

the opposite effect to  $\chi_{AC}$  except the interfacial tension among the interfacial properties, even if not shown in this paper.

**Acknowledgment.** The present study was supported (in part) by the Basic Science Research Institute Program, Ministry of Education, Korea, 1993. Project No. BSRI-93-309.

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## Structures and Barrier Heights for the Internal Rotation of Ethyl Halides Calculated by *ab initio* Methods

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Received October 13, 1993

The barrier heights of the internal rotations for ethyl halides calculated by *ab initio* methods differ from those of experiments by more than 0.2 kcal/mol. The use of basis sets larger than the 6-31G\* set and the inclusion of correlation do not improve the agreement between the calculated and experimental values. The zero-point vibration corrections are substantial in the HF calculations with 6-31G\* basis sets, but become negligible in the MP2 calculations with 6-311G\*\* basis sets for C<sub>2</sub>H<sub>5</sub>F and C<sub>2</sub>H<sub>5</sub>Cl. It is shown that the rigid rotor approximation and the assumed shape of the potential curve as a cos2 $\theta$  curve could also be the sources of discrepancies between calculated and experimental values. Higher order perturbation corrections narrow the gap between experimental and theoretical values, but there still remains about 10% overestimate of 0.3 kcal/mol. Optimized geometries from the HF and MP2 calculations are in good agreement with those from experiments. Dipole moments calculated from the MP2 densities show slightly better agreement with experiments than those from the HF densities.

## Introduction

Ethyl halides are one of the simplest systems that exhibit

internal rotations. Barrier heights of internal rotations for ethyl halides (C<sub>2</sub>H<sub>5</sub>X where X=F, Cl, Br and I) do not display any apparent trends as the halogen atom varies from

fluorine to iodine. Another property that does not have simple trends is dipole moment. Experimental values for dipole moments and rotational barriers are available<sup>1-5</sup>, but may not provide detailed informations which are helpful in understanding these systems. Simple argument based upon the size and electronegativity of halogen atoms is not suitable to explain the relative magnitude of barrier heights or dipole moments. Electronic structure calculations may shed some lights in explaining these properties. Since the ethyl halides are small enough to apply various methods of electronic structure calculations, we have studied the ground states of the molecules with *ab initio* methods in GAUSSIAN packages<sup>6</sup>.

It is generally accepted that Hartree-Fock(HF) calculations for small saturated molecules with a basis set of reasonable size yield the barrier heights of the internal rotation in good agreement with experiment since the number and characteristics of bonds remain unchanged during the internal rotation<sup>7,8</sup>. Our previous study indicates that HF calculations overestimate the barrier heights of internal rotation by about 0.3 kcal/mol in all ethyl halides<sup>9</sup>. This 0.3 kcal/mol is a small quantity but this corresponds to about 10% of the rotational barriers. Semiempirical methods available in MOPAC<sup>10</sup>, namely MINDO/3, MNDO, AM1 and PM3, produce barriers too small to be useful for the present study, although the geometry of the staggered form is in good agreement with experiment. Therefore, we limit the present report to *ab initio* results. In the *ab initio* calculations, our primary goal is to investigate whether the 10% discrepancy in barrier heights can be reduced by using larger basis sets and/or by the inclusion of more correlations. Most extensive study is done for the ethyl fluoride since the fluorine is the smallest. After performing test calculations using various kinds of basis sets, 6-31G\* and 6-311G\*\* basis sets are selected as the compromise between accuracy and computational economy for the study of correlation effect.

The present study also considers other factors influencing barrier heights such as the zero-point energy and the frozen rotor approximation. In order to include the zero-point energy contribution to the barrier heights of internal rotations, harmonic vibrational frequencies are calculated and thermal corrections are conducted at the HF and the MP2 levels. The validity of the rigid rotor approximation is tested at the HF level using 6-311G\*\* basis set for the C<sub>2</sub>H<sub>5</sub>F molecule. Results of these calculations are described after a brief section explaining computational method.

### Computational Methods

Calculations have been performed using the GAUSSIAN88 program with various kinds of internally stored basis sets for C, H, F and Cl atoms<sup>6</sup>. For C<sub>2</sub>H<sub>5</sub>Br and C<sub>2</sub>H<sub>5</sub>I molecules, effective core potentials (ECP) of Hay and Wadt<sup>11</sup> are used for Br and I in order to reduce the size of calculations and also to include the relativistic effects. The reliability of ECP is partially tested by performing both all electron and ECP calculations for ethyl chloride.

For most molecules, correlation effects are considered by a routinely available method, Møller Plesset perturbation theory expansion up to the second order(MP2). Geometries are optimized for staggered and eclipsed conformers using each selected basis set at the HF level. For MP2 geometry

**Table 1.** The Barrier Heights for the Internal Rotation of C<sub>2</sub>H<sub>5</sub>F and C<sub>2</sub>H<sub>5</sub>Cl Calculated by the HF Method.

Basis	$\Delta E(\text{kcal/mol})$	
	C <sub>2</sub> H <sub>5</sub> F	C <sub>2</sub> H <sub>5</sub> Cl
3-21G	3.33	3.64
3-21G*	3.66	
4-31G	3.27	3.69
4-31G*	3.58	3.97
6-31G*	3.62	3.87
6-31G**	3.64	3.88
6-311G*	3.64	
6-311G**	3.73	3.94
Expt. <sup>a</sup>	3.33 ± 0.05	3.70 ± 0.04

<sup>a</sup>From Ref. 2 and 3.

optimizations, only 6-31G\* and 6-311G\*\* basis sets are used. Since both the staggered and the eclipsed forms of alkyl halides have the plane of symmetry, this symmetry is assumed throughout calculations in order to reduce the required computation time and to improve energies. All other geometrical parameters are optimized simultaneously. As a first approximation, the barrier height for the internal rotation is computed by taking the difference between total energies of staggered and eclipsed forms. In order to include the zero-point energy correction, harmonic vibrational frequencies are calculated at the HF and MP2 levels at the HF and MP2 optimized geometries, respectively.

### Results and Discussion

Effects of the basis set size for the barrier heights are shown in Table 1 for C<sub>2</sub>H<sub>5</sub>F and C<sub>2</sub>H<sub>5</sub>Cl systems. Polarization functions on heavy atoms affect the barrier heights by about 0.3 kcal/mol for C<sub>2</sub>H<sub>5</sub>F and C<sub>2</sub>H<sub>5</sub>Cl at the HF level, but the additional *p* functions on the H atoms have smaller effects. When the basis set is larger than the 4-31G\* set, the calculated barrier heights for the internal rotation seem to increase with the increasing size of the basis set. As a result, the agreement with experiment gets worse for the larger basis sets. Although it is very difficult to suggest a good basis set for the calculation of barrier heights from the data in Table 1, we use the 6-31G\* basis set as the standard basis set. The 6-311G\*\* basis set is also employed whenever more information on basis set effects are desirable.

In order to estimate the effect of correlation, barrier heights are calculated for C<sub>2</sub>H<sub>5</sub>F and C<sub>2</sub>H<sub>5</sub>Cl using 6-31G\* basis sets and various routinely available methods. The results are summarized in Table 2. Energies of staggered and eclipsed forms are calculated at the MP2 optimized geometries by MP2, MP3, MP4, CISD, and CCD methods. The barrier height for C<sub>2</sub>H<sub>5</sub>F is also computed at the MP3 optimized geometries, but the results are essentially identical to those in Table 2. The correlation effects on the barrier heights are about 0.2 kcal/mol in the direction of increasing the barrier heights compared with the HF values. Correlation effects worsen the agreement between calculated and experimental values. In Table 2, MP2 results overestimates the more ac-

**Table 2.** The Barrier Heights of the Internal Rotation of  $C_2H_5F$  and  $C_2H_5Cl$  Calculated with 6-31G\* Basis Sets at Various Levels of Electron Correlations

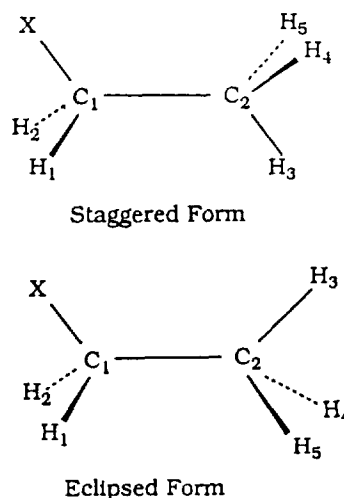
Method	$\Delta E(\text{kcal/mol})$	
	$C_2H_5F$	$C_2H_5Cl$
HF	3.64	3.88
MP2	3.92	4.10
MP3	3.74	3.93
MP4	3.82	3.95
CISD	3.75	3.93
CCD	3.71	3.89
Expt. <sup>a</sup>	$3.33 \pm 0.05$	$3.70 \pm 0.04$

<sup>a</sup>From Ref. 2 and 3.

curate MP4 values by 0.20 and 0.15 kcal/mol for  $C_2H_5F$  and  $C_2H_5Cl$ , respectively. CISD and CCD calculations lower the barrier heights even further from the MP4 values, but the calculated barrier heights are still larger than the HF values. It is very unlikely that the barrier heights calculated with the 6-31G\* basis set will reach the experimental values by including more correlation effects.

The HF theory with large basis sets reproduces experimental geometries quite well. Theoretical and experimental geometries agree within 0.01 Å for bond lengths and 1° for bond angles<sup>8</sup>. Geometries are optimized at the HF and MP2 levels using 6-31G\* and 6-311G\*\* basis sets for  $C_2H_5F$  and  $C_2H_5Cl$ . For  $C_2H_5Br$  and  $C_2H_5I$ , ECPs are used for the Br and I atoms and 6-31G\* basis sets are used for other atoms. Since the improvement of geometrical parameters from including the third order perturbation effect for  $C_2H_5F$  is rather small and the time required for the inclusion of third order effect is quite large, MP3 geometry optimizations are performed only for ethyl fluorides. The geometric parameters are defined as shown in Figure 1.

The optimized geometries for ethyl fluorides are collected in Table 3 and Table 4 for staggered and eclipsed forms, respectively. When the basis sets are enlarged from 4-31G\* to 6-311G\*\*, there are almost no change in the calculated

**Figure 1.** Definition of geometrical parameters.

geometries. For geometrical parameters at the HF level, even 4-31G\* values are nearly identical to those of the more extensive 6-311G\*\* basis. When correlation effects are included using MP2 method, the geometrical parameters agree quite well with experimental values. The difference in bond distances and bond angles are less than 0.005 Å and 1°, respectively. The biggest differences in geometrical parameters between two rotational conformers are the C-C bond length, elongated by 0.016 Å for the eclipsed form, the angle  $H_3C_2C_1$ , increased by 2.0°, and the angle  $H_4C_2C_1$ , increased by 1.7°. All other geometric parameters remain nearly constant during the rotation.

Table 5 and Table 6 show the optimized geometries for  $C_2H_5Cl$  using 6-31G\*, 6-311G\*\* and EP 6-31G\* basis sets employing the HF and MP2 methods. For the 6-311G\*\*/MP2 case, which is the most elaborate calculation, the agreement with experiment is quite good. The deviations from experimental values in bond lengths and bond angles are again less than 0.005 Å and 1.0°, respectively. The C-C bond elongates by 0.017 Å and the  $ClC_1C_2$  bond angle increase by 1.7° for the eclipsed form during the internal rotation. The geometrical parameters obtained with the EP 6-31G\* basis

**Table 3.** Optimized Geometries of Staggered  $C_2H_5F$ 

Method	HF				MP2		MP3	Expt. <sup>a</sup>
	4-31G*	6-31G*	6-311G*	6-311G**	6-31G*	6-311G**	6-31G*	
$r_{C_1F}$	1.371	1.373	1.371	1.372	1.399	1.395	1.390	1.387
$r_{C_1C_2}$	1.511	1.512	1.510	1.511	1.509	1.513	1.510	1.512
$r_{C_1H_1}$	1.082	1.083	1.082	1.084	1.094	1.095	1.093	1.094
$r_{C_2H_3}$	1.085	1.086	1.085	1.086	1.093	1.095	1.093	1.093
$r_{C_2H_4}$	1.083	1.084	1.084	1.085	1.092	1.093	1.091	1.093
$\angle FC_1C_2$	109.5	109.5	109.7	109.7	109.2	109.2	109.6	109.3
$\angle H_1C_1C_2$	111.5	111.5	111.7	111.6	111.7	111.8	111.4	112.1
$\angle H_3C_2C_1$	110.4	110.3	110.3	110.1	110.4	110.4	110.2	109.4
$\angle H_4C_2C_1$	110.4	110.5	110.6	110.5	110.2	110.2	110.3	110.2
$\angle H_1C_1F$	107.8	107.7	107.3	107.4	107.7	107.6	107.7	106.5
$\angle H_4C_2H_3$	108.6	108.6	108.5	108.6	108.7	108.7	108.7	108.5

<sup>a</sup>From Ref. 5

**Table 4.** Optimized geometries of eclipsed  $C_2H_5F$ 

Method	HF				MP2		MP3	Expt. <sup>a</sup>
	4-31G*	6-31G*	6-311G*	6-311G**	6-31G*	6-311G**	6-31G*	
$r_{C_1F}$	1.372	1.374	1.372	1.373	1.400	1.397	1.391	1.387
$r_{C_1C_2}$	1.528	1.529	1.526	1.528	1.526	1.529	1.527	1.512
$r_{C_1H_1}$	1.081	1.082	1.081	1.082	1.093	1.094	1.092	1.094
$r_{C_2H_3}$	1.082	1.083	1.083	1.084	1.091	1.092	1.091	1.093
$r_{C_2H_4}$	1.083	1.084	1.084	1.085	1.092	1.093	1.091	1.093
$\angle FC_1C_2$	110.2	110.2	110.3	110.2	110.0	109.9	110.2	109.3
$\angle H_2C_1C_2$	111.8	111.9	112.0	111.9	112.0	112.1	111.7	112.1
$\angle H_3C_2C_1$	108.9	108.9	109.1	108.9	108.2	108.3	108.2	109.4
$\angle H_4C_2C_1$	111.9	111.9	112.0	111.8	112.0	112.0	112.0	110.2
$\angle H_1C_1F$	107.2	107.1	106.8	106.9	107.2	107.1	107.2	106.5
$\angle H_4C_2H_3$	108.0	108.0	107.9	108.1	108.1	108.2	108.1	108.5

<sup>a</sup>Experimental values are for the staggered form from Ref. 5.**Table 5.** Optimized Geometries of Staggered  $C_2H_5Cl$ 

	HF			MP2			Expt. <sup>a</sup>
	6-31G*	6-311G**	EP 6-31G*	6-31G*	6-311G**	EP 6-31G*	
$r_{C_1Cl}$	1.799	1.804	1.792	1.789	1.786	1.777	1.789
$r_{C_1C_2}$	1.517	1.516	1.517	1.514	1.515	1.517	1.520
$r_{C_1H_1}$	1.079	1.079	1.079	1.090	1.089	1.091	1.089
$r_{C_2H_3}$	1.086	1.087	1.086	1.094	1.094	1.094	1.092
$r_{C_2H_4}$	1.083	1.084	1.083	1.091	1.091	1.092	1.092
$\angle ClC_1C_2$	111.5	111.5	111.3	111.3	111.0	111.2	111.0
$\angle H_1C_2C_1$	111.8	111.9	111.8	111.5	111.4	111.5	111.4
$\angle H_3C_2C_1$	109.3	109.1	109.4	109.5	109.7	109.6	109.2
$\angle H_4C_2C_1$	111.0	111.0	111.0	110.9	110.7	110.7	110.3
$\angle H_1C_1Cl$	106.2	106.0	106.3	106.8	107.0	107.0	106.3
$\angle H_4C_2H_3$	108.5	108.5	108.5	108.6	108.7	108.6	109.1

<sup>a</sup>From Ref. 5**Table 6.** Optimized Geometries of Eclipsed  $C_2H_5Cl$ 

	HF			MP2			Expt. <sup>a</sup>
	6-31G*	6-311G**	EP 6-31G*	6-31G*	6-311G**	EP 6-31G*	
$r_{C_1Cl}$	1.801	1.806	1.793	1.791	1.788	1.779	1.789
$r_{C_1C_2}$	1.534	1.533	1.534	1.531	1.532	1.534	1.520
$r_{C_1H_1}$	1.078	1.078	1.078	1.090	1.089	1.090	1.089
$r_{C_2H_3}$	1.081	1.082	1.081	1.090	1.090	1.090	1.092
$r_{C_2H_4}$	1.084	1.084	1.084	1.092	1.092	1.092	1.092
$\angle ClC_1C_2$	112.8	112.8	112.7	112.7	112.7	112.6	111.0
$\angle H_1C_2C_1$	112.0	112.1	112.0	111.7	111.5	111.6	111.4
$\angle H_3C_2C_1$	111.5	111.5	111.4	111.2	111.1	110.9	109.2
$\angle H_4C_2C_1$	110.7	110.7	110.8	110.9	111.0	110.9	110.3
$\angle H_1C_1Cl$	105.6	105.3	105.6	106.1	106.3	106.3	106.3
$\angle H_4C_2H_3$	107.9	107.9	107.9	107.8	107.7	107.9	109.1

<sup>a</sup>Experimental values of the staggered form from Ref. 4.

set are in good agreement with those from the 6-31G\* basis set, implying that the use of ECP for geometry calculations can be justified.

The calculated geometrical parameters for  $C_2H_5Br$  are shown in Table 7. The geometrical parameters agree well, with experimental values. The EP 6-31G\* basis gives quite

**Table 7.** EP 6-31G\* Optimized Geometries for C<sub>2</sub>H<sub>5</sub>Br

	Staggered		Eclipsed		Expl. <sup>a</sup>
	HF	MP2	HF	MP2	
<i>r</i> C <sub>1</sub> Br	1.974	1.974	1.977	1.976	1.950
<i>r</i> C <sub>1</sub> C <sub>2</sub>	1.517	1.515	1.533	1.532	1.519
<i>r</i> C <sub>1</sub> H <sub>1</sub>	1.078	1.090	1.077	1.089	1.087
<i>r</i> C <sub>2</sub> H <sub>3</sub>	1.087	1.095	1.081	1.090	1.092
<i>r</i> C <sub>2</sub> H <sub>4</sub>	1.083	1.092	1.084	1.093	1.092
∠BrC <sub>1</sub> C <sub>2</sub>	111.6	111.3	113.1	112.7	111.3
∠H <sub>1</sub> C <sub>1</sub> C <sub>2</sub>	112.4	112.4	112.6	112.6	112.2
∠H <sub>3</sub> C <sub>2</sub> C <sub>1</sub>	109.1	109.2	112.1	111.7	108.5
∠H <sub>4</sub> C <sub>2</sub> C <sub>1</sub>	111.2	111.0	110.5	110.6	110.4
∠H <sub>1</sub> C <sub>1</sub> Br	105.3	105.5	104.5	104.8	105.3
∠H <sub>4</sub> C <sub>2</sub> H <sub>3</sub>	108.4	108.5	107.8	107.8	109.2

<sup>a</sup>Experimental values for the staggered form from Ref. 5.**Table 8.** EP 6-31G\* Optimized Geometries for C<sub>2</sub>H<sub>5</sub>I

	Staggered		Eclipsed		Expl. <sup>a</sup>
	HF	MP2	HF	MP2	
<i>r</i> C <sub>1</sub> I	2.175	2.175	2.178	2.178	2.151
<i>r</i> C <sub>1</sub> C <sub>2</sub>	1.518	1.516	1.534	1.533	1.521
<i>r</i> C <sub>1</sub> H <sub>1</sub>	1.078	1.090	1.077	1.089	1.086
<i>r</i> C <sub>2</sub> H <sub>3</sub>	1.087	1.096	1.080	1.090	1.093
<i>r</i> C <sub>2</sub> H <sub>4</sub>	1.083	1.092	1.084	1.093	1.093
∠IC <sub>1</sub> C <sub>2</sub>	112.3	111.9	113.9	113.6	111.4
∠H <sub>1</sub> C <sub>1</sub> C <sub>2</sub>	112.5	112.6	112.7	112.8	112.3
∠H <sub>3</sub> C <sub>2</sub> C <sub>1</sub>	108.9	109.0	112.9	112.6	108.4
∠H <sub>4</sub> C <sub>2</sub> C <sub>1</sub>	111.4	111.3	110.3	110.4	110.5
∠H <sub>1</sub> C <sub>1</sub> I	104.7	105.0	103.9	104.1	104.5
∠H <sub>4</sub> C <sub>2</sub> H <sub>3</sub>	108.2	108.4	107.6	107.6	109.2

<sup>a</sup>Experimental values for the staggered form from Ref. 5.

accurate geometrical values especially when the MP2 method is used. The C-C bond length changes by 0.017 Å and the BrC<sub>1</sub>C<sub>2</sub> and H<sub>3</sub>C<sub>2</sub>C<sub>1</sub> angles change by 1.4° and 2.5°, respectively, during the internal rotation.

The calculated geometrical parameters for C<sub>2</sub>H<sub>5</sub>I shown in Table 8 are in reasonable agreement with experimental values except for the C-I bond length which is 0.024 Å longer than the experimental value. During the internal rotation C-C bond length elongates by 0.017 Å and the IC<sub>1</sub>C<sub>2</sub> and H<sub>3</sub>C<sub>2</sub>C<sub>1</sub> angles increase by 1.7° and 3.6°, respectively.

Charge distributions and dipole moments for the staggered form of C<sub>2</sub>H<sub>5</sub>X molecules are collected in Table 9. The correlation effect reduces the charge, but the trends shown by the net charges of the halogen and carbon atoms are not modified very much by the use of MP2 densities. The charge for the C<sub>1</sub> carbon is negative except for the fluoride. Since fluorine withdraws electrons from the bonded carbon, the C<sub>1</sub> carbon is positively charged. For other system, the electronegativity is not so large and the carbon-halogen bond length are longer than the carbon-fluorine bond length. The electron withdrawing effect of the halogen atom is not so prominent and the carbon atom is negatively charged.

**Table 9.** Charges and Dipole Moments for the Staggered Forms of C<sub>2</sub>H<sub>5</sub>X Molecules. 6-311G\*\* Basis Sets are Used for the Fluoride and the Chloride, and EP 6-31G\* Basis Sets for the Bromide and Iodide Charges (*a.u.*)

X	HF density				MP2 density			
	F	Cl	Br	I	F	Cl	Br	I
X	-0.37	-0.16	-0.20	-0.10	-0.29	-0.11	-0.16	-0.07
C <sub>1</sub>	0.21	-0.21	-0.31	-0.44	0.12	-0.28	-0.34	-0.46
C <sub>2</sub>	-0.28	-0.24	-0.47	-0.46	-0.33	-0.28	-0.49	-0.48
H <sub>1</sub>	0.08	0.14	0.22	0.23	0.09	0.15	0.22	0.22
H <sub>3</sub>	0.09	0.10	0.17	0.17	0.10	0.11	0.18	0.18
H <sub>4</sub>	0.10	0.11	0.19	0.19	0.12	0.13	0.19	0.19

Dipole Moments (Debye)

	HF density				MP2 density			
	F	Cl	Br	I	F	Cl	Br	I
Calc.	2.15	2.41	2.38	2.28	1.83	2.12	2.18	2.08
Expl. <sup>a</sup>	1.94	2.05	2.03	1.91	1.94	2.05	2.03	1.91

<sup>a</sup>From Ref. 5

The dipole moments calculated from the HF density overestimate the experimental values substantially for all ethyl halides as shown in Table 9, but those from the MP2 density are in far better agreements. The variations in observed and calculated dipole moments can be explained qualitatively from the charge distribution and geometry. For the fluoride there exist two kinds of bond dipoles in opposite directions which cancel with each other to produce a smaller dipole moment. The charge on Br is larger than that on Cl or I. The chloride in Table 9 is calculated with 6-311G\*\* while the bromide is calculated with Ep 6-31G\*, but the charge on Cl is similar (-0.15) even in the HF calculations using EP 6-31G\*.

The C-C bond length of the eclipsed form is longer than that of the staggered form by 0.017 Å regardless of the attached halide atom. For the chloride, the bromide and the iodide, the angle between the halogen and the hydrogen atoms are larger for the eclipsed form because there are larger steric repulsions between the halogen atom and the asymmetric hydrogen atom. This steric repulsion overweighs the electrostatic attraction between the halogen and the hydrogen. For the fluoride, the situation is slightly different. The angle between the F and H atoms becomes narrower for the eclipsed form as shown in Tables 3 and 4 probably due to the electrostatic interaction between the negatively charged fluorine and positively charged hydrogen on the same carbon atom.

The energy differences between the staggered and eclipsed forms are collected in Table 10. The barrier heights at the HF level are larger than experimental values by 0.2 to 0.3 kcal/mol for all ethyl halides. The results obtained at the MP2 level using same basis sets are in worse agreement with experiment than the HF results. Basis set and correlation effects mentioned earlier seem to imply that this discrepancy may not be removed easily by improving quality of basis set and/or electron correlations. In an effort to locate

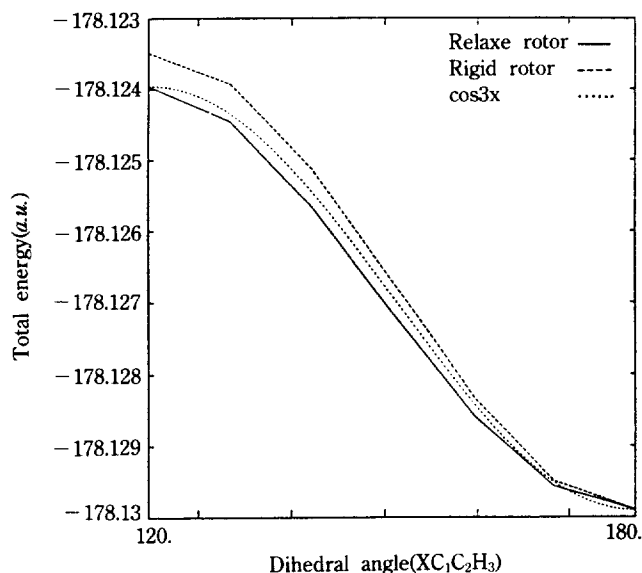
**Table 10.** Barrier Heights (kcal/mol) of the Internal Rotation for  $C_2H_5X$  with and without Zero-point Energy Corrections Without zero-point energy correction

	EP 6-31G*		6-31G*		6-311G**		Expl. <sup>a</sup>
	HF	MP2	HF	MP2	HG	MP2	
F			3.62	3.92	3.73	3.96	3.32
Cl	3.94	4.15	3.87	4.10	3.94	4.39	3.7
Br	3.89	4.02					3.7
I	3.87	4.03					3.66

With zero-point energy and MP4 corrections

	6-31G*		6-311G**		Expl. <sup>b</sup>
	MP2	MP2	MP2	MP4	
F		3.59	3.54	3.44	2.97
Cl		3.83	3.97	3.81	3.34

<sup>a</sup>From Ref. 3, 4, and 5. <sup>b</sup>Experimental values are also corrected for the zero-point energies using experimental vibrational frequency for the torsional motion.

**Figure 2.** Potential energy curves for the torsional motion of the ethyl fluoride calculated by the HF method using 6-311G\*\* basis set.

the probable source of the discrepancies in other factors, we perform some additional calculations.

In order to estimate the error which may be caused by the rigid rotor approximation, we have carried out HF calculations for  $C_2H_5F$  with and without the rigid rotor approximation using 6-311G\*\* basis set. For the rigid rotor approximation, geometric parameters for the staggered form are optimized imposing the equivalence restriction of three hydrogens of methyl group. During the rotation around the CC bond, the geometric parameters of the methyl group are kept constant. For the relaxed rotor, all geometric parameters are optimized at each given torsional angle. The resulting potential curves are shown in Figure 2. When the rigid rotor approximation is employed, the calculated barrier height in-

**Table 11.** The Differences ( $cm^{-1}$ ) of the Sum of Vibrational Frequencies between Staggered and Eclipsed Forms. The Torsional Frequency Corresponding to the Internal Rotation is not Included in the Sum. The Sum is Larger for the Eclipsed Forms than for the Staggered Forms.

	SCF frequencies		MP2 frequencies	
	6-31G*	6-311G**	6-31G*	6-311G**
$C_2H_5F$	91.2	74.7	40.7	0.9
$C_2H_5Cl$	129.5	100.5	91.2	5.0
$C_2H_5Br$	122.1		81.4	
$C_2H_5I$	122.8		89.5	

creases by 0.32 kcal/mol due to the higher energy for the eclipsed form. Barrier heights for the internal rotation cannot be directly measured in experiments. Experimental values for the barrier heights are usually derived based upon the assumption that the potential energy curve for the torsional motion has  $\cos 3\theta$  dependence<sup>13</sup>. Rigid rotor approximation is also implicit in the interpretation of the experimental data since the torsional motion is assumed as being independent from other vibrational motions. In Figure 2, there are also differences between the relaxed rotor curve and the  $\cos 3\theta$  curve. Therefore, both approximations could be the source of some discrepancy between calculated and experimental barrier heights, but the actual magnitude is difficult to estimate<sup>13</sup>.

Along the similar line, comparisons between rotational barriers determined by *ab initio* and spectroscopic methods require special care due to the zero point energies<sup>12</sup>. The spectroscopic rotation barriers are effective potential barrier which can be best modeled by a ground-state vibrationally adiabatic potential barrier since it was obtained by fitting an one-dimensional potential for a motion along the torsional coordinate in the presence of all other modes. The resulting barrier neglects the effect of zero-point vibration energy for the torsional mode but the zero-point vibration energies in all the other modes are included. This effect is estimated using vibrational frequencies from *ab initio* calculations. It is known that the HF and MP2 calculations with large basis sets tend to overestimate the vibrational frequencies by 6-10% and less than 5%, respectively<sup>8</sup>.

In order to include zero-point energy correction, harmonic vibrational frequencies are obtained and all vibrational frequencies except the torsional mode frequencies are summed for both staggered and eclipsed conformers. The differences in the sums are collected in Table 11. For all ethyl halides, the sums for eclipsed forms are larger than those for staggered forms, worsening the agreement between calculation and experiment, although the difference is reduced both by the larger basis set and the inclusion of electron correlation. The differences around  $100\text{ cm}^{-1}$  at the HF level with 6-31G\* become less than  $5\text{ cm}^{-1}$  for MP2 calculations with 6-311G\*\* for  $C_2H_5F$  and  $C_2H_5Cl$ .

There is another point to consider in the zero point energy. The staggered forms has one extra torsional mode which contributes to the potential curve. In order to be fair in the comparison, both spectroscopic and *ab initio* values need to be corrected by their respective vibrational frequencies

for this torsional motion. The torsional frequency differences between experiment and theory are less than  $30\text{ cm}^{-1}$  which is equivalent to  $0.085\text{ kcal/mol}$ . The barrier heights corrected for this zero point energy are also listed in Table 10. The zero point correction is large for the HF calculations with 6-31G\* basis sets, and in the direction of worsening the agreement with experiment. But at the MP2 level with 6-311 G\*\* basis set, there is almost no difference whether the zero point correction is included or not, at least for  $\text{C}_2\text{H}_5\text{F}$  and  $\text{C}_2\text{H}_5\text{Cl}$ .

In order to include the correlation effect further, MP4 energies are obtained at MP2 optimized geometries using 6-311G\*\* basis sets for the fluoride and the chloride. This higher order correlation energy reduces the barrier heights by  $0.11\text{ kcal/mol}$  and  $0.16\text{ kcal/mol}$  for  $\text{C}_2\text{H}_5\text{F}$  and  $\text{C}_2\text{H}_5\text{Cl}$ , respectively, as shown in Table 10. These lowerings are about the same as those in Table 2 for 6-31G\* basis sets. We expect that more correlations will probably bring the barrier value to that of the HF level, but not much lower.

Without any considerations about the rigid rotor approximation, the best estimate of the barrier from the present *ab initio* calculations for  $\text{C}_2\text{H}_5\text{F}$  is still  $0.37\text{ kcal/mol}$  higher than experimental values. The situation is similar for  $\text{C}_2\text{H}_5\text{Cl}$  in that theoretical values are higher by  $0.47\text{ kcal/mol}$ . Theoretical values also overestimate the experimental values by  $0.3\text{ kcal/mol}$  both for  $\text{C}_2\text{H}_5\text{Br}$  and  $\text{C}_2\text{H}_5\text{I}$ . Results for the fluoride and the chloride seem to indicate that improved *ab initio* calculations are not warranted at this point as far as the barrier heights are concerned.

### Conclusion

The barrier heights of the internal rotations for ethyl halides are calculated by *ab initio* methods. The use of larger basis set and the inclusion of correlation do not improve the agreement between the calculated and experimental values. The zero-point vibration correction is also considered. In the HF calculations with 6-31G\* basis sets, this correction is significant, but becomes negligible in the MP2 calculations with 6-311G\*\* basis sets for  $\text{C}_2\text{H}_5\text{F}$  and  $\text{C}_2\text{H}_5\text{Cl}$ . The rigid rotor approximation and the assumed shape of the potential curve as a  $\cos 3\theta$  curve are not strictly valid and could cause deviations in deriving barrier heights. However, the present study does not provide the clue to why the calculated barrier should be higher. Higher order perturbation corrections narrows the gap between experimental and theoretical values, but there still remains about 10% overestimate of 0.3

kcal/mol.

It appears that the calculated barrier heights from elaborate calculations with added corrections are in good agreement with the starting point of the present study, HF/6-31G\* values. One may use the barrier heights from the HF/6-31G\* calculations with the understanding that the calculated values will overestimate the experimental ones by about 10% whenever the reference is needed for the torsional motion of a halogen-containing carbon. Calculations beyond the level of the present study will greatly increase the computational time without too much improvement in the description of the internal rotation.

**Acknowledgment.** This study is, in part, supported by the Korea Science and Engineering Foundation.

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