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Conformational Properties of 1,3-Difluoropropane

D. Wu and A. Tian

Department of Chemistry, Sichuan University, Chengdu, Sichuan, People's Republic of China

H. Sun*

Molecular Simulations, Inc., San Diego, California 92121-3752

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The conformational energy order of 1,3-difluoropropane is identified as GG < AG < AA < GG′ at various ab initio calculation levels. This result is analyzed on the basis of the molecular structures, partial charge distributions, and a molecular mechanics calculation. It is demonstrated that a strong dipole−dipole interaction between the highly polarized C−F bonds is the decisive factor determining the conformational energy preference between two gauche-gauche conformers (GG and GG′). This observation suggests that, in addition to the gauche effect, the intramolecular electrostatic interaction should be considered for studying conformational behaviors of molecules with highly polarized bonds in general. The conformational energies obtained in this work propose a challenge to earlier interpretations of experimental data for 1,3-difluoropropane.

Introduction

Conformational analysis of rotational isomerism of halogenated alkanes has been the subject of considerable interest. For simple molecules, such as 1,2-difluoroethane, their conformational behaviors are well studied.[1,2] As a classical example that illustrates the anomeric effect, 1,2-difluoroethane is known to favor a gauche conformation in which the F−C−C−F dihedral angle is approximately 60°.[1] The gauche conformation is stabilized due to the "anomeric effect" that has an origin of electron donation from lone-pair orbitals of the fluorine atom to the antibonding orbitals of the C−C bond.[2−4] For the same reason, the most stable conformation of 1-fluoropropane has the C−C−C−F angle in the gauche position (see Figure 1). This conclusion is confirmed by both theoretical calculations and experimental measurements.[5−8]

Four staggered conformations can be identified for 1,3-difluoropropane, namely GG, AG, AA, and GG′, as illustrated in Figure 2. On the basis of the argument of the gauche effect, it is not a surprise to see that the GG is a stable conformer. However, controversial results have been reported for the relative energies of the other three conformational isomers.[9−13] Lere-Porte et al. conducted IR spectroscopic measurements[9] and subsequently published their semiempirical calculations[10] that predict the conformational energies in the following order: GG (0.0 kcal/mol), AG (0.1 kcal/mol), AA (0.4 kcal/mol), and the GG′ (1.1 kcal/mol). Meyer[11] performed molecular mechanics calculations and obtained very similar results: GG (0.0), GA (0.12), AA (0.33), and GG′ (0.76) (all in kcal/mol). Klaeboe et al.[12] investigated this molecule using electron diffraction and IR/Raman spectroscopy measurements in gas, liquid, and solid phases. Using a force field calculation, they interpreted the energies relative to GG as follows: GG′, 0.5−1.2 kcal/mol; AG, 1.2 kcal/mol. Hammarstrom et al.[13] calculated the conformers using the modified MM2 force field. They found the GG′ is about 2.35 kcal/mol higher in energy than the GG conformer and that GA and AA are 0.08 and 0.71 kcal/mol higher in energy, respectively.

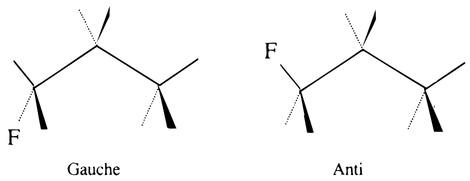

Figure 1. The two conformers of 1-fluoropropane.

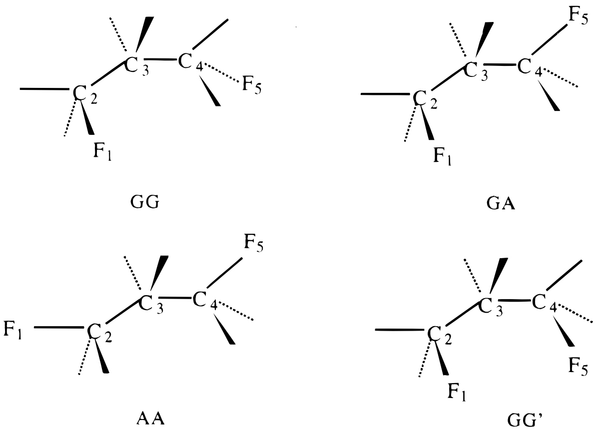

Figure 2. The four conformational isomers of 1,3-difluoropropane.

1,3-Difluoropropane is the simplest fluorinated alkane that contains two adjacent C−C−C−F torsion angles. Studying its conformational behavior is significant for understanding complex chain conformations of this type of molecules including polymers. If one assumes the gauche effect being a decisive factor, the GG′ conformer would be expected to be a stable one. This assumption was indeed used in previous force field parametrizations.[11,12] To our best knowledge, the reported quantum mechanics calculations for this molecule[10] were based on empirical methods (e.g. CNDO/2 or PCILO), which are known to be insufficient for characterizing conformational energies in general. Therefore, we found it necessary to carry out high-quality ab initio calculations for this molecule. It was

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TABLE 1: Comparison of Conformation Energies of 1-Fluoropropane ($CH_3CH_2CH_2F$)

	method	ΔE (kcal/mol)	ref
calcn	HF/6-31G*	0.282	
	HF/6-31G**	0.256	5
	MP2/6-31G*	0.585	
	MP2/6-31+G**	0.332	
	BLYP/6-31G*	0.435	
	BLYP/6-31+G**	0.114	
	SVWN/6-31G*	0.621	
	SVWN/6-31+G**	0.361	
expt	IR/Raman	0.349	6
	MW	0.47	7
	NMR (liquid)	0.22	8

our hope that this study would not only clarify some of the confusions found in the literature but also provide certain guidance for future investigation and modeling of similar molecular systems.

Computational Methods

In this study, ab initio calculations were performed at various levels of theory, including the restricted Hartree−Fock (RHF) method, the second-order Møller−Plesset perturbation theory (MP2), and the density functional theory (DFT) with SVWN[14] and BLYP[15] functionals. Two basis sets, 6-31G* and 6-31+G**, were used for comparison. The conformational structures were fully optimized using analytical gradient methods. Normal-mode analyses were performed to verify that the optimized structures are in their minimum-energy states. Finally, CCSD energy calculations with the correlation-consistent cc-pvtz basis set were carried out on the basis of MP2/6-31+G** optimized structures to further evaluate the accuracy of the calculations. These calculations were carried out using Gaussian 92 and Gaussian 94 packages.[16] The CHELPG method[17] was used to calculate the atomic partial charges on the basis of electrostatic potentials (ESP). The conformation properties were analyzed using a simple molecular mechanics model. In addition, calculations were also performed using a recently developed ab initio force field−COMPASS.[18]

Results and Discussion

1. A Benchmark: Calculated Results for 1-Fluoropropane. We first carried out the calculation for 1-fluropropane. This is necessary because good agreement between calculation and experiment has been reported in the literature for this molecule, which provides a good validation case for the ab initio methods used in this study. In addition, 1-fluoropropane is closely related to the subject molecule with simpler conformational isomers. A comparison of the calculated results for this molecule with those for 1,3-difuoropropane can be useful.

The calculated and experimental results are summarized in Table 1. The conformational energies of 1-fluoropropane were determined experimentally in the gas phase using IR and Raman spectra[6] and microwave measurements[7] and in the liquid state using NMR spectroscopy.[8] In both gaseous and liquid states, the gauche conformer is found to be more stable than the anti form. The reported energy differences are 0.349[6] and 0.47 kcal/mol[7] for molecules in the gaseous phase and 0.22 kcal/mol for those in the liquid state.[8] The ab initio results, as given in Table 1, are generally in good agreement with the experimental data. In particular, the results obtained using MP2 and SVWN methods with a large basis set (6-31+G**) yield good agreements with the gas phase experimental data. The zero-point energy (ZPE) correction to the energy difference between the gauche and anti forms is estimated to be about −0.07 kcal/mol at the HF/6-31G* level. This is estimated on the basis of the calculated HF/6-31G* frequencies, which were subsequently scaled by using a factor of 0.89.

The structural parameters, bond lengths and angles and torsion angles, are listed in Table 2. Generally speaking, all ab initio results agree reasonably well with the experimental data[19] within a few percent of deviation. However, the overall best agreement appears to be obtained at the MP2/6-31+G** and SVWN/6-31+G** levels.

2. Conformational Energies of 1,3-Difluoropropane. Vibration analyses at the HF/6-31G* and HF/6-31+G** levels were performed to confirm that all four conformational isomers (Figure 2) correspond to minimum (or local minimum) energy states. In Table 3, we list the optimized conformation energies of these conformers calculated at different levels of theory.

At every level of the theories that we considered, the GG conformer is found to be the most stable, which agrees with what is reported in the literature. The second most stable conformer is AG according to our calculation, which is 0.81−1.16 kcal/mol higher in energy than the GG. The AA is 2.04−2.63 kcal/mol higher in energy than the GG. The least stable conformer is the GG′. The energy increments between the GG and GG′ range from 2.67 to 3.33 kcal/mol. We did zero-point-

TABLE 2: Comparison of Structural Parameters for Two Conformers of 1-Fluoropropane[a]

method	conf	C−F	C−C	C(F)−C	C(F)−H	CCC	FCC	FCCC
HF/6-31G*	G	1.374	1.527	1.515	1.084	112.9	109.8	60.6
	A	1.372	1.528	1.515	1.084	112.2	109.7	180.0
HF/6-31G**	G	1.374	1.527	1.514	1.084	112.9	109.8	60.5
	A	1.372	1.528	1.514	1.085	112.2	109.7	180.0
MP2/6-31G*	G	1.402	1.525	1.513	1.094	112.2	109.3	59.8
	A	1.400	1.527	1.512	1.096	111.8	109.6	180.0
MP2/6-31+G**	G	1.416	1.525	1.511	1.090	112.9	109.7	62.1
	A	1.414	1.527	1.510	1.091	111.2	109.9	180.0
BLYP/6-31G*	G	1.412	1.542	1.531	1.106	113.0	110.0	60.4
	A	1.410	1.543	1.531	1.107	112.6	109.9	180.0
BLYP/6-31+G**	G	1.434	1.544	1.529	1.103	114.0	110.4	63.7
	A	1.432	1.547	1.529	1.104	111.9	110.1	180.0
SVWN/6-31G*	G	.377	1.511	1.501	1.109	111.4	109.5	58.3
	A	1.373	1.511	1.501	1.111	111.6	110.4	180.0
SVWN/6-31+G**	G	1.392	1.512	1.499	1.107	112.4	109.9	61.2
	A	1.388	1.513	1.500	1.108	111.0	110.7	180.0
expt MW[19]	G	1.390	1.526	1.506	1.097	112.9	110.0	62.6
	A	1.401	1.534	1.501	1.095	110.6	110.0	180.0

[a] Distances are in angstroms; angles are in degrees. C(F) represents the fluorinated carbon atom.

TABLE 3: Comparison of Conformational Energies (kcal/mol) of 1,3-Difluoropropane

method	GG	AG	AA	GG′
HF/6-31G*	0.0	1.09	2.57	3.04
HF/6-31+G**	0.0	0.87	2.19	3.22
MP2/6-31+G**	0.0	1.16	2.41	3.33
CCSD/cc-pvtz//MP2/6-31+G**	0.0	1.03	2.27	2.75
BLYP/6-31+G**	0.0	0.81	2.04	2.81
SVWN/6-31+G**	0.0	1.13	2.63	2.91
CCSD/cc-pvtz//MP2/6-31+G**	0.0	1.10	2.54	2.81
expt[12]	0.0	1.1 ± 0.4	1.2	

TABLE 4: Comparison of Conformational Energies (kcal/mol) Calculated Using Force Field and Semiempirical Methods

method	GG	AG	AA	GG′
Mayer[11]	0.0	0.12	0.33	0.76
Klaeboe et al.[12]	0.0	1.2	2.4	0.3
modified MM2[13]	0.0	0.08	0.71	2.35
CNDO/2, PCILO[10]	0.0	0.1	0.4	1.1
COMPASS[18]	0.0	1.29	3.24	2.90

energy corrections at the HF/6-31G* and HF/6-31+G** levels and found that the corrections are small and do not change the order of energies.

Comparing the calculation results with the experimental data,[12] which are also listed in Table 3, one sees that an agreement is obtained for the AG conformer. For the GG′ conformer, the reported value (1.2 kcal/mol) is substantially less than the theoretical values obtained in this work. To our best knowledge, the ED and IR/Raman work reported by Klaeboe et al.[12] is the only "direct" measurement of the conformational population for this molecule reported in the literature. In their work, the measured radial distribution function was interpreted under the influence of their force field calculations that predicted the GG′ conformer is only 0.3 kcal/mol higher in energy than the most stable GG conformer (Table 4). Their fitting of experimental data (radial distribution function) was conducted with a constraint that enforces the population of the GG′ conformer complementary to the populations of GG and AG: $a(\mathrm{GG}') = 100 - [a(\mathrm{GG}) + a(\mathrm{GA})]$.[12] On the basis of the high-level ab initio results presented in this paper, we find it difficult to accept the assumption of a strong population for the GG′ conformer.

As mentioned in the Introduction, several empirical force field calculations were published in the literature. These results, together with those obtained using semiempirical methods, are listed in Table 4 for comparison. It should be noted that Mayer's force field and the modified MM2 force field yield relatively high energy for the GG′ conformer. Both force fields have bond dipoles accounted for in the electrostatic interactions. The importance of including this term will be discussed later in this paper. The semiempirical CNDO/2 and PCILO results also predict the GG′ to be least stable. Quantitatively, all of the published force field and semiempirical results are in large discrepancy with the high-level ab initio results reported in this work. However, using the new COMPASS force field,[18] which was parametrized using ab initio data and condensed-phase properties, we obtained good agreement with the ab initio data in general. The only exception is that the energy calculated for the AA conformer is slightly too high.

TABLE 5: Comparison of Structural Parameters for Conformers of 1,3-Difluoropropane[a]

	MP2/6-31+G**				
	GG	AG	AA	GG′	expt[b]
	Bond Lengths				
F1−C2	1.414	1.411	1.408	1.405	1.391(0.002)
C2−C3	1.510	1.512	1.513	1.512	1.513(0.003)
C3−C4	1.510	1.510	1.513	1.512	1.513(0.003)
C4−F5	1.414	1.411	1.408	1.405	1.391(0.002)
C2−H6	1.088	1.090	1.089	1.090	1.094(0.005)
C2−H7	1.087	1.087	1.089	1.089	1.094(0.005)
C3−H8	1.091	1.091	1.089	1.090	1.094(0.005)
C3−H9	1.091	1.091	1.089	1.094	1.094(0.005)
C4−H10	1.088	1.088	1.089	1.089	1.094(0.005)
C4−H11	1.087	1.087	1.089	1.090	1.094(0.005)
	Bond Angles				
F1−C2−C3	108.9	108.9	109.1	110.7	110.1(0.3)
C2−C3−C4	112.6	112.0	111.3	115.0	112.9(0.8)
C3−C4−F5	108.9	109.4	109.1	110.7	110.1(0.3)
H6−C2−C3	111.8	111.7	112.1	111.6	112.1(1.4)
H7−C2−C3	111.9	112.0	112.1	111.1	112.1(1.4)
H8−C3−C2	109.0	109.0	109.3	109.6	108.5(*)
H9−C3−C2	109.2	109.2	109.3	107.5	108.5(*)
H10−C4−C3	111.8	111.8	112.1	111.1	112.1(1.4)
H11−C4−C3	111.9	111.9	112.1	111.6	112.1(1.4)
	Torsional Angles				
F1−C2−C3−C4	63.5	176.6	180.0	−70.1	64(2), 178(2), na, −64(2)
C2−C3−C4−F5	63.5	61.2	180.0	70.0	64(2), 62(2), na, 64(2)
H6−C2−C3−C4	−178.5	58.7	61.8	49.0	
H7−C2−C3−C4	−54.5	−64.9	−61.8	171.3	
H8−C3−C2−F1	−175.1	56.5	59.1	53.9	
H9−C3−C2−F1	−57.6	−61.4	−59.1	170.3	
H10−C4−C3−C2	−178.6	179.6	61.8	−171.5	
H11−C4−C3−C2	−54.6	−56.9	−61.8	−49.1	

[a] Bond lengths are in angstroms; angles are in degrees. [b] Reference 12. Results of gas phase electron diffraction. The standard deviations are given in parentheses. The torsion angles are given for GG, AG, and GG′ only.

3. Molecular Structures and Charge Distribution of 1,3-Difluoropropane. The MP2/6-31+G** optimized structural parameters for the four conformers are given in Table 5. For comparison, the electron diffraction data, which are "average" values based on measurements[12] are listed in the table for comparison. The standard deviations[12] are given in parentheses. Three conformers were reported; their corresponding torsion angles are listed in the table (in a sequence of GG, AG, AA, and GG′). Comparison of the calculated results with the experimental data appears to be satisfactory. The largest discrepancy, however, is found for the torsion angles of the GG′ conformer. The ab initio angles are about ±70°, where the reported experimental data are ±64°.

Close examination of the structure parameters is interesting. The calculated C−F bond lengths (F1−C2 and C4−F5) are different among the conformers. The longest bond length is associated with the most stable GG conformer. This seems to be consistent with that found in 1-fluoropropane. However, the shortest bond length is found in the least stable conformer GG′. Although, in both GG and GG′, the C−F bonds are in gauche positions, very different behaviors in the C−F bond lengths are observed. This indicates that the bond lengths may be related to some factors other than the gauche effect. For bond angles, the most significant differences among the four conformers are found for the F−C−C and C−C−C angles. The values obtained for the GG′ are significantly larger than those obtained for other conformers. Associated with the high energy, the GG′ conformer appears to be in high internal tension. Examination of the deviations from the "standard" gauche angle (60°) leads to the same conclusion. The largest deviations are found in the GG′ conformation. The values range from 49 to 70°.

The ESP charges calculated using the CHELPG method[17] are given in Table 6. These data are based on HF/6-31G*

TABLE 6: Electrostatic Potential (ESP) Derived Partial Charges for 1,3-Difluoropropane Conformers

	GG	AG	AA	GG′
F1	−0.300	−0.319	−0.294	−0.291
C2	0.284	0.336	0.259	0.288
C3	−0.074	−0.072	−0.084	−0.059
C4	0.295	0.199	0.246	0.291
F5	−0.302	−0.288	−0.291	−0.291
H6	0.006	−0.005	0.011	0.005
H7	0.020	0.008	0.012	0.004
H8	0.026	0.025	0.055	0.052
H9	0.026	0.052	0.055	−0.006
H10	0.003	0.038	0.015	0.003
H11	0.017	0.025	0.015	0.005

TABLE 7: Calculated Molecular Dipole Moments (D) for 1,3-Difluoropropane Conformers

	GG	AG	AA	GG′
HF/6-31G*	2.21	2.07	2.02	3.69
HF/6-31+G**	2.37	2.29	2.26	4.12
MP2/6-31+G**	2.57	2.48	2.41	4.43
BLYP/6-31+G**	2.27	2.17	2.10	3.94
SVWN/6-31+G**	2.19	2.10	1.89	3.70

calculations. Using a large basis set (6-31+G**) does not change the values significantly. As shown in this table, the C−F bond is significantly polarized. The ESP charges for the fluorine atom are about −0.3 electron. Since the C−C bond is nearly nonpolar, the charge separation reflects the polarization only between the carbon and fluorine atoms. Since the bond length is roughly 1.4 Å, the charge separation corresponds to a bond dipole of approximately 2.02 D. It should be noted that hydrogen atoms are not strongly polarized. Therefore, intramolecular hydrogen bonds must be a weak phenomenon.

The calculated molecular dipole moments are listed in Table 7. Similar results are obtained at different levels of theory. The calculated molecular dipole moments are about 2 D for conformers GG, AG, and AA, while the values obtained for conformer GG′ are significantly larger. This difference should not have much influence on the conformational populations for this molecule in the gas phase but may be a significant factor to be considered for molecules in condensed phases. The strong dipole−dipole intermolecular interaction may further stabilize the conformation of GG′ in condensed phases.

4. Analysis of the Energy Differences between the GG and GG′ Conformations. A few factors may influence the structural and conformational behavior of 1,3-difluoropropane. The anomeric effect has direct impact on bond lengths and bond angles. A typical anomeric effect can be found in molecules that have the X−Y−A type of structure where A is an electronegative and electron-rich atom (with a lone-pair electron).[2,3] The interaction between the lone-pair electrons of atom A and the antibond orbital of the X−Y bond enforces the Y−A bond. Related is the so-called gauche effect. Since the anomeric effect requires a match of orbital symmetries, a certain geometric arrangement of atoms in the space is favored. It is due to this interaction that the gauche conformer of 1-fluoropropane is more stable than the anti form. Consequently, the GG conformer is more stable than the AG and AA conformers of 1,3-difluoropropane. However, in order to explain the stability of the GG′ conformer, the gauche effect alone is clearly not sufficient.

As we discussed above, the C−F bonds are highly polarized, forming strong bond dipole moments. Consequently, the through-space dipole−dipole interaction must play an important role in determining the molecular conformational properties. As illustrated in Figure 2, the two bond dipoles of the C−F bonds are in different positions relative to each other in the GG and GG′ conformations. In GG, the two dipoles form an angle of roughly 120°, so that both have significant projection components in an antiparallel fashion, while, in GG′, the two dipoles are very much parallel to each other. Consequently, the dipole−dipole interaction stabilizes the GG conformer but destabilizes the GG′ conformer.

TABLE 8: Comparison of Energetic Components (kcal/mol) between GG and GG′ Conformers of 1,3-Difluoropropane, Calculated Using a Simple Molecular Mechanics Model (See Text)

energy	GG	GG′
torsion	0.0	0.529
LJ(6−9)	0.0	−0.147
dipole (C−F/C−F only)	0.0	2.716 (2.719)
total	0.0	3.098

To quantitatively assess this argument, we carried out a simple molecular mechanics analysis using a model consisting of a 3-fold torsion function, a dipole−dipole electrostatic interaction term, and van der Waals interactions. The torsion function is

$$V(\phi) = (V_0/2)(1 - \cos 3\phi) \qquad (1)$$

where ϕ is the torsion angle of (∗)−C−C−(∗). To the first degree of approximation, we assume that the torsion term is generic: all torsion angles (F−C−C−C, F−C−C−H, C−C−C−H, etc.) share the same parameters. The barrier height V_0 is determined using the known barrier height of rotation about the C−C bond in ethane (2.88 kcal/mol). Since there are nine torsion angles defined about the C−C bond in 1,3-difluoropropane (two F−C−C−H, two H−C−C−C, four H−C−C−H, and one F−C−C−C), $V_0 = 0.32$ kcal/mol is used. The van der Waals interaction is represented by a Lennard-Jones (6−9) potential with parameters taken from the COMPASS force field.[18] The vdW parameters were optimized using MD simulations of molecular liquids. The electrostatic interaction is written in terms of dipole−dipole interactions in which the ESP charges given in Table 4 were used:

$$V_{\text{dipole}} = \frac{\mu_i \mu_j}{r_{ij}^{\,3}}(\cos \chi - 3 \cos \alpha_i \alpha_j) \qquad (2)$$

Here, χ is the angle between the two bond moments μ_i and μ_j and α_i and α_j are the angles between the bond moments and the vector connecting the two centers of the bond moments.

Using the ab initio optimized structures, we calculated the components of the three energy terms, torsion, vdW, and dipole−dipole, for GG and GG′ conformers. The dipole−dipole terms were further separated into two subcategories: one for all dipoles including very weak C−H dipoles and the other including only C−F dipoles. The results are listed in Table 8. The simple MM calculation shows that the conformational energies are dominated by the dipole−dipole interaction. The contribution from the torsion term is less than 0.6 kcal/mol, the vdW term contributes less than 0.3 kcal/mol, and the most significant contribution (up to 2.7 kcal/mol) comes from the dipole−dipole term. For the dipole−dipole energy, almost all contributions come from the C−F/C−F bond dipole interaction only (given in the parentheses).

5. Conformational Population. On the basis of the analysis presented above, we believe the conformational energies of 1,3-difluoropropane obtained in this study are accurate. It may be necessary to re-evaluate the early analysis of electron diffraction

TABLE 9: Theoretical Thermodynamic Properties and Conformational Composition Calculated Using the ab Initio Data

	GG	AG	AA	GG′
ΔE(MP2)^b	0.0	1.16	2.41	3.33
E_{TE}	3.35	3.41	3.48	3.32
$E_{\mathrm{ZPE}}{}^c$	60.40	60.33	60.27	60.22
$\Delta H_i{}^b$	58.30	59.46	60.72	61.44
S_{I}	74.45	74.89	75.39	75.49
%	72.6	25.9	1.0	0.5
expt^9 %	63(4)	27(2)	0	10(5)

[a] E_{TE} and E_{ZPE} in kcal/mol; S in cal/(mol·K). [b] $E_{\mathrm{ele}} = E_{\mathrm{ele}}{}^0 + \Delta E$(MP2); $H_i = E_{\mathrm{ele}}{}^0 + \Delta Hi$; $E_{\mathrm{ele}}{}^0$ is the conformational energy of GG at the MP2/6-31G** level. [c] The zero-point energies unscaled at the HF/6-31G** level.

data[12] with the aid of the new theoretical data. To provide a direct comparison with the measurements, we estimated the conformational populations based on the Boltzmann distribution:

$$\frac{n_i}{N} = \frac{g_i \exp[-(H_i - TS_i)/RT]}{\sum_i g_i \exp[-(H_i - TS_i)/RT]} \tag{3}$$

where g_i is the degeneracy of the ith state number and H_i and S_i are the enthalpy and entropy of the ith conformation which can be estimated using results of quantum mechanics calculation.[20] We calculated these quantities using Gaussian 92[16] at the MP2/6-31+G** level. The predicted populations of the conformations are summarized in Table 9. In comparison with the early assignment,[12] we predict a slightly larger population for the GG state, a very similar population for the AG state, and almost zero populations for both AA and GG′.

Although the experimental work of Klaeboe et al.[12] was conducted in vapor, liquid, and solid phases, the population analysis was referred to molecules in gas phase only by the authors. In this paper, our discussion is focused on the gas phase, too. It should be pointed out, however, that the populations of different conformers in condensed phases may be quite different from those in the gas phase. According to our calculated results given in Table 7, the GG′ conformer has significantly larger molecular dipole moments than other conformers do. This difference may have an influence on the conformational populations of the molecule in condensed phases.

Conclusions

The good agreement between calculated and experimental data for 1-fluoropropane suggests that high-level ab initio calculations, particularly those performed at the MP2/6-31+G** level and by the DFT method at the SVWN/6-31+G** level, seem to be adequate to characterize the conformational behaviors of fluorinated alkanes. Using these methods, we predict that the order of conformational energies of 1,3-difluoropropane is GG < AG < AA < GG′. Our high-level ab initio results appear to be consistent, both internally (with different levels of theory) and externally (with comparison of 1-fluoropropane). Further analyses of molecular structures and electrostatic charge distributions support this conclusion.

The conformational stability of GG and AG isomers with respect to the AA conformers can be explained using the concept of the gauche effect. However, the gauche effect alone is not enough to explain why GG′ is so significantly less stable than the GG form. It is perhaps because of this reason that controversial results have been reported in the literature. Using a simple molecular mechanics model, we demonstrated that, in addition to the well-known gauche effect, a through-space dipole−dipole interaction between the C−F bonds is an important factor in determining the conformational behavior of this molecule. Since this phenomenon is due to the strong polarization of the C−F bond, the observed importance of dipole−dipole interactions can be extended to any molecules that have strong polar bonds and, in particular, to all halogenated alkanes.

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