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(15) Approximately this same ratio is also obtained if $[C_3H_7^+]$ is corrected for the abundances of those ions which should arise from the decomposition of $C_3H_7^+$;[14] similar $[C_3H_7^+]/[HA^+]$ values were found in measurements made with H_3S^+ protonation and in connection with the previous ICR study.[6]
(16) ΔH(*sec*-$C_3H_7^+ \rightarrow CH_3CH{=}CH_2^+$) = 89 kcal/mol; ΔH(*sec*-$C_3H_7^+ \rightarrow C_3H_5^+$) = 24 kcal/mol; ΔH(*sec*-$C_3H_7^+ \rightarrow C_3H_3^+$) = 63 kcal/mol; and ΔH(*sec*-$C_3H_7^+ \rightarrow C_2H_3^+$) = 59 kcal/mol.[5,17]
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Molecular Orbital Theory of the Electronic Structure of Organic Compounds. 25. Conformations of Methyl- and Fluoro-Substituted Cyclopentanes and Cyclohexanes

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Abstract: Ab initio molecular orbital theory is used to study the influence of single methyl and fluoro substituents on the conformational potential surface for cyclopentane and cyclohexane. The theory indicates that both substituents favor the envelope (E) form of cyclopentane leading to two separate potential minima for axial and equatorial substitution. The equatorial form of methylcyclopentane is more stable but the reverse is true for fluorocyclopentane. For the substituted cyclohexanes, both substituted molecules are more stable in the equatorial form. These theoretical results are in reasonable agreement with available experimental data. Comparison is also made with related 1-propanes.

In a previous paper,[1] we presented an ab initio molecular orbital study of the pseudorotational potential surface for cyclopentane. The results were in reasonable agreement with experimental data, indicating almost free pseudorotational motion interconverting among the various envelope (E) and twist (T) conformations and a significantly higher barrier for inversion through a form with a planar carbon skeleton. For cyclohexane, it is generally recognized that the lowest-energy conformation is a puckered chair form with a high barrier to inversion. An initial aim of this paper is to determine the puckering amplitude of cyclohexane by the same theoretical technique used previously for cyclopentane.

The main objective of the present work is to make a theoretical study of the influence of single methyl or fluoro substituents on the potential surfaces for these ring systems. For the cyclopentanes, the first aim of such a study is to find whether a substituent significantly hinders pseudorotational motion or changes the barrier to direct inversion. If a pseudorotational barrier is introduced, it should then be possible to determine the minima, corresponding to different pseudorotational conformers and their relative energies. For the E-type ring conformation, for example, the relative stabilities of axially and equatorially substituted forms can be compared. At the present time, there is only limited experimental information on these systems. For the substituted cyclohexanes, the ring is already locked in a chair-type arrangement, but this level of theory should again allow comparison of the energies of the axially and equatorially substituted conformations. Finally we shall give a comparative discussion of the interactions and their relation to similar interactions in substituted propanes.

Methods

Since the compounds considered in this study are relatively large, only simple quantum mechanical techniques can be used. Throughout we shall use single-determinant molecular orbital theory (restricted Hartree–Fock or RHF) in conjunction with two Gaussian-type basis sets. The simpler of these is the min-

imal STO-3G set.[2] The other larger basis is the split-valence set 4-31G.[3] Both were used in our previous study of cyclopentane,[1] but presently available computer capacity limits the use of 4-31G among the substituted molecules of fluorocyclopentane (72 basis functions).

In view of the large extent of these computations (some of which involve more than a million two-electron integrals), it is important to establish that round-off errors and other approximations in the energy calculations do not exceed the relatively small differences that are of interest. In a separate study[4] of comparable calculations on pentane using the same program, such errors have been found to be less than 10^{-5} hartree or about 0.01 kcal mol^{-1}.

In both cyclopentanes and cyclohexanes we have used a geometrical model which allows partial flexibility. For the cyclopentane ring, the displacements z_j ($j = 1, \ldots, 5$) perpendicular to a suitably defined mean plane are related to pseudorotational coordinates (q, φ) by[1]

$$z_j = (2/5)^{1/2} q \cos [\varphi + 4\pi(j-1)/5] \qquad (1)$$

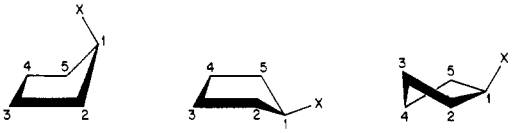
where q is the puckering amplitude and φ is a phase angle describing the type of displacement. All bond lengths are kept fixed at standard values.[5] The $-CH_2-$ are kept as rigid C_{2v} units with tetrahedral HCH angles, but all other geometrical variables are optimized (by energy variation) for each value of q and φ. This leads to a pseudorotational potential surface $V(q, \varphi)$ which is characteristic of the inversion-pseudorotation degrees of freedom.

For the cyclohexane ring, we consider only "pure chair" distortion in which displacements relative to a mean plane are

$$z_j = (1/6)^{1/2} q_3 (-1)^{j-1} \qquad (2)$$

The amplitude q_3 is the only degree of freedom varied in this model, all CCC angles being equal and the $-CH_2-$ again being treated as C_{2v} units with tetrahedral HCH angles. The other type of displacement leading to boat or twist structures is not considered.

Finally, the geometry of the substituent has to be specified. Standard bond lengths and angles are used.[5] For the methyl group, a conformation with a CH trans to the methine hydrogen is chosen. For the cyclopentane ring, the substituent X is placed in the axial position for carbon atom 1 in the E form I corresponding to $\varphi = 0$. Advance of φ to 180° then leads by pseudorotation to the equatorially substituted E form II. In between (at $\varphi = 90$ and 270°) lie two equivalent T forms such as III.



I II III

In applying the theory to substituted cyclopentanes, we have proceeded in the following manner. Starting with the previously determined $V(q, \varphi)$ surface for cyclopentane, we select the amplitude q which minimizes the energy for each φ (for the unsubstituted molecule). Then for a series of values of φ along this path, single calculations are carried out with one of the hydrogens replaced by the substituent. In this way, a modified potential $V(\varphi)$ characteristic of the substituted compounds is found. This procedure should give the principal changes in the pseudorotational potential. However, it should be noted that it does not allow for possible changes in the ring skeleton *caused* by the substituent. For cyclohexanes, a similar procedure is followed, single calculations being carried out for axially and equatorially substituted molecules at the puckering amplitude q_3 determined for cyclohexane itself.

Table I. Cyclohexane Chair Geometries and Energies[a]

	RHF/STO-3G		Exptl	
Parameter	Standard	Optimized q_3	Ref 6	Ref 7
q_3	(0.63)	0.58	0.57	0.56
CCC angle	(109.5)	111.0	111.1	111.4
CCCC torsion	(60)	56.0	55.9	54.9
CC length	(1.54)	(1.54)	1.53	1.54
CH length	(1.09)	(1.09)	1.12	1.12
HCH angle	(109.5)	(109.5)	111.0	107.5
Energy	−231.48017	−231.48146		

[a] Bond lengths in ångströms, angles in degrees, and energies in hartrees; parameters in parentheses are assumed standard values (ref 5).

Ideally, it would be desirable to reoptimize the puckering coordinates for the substituted molecule. The only case in which this has been done is in the RHF/STO-3G study of methylcyclohexane where the 1,3-overlap effect is likely to be most important. For this molecule, q_3 has been reoptimized.

Results

Cyclohexane. Calculations with the RHF/STO-3G theory are straightforward and are summarized in Table I. If all bond angles are tetrahedral (full standard model), the value of q_3 is 0.63 Å and the total energy is −231.480 17 hartrees. Reoptimization of the energy by varying q_3 (and hence the CCC bond angles and CCCC torsion angles) gives $q_3 = 0.58$ Å and an energy of −231.481 46 hartrees. The lowering of 0.8 kcal mol^{-1} is presumably associated with relief of the steric repulsion of 1,3 axial hydrogens. Experimentally, the electron diffraction results[6,7] show a similar distortion.

Methylcyclopentane. Results are listed in Table II. The STO-3G energies suggest that the two envelope E forms with methyl substitution at the apex (I and II) are both local minima in the potential curve, the corresponding T forms (III) being about 0.4 kcal mol^{-1} higher in energy. Unreported calculations with other values of φ indicate that $\varphi = 0$ and 180° are the only minima in $V(\varphi)$. The lowest energy is found for the E form with equatorial substituent ($\varphi = 180°$), the axial conformer being about 0.3 kcal mol^{-1} less stable. Compared with cyclopentane, the barrier to ring inversion via the planar form has increased compared with cyclopentane (from 3.4 to 4.0 kcal mol^{-1}), so that conformational changes still occur mainly by pseudorotation (for which the barrier is only 0.5 kcal mol^{-1}).

The available experimental data are consistent with these findings although it should be borne in mind that some of it refers to the liquid phase at elevated temperatures whereas the theoretical results really apply to the gas phase at 0 °K. A NMR study[8] of the vicinal proton–proton coupling constants for various deuterated methylcyclopentanes demonstrated that the ring can no longer undergo free pseudorotation but is somewhat restricted to those conformations in which the substituent is equatorially bonded ($\varphi = 180 \pm 54°$). In addition, the NMR investigation provided evidence that the degree of puckering varies somewhat with the phase angle φ, but this has not been investigated. Further evidence for the dominance of the equatorially substituted cyclopentane was found in a study of the ^{13}C chemical shifts of methylcyclopentanes.[9] The measured β and γ effects compared with the known effects for methylcyclohexanes reflect unfavorable 1,3 interactions for an axial methyl group. This parallels an investigation[10] on *cis*-1,3-dimethylcyclopentane which has both substituents in the equatorial position. The cis compound is more stable by 0.5 kcal mol^{-1} than the corresponding trans derivative where one methyl group has to occupy an axial position. Finally, it might

Table II. Energies of Methylcyclopentane and Fluorocyclopentane

Molecule	φ, deg	q, Å	Conformation	Energy[a] Total	Energy[a] Rel
Methylcyclopentane					
RHF/STO-3G		0	Planar (C_s)	−231.464 38	4.00
	0	0.371	E(C_s); CH_3 axial	−231.470 48	0.17
	90	0.373	T(C_1); CH_3 intermediate	−231.469 98	0.49
	180	0.371	E(C_s); CH_3 equatorial	−231.470 76	0
Fluorocyclopentane					
RHF/STO-3G		0	Planar (C_s)	−290.338 17	3.16
	0	0.371	E(C_s); F axial	−290.342 68	0.33
	90	0.373	T(C_1); F intermediate	−290.343 21	0
	180	0.371	E(C_s); F equatorial	−290.342 04	0.73
Fluorocyclopentane					
RHF/4-31G	0	0.392[b]	E(C_s); F axial	−293.611 52	0
	90	0.394	T(C_1); F intermediate	−293.610 32	0.75
	180	0.392[b]	E(C_s); F equatorial	−293.610 86	0.41

[a] Total energy in hartrees; relative energies in kcal mol^{-1}. [b] The 4-31G optimization of E-type puckered cyclopentane which was not included in ref 1 gave the following results: $E = -194.877\ 84$; $q = 0.392$; $\alpha = 102.89°$.

be mentioned that an empirical study of methylcyclopentane conducted by Allinger et al.[11] led to a potential $V(\varphi)$ similar to ours with the E minimum at $\varphi = 180°$, being lower in energy by 0.85 kcal mol^{-1} than the T forms ($\varphi = 90$ and 270°).

Fluorocyclopentane. As mentioned in the previous section, fluorocyclopentane has been investigated by both the RHF/STO-3G and RHF/4-31G methods. The results (shown in Table II) are not consistent between the methods. The minimal basis results indicate that a structure close to the T form (III) has lowest energy whereas the split-valence (4-31G) basis predicts the axially substituted E conformer to be most stable.

There is some reason to distrust the predictions of the RHF/STO-3G method that the T conformations are most stable for fluorocyclopentane. This is because the same level of theory does not satisfactorily reproduce the influence of fluorination on the torsional potentials for C-C bonds. Experimentally, it is found that the rotational barrier in fluoroethane[12] (3.30 kcal mol^{-1}) is greater than in ethane[13] (2.93 kcal kcal mol^{-1}). However, the STO-3G basis underestimates the barrier to rotation in fluoroethane by 0.5 kcal mol^{-1} while the result for ethane itself (3.3 kcal mol^{-1}) is somewhat too large. As a result, those ring conformations of fluorocyclopentane which involve high CH_2-CHF-CH_2 eclipsing (i.e., the T forms III) will be preferred at the STO-3G level. The 4-31G basis, on the other hand, gives a good description of the barrier increase for ethane → fluoroethane[14] and this is consistent with the higher calculated energy for the T conformers of fluorocyclopentane. Also, it is worth noting that the relative energies of the two E forms I and II (where the amounts of CH_2-CHF-CH_2 eclipsing are comparable) are consistently described by the two theoretical methods.

There is a limited amount of experimental information on fluoro and other monohalogenocyclopentanes based on infrared, Raman, and nuclear magnetic resonance studies. The interpretation of these data has mostly been based on the assumption that E forms are more stable than T forms as suggested by some calculations with empirical force fields.[15,16] Under this assumption, the conformers with axial fluorine were found to dominate.[17] Quantitative studies on chlorocyclopentane and bromocyclopentane led to enthalpy differences of 0.3 and 0.6 kcal mol^{-1} respectively between axial and equatorial forms.[18] A recent NMR investigation of monosubstituted cyclopentanes gave further evidence for a slight conformational preference of the E forms in the pseudorotational surface.[19]

Table III. Energies of Methylcyclohexane and Fluorocyclohexane (RHF/STO-3G)

Molecule	Substituent position	Energy[a] Total	Energy[a] Rel
Methylcyclohexane	Axial	−270.054 68	4.07
	Axial	−270.055 81[b]	3.36
	Equatorial	−270.061 17	0
Fluorocyclohexane	Axial	−328.931 88	0.13
	Equatorial	−328.932 09	0

[a] Total energy in hartrees; relative energies in kcal mol^{-1}. [b] q_3 reoptimized to 0.54 Å.

Methylcyclohexane. The results (Table III) indicate that the equatorial form is more stable. The energy of axial methylcyclohexane is 4.1 kcal mol^{-1} higher using the skeletal geometry for cyclohexane itself. However, this involves considerable 1,3 steric repulsion so reoptimization of q_3 was carried out. For the axial conformation, this lowered q_3 to 0.54 Å while the equatorial conformation was unmodified. The axial-equatorial energy gap was decreased to 3.4 kcal mol^{-1}. A fuller treatment should also allow for flexibility in other puckering coordinates, presumably lowering this energy gap further, but this has not yet been done. Experimental results also show the equatorial conformation to be most stable. From a wide variety of spectroscopic and thermodynamic studies an average value of 1.70 kcal mol^{-1} has been found for the energy difference.[20]

Fluorocyclohexane. Again the RHF/STO-3G results indicate that the equatorial is more stable than the axial conformer. However, the energy difference is small (0.13 kcal mol^{-1}) using the cyclohexane skeletal q_3 (0.58 Å). Reoptimization of q_3 led to no significant change for either conformer. However, it should be emphasized that full reoptimization of all puckering coordinates was not carried out and may change this small energy difference. Experimentally, electron diffraction and spectroscopic data[20] indicate that the equatorial form is more stable than axial by an average of 0.15 kcal mol^{-1}.

Discussion

As indicated in the previous section, the theory supports the existence of two local potential minima for the axially and

Table IV. Comparison of the Relative Stabilities (kcal mol^{-1}) of Axial and Equatorial Conformations for Monosubstituted Cyclohexanes and Cyclopentanes Together with Gauche-Trans Energy Difference for 1-Propanes

	E(axial) − E(equatorial)					
	Cyclohexanes		Cyclopentanes		E(gauche) − E(trans) for 1-propanes	
Substituent	Theory	Exptl	Theory	Exptl	Theory	Exptl
CH_3	3.37[a]	1.70[b]	0.17[c]	0.5[d]	1.09[e]	0.77[f]
NH_2		1.20[b]			0.11[g]	~0[h]
OH		0.52[b]		<0[i]	−0.18[g]	−0.29[j]
F	0.13[a]	0.15[b]	−0.41[k]	−0.3[l]	−0.09[e]	−0.47[m]

[a] STO-3G result after reoptimization of puckering amplitude. [b] Reference 20. [c] STO-3G result without reoptimization of puckering amplitude. [d] Difference between *cis*- and *trans*-1,3-dimethylcyclopentane (ref 10). No direct value available. [e] 4-31G results with optimized dihedral angles. L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **95**, 693 (1973). [f] G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, **16**, 704 (1948). [g] 4-31G results with standard geometries (ref 22). [h] D. W. Scott, *J. Chem. Thermodyn.*, **3**, 843 (1971). [i] I. O. C. Ekejiuba and H. E. Hallam, *J. Chem. Soc. B*, 209 (1970). [j] A. A. Abdurahmanov, R. A. Rahimova, and L. M. Imanov, *Phys. Lett. A*, **32**, 123 (1970). [k] 4-31G result without reoptimization of puckering amplitude. [l] Result for chlorocyclopentane from ref 18. [m] E. Hirota, *J. Chem. Phys.*, **37**, 283 (1962).

equatorially substituted forms of the envelope conformations of the cyclopentanes. This applies to both methyl and fluoro substituents, neither of which favors a twist conformation. The available information for the axial-equatorial energy difference for both cyclopentanes and cyclohexanes is displayed in Table IV which also covers the amino and hydroxyl substituents. The table also gives trans-gauche energy differences for 1-propanes where there are similar long-range interatomic interactions (trans corresponding to equatorial and gauche to axial). Each theoretical entry refers to the highest level of theoretical calculation carried out in this laboratory.

The following points about this comparison are noteworthy:

1. For both cyclohexanes and cyclopentanes, the axial-equatorial energy difference becomes less positive as we proceed along the series of substituents Me, NH_2, OH, and F. The same trend is found for gauche-trans energy difference in 1-propanes. These trends are found consistently both theoretically and experimentally. They may be partly explained by reduced steric repulsion, but it is evident that additional effects must be operating to make the axial forms more stable in some cases.

2. The axial-equatorial energy differences for cyclopentanes are less positive than for cyclohexanes. Again this is indicated in theory and experiment. It can be partly interpreted in terms of reduced 1,3 steric repulsion in cyclopentanes since the corresponding separations are larger than in cyclohexanes.

3. Theory and experiment both give fluorocyclohexane to be most stable in the equatorial form even though the corresponding 1-propane has a gauche conformation. In view of the similar interatomic distances, this might not be expected. However, Allinger et al.[21] have pointed out that relief from steric repulsion in molecules such as 1-fluoropropane can be achieved by change of dihedral angle whereas this mechanism is not available in fluorocyclohexane because of the stiffness of the ring. The existence of two close 1,3 steric repulsions involving the substituent in the axial conformation (compared with only one such interaction in the 1-propane) may also be a contributing factor.

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