protonated Cyclopropane (MINDO/3)[a]

species	C–C distance (α-β or between bridgeheads)	C–H distance (bridging C–H)	Cα or C bridge[b]	H_β or H bridge[b]
1	1.46, 1.46		421	096, 078, 099, 077
2	1.43, 1.48		336	114, 073, 078, 064
3	1.42	1.30	183	121
4	1.81	1.30	196	043
5	2.04	1.30	249	−010
6	1.72	1.28	177	121

[a] All distances are given in Å. [b] Given as charge times 10^3.

The calculated activation energies for the various hydride shifts are also presented in Table II, while the structures of the transition-states are indicated in **1–3**. MINDO/3 predicts the activation energies for the hydride shifts to be in the order 1–2 < 1–3 < 1–4 while MNDO predicts 1–2 < 1–3 ≃ 1–4. The MNDO values are all much higher than the MINDO/3 values. MINDO/3 predicts a negative (−2.0 kcal) activation for the 1–2 shift and a protonated cyclopropane-like transition state for the 1–3 shift. Cyclopropane, protonated cyclopropane, **6**, and protonated and unprotonated bicyclo[3.1.0]hexane and bicyclo[2.2.0]hexane were calculated by use of using the same methods. The results of these calculations are presented in Table III. Protonated bicyclo[3.1.0]hexane was identical to the transition state for the 1–3 hydride shift as calculated by MINDO/3. Protonated cyclopropanes have been extensively reported in both the theoretical[20] and experimental[21] literature.

The facile rearrangement to methylcyclopentyl cation, which has been reported for unstabilized cyclohexyl cations,[8–10] was observed during the calculations, but the re-

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action path to this product was not studied in detail.

Discussion

The two open, "classical", conformations of cyclohexyl cation, chair and boat, are much closer to planarity than the corresponding conformation of cyclohexane and virtually identical in energy. This result suggests that the conformation of an intermediate that resembles the cyclohexyl cation, such as those likely to be involved in certain solvolyses of cyclohexyl derivatives, can easily change under the influence of even weak interactions, with its surroundings. Also, the most stable conformation, which contains a 1–2 H-bridge, is sufficiently close in energy to the open structures so that the lowest energy conformation of such intermediates can presumably be either bridged or not, depending upon the interactions with its surroundings. These results seem to agree well with the observations of various amounts of 1–2 deuterium shifts in the solvolyses of cyclohexyl derivatives in different solvents. One should note that when the β C–H bonds are constrained to be equal in the calculation, one of the β H's bends much closer to the α carbon than do the others (see Table IV). This result is of interest in the context of an explanation some of us have proposed for the observed deuterium distributions in the olefinic products of the acetolyses of 2,2,6,6-tetradeuteriocyclohexyl tosylate.[3] The lack of observed deuterium migration in the olefinic products in the absence of added salts, despite the persistence of a 15% 1–2 shift in the acetate product, led us to propose that the deuterium that migrates must be the deuterium that is eliminated.[3b] For this to be true, one of the four β hydrogens would have to interact more strongly with the cationic center. This suggestion is consistent with the report that the β-deuterium isotope effects for cyclohexyl derivatives are not additive in the usual manner.[22]

The 1–2 hydrogen-bridged cation, **3**, is the most stable cyclohexyl species by about 2 kcal/mol (see Table I). This value seems quite reasonable since secondary alkyl cationic intermediates that can form symmetrical hydrogen bridges seem to exist in either the bridged[3,5] or open form in different media. Here, the manner in which the medium stabilizes the cation may play an important role. When specific solvation of a cationic center occurs, it is likely that the open structure is favored. Less specific stabilization by a species that interacts at greater distance from the cation should favor the bridged structure, which has its charge more delocalized internally.

It is of particular interest to compare the transition states for the 1–3 and 1–4 shifts, **4** and **5**. Although **4** and **5** are identical with the structure obtained by optimizing symmetrically edge-protonated bicyclo[3.1.0]hexane and bicyclo[2.2.0]hexane, respectively, there is a significant amount of bonding between the carbons exchanging the hydride in **4** but much less in **5**. Table IV compares several features of **3**, **4**, **5**, and protonated cyclopropane **6**. In **3**, **4**, and protonated cyclopropane 5, the "hydride" being transferred is actually *positive*. The electron pair is being transferred through the C–C bond, i.e., the π-bond for the 1–2 shift, where the bridged structure can be thought of as a protonated alkene, and the σ bond of the protonated bicyclo[3.1.0]hexane for the 1–3 shift. The observation that 1–3 hydride shifts occur in the formation of the olefinic product of the acetolysis of 2,2,6,6-tetradeuteriocyclohexyl tosylate in the presence of sodium acetate[3a,b] might be explained by the stabilization of the (positively charged) migrating H by either an acetic acid molecule or an acetate ion. An NMR of the 1–3 and 1–4 hydride shifts in 1,3-dimethylcyclohexyl cation and 1,4-dimethylcyclohexyl cation, respectively, has come to similar qualitative conclusions. The 1–4 shift was similar to that expected for an acyclic system, but the 1–3 shift was affected by the ring.[6]

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Registry No. Cyclohexyl cation, 22499-63-4.

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