

Staggered and eclipsed conformations of C_2F_6 : A systematic ab initio study

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Abstract

Molecular geometries, energies, and vibrational frequencies for eclipsed and staggered conformers of perfluoroethane were determined by ab initio calculations. Basis set effects were investigated systematically with progressively larger basis sets, up to triple zeta, d and f polarization functions plus diffuse functions on all atoms. Electron correlation was included by means of Møller–Plesset perturbation calculations to the third order. Vibrational frequencies, calculated at both Hartree–Fock (HF) and second order Møller–Plesset perturbation (MP2) methods, were used to make zero-point energy and thermal corrections to electronic energies. Some semi-empirical methods and molecular mechanics force fields were also employed for comparison. The rotational barrier (3.81 kcal mol⁻¹) predicted from the HF/6-311 + G(3df) method is close to the measured electron diffraction value of 4.40 kcal mol⁻¹ (−0.90, +1.10). The MP2/6-311G(d) level gives a lower barrier of 3.33 kcal mol⁻¹, and the best MP3 calculation, MP3/6-311 + G(3df)//MP2/6-311G(d), a value of 3.55 kcal mol⁻¹. © Elsevier Science S.A.

Keywords: Ab initio; Perfluoroethane; Rotational barrier

1. Introduction

It is well known that saturated fluorocarbons exhibit an uncommon set of both physical and chemical properties, which in most instances are quite different from those of their analogous hydrocarbons [1]. These properties make them useful in a great number of application. In particular, several papers have dealt with hexafluoroethane in environmental [2], theoretical [3] and solid-state [4] chemistry, as well as in materials science [5] and medicine [6,7].

Since certain properties of organic compounds are closely related to preferred conformations [8], a reliable determination of the structural differences among conformers is desired. There exist a number of chemical and physical methods to get this information [9,10]. Because chemical methods may produce questionable results [9], physical methods now predominate. Computational determinations are paramount for those conformations which show superimposed spectra in the vapor and liquid states, and in general for those which are difficult to elucidate by other physical methods.

Hexafluoroethane has proven to be elusive to various physical methods applied to the structure of its staggered and eclipsed conformers and the corresponding rotational barrier, [11–20]. Table 1 summarizes the experimental and theoret-

ical structural parameters of the staggered conformer and the rotational barrier values reported so far.

Since the torsional frequency for C_2F_6 cannot be directly measured from either IR or Raman spectroscopy, and the large error bar of the electron diffraction data (Table 1) prevents a firm determination of the rotational barrier, we have carried out a systematic set of ab initio M.O. calculations to provide the rotational barrier and structural parameters for each conformer. We have also calculated the vibrational frequencies at HF and MP2 levels to make zero-point energy and thermal corrections to the calculated electronic energies. In addition, some single-point energy calculations at the MP3 level for the MP2/6-311G(d) optimized geometry were completed. No thermal correction to the internal energy of the conformers was considered in getting the ab initio rotational barrier indicated in Table 1. For comparison, some common semi-empirical and molecular mechanics force field methods were used for geometry optimizations and relative energies of conformers.

2. Computational methods

2.1. Ab initio calculations

Ab initio MO calculations were performed using the Gaussian 94 program [22]. Complete self-consistent field (SCF)

Table 1

Different experimental and theoretical values reported for the rotational barrier and for the structural parameters of hexafluoroethane. First row shows the year of publication

	Experiment							Theory	
	1948 ^a	1953 ^b	1954 ^c	1955 ^d	1966 ^e	1969 ^f	1974 ^g	1988 ^h	1996 ⁱ
r_{C-F} (Å)	1.35	1.33	1.33	1.32	1.32	1.32	1.326	1.31	1.339
r_{C-C} (Å)	1.45	1.48	1.51	1.56	1.56	1.56	1.545	1.528	1.535
$\angle FCC$ (deg)	109.5	109.5	108	109.5	109.5	110	109.7	109.8	110.1
ΔE (kcal mol ⁻¹)	4.35	3.92			4.30	4.20	3.67 4.40	3.90	3.80

^a Barrier height estimated from thermodynamic data (Pace and Aston [11]). These authors measured the entropy at 176.15 K and 194.87 K and found that $S = 67.92$, and $S = 69.88$ (± 0.20 cal K⁻¹ mol⁻¹), respectively. They also matched the calculated statistical-mechanical entropy with experiment by adjusting the height of the barrier to internal rotation.

^b Rotational barrier based on Pace and Aston's work, but revised using the new structural parameters [12].

^{c,d} Data taken from [13] and [14] respectively.

^e Rotational barrier obtained from electron diffraction data at 295 K [17]. Error in the barrier height is estimated to extend to 30% above and 20% below the given value.

^f Rotational barrier based on Pace and Aston's work, but revised using the structural data given by Karle [14], and the moments of inertia and vibrational frequencies (except for the torsional mode) given by Carney [15], but assuming free internal rotation [21].

^g Barrier from electron diffraction with sample cooling during experiment: 3.67 (-0.75 , $+0.91$) at 250 K, and 4.40 (-0.90 , $+1.10$) at 300 K [18].

^h Data obtained by ab initio molecular orbital calculations [19].

ⁱ Data obtained by ab initio density functional calculations [20].

geometry optimizations and frequency calculations were done for C₂F₆ conformers with each basis set. The normal vibration frequencies obtained were scaled by a factor of 0.900 to compensate for anharmonicity and electron correlation. MP2 optimizations and the corresponding frequencies were carried out up to the 6-311G(d) basis set. MP2 frequencies were scaled by 0.980 to account for anharmonicity. MP3 single-point energies were calculated using the MP2/6-311G(d) optimized geometry with some basis sets. Eclipsed conformer geometry was confirmed by the presence of a single imaginary frequency. The scaled frequencies and molecular structures were used with standard formulae [23,24] to calculate the zero-point vibrational energies (ZPVE) and thermal contributions to the enthalpy for each of the stationary states: $(H(T) - H(0) = H_{298}^0 - H_0^0)$.

2.2. Semi-empirical calculations

The MNDO [25,26], CNDO [27], INDO [28], and PM3 [29,30] semi-empirical methods, implemented in the Gaussian 94 package were used for geometry optimizations and frequency calculations for each conformer.

2.3. Molecular mechanics calculations

The MM2, TRIPOS, and UFF force fields, implemented in the CS Chem 3D Pro (version 3.2), Sybyl (version 6.1) and Cerius2 (version 2.0) programs, respectively, were used for energy minimization.

3. Results and discussion

3.1. Geometries

The staggered and eclipsed conformers of perfluoroethane have D_{3d} and D_{3h} symmetry respectively. The geometry parameters given by the ab initio calculations are shown in Table 2, and compared with the most recent experimental values [18]. The $\angle FCC$ is independent of the basis set and the agreement with the experimental value is remarkable. When compared to the staggered $\angle FCC$ at both HF and MP2 methods, the $\angle FCC$ of the eclipsed conformer is 0.2° larger within the 3-21G basis set, and about 0.45° larger within the others.

The predicted C–F distance for the eclipsed conformer is similar to that of the staggered conformer at all levels of theory used. However, it should be said that the two smallest basis sets greatly overestimate this parameter. This is more evident at the MP2 level where the predicted C–F bond is 0.03 Å (3-21G) and 0.04 Å (6-31G) longer than that predicted at the HF level. The calculated value using the other basis sets remains essentially unchanged, although the calculated C–F bond is, as expected, 0.016–0.025 Å shorter than the experimental value when no correlation effects are included. This difference range is very similar to that found in some other fluorocarbons [31,32].

The C–C bond in the eclipsed conformer is about 0.03 Å longer than in the staggered form. In general, the predicted C–C distance becomes closer to experiment as extra valence functions are added to the split valence basis set 6-31G(d) and as the number of d and f polarization functions is increased. Adding diffuse functions slightly improves the calculated C–C bond. MP2 enhances predictions for this par-

Table 2
Geometrical parameters for the staggered and eclipsed conformers of C₂F₆, as given by ab initio molecular orbital calculations^a

	3-21G	6-31G	6-31G(d)	6-311G(d)	6-31G(2d)	6-31G(3d)	6-31G(2df)	6-311G(2df)	6-31G(3df)	6-311G(3df)	6-311 + G(3df)
HF method											
Staggered											
r _{C-C}	1.503	1.517	1.526	1.529	1.526	1.536	1.532	1.530	1.539	1.536	1.538
r _{C-F}	1.338	1.350	1.311	1.306	1.306	1.306	1.303	1.302	1.303	1.302	1.302
∠FCC	109.8	109.9	109.8	109.8	109.8	109.8	109.8	109.8	109.8	109.8	109.8
Eclipsed											
r _{C-C}	1.533	1.546	1.555	1.558	1.557	1.565	1.563	1.562	1.5684	1.566	1.569
r _{C-F}	1.337	1.349	1.310	1.306	1.305	1.305	1.302	1.302	1.302	1.301	1.301
∠FCC	110.0	110.5	110.3	110.3	110.3	110.2	110.2	110.3	110.2	110.3	110.3
MP2 method											
Staggered											
r _{C-C}	1.519	1.536	1.530	1.538	Exp. ^b	1.545					
r _{C-F}	1.368	1.391	1.340	1.330	1.326	1.326					
∠FCC	109.7	109.9	109.7	109.7	109.7						
Eclipsed											
r _{C-C}	1.552	1.566	1.560	1.569							
r _{C-F}	1.366	1.390	1.339	1.330							
∠FCC	109.9	110.4	110.1	110.2							

^a Bond distances in ångströms; angles in degrees.^b See Ref. [18].

ticular bond compared with the HF method for corresponding basis sets.

The geometrical parameters by some semi-empirical and molecular mechanics methods are collected in Table 3. The overall performance of the force fields is better than that of the semi-empirical methods. Nevertheless, both are of poor quality compared with ab initio results.

In summary, not only does the size of the basis set need to be augmented, but its shape needs to be changed (by adding d and f polarization functions) and correlation effects included to correctly predict structural parameters of the C₂F₆ conformers.

3.2. Vibrational analyses

The calculated vibrational frequencies are given in Tables 4–7. The symmetry of the normal modes has been assigned by the point group of each conformer [33]. Because frequency calculations use the harmonic oscillator model, neglecting anharmonic effects, and since the HF approach (Tables 4 and 6) also neglects correlation, the SCF and MP2 frequencies are scaled by factors of 0.900 and 0.980 respectively to bring them closer to experimental values. The experimental values [20] and the available theoretical results [19,20] are also displayed in Table 4.

A possible explanation for the effect of d and f functions on the predicted frequencies can be developed by considering the types of vibrations. Tables 5 and 7 show the coordinates associated with the symmetry of vibrational modes. The first frequency is generated by torsion and convergence is achieved. The last five frequencies are stretching modes. The remaining vibrational modes are bending modes. Since spatial distortion by bending is larger than that caused by stretching, the former require slightly more flexibility in choice of basis.

Polarized basis sets allow orbitals to change shape by adding orbitals with angular momentum beyond what is needed for the ground state. Accordingly, the low frequencies given by 6-31G(3d) are closer to experimental values than those given by 6-31G. The addition of one f function should improve the predicted values. In fact, adding f functions does not improve the prediction, because in this particular molecule the stretching modes are not shape dependent.

In short, the bending modes for C₂F₆ are best described by allowing the orbitals to change shape, i.e. adding d and f polarization functions, and stretching modes by increasing the size of the basis set. A combination of both basis set size and shape leads to high quality prediction of vibrational spectra. The difference in the magnitudes of the values for the D_{3d} and D_{3h} can be explained by steric hindrance and by the change of the C–C bond length (structure dependence). There is excellent agreement of calculated spectra with experiment. The global error varies from 6% to 1.3% within the HF method and from 6.71% to 0.95% within the MP2 method as the basis sets are improved. The errors with Dixon's basis

Table 3
Geometrical parameters of C_2F_6 , as given by some molecular mechanics and semi-empirical methods

Force field	Staggered			Eclipsed		
	r_{C-C}	r_{C-F}	$\angle FCC$	r_{C-C}	r_{C-F}	$\angle FCC$
MM2	1.497	1.328	111.4	1.511	1.328	112
UFF	1.525	1.383	109.1	1.542	1.384	110.5
TRIPOS	1.542	1.36	109.6	1.550	1.361	110.3
Exp. [18]	1.545	1.326	109.7			
Semi-empirical						
CNDO	1.489	1.347	112.5	1.49	1.347	112.7
INDO	1.491	1.349	112.6	1.493	1.349	112.8
MNDO	1.674	1.346	110.7	1.682	1.347	110.0
PM3	1.633	1.343	112.4	1.633	1.343	112.4

Bond distances in ångströms; angles in degrees.

Table 4
Normal vibration frequencies (cm^{-1}) for the staggered conformer (D_{3h}) of C_2F_6 , as given by HF method and different basis sets ^a

Symmetry	6-31G			6-31G(d)			6-31G(2d)			6-31G(3d)			6-31G(2df)			6-31G(3df)			6-31G(3df) + G			6-31G*(C) ^c	
	3-21G	6-31G	6-31G(d)	6-31G(d)	6-31G(2d)	6-31G(3d)	6-31G(2d)	6-31G(3d)	6-31G(2df)	6-31G(3df)	6-31G(3df)	6-31G(2df)	6-31G(3df)	6-31G(3df)	6-31G(3df)	6-31G(3df)	6-31G(3df)	6-31G(3df)	6-31G(3df)	6-31G(3df)	6-31G(3df)	6-31G(3df)	6-31G(3df)
A_{1u}	58	66	64	66	70	66	68	68	68	68	68	68	67	67	69	70	68	63					
E_u	197	204	207	212	210	211	206	208	208	206	211	210	210	210	212	212	219	210	210	210	210	210	210
A_{1g}	330	330	340	340	339	340	339	341	341	340	340	340	340	340	342	341	348	340	340	340	340	340	340
E_g	357	354	374	378	375	375	375	377	377	375	375	377	377	377	379	379	372	376	376	376	376	376	376
E_u	484	473	508	516	512	514	515	517	517	515	514	515	518	518	518	518	522	513	513	513	513	513	513
E_g	586	575	607	610	608	610	611	613	613	611	610	611	615	615	615	614	620	607	607	607	607	607	607
A_{2u}	652	644	697	706	698	703	707	708	708	707	703	707	709	710	710	711	714	696	696	696	696	696	696
A_{1g}	757	748	798	802	794	798	806	806	806	806	798	806	806	806	806	806	807	794	794	794	794	794	794
A_{2u}	1111	1077	1119	1109	1103	1103	1118	1116	1116	1118	1103	1118	1115	1116	1116	1113	1116	1112	1112	1112	1112	1112	1112
E_g	1289	1248	1283	1266	1253	1256	1275	1272	1272	1275	1256	1272	1269	1268	1268	1264	1250	1276	1276	1276	1276	1276	1276
E_u	1315	1256	1290	1273	1261	1263	1285	1281	1281	1285	1263	1275	1276	1275	1275	1270	1250	1283	1283	1283	1283	1283	1283
A_{1g}	1384	1392	1464	1450	1447	1437	1447	1447	1447	1447	1437	1447	1434	1443	1443	1432	1417	1442	1442	1442	1442	1442	1442

^a All frequencies have been scaled by a factor of 0.900.

^b See Ref. [20].

^c This is the basis set used by Dixon (see Ref. [19]) to calculate the frequencies. In this basis set d polarization functions have been added to each carbon atom. Their corresponding frequencies have also been scaled by 0.900.

Table 5
Normal vibration frequencies (cm^{-1}) for the staggered conformer (D_{3d}) of C_2F_6 given by the MP2 method with different basis sets and by density functional theory

Symmetry	Coordinate ^b	3-21G	6-31G	6-31G(d)	6-311G(d)	LDA ^a	Exp.
A_{1u}	$\chi_{\text{CF}3}$	62	65	65	69	77	68
E_u	γ_{CCF}	201	207	210	217	206	219
A_{1g}	γ_{FCF}	340	334	347	351	325	348
E_g	γ_{CCF}	357	345	370	379	349	372
E_u	γ_{FCF}	491	465	506	518	481	522
E_g	γ_{FCF}	595	570	609	615	578	620
A_{2u}	γ_{FCF}	653	628	692	708	660	714
A_{1g}	ν_{CC}	759	727	796	803	779	807
A_{2u}	ν_{CF}	1119	1058	1127	1120	1084	1116
E_g	ν_{CF}	1271	1190	1265	1247	1194	1250
E_u	ν_{CF}	1300	1197	1279	1261	1120	1250
A_{1g}	ν_{CF}	1377	1366	1471	1449	1363	1417

^a Data taken from Ref. [20]. LDA stands for local density approximation.

^b χ : torsional mode; γ : bending mode; ν : stretching mode. See Ref. [20].
Frequencies scaled by 0.980.

Table 6

Normal vibration frequencies (cm^{-1}) for the eclipsed conformer (D_{3h}) of C_2F_6 , as given by the HF method with different basis sets^a

Symmetry	3-21G	6-31G	6-31G(d)	6-311G(d)	6-31G(2d)	6-31G(2df)	6-31G(3d)	6-31G(2df)	6-311G(2df)	6-31G(3df)	6-311G(3df)	6-311 + G(3df)
A_1''	-54	-65	-63	-62	-61	-61	-62	-61	-63	-62	-65	-65
E_1'	257	267	275	271	267	267	269	267	268	268	266	267
A_1'	353	346	367	367	365	365	365	365	366	365	365	364
E_2''	356	357	370	372	370	370	368	370	370	370	370	370
E_1'	482	476	513	521	517	519	518	519	520	522	524	523
E_2''	580	567	603	608	608	608	608	610	610	612	612	611
A_2''	660	650	702	712	704	710	710	712	714	716	716	716
A_1'	752	743	797	800	792	797	797	803	803	805	804	804
A_2''	1104	1068	1113	1105	1098	1099	1099	1113	1112	1110	1111	1107
E_1'	1300	1241	1283	1265	1252	1255	1255	1277	1271	1267	1266	1262
E_2''	1303	1253	1289	1273	1258	1263	1263	1282	1276	1274	1273	1268
A_1'	1332	1340	1421	1406	1399	1393	1393	1400	1400	1391	1399	1389

^a All frequencies are scaled by a factor of 0.900.

Table 7
Normal vibration frequencies (cm^{-1}) for the eclipsed conformer (D_{3h}) of C_2F_6 by the MP2 method with different basis sets

Symmetry	Coordinate ^a	3-21G	6-31G	6-31G(d)	6-311G(d)
A_1''	χ_{CF_3}	–54	–67	–67	–65
E'	γ_{CCF}	258	271	282	279
A_1'	γ_{FCF}	355	334	362	370
E''	γ_{CCF}	358	361	379	376
E'	γ_{FCF}	488	468	511	523
E''	γ_{FCF}	584	557	601	612
A_2''	γ_{FCF}	662	636	698	714
A_1'	ν_{CC}	752	722	793	799
A_2''	ν_{CF}	1111	1047	1118	1112
E'	ν_{CF}	1283	1182	1271	1250
E''	ν_{CF}	1289	1193	1271	1252
A_1'	ν_{CF}	1315	1306	1420	1397

^a χ , torsional mode; γ , bending mode; ν , stretching mode. See Ref. [20].
All frequencies scaled by 0.980.

Table 8
HF and MP2 total energies (hartrees) and their relative differences, ΔE (kcal mol⁻¹), for the staggered and eclipsed conformers of C_2F_6 . Where appropriate, second row shows the corresponding MP2 values

Basis set	Staggered (S)		Eclipsed (E)		Differences (E–S)		
	Electronic	ZPVE	$H(S) = H(T) - H(0)$	Electronic	ZPVE	$H(E) = H(T) - H(0)$	$\Delta E(\text{el} + \text{zpv} + \text{the})$
3-21G	–668.7448992	0.0290331	0.0079361	–668.7396722	0.0290583	0.0069162	3.28
	–669.6277134	0.0290198	0.0078773	–669.6228397	0.0289521	0.0069027	3.06
6-31G	–672.1459630	0.0284148	0.0079521	–672.1388068	0.0283770	0.0069640	4.49
	–673.0576471	0.0276233	0.0080059	–673.0510968	0.0275213	0.0070265	4.11
6-31G(d)	–672.3844817	0.0296505	0.0077449	–672.3781981	0.0297504	0.0067250	3.94
	–673.6523798	0.0295597	0.0077409	–673.6463102	0.0296136	0.0067185	3.81
6-311G(d)	–672.5651207	0.0295758	0.0076971	–672.5586904	0.0296334	0.0067091	4.04
	–674.0444942	0.0295568	0.0076609	–674.0382023	0.0295568	0.0066751	3.95
6-31G(2d)	–672.3928455	0.0293607	0.0079361	–672.3861752	0.0293886	0.0069162	4.19
6-31G(3d)	–672.4185030	0.0294012	0.0077130	–672.4119331	0.0294453	0.0067250	4.12
6-31G(2df)	–672.4222111	0.029664	0.0077130	–672.4157506	0.0297090	0.0067250	4.05
6-311G(2df)	–672.6110793	0.0296658	0.0076971	–672.6043297	0.0296802	0.0067091	4.24
6-31G(3df)	–672.4428001	0.0296091	0.0076971	–672.4363087	0.0296460	0.0067091	4.07
6-311G(3df)	–672.625803	0.0296604	0.0081114	–672.618781	0.0296496	0.0070915	4.41
6-311+G(3df)	–672.6372545	0.0295929	0.007681152	–672.6302104	0.0295767	0.006724992	4.42

1 hartree = 627.51 kcal mol⁻¹.

Table 9
Total electronic energies (hartrees) for the staggered and eclipsed conformers of C_2F_6 , as given by MP2 and MP3 single point energy calculations using the MP2/6-311G(d) and HF/6-311 + G(3df) optimized geometries. The value within parenthesis corresponds to the relative energy after thermal correction

MP2 geometry	Staggered		Eclipsed		ΔE (kcal mol ⁻¹)	
	MP2	MP3	MP2	MP3	MP2	MP3
6-311G(d)	-674.0444942	-674.0286410	-674.0382023	-674.0222407	3.95 (3.33)	4.02 (3.40)
6-31G(2d)	-673.8722498	-673.8674718	-673.8658534	-673.8610311	4.01 (3.39)	4.04 (3.42)
6-31G(3d)	-673.9742849	-673.9664915	-673.9679781	-673.9601875	3.96 (3.34)	3.96 (3.34)
6-311G(3df)	-674.4169589	-674.4234034	-674.4234034	-674.4234034	4.04 (3.42)	4.04 (3.42)
6-311 + G(3df)	-674.4451953	-674.4319920	-674.4386510	-674.4253508	4.11 (3.49)	4.17 (3.55)
HF geometry						
6-311G(d)	-674.039173	-674.025765	-674.032846	-674.019334	3.97 (3.35)	4.04 (3.42)

set [19] and for the LDA [20] are 2.5% and 6.6% respectively.

3.3. Energetics

The electronic energy of each conformer after geometry optimization is associated with an isolated rigid molecule at 0 K. It is made comparable with experimental values by zero-point vibrational energy and thermal corrections to the electronic energy [23,24].

Correlation effects lead to a decrease in the rotational barrier (Table 8). The lowest barrier is provided by 3-21G and the highest barrier is given by 6-31G, the smallest basis sets considered. The value of the barrier oscillates with the addition of d functions to 6-31G, but f functions consistently decrease the barrier compared with corresponding basis sets with only d functions. The effect of extra valence functions is to substantially increase the barrier; for instance the 6-311G(3df) barrier is 0.30 kcal mol⁻¹ higher than that of the 6-31G(3df). The main correction of -0.62 kcal mol⁻¹ is due to the change in enthalpy on going from 0 to 298.15 K. The zero-point contribution is small and tends to decrease as the basis sets are improved. The thermal correction turns out to be independent of both the basis set and the correlation effects. The small zero-point energy depends on the basis set chosen and on correlation.

The highest basis set considered within the HF method (6-311 + G(3df)) gives a corrected barrier 0.59 kcal mol⁻¹ lower than the value estimated at 300 K from electron diffraction data [18] (4.40 kcal mol⁻¹), whereas the 6-31G basis set gives a value 0.55 kcal mol⁻¹ lower. The apparent good agreement with experiment with the 6-31G basis set is fortuitous. It is well-known that this basis set gives too long a bond length for the C-F bonds, leading to decreased stretching frequencies and consequently better agreement with experiment. At the MP2 level, all basis sets give a barrier notably lower than the thermodynamic value.

Dixon [19] predicts a barrier, after zero-point correction, of 3.90 kcal mol⁻¹ at the HF level and with a basis set size between our 6-31G and 6-31G(d) close to the thermodynamic value (3.92 kcal mol⁻¹). However, this value cannot be directly compared with experiment since no thermal corrections were made. If corrected using our average thermal contribution, it drops to 3.28 kcal mol⁻¹. The local density approximation [20] gives a rotational barrier of 3.80 kcal

Table 10
Total energies and their relative differences ΔE for the staggered and eclipsed conformers of C_2F_6 by molecular mechanics methods

Force field	Staggered	Eclipsed	ΔE (kcal mol ⁻¹)
TRIPOS	-0.0704	2.089	2.1594
MM2	23.3141	27.4343	4.1202
UFF	1.7148	7.007	5.2922

Table 11
Semiempirical total energies and their differences, ΔE (kcal mol⁻¹), for the staggered and eclipsed conformers of C₂F₆. ZPVE and Thermal energies in kcal mol⁻¹. Electronic energies in hartrees

Method	Staggered (S)			Eclipsed (E)			Differences (E-S)		
	Electronic	ZPVE	Thermal	Electronic	ZPVE	Thermal	ΔE (elect.)	ΔE (el + zve)	ΔE (el + zve + the)
MNDO	-0.4776420	19.25	4.94	-0.4743467	19.22	4.36	2.07	2.04	1.46
PM3	-0.5065872	18.31	5.16	-0.5035464	18.19	4.59	1.91	1.79	1.22
INDO	-172.4128617	25.30	5.10	-172.4113635	25.31	4.51	0.94	0.95	0.36
CNDO	-180.7542223	25.68	5.08	-180.7528337	25.69	4.48	0.87	0.88	0.28

Table 12
Free energy ($\Delta G_{298.15}^0$) differences between the staggered and eclipsed conformers of C₂F₆ in kcal mol⁻¹

Basis Set	Staggered			Eclipsed			Differences				
	$H(T) - H(0)$	ZPVE	S(T)	$H(T) - H(0)$	ZPVE	S(T)	$\Delta ZPVE$	$\Delta H(T-0)$	$\Delta H = H(E) - H(S)$	$\Delta S(T)$	$\Delta G(T)$
3-21G	4.98	18.219	0.0846	4.34	18.234	0.0790	0.016	-0.64	2.66	-0.0056	4.33
	4.94	18.210	0.0842	4.33	18.168	0.0789	-0.042	-0.61	2.40	-0.0053	3.98
6-31G	4.99	17.831	0.0844	4.37	17.807	0.0790	-0.024	-0.62	3.85	-0.0053	5.44
	5.02	17.334	0.0845	4.41	17.270	0.0793	-0.064	-0.61	3.43	-0.0052	4.98
6-31G(d)	4.86	18.606	0.0837	4.22	18.669	0.0782	0.063	-0.64	3.37	-0.0055	5.00
	4.86	18.549	0.0836	4.22	18.583	0.0782	0.034	-0.64	3.21	-0.0054	4.82
6-311G(d)	4.83	18.559	0.0834	4.21	18.595	0.0782	0.036	-0.62	3.45	-0.0052	5.00
	4.81	18.547	0.0832	4.19	18.547	0.0781	0.000	-0.62	3.33	-0.0051	4.85
6-31G(2d)	4.85	18.424	0.0834	4.23	18.442	0.0743	0.018	-0.62	3.56	-0.0091	6.27
6-31G(3d)	4.84	18.450	0.0794	4.22	18.477	0.0743	0.028	-0.62	3.53	-0.0051	5.06
6-31G(2df)	4.84	18.614	0.0804	4.22	18.643	0.0743	0.028	-0.62	3.46	-0.0061	5.29
6-311G(2df)	4.83	18.616	0.0794	4.21	18.625	0.0742	0.009	-0.62	3.62	-0.0052	5.17
6-31G(3df)	4.83	18.580	0.0794	4.21	18.603	0.0742	0.023	-0.62	3.48	-0.0052	5.03
6-311G(3df)	4.82	18.612	0.0793	4.21	18.605	0.0743	-0.007	-0.61	3.78	-0.0050	5.27
6-311 + G(3df)	4.82	18.570	0.0792	4.22	18.560	0.0743	-0.010	-0.60	3.81	-0.0050	5.29

Table 13
Polarizabilities and quadrupole moments for the two conformers of C_2F_6 , as predicted by the HF/6-311 + G(3df) level ^a

	α_{xx}	α_{yy}	α_{zz}	α	q_{xx}	q_{yy}	q_{zz}
Staggered	27.258	27.258	27.409	27.308	-41.794	-41.794	-41.418
Eclipsed	27.142	27.142	27.860	27.381	-41.719	-41.791	-41.841

^a Polarizabilities are in a.u.³. The quadrupole moments are in Debye Å.
1 a.u. = 1 Bohr = 0.529 Å.

mol⁻¹, the same as predicted by the highest basis set at the HF level.

In order to check the effect of a higher order correlation on the relative energies, single point energy calculations were performed in a number of basis sets at the MP3 level using the MP2/6-311G(d) optimized geometry. A single point energy at the MP3/6-311G(d) level was also carried out with the HF/6-311 + G(3df) geometry (Table 9). The barriers obtained with the HF geometry are close to those obtained with the MP2 geometry. Furthermore, all the MP2 and MP3 calculations are fairly similar. After applying thermal corrections and ignoring zero-point energies, lower bound values for the barriers are 3.33 kcal mol⁻¹ and 3.40 kcal mol⁻¹ with MP2 and MP3 respectively. The upper bound values are 3.49 kcal mol⁻¹ and 3.55 kcal mol⁻¹, respectively. These values are lower than the reported experimental rotational barriers.

3.4. Molecular mechanics and semi-empirical energies

Tables 10 and 11 show the energies for some semi-empirical methods and molecular mechanics force fields. The semi-empirical methods largely underestimate the rotational barrier. Using the 0.900 correction factor, the MM2 force field gives a rotational barrier only 0.28 kcal mol⁻¹ lower than the barrier obtained from electron diffraction data at 300 K [18]. The other fields give a poorer performance but better than with any of the semi-empirical methods.

3.5. Thermodynamic properties

The calculated frequencies, along with the corresponding optimized geometries, were employed to get some thermo-

Table 14
Some molecular orbital eigenvalues (eV) for perfluoroethane conformers at the HF/6-311 + G(3df) level

Orbital ^a	Staggered	Eclipsed
occ	-18.76 (a _{1u})	-18.65 (e'')
occ	-18.52 (a _{2g})	-18.45 (a ₁ '')
HOMO	-16.01 (a _{1g})	-16.05 (a ₁ '')
LUMO	2.11 (a _{1g})	2.11 (a ₁ '')
unocc	2.46 (a _{2u})	2.45 (a ₂ '')

^a Orbitals given in order of increasing energy with symmetry in parenthesis. occ = occupied. unocc = unoccupied. HOMO = highest occupied molecular orbital. LUMO = lowest unoccupied molecular orbital.

dynamic properties displayed in Table 12 [23,24]. The best basis set within the HF method predicts a value of 5.29 kcal mol⁻¹ for the Gibbs free energy change; the best basis set within the MP2 level predicts a value of 4.82 kcal mol⁻¹. The value predicted for $H(T) - H(0)$ is a constant at both levels of theory considered.

3.6. Electronic properties

The Mulliken charge distribution depends on the basis set. Carbon takes a charge which varies between 1.8 and 0.57. The tensor components of the molecular polarizabilities and quadrupole moments determined by the HF/6-311 + G(3df) level of theory are given in Table 13. Table 14 shows the eigenvalues and the symmetries for some molecular orbitals of the D_{3d} and D_{3h} conformers. The HOMO of the eclipsed conformer is 0.90 kcal mol⁻¹ more stable than the HOMO of the staggered. The negatives of the eigenvalues of filled molecular orbitals, according to Koopman's theorem [34], correspond to their ionization potentials.

4. Conclusions

The rotational barrier of hexafluoroethane and the structural parameters of its staggered and eclipsed conformers have been systematically studied by means of ab initio molecular orbital theory. Both HF and MP2 levels were used to perform geometry optimizations and frequency calculations with a number of progressively larger basis sets. The C–C bond and ∠FCC are accurately predicted by HF and MP2; the C–F bond is better predicted by MP2, while HF underestimates it. Basis set and electron correlation effects have a great influence on the calculated rotational barrier. Zero-point vibrational energy correction to the barrier is very small (-0.007 to -0.065 kcal mol⁻¹), but thermal correction is significant (-0.62 kcal mol⁻¹) and is independent of basis set and correlation. The best Hartree–Fock rotational barrier, after zero-point energy and thermal corrections, is 3.81 kcal mol⁻¹, close to the measured thermodynamic barrier of 3.92 kcal mol⁻¹. Correlation effects greatly lower the barrier predicted by the HF method. The MP2/6-311g(d) level predicts a barrier, after all corrections, of 3.33 kcal mol⁻¹. Higher-order correlation corrections were made by performing single-point energy calculations at the MP3 level with several basis sets. The MP2/6-311g(d) geometry was used to perform MP3 calculations. The best MP3 calculation

(MP3/6-311 + G(3df)//MP2/6-311G(d)) gives a value for the rotational barrier of $3.55 \text{ kcal mol}^{-1}$, after applying only a thermal correction of $-0.62 \text{ kcal mol}^{-1}$. Semi-empirical and molecular mechanics methods are unsatisfactory.

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References

- [1] R.E. Banks, *Fluorocarbons and their Derivatives*, Macdonald, London, 1970, p. 15–20.
- [2] C. Roehl, D. Boglu, C. Bruhl, G. Moortgat, *Geophys. Res. Lett.* 22 (1995) 815.
- [3] T. Takagi, L. Boesten, H. Tanaka, M. Dillon, *J. Phys. B.* 27 (1994) 5389.
- [4] G.T. Andrews, H. Kiefte, M.J. Clouter, *J. Chem. Phys.* 99 (1993) 5430.
- [5] H. Park, K. Kwon, J. Lee et al., *J. Appl. Phys.* 76 (1994) 4596.
- [6] T. Bochow, R. Olk, J. Hershey, *Archiv. Ophthalmol.* 11 (1992) 1723.
- [7] U. Gross, G. Papke, S. Rudiger, *J. Fluorine Chem.* 61 (1993) 11.
- [8] M. Hanack, *Conformation Theory*, Academic Press, New York, 1965, p. 24.
- [9] W.J. Orville-Thomas, in: *Internal Rotation in Molecules*, Wiley-Interscience, New York, 1974, p. 13.
- [10] P. Klaeboe, *Vibrational Spectrosc.* 9 (1995) 3.
- [11] E.L. Pace, G.J. Aston, *J. Am. Chem. Soc.* 70 (1948) 566.
- [12] D.E. Man, E.K. Plyler, *J. Chem. Phys.* 21 (1953) 1116.
- [13] L.J. Brandt, R.L. Livingston, *J. Am. Chem. Soc.* 76 (1954) 2096.
- [14] D.A. Swick, I.L. Karle, *J. Chem. Phys.* 23 (1955) 1499.
- [15] A.R. Carney, E.A. Piotrowski, A.G. Meister, J.H. Braun, *J. Molec. Spectrosc.* 7 (1961) 209.
- [16] H.P. Bucker, J.R. Nielsen, *J. Molec. Spectrosc.* 11 (1963) 243.
- [17] J. Karle, *J. Chem. Phys.* 45 (1966) 4149.
- [18] K.L. Gallaher, A. Yokozeki, H. Bauer, *J. Phys. Chem.* 78 (1974) 2389.
- [19] D.A. Dixon, F.A. Catledge, *Int. J. Supercomputer Appl.* 2 (1988) 62.
- [20] U. Rothlisberger, K. Laasonen, M.L. Klein, *J. Chem. Phys.* 104 (1996) 3692.
- [21] H.-W. Ko, W.A. Steele *J. Chem. Phys.* 51 (1969) 4595.
- [22] M.J. Frish, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheesman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, C.Y. Peng, P.Y. Ayala, W. Cheng, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, A. Pople, *Gaussian 94, Revision B.3*, Gaussian, Pittsburgh PA, 1995.
- [23] T.L. Hill, *An Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, MA, 1960, p. 167.
- [24] D.A. McQuarrie, *Statistical Thermodynamics*, Harper and Row, New York, 1973, p. 156.
- [25] M.J.S. Dewar, C.H. Reynolds, *J. Comp. Chem.* 2 (1986) 140.
- [26] M.J.S. Dewar et al., *Organometallics* 4 (1985) 1964.
- [27] G. Segal, J.A. Pople, *J. Chem. Phys.* 44 (1966) 3289.
- [28] J.A. Pople, D.L. Beveridge, P.A. Dobosh, *J. Chem. Phys.* 47 (1967) 2026.
- [29] J.J.P. Stewart, *J. Comp. Chem.* 10 (1989) 209.
- [30] J.J.P. Stewart, *J. Comp. Chem.* 10 (1989) 221.
- [31] D.A. Dixon, *J. Phys. Chem.* 90 (1986) 2038.
- [32] D.A. Dixon, T. Fukunaga, B.E. Smart, *J. Am. Chem. Soc.* 108 (1986) 4027.
- [33] F.A. Cotton, *Chemical Applications of Group Theory*, Wiley-Interscience, New York, 1990, p. 309.
- [34] W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley-Interscience, New York, 1986, p. 116.

Note added in proof

Recently we calculated the rotational barrier (with thermal correction) at the MP4 (SDTQ)/6-311G(d) method using the MP2/6-311G(d) geometry. The predicted value is $3.12 \text{ kcal mol}^{-1}$.