Ab Initio Study of the Conformations of the Cyclohexyl and 1-Hydroxycyclohexyl Radicals

Roger V. Lloyd,* J. Guy Causey, and Frank A. Momany

Contribution from the Department of Chemistry, Memphis State University, Memphis, Tennessee 38152. *Received August 3, 1979*

Abstract: The GAUSSIAN 70 program at the STO-3G level was used to calculate the energies of the cyclohexyl and 1-hydroxycyclohexyl radicals. All possible radical sites in the chair, boat, and twist-boat conformers were considered, and in each case the energy was optimized with respect to the angle that the α substituent (H or OH) makes with the plane of the carbon atoms at the radical site. For both radicals the twist-boat was ~5 kcal/mol and the boat ~7 kcal/mol higher in energy than the chair form. The calculations suggest that the radicals undergo chair-to-chair inversion via a twist-boat intermediate with simultaneous radical site inversion.

Introduction

Experimental EPR spectra for various cyclohexyl radicals have shown the phenomenon of line-width alternation,[1-3] and this has been attributed by some authors[4] to the interchange of β protons (protons attached to carbons β to the radical site) at rates comparable to the difference in their hyperfine splitting constants.[4] It has been suggested that the interchange is caused by ring inversion between two equivalent chair forms,[1] even though the experimental results in themselves do not actually allow conclusions to be drawn concerning the mechanism responsible for the observed line broadening. The calculations carried out here were designed to help distinguish between different mechanisms which are consistent with the experimental results.

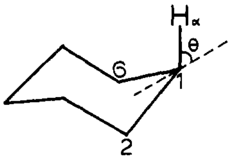
No theoretical investigations to date have been carried out on cyclohexyl radicals, but a few calculations have been made on the parent molecule. In a recent ab initio study, Cremer et al.[5] optimized the geometry of the chair form of cyclohexane. Hendrickson[6] had earlier studied cyclohexane using empirical potential energy functions. He obtained a value of 6.93 kcal/mol for the energy difference between chair and boat with the twist-boat 1.6 kcal/mol lower in energy than the boat. These calculations of possible intermediates[6] were consistent with the popular view that the twist-boat form is a logical choice for the higher energy intermediate in the chair-to-chair inversion process.[7] Whether the radicals invert in the same manner as the closed-shell molecules or if they have similar geometry is still unanswered. Our purpose is thus to examine the radical site geometries and obtain relative energies for several reasonable conformers of the cyclohexyl radical, that is, the chair, boat, and twist-boat forms.

Methods

Energies were calculated using GAUSSIAN 70 at the STO-3G level.[8] Standard C-C and C-H bond lengths,[9] tetrahedral H-C-H bond angles, and the optimized value for the C-C-C bond angles of 111° obtained by Cremer et al.[5] were used. The O-H bond length and C-O-H angle were taken from Lathan's ab initio study of methanol[10] (Table I). For the chair and boat forms dihedral angles of 56 or 0° were used[5] and for the twist-boat the angles were derived from Hendrickson's equations[6] applied to our set of parameters. Dihedral angles for the carbon skeleton in each of the three conformations are given in Table II along with their respective energies. Our calculated energy for the chair form of cyclohexane is −231.481 46 hartrees, in agreement with the value found by Cremer et al.[5]

In the chair form all carbons are equivalent and thus there can be only one radical site with two different substituent positions, axial (A) or equatorial (E), assuming that the radical site does not become planar. The boat contains two inequivalent carbons which we designate as "bow" and "midships" so that there are two radical sites with four different substituents. The twist-boat is similar except that the substituents on the "bow" carbon are geometrically equivalent.

The energy of each cyclohexyl radical was calculated as a function of the angle θ, formed by the C_1-H_α bond with the C_6-C_1-C_2 plane as shown below. H_α was maintained in the plane which bisects the C_6-C_1-C_2 angle and which is perpendicular to the C_6-C_1-C_2 plane. The angle θ, at which the energy is a minimum, was determined by fitting a set of calculated values to a parabola, and recalculating at this angle to give the final reported energy and unpaired electron spin densities.



For the 1-hydroxy radicals, a similar method was employed to determine the minimum-energy angle which the C_1-O bond makes to the ring. The hydroxyl hydrogen position was initially held constant, and, when the C_1-O bond was set at its optimum angle, the hydroxyl hydrogen was then rotated between 0 (directly away from the ring) and 180° (directly over the ring) in 60° increments to find its minimum-energy position.

Results

The α-hydrogen angles at minimum-energy positions for cyclohexyl radical are reported in Table III (with the constraint that the total geometry was not varied in the energy minimization). As expected the chair form is found to be of lowest energy, although the A substituent is slightly favored over the E by 0.14 kcal/mol. This energy difference is sufficiently small that the A and E can be considered as essentially equal in energy. The greatest difference between A and E positions is 0.6 kcal/mol for the boat "bow" radical site. The twist-boat radicals are 5.0-5.8 kcal/mol and the boat forms 6.4-7.7 kcal/mol higher than the chair configuration.

Table I. Standard Values of Geometric Parameters[a]

parameter	value	parameter	value
C-C length	1.540 Å	C-C-C angle	111.000°
C-H length	1.090 Å	H-C-H angle	109.471°
C-O length	1.439 Å	C-O-H angle	104.600°
O-H length	0.989 Å		

[a] Values taken from ref 5 and 10.

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Table II. Dihedral Angles and Energies for Cyclohexane[a,b]

form	1	2	3	4	5	6	energy total	energy rel
chair	+56.05	−56.05	−56.05	+56.05	−56.05	−56.05	−231.481 46	0.0
twist-boat	+65.79	−31.21	−31.21	+65.79	−31.21	−31.21	−231.470 63	6.8
boat	0.00	+56.05	+56.05	0.00	−56.05	−56.05	−231.467 74	8.6

[a] Dihedral angle 1 is defined by the atoms C_1-C_2-C_3-C_4 for rotation about the C_2-C_3 bond. Other angles follow sequentially. [b] Angles in degrees, total energies in hartrees, and relative energies in kcal/mol.

Table III. Geometries and Energies for the Cyclohexyl Radical

form	substituent[a] position	hydrogen[b] angle (θ)	energy[c] total	energy[c] rel
chair	A	32.4	−230.840 99	0.0
	E	30.9	−230.840 76	0.14
boat (midships)	A	28.23	−230.830 86	6.4
	E	27.96	−230.830 78	6.4
boat (bow)	A	29.6	−230.828 68	7.7
	E	31.6	−230.829 65	7.1
twist-boat (midships)	A	29.0	−230.831 82	5.8
	E	29.2	−230.832 52	5.3
twist-boat (bow)[d]		28.2	−230.833 05	5.0

[a] A = axial, E = equatorial, referring to corresponding position in the parent molecule. [b] See text for definition. [c] Total energies in hartrees, relative energies in kcal/mol. [d] A and E are geometrically equivalent.

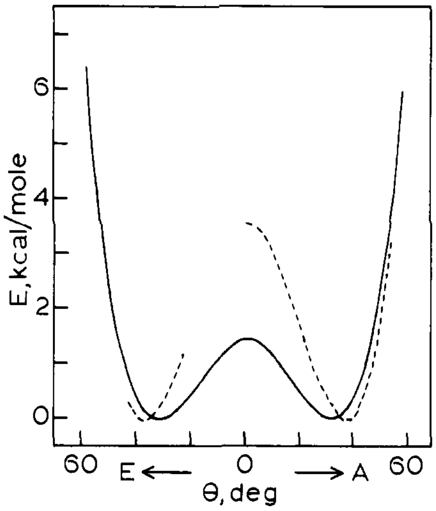

Figure 1. The relative energies (kcal/mol) of the chair form of the cyclohexyl radical (—) and the 1-hydroxycyclohexyl radical (- - -) as functions of the substituent angle θ. See text for the definition of θ. E = equatorial, A = axial.

The hydrogen 1s atomic orbital unpaired electron spin densities as calculated by GAUSSIAN 70 are given in Table IV. In this table the Greek letters refer to the carbon to which the protons are attached, i.e., the radical site carbon is C_α, the two carbons directly bonded to it are C_β, and so on. Each proton is further designated as axial (A) or equatorial (E) according to its stereochemistry relative to the substituent on C_α. The spin densities show the expected sign alternation and the magnitudes decrease rapidly after the β protons.

Figure 1 shows the curves of relative energy vs. θ for the chair forms of the cyclohexyl and 1-hydroxycyclohexyl radicals that were obtained when θ was varied as described above. In this figure as well as in Tables IV and VI the original tetrahedral geometry of the parent molecules corresponds to θ = 54.75°, and a planar radical site geometry corresponds to θ = 0°. The curves shown are representative of the results obtained when θ is varied in the different radicals. The angle θ of lowest energy obtained for the cyclohexyl radical is found to be slightly more planar than that obtained for the 1-hydroxy radical in both A and E positions. The barriers to planarity of the α substituent, which corresponds to the barrier for radical site inversion, were found to be 1.5 kcal/mol for the cyclohexyl radical and 3.5 kcal/mol for the 1-hydroxy radical.

The results for the 1-hydroxy radical are given in Tables V and VI. The hydroxyl hydrogens were found to prefer the gauche conformation in all cases, with the change in energy upon going from the hydrogen at 0° to the lowest energy angle being typically 2 kcal/mol. The relative energies of the various backbone conformers are quite similar to those found for the unsubstituted radical, and the difference between the A and E configurations is at most 0.3 kcal/mol. The spin densities also show the same pattern as the cyclohexyl radical, and there is very little delocalization of the unpaired electron onto the oxygen atom.

Discussion

Both ESR experiments and INDO calculations suggest that

Table IV. Hydrogen 1s Atomic Orbital Unpaired Electron Spin Densities for Cyclohexyl Radical[a]

form	position	β,ax	β,eq	γ,ax	γ,eq	δ,ax	δ,eq	α
chair	A	0.0206	0.0092	−0.0043	−0.0009	0.0012	0.0027	−0.0758
	E	0.0429	0.0105	−0.0023	−0.0029	0.0005	0.0013	−0.0773
boat	A	{0.0235	0.0089	−0.0043	−0.0001	0.0007	0.0007	−0.0799
(midships)		0.0274	0.0355	−0.0016	−0.0025			
	E	{0.0431	0.0104	−0.0023	−0.0025	0.0006	0.0005	−0.0799
		0.0349	0.0276	−0.0019	−0.0022			
boat (bow)	A	0.0229	0.0091	−0.0029	−0.0028	−0.0002	0.0011	−0.0786
	E	0.0443	0.0114	−0.0027	−0.0021	−0.0009	0.0006	−0.0764
twist-boat	A	{0.0339	0.0109	−0.0010	−0.0039	0.0005	0.0009	−0.0793
(midships)		0.0189	0.0110	−0.0029	−0.0020			
	E	{0.0426	0.0216	−0.0031	−0.0023	0.0003	0.0006	−0.0788
		0.0424	0.0091	−0.0015	−0.0025			
twist-boat		{0.0336	0.0110	−0.0034	−0.0010	0.0007	0.0005	−0.0798
(bow)		0.0421	0.0210	−0.0015	−0.0027			

[a] Bracketed spin densities indicate conformers that no longer have a plane of symmetry, so that the four β protons are all inequivalent.

Table V. Geometries and Energies for the 1-Hydroxycyclohexyl Radical[a]

form	substituent position	angle oxygen (θ)	angle hydroxyl proton[b]	energy total	energy rel
chair	A	36.3	68.2	−304.683 81	0.0
	E	35.7	67.5	−304.683 37	0.3
boat (midships)	A	36.9	58.4	−304.673 55	6.4
	E	36.0	68.0	−304.673 11	6.7
boat (bow)	A	35.0	56.3	−304.671 72	7.6
	E	35.5	63.8	−304.672 16	7.3
twist-boat (midships)	A	38.2	66.9	−304.675 13	5.5
	E	36.8	70.3	−304.675 22	5.4
twist-boat (bow)		36.9	69.6	−304.675 94	4.9

[a] See footnotes for Table III. [b] A positive angle refers to clockwise rotation of the O–H bond when looking down the C_1–O bond toward C_1.

Table VI. Hydrogen 1s Atomic Orbital Unpaired Electron Spin Densities for 1-Hydroxycyclohexyl Radical[a]

form	position	β,ax	β,eq	γ,ax	γ,eq	δ,ax	δ,eq	O[b]	^{H}OH
chair	A	0.0139	0.0073	−0.0040	0.0001	0.0012	0.0025	0.0245	−0.0023
		0.0148	0.0084	−0.0040	−0.0006				
	E	0.0402	0.0097	−0.0017	−0.0026	0.0003	0.0009	0.0224	−0.0018
		0.0402	0.0085	−0.0016	−0.0025				
boat (midships)	A	0.0140	0.0067	−0.0040	0.0011	0.0007	0.0007	0.0183	0.0000
		0.0214	0.0303	−0.0016	−0.0019				
	E	0.0407	0.0098	−0.0016	−0.0025	0.0005	0.0005	0.0213	−0.0023
		0.0280	0.0214	−0.0020	−0.0011				
boat (bow)	A	0.0151	0.0071	−0.0020	−0.0024	0.0007	0.0010	0.0138	0.0017
		0.0085	0.0167	−0.0022	−0.0027				
	E	0.0417	0.0108	−0.0022	−0.0017	−0.0010	0.0005	0.0193	−0.0005
		0.0094	0.0416	−0.0021	−0.0016				
twist-boat (midships)	A	0.0244	0.0074	−0.0036	−0.0000	0.0007	0.0009	0.0262	−0.0023
		0.0101	0.0092	−0.0028	−0.0014				
	E	0.0369	0.0186	−0.0016	−0.0028	0.0002	0.0004	0.0229	−0.0023
		0.0406	0.0079	−0.0011	−0.0017				
twist-boat (bow)		0.0244	0.0076	−0.0034	−0.0002	0.0006	0.0004	0.0239	−0.0027
		0.0365	0.0183	−0.0021	−0.0009				

[a] Because of the hydroxyl hydrogen the radicals do not have a plane of symmetry, so that the protons on the two β and the two γ carbons are inequivalent. [b] Atomic spin density on oxygen.

α-hydroxyalkyl radicals are nonplanar at the radical site,[11] but the contrary view is commonly held for unsubstituted alkyl radicals.[12] Our results suggest that *both* the cyclohexyl and the 1-hydroxycyclohexyl radicals are nonplanar at the radical site (see Figure 1), with the latter being slightly more nonplanar, as would be expected because of the more electronegative substituent.[13] The nonplanar structure found for the cyclohexyl radical is also consistent with studies on the *tert*-butyl radical.[14-16] Therefore one should consider radical site inversion as a possible mechanism for the observed β-proton interchange.

From Figure 1, the energy barrier for passage through planarity is predicted to be ~1.5 kcal/mol for cyclohexyl and ~3.5 kcal/mol for the 1-hydroxycyclohexyl radical. For comparison, a barrier of only 0.5–0.6 kcal/mol was determined for the inversion of the *tert*-butyl radical.[15,16] These are all considerably lower than the 5.0 kcal/mol found experimentally for the cyclohexyl radical.[1] Also, the calculated s orbital spin densities (Tables IV and VI), which should predict the relative magnitudes of the ESR hyperfine splitting constants (hfsc), show that a simple interchange of the substituent between the A and E configurations cannot by itself explain the experimental results for cyclohexyl radicals.[1-3] Experimentally, the β protons show one large and one small hfsc, because the observed hfsc's are inversely proportional to the dihedral angle between the C_β–H_β bond and the unpaired electron orbital.[12] This is correctly predicted for both the cyclohexyl and 1-hydroxycyclohexyl radicals in the E form, but upon inversion to the A form the spin densities for the β protons do not show the required interchange. Taken together these results strongly suggest that radical site inversion cannot be the only motion the radical undergoes.

From consideration of the calculations reported here, the most probable radical motion involves a chair-to-chair ring inversion, accompanied by simultaneous radical site inversion. Since the entire potential energy surface was not explored, we can discuss the relative energies of the conformers examined but not the high energy barriers between conformers. However, our results for cyclohexane (Table II), for which more information is available, are consistent with previous calculations,[5,6] as well as experimental determinations.[17,18] For example, in an infrared study the chair to twist-boat energy difference was found to be 5.5 kcal/mol, with a barrier through the high-energy transition state of 10.8 kcal/mol. These values should be compared with our calculated values of 6.8 and 8.6 kcal/mol for the chair vs. twist-boat and chair vs. classical boat, respectively. The fact that our predicted twist-boat vs. boat energy difference is too small may be the result of the fact that we did not carry out complete geometry optimizations for each conformer. Since our results for the molecule and the radicals show very similar relative energies, we suggest that the inversion mechanisms are the same in all cases.

Specifically, a mechanism consisting of chair-to-chair inversion through the twist-boat "bow" intermediate is a likely choice. The simultaneous radical site inversion would allow the substituent to remain in the E configuration. This could be quite easily accomplished with the twist-boat "bow" form, since only in this form are the A and E substituents geometrically equivalent. On this basis we would predict barriers of 5 kcal/mol for both the cyclohexyl and 1-hydroxycyclohexyl radicals, if the inversion pathway does not involve higher energy conformers, and at least 6.4 kcal/mol if the boat is an intermediate between chair and twist-boat. In either case we do not agree with the proposal that the 1-hydroxycyclohexyl radical has the twist-boat form as the most stable conformation.[3]

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Molecular Orbital Study of Tetrahedral, Planar, and Pyramidal Structures of the Isoelectronic Series BH_4^-, CH_4, NH_4^+, AlH_4^-, SiH_4, and PH_4^+

Mary-Beth Krogh-Jespersen,[1a] Jayaraman Chandrasekhar, Ernst-Ulrich Würthwein, John B. Collins,[1b] and Paul von Ragué Schleyer*

Contribution from the Institut für Organische Chemie, Universität Erlangen-Nürnberg, D-8520 Erlangen, West Germany. *Received August 15, 1979*

Abstract: Eight valence electron ZH_4 systems strongly prefer tetrahedral geometry. Alternative geometries, square planar (D_{4h}) and pyramidal (C_{4v}), were investigated in detail theoretically; electronic structures reveal how substituents might stabilize these forms preferentially. With the possible exception of BH_4^-, all ZH_4 planar (D_{4h}) and pyramidal (C_{4v}) species studied prefer singlet to triplet states. For the planar forms, two alternative singlet lumomers compete. CH_4 and NH_4^+ (both D_{4h}) prefer HOMOs of $\pi(a_{2u})$ symmetry because of the greater electronegativity of the central atom. σ-Donor, π-acceptor substituents should stabilize these forms. Planar BH_4^-, AlH_4^-, SiH_4, and PH_4^+ prefer HOMOs with $\delta(b_{1g})$ symmetry because of the lower central atom electronegativity, the longer Z-H bonds, and, for the second-row species, the participation of d orbitals. π-Acceptor, σ-donor substituents should stabilize these forms. Pyramidal (C_{4v}) singlet ($^1A_1$) structures are preferred over planar singlets for CH_4, NH_4^+, and PH_4^+. The electron density is more evenly distributed upon pyramidalization; this is favored when Z is less electronegative. AlH_4^-, of all the species investigated, is indicated to require the least amount of energy to achieve planarity; SiH_4 is next best. Planarity is least favorable for CH_4. These results indicate how much inherent energetic opposition must be overcome in order to achieve planar or pyramidal structures.

Introduction

Eight valence electron ZH_4 molecules prefer to be tetrahedral.[2] Alternative geometries are very unstable. Planar methane, for example, not only is calculated to be more than 150 kcal/mol higher in energy than the tetrahedral form,[3a] but also to be unstable toward dissociation. Planar NH_4^+ [3a,4a] and nontetrahedral D_{4h} and C_{4v} forms of SiH_4[4b,c] are similarly indicated to be only somewhat more favorable in these respects. The energy difference between planar and tetrahedral tetracoordinate carbon and silicon compounds can, however, be reduced significantly through substitution.[3,4c,d] Molecules which prefer planar geometries have been demonstrated,[3c] claimed,[4c] or suggested.[3a,b,4d]

In this paper we extend our investigation to include the entire set of isoelectronic ZH_4 species: BH_4^-, CH_4, NH_4^+, AlH_4^-, SiH_4, and PH_4^+. Using ab initio molecular orbital theory,[5] the structures and energies of tetrahedral (T_d), planar (D_{4h}), and pyramidal (C_{4v}) forms have been studied at uniform levels of approximation. The results reveal significant quantitative and qualitative differences among these species. Variations in the electronic structure have important implications for choice of substituents which might be used to help attain unusual geometries.

Computational Method

The structure of the first-row hydrides, BH_4^-, CH_4, and NH_4^+, were optimized using the 6-31G* basis set[6] (a split-valence basis including d-type polarization functions on the heavy atom). For the second-row hydrides, AlH_4^-, SiH_4, and PH_4^+, geometry optimizations were carried out with the STO-3G* basis set,[7] a minimal basis augmented by a set of d orbitals on the second-row atom. Singlets were calculated using the restricted Hartree-Fock method.[8a] The unrestricted Hartree-Fock (UHF) method[8b] was used for triplets. Estimates of correlation energy were made using second-order Møller-Plesset theory (MP2).[9] Results are designated thus: MP2/6-31G*//6-31G* (this indicates a single-point MP2/6-31G* calculation carried out on the 6-31G* optimized geometry). Mulliken population analyses[10] employed STO-3G[11] wave functions with STO-3G optimum geometries.

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