Rotational Barriers in Propene and Its Fluoro Derivatives

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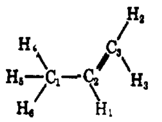
Abstract: Rotational barriers for propene, *cis*-fluoropropene, and *trans*-fluoropropene have been calculated from *ab initio* LCAO molecular orbital wave functions. The correct ordering and reasonable agreement with the experimentally determined magnitudes obtained substantiate the fact that quantitative prediction of barriers to internal rotation are realizable within the framework of the Hartree–Fock approximation. Energy-component analysis elucidates the barrier mechanism for this series of molecules as it has in many other cases. The *cis*-fluoro barrier is *attractive* dominant, while the barriers in propene and the other fluoro derivatives are almost certainly dominated by repulsive interactions. The effects on the observed barrier magnitudes of uncertainties in the geometry are also examined by means of semiempirical methods.

The understanding of barriers to internal rotation in molecules is a problem of continuing interest to chemists. Propene and the monofluoropropenes are an important series for rotation barrier studies, both because there are adequate experimental data[1–5] and because a correct explanation of the anomalously low barrier for *cis*-fluoropropene has heretofore been lacking.

In the present work, *ab initio* molecular orbital wave functions, employing double-ζ-quality atomic orbitals as a basis, have been obtained for each of the molecules studied, and energy-component analyses have been performed. Preliminary investigations of the effect of uncertainties in the geometry on the barrier height are also discussed.

Table I. Molecular Coordinates (au)



Atom	Propene X	Propene Y	Propene Z	*cis*-Fluoropropene X	*cis*-Fluoropropene Y	*cis*-Fluoropropene Z	*trans*-Fluoropropene X	*trans*-Fluoropropene Y	*trans*-Fluoropropene Z
C_1	0.0	0.0	0.0	−1.59846	−2.34326	0.0	−1.59846	−2.34326	0.0
C_2	2.83651	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_3	4.25924	2.08565	0.0	2.52472	0.0	0.0	2.52472	0.0	0.0
H_1	3.76202	−1.84018	0.0	−0.99863	1.80158	0.0	−0.99863	1.80158	0.0
H_2, F (cis)	3.38140	3.95114	0.0	3.88361	−2.14127	0.0	3.57173	−1.77696	0.0
H_3, F (trans)	6.29961	1.98586	0.0	3.59210	1.74180	0.0	3.80421	2.18961	0.0
H_4 (E)	−0.74488	1.92042	0.0	−0.43175	−4.04082	0.0	−0.43175	−4.04083	0.0
H_5 (E)	−0.74488	−0.96021	1.66313	−2.81146	−2.41750	1.66315	−2.81146	−2.41750	1.66315
H_6 (E)	−0.74488	−0.96021	−1.66313	−2.81146	−2.41750	−1.66315	−2.81146	−2.41750	−1.66315
H_4 (S)	−0.74488	−1.92042	0.0	−3.60470	−1.87639	0.0	−3.60470	−1.87639	0.0
H_5 (S)	−0.74488	0.96021	1.66313	−1.22499	−3.49972	1.66315	−1.22499	−3.49972	1.66315
H_6 (S)	−0.74488	0.96021	−1.66313	−1.22499	−3.49972	−1.66315	−1.22499	−3.49972	−1.66315

Methods of Calculation

The barriers for propene, *cis*-fluoropropene, and *trans*-fluoropropene were calculated by computing *ab initio* LCAO–MO–SCF wave functions for the eclipsed and staggered configurations of each of the molecules. (Herein, the terms eclipsed and staggered refer to the relative orientation of the methyl-group hydrogens with respect to the carbon–carbon double bond.) The calculations were performed with the aid of programs written at Princeton.[6] Essentially double-ζ-quality atomic orbitals were used as a basis set: (10s,5p) Gaussian basis functions on carbon and fluorine and 5s Gaussian functions on hydrogen.[7] The s Gaussians on the heavy centers were contracted to three group functions, and the p Gaussians on the heavy centers were contracted into one group function. The s Gaussians on hydrogen were contracted into one group function and a scale factor of 1.41 was employed. The self-consistent-field molecular orbital calculations were carried out following Roothaan's procedure.[8]

The geometries employed in the calculations are essentially those reported by Baudet and Wilson.[9] Nuclear coordinates are given in Table I.

Results and Discussion

The results for the total energies, as well as the component analyses, for the present calculations are exhibited in Tables II, III, and IV, for propene, *cis*-fluoropropene, and *trans*-fluoropropene, respectively. The scaled quantities are the values for the energy compo-

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Table II. Total Energies and Component Analysis for Propene (au)

	Eclipsed (E)	Staggered (S)	E − S
Unscaled			
E_{tot}	−116.92656	−116.92457	
$E_{electronic}$	−187.65699	−187.64229	
V_{nn}	70.73042	70.71773	
V_{ne}	−411.87512	−411.87450	
V_{ee}	107.85140	107.85565	
V_{tot}	−233.29340	−233.30111	
T	116.36673	116.37655	
$-V/2T$	1.00240545	1.00235451	
$V_{nn} + V_{ee} + T$	294.94856	294.94993	
$V_{nn} + V_{ne} + T$	−224.77796	−224.78022	
Scaled			
V_{nn}	70.90056	70.88423	0.01633
V_{ne}	−412.86587	−412.84426	−0.02161
V_{ee}	108.11083	108.10960	0.00123
V_{tot}	−233.85447	−233.85042	−0.00405
T	116.92724	116.92521	0.00202
$V_{nn} + V_{ee} + T$	295.93863	295.91905	0.01958
$V_{nn} + V_{ne} + T$	−225.03870	−255.03481	−0.00325

Table III. Total Energies and Component Analysis for *cis*-Fluoropropene (au)

	Eclipsed (E)	Staggered (S)	E − S
Unscaled			
E_{tot}	−215.71120	−215.70950	
$E_{electronic}$	−331.47121	−331.39694	
V_{nn}	115.76001	115.68744	
V_{ne}	−739.41176	−739.28490	
V_{ee}	192.42914	192.37422	
V_{tot}	−431.22262	−431.22325	
T	215.51141	215.51374	
$-V/2T$	1.00046354	1.00045417	
$V_{nn} + V_{ee} + T$	523.70056	523.57540	
$V_{nn} + V_{ne} + T$	−408.14034	−408.08372	
Scaled			
V_{nn}	115.81367	115.73998	0.07369
V_{ne}	−739.75451	−739.62066	−0.13385
V_{ee}	192.51834	192.46159	0.05675
V_{tot}	−431.42251	−431.41909	−0.00341
T	215.71125	215.70955	0.00171
$V_{nn} + V_{ee} + T$	524.04326	523.91112	0.13214
$V_{nn} + V_{ne} + T$	−408.22959	−408.17114	−0.05845

Table IV. Total Energies and Component Analysis for *trans*-Fluoropropene (au)

	Eclipsed (E)	Staggered (S)	E − S
Unscaled			
E_{tot}	−215.70738	−215.70524	
$E_{electronic}$	−328.95399	−328.93852	
V_{nn}	113.24661	113.23328	
V_{ne}	−734.32517	−734.33061	
V_{ee}	189.86118	189.87065	
V_{tot}	−431.21738	−431.22668	
T	215.51000	215.52144	
$-V/2T$	1.00045794	1.00042642	
$V_{nn} + V_{ee} + T$	518.61779	518.62537	
$V_{nn} + V_{ne} + T$	−405.56856	−405.57589	
Scaled			
V_{nn}	113.29847	113.28156	0.01691
V_{ne}	−734.66144	−734.64374	−0.01770
V_{ee}	189.94812	189.95162	−0.00349
V_{tot}	−431.41485	−431.41056	−0.00428
T	215.70742	215.70528	0.00214
$V_{nn} + V_{ee} + T$	518.95402	518.93846	0.01556
$V_{nn} + V_{ne} + T$	−405.65555	−405.65690	0.00135

nents upon application of a coordinate scale factor to the *ab initio* results in order to satisfy the virial theorem in the form $V/2T = -1$. Since the eclipsed configuration approximates the equilibrium geometry (which corresponds to a generalized minimum in the total energy surface), and since the staggered configuration approximates the geometry at the top of the barrier for the molecular mode under consideration (which corresponds to a generalized saddle point in the total energy surface), both the exact and the Hartree–Fock wave functions should satisfy the virial theorem in this form, for both the eclipsed and the staggered configurations.

Calculated barrier heights are displayed in Table V, along with the experimentally determined quantities and the values obtained with a cruder basis set for comparison. The fact that the barriers obtained lie in the proper order confirms the presumption that the problem of the anomalously low barrier for the cis isomer is amenable to solution within the framework of the Hartree–Fock approximation. Since there is little reason to believe that the barrier for 2-fluoropropene would not fall into line with the other results, calculation of this wave function was deemed unnecessary. Our calculated barrier for the cis isomer agrees exactly with the experimental value; the discrepancy between the calculated values and the experimental values for propene and *trans*-fluoropropene is larger. Although the agreement for the cis isomer is to be viewed as largely fortuitous, the fact that the magnitudes of the changes in the energy components upon traversing the barrier are approximately an order of magnitude larger for the cis isomer than for the other two molecules allows one to postulate that the barrier for the cis isomer may indeed be more accurately described than the barriers for the other two systems. It may be said that the cis isomer, owing to the presence of the L-shell atomic orbitals on the fluorine atom, is less "function-poor" in the through-space region that gives rise to the barrier.

Table V. Barrier Heights (kcal/mol)

	Exptl	Basis A[a]	Basis B[b,e]
Propene	1.98	1.48[c]	1.25
cis-Fluoropropene	1.06	1.58[d]	1.07
trans-Fluoropropene	2.20	1.53[d]	1.34
2-Fluoropropene	2.45	1.20[d]	

[a] Uncontracted Gaussian basis set of (5s, 2p) on the heavy centers and 3s on hydrogen. [b] Gaussian basis set of (10s, 5p) contracted to [3s, 1p] on heavy centers and 5s contracted to [1s] on hydrogen. [c] M. L. Unland, J. R. VanWazer, and J. H. Letcher, *J. Amer. Chem. Soc.*, **91**, 1045 (1969). [d] M. L. Unland, J. H. Letcher, and J. R. VanWazer, personal communication. [e] Present work.

Changes in the overlap populations upon traversing the barrier can give some information concerning the regions in which the electron density is changing during rotation. The largest change in overlap population for propene and *trans*-fluoropropene is that between the methyl carbon and the nearest ethylene carbon. When the fluorine is in the cis position, this change is reduced somewhat, but is compensated for by a change in the overlap population between the methyl carbon and the fluorine. This reflects the fact that there is indeed an appreciable change in the electron density in the through-space regions close to the methyl group.

Decomposition of the total energy into its various components has proved a useful aid to the analysis of chemical binding and, in particular, rotational barriers.[10] For many barriers, the nuclear–nuclear repulsion component (V_{nn}) alone predicts the correct equilibrium geometry; however, in the molecules of the present work, the V_{nn} predicts the staggered configurations to be stable rather than the equilibrium eclipsed configurations. This means that the sum of the ΔV_{ne} and ΔV_{ee} terms must account for the actual equilibrium configuration ($\Delta V_{tot} = \Delta V_{nn} + \Delta V_{ne} + \Delta V_{ee} = 2\Delta E_{tot}$). The results of the present work (scaled to satisfy the virial theorem) indicate that it is primarily the ΔV_{ne} term which is responsible for making the eclipsed configuration more stable. Accordingly the energy components yield an attractive dominant barrier[10] for all three systems. For the cis isomer, the nuclear–nuclear repulsions and the electron–electron repulsions both quite strongly favor the staggered configuration, while the nuclear–electronic attraction even more strongly favors the eclipsed configuration. For propene and the trans isomer the changes in the components are much smaller, but the same trends prevail, except that, for the trans isomer, the electron–electron repulsions slightly favor the equilibrium eclipsed configuration. It is felt that improving the basis set in the through-space regions for propene and the trans isomer will make both the ΔV_{ne} and ΔV_{ee} terms more positive, resulting in a repulsive dominant barrier in these molecules.

Realization that some barriers are attractive dominant and others are repulsive dominant is an important key to the systemization and understanding of rotational barriers. Until this observation was made, it was commonly assumed that the nonbonded hindering potential giving rise to rotational barriers was always repulsive. The qualitative model long adopted has been that analogous to two helium atoms moving past one another. This model is still adequate for explaining most barriers, but there are others such as *cis*-fluoropropene, acetaldehyde,[11] and nitrosomethane,[12] for which the change in the interaction has a net attractive nature, and the magnitudes of the barriers for these cases show a different trend than that for the repulsive dominant cases. Qualitatively, the attractive interaction in *cis*-fluoropropene is analogous to that in diatomic hydrogen fluoride at double or triple its equilibrium bond length. However, as pointed out previously for propene,[13] several parts of these molecules are simultaneously undergoing changes in their interactions and a complex balance of effects is taking place.

Since one does not expect any significant change in the correlation energy upon traversing the barrier to rotation in the molecules studied, and as indicated below, the uncertainties in geometry cannot account for the discrepancy between the calculated and experimental barriers, it appears that the discrepancy is almost entirely due to the use of an inadequate basis set. The primary deficiency of the basis set employed is the rigidity of the LCAO approximation. Obviously, the flexibility introduced by splitting out the basis would lead to a more accurate wave function; splitting out the "tail components" of the basis functions would yield more flexibility in the critical through-space regions, and it is reasonable to expect that such splitting would lead to a marked improvement in the barrier magnitudes. The addition of higher order harmonic functions to the basis lowers total energies, but there are no hybridization or symmetry arguments that indicate a significant improvement in predicted magnitudes.

Effect of Uncertainties in Geometry

By an examination of the microwave spectra of several isotopically substituted propenes, Lide and Christensen[3] determined the geometry of propene with an estimated uncertainty in most bond lengths of ±0.004 Å and an uncertainty on the order of ±0.3° for most bond angles. The out-of-plane methyl hydrogens were more difficult to determine, with an estimated uncertainty of ±0.014 Å in CH bond length and ±1.8° in HCH angles. The geometries for the fluoropropenes have been less accurately determined. The assumed geometries have been obtained by keeping the basic propene structure fixed and adjusting the position of the fluorine atom to fit the spectroscopically observed moments of inertia. In addition, the methyl groups were "symmetrized" by symmetrically disposing the methyl hydrogens around the C–C bond axis.[9]

The calculations reported in this section were carried out with the CNDO/2 approximation.[14] The CNDO method has had rather limited success for barrier calculations, but in the present case we have the fortunate circumstance that the CNDO/2 method yields essentially the same barrier as the present *ab initio* calculations for propene and *trans*-fluoropropene. Therefore, it is not unreasonable to expect, considering the small displacements being investigated, that the results from the CNDO/2 calculation for these molecules should roughly reflect what would be obtained from *ab initio* calculations.

In order to obtain a rough estimate of the effect of the uncertainty in geometry on the height of the barrier to internal rotation, calculations were performed with different molecular coordinates for *trans*-fluoropropene. Experimentally the effect on the geometry[3] of ethylene is more dramatic when a hydrogen is replaced by a fluorine atom than when a hydrogen is replaced by a methyl group, and it is characterized by movement of the vicinal CH bond 9–10° away from the carbon–carbon double bond, shortening the carbon–carbon double bond by 0.004 Å, shortening the *trans*-CH bond by 0.01 Å, and swinging the *trans*-CH bond 2° toward the carbon–carbon bond. It is not unreasonable to expect that the effect of replacing a hydrogen by a fluorine in propene may well be quite similar to this. In order to assay the effect that such changes would have on the calculated barrier height for *trans*-fluoropropene, two calculations were performed, one in which the CH bond vicinal to the fluorine was swung 9° away from the carbon–carbon double bond (denoted "displaced coordinate I" in Table VI), and a second which added to this a double-bond shortening of 0.004 Å and a methyl carbon–ethylene carbon bond shortening along with a 2° swing toward the carbon–carbon double bond (denoted "displaced coordinate II" in Table VI). The

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Table VI. CNDO/2 Barriers for Variation in Geometry for *trans*-Fluoropropene

	Barriers, au
Equilibrium geometry	0.0022
Displaced coordinate I	0.0021
Displaced coordinate II	0.0023

Table VII. CNDO/2 Results for Rigid Rotation of Equilibrium Asymmetric Methyl Group in Propene (0–180°)

	Total energy, au	Barrier,[a] au
Eclipsed 1	−25.7748	
Intermediate 1	−25.7738	0.0021
Staggered 1	−25.7727	
Intermediate 2	−25.7735	0.0019
Eclipsed 2	−25.7746	
Intermediate 3	−25.7737	0.0019
Staggered 2	−25.7727	

[a] CNDO/2 barrier for symmetrized coordinates employed in *ab initio* calculation is 0.0019 au.

actual molecular mode under consideration has a symmetric threefold barrier. In the calculations, this mode is simulated by a rigid rotation of the methyl group. An exact calculation for a rigid rotation of the methyl group, employing the exact equilibrium geometry, should yield an upper bound to the barrier height for the actual mode. It was decided to compute the difference in the barrier for a rigid rotation of the experimentally determined, asymmetric methyl group for propylene, with respect to that for the symmetrized methyl group of the present calculations. The results of this calculation are presented in Table VII.

In summary, the results of this section indicate that the uncertainties in the geometry do not dramatically affect the accuracy of the calculated barriers. However, they do indicate that, without extensive optimization of geometry, the uncertainty in the barrier for an *ab initio* calculation may well be as much as ±0.2 kcal.

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Molecular Motion in Spin-Labeled[1a] Phospholipids and Membranes

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Abstract: L-α-Lecithins having a paramagnetic *N*-oxyl-4′,4′-dimethyloxazolidine ring at selected positions on a fatty acid chain have been prepared. A quantitative analysis of the paramagnetic resonance spectra of these "spin-labeled" lecithins in aqueous dispersions of natural phospholipids is given in terms of an effective spin Hamiltonian that results from rapid anisotropic motions of the paramagnetic *N*-oxyloxazolidine ring. Good agreement is obtained between the observed and calculated resonance line shapes. Similar studies are presented for *N*-oxyl-4′,4′-dimethyloxazolidine derivatives of saturated fatty acids in aqueous dispersions of phospholipids and in the walking leg nerve fiber of *Homarus americanus*. The rapid anisotropic molecular motion determined from the resonance spectra can be accounted for in terms of a realistic model of rapidly interconverting isomeric states of a polymethylene chain. The analysis of the resonance data in terms of this model makes it possible to estimate the probabilities of gauche and trans conformations about carbon–carbon single bonds at various positions in fatty acid chains in phospholipid bilayers and in membranes. These calculations indicate that, for example, the fatty acid polymethylene chain in aqueous dispersions of lecithin–cholesterol (2:1 mole ratio) may be thought of as relatively "rigid rods" for a region of up to about eight carbon atoms from the fatty acid–glycerol ester linkage, with rapidly increasing probabilities for gauche states at larger distances. Similar studies with spin-labeled fatty acids bound to nerve fiber membranes indicate that the polymethylene chains on the membrane phospholipids show motional characteristics very similar to those of the 2:1 egg lecithin–cholesterol system. Qualitatively one may say that the hydrophobic regions of phospholipid bilayers and membranes become more and more "fluid" as one moves toward the terminal methyl groups of the phospholipid fatty acids.

A variety of physical techniques have been applied to the study of the structure and kinetic properties of phospholipid dispersions and membranes. Included among these techniques are, for example, X-ray diffraction, differential thermal analysis, electron microscopy, infrared spectroscopy, optical rotatory dispersion, circular dichroism, and nuclear magnetic resonance. The results of such studies have been described recently by Chapman and Wallach,[2] Levine, Bailey, and Wilkins,[3] Luzzati,[4] Lenard and Singer,[5] Robertson,[6a] Stoeckenius,[6b] and Steim, *et al.*[7]

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