

Rotational Barrier for 1,1-Difluoroethane, 1,1,1,2-Tetrafluoroethane, Pentafluoroethane, and Hexafluoroethane: A Density Functional and *ab Initio* Molecular Orbital Study

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The structures and vibrational frequencies for eclipsed and staggered conformers of CF_2HCH_3 , CF_3CFH_2 , $\text{C}_2\text{F}_5\text{H}$, and C_2F_6 have been calculated by using B3LYP and MP2 *ab initio* methods. A reassignment of the experimental IR spectra of CF_3CFH_2 and C_2F_6 is suggested. Relative electronic energies are determined with a number of basis sets. Electron correlation is included by means of Møller–Plesset perturbation methods up to the fourth order. Scaled vibrational frequencies are used to account for zero-point energy and thermal contributions to electronic energies. Temperature dependence of the rotational barriers is studied at 20 K intervals from 0 to 300 K.

Introduction

Several fluorinated compounds have been proposed as acceptable alternative compounds to chlorofluorocarbons by the Alternative Fluorocarbons Environmental Acceptability Study program (AFEAS) and the Program of Alternative Fluorocarbon Toxicity Testing (PAFT).¹ 1,1-Difluoroethane, 1,1,1,2-tetrafluoroethane, and pentafluoroethane are among these alternative molecules. The numerical codes for these compounds are respectively R152a, R134a, and R125a. On the other hand, hexafluoroethane has been found useful in many fields including materials science² and even medicine.³ Several publications have dealt with the experimental and theoretical determination of the structure and rotational barrier for 1,1-difluoroethane,^{4–8} pentafluoroethane,^{9–11} and hexafluoroethane.^{12–15} A systematic density functional study of fluorination in ethane has also been published lately.¹⁶ With the exception of C_2F_6 ,¹⁵ previous theoretical studies did not consider the effect of zero-point energy and/or thermal corrections to the calculated rotational barriers. In this paper we examine the structural parameters, vibrational frequencies, and the temperature dependence of the height of the rotational barrier for these molecules by means of density functional theory and conventional *ab initio* molecular orbital methods. In particular, we recently reported an extensive and systematic *ab initio* study of C_2F_6 .¹⁵ Here we extend that work by including the results of the B3LYP density functional method and by considering some basis sets different from those used in the previous work. Furthermore, a reassignment of some of the normal modes of C_2F_6 is suggested. We found that for 1,1,1,2-tetrafluoroethane there were some discrepancies between the vibrational assignment proposed by Ward et al.¹⁷ and that by Nielsen and Halley.¹⁸ We reassign the fundamental frequencies of this molecule based on animation of the calculated normal modes of the equilibrium structure.

Computational Details

Calculations were carried out using the Gaussian 94 program.¹⁹ Complete geometry optimizations and frequency calculations were done for the staggered and eclipsed conformers

of each molecule at the B3LYP/6-31G(d') and MP2/6-311G(d,p) levels of theory. The 6-31G(d') basis set is defined as part of the Complete Basis Set model chemistry, and it is intended to correct some deficiencies in the standard 6-31G(d) basis set.²⁰ Single-point energy calculations were done for the MP2/6-311G(d,p) optimized geometries using progressively larger basis sets up to 6-311++G(3df,3p). Frozen-core correlation corrections were included using Møller–Plesset perturbation methods up to fourth order with single, double, triple, and quadruple substitutions, i.e., MP4(SDTQ). To correct for anharmonicity, we scaled the B3LYP frequencies by a factor of 0.98 and the MP2 frequencies by a factor of 0.97.²⁰ Zero-point vibration energy (ZPVE) and thermal corrections to the electronic energies were accounted for using standard formulas and the scaled vibrational frequencies. Torsion modes were considered as harmonic oscillators.

Results and Discussion

Geometries. Calculated and experimental structural parameters for the fluoroethanes considered in this paper are shown in Table 1. Although the density functional B3LYP method consistently predicts bond lengths longer than those predicted by the MP2 method, we see that both methods reproduce the experimental trend very well. In particular, the C–C bond length increases with increasing fluorine substitution, whereas the C–F bond length decreases.^{7,9,12,21} In each case the major structural change going from the staggered to the eclipsed conformation is an increase of the C–C bond length by about 0.020 Å for CF_2HCH_3 and CF_3CFH_2 and 0.030 Å for $\text{C}_2\text{F}_5\text{H}$ and C_2F_6 . Except for 1,1-difluoroethane, changes in some $\angle\text{CCF}$ and $\angle\text{CCH}$ angles are also significant (up to $\sim 3^\circ$).

Vibrational Frequencies. A careful assignment for the fundamentals of pentafluoroethane has recently been made using *ab initio* calculations as well as infrared and Raman spectra of the gas and solid.¹¹ The assignment for the normal modes of 1,1-difluoroethane has also been done using *ab initio* calculations at the MP2 level and the same basis set as in this work.⁷ Unscaled vibrational frequencies for these two molecules, obtained with the B3LYP/6-31G(d') and MP2/6-311G(d, p), are

TABLE 1: Structural Parameters (Bonds in Å; Angles in degs)

	staggered conformation			eclipsed conformation	
	B3LYP	MP2	exp ^a	B3LYP	MP2
1,1-Difluoroethane					
rC1–C2	1.511	1.503	1.498	1.529	1.520
rC1–F	1.368	1.364	1.364	1.368	1.364
rC1–H	1.099	1.093	1.081	1.098	1.092
∠C2C1F	110.36	110.32	110.70	110.83	110.71
∠C2C1H	113.06	113.23	111.00	113.32	113.52
∠C1C2H	109.71	109.67	111.00	109.09	109.09
1,1,1,2-Tetrafluoroethane					
rC1–C2	1.526	1.516	1.501	1.553	1.542
rC1–F ^c	1.350	1.345	1.334	1.337	1.331
rC1–F	1.340	1.335	1.334	1.345	1.340
rC2–F	1.376	1.372	1.389	1.374	1.371
rC2–H	1.096	1.091	1.077	1.096	1.090
∠C2C1F ^c	107.99	108.03	110.40	110.40	110.74
∠C2C1F	110.61	110.58	110.40	109.41	109.23
∠C1C2F ^c	109.72	109.52	112.30	110.45	110.86
∠C1C2H	108.84	108.60	106.10	108.91	108.50
Pentafluoroethane					
rC1–C2	1.540	1.529	1.520	1.568	1.559
rC1–F	1.338	1.333	1.335	1.336	1.331
rC2–F	1.353	1.348	1.345	1.351	1.347
rC2–H	1.097	1.091	1.100	1.096	1.090
∠C2C1F ^c	109.12	109.08	109.20	110.56	110.71
∠C2C1F1	109.90	109.87	109.20	109.35	109.32
∠C2C1F2	109.99	109.96	109.20	109.19	109.06
∠C1C2F3	109.01	108.86	109.60	109.70	109.94
∠C1C2F ^c	109.10	108.93	109.60	109.54	109.75
∠C1C2H	110.51	110.44	110.00	110.16	109.82
Hexafluoroethane ^b					
rC–C	1.550	1.538	1.545	1.576	1.569
rC–F	1.336	1.330	1.326	1.335	1.330
∠CCF	109.92	109.72	109.70	110.15	110.20

^a See refs 7, 21, 9, and 12 for C₂F₂H₄, C₂F₄H₂, C₂F₅H, and C₂F₆, respectively. ^b MP2 data from ref 15. ^c Fluorine atom trans to fluorine atom.

given in Table 2, together with experimental data. For hexafluoroethane, however, we found that in the assignments suggested in ref 14 some important contributions were not considered. For 1,1,1,2-tetrafluoroethane no recent assignments for its normal modes were found. A detailed assignment and description based on animation of the normal modes for

the equilibrium structures of hexafluoroethane and 1,1,1,2-tetrafluoroethane are given in Tables 3 and 4, respectively.

Hexafluoroethane. The calculated harmonic frequencies are in very good agreement with the observed values. The B3LYP method in particular does a remarkable job in the prediction of the frequencies. We found that the highest mode is due mainly to a C–C stretch and not to a C–F stretch as suggested in ref 14. The presence of a C–C stretch mode at such a high frequency is in agreement with the observation that fluorine atoms, adjacent to a C–C bond, stabilize it.²² We also found that the C–C stretch mode contributes significantly to the low frequency at 348 cm⁻¹. The band at 807 cm⁻¹ is due not only to the C–C stretch but also to a symmetric CF₃ deformation.

1,1,1,2-Tetrafluoroethane. Danti and Wood²³ reported the far-infrared gas spectrum of 1,1,1,2-tetrafluoroethane. Ward et al.¹⁷ measured the infrared and Raman spectra of the liquid, whereas Nielsen and Halley¹⁸ obtained the infrared gas spectrum and the Raman liquid spectrum. Since the assignment of some of the fundamental frequencies made by these researchers differs from one another, we have reassigned the fundamental modes based on animation of the calculated normal modes. It should be noted that both B3LYP and MP2 methods result in the same assignment. The observed and calculated frequencies, along with a description of each of the normal modes, are given in Table 4. The assignment of the three highest frequencies are the same as those derived from experiment. The next mode, however, is assigned differently in the two experimental papers. Ward et al. interpreted this band as CH₂ twist (A''), although they mentioned that polarization data were inconclusive for this band and that consequently their assignment had relied largely on the group vibration theory. On the other hand, Nielsen and Halley interpreted this band as a fundamental associated primarily with a C–F stretch (A'). Our results indicate that this band is due to a CH₂ wag (A'). The next three bands are assigned to C–F stretching motions (A', A'', A') in both experimental papers. The ab initio results show that these bands result from combination of different types of motions including the C–F stretch. Our calculation also indicates that the symmetries of these modes are A'', A', and A''. The contribution of CH₂ motions is not surprising as this region is commonly associated with the CH₂ group. The C–C stretch mode appearing at high frequencies was already considered in

TABLE 2: Experimental and Calculated Vibrational Frequencies (cm⁻¹)

1,1-difluoroethane					pentafluoroethane				
staggered			eclipsed		staggered			eclipsed	
B3LYP	MP2	exp ^a	B3LYP	MP2	B3LYP	MP2	exp ^b	B3LYP	MP2
251	258	222	-236	-252	66	81	75	-65	-76
375	388	383	408	423	205	218	212	274	285
458	470	470	479	490	240	251	250	290	301
561	571	571	578	589	357	369	364	367	378
875	891	868	893	909	409	422	420	400	410
967	981	930	948	965	517	527	523	521	533
1151	1181	1129	1106	1132	570	583	578	571	585
1173	1187	1143	1161	1188	579	593	592	582	596
1174	1197	1169	1185	1206	719	735	727	715	732
1405	1413	1372	1386	1399	869	891	868	855	878
1427	1450	1360	1423	1448	1147	1169	1146	1149	1170
1449	1473	1414	1439	1462	1165	1198	1142	1168	1197
1508	1507	1460	1504	1506	1212	1239	1199	1216	1241
1511	1510	1460	1511	1511	1246	1271	1225	1250	1274
3063	3102	2963	3065	3106	1315	1351	1310	1293	1333
3067	3141	2979	3073	3144	1413	1434	1356	1415	1439
3151	3205	3001	3152	3206	1452	1496	1392	1423	1466
3155	3207	3018	3165	3215	3098	3176	3002	3102	3179

^a From ref 7. ^b From ref 11.

TABLE 3: Vibrational Frequencies of Hexafluoroethane (cm⁻¹)

sym ^d	assign ^b	staggered			eclipsed	
		B3LYP	MP2 ^c	exp ^d	B3LYP	MP2 ^c
A _{1u}	torsion	45	70	68	-60	-66
E _u	b(FCC)	209	221	219	271	285
A _{1g}	δ _s (CF ₃) + ν(CC)	345	358	348	370	378
E _g	b _s (CF ₂) + δ _{as} (CF ₃)	375	387	372	369	384
E _u	b _s (CF ₂)	519	529	522	522	534
E _g	b _s (CF ₂) + δ _{as} (CF ₃)	613	628	620	610	624
A _{2u}	δ _s (CF ₃)	705	722	714	712	729
A _{1g}	δ _s (CF ₃) + ν(CC)	802	819	807	799	815
A _{2u}	ν _s (CF ₃)	1120	1143	1116	1115	1135
E _g	ν _{as} (CF ₂)	1248	1272	1250	1254	1276
E _u	ν _{as} (CF ₂)	1258	1287	1250	1257	1278
A _{1g}	ν(CC)	1411	1479	1417	1371	1426

^a Symmetry assigned to the staggered form. ^b Fundamental vibration nomenclature as follows: b, bend; δ, deformation; ν, stretching; the subscripts s and as stand for symmetric and asymmetric, respectively. ^c From ref 15. ^d From ref 14.

hexafluoroethane. The next frequency is observed by Ward et al. as a strong band at 1067 cm⁻¹, and they identified it as symmetric C–F stretch. On the other hand, Nielsen and Halley observed a weak band at 1065 cm⁻¹, but they were not certain whether it was a fundamental mode. The ab initio results show that this is the most intense band and that it is due to a combination of a C–F stretch and a CH₂ wag. The C–F stretch is for the fluorine atom trans to the fluorine atom of the CH₂F group. Therefore, our results support the assignment made by Ward et al. The next band is observed at the same frequency in both experimental works, but the assignment is different. Nielsen and Halley interpreted this band as CH₂ wag (A'), whereas Ward et al. assigned it to CH₂ rock (A''). Our results show that this band is associated essentially with the C–F stretch in the CH₂F group. The next frequency is observed by Ward et al. at 908 cm⁻¹ and assigned to the symmetric CH₂ wag (A'). Nielsen and Halley observed a weak band at 885 cm⁻¹, but again they were not certain whether it was a fundamental mode. We found this band associated with a mixing of CH₂ rock and CF₂ asymmetric stretch. The next band is assigned to the C–C stretch in both experimental works. We found that it also contains some CF₃ symmetric stretching motions. For the

remaining frequencies, we can say that our assignments are basically the same as those found in the quoted experimental papers.

Relative Energies. The MP2/6-311G(d,p) geometries were used to perform single point energy calculations with a number of basis sets and correlation methods up to MP4(SDTQ). The relative electronic energies (eclipsed – staggered) are given in Table 5. For 1,1-difluoroethane, one observes that addition of diffuse functions to heavy atoms lowers the barrier height. Also, the relative energies as given by the MP3 and all MP4 methods become the same. Adding diffuse functions to the hydrogen atoms leaves the relative energies unchanged. However, the effect of an additional set of d orbitals is to further reduce the barrier height for all methods. Moreover, the MP2 relative energy becomes closer to that given by the higher correlated methods. The largest basis set gives a value for the relative energy at the MP2 level which is the same as that obtained at the MP3 and MP4 levels with the 6-311+G(2d,p) basis set. We also observe that, for each of the smaller basis sets, there is a decrease in barrier height of approximately 0.10 kcal/mol when proceeding from the MP2 energy to one of the MP4 barriers (which are all close to equal). Therefore, we speculate that, were the calculation feasible, one would also expect the MP2/6-311+G(3df,3p) barrier to be decreased by a similar amount. Hence, a better estimate of the barrier height would be 3.20 – 0.10 = 3.10 kcal/mol. One also finds decreases in barrier heights going from MP2 to MP4 in the other three molecules. Thus, one may think that the MP2 barriers with the biggest bases are still too high for these. One also finds that, except for 1,1-difluoroethane, addition of diffuse functions to heavy atoms significantly increases the relative energies at all levels of theory. For instance, the relative energy for hexafluoroethane increases from 3.95 to 5.01 kcal/mol at the MP2 level. Nevertheless, as the basis set is improved, the correlated relative energies are consistently reduced, and we expect that the MP2 calculations give results very close to the MP3 and MP4 values. In general, we observe that the HF relative energies using the highest basis set are in each case higher than those given by the other methods. However, the HF barriers calculated with the smallest basis set are in each case relatively close to the corresponding MP2 barriers. It is also worthy to note that, except for 1,1-

TABLE 4: Vibrational Frequencies of 1,1,1,2-Tetrafluoroethane (cm⁻¹)

sym ^d	assignment ^b	staggered				eclipsed	
		B3LYP	MP2	exp ^c	exp ^d	B3LYP	MP2
A''	torsion	104	118	120	124	-119	-128
A'	ρ(CF ₃) + ρ(CFH ₂)	210	222	225	201	274	284
A''	ρ(CH ₂) + ρ(CF ₃)	355	366	352	358	361	373
A'	ρ(CH ₂ F) + ρ(CF ₃)	404	416	408	407	400	411
A''	δ _{as} (CF ₃)	529	540	539	541	535	546
A'	δ _s (CF ₃)	533	547	549	550	537	552
A'	δ _s (CF ₃) + δ(CH ₂ F)	657	675	665	666	650	669
A'	ν(CC) + ν _s (CF ₃)	841	862	843	844	830	852
A''	ρ(CH ₂) + ν _{as} (CF ₂)	998	1008	885(?)	908	981	1000
A'	ν(CF)	1116	1144	972	972	1121	1147
A'	ν(CF) + χ(CH ₂)	1200	1227	1065(?)	1067	1217	1245
A''	τ(CH ₂) + ν _{as} (CF ₂)	1222	1246	1103	1096	1222	1245
A'	χ(CH ₂) + ν(CC) + ν _s (CF ₂)	1303	1341	1182	1189	1280	1322
A''	τ(CH ₂) + ν _{as} (CF ₂)	1333	1353	1298	1296	1318	1346
A'	χ(CH ₂)	1459	1489	1427	1374	1441	1478
A'	b _s (CH ₂)	1517	1524	1464	1431	1519	1532
A'	ν _s (CH ₂)	3073	3135	2984	2984	3074	3136
A''	ν _{as} (CH ₂)	3133	3207	3013	3015	3134	3208

^a Symmetry assigned to the staggered form. ^b Fundamental vibration nomenclature as follows: b, bend; δ, deformation; ν, stretching; χ, wag; τ, twist; ρ, rock; the subscripts s and as stand for symmetric and asymmetric, respectively. ^c From ref 18. ^d From ref 17.

TABLE 5: Relative Electronic Energies (kcal/mol)

basis set	HF	MP2	MP3	MP4		
				DQ	SDQ	SDTQ
1,1-Difluoroethane						
6-311G(d,p)	3.61	3.78	3.59	3.60	3.64	3.68
6-311+G(d,p)	3.56	3.60	3.47	3.47	3.48	3.48
6-311++G(d,p)	3.56	3.60	3.48	3.48	3.49	3.49
6-311+G(2d,p)	3.46	3.30	3.20	3.21	3.20	
6-311+G(3df,p)	3.43	3.23				
6-311++G(3df,3p)	3.39	3.20				
1,1,1,2-Tetrafluoroethane						
6-311G(d,p)	4.41	4.36	4.24	4.24	4.23	4.18
6-311+G(d,p)	4.67	4.96	4.80	4.80	4.81	4.81
6-311+G(2d)	4.69	4.76	4.64	4.65	4.64	
6-311+G(2d,p)	4.55	4.52	4.40	4.41	4.40	
6-311++G(3d,3p)	4.56	4.33				
Pentafluoroethane						
6-311G(d,p)	4.07	3.94	3.95	3.94	3.86	3.73
6-311+G(d,p)	4.30	4.77	4.68	4.67	4.65	4.64
6-311+G(2d)	4.34	4.36				
6-311+G(2d,p)	4.26	4.24				
6-311++G(3d,3p)	4.38	4.05				
Hexafluoroethane						
6-311G(d,p) ^a	4.07	3.95	4.02	4.01	3.90	3.74
6-311+G(d)	4.32	5.01	4.91	4.92	4.90	
6-311+G(2d)	4.28	4.33				
6-311+G(3df) ^a	4.43	4.11	4.17			

^a Data taken from ref 15.TABLE 6: Experimental and Calculated Rotational Barriers (kcal/mol)^a

	B3LYP ^b	MP2 ^c	exp ^d
1,1-Difluoroethane			
ΔE_1	3.48	3.20	
ΔE_2	3.14	2.88	
ΔE_3 (260.15 K)	2.87	2.61	3.32
1,1,1,2-Tetrafluoroethane			
ΔE_1	3.75	4.33	
ΔE_2	3.62	4.23	
ΔE_3 (298.15 K)	3.10	3.73	4.20
Pentafluoroethane			
ΔE_1	2.85	4.05	
ΔE_2	2.87	4.04	
ΔE_3 (298.15 K)	2.26	3.45	3.40
Hexafluoroethane			
ΔE_1	2.53	4.11	
ΔE_2	2.53	4.11	
ΔE_3 (250.15 K)	1.97	3.62	3.67

^a ΔE_1 = relative electronic energy, ΔE_2 = relative energy including zero-point vibrational energy correction, and ΔE_3 = relative energy including both zero-point and thermal energy correction. ^b Using the 6-31G(d') basis set. ^c Using 6-311++G(3df,3p), 6-311++G(3d,3p), 6-311++G(3d,3p), and 6-311+G(3df) for CF₂HCH₃, CF₃CFH₂, C₂F₅H, and C₂F₆, respectively. ^d From refs 8, 23, 11, and 12 in order of increasing fluorine substitution.

difluoroethane, the MP2 barriers calculated with the highest basis set are quite similar to those obtained with the smallest basis set.

Zero-Point Vibrational Energy Difference. The relative energies shown in Table 5 correspond to the internal energy difference for the eclipsed and staggered conformer of each molecule at equilibrium geometries at 0 K without nuclear motion. To account for zero-point energies, we used the scaled vibrational frequencies calculated at the MP2/6-311G(d,p) level. The results are displayed in Table 6. The values obtained using the B3LYP/6-31G(d') method are also shown. Both MP2 and B3LYP methods produce similar zero-point energy corrections.

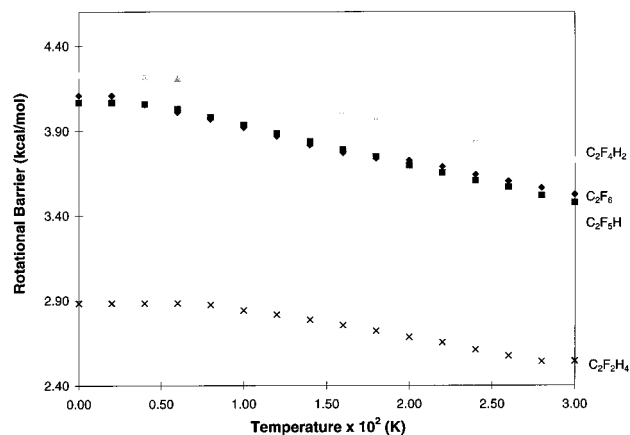


Figure 1. Temperature dependence of the rotational barriers.

One observes that the barrier for 1,1-difluoroethane is lowered by more than 0.30 kcal/mol after zero-point energy correction. However, the zero point energy effect is small for 1,1,1,2-tetrafluoroethane, and it becomes negligible for penta- and hexafluoroethane.

Temperature Dependence of the Rotational Barriers. Thermal contributions to the enthalpy [$H(T) - H(0)$] were calculated from the scaled frequencies using standard formulas.²⁵ Thermal corrections were made at 20 K intervals from 0 to 300 K. In general, the corrections given by B3LYP are essentially the same as those given by MP2. The MP2 rotational barriers, with the highest basis set for each molecule, as a function of temperature after zero-point and thermal correction are shown in Figure 1. One sees that for low temperatures ($T < 100$ K) the barrier height for each molecule remains fairly constant. There is a much larger effect as the temperature goes above 100 K. In fact, the rotational barrier decreases linearly with temperature for $T > 100$ K. This behavior is common to all four molecules. One also observes that the ordering of the barrier height among the molecules is conserved through the entire temperature range. For instance, the rotational barrier for 1,1-difluoroethane is always smaller than that of the other molecules. The lowering of the barrier may be considered as a result of the low-frequency torsion mode in the staggered conformer, of each molecule. This low frequency increases the energy of the staggered conformer and consequently the barrier height is reduced. We expect this effect to be more pronounced as the torsion frequency becomes smaller. In fact, the barrier is reduced in 0.34, 0.50, 0.59, and 0.58 kcal/mol for CHF₂CH₃, CF₃CH₂F, C₂F₅H, and C₂F₆, respectively, on going from 0 to 300 K, which is consistent with the value of the corresponding torsion frequencies 258, 118, 81, and 70 cm⁻¹.

Comparison with Experiment. To judge the agreement with experiment, we correct the B3LYP and MP2 energies obtained with the highest basis set for differences in zero-point energies and for the change in enthalpy on going from 0 to the temperature of the experimental determination (see Figure 1). Table 6 shows the corrected rotational barriers along with some recent experimental values. It is seen that relative energies given by B3LYP are significantly smaller than those given by MP2, except for 1,1-difluoroethane. The experimental ordering of the rotational barriers among the four molecules is well reproduced by the MP2 method but not by the B3LYP method. It is seen also that the MP2 rotational barriers for pentafluoroethane and hexafluoroethane agree very well with the corresponding experimental values. Disagreement is observed, however, for the other two molecules. In fact, the MP2 barriers for 1,1,1,2-tetrafluoroethane and 1,1-difluoroethane are 0.47 and

0.71, kcal/mol respectively, lower than the experimental values. For 1,1,1,2-tetrafluoroethane we may say that the discrepancy is due in part to the poor assumed structural parameters used by Danti and Wood²³ as compared to the more recently determined values.²¹ It is known that when the accuracy of structural parameters is very poor, it could be a major source of error in the determination of the rotational barrier from torsional frequencies.²⁵ For 1,1-difluoroethane we believe that convergence has been achieved at the MP2 level. However, the discrepancy with experiment cannot be explained in terms of structural parameters. Accordingly, the rotational barrier of CHF₂CH₃ is still open for further research.

Concluding Remarks

The geometries, vibrational frequencies, and rotational barriers for 1,1-difluoroethane, 1,1,1,2-tetrafluoroethane, pentafluoroethane, and hexafluoroethane have been systematically studied by means of B3LYP density functional method and conventional molecular orbital methods. Experimental trends in the structural parameters are well reproduced by both theoretical methods. Calculated vibrational frequencies are also in good agreement with experiments. Rotational barriers calculated at the Hartree-Fock and MP2 methods with the highest basis set for each molecule show the same qualitative ordering as those found from experiments. At the room temperature the rotational barriers in order of increasing fluorine substitution are 2.54, 3.73, 3.48, and 3.53 kcal/mol (Figure 1). The smaller \angle CCF angle and the longer C-F length found in the CF₃ group of CF₃CH₂F for the fluorine atom trans to the fluorine atom suggest an important nonbonding interaction of this fluorine atom with the CH₂F group. This interaction may stabilize greatly the staggered conformer and hence contribute to the observed high barrier in this molecule. The magnitude as well as the ordering of the rotational barriers calculated using the B3LYP/6-31G-(d') method is in disagreement with both experiments and molecular orbital calculations. In this paper we provide the highest level of calculations (within the scope of our computer capabilities) of the rotational barrier for CF₂HCH₃, CF₃CH₂F, and C₂F₅H. We demonstrate that the barrier heights of these molecules, including C₂F₆, decrease linearly with temperature. We provide a new assignment for the normal modes of vibration of both CF₃CH₂F and C₂F₆.

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