

THEORETICAL STUDY OF INTERNAL ROTATION AND RING INVERSION IN 4-CYCLOPENTENECARBOXYLIC ACID HALIDES

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1. INTRODUCTION

The structure of a series of small ring compounds containing CXO group (where X is: H, F, and Cl) have been investigated by both experimental techniques and theoretical methods [1–7]. The information obtained from theoretical calculations and from the interpretation of molecular spectra of these compounds provided better understanding for the nature of forces in these ring compounds and hence for their structural stability.

When the ring was three-membered, the molecules were found to exist in the planar *cis* and *trans* conformations [6, 8–10]. For the less strained four-, five-, and six-membered rings the nonplanar *gauche* conformation was determined to be the lowest energy conformer [1–5, 7]. Cyclic molecules with *N* ring atoms generally exhibit *N*–3 out-of-plane ring vibrations. The presence of double bonds in the ring hinders these motions. Therefore, 4-cyclopentenecarboxylic acid halides have similar ring behavior to the corresponding cyclobutanes. They have the ring puckering vibration as the only ring motion that gives rise to axial and equatorial configurations of the ring. For many years we were particularly interested in unsaturated hydrocarbons for their important applications in synthetic and polymer chemistry. Therefore, in the present study, the conformational equilibrium and the internal rotation in 4-cyclopentenecarboxylic acid fluoride and chloride were investigated by *ab initio* calculations for comparison purposes. The results of this work are presented herein.

2. AB INITIO CALCULATIONS

The GAUSSIAN 94 program [11] running on IBM RS/6000 model 7015–R24 workstation, was used to carry out the LCAO–MO–SCF restricted Hartree–Fock calculation with the extended 6-31G* basis set. The calculations were extended to the second order Moller–Plesset (MP2) level to investigate the effect of electron correlation on the optimization of the energies and the barriers in 4-cyclopentenecarboxylic acid fluoride and chloride. The possible conformers for each of the two molecules are: the *cis* (oxygen of the carbonyl group eclipses the ring); the *trans* (oxygen of the carbonyl group eclipses the methyl group), and the *gauche* conformers in both the axial and the equatorial cyclopentene ring (see Figure 1). The structural parameters of all the stable conformers of the molecules were optimized by minimizing the energy with respect to the geometrical parameters. From preliminary calculations the equatorial was found to be more preferable than the axial configuration for the ring. The *cis*-axial and the *trans*-axial of the molecules were found to turn into the corresponding equatorial forms upon completion of optimization. Only the *gauche*-axial was predicted to have a noticeable stability that decreases as going from the fluoride to the chloride. The calculated structural parameters, energies, total dipole moments and rotational constants of the two molecules in the *gauche*- and *trans*-equatorial conformers are given in Tables 1–6.

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2.1 Potential Surface

The potential surface scan for the internal rotation about the C–C single bond was obtained by allowing the CXO torsional angle (ϕ) to vary by 10° increments from 0° (*cis* position) to 180° (*trans* position). Only the equatorial configuration of the ring was adopted. All the remaining parameters were held constant at the optimized parameters for the stable conformers. Full geometry optimizations at each of the fixed CXO dihedral angles (ϕ): 15° , 30° , 45° , 60° , 75° , 90° , 105° , 120° , 135° , 150° , and 165° were then carried out at various levels of calculations. The torsional potential was represented as a fourier cosine series in the dihedral angle (ϕ): $V(\phi) = \sum (V_n/2) [1 - \cos(n\phi)]$, where the potential coefficients from V_1 to V_6 are considered adequate to describe the potential function. The results of the energy optimizations at ϕ from 15° to 180° were used to calculate the six coefficients by least-squares fitting. The barrier to internal rotation was calculated and listed in Tables 2 and 4, and the potential functions for the three molecules are shown in Figure 2.

Table 1. Optimized Structural Parameters of 4-Cyclopentenecarboxylic Acid Fluoride in *Trans*- and *gauche*-Equatorial Conformations.

| Parameter ^a | HF/6-31G* | | MP2/6-31G* | | Microwave ^b |
|-------------------------------|--------------|---------------|--------------|---------------|------------------------|
| | <i>Trans</i> | <i>Gauche</i> | <i>Trans</i> | <i>Gauche</i> | <i>Gauche</i> |
| Bond lengths (Å) | | | | | |
| $r(C_1 = C_2)$ | 1.317 | 1.318 | 1.340 | 1.341 | |
| $r(C_1 - C_5 = C_2 - C_3)$ | 1.509 | 1.509 | 1.507 | 1.507 | 1.550 |
| $r(C_3 - C_4 = C_5 - C_4)$ | 1.555 | 1.548 | 1.550 | 1.545 | 1.535 |
| $r(C_4 - C_6)$ | 1.500 | 1.500 | 1.495 | 1.496 | 1.509 |
| $r(C_6 = O)$ | 1.170 | 1.169 | 1.200 | 1.200 | 1.188 |
| $r(C_6 - F)$ | 1.330 | 1.329 | 1.376 | 1.374 | 1.348 |
| $r(C_4 - H)$ | 1.081 | 1.086 | 1.093 | 1.097 | 1.100 |
| $r(C_1 - H)$ | 1.075 | 1.075 | 1.086 | 1.086 | |
| $r(C_2 - H)$ | 1.075 | 1.075 | 1.086 | 1.086 | |
| $r(C_3 - H_1)$ | 1.086 | 1.085 | 1.097 | 1.097 | 1.081 |
| $r(C_3 - H_2)$ | 1.085 | 1.085 | 1.095 | 1.095 | 1.081 |
| $r(C_5 - H_1)$ | 1.086 | 1.088 | 1.097 | 1.099 | 1.081 |
| $r(C_5 - H_2)$ | 1.085 | 1.084 | 1.095 | 1.094 | 1.081 |
| Bond angles (deg) | | | | | |
| $(C_1 C_2 C_3 = C_2 C_1 C_5)$ | 112.5 | 112.5 | 112.0 | 112.0 | |
| $(C_3 C_4 C_5)$ | 105.5 | 106.1 | 105.4 | 106.1 | 89.7 |
| $(C_4 C_6 O)$ | 128.3 | 129.4 | 129.4 | 129.8 | 129.7 |
| $(C_4 C_6 F)$ | 111.7 | 110.6 | 110.5 | 109.9 | 109.7 |
| $(C_6 C_4 H)$ | 106.2 | 106.0 | 106.8 | 106.8 | 108.5 |
| $(C_2 C_3 H_1)$ | 112.1 | 112.1 | 111.4 | 111.5 | |
| $(C_2 C_3 H_2)$ | 111.3 | 111.8 | 111.3 | 111.8 | |
| $(C_1 C_5 H_1)$ | 112.1 | 111.5 | 111.4 | 110.8 | |
| $(C_1 C_3 H_2)$ | 111.3 | 111.7 | 111.3 | 111.9 | |
| $(C_3 C_2 H)$ | 122.2 | 122.2 | 122.8 | 122.7 | |
| $(C_5 C_1 H)$ | 122.2 | 122.4 | 122.8 | 123.0 | |
| $(C_1 C_4 C_5 H)$ | 119.0 | 119.1 | 118.8 | 118.9 | |
| $(C_2 C_4 C_3 H)$ | 121.1 | 121.4 | 121.5 | 121.9 | |
| θ | 130.8 | 132.0 | 130.0 | 131.2 | 130.0 |
| ϕ | 180.0 | 62.2 | 180.0 | 62.9 | 54.7 |

^a θ and ϕ are the angle of the carbonyl group with the ring and the CFO torsional angle respectively.

^b Structural parameters of cyclobutanecarboxylic acid fluoride obtained from reference [1].

3. DISCUSSION

The structural stability of small ring compounds has attracted attention for many years [1–10]. The structure of the smallest member, the three-membered ring, in the gas phase is of particular interest. The formation of the ring by the overlap between the sp^3 hybridized orbitals of the carbons (bond angle is near 109°) leads to a highly strained three-membered ring (bond angle is about 60°). The stability of many substituted cyclopropanes was explained by adopting the sp^2 hybridization model, in which three sp^2 lobes are arranged on each carbon atom forming three-center-three-electron bonds [12, 13]. The remaining two lobes of each carbon in the ring are directed above and below the plane of the ring to form bonds to hydrogen atoms of cyclopropane ring. The pure $2p$ orbitals overlap in the ring plane creating a bonding molecular orbitals.

For the relatively higher-order cyclic compounds, there are two forces that control the conformational behavior of the ring. First is the ring strain which tends to keep the ring skeleton planar. Second is the torsional forces between the methylene groups, which tend to pucker the ring. These forces compete with each other in determining the equilibrium structure of

Table 2. Calculated Total Energies (Hartrees) and Relative Energies (kcal/mol) of Stable Conformers of 4-Cyclopentenecarboxylic Acid Fluoride.

| Conformation | HF/6-31G* | | | MP2/6-31G* | | |
|---------------------------|-------------------|--------------|-----------------|-------------------|--------------|-----------------|
| | $(\phi, \beta)^a$ | Total Energy | Relative Energy | $(\phi, \beta)^a$ | Total Energy | Relative Energy |
| <i>Gauche</i> -Equatorial | (62,21) | -405.58356 | 0.000 | (63,24) | -406.69124 | 0.101 |
| <i>Trans</i> -Equatorial | (180,21) | -405.58296 | 0.374 | (180,24) | -406.69112 | 0.180 |
| <i>Cis</i> -Equatorial | (0,23) | -405.58150 | 1.294 | (0,26) | -406.68965 | 1.102 |
| <i>Gauche</i> -Axial | (59,16) | -405.58274 | 0.518 | (60,25) | -406.69141 | 0.000 |
| Planar | (0, 0) | -405.58024 | 2.085 | (0, 0) | -406.68829 | 1.953 |

^a ϕ and β are CFO torsional angle and ring puckering angle respectively.

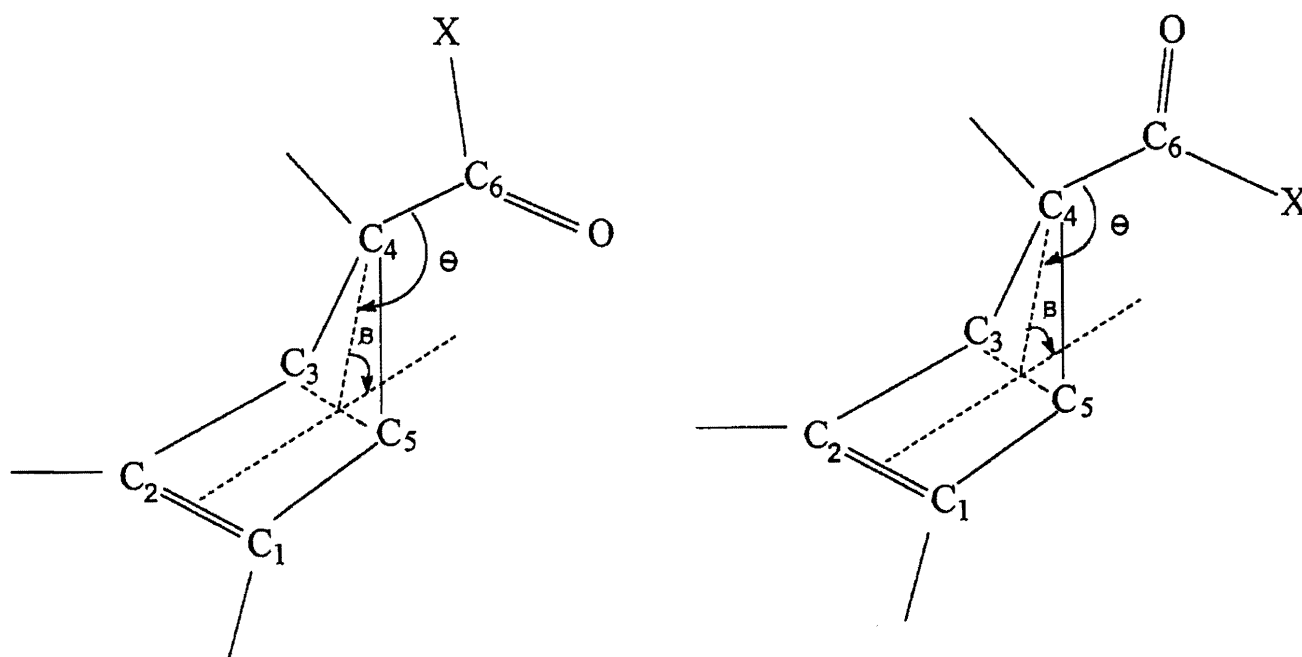


Figure 1. Molecular structure of 4-cyclopentenecarboxylic acid fluoride (X=F) and chloride (X=Cl) in cis-equatorial (right) and trans-equatorial (left) conformations.

the molecules. The corresponding four [1, 2, 5], and six [7] membered ring compounds were found to have the equatorial, and the five [3, 4] membered ring to have the twist, for the lower energy ring configuration.

From energy optimization of various stable conformers of 4-cyclopentenecarboxylic acid fluoride and chloride, the molecules were predicted to exist as a complex mixture of both axial and equatorial conformations at ambient temperatures. This behavior can be attributed to a relatively low ring barrier to inversion in the molecules. As shown in Tables 2, and 4 the planar was predicted to be about 2 kcal/mol lower in energy than the equatorial form.

Furthermore, the *gauche* to *trans* barrier and hence the relative stability of the *gauche* conformer was predicted to increase in the order: chloride > fluoride. A comparison between the calculated total dipole moments, shows insignificant change in going from the *trans* to the *gauche* conformations of both molecules. About 0.35 debye difference is calculated between the dipole moments of the two conformers. The calculated small difference in the dipole moments implies small charge density variation with the rotation of the carbonyl group. Thus, the steric forces are expected to play a more important role than the dipolar effects in determining the conformational equilibrium in these molecules. This explains the increase in the relative stability of the *gauche* conformation as the size of the substituent increases.

The calculated structural parameters at the two levels for the stable conformers of the molecules, were compared to those obtained from microwave data for cyclobutylcarboxylic acid fluoride [1] and chloride [2]. From the data, the inclusion of electron correlation was shown to improve the C–H and the C=O bond lengths in the two molecules. In the case of the chloride, some of the structural parameters were found to be slightly influenced by the rotation of the CClO rotor. A small change in the CCO and the CClC bond angles is noticed going from *trans* to the *gauche* conformer in the molecule. The calculated bond angles are generally consistent with the reported angles within the expected experimental uncertainties.

Table 3. Barrier to Internal Rotation (kcal/mol), Potential Coefficients (kcal/mol), Total Dipole Moments (Debye), and Rotational Constants (MHz) of Equatorial 4-Cyclopentenecarboxylic Acid Fluoride.

| Parameter | HF/6-31G* | | MP2/6-31G* | |
|---------------------------------------|--------------|---------------|--------------|---------------|
| | <i>Trans</i> | <i>Gauche</i> | <i>Trans</i> | <i>Gauche</i> |
| Barrier to internal rotation | | | | |
| <i>Trans</i> to <i>gauche</i> barrier | 2.115 | | 2.303 | |
| <i>Gauche</i> to <i>trans</i> barrier | 2.489 | | 2.382 | |
| V_1 | 1.523 | | 1.366 | |
| V_2 | 0.413 | | 0.521 | |
| V_3 | -1.553 | | -1.571 | |
| V_4 | 0.891 | | 0.917 | |
| V_5 | 0.362 | | 0.268 | |
| V_6 | 0.499 | | 0.441 | |
| Dipole moment | | | | |
| μ_t | 3.45 | 3.26 | 3.62 | 3.44 |
| Rotational constants | | | | |
| A | 4513 | 4429 | 4428 | 4326 |
| B | 1415 | 1509 | 1404 | 1506 |
| C | 1353 | 1208 | 1349 | 1196 |

Table 4. Optimized Structural Parameters of 4-Cyclopentenecarboxylic Acid Chloride in *trans*- and *gauche*-Equatorial Conformations.

| Parameter ^a | HF/6-31G* | | MP2/6-31G* | | Microwave ^b |
|--------------------------|--------------|---------------|--------------|---------------|------------------------|
| | <i>Trans</i> | <i>Gauche</i> | <i>Trans</i> | <i>Gauche</i> | <i>Gauche</i> |
| Bond lengths (Å) | | | | | |
| $r(C_1=C_2)$ | 1.317 | 1.318 | 1.340 | 1.341 | |
| $r(C_1-C_5 = C_2-C_3)$ | 1.509 | 1.509 | 1.507 | 1.507 | 1.550 |
| $r(C_3-C_4 = C_5-C_4)$ | 1.552 | 1.549 | 1.549 | 1.546 | 1.535 |
| $r(C_4-C_6)$ | 1.511 | 1.509 | 1.504 | 1.501 | 1.509 |
| $r(C_6=O)$ | 1.168 | 1.168 | 1.202 | 1.202 | 1.191 |
| $r(C_6-Cl)$ | 1.792 | 1.792 | 1.810 | 1.807 | 1.790 |
| $r(C_4-H)$ | 1.082 | 1.084 | 1.095 | 1.096 | 1.100 |
| $r(C_1-H)$ | 1.075 | 1.075 | 1.086 | 1.086 | |
| $r(C_2-H)$ | 1.075 | 1.075 | 1.086 | 1.086 | |
| $r(C_3-H_1)$ | 1.085 | 1.085 | 1.097 | 1.097 | 1.085 |
| $r(C_3-H_2)$ | 1.085 | 1.085 | 1.095 | 1.095 | 1.085 |
| $r(C_5-H_1)$ | 1.085 | 1.088 | 1.097 | 1.099 | 1.085 |
| $r(C_5-H_2)$ | 1.085 | 1.083 | 1.095 | 1.094 | 1.085 |
| Bond angles (deg) | | | | | |
| $(C_1C_2C_3=C_2C_1C_5)$ | 112.6 | 112.5 | 112.1 | 111.9 | |
| $(C_3C_4C_5)$ | 106.0 | 105.9 | 105.8 | 105.9 | |
| (C_4C_6O) | 126.1 | 128.0 | 126.8 | 128.1 | 123.2 |
| (C_4C_6Cl) | 114.9 | 112.6 | 113.5 | 111.7 | 112.7 |
| (C_6C_4H) | 103.9 | 106.7 | 104.8 | 107.3 | 110.1 |
| $(C_2C_3H_1)$ | 112.5 | 112.0 | 111.8 | 111.4 | |
| $(C_2C_3H_2)$ | 111.0 | 111.8 | 111.1 | 111.8 | |
| $(C_1C_5H_1)$ | 112.5 | 111.6 | 111.8 | 110.9 | |
| $(C_1C_3H_2)$ | 111.0 | 111.5 | 111.1 | 111.7 | |
| (C_3C_2H) | 122.1 | 122.1 | 122.6 | 122.7 | |
| (C_5C_1H) | 122.1 | 122.4 | 122.6 | 122.9 | |
| $(C_1C_4C_5H)$ | 119.2 | 119.0 | 118.8 | 118.8 | |
| $(C_2C_4C_3H)$ | 120.8 | 121.3 | 121.3 | 121.9 | |
| θ | 133.7 | 131.0 | 133.0 | 130.5 | 130.0 |
| ϕ | 180.0 | 53.3 | 180.0 | 54.9 | 61.1 |

^a θ and ϕ are the angle of the carbonyl group with the ring and the CClO torsional angle respectively.

^b Structural parameters of cyclobutanecarboxylic acid chloride obtained from reference [2].

Table 5. Calculated Total Energies (Hartrees) and Relative Energies (kcal/mol) of Stable Conformers of 4-Cyclopentenecarboxylic Acid Chloride.

| Conformation | HF/6-31G* | | | MP2/6-31G* | | |
|---------------------------|-------------------|--------------|-----------------|-------------------|--------------|-----------------|
| | $(\phi, \beta)^a$ | Total Energy | Relative Energy | $(\phi, \beta)^a$ | Total Energy | Relative Energy |
| <i>Gauche</i> -Equatorial | (53,22) | -765.61621 | 0.000 | (55,25) | -766.69051 | 0.000 |
| <i>Trans</i> -Equatorial | (180,19) | -765.61427 | 1.220 | (180,24) | -766.68890 | 0.010 |
| <i>Cis</i> -Equatorial | (0,23) | -765.61430 | 1.198 | (0,26) | -766.68892 | 0.998 |
| <i>Gauche</i> -Axial | (48,16) | -765.61527 | 0.592 | (49,25) | -766.69051 | 0.000 |
| Planar | (0, 0) | -765.61307 | 1.971 | (0, 0) | -766.68758 | 1.842 |

^a ϕ and β are CClO torsional angle and ring puckering angle respectively.

Table 6. Barrier to Internal Rotation (kcal/mol), Potential Coefficients (kcal/mol), Total Dipole Moments (Debye), and Rotational Constants (MHz) of Equatorial 4-Cyclopentenecarboxylic Acid Chloride.

| Parameter | HF/6-31G* | | MP2/6-31G* | |
|---------------------------------------|--------------|---------------|--------------|---------------|
| | <i>Trans</i> | <i>Gauche</i> | <i>Trans</i> | <i>Gauche</i> |
| Barrier to internal rotation | | | | |
| <i>Trans</i> to <i>gauche</i> barrier | 3.054 | | 2.812 | |
| <i>Gauche</i> to <i>trans</i> barrier | 4.274 | | 3.822 | |
| V_1 | 3.376 | | 3.007 | |
| V_2 | 1.132 | | 0.940 | |
| V_3 | -2.430 | | -2.205 | |
| V_4 | 0.805 | | 0.828 | |
| V_5 | 0.252 | | 0.208 | |
| V_6 | 0.565 | | 0.512 | |
| Dipole moment | | | | |
| μ_t | 3.11 | 2.84 | 3.32 | 3.00 |
| Rotational constants | | | | |
| <i>A</i> | 6782 | 6014 | 6748 | 5973 |
| <i>B</i> | 1811 | 2011 | 1791 | 2001 |
| <i>C</i> | 1521 | 1638 | 1507 | 1632 |

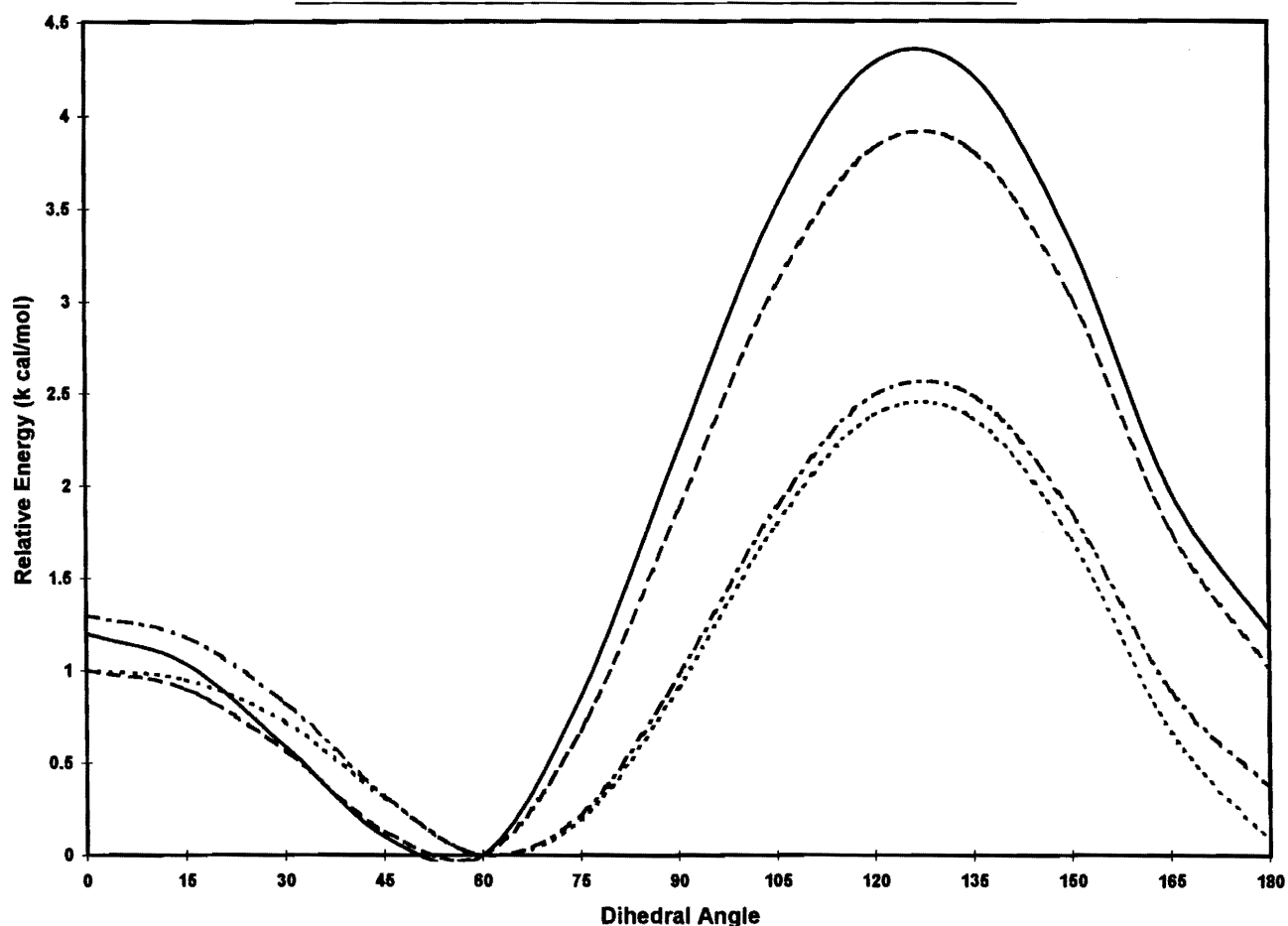


Figure 2. The determined potential surface for 4-cyclopentenecarboxylic acid fluoride and chloride by *ab initio* HF/6-31G* (solid and dashed-dotted lines) and MP2/6-31G* (dashed and dotted lines) levels respectively.

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