

A density functional study of mono- and difluoropropenes

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Received 30 May 1997; accepted 22 August 1997

Abstract

A number of physical and chemical properties of all possible mono- and selected difluoropropenes have been investigated using semiempirical, standard ab initio and density functional methods, with particular emphasis on hybrid HF-DFT functionals that mix part of the exact Hartree–Fock exchange in with the density functional. We have included two hybrid functionals in our study—Becke’s original 3-parameter ACM functional (also known as B3PW91) and the popular B3LYP functional. Results for the two functionals are very similar and generally among the best reported, although the ACM functional seems to be better for geometries than B3LYP. The semiempirical methods (especially MNDO) give a poor picture of the chemistry of the monofluoropropenes, with relative energies and derived potential energy surfaces often qualitatively incorrect. We make a number of predictions as to the geometries and energetics of the difluoropropenes; we consider our ‘best’ theoretical bond lengths to have a *maximum* error of 0.02 Å. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Difluoropropene; Monofluoropropene; ACM functional; B3LYP functional

1. Introduction

There are a number of fairly subtle conformational (and related) effects following substitution of hydrogen by fluorine in hydrocarbons. Perhaps the most well known is the *geminal* effect whereby C–F bond strength *increases* with increasing fluorine substitution on the *same* carbon atom (and C–F bond lengths correspondingly *decrease* with increasing substitution) [1]. There is also a tendency for π C=C bond strength to *decrease* with increasing vicinal fluorine substitution at the carbon atoms concerned [2]. Other conformational preferences include the so-called *gauche* effect (partially substituted fluorocarbons tend to prefer *gauche* conformations over *anti*, in contrast to unsubstituted hydrocarbons for which the preference is *anti* over *gauche* [3]) and the often greater stability of *cis* difluoro substituted alkenes compared to *trans*, which runs counter to expectations based on electrostatic and steric arguments [4] (the *cis* effect). For a more thorough discussion of these and other effects along with possible theoretical explanations, see the review article by Smart [5].

We have previously undertaken a comprehensive study of the ability of commonly used theoretical methods, especially the increasingly popular density functional methods, to accurately predict the geometries and relative conformational sta-

bilities of fluorinated methanes, ethylenes and ethanes [6]. This stemmed from an earlier study of organic reactions comparing calculated geometries, heats of reaction and barrier heights with experimental data which found that density functional theory (DFT) provided better overall agreement with experiment than more traditional ab initio methods such as MP2 [7]. Of particular note in both these studies [6,7] was the performance of hybrid HF-DFT functionals—we used Becke’s original three-parameter approximation to the ‘adiabatic connection’ formula (hereafter referred to as the Adiabatic Connection Method or ACM [8])—which mix a portion of the exact Hartree–Fock exchange into the density functional. In our previous fluorination study especially [6], the ACM functional gave excellent agreement with experiment for geometries, relative energetics, rotational barriers and dipole moments for all systems examined and was clearly the most accurate method of all those included in the study. There is now overwhelming evidence that hybrid HF-DFT functionals can provide results of a similar quality to fairly high-level post Hartree–Fock calculations at a fraction of the computational cost [9].

This article presents a study of all possible mono- and selected difluoropropenes. As with our previous fluorination study [6], we focus on the capability of theory to reproduce known experimental trends in geometry, conformation, energetics and dipole moments, in both relative and absolute

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terms. Again, a range of theoretical methods have been used, including semiempirical, traditional ab initio and density functional theory. There is very little experimental data available for the difluoropropenes and, based on our best ab initio results, we make a number of predictions as to geometries, relative energetics, and dipole moments.

2. Computational details

Calculations were carried out at the MNDO [10], AM1 [11] and PM3 [12] semiempirical levels, at the Hartree–Fock and MP2 levels, and with various density functionals, namely the local SVWN functional (which comprises Slater’s exchange term [13] plus Vosko et al.’s [14] parameterization of the exact uniform gas results of Ceperley and Alder [15]), the nonlocal BP and BLYP functionals (combining Becke’s nonlocal exchange functional [16] with the correlation functionals of Perdew [17] and Lee Yang, and Parr [18], respectively) and the hybrid ACM functional [8]. Additionally, we have also included the hybrid B3LYP functional, which uses Becke’s original parameterization scheme [8], but substitutes the correlation functional of Perdew [17] with that of Lee Yang, and Parr [18]. The currently greater popularity of B3LYP compared to the original ACM functional (which can also be termed B3PW91) appears to be purely fortuitous, arising solely from the fact that in the first DFT version of the extremely popular GAUSSIAN program, Perdew’s 1991 functional was not available (it simply had not been coded) and Lee et al.’s functional (which had been) was substituted instead. To the best of our knowledge there has been no systematic comparison of these two hybrid functionals to determine whether, or under what circumstances, one of them might be consistently ‘better’ than the other.

For calculations at the HF level and beyond, including all the density functional calculations, we used two basis sets—the standard split-valence + polarization 6-31G* basis developed by Hariharan and Pople [19] and a triple-zeta double-polarization (TZ2P) basis developed by Schafer et al. [20]. In all cases we used five spherical harmonic as opposed to six Cartesian components in the d-polarization functions.

Energies and gradients for all three semiempirical methods (MNDO, AM1 and PM3) as well as for the HF/6-31G* and some of the MP2 calculations were computed using GAUSSIAN 94 [21]. For all other levels of theory, including almost all the density functional calculations, we used TURBOMOLE [22]; the exception was for calculations using the hybrid B3LYP functional, where we again used GAUSSIAN 94 [21]. All geometry optimizations, for both minima and transition states, were carried out with the EF algorithm [23], using the general purpose stand-alone optimization package OPTIMIZE [24]. In the majority of our calculations, we used standard convergence criteria of 0.0003 a.u. on the maximum gradient component and either an energy change from the previous cycle of less than 10^{-6} hartree or a maximum predicted displacement of less than 0.0003 a.u. per coordinate. For several of the *gauche* structures (which have no sym-

metry) we tightened the convergence to ensure in particular that dihedral angles were well converged. All stationary points were characterized at the HF/6-31G* level by vibrational analysis.

3. Results

A table of total energies for all species examined at all levels of theory together with Hartree–Fock zero-point vibrational energies (ZPVEs) is given in Appendix A. In this section we discuss the various mono- and difluoropropenes in turn, comparing geometries, dipole moments, relative stabilities and rotational barriers between each level of theory and with experiment. Relative energies are reported in kcal/mol and we have adopted the standard practice of correcting all our ab initio energies with the zero-point vibrational energy calculated at the HF/6-31G* level, scaled by a factor of 0.89.

3.1. Monofluoropropenes

All possible monofluoropropenes and their rotational transition states are shown schematically in Fig. 1.

Calculated geometrical parameters are reported in Table 1 together with experimental values where available. The amount of *reliable* experimental structural data for the fluoropropenes is rather limited; in many cases difficulties in interpreting the (usually) microwave experiments have led to several bond distances and angles (typically those involving hydrogen atoms which are notoriously difficult to pin down accurately) either being given ‘assumed’ values or values calculated theoretically (such values are starred in Table 1). An interesting example is provided by the two sets of experimental parameters [27,28] given for 3-fluoropropene (both from the same group), which is probably the most studied isomer.

The first (and earlier) set of experimental (microwave) data [27] was derived with no theoretical assistance and no parameters given preordained values. This set looks reasonable for *cis*-3-fluoropropene, and is in fact in good agreement with the better quality ab initio calculations (see later). Some of the experimental C–H bond lengths are perhaps too long, but in view of the difficulties with hydrogen atoms, this is not surprising. Although nothing seems obviously amiss with the experimental parameters for *gauche*-3-fluoropropene [27], if we compare the experimental C–F bond lengths between the *cis* and *gauche* isomers, we see that experimentally the C–F distance is significantly *shorter* in *gauche*-3-fluoropropene than in *cis*, whereas all the ab initio calculations, at all levels of theory, predict precisely the opposite.

The second (and later) experimental set [28] essentially comprises a complete refit of the original microwave data with many of the distances and angles involving hydrogen atoms given values calculated from MP2/6-31G* optimizations. The authors note in Ref. [28] that previously derived

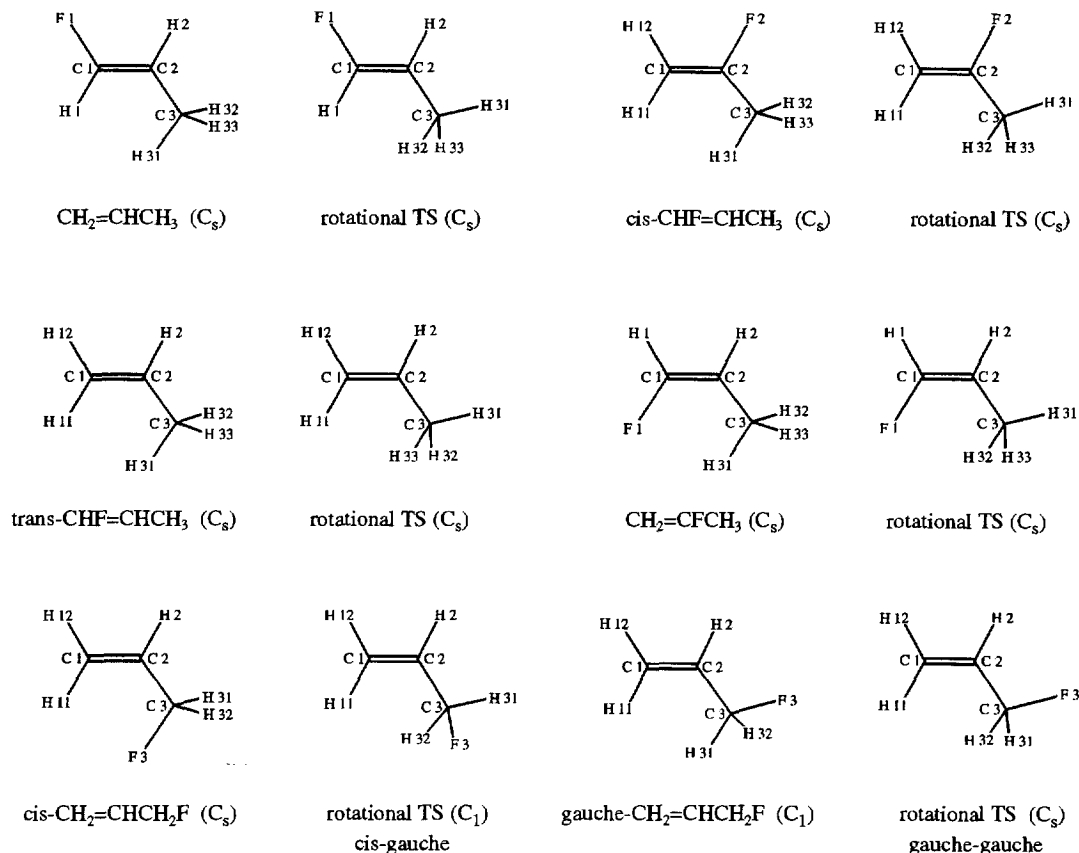


Fig. 1. Structures and labelling scheme for the monofluoropropenes.

C–H distances were ‘artefacts of the experimental data’. The refit has dramatically altered some of the ‘experimental’ parameters, particularly for the *gauche* isomer. The C–F bond length in *gauche*-3-fluoropropene has increased by 0.030 Å, and is now *longer* than in the *cis* isomer and in excellent agreement with the best theoretical calculations. The C–C single bond length has also changed significantly, decreasing by 0.033 Å. There are also changes in the geometry of the *cis* isomer, but these are not so marked (only two C–H distances were fixed during the refit). The second set of data [28] is clearly in much better agreement with our best calculations than is the first set [27].

This example clearly shows that theory has a lot to offer the experimentalist when it comes to deriving a reliable set of geometrical parameters from microwave or other (e.g., X-ray) data. Some interesting comments on the difficulties in obtaining absolute geometries from microwave spectroscopy are given in the theoretical study by Boggs and Fan [29] of successive fluorination on the structure of cyclopropane. One cannot help wondering what percentage of the experimentally determined molecular structures quoted in the literature are really accurate. The experimental geometries we have quoted in Table 1 seem ‘reasonable’ to us. Note that the only experimental geometry we were able to find for 2-fluoropropene (a microwave study by Pierce and O’Reilly [30]) had almost all parameters except those involving fluorine ‘assumed’; we

consider their derived C–F bond distance, 1.324 ± 0.015 Å, to be too short and hence have not included it in the table.

At the end of Table 1 we have compiled a listing of the errors in C–F and in ‘all’ calculated bond lengths vs. experiment (in the latter case we have excluded any experimentally ‘assumed’ bond distances from the analysis). The best theoretical methods, judged by the lowest average/maximum errors in predicted bond lengths, are—for the C–F bond lengths—ACM/TZ2P, ACM/6-31G* and MP2/TZ2P—and taking ‘all’ bond lengths—ACM/6-31G*, B3LYP/6-31G*, ACM/TZ2P and MP2/6-31G*. This is precisely what was found in our previous fluorination study [6], namely that ACM and MP2 were clearly the best methods, with ACM generally superior overall, but MP2 being better than any of the other non-hybrid density functionals. As usual, HF bond lengths are too short.

What is clear from the error analysis is that the two hybrid DFT functionals (ACM and B3LYP) are *not* equivalent, at least for geometries. Examination of Table 1 shows that, although the two functionals show very little difference for bond angles and C–H and C=C double bond lengths, there are quite significant variations for C–C single and, in particular, C–F bonds. All fluoropropene C–C single bonds are ~ 0.004 Å longer with B3LYP than with ACM, and C–F bonds are around 0.006 Å (6-31G*) and 0.010 Å (TZ2P) longer. This increase makes calculated B3LYP/TZ2P C–F

Table 1
Selected geometrical parameters for propene and the monofluoropropenes (bond lengths in Å; bond angles in degrees)

Parameter	TZ2P basis											Ref. [25]						
	6-31G* basis					TZ2P basis												
	MNDO	AMI	PM3	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	HF		MP2	SVWN	BP	BLYP	ACM	B3LYP
<i>Propene (C₃)</i>																		
rC ₁ C ₂	1.340	1.331	1.328	1.319	1.338	1.334	1.343	1.344	1.333	1.334	1.315	1.331	1.326	1.335	1.337	1.326	1.327	1.336
rC ₂ C ₃	1.496	1.476	1.480	1.502	1.499	1.484	1.505	1.511	1.498	1.502	1.500	1.497	1.478	1.500	1.507	1.493	1.497	1.501
rC ₁ H ₁₁	1.089	1.098	1.087	1.077	1.087	1.100	1.095	1.096	1.089	1.088	1.074	1.079	1.095	1.091	1.090	1.084	1.083	1.091
rC ₁ H ₁₂	1.089	1.097	1.086	1.076	1.085	1.097	1.094	1.094	1.087	1.087	1.073	1.077	1.092	1.088	1.087	1.082	1.081	1.081
rC ₃ H ₂₁	1.096	1.103	1.097	1.079	1.089	1.102	1.098	1.099	1.091	1.091	1.076	1.082	1.098	1.093	1.092	1.087	1.086	1.090
rC ₃ H ₃₁	1.109	1.118	1.098	1.084	1.093	1.105	1.102	1.103	1.095	1.095	1.081	1.086	1.100	1.096	1.096	1.090	1.089	1.085
rC ₃ H ₃₂	1.111	1.119	1.098	1.087	1.095	1.108	1.105	1.106	1.098	1.099	1.084	1.088	1.103	1.100	1.099	1.093	1.093	1.098
∠C ₁ C ₂ C ₃	126.9	124.3	123.4	125.3	124.6	124.8	125.3	125.3	125.2	125.3	124.4	124.8	124.8	125.4	125.4	125.3	125.4	124.3
∠H ₁₁ C ₁ C ₂	124.3	122.8	123.2	121.8	121.5	121.1	121.6	121.7	121.6	121.7	121.7	121.7	120.9	121.5	121.6	121.5	121.6	120.5
∠H ₁₂ C ₁ C ₂	122.3	122.3	122.7	121.6	121.7	122.0	121.8	121.9	121.8	121.8	121.4	121.3	121.8	121.6	121.6	121.6	121.6	121.5
∠C ₁ C ₂ H ₂₁	119.3	120.9	120.8	118.9	118.9	118.9	118.8	118.9	118.8	118.9	118.7	118.7	118.7	118.6	118.7	118.7	118.7	119.0
∠C ₂ C ₃ H ₃₁	113.0	111.9	112.9	111.5	111.0	111.4	111.7	111.6	111.6	111.5	111.3	110.9	111.3	111.6	111.6	111.5	111.5	111.2
∠C ₂ C ₃ H ₃₂	110.4	110.1	110.5	110.9	111.1	111.5	111.2	111.3	111.1	111.2	110.6	110.9	111.3	111.0	111.0	111.0	111.0	111.2
∠H ₁₂ C ₂ H ₃₃	107.7	108.1	107.5	107.0	107.1	106.1	106.4	106.4	106.6	106.6	107.2	107.1	106.1	106.4	106.5	106.6	106.6	106.2
<i>Rotational TS (C₂)</i>																		
rC ₁ C ₂	1.341	1.331	1.328	1.319	1.338	1.335	1.343	1.344	1.333	1.334	1.315	1.332	1.326	1.335	1.337	1.326	1.327	1.336
rC ₂ C ₃	1.497	1.478	1.482	1.512	1.507	1.494	1.515	1.522	1.507	1.513	1.511	1.507	1.488	1.510	1.517	1.503	1.508	1.508
rC ₁ H ₁₁	1.089	1.098	1.086	1.078	1.087	1.100	1.096	1.096	1.089	1.089	1.075	1.080	1.095	1.091	1.090	1.085	1.084	1.084
rC ₁ H ₁₂	1.089	1.097	1.085	1.076	1.085	1.097	1.094	1.094	1.087	1.087	1.073	1.077	1.092	1.088	1.087	1.082	1.081	1.081
rC ₃ H ₂₁	1.095	1.103	1.096	1.078	1.088	1.101	1.097	1.098	1.090	1.090	1.075	1.081	1.097	1.092	1.091	1.086	1.084	1.084
rC ₃ H ₃₁	1.109	1.117	1.097	1.084	1.092	1.103	1.101	1.102	1.094	1.094	1.081	1.085	1.098	1.095	1.095	1.089	1.089	1.089
rC ₃ H ₃₂	1.110	1.119	1.098	1.086	1.094	1.107	1.104	1.105	1.097	1.097	1.083	1.087	1.102	1.098	1.098	1.092	1.091	1.091
∠C ₁ C ₂ C ₃	126.2	123.8	122.8	124.9	124.2	124.7	125.1	125.1	125.0	125.0	124.9	124.2	124.8	125.2	125.2	125.1	125.1	125.1
∠H ₁₁ C ₁ C ₂	124.2	122.7	123.1	122.0	121.7	121.5	122.0	122.0	121.9	121.9	121.9	121.4	121.4	121.9	121.9	121.8	121.9	121.9
∠H ₁₂ C ₁ C ₂	122.4	122.3	122.7	121.5	121.6	121.7	121.6	121.7	121.6	121.7	121.3	121.2	121.5	121.4	121.5	121.4	121.4	121.4
∠C ₁ C ₂ H ₂₁	119.2	120.7	120.6	118.5	118.6	118.3	118.3	118.5	118.4	118.5	118.4	118.4	118.2	118.2	118.4	118.3	118.3	118.3
∠C ₂ C ₃ H ₃₁	111.1	111.0	111.8	111.2	111.4	112.1	111.6	111.5	111.6	111.5	111.1	111.4	112.1	111.6	111.5	111.5	111.5	111.5
∠C ₂ C ₃ H ₃₂	111.5	110.7	111.3	111.3	111.2	111.6	111.6	111.6	111.4	111.5	111.1	111.0	111.4	111.4	111.4	111.3	111.3	111.3
∠H ₁₂ C ₂ H ₃₃	107.7	108.0	107.4	107.7	107.5	106.7	107.0	107.0	107.2	107.1	107.8	107.6	106.8	107.1	107.2	107.3	107.3	107.3
<i>cis-1-Fluoropropene (C₃) (this structure is a rotational TS at MNDO)</i>																		
rC ₁ C ₂	1.356	1.345	1.339	1.311	1.331	1.331	1.339	1.340	1.328	1.328	1.306	1.324	1.321	1.330	1.331	1.320	1.320	1.336*
rC ₂ C ₃	1.494	1.473	1.476	1.501	1.497	1.483	1.503	1.510	1.496	1.501	1.500	1.496	1.477	1.498	1.505	1.491	1.496	1.501*
rC ₁ H ₁₁	1.100	1.104	1.093	1.071	1.084	1.098	1.093	1.093	1.086	1.086	1.070	1.076	1.093	1.088	1.086	1.081	1.079	1.081*
rC ₁ F ₁	1.323	1.350	1.337	1.334	1.360	1.338	1.359	1.367	1.347	1.353	1.328	1.351	1.340	1.363	1.374	1.347	1.356	1.342
rC ₂ H ₂	1.095	1.102	1.096	1.076	1.086	1.098	1.095	1.095	1.088	1.088	1.073	1.079	1.094	1.099	1.094	1.083	1.082	1.090*
rC ₃ H ₃₁	1.108	1.118	1.098	1.082	1.091	1.104	1.100	1.100	1.093	1.093	1.079	1.084	1.099	1.094	1.094	1.088	1.087	1.090*
rC ₃ H ₃₂	1.111	1.119	1.098	1.086	1.094	1.107	1.105	1.106	1.097	1.098	1.083	1.087	1.102	1.099	1.099	1.092	1.092	1.090*
∠C ₁ C ₂ C ₃	129.5	125.3	125.1	125.6	124.5	123.8	125.5	125.3	125.3	125.1	126.1	125.2	124.8	126.4	126.4	126.1	126.0	124.3*
∠H ₁₁ C ₁ C ₂	121.8	123.1	125.4	125.4	125.9	125.5	125.4	125.7	125.3	125.6	125.0	125.5	125.8	125.7	126.1	125.5	125.8	121.5*
∠F ₁ C ₁ C ₂	124.8	124.0	123.0	122.7	122.1	122.0	122.8	122.6	122.7	122.5	122.8	122.3	121.9	122.6	122.4	122.6	122.4	122.4
∠C ₁ C ₂ H ₂	116.6	118.6	118.4	116.3	116.4	116.6	116.0	116.2	116.1	116.4	115.7	115.3	115.8	115.3	115.5	115.4	115.7	119.0*

Table 1 (continued)

Parameter	6-31G* basis			TZ2P basis												
	AM1	PM3	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP
$\angle C_2C_3H_{31}$	113.6	113.3	111.3	110.6	110.6	111.3	111.1	111.2	111.0	111.4	111.0	111.2	111.7	111.6	111.6	111.5
$\angle C_2C_3H_{32}$	110.1	110.3	110.7	111.0	111.6	111.2	111.2	111.1	111.1	110.4	110.7	111.3	110.8	110.8	110.8	110.8
$\angle H_{32}C_3H_{33}$	107.7	107.5	107.3	107.3	106.5	106.7	106.7	106.9	106.9	107.5	107.4	106.5	106.8	106.8	106.9	107.7*
<i>Rotational TS (C_s) (this structure is a minimum at MNDO)</i>																
rC ₁ C ₂	1.356	1.346	1.339	1.310	1.331	1.338	1.339	1.327	1.328	1.306	1.324	1.321	1.330	1.330	1.320	1.320
rC ₂ C ₃	1.494	1.478	1.508	1.502	1.489	1.509	1.517	1.502	1.507	1.507	1.502	1.483	1.505	1.512	1.498	1.503
rC ₁ H ₁	1.099	1.104	1.092	1.071	1.084	1.093	1.093	1.086	1.086	1.069	1.076	1.093	1.088	1.086	1.081	1.079
rC ₁ F ₁	1.323	1.350	1.337	1.334	1.360	1.359	1.368	1.347	1.353	1.328	1.351	1.340	1.363	1.374	1.347	1.356
rC ₃ H ₂	1.094	1.101	1.095	1.085	1.097	1.094	1.094	1.087	1.087	1.072	1.077	1.093	1.089	1.088	1.082	1.081
rC ₁ H ₃₁	1.109	1.117	1.097	1.083	1.091	1.100	1.101	1.093	1.093	1.080	1.084	1.097	1.094	1.094	1.088	1.088
rC ₃ H ₃₂	1.110	1.120	1.099	1.085	1.094	1.104	1.104	1.096	1.097	1.082	1.087	1.102	1.098	1.097	1.091	1.091
$\angle C_1C_3C_1$	128.4	124.5	123.5	124.4	123.0	124.3	124.1	124.1	124.0	125.0	124.0	123.8	125.4	125.4	125.1	125.0
$\angle H_1C_1C_2$	122.0	123.2	125.8	125.9	126.7	126.0	126.3	125.9	126.2	125.5	126.1	126.3	126.2	126.6	125.9	126.3
$\angle F_1C_1C_2$	124.5	123.7	122.3	121.9	120.9	121.9	121.6	121.8	121.6	122.0	121.4	121.0	121.9	121.7	121.9	121.6
$\angle C_1C_2H_2$	116.7	118.6	118.6	116.6	116.9	116.3	116.5	116.4	116.6	115.9	115.7	116.0	115.4	115.6	115.6	115.8
$\angle C_2C_3H_{31}$	110.7	111.0	111.8	111.1	111.9	111.2	111.2	111.2	111.2	110.6	110.9	111.7	111.0	110.9	111.0	111.0
$\angle C_2C_3H_{32}$	111.5	110.5	111.1	111.1	111.5	111.5	111.5	111.4	111.4	111.1	111.1	111.4	111.5	111.4	111.4	111.4
$\angle H_{32}C_3H_{33}$	107.9	107.7	107.3	107.5	107.2	106.8	106.7	106.9	106.9	107.6	107.3	106.3	106.8	106.9	107.0	107.0
<i>trans-1-Fluoropropene (C_s)</i>																
rC ₁ C ₂	1.356	1.340	1.310	1.331	1.330	1.338	1.339	1.327	1.328	1.305	1.323	1.320	1.329	1.329	1.319	1.319
rC ₂ C ₃	1.494	1.478	1.502	1.497	1.483	1.504	1.511	1.496	1.502	1.500	1.497	1.478	1.499	1.507	1.492	1.498
rC ₁ H ₁	1.099	1.104	1.093	1.073	1.085	1.095	1.095	1.087	1.087	1.071	1.078	1.096	1.089	1.088	1.083	1.081
rC ₁ F ₁	1.324	1.351	1.338	1.333	1.358	1.357	1.364	1.344	1.350	1.327	1.350	1.337	1.362	1.373	1.346	1.342
rC ₂ H ₂	1.094	1.101	1.097	1.077	1.087	1.095	1.096	1.088	1.088	1.074	1.079	1.096	1.091	1.090	1.084	1.083
rC ₃ H ₃₁	1.109	1.118	1.098	1.085	1.094	1.102	1.103	1.095	1.096	1.082	1.087	1.101	1.096	1.096	1.090	1.090*
rC ₃ H ₃₂	1.111	1.119	1.098	1.086	1.094	1.105	1.106	1.098	1.098	1.083	1.087	1.103	1.099	1.099	1.092	1.090*
$\angle C_1C_2C_3$	125.0	122.7	121.8	123.5	122.7	123.2	123.3	123.2	123.4	123.4	122.3	122.8	123.2	123.4	123.2	123.4
$\angle H_1C_1C_2$	124.0	124.0	126.2	125.9	124.4	125.4	125.5	125.4	125.5	125.7	125.5	125.1	126.0	126.4	125.7	126.1
$\angle F_1C_1C_2$	122.6	122.7	121.7	122.1	122.8	122.6	122.5	122.5	122.3	122.1	122.1	122.4	122.2	122.0	122.2	122.0
$\angle C_1C_2H_2$	120.7	121.0	121.4	118.1	118.3	118.3	118.3	118.2	118.1	118.3	118.2	117.9	118.2	118.3	118.2	118.1
$\angle C_2C_3H_{31}$	113.2	112.1	113.0	111.6	111.5	111.7	111.7	111.7	111.6	111.4	111.1	111.3	111.7	111.7	111.6	111.6
$\angle C_2C_3H_{32}$	110.3	110.0	110.4	110.9	111.1	111.3	111.3	111.2	111.3	110.7	111.0	111.6	111.1	111.1	111.1	111.0
$\angle H_{32}C_3H_{33}$	107.8	108.1	107.5	107.3	106.4	106.7	106.7	106.9	106.9	107.5	107.5	106.5	106.8	106.9	106.9	107.0
<i>Rotational TS (C_s)</i>																
rC ₁ C ₂	1.357	1.346	1.310	1.331	1.330	1.338	1.339	1.327	1.328	1.305	1.323	1.320	1.329	1.329	1.319	1.319
rC ₂ C ₃	1.495	1.474	1.480	1.511	1.493	1.514	1.521	1.507	1.512	1.511	1.507	1.488	1.510	1.518	1.503	1.508
rC ₁ H ₁	1.099	1.103	1.093	1.073	1.086	1.095	1.095	1.088	1.087	1.071	1.078	1.096	1.089	1.088	1.083	1.081
rC ₁ F ₁	1.324	1.350	1.338	1.333	1.358	1.357	1.365	1.345	1.351	1.327	1.350	1.338	1.362	1.373	1.346	1.355
rC ₂ H ₂	1.094	1.101	1.096	1.076	1.086	1.095	1.095	1.088	1.088	1.073	1.079	1.095	1.090	1.089	1.084	1.082
rC ₃ H ₃₁	1.109	1.118	1.097	1.083	1.091	1.100	1.101	1.093	1.094	1.080	1.084	1.098	1.095	1.094	1.088	1.088
rC ₃ H ₃₂	1.111	1.119	1.099	1.085	1.094	1.104	1.105	1.097	1.097	1.082	1.086	1.101	1.098	1.097	1.091	1.091
$\angle C_1C_2C_3$	124.3	122.2	121.3	123.7	122.9	123.6	123.7	123.6	123.8	123.6	122.7	123.6	123.7	123.8	123.7	123.8
$\angle H_1C_1C_2$	123.9	123.9	126.1	126.0	125.0	125.7	125.9	125.7	125.8	125.9	125.9	125.7	126.4	126.8	126.1	126.4

Ref. [26]

Table 1 (continued)

Parameter	6-31G* basis					TZ2P basis					Ref.[27]	Ref.[28]							
	PM3	MINDO	AMI	PM3	HF	MP2	SVWN	BP	BLYP	ACM			B3LYP	HF	MP2	SVWN	BP	BLYP	ACM
$\angle \text{F}_1\text{C}_1\text{C}_2$	122.6	122.8	121.7	121.8	122.0	121.8	122.5	122.4	122.3	122.3	122.2	122.0	121.9	122.1	122.0	121.8	122.0	121.9	121.9
$\angle \text{C}_1\text{C}_2\text{H}_2$	120.6	120.8	121.1	117.6	117.6	117.6	117.1	117.6	117.6	117.5	117.5	117.7	117.6	117.0	117.5	117.7	117.5	117.5	117.5
$\angle \text{C}_1\text{C}_2\text{H}_{31}$	110.8	110.6	111.5	110.3	110.4	110.3	111.0	110.6	110.5	110.6	110.5	110.2	110.3	111.0	110.5	110.4	110.5	110.5	110.5
$\angle \text{C}_2\text{C}_3\text{H}_{12}$	111.6	110.9	111.4	111.8	111.8	111.9	112.4	112.2	112.2	112.1	112.1	111.7	111.7	112.2	112.0	112.0	111.9	112.0	112.0
$\angle \text{H}_{12}\text{C}_3\text{H}_{31}$	107.8	108.0	107.5	107.8	107.8	107.8	107.0	107.3	107.2	107.4	107.4	108.1	107.9	107.2	107.5	107.5	107.6	107.6	107.6
2-Fluoropropene (C₃)																			
rC ₁ C ₂	1.358	1.344	1.338	1.312	1.312	1.332	1.331	1.339	1.340	1.329	1.329	1.308	1.325	1.322	1.331	1.331	1.321	1.321	1.321
rC ₂ C ₃	1.518	1.491	1.492	1.491	1.491	1.488	1.477	1.497	1.503	1.489	1.493	1.489	1.486	1.469	1.490	1.495	1.483	1.487	1.487
rC ₁ H ₁	1.087	1.095	1.085	1.072	1.072	1.082	1.094	1.090	1.091	1.083	1.083	1.069	1.074	1.089	1.085	1.084	1.079	1.078	1.078
rC ₁ H ₂	1.088	1.096	1.086	1.073	1.073	1.082	1.094	1.091	1.091	1.084	1.084	1.071	1.075	1.090	1.086	1.085	1.080	1.079	1.079
rC ₂ F ₂	1.331	1.359	1.347	1.338	1.338	1.365	1.342	1.365	1.374	1.352	1.358	1.332	1.357	1.347	1.372	1.383	1.354	1.362	1.362
rC ₃ H ₃₁	1.108	1.116	1.097	1.082	1.082	1.091	1.102	1.099	1.100	1.092	1.093	1.079	1.084	1.097	1.094	1.094	1.088	1.087	1.087
rC ₃ H ₃₂	1.109	1.118	1.098	1.085	1.085	1.094	1.107	1.104	1.105	1.097	1.097	1.083	1.087	1.102	1.098	1.098	1.092	1.091	1.091
$\angle \text{C}_1\text{C}_2\text{C}_3$	125.0	123.8	124.7	128.7	128.7	128.8	128.1	128.5	128.7	128.4	128.6	128.7	128.7	128.8	129.2	129.6	128.9	129.2	129.2
$\angle \text{H}_1\text{C}_1\text{C}_2$	122.2	121.2	121.7	120.4	120.4	120.2	120.2	120.3	120.4	120.3	120.4	120.0	119.3	119.8	119.9	120.0	119.9	120.0	120.0
$\angle \text{H}_2\text{C}_1\text{C}_2$	123.7	122.4	123.3	121.0	121.0	120.8	120.9	121.2	121.2	121.1	121.1	121.0	120.8	120.8	121.2	121.2	121.0	121.1	121.1
$\angle \text{C}_1\text{C}_2\text{F}_2$	120.1	121.4	120.6	119.7	119.7	119.4	119.9	119.6	119.5	119.7	119.6	119.6	119.4	119.4	119.1	118.9	119.3	119.1	119.1
$\angle \text{C}_2\text{C}_3\text{H}_{31}$	111.1	110.4	111.2	111.0	111.0	110.7	111.2	111.1	111.0	111.1	111.0	110.6	110.3	110.8	110.7	110.6	110.7	110.7	110.7
$\angle \text{C}_2\text{C}_3\text{H}_{32}$	110.9	110.0	110.9	110.1	110.1	110.2	110.6	110.6	110.6	110.4	110.5	109.9	110.1	110.4	110.4	110.4	110.3	110.3	110.3
$\angle \text{H}_{12}\text{C}_3\text{H}_{31}$	108.2	108.3	107.6	107.6	107.6	107.7	106.8	107.1	107.1	107.2	107.2	107.9	107.9	107.1	107.4	107.4	107.5	107.5	107.5
Rotational TS (C₃)																			
rC ₁ C ₂	1.358	1.345	1.338	1.312	1.312	1.332	1.331	1.339	1.340	1.329	1.329	1.308	1.325	1.321	1.330	1.331	1.321	1.321	1.321
rC ₂ C ₃	1.518	1.492	1.494	1.502	1.502	1.499	1.488	1.509	1.515	1.501	1.505	1.502	1.497	1.480	1.501	1.507	1.494	1.498	1.498
rC ₁ H ₁	1.087	1.095	1.085	1.073	1.073	1.082	1.094	1.091	1.091	1.084	1.084	1.070	1.075	1.090	1.086	1.085	1.079	1.079	1.079
rC ₁ H ₂	1.088	1.096	1.085	1.073	1.073	1.082	1.094	1.091	1.091	1.084	1.084	1.071	1.075	1.090	1.086	1.085	1.080	1.079	1.079
rC ₂ F ₂	1.331	1.359	1.346	1.337	1.337	1.365	1.342	1.365	1.373	1.352	1.358	1.331	1.357	1.347	1.371	1.383	1.354	1.362	1.362
rC ₃ H ₃₁	1.108	1.117	1.098	1.082	1.082	1.091	1.103	1.099	1.100	1.093	1.093	1.079	1.084	1.098	1.094	1.093	1.088	1.087	1.087
rC ₃ H ₃₂	1.109	1.117	1.098	1.084	1.084	1.093	1.105	1.102	1.103	1.095	1.096	1.081	1.085	1.100	1.096	1.096	1.090	1.089	1.089
$\angle \text{C}_1\text{C}_2\text{C}_3$	124.2	123.2	124.0	128.1	128.1	128.2	127.9	128.1	128.3	128.0	128.2	128.1	128.2	128.5	128.8	129.1	128.5	128.7	128.7
$\angle \text{H}_1\text{C}_1\text{C}_2$	122.0	121.0	121.4	120.3	120.3	120.1	120.2	120.3	120.3	120.3	120.4	119.9	119.3	119.8	119.9	120.0	119.9	120.0	120.0
$\angle \text{H}_2\text{C}_1\text{C}_2$	123.8	122.5	123.4	121.0	121.0	120.9	120.9	121.2	121.2	121.1	121.1	121.1	120.9	120.8	121.2	121.3	121.1	121.1	121.1
$\angle \text{C}_1\text{C}_2\text{F}_2$	120.1	121.4	120.5	119.4	119.4	119.1	119.5	119.3	119.2	119.3	119.2	119.3	119.0	119.0	118.8	118.6	119.0	118.9	118.9
$\angle \text{C}_2\text{C}_3\text{H}_{31}$	112.6	111.0	112.8	109.7	109.7	109.3	109.6	109.8	109.7	109.7	109.7	109.7	109.6	109.8	110.0	109.9	109.9	109.9	109.9
$\angle \text{C}_2\text{C}_3\text{H}_{32}$	110.3	109.8	110.4	111.1	111.1	111.2	111.7	111.4	111.5	111.4	111.4	110.8	111.3	111.3	111.1	111.1	111.1	111.1	111.1
$\angle \text{H}_{12}\text{C}_3\text{H}_{31}$	108.1	108.6	107.8	108.0	108.0	108.1	107.5	107.6	107.6	107.7	107.7	108.3	108.3	107.8	107.9	107.9	108.0	108.0	108.0
cis-3-Fluoropropene (C₃)																			
rC ₁ C ₂	1.340	1.329	1.326	1.316	1.316	1.336	1.332	1.340	1.342	1.331	1.331	1.312	1.329	1.324	1.333	1.334	1.323	1.324	1.333
rC ₂ C ₃	1.517	1.495	1.496	1.497	1.497	1.495	1.483	1.502	1.508	1.495	1.499	1.496	1.493	1.474	1.496	1.501	1.489	1.493	1.495
rC ₁ H ₁₁	1.089	1.099	1.087	1.074	1.074	1.083	1.097	1.092	1.093	1.086	1.085	1.072	1.077	1.093	1.088	1.087	1.082	1.080	1.083
rC ₁ H ₁₂	1.090	1.098	1.086	1.075	1.075	1.084	1.096	1.093	1.093	1.086	1.086	1.072	1.077	1.091	1.087	1.087	1.081	1.080	1.084*
rC ₂ H ₂	1.096	1.102	1.096	1.079	1.079	1.089	1.101	1.097	1.098	1.090	1.090	1.076	1.081	1.097	1.093	1.092	1.086	1.085	1.089*
rC ₂ F ₃	1.352	1.382	1.359	1.367	1.367	1.395	1.369	1.394	1.403	1.380	1.387	1.363	1.389	1.376	1.402	1.415	1.384	1.394	1.388
rC ₃ H ₃₁	1.125	1.128	1.104	1.084	1.084	1.096	1.114	1.109	1.109	1.100	1.100	1.083	1.088	1.107	1.102	1.100	1.095	1.093	1.096

Table 1 (continued)

Parameter	6-31G* basis					TZ2P basis													
	MNDO	AMI	PM3	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP		
$\angle C_1C_2C_3$	129.3	125.0	124.9	124.7	123.6	122.5	124.3	124.3	124.2	124.1	125.4	124.3	123.8	125.5	125.6	125.2	124.4	124.5	
$\angle H_{11}C_1C_2$	124.9	122.4	123.6	121.5	121.1	119.9	121.0	121.0	121.0	121.0	121.6	120.9	120.3	121.3	121.4	121.3	120.8	121.1	
$\angle H_{12}C_1C_2$	121.8	122.3	121.3	121.3	121.3	122.0	121.6	121.5	121.5	121.6	120.8	120.7	121.5	121.0	121.1	121.0	121.1	121.3	
$\angle C_1C_2H_3$	119.3	121.9	121.3	120.6	120.9	121.7	120.9	121.1	120.9	121.0	120.4	120.5	121.1	120.4	120.5	120.5	120.6	120.9	
$\angle C_2C_3F_1$	115.1	114.2	114.4	111.3	111.0	111.3	112.0	111.7	111.8	111.6	111.8	111.5	111.7	112.4	112.1	112.1	111.9	111.5	
$\angle C_2C_3H_{11}$	108.4	108.9	110.3	110.7	111.0	110.5	110.5	110.7	110.5	110.7	110.5	110.7	110.8	110.7	111.0	110.6	110.8	111.1	
$\angle H_{11}C_1H_{12}$	106.6	108.3	108.5	108.2	108.1	106.6	107.2	107.2	107.4	107.4	108.4	108.5	107.4	107.9	108.2	107.9	107.9	108.0	
<i>gauche-3-Fluoropropene (C₁) (this structure does not exist at MNDO and AM1)</i>																			
rC_1C_2	–	–	1.327	1.318	1.338	1.333	1.342	1.343	1.332	1.333	1.313	1.331	1.325	1.334	1.336	1.325	1.326	1.338	Ref.[28]
rC_2C_3	–	–	1.499	1.496	1.492	1.482	1.501	1.506	1.494	1.497	1.495	1.489	1.474	1.494	1.498	1.488	1.491	1.523	1.490
rC_1H_{11}	–	–	1.087	1.077	1.086	1.100	1.095	1.096	1.089	1.088	1.074	1.079	1.095	1.090	1.089	1.084	1.083	1.072	1.086*
rC_1H_{12}	–	–	1.086	1.075	1.085	1.097	1.093	1.094	1.087	1.086	1.072	1.077	1.092	1.088	1.087	1.082	1.081	1.096	1.084*
rC_2H_2	–	–	1.097	1.077	1.088	1.101	1.097	1.097	1.090	1.090	1.075	1.080	1.097	1.092	1.091	1.085	1.084	1.074	1.088*
rC_2F_3	–	–	1.360	1.373	1.402	1.377	1.404	1.413	1.389	1.395	1.370	1.400	1.387	1.416	1.430	1.396	1.406	1.364	1.394
rC_3H_{11}	–	–	1.103	1.082	1.094	1.111	1.105	1.105	1.097	1.097	1.080	1.087	1.105	1.098	1.097	1.091	1.090	1.115	1.095*
rC_3H_{12}	–	–	1.104	1.083	1.095	1.113	1.107	1.108	1.099	1.099	1.082	1.087	1.106	1.100	1.099	1.094	1.092	1.097	1.095*
$\angle C_1C_2C_3$	–	–	121.6	124.1	123.3	123.6	124.1	124.1	124.0	124.1	123.8	122.8	123.3	123.7	123.9	123.7	123.8	124.4	123.3
$\angle H_{11}C_1C_2$	–	–	123.2	121.9	121.5	121.1	121.7	121.7	121.7	121.7	121.7	120.9	120.8	121.5	121.6	121.4	121.5	122.4	121.5*
$\angle H_{12}C_1C_2$	–	–	122.6	121.7	121.7	122.1	121.9	121.9	121.8	121.9	121.5	121.5	122.0	121.7	121.7	121.6	121.7	119.3	121.8*
$\angle C_1C_2H_3$	–	–	121.6	120.5	120.7	120.8	120.5	120.5	120.5	120.6	120.4	120.5	120.7	120.4	120.4	120.5	120.5	119.5	120.7*
$\angle C_2C_3F_1$	–	–	112.4	109.9	109.7	110.6	110.5	110.2	110.4	110.2	110.1	110.1	110.5	110.4	110.1	110.4	110.1	109.5	110.4
$\angle C_2C_3H_{11}$	–	–	111.9	111.5	111.2	110.5	111.1	111.2	111.1	111.2	111.3	110.9	110.9	111.6	111.8	111.4	111.6	107.2	111.5*
$\angle C_2C_3H_{12}$	–	–	110.6	111.1	111.5	110.5	110.7	111.0	110.8	110.9	110.9	111.5	111.1	111.3	111.7	111.1	111.4	105.5	111.2*
$\angle H_{11}C_1H_{12}$	–	–	108.4	109.0	108.9	107.8	108.3	108.5	108.4	108.5	109.3	109.5	108.8	109.2	109.6	109.1	109.2	111.3	108.9*
$rC_1C_2C_3F_1$	–	–	165.1	130.2	127.6	130.7	129.2	127.8	130.1	128.6	126.9	122.8	127.2	125.0	123.4	126.4	124.7	124.3	124.6
$rC_1C_2C_3H_{11}$	–	–	45.1	10.2	7.9	9.1	8.3	7.1	9.4	8.1	7.1	3.4	6.8	5.3	4.1	6.4	5.1	–	–
$rC_1C_2C_3H_{12}$	–	–	75.9	111.5	113.9	110.0	112.2	113.7	111.2	112.8	114.9	118.9	114.2	117.1	119.1	115.4	117.4	–	–
<i>gauche-gauche Rotational TS (C₁) (this structure is a trans minimum at MNDO and AM1)</i>																			
rC_1C_2	1.341	1.330	1.327	1.317	1.337	1.333	1.341	1.342	1.331	1.332	1.313	1.330	1.324	1.334	1.335	1.324	1.325	1.338	1.335
rC_2C_3	1.519	1.497	1.499	1.505	1.502	1.491	1.511	1.517	1.503	1.507	1.504	1.501	1.482	1.504	1.510	1.497	1.501	1.523	1.490
rC_1H_{11}	1.089	1.098	1.087	1.078	1.087	1.100	1.096	1.096	1.089	1.089	1.075	1.079	1.095	1.090	1.090	1.084	1.083	1.072	1.086*
rC_1H_{12}	1.089	1.098	1.086	1.075	1.084	1.096	1.093	1.093	1.086	1.086	1.072	1.077	1.091	1.087	1.087	1.081	1.080	1.096	1.084*
rC_2H_2	1.094	1.102	1.097	1.076	1.087	1.101	1.096	1.096	1.089	1.089	1.074	1.079	1.097	1.091	1.090	1.085	1.083	1.074	1.088*
rC_2F_3	1.353	1.383	1.360	1.370	1.398	1.372	1.397	1.406	1.384	1.390	1.368	1.394	1.381	1.407	1.420	1.389	1.399	1.364	1.394
rC_3H_{11}	1.124	1.127	1.103	1.083	1.095	1.112	1.106	1.107	1.098	1.098	1.081	1.087	1.105	1.100	1.098	1.093	1.091	1.115	1.095*
$\angle C_1C_2C_3$	124.6	122.7	121.5	124.5	124.0	125.1	125.1	125.0	124.9	124.9	124.4	123.7	124.9	124.9	124.8	124.8	124.7	124.5	124.5
$\angle H_{11}C_1C_2$	124.2	122.9	123.2	122.2	122.1	121.9	122.3	122.3	122.2	122.3	122.0	121.7	121.8	122.2	122.2	122.2	122.2	122.2	122.2
$\angle H_{12}C_1C_2$	122.2	122.1	122.6	121.4	121.3	121.5	121.4	121.5	121.4	121.4	121.2	121.0	121.3	121.2	121.2	121.2	121.2	121.2	121.2
$\angle C_1C_2H_3$	119.6	122.1	121.5	120.7	120.9	120.9	120.5	120.7	120.6	120.7	120.6	120.9	120.9	120.5	120.7	120.6	120.7	120.9	120.9
$\angle C_2C_3F_1$	112.9	112.3	112.4	109.4	109.4	110.1	110.1	109.8	109.9	109.7	109.6	109.8	110.3	110.2	110.0	110.2	109.9	111.7	109.9
$\angle C_2C_3H_{11}$	109.7	109.8	111.3	111.6	111.7	111.0	111.3	111.5	111.4	111.5	111.5	111.5	111.4	111.7	111.9	111.5	111.7	111.2*	108.9*
$\angle H_{11}C_1H_{12}$	106.6	108.4	108.4	108.8	108.6	107.3	107.9	107.9	108.0	108.1	109.1	109.1	108.2	108.7	109.0	108.7	108.7	108.7	108.7

Table 1 (continued)

Parameter	6-31G* basis						TZ2P basis										
	MNDO	AM1	PM3	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP
<i>cis-gauche Rotational TS (C₁) (this structure is a cis-trans rotational TS at MNDO and AM1)</i>																	
rC ₁ C ₂	1.340	1.330	1.327	1.318	1.338	1.334	1.342	1.344	1.332	1.333	1.313	1.331	1.325	1.334	1.336	1.325	1.326
rC ₂ C ₃	1.521	1.500	1.502	1.507	1.502	1.494	1.513	1.518	1.505	1.509	1.507	1.501	1.487	1.506	1.511	1.500	1.503
rC ₁ H ₁₁	1.089	1.099	1.087	1.077	1.086	1.100	1.095	1.095	1.088	1.088	1.074	1.079	1.095	1.090	1.089	1.084	1.082
rC ₁ H ₁₂	1.090	1.098	1.086	1.075	1.085	1.097	1.094	1.094	1.087	1.087	1.072	1.077	1.092	1.088	1.087	1.082	1.081
rC ₂ H ₂	1.094	1.101	1.095	1.077	1.087	1.100	1.096	1.096	1.089	1.089	1.074	1.079	1.095	1.091	1.090	1.084	1.083
rC ₁ F ₃	1.354	1.384	1.361	1.373	1.403	1.379	1.405	1.414	1.390	1.396	1.370	1.400	1.388	1.415	1.429	1.396	1.405
rC ₃ H ₃₁	1.123	1.126	1.102	1.081	1.093	1.109	1.104	1.104	1.096	1.096	1.079	1.085	1.102	1.097	1.096	1.091	1.089
rC ₃ H ₃₂	1.124	1.127	1.103	1.082	1.094	1.111	1.105	1.106	1.097	1.097	1.080	1.086	1.105	1.099	1.098	1.092	1.091
∠C ₁ C ₂ C ₃	126.3	123.4	122.1	123.1	121.9	122.0	123.2	123.1	122.9	123.0	123.4	122.3	122.3	123.7	123.8	123.4	123.4
∠H ₁₁ C ₁ C ₂	124.3	122.6	123.0	121.7	121.3	121.0	121.6	121.6	121.6	121.6	121.7	121.1	121.0	121.7	121.7	121.6	121.6
∠H ₁₂ C ₁ C ₂	122.2	122.3	122.7	121.7	121.8	122.1	121.8	121.9	121.8	121.8	121.3	121.2	121.8	121.4	121.4	121.4	121.5
∠C ₁ C ₂ H ₂	119.9	121.7	121.7	119.8	120.0	120.0	119.6	119.8	119.7	119.8	119.8	119.9	119.9	119.6	119.7	119.7	119.8
∠C ₂ C ₃ F ₃	112.9	112.8	111.9	110.9	110.4	110.9	111.2	111.1	111.1	111.0	111.2	110.7	110.8	111.3	111.2	111.1	111.1
∠C ₂ C ₃ H ₃₁	109.1	109.7	111.6	111.2	111.6	111.2	111.0	111.0	111.1	111.1	110.9	111.4	111.6	111.4	111.5	111.3	111.4
∠C ₂ C ₃ H ₃₂	110.1	109.7	111.6	111.2	111.2	110.3	110.9	111.1	110.9	111.0	111.2	111.4	111.0	111.5	111.8	111.3	111.6
∠H ₃₁ C ₃ H ₃₂	106.1	108.3	108.3	108.7	108.8	107.7	108.2	108.3	108.3	108.3	108.9	109.2	108.5	108.9	109.1	108.8	108.8
rC ₁ C ₂ C ₃ F ₃	76.2	72.7	76.9	62.9	62.4	64.5	63.1	62.7	63.6	62.9	60.3	58.4	61.3	58.7	57.2	59.8	59.1
rC ₁ C ₂ C ₃ H ₃₁	162.2	166.8	163.8	177.5	177.9	174.5	176.5	177.1	176.1	176.9	179.8	177.7	178.8	178.0	176.2	179.3	178.4
rC ₁ C ₂ C ₃ H ₃₂	46.2	47.9	42.5	56.3	56.3	55.0	56.3	56.5	55.7	56.3	58.8	60.2	57.5	60.1	61.2	59.2	59.6
Value fixed by calculation (usually at the MP2/6-31G level)																	
Error in C–F bond lengths																	
Ave. error	0.024	0.008	0.018	0.015	0.012	0.012	0.012	0.020	0.005	0.005	0.020	0.006	0.007	0.019	0.032	0.004	0.011
Max. error	0.036	0.009	0.034	0.021	0.018	0.019	0.017	0.025	0.008	0.011	0.025	0.009	0.012	0.022	0.036	0.005	0.014
Average error in all bond lengths (excluding # fixed)																	
Ave. error	0.014	0.014	0.010	0.011	0.005	0.011	0.009	0.013	0.003	0.004	0.014	0.006	0.010	0.007	0.010	0.005	0.006

bonds too long, and although the average error in C–F bond lengths with this basis is certainly better than for the BP or BLYP functionals alone, it is much worse than for ACM and worse even than for SVWN. The B3LYP/6-31G* results are much better for bond lengths, and the average error here (for C–F bonds and for ‘all’ bond lengths) is very similar to that for the ACM functional.

Geometrical trends with the ACM and B3LYP hybrid functionals not surprisingly mirror those of the BP and BLYP functionals that comprise them. ACM bond lengths are lower than those with the BP functional, and correspondingly, B3LYP bond lengths are lower than with BLYP. However, although both BP and BLYP bond distances are generally too long, BLYP are usually longer, and in worse agreement with experiment. Inclusion of HF exchange in the hybrid functional reduces calculated bond distances by about the same amount for each functional, but whereas for ACM this reduction brings values down nicely to close agreement with experiment, it is insufficient for B3LYP. However, it should be noted that—apart from the C–F bond lengths—BP and BLYP bond distances are as good as those from any other method, and their errors when ‘all’ bond lengths are considered are significantly reduced.

The best of the semiempirical methods for predicting C–F bond lengths is AM1, which is almost as good as MP2/TZ2P (and better than all but the best of the ab initio methods); however, if ‘all’ bond lengths are considered, AM1 is now one of the worst methods, and PM3 is noticeably better.

Table 2a reports relative energies between the various fluoropropene isomers and rotational barrier heights. Before commenting on the energetics, some remarks as to the nature of some of the optimized structures are in order. Experimentally, and in all the ab initio calculations, the fluoropropene structures and their nature are as depicted in Fig. 1. With AM1 and, especially, MNDO, the character of some of the stationary points changes, and in consequence the corresponding potential energy surfaces (PES) are incorrect.

The most problems occur with 3-fluoropropene. Experimentally there are two minima, a *cis* isomer (with C_s symmetry) and a *gauche* (with C_1). These are connected (rotating about the C–C single bond) by a C_s *trans* structure, which connects two symmetry equivalent *gauche* isomers and is therefore a *gauche–gauche* rotational TS, and by another *gauche*-like (C_1) structure which is the *cis–gauche* TS. This situation is depicted in Fig. 2a. With MNDO and AM1, the *cis* minimum exists but the *gauche* minimum does not; instead what was the *gauche–gauche* TS is now a *trans* minimum and the *cis* and *trans* minima are connected by a *gauche*-like TS (which is structurally very like the *cis–gauche* rotational TS but is in fact now a *cis–trans* TS). This is depicted schematically in Fig. 2b. Note that the PES is qualitatively correct with PM3 (to its credit), although the CCCF dihedral angle in the *gauche* isomer differs by some 40° from its true value (see Table 1), and the PM3 *gauche* minimum looks very much like the *gauche–gauche* TS.

Additionally, MNDO has a further anomaly. This occurs for *cis*-1-fluoropropene where the rotational TS is actually a *minimum*, and what is structurally the minimum at all other levels of theory is the rotational TS, i.e., the two structures have switched. This is accounted for in Table 4a by the *negative* rotational barrier with MNDO for *cis*-1-fluoropropene.

Turning to the actual values, agreement with the experimental energy differences and barriers is perhaps best described as fair. Apart from the energy difference between *cis*- and *gauche*-3-fluoropropene, ab initio results with the smaller 6-31G* basis are almost identical to those with the TZ2P basis with all methods giving very similar values, although there is a tendency for values with the larger basis to be slightly smaller and also for SVWN to give higher values than the other methods. Compared to the quoted experimental quantities, the ab initio values are on the low side. For rotational barriers, much of this can be ‘blamed’ on the ZPVE correction, the uncorrected barrier heights are in much better agreement. (For example, the ZPVE correction to the rotational barrier in propene is 0.9 kcal/mol, adding this back to the calculated values improves the agreement significantly.)

For 3-fluoropropene, the *cis–gauche* energy difference reduces substantially between the two basis sets (in fact BLYP/TZ2P erroneously predicts the *gauche* conformer to be more stable than the *cis*). However, as can be seen from the two quoted experimental values, evidence can be found to support either set of results. The larger experimental value (0.8 kcal/mol) is the more recent, and in calculating the theoretical errors, this was the value taken.

Surprisingly, the best results overall for the energetics are provided by SVWN/TZ2P, with an average error of 0.3 kcal/mol, followed by HF/TZ2P, HF/6-31G* and B3LYP/6-31G*, all with average errors of 0.4 kcal/mol. Hartree–Fock also gave good rotational barriers for the fluoroethanes [6]. Most of the other ab initio methods have an average error of 0.5 kcal/mol. Although the worst average error (for BP/TZ2P and BLYP/TZ2P) is only 0.7 kcal/mol, this is quite a large error in percentage terms, as the energy differences we are considering are all fairly small.

The B3LYP and ACM functionals give almost identical energetics. However, for three of the reported rotational barriers, B3LYP/6-31G* values are fractionally (0.1 kcal/mol) higher than the corresponding ACM values, and this is sufficient to make the average error with B3LYP lower than for ACM. This is hardly significant and average (and maximum) errors with the TZ2P basis for the two hybrids are identical.

The semiempirical results are poor. Barrier heights are far too low and the relative energies between the stable structures often have the wrong order. For example, apart from the slight misordering between *cis*- and *gauche*-3-fluoropropene at BLYP/TZ2P (noted above), all the ab initio methods predict that the energy ordering among the various monofluoropropene isomers is: 2-fluoro > *cis*-1-fluoro > *trans*-1-fluoro > *cis*-3-fluoro > *gauche*-3-fluoro. The available experimental data supports this relative stability—the ordering *cis*-1-fluoro > *trans*-1-fluoro and *cis*-3-fluoro > *gauche*-3-fluoro is

Table 2
a. Relative energies and barrier heights for propene and the monofluoropropenes (kcal/mol)

Species	6-31G* basis						TZ2P basis						Expt.					
	MNDO	AMI	PM3	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	HF	MP2		SVWN	BP	BLYP	ACM	B3LYP
Rotational barrier in propene	0.2	0.6	0.7	1.2	1.1	1.4	1.1	1.2	1.1	1.2	1.3	1.1	1.3	1.0	1.0	1.1	1.1	Ref. [25]
Energy of <i>trans</i> -1-fluoropropene relative to <i>cis</i> -1-fluoropropene	-0.4	-0.4	-0.2	0.5	0.6	0.7	0.4	0.5	0.4	0.5	0.4	0.6	0.7	0.4	0.4	0.4	0.5	Ref. [31]
Rotational barrier in <i>cis</i> -1-fluoropropene	-0.1	0.5	0.3	0.9	0.7	0.8	0.8	0.8	0.8	0.9	0.9	0.7	0.9	0.7	0.6	0.7	0.7	Ref. [26]
Rotational barrier in <i>trans</i> -1-fluoropropene	0.2	0.6	0.7	1.7	1.5	1.9	1.6	1.6	1.6	1.6	1.9	1.7	1.8	1.5	1.5	1.6	1.6	Ref. [32]
Rotational barrier in 2-fluoropropene	0.2	0.3	0.6	2.1	1.9	2.0	1.8	1.8	1.9	1.9	2.2	2.0	1.8	1.6	1.7	1.8	1.8	Ref. [30]
Energy of <i>gauche</i> -3-fluoropropene relative to <i>cis</i> -3-fluoropropene	-	-	0.1	0.5	0.7	1.6	0.7	0.7	0.7	0.7	0.1	0.0	1.0	0.0	-0.2	0.2	0.0	Ref. [27]
<i>gauche-gauche</i> rotational barrier in 3-fluoropropene	-	-	0.0	1.0	1.2	1.2	1.1	1.2	1.0	1.1	1.3	1.6	1.4	1.4	1.5	1.2	1.4	Ref. [33]
<i>cis-gauche</i> rotational barrier in 3-fluoropropene	-	-	1.4	2.9	2.7	4.2	2.9	2.8	3.0	3.0	2.7	2.3	3.5	2.3	2.0	2.5	2.4	Ref. [30]
Relative energy of fluoropropene minima relative to 2-fluoropropene	-3.4	-3.9	0.2	4.0	3.9	4.2	3.8	3.9	4.0	4.0	4.1	4.0	4.1	3.6	3.7	3.8	3.8	Ref. [30]
<i>cis</i> -1	-3.8	-4.3	0.0	4.5	4.5	4.9	4.2	4.4	4.4	4.5	4.5	4.6	4.8	4.0	4.1	4.2	4.3	Ref. [30]
<i>cis</i> -3	1.5	-0.9	4.3	6.8	8.5	11.8	10.4	9.7	9.9	9.3	5.9	7.6	10.0	8.8	8.0	8.3	7.8	Ref. [30]
<i>gauche</i> -3	-	-	4.4	7.3	9.2	13.4	11.1	10.4	10.6	10.0	6.0	7.6	11.0	8.8	7.8	8.5	7.8	Ref. [30]
Errors for all reported energy differences/barriers	1.7	1.4	1.3	0.4	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.5	0.3	0.7	0.7	0.6	0.6	Ref. [30]
Ave. error	2.2	2.1	1.9	0.8	0.9	0.9	0.9	0.8	0.9	0.8	0.7	1.0	0.7	1.0	1.3	0.9	0.9	Ref. [30]
Max. error	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Ref. [30]

Species	6-31G* basis						TZ2P basis						Expt.					
	MNDO	AMI	PM3	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	HF	MP2		SVWN	BP	BLYP	ACM	B3LYP
Propene	0.04	0.23	0.23	0.31	0.28	0.43	0.38	0.37	0.36	0.36	0.39	0.34	0.48	0.43	0.42	0.42	0.41	0.37 ^a
<i>cis</i> -1-Fluoro	1.63	1.38	1.40	1.55	1.40	1.10	1.18	1.19	1.27	1.29	1.57	1.44	1.33	1.40	1.48	1.43	1.50	1.46 ^b
<i>trans</i> -1-Fluoro	1.68	1.60	1.59	1.79	1.66	1.35	1.43	1.43	1.52	1.53	1.89	1.75	1.66	1.72	1.80	1.75	1.82	1.85 ^c
2-Fluoro	1.82	1.53	1.52	1.63	1.53	1.29	1.34	1.33	1.41	1.41	1.70	1.62	1.54	1.58	1.63	1.60	1.65	1.60 ^d
<i>cis</i> -3-Fluoro	1.75	1.55	1.45	1.82	1.70	1.47	1.52	1.52	1.60	1.60	1.87	1.78	1.68	1.72	1.78	1.75	1.80	1.76 ^e
<i>gauche</i> -3-Fluoro	-	-	1.55	1.99	1.90	1.56	1.65	1.65	1.73	1.74	2.00	1.96	1.80	1.88	1.97	1.90	1.96	1.93 ^e
Ave. error	0.18	0.15	0.21	0.06	0.08	0.32	0.25	0.25	0.18	0.17	0.08	0.04	0.12	0.06	0.04	0.04	0.04	0.04

^a Ref. [35], ^b Ref. [26], ^c Ref. [36], ^d Ref. [30], ^e Ref. [33].

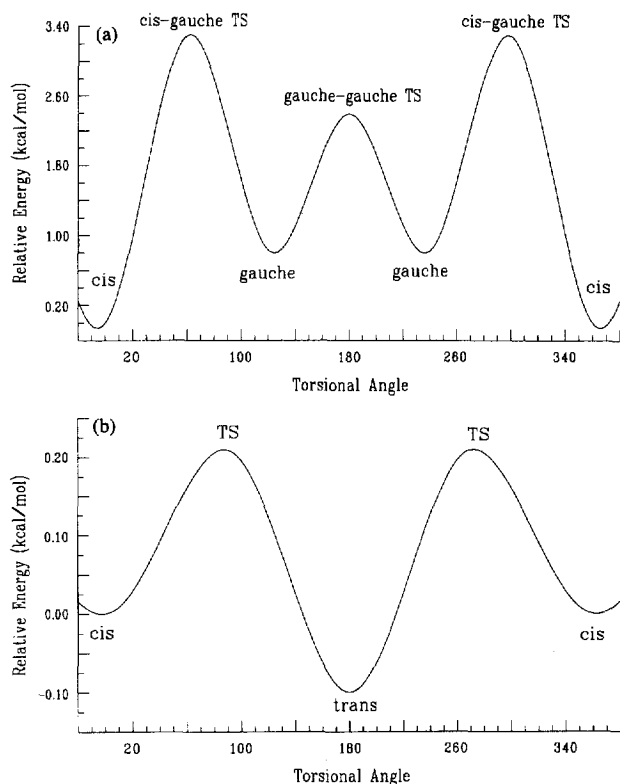


Fig. 2. (a) Schematic of the potential energy surface for rotation about the C–C single bond in 3-fluoropropene at all ab initio levels and experimentally. Starting at the *cis* isomer (C_s ; 0°), there is a *cis-gauche* TS, a *gauche* minimum (ca. 1 kcal/mol higher than the *cis*), a *gauche-gauche* TS (C_s ; 180°), a second (equivalent) *gauche* minimum, a *cis-gauche* TS and back to the *cis* minimum (360°). (b) Schematic of the potential energy surface for rotation about the C–C single bond in 3-fluoropropene at the MNDO and AM1 semiempirical levels. There is no *gauche* minimum; instead the *gauche-gauche* TS is now a *trans* minimum which is lower in energy than the *cis* isomer (see text).

shown in Table 2a and according to Abell and Adolf [34], *cis*-1-fluoropropene is more stable than *cis*-3-fluoropropene by 4.15 ± 0.1 kcal/mol (our best ab initio values are 4.0 kcal/mol at B3LYP/TZ2P, 4.3 kcal/mol at BLYP/TZ2P and 4.5 kcal/mol at ACM/TZ2P). Only PM3 gets anywhere near this ordering; MNDO and AM1 are hopelessly wrong—*gauche*-3-fluoropropene does not exist at all and AM1 has 2-fluoropropene as the *least* stable isomer.

Calculated and experimental dipole moments are given in Table 2b. As can be seen from the table, DFT/6-31G* dipole moments are often far too low and in poor agreement with experimental values. However, they increase—often considerably—with the larger TZ2P basis, and agreement with experiment improves substantially. HF dipole moments, on the other hand, worsen with the larger basis, as 6-31G* values are already slightly too high. MP2 dipoles also increase with the TZ2P basis, and agreement with experiment improves, but to a much lesser extent than with DFT. Exactly the same trends were observed in our previous fluorination study [6], and it does seem that larger basis sets are required to give good dipole moments with DFT compared to the more traditional ab initio methods. Having said that, the best agree-

ment with experiment is provided by ACM/TZ2P, B3LYP/TZ2P, BLYP/TZ2P and MP2/TZ2P, all four methods having an average error of just 0.04 D.

B3LYP dipole moments tend to be larger than for ACM. The effect is only slight with the 6-31G* basis, but is clear with the TZ2P, with all dipoles for the monofluoropropenes greater than the corresponding ACM values by ~ 0.06 D. However, the average error with the two methods (as reported above) is the same, as ACM values are slightly too low by about the same amount that B3LYP values are slightly too high.

Semiempirical dipole moments, although on average better than DFT/6-31G* values, are not particularly good, and experimental trends are not well reproduced. PM3 results appear to be the worst, although one should recall that both AM1 and MNDO erroneously have *no gauche* isomer for 3-fluoropropene, so the comparison is not really fair.

Experimentally, the dipole moment ordering in the monofluoropropenes is *gauche*-3-fluoro > *trans*-1-fluoro > *cis*-3-fluoro > 2-fluoro > *cis*-1-fluoro. This ordering is only reproduced with HF/TZ2P, BLYP/TZ2P and B3LYP/TZ2P—all the 6-31G* calculations along with MP2/TZ2P and SVWN/TZ2P switch the ordering of *trans*-1-fluoropropene and *cis*-3-fluoropropene. With ACM/TZ2P and BLYP/TZ2P, dipole moments for these two compounds are the same (to two decimal places). In general, experimental dipole moments are less prone to error than are, for example, bond lengths, so we expect the experimental values quoted in Table 2b to be reliable. However, apart from B3LYP/TZ2P, our best theoretical methods show the largest error with respect to the quoted experimental values for *trans*-1-fluoropropene and calculated B3LYP/TZ2P and HF/6-31G* dipole moments for all the monofluoropropenes are larger than experiment for *all* species *except trans*-1-fluoropropene. None of this is conclusive of course, but we do consider it a possibility that the experimental dipole moment for *trans*-1-fluoropropene—while not necessarily lower than that of *cis*-3-fluoropropene—*may* be too high.

3.2. Difluoropropenes

Our study includes 1,1-difluoropropene, 1,2-difluoropropene and 3,3-difluoropropene. These have been selected primarily to investigate the fluorine ‘effects’ mentioned in the introduction, i.e., the *geminal* effect (1,1- and 3,3-difluoropropene), and the *cis* effect and the effect of vicinal fluorine substitution across the C=C double bond (1,2-difluoropropene). It is also known experimentally that 3,3-difluoropropene is more stable than 1,1-difluoropropene [31], and this provides another test for the various theoretical models. Structures of all the difluoropropenes we have included in this work and their rotational transition states are shown in Fig. 3.

We were unable to find any experimental geometries for the difluoropropenes. Consequently our comments as to both the absolute values and to trends in the geometrical param-

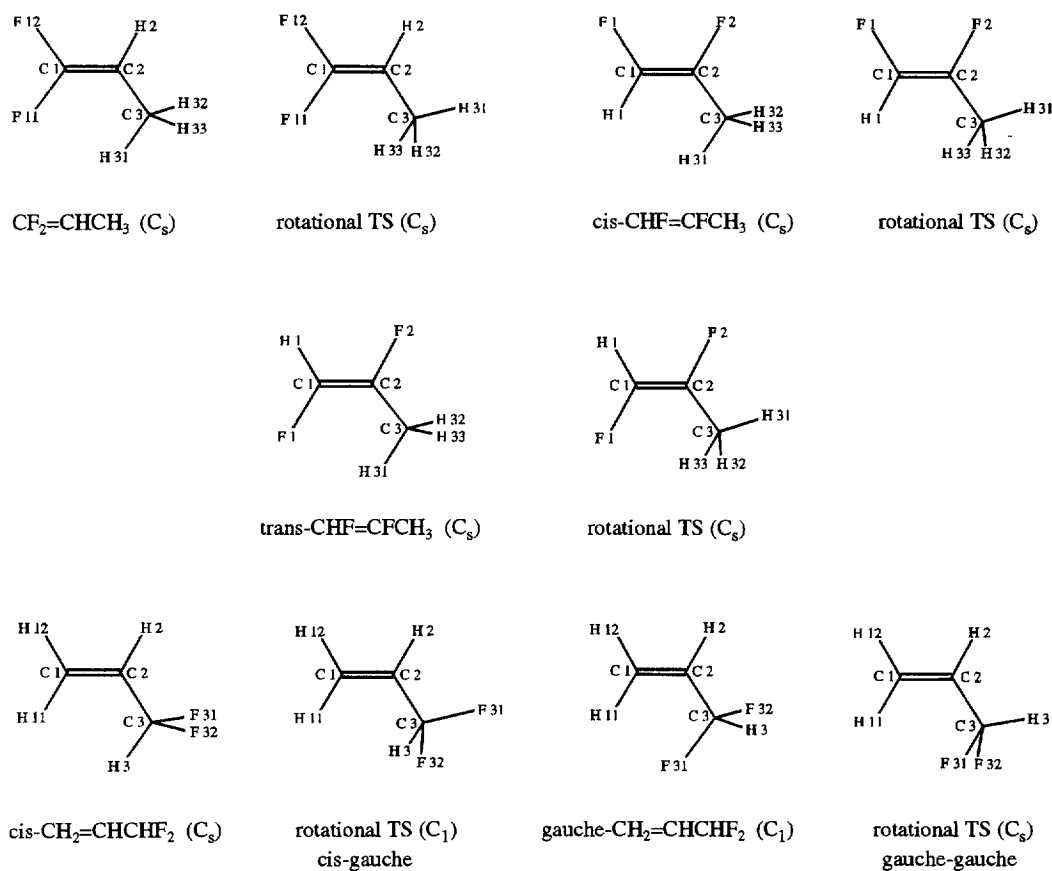


Fig. 3. Structures and labelling scheme for the difluoropropenes.

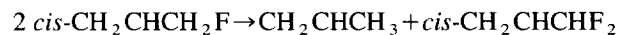
ters should be taken as predictions, which we hope will be confirmed by subsequent experimental studies. Not surprisingly, based on our previous results for the fluorinated methanes, ethylenes and ethanes [6], and results in this work for the monofluoropropenes, we consider the most reliable values for C–F bond lengths to be ACM/TZ2P, especially if these values are supported by MP2/TZ2P calculations. We consider the bond lengths predicted by our best theoretical methods to have a *maximum* error of ± 0.02 Å.

There is clear evidence for the operation of the *geminal* effect in the fluoropropenes, as can be seen by comparing calculated C–F bond lengths in *cis*- or *trans*-1-fluoropropene (Table 1) with those in 1,1-difluoropropene (Table 3), and in *cis*- and *gauche*-3-fluoropropene with those in the corresponding 3,3-difluoropropenes. Looking at the ACM/TZ2P values, then the C–F bond length contraction between *cis*-1-fluoropropene and 1,1-difluoropropene is 0.024 Å, and that between 3-fluoropropene and 3,3-difluoropropene is 0.026 Å (average value). These changes in C–F bond length compare exceptionally well with the corresponding reductions between fluoroethylene and 1,1-difluoroethylene of 0.024 Å, and between fluoromethane and difluoromethane of 0.026 Å [6].

Examination of Tables 1 and 3 show that similar reductions in C–F bond length are predicted by all the *ab initio* methods. However—as was the case in the previous study [6]—there

is little or no evidence for the *geminal* effect in the semiempirical bond lengths. The change in C–F bond length between *cis*-1-fluoropropene and 1,1-difluoropropene with MNDO, AM1 and PM3 is +0.001 Å, –0.005 Å and –0.005 Å, respectively, and between *cis*-3-fluoropropene and *cis*-3,3-difluoropropene is +0.006 Å, –0.002 Å and –0.001 Å, respectively. As can be seen, the bond length contraction is minimal, and C–F bonds lengths actually *increase* with MNDO.

Energetically, evidence for the *geminal* effect can be obtained by looking at the following two reactions



We have no experimental data on the first of these reactions, but the second has a reported incremental *geminal* stabilization of –6.6 kcal/mol [31]. Calculated IGSTABs for both of the above reactions—along with other relative energies and rotational barrier heights—are reported in Table 4a.

At the *ab initio* level both reactions are exothermic, with the smaller 6-31G* basis set results giving the best agreement with the experimental IGSTAB [31]. Reaction exothermicity decreases with the larger TZ2P basis. However, the experimental result is not particularly reliable beyond the fact that the heat of reaction is negative, indicating that the *geminal*

Table 3 (continued)

Parameter	6-31G* basis						TZ2P basis											
	MNDO	AM1	PM3	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	
$\angle C_2C_3H_{32}$	110.7	109.8	110.8	110.1	110.3	111.0	110.8	110.8	110.6	110.6	110.0	110.3	110.8	110.6	110.6	110.5	110.5	
$\angle H_{32}C_3H_{33}$	108.2	108.3	107.6	107.8	107.9	107.2	107.4	107.3	107.5	107.4	108.2	108.2	107.6	107.8	107.9	107.9	107.9	
<i>Rotational TS (C₂)</i>																		
rC ₁ C ₂	1.375	1.360	1.351	1.309	1.333	1.335	1.342	1.343	1.330	1.330	1.306	1.326	1.326	1.335	1.335	1.323	1.323	
rC ₂ C ₃	1.516	1.489	1.491	1.502	1.497	1.485	1.506	1.513	1.498	1.503	1.501	1.496	1.478	1.500	1.507	1.493	1.498	
rC ₁ H ₁	1.097	1.101	1.092	1.070	1.082	1.097	1.092	1.092	1.084	1.084	1.068	1.075	1.092	1.086	1.085	1.080	1.078	
rC ₁ F ₁	1.319	1.346	1.334	1.328	1.353	1.332	1.354	1.361	1.341	1.346	1.321	1.343	1.332	1.354	1.364	1.339	1.346	
rC ₂ F ₂	1.326	1.354	1.341	1.332	1.359	1.339	1.361	1.369	1.347	1.353	1.325	1.349	1.340	1.363	1.373	1.346	1.353	
rC ₃ H ₃₁	1.108	1.117	1.098	1.082	1.091	1.103	1.100	1.101	1.093	1.093	1.079	1.084	1.099	1.094	1.094	1.088	1.088	
rC ₃ H ₃₂	1.110	1.118	1.098	1.084	1.093	1.106	1.103	1.103	1.095	1.096	1.081	1.085	1.100	1.096	1.096	1.090	1.089	
$\angle C_1C_2C_3$	122.8	121.4	123.0	126.3	126.3	126.1	126.0	126.3	126.0	126.3	126.0	125.8	126.5	126.3	126.7	126.2	126.5	
$\angle H_1C_1C_2$	122.3	122.0	124.8	123.6	123.8	123.0	123.3	123.5	123.3	123.5	123.1	122.9	123.1	123.3	123.7	123.2	123.5	
$\angle F_1C_1C_2$	123.2	123.5	121.6	122.2	121.7	121.9	122.5	122.4	122.4	122.2	122.6	122.3	121.9	122.6	122.4	122.5	122.3	
$\angle C_1C_2F_2$	120.7	122.1	120.3	119.4	118.8	118.8	119.2	119.0	119.2	119.1	119.6	119.3	118.7	119.1	118.9	119.2	119.1	
$\angle C_2C_3H_{31}$	112.3	110.6	112.4	108.6	108.1	108.2	108.6	108.6	108.6	108.5	108.6	108.4	108.4	108.7	108.7	108.7	108.7	
$\angle C_2C_3H_{32}$	110.4	110.1	110.6	111.7	111.9	112.7	112.3	112.3	112.2	112.2	111.4	111.7	112.3	111.9	111.9	111.8	111.8	
$\angle H_{32}C_3H_{33}$	108.1	108.7	107.8	108.3	108.4	107.8	107.9	107.9	108.0	108.0	108.6	108.7	108.0	108.3	108.3	108.3	108.4	
<i>trans-1,2-Difluoropropene (C₂) (this structure is a rotational TS at MNDO)</i>																		
rC ₁ C ₂	1.376	1.361	1.352	1.309	1.333	1.335	1.342	1.343	1.330	1.330	1.305	1.326	1.325	1.334	1.334	1.323	1.323	
rC ₂ C ₃	1.516	1.487	1.489	1.487	1.483	1.471	1.491	1.497	1.484	1.488	1.486	1.480	1.463	1.484	1.490	1.478	1.482	
rC ₁ H ₁	1.098	1.102	1.093	1.070	1.082	1.096	1.092	1.091	1.084	1.084	1.068	1.074	1.092	1.086	1.084	1.079	1.078	
rC ₁ F ₁	1.320	1.347	1.335	1.333	1.358	1.337	1.358	1.366	1.346	1.351	1.326	1.349	1.338	1.360	1.371	1.345	1.352	
rC ₂ F ₂	1.330	1.357	1.345	1.337	1.363	1.340	1.365	1.372	1.351	1.357	1.331	1.355	1.344	1.369	1.380	1.352	1.360	
rC ₃ H ₃₁	1.107	1.117	1.097	1.081	1.090	1.103	1.099	1.100	1.092	1.092	1.078	1.084	1.099	1.094	1.094	1.088	1.087	
rC ₃ H ₃₂	1.110	1.118	1.098	1.085	1.094	1.107	1.104	1.105	1.097	1.097	1.083	1.087	1.102	1.098	1.098	1.092	1.091	
$\angle C_1C_2C_3$	127.8	124.7	126.0	128.7	128.1	126.2	127.9	127.9	127.9	127.9	128.9	128.5	127.6	129.1	129.4	128.8	129.0	
$\angle H_1C_1C_2$	123.2	123.2	125.5	124.8	125.1	124.2	124.5	124.8	124.5	124.7	124.4	124.7	124.5	124.9	125.3	124.6	125.0	
$\angle F_1C_1C_2$	122.7	122.4	121.6	120.9	120.2	120.6	121.1	120.9	121.0	120.9	121.1	120.5	120.5	120.9	120.7	121.0	120.8	
$\angle C_1C_2F_2$	117.2	119.2	118.6	117.4	117.1	118.1	117.2	117.3	117.4	117.4	117.3	116.9	117.4	116.6	116.5	116.9	116.8	
$\angle C_2C_3H_{31}$	111.9	110.2	111.7	110.6	109.9	109.6	110.1	110.1	110.3	110.2	110.5	109.9	109.9	110.3	110.3	110.3	110.3	
$\angle C_2C_3H_{32}$	110.6	110.0	110.7	110.1	110.3	111.1	110.8	110.8	110.6	110.6	109.8	110.1	110.7	110.5	110.5	110.3	110.3	
$\angle H_{32}C_3H_{33}$	108.2	108.3	107.6	107.8	108.0	107.3	107.4	107.4	107.5	107.5	108.2	108.2	107.6	107.8	107.9	107.9	107.8	
<i>Rotational TS (C₂) (this structure is a minimum at MNDO)</i>																		
rC ₁ C ₂	1.377	1.362	1.353	1.309	1.332	1.333	1.342	1.342	1.329	1.329	1.305	1.325	1.325	1.334	1.334	1.322	1.322	
rC ₂ C ₃	1.516	1.487	1.489	1.497	1.492	1.481	1.501	1.507	1.493	1.498	1.496	1.490	1.472	1.493	1.499	1.487	1.491	
rC ₁ H ₁	1.098	1.101	1.093	1.069	1.082	1.096	1.091	1.091	1.083	1.083	1.068	1.074	1.091	1.086	1.084	1.079	1.078	
rC ₁ F ₁	1.320	1.347	1.335	1.334	1.359	1.337	1.359	1.367	1.346	1.352	1.327	1.350	1.338	1.361	1.372	1.345	1.353	
rC ₂ F ₂	1.329	1.355	1.343	1.336	1.362	1.339	1.364	1.371	1.350	1.356	1.330	1.354	1.343	1.368	1.379	1.351	1.359	
rC ₃ H ₃₁	1.108	1.117	1.098	1.082	1.091	1.103	1.099	1.100	1.093	1.093	1.079	1.084	1.098	1.094	1.094	1.088	1.087	
rC ₃ H ₃₂	1.109	1.118	1.098	1.084	1.093	1.106	1.102	1.103	1.095	1.096	1.081	1.086	1.101	1.097	1.097	1.090	1.090	
$\angle C_1C_2C_3$	126.6	123.8	124.5	127.4	126.6	125.3	126.8	126.8	126.8	126.8	127.6	127.3	126.8	128.1	128.4	127.8	128.0	
$\angle H_1C_1C_2$	123.4	123.5	125.9	125.5	126.2	125.3	125.7	125.7	125.4	125.6	125.2	125.5	125.3	126.1	126.1	125.3	125.7	
$\angle F_1C_1C_2$	122.4	122.0	120.8	119.8	118.8	119.2	119.9	119.7	119.8	119.7	120.1	119.4	119.3	119.9	119.7	120.0	119.8	

Table 3 (continued)

Parameter	TZ2P basis													
	6-31G* basis					TZ2P basis								
	PM3	AM1	MNDO	6-31G* basis	BLYP	ACM	B3LYP	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP
$\angle C_1C_2F_2$	117.4	119.5	118.9	117.6	117.5	117.6	117.7	117.7	117.2	117.6	116.7	116.6	117.1	117.0
$\angle C_2C_3H_{31}$	112.2	111.0	112.7	109.2	109.0	109.4	109.3	109.3	109.0	109.3	109.3	109.3	109.3	109.3
$\angle C_2C_3H_{32}$	110.4	109.7	110.3	111.1	111.1	111.8	111.5	111.4	111.0	111.5	111.3	111.3	111.2	111.2
$\angle H_{32}C_3H_{33}$	108.3	108.3	107.6	107.9	107.8	107.1	107.5	107.5	108.0	107.4	107.7	107.7	107.8	107.8
<i>cis</i> -3,3-Difluoropropene (C_2)														
rC ₁ C ₂	1.339	1.328	1.326	1.316	1.336	1.332	1.330	1.331	1.329	1.323	1.333	1.335	1.323	1.324
rC ₂ C ₃	1.540	1.515	1.517	1.491	1.486	1.479	1.490	1.493	1.486	1.473	1.492	1.495	1.487	1.488
rC ₁ H ₁₁	1.089	1.099	1.088	1.076	1.086	1.099	1.088	1.088	1.079	1.095	1.089	1.089	1.084	1.083
rC ₁ H ₁₂	1.090	1.099	1.086	1.074	1.084	1.096	1.086	1.086	1.072	1.092	1.088	1.087	1.082	1.080
rC ₁ H ₂	1.094	1.100	1.096	1.076	1.087	1.100	1.088	1.088	1.074	1.095	1.089	1.089	1.084	1.083
rC ₃ H ₃	1.135	1.133	1.111	1.078	1.093	1.113	1.105	1.096	1.086	1.107	1.099	1.096	1.092	1.090
rC ₃ F ₃₁	1.358	1.380	1.358	1.346	1.375	1.358	1.366	1.371	1.368	1.362	1.387	1.397	1.368	1.375
$\angle C_1C_2C_3$	124.8	122.3	121.5	122.9	122.0	122.4	122.8	122.9	121.6	122.0	122.5	122.7	122.4	122.5
$\angle H_{11}C_1C_2$	124.6	123.1	123.4	121.9	121.5	121.0	121.7	121.7	121.0	120.8	121.5	121.6	121.5	121.6
$\angle H_{12}C_1C_2$	122.0	122.0	122.4	121.7	121.7	122.1	121.8	121.8	121.4	122.0	121.6	121.6	121.6	121.6
$\angle C_1C_2H_2$	120.5	123.2	122.7	121.9	122.2	122.5	122.0	122.1	122.0	122.6	122.1	122.1	122.2	122.1
$\angle C_2C_3H_3$	110.3	110.9	113.2	113.4	113.7	112.7	113.3	113.3	113.0	113.1	113.9	114.4	113.4	113.8
$\angle C_2C_3F_{31}$	111.6	112.2	111.9	110.1	109.8	109.7	109.9	109.9	110.3	110.2	110.2	110.2	110.3	110.3
$\angle F_{31}C_3F_{32}$	105.6	102.2	102.8	106.5	106.8	107.0	106.9	106.8	106.6	106.5	106.5	106.2	106.5	106.3
<i>gauche</i> -3,3-Difluoropropene (C_1) (this structure does not exist at MNDO)														
rC ₁ C ₂	1.328	1.326	1.326	1.316	1.336	1.331	1.330	1.331	1.328	1.322	1.332	1.333	1.322	1.323
rC ₂ C ₃	1.512	1.514	1.495	1.495	1.492	1.485	1.496	1.499	1.492	1.479	1.498	1.502	1.492	1.494
rC ₁ H ₁₁	1.100	1.087	1.074	1.074	1.083	1.097	1.086	1.085	1.071	1.093	1.088	1.087	1.082	1.080
rC ₁ H ₁₂	1.098	1.086	1.074	1.074	1.084	1.096	1.086	1.086	1.072	1.092	1.088	1.087	1.082	1.080
rC ₃ H ₃	1.101	1.096	1.076	1.076	1.099	1.113	1.106	1.098	1.074	1.095	1.090	1.089	1.084	1.083
rC ₃ F ₃₁	1.379	1.357	1.357	1.342	1.371	1.354	1.361	1.366	1.362	1.356	1.378	1.388	1.360	1.367
rC ₃ F ₃₂	1.380	1.358	1.347	1.347	1.377	1.360	1.368	1.373	1.371	1.364	1.390	1.401	1.370	1.377
$\angle C_1C_2C_3$	123.4	122.9	124.0	124.0	123.0	122.1	123.6	123.6	124.2	122.8	124.3	124.4	124.0	124.2
$\angle H_{11}C_1C_2$	122.5	123.5	121.8	121.8	121.4	120.2	121.3	121.3	121.1	120.4	121.5	121.5	121.4	121.5
$\angle H_{12}C_1C_2$	122.1	122.3	121.1	121.1	121.1	121.9	121.5	121.4	120.8	121.5	121.0	121.0	121.0	121.0
$\angle C_1C_2H_2$	123.1	122.2	121.5	121.5	121.8	122.5	121.7	121.8	121.5	122.3	121.5	121.6	121.7	121.6
$\angle C_2C_3H_3$	109.0	110.9	113.0	113.0	113.8	112.9	113.4	113.1	113.5	113.3	113.4	113.9	113.0	113.4
$\angle C_2C_3F_{31}$	104.2	113.9	111.5	111.5	111.1	110.8	111.3	111.3	111.6	111.9	112.1	112.1	111.9	111.9
$\angle C_2C_3F_{32}$	112.5	112.3	109.7	109.7	109.2	109.5	109.4	109.5	109.8	109.7	109.6	109.6	109.7	109.7
$\angle F_{31}C_3F_{32}$	102.5	102.7	107.6	107.6	107.7	108.2	108.0	108.0	107.3	107.5	107.4	107.2	107.4	107.3
$\pi H_{12}C_2C_3H_3$	83.8	85.5	66.9	66.9	66.9	65.5	65.1	66.6	66.0	64.9	63.8	63.6	64.8	65.0
<i>gauche-gauche</i> Rotational TS (C_1) (this structure is a trans minimum at MNDO)														
rC ₁ C ₂	1.340	1.329	1.326	1.316	1.337	1.332	1.331	1.332	1.330	1.323	1.333	1.334	1.323	1.324
rC ₂ C ₃	1.539	1.514	1.515	1.503	1.497	1.494	1.504	1.506	1.499	1.487	1.506	1.509	1.500	1.502
rC ₃ H ₃	1.089	1.100	1.087	1.075	1.085	1.098	1.087	1.087	1.073	1.094	1.089	1.088	1.083	1.081
rC ₁ H ₁₁	1.090	1.099	1.086	1.075	1.084	1.096	1.086	1.086	1.072	1.092	1.088	1.087	1.082	1.081
rC ₁ H ₁₂	1.093	1.100	1.094	1.076	1.086	1.098	1.087	1.088	1.073	1.094	1.089	1.088	1.083	1.082

Table 3 (continued)

Parameter	6-31G* basis						TZ2P basis										
	MNDO	AM1	PM3	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP
rC ₃ H ₃	1.135	1.133	1.110	1.078	1.092	1.111	1.104	1.104	1.095	1.095	1.078	1.085	1.105	1.098	1.096	1.091	1.089
rC ₃ F ₃₁	1.358	1.380	1.358	1.346	1.375	1.359	1.382	1.389	1.366	1.371	1.341	1.369	1.363	1.386	1.397	1.367	1.375
∠C ₁ C ₂ C ₃	127.4	123.5	122.1	122.4	120.9	120.9	122.8	122.6	122.4	122.2	122.9	121.6	121.5	123.2	123.3	122.9	122.9
∠H ₁₁ C ₁ C ₂	124.6	122.3	122.7	121.7	121.2	120.8	121.6	121.5	121.6	121.5	121.7	121.1	120.9	121.7	121.7	121.6	121.6
∠H ₁₂ C ₁ C ₂	121.8	122.3	122.7	121.5	121.6	122.0	121.5	121.7	121.6	121.7	121.1	121.0	121.6	121.2	121.2	121.2	121.2
∠C ₁ C ₂ H ₂	120.3	122.7	122.6	121.1	121.4	121.5	120.9	121.1	121.0	121.2	121.1	121.3	121.6	121.1	121.1	121.1	121.2
∠C ₂ C ₃ H ₃	108.3	109.7	112.3	112.8	113.9	113.2	113.0	113.1	112.9	113.1	112.4	113.5	113.7	113.4	113.7	113.1	113.3
∠C ₂ C ₃ F ₃₁	112.7	113.1	112.5	110.9	110.4	110.2	110.7	110.7	110.7	110.7	111.2	110.8	110.6	111.1	111.1	111.1	111.1
∠F ₃₁ C ₃ F ₃₂	105.5	102.1	102.7	106.4	106.5	106.7	106.9	106.7	106.8	106.6	106.3	106.5	106.3	106.4	106.2	106.4	106.2
<i>cis-gauche Rotational TS (C₁) (this structure is a cis-trans rotational TS at MNDO)</i>																	
rC ₁ C ₂	1.339	1.328	1.326	1.316	1.336	1.331	1.340	1.342	1.330	1.331	1.311	1.329	1.322	1.332	1.334	1.323	1.324
rC ₂ C ₃	1.538	1.514	1.516	1.501	1.497	1.491	1.510	1.514	1.502	1.505	1.503	1.497	1.485	1.505	1.508	1.498	1.500
rC ₂ H ₁₁	1.089	1.099	1.087	1.077	1.086	1.099	1.095	1.095	1.088	1.088	1.074	1.079	1.095	1.089	1.088	1.083	1.082
rC ₁ H ₁₂	1.090	1.099	1.086	1.074	1.084	1.096	1.093	1.093	1.086	1.086	1.072	1.077	1.092	1.088	1.087	1.081	1.080
rC ₂ H ₂	1.094	1.101	1.096	1.075	1.086	1.099	1.095	1.095	1.088	1.087	1.072	1.078	1.095	1.089	1.088	1.083	1.082
rC ₃ H ₃	1.137	1.134	1.111	1.078	1.093	1.112	1.105	1.105	1.096	1.096	1.078	1.086	1.107	1.100	1.097	1.093	1.091
rC ₃ F ₃₁	1.357	1.379	1.358	1.344	1.372	1.355	1.378	1.385	1.363	1.368	1.339	1.365	1.358	1.382	1.392	1.364	1.371
rC ₃ F ₃₂	1.358	1.380	1.359	1.346	1.376	1.359	1.383	1.391	1.366	1.372	1.340	1.369	1.363	1.387	1.398	1.368	1.375
∠C ₁ C ₂ C ₃	127.8	122.3	121.0	122.9	121.8	122.3	123.1	123.1	122.9	122.9	122.9	121.9	122.4	123.2	123.3	123.0	123.0
∠H ₁₁ C ₁ C ₂	125.1	122.9	123.2	122.0	121.7	121.3	121.9	121.9	121.9	121.9	121.9	121.4	121.2	121.9	122.0	121.8	121.9
∠H ₁₂ C ₁ C ₂	121.6	122.0	122.5	121.4	121.4	121.8	121.5	121.6	121.5	121.5	121.1	121.0	121.5	121.1	121.2	121.2	121.2
∠C ₁ C ₂ H ₂	119.8	123.1	122.5	121.7	121.9	122.1	121.5	121.7	121.7	121.8	121.7	121.9	122.3	121.7	121.7	121.8	121.8
∠C ₂ C ₃ H ₃	107.5	110.1	112.5	113.5	114.1	113.1	113.6	113.8	113.4	113.6	113.2	114.0	113.7	114.2	114.7	113.8	114.1
∠C ₂ C ₃ F ₃₁	114.3	112.3	112.5	109.5	109.4	109.4	109.4	109.3	109.5	109.4	109.6	109.7	109.8	109.7	109.6	109.7	109.7
∠C ₂ C ₃ F ₃₂	111.8	113.1	112.1	111.1	110.6	110.5	110.8	110.7	110.9	110.8	111.4	110.8	110.8	111.2	111.2	111.2	111.2
∠F ₃₁ C ₃ F ₃₂	105.2	102.3	102.8	107.3	107.6	108.1	108.0	108.0	107.9	107.8	107.1	107.4	107.5	107.4	107.2	107.4	107.2
πH ₃ C ₂ C ₃ H ₃	72.6	132.5	140.8	122.2	123.5	124.2	122.4	122.9	123.2	122.3	119.5	119.2	120.9	117.6	117.5	119.1	118.2

effect is indeed operating in the fluoropropenes. Despite the minimal bond length contraction, there does seem to be evidence for the *geminal* effect in the semiempirical energetics, with reaction (1b) showing a small negative IGSTAB with all three semiempirical methods. However, only PM3 gives a negative IGSTAB for reaction (1a); AM1 is thermoneutral at best, and MNDO is slightly endothermic.

Looking at the effect of vicinal fluorine substitution across the C=C double bond, then all of the ab initio methods except Hartree–Fock predict a small increase (~ 0.004 Å) in C=C bond length following substitution of the second fluorine atom [compare C=C bond lengths in *cis*-1-fluoropropene (Table 1) and *cis*-1,2-difluoropropene (Table 3)]. Exactly the same trend can be seen in the fluoroethylenes [6], although this was not commented on at the time. This does lend some support to the commonly held assertion that C=C bond strength *decreases* with increasing vicinal fluorine substitution across the double bond. However, the overall effect is a combination of separate σ and π bond effects, which tend to oppose each other. Although it is now established that the π bond weakens [2,5], the σ bond may actually get stronger.

One trend that was commented on in Ref. [6] is the decrease in C=C bond length along the series $\text{CH}_2\text{CH}_2 > \text{CH}_2\text{CHF} > \text{CH}_2\text{CF}_2$. This same decrease is also seen with the ab initio methods for the corresponding propene series $\text{CH}_3\text{CH}=\text{CH}_2 > \text{CH}_3\text{CH}=\text{CHF} > \text{CH}_3\text{CH}=\text{CF}_2$, with the bond length changes being very similar for both series.

The predictions at the semiempirical level for these two C=C bond length trends are again at odds with the ab initio predictions. An increase in C=C bond length following vicinal fluorine substitution *is* predicted, only its magnitude is around four times larger than that predicted at the ab initio level (increases of 0.018 Å, 0.0015 Å and 0.012 Å at MNDO, AM1 and PM3, respectively), and the observed trend with increasing *geminal* fluorine substitution is exactly the opposite of the ab initio prediction, with all C=C bond lengths *increasing* significantly instead of decreasing.

We were unable to find an experimental estimate of the relative stability of *cis*- and *trans*-1,2-difluoropropene; thus we have no experimental evidence as to whether or not the *cis* effect is operational in the fluoropropenes. Looking to our previous study for guidance [6], for 1,2-difluoroethylene the *cis* isomer is more stable than the *trans* (by about 1.4 kcal/mol). This was predicted theoretically, but there was a clear basis set effect—the *trans* isomer was the more stable with the 6-31G* basis, the stability reversing with the TZ2P basis, although the relative energy difference was underestimated. Here, we find that *trans*-1,2-difluoropropene is clearly predicted to be the more stable isomer at the 6-31G* level; however, the relative energy difference reduces to 0.2 kcal/mol or less with the TZ2P basis (Table 4a). It may be that very large basis sets are required to account for the subtle factors that give rise to the *cis* effect. To test this hypothesis we have carried out single-point ACM energy calculations on both *cis*- and *trans*-1,2-difluoropropene using Dunning's correlation-consistent aug-cc-pVTZ basis [39] (11s6p3d2f

on carbon and oxygen, 7s3p2d on hydrogen). With this large basis set, the *cis* isomer is indeed more stable than the *trans* (by 0.7 kcal/mol). Both MNDO and PM3 (but less so AM1) firmly favour the *cis* isomer, almost the only occasion in which the semiempirical results appear to be better than the ab initio.

Comparing the absolute values for calculated ab initio bond lengths in the difluoropropenes, then all the usual trends are there: HF bond lengths (except for the C–C single bond) are consistently shorter than those for the other methods, and BP and, especially, BLYP are consistently longer. As was the case with the monofluoropropenes, B3LYP and ACM geometrical parameters are very similar *except* for C–C single bond lengths, which are ~ 0.003 Å longer at B3LYP, and C–F bond lengths, which are around 0.005 Å (6-31G*) and 0.007 Å (TZ2P) longer (these differences are somewhat less for the di- than for the monofluoropropenes).

Another trend that we can directly compare with the fluoroethylenes is the angle contraction $\angle\text{HCH} > \cdot\angle\text{HCF} > \cdot\angle\text{FCF}$ in propene, 1-fluoropropene and 1,1-difluoropropene, respectively. The calculated bond angles (ACM/TZ2P) of around 117°, 112° and 110° (calculated from Tables 1 and 3) are essentially the same as the corresponding angles in ethylene, fluoroethylene and 1,1-difluoroethylene [6]. As with the fluoroethylenes, this trend is reproduced at all levels of theory, including semiempirical.

Before commenting on the rest of the energetics in Table 4a, we look at the nature of the various stationary points on the PES. As was the case with the monofluoropropenes, there are some major anomalies with MNDO (although not this time with AM1). The most problems occur with 3,3-difluoropropene. Experimentally, and in all the other calculations (including AM1 and PM3), there are four relevant stationary points: a *cis*-minimum (C_s symmetry), a *gauche* minimum (C_1), a *cis*-*gauche* rotational TS (C_1) and a *gauche*-*gauche* rotational TS (C_s). With MNDO there is *no gauche* minimum; instead the *gauche*-*gauche* rotational TS is now a *trans*-minimum and the *cis*-*gauche* TS is now a *cis*-*trans* TS. The situation is exactly equivalent to the corresponding picture with 3-fluoropropene (see the discussion given with the monofluoropropenes). Additionally, the same switching of the minimum and rotational TS that occurred with MNDO for *cis*-1-fluoropropene also occurs for both 1,1- and *trans*-1,2-difluoropropene, i.e., what is structurally the minimum at all other levels of theory is a TS with MNDO, and vice versa. As before, this is indicated in Table 4a by the negative rotational barriers quoted for these two species.

We should note that there were difficulties characterizing some of the semiempirical stationary points by vibrational analysis. Specifically, *cis*-3,3-difluoropropene—which we have taken to be a minimum at all levels of theory—has one imaginary frequency at MNDO and PM3. This imaginary frequency persists even with very tight convergence criteria. We were unable to locate any nearby lower energy structures with a potential scan, and we consider the imaginary frequency to be an artefact of the second derivative implemen-

Table 4
 a. Relative energies and barrier heights for the difluoropropenes (kcal/mol)

Species	6-31G* basis										TZ2P basis					Expt.		
	MNDO	AM1	PM3	HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	HF	MP2	SVWN	BP	BLYP		ACM	B3LYP
Rotational barrier in 1,1-difluoropropene																		
barrier	-0.1	0.5	0.4	0.9	0.7	1.1	0.8	0.8	0.8	0.9	1.0	0.8	1.0	0.7	0.7	0.8	0.8	Ref.[37] 1.3
Energy of <i>trans</i> -1,2-difluoropropene relative to <i>cis</i> -1,2-difluoropropene																		
<i>trans</i>	1.2	0.2	1.7	-1.1	-1.1	-0.9	-0.7	-0.8	-0.8	-0.9	-0.1	-0.1	-0.2	0.0	-0.2	-0.1	-0.2	
Rotational barrier in <i>cis</i> -1,2-difluoropropene																		
barrier	0.1	0.3	0.6	2.6	2.4	2.6	2.4	2.4	2.4	2.4	2.9	2.7	2.6	2.3	2.3	2.5	2.5	
Rotational barrier in <i>trans</i> -1,2-difluoropropene																		
barrier	-0.2	0.3	0.3	1.8	1.5	1.9	1.6	1.6	1.6	1.7	1.9	1.7	1.7	1.5	1.4	1.6	1.6	
Energy of <i>gauche</i> -3,3-difluoropropene relative to <i>cis</i> -3,3-difluoropropene																		
<i>gauche</i>	-	-0.1	-0.3	0.3	0.1	-0.1	0.5	0.4	0.3	0.2	0.6	0.7	0.4	1.0	1.0	0.8	0.8	Ref.[38] 0.7
<i>gauche-gauche</i> Rotational barrier in 3,3-difluoropropene																		
barrier	-	1.2	0.7	5.3	2.7	3.3	2.5	2.5	2.7	2.8	3.0	2.3	2.7	2.1	2.0	2.4	2.3	1.5
<i>cis-gauche</i> Rotational barrier in 3,3-difluoropropene																		
barrier	-	0.1	0.1	1.9	1.8	2.2	2.0	2.0	1.9	1.9	2.1	2.1	2.2	2.2	2.1	2.1	2.1	0.8
Relative energy of difluoropropene minima relative to <i>cis</i> -3,3-difluoropropene																		
<i>gauche</i> -3,3	-	-0.1	-0.3	0.3	0.1	-0.1	0.5	0.4	0.3	0.2	0.6	0.7	0.4	1.0	1.0	0.8	0.8	
1,1-Difluoro	-6.4	-2.6	-5.1	2.2	-3.2	-7.0	-4.7	-3.2	-3.8	-2.6	3.5	1.0	-4.0	-1.9	0.0	-1.4	0.2	2.5
<i>trans</i> -1,2	-1.7	2.9	3.0	8.3	6.2	0.4	1.4	2.4	2.9	3.3	8.6	7.0	2.0	3.2	4.1	6.5	4.7	
<i>cis</i> -1,2	-2.9	2.7	1.3	9.4	7.3	1.3	2.1	3.2	3.7	4.2	8.7	7.1	2.2	3.2	4.3	6.6	4.9	
Incremental geminal stabilization energies for fluorine in 1,1- and 3,3-difluoropropene																		
1,1-Difluoro	0.1	0.0	-3.0	-2.2	-2.1	-2.6	-2.2	-1.9	-2.3	-2.0	-1.5	-1.5	-1.6	-1.1	-0.7	-1.3	-1.0	
3,3-Difluoro	-1.6	-1.7	-4.6	-6.0	-6.5	-6.7	-6.5	-6.1	-6.3	-6.1	-5.0	-5.7	-5.3	-5.3	-5.0	-5.2	-5.0	-6.6
b. Calculated dipole moments for the difluoropropenes (debye)																		
Species	MNDO	AM1	PM3	6-31G* basis			TZ2P basis					Expt.						
				HF	MP2	SVWN	BP	BLYP	ACM	B3LYP	HF		MP2	SVWN	BP	BLYP	ACM	B3LYP
1,1-Difluoro	2.07	1.83	1.89	1.61	1.51	1.18	1.28	1.30	1.37	1.40	1.74	1.61	1.52	1.61	1.71	1.64	1.73	0.89 ^a
<i>cis</i> -1,2-Difluoro	3.06	2.66	2.65	3.00	2.76	2.29	2.37	2.36	2.54	2.53	3.03	2.83	2.66	2.70	2.80	2.78	2.86	
<i>trans</i> -1,2-Difluoro	0.37	0.47	0.47	0.60	0.56	0.59	0.61	0.60	0.61	0.60	0.71	0.65	0.73	0.75	0.75	0.73	0.73	
<i>cis</i> -3,3-Difluoro	2.90	2.53	2.40	2.46	2.31	1.90	1.99	2.00	2.12	2.13	2.56	2.45	2.29	2.36	2.45	2.40	2.47	2.47 ^b
<i>gauche</i> -3,3-Difluoro	-	2.36	2.20	2.25	2.08	1.73	1.84	1.84	1.94	1.95	2.31	2.20	2.06	2.14	2.23	2.17	2.24	2.12 ^b

^a Ref. [37], ^b Ref. [38]

tation for semiempirical wavefunctions within GAUSSIAN 94 (which, as far as we know, is based on the original finite-difference code in AMPAC) and of the very flat PES with these two methods.

At the ab initio level, the various rotational barriers among the difluoropropenes all have similar values for a given system. For the monofluoropropenes, the calculated ab initio barriers tended to be lower than experiment (see Table 4a). This was also the case for rotational barriers in the fluoroeethanes (see Table 3d in Ref. [6]). The same thing is true for 1,1-difluoropropene, but *not* for either of the 3,3-difluoropropenes, at least for the experimental values we have quoted [38]. We have rather more confidence in our theoretical values than the experimental barriers of Ref. [38] (derived from microwave spectroscopy), which we consider to be too low. The semiempirical rotational barriers are even lower than the (too low) experimental barriers, particularly for the *cis-gauche* rotational barrier in 3,3-difluoropropene.

Although we are not completely sure, we consider that the most likely energy ordering among the difluoropropenes examined here is: *cis*-3,3-difluoro > *gauche*-3,3-difluoro > 1,1-difluoro > *cis*-1,2-difluoro > *trans*-1,2-difluoro. There is reasonable experimental evidence for the ordering of the first three [31,38], and all our calculations (except for MNDO) predict that 1,2-difluoropropene is the least stable isomer (the relative stability of the *cis* and *trans* isomers has been discussed above). None of the methods fully reproduces this energy ordering, but HF/TZ2P and MP2/TZ2P are almost right, with a slight mis-ordering between *cis*- and *trans*-1,2-difluoropropene. A majority of the ab initio methods—including ACM—incorrectly predict that 1,1-difluoropropene is the most stable isomer. At the semiempirical level, AM1 and PM3 both predict 1,1-difluoro- and *gauche*-3,3-difluoropropene to be more stable than *cis*-3,3-difluoropropene, and with MNDO *all* isomers are more stable than *cis*-3,3-difluoropropene (except *gauche*-3,3-difluoropropene, which does not exist).

Calculated and experimental dipole moments are given in Table 4b. We were not able to find experimental dipoles for the 1,2-difluoropropenes, and the only value we could find for 1,1-difluoropropene [37] we consider to be horribly wrong (it is far too low). Consequently the only dipole moments we can compare with experiment are those for the two 3,3-difluoropropene isomers. On this rather flimsy basis then the best methods overall are MP2/TZ2P, ACM/TZ2P and B3LYP/TZ2P. All the trends among the ab initio dipole moments that were found for the monofluoropropenes hold for the difluoropropenes; thus the DFT values are all too low with the 6-31G* basis and improve substantially with the TZ2P basis, HF dipoles worsen with the larger basis (they are all too high), and B3LYP dipole moments—which are similar to ACM at the 6-31G* level—are consistently larger with the TZ2P basis. Note that all our calculations (including semiempirical) predict the same dipole moment order: *cis*-1,2-difluoro > *cis*-3,3-difluoro > *gauche*-3,3-difluoro > 1,1-difluoro > *trans*-1,2-difluoro.

4. Summary

We have carried out a systematic series of calculations on the geometries, energetics, dipole moments and, where appropriate, the rotational barriers, of all possible mono- and selected difluoropropenes. Semiempirical (MNDO, AM1 and PM3) and standard ab initio (HF and MP2) techniques were compared with density functional methods (SVWN, BP, BLYP, ACM [aka B3PW91] and B3LYP). Our conclusions are discussed below.

4.1. Geometries

The best method for reproducing the experimental geometries, both in terms of the trends with increasing fluorine substitution and in absolute terms, is ACM/TZ2P. We reached exactly the same conclusion in our previous study of all possible fluorinated methanes, ethylenes and ethanes [6]. Unlike our earlier study, in this work we also included the other popular hybrid density functional, B3LYP. Although in general giving similar geometrical parameters to ACM, all fluoropropene C–C single bond and—in particular—C–F bond lengths were overestimated with the B3LYP functional. Consequently, we consider the ACM functional to be better suited for predicting fluorocarbon geometries than B3LYP. Having said this however, B3LYP is certainly a better choice than any of the other commonly used density functionals and is generally on a par with MP2.

Although the other ab initio methods reliably reproduce trends, HF bond lengths are typically too short, and BP and (especially) BLYP bond lengths are consistently too long. The semiempirical methods are clearly totally unreliable; in many cases the calculated trends are the reverse of what is observed experimentally and the average errors in bond length are both large and unsystematic.

We consider our predicted ACM/TZ2P bond lengths to be accurate to at least ± 0.02 Å.

4.2. Energetics

All of the ab initio methods examined here perform similarly in reproducing relative energies and barrier heights, and no single method is clearly superior to any other. However, based on both the results reported in this work and on our previous study [6], the marginally best method overall is probably HF/TZ2P. ACM and B3LYP have a very similar performance; of the eleven rotational barriers reported in Tables 2a and 4a, the two hybrid functionals give identical values with the TZ2P basis (to the accuracy reported) for eight of them. The semiempirical methods are again noticeably worse than any of the ab initio. MNDO in particular often gives a qualitatively incorrect picture of the PES, with minima and transition state structures switching for *cis*-1-fluoropropene, *trans*-1,2-difluoropropene and 1,1-difluoropropene, and qualitative differences for 3-fluoro- and 3,3-difluoropropene (see Fig. 2).

4.3. Dipole moments

The same conclusions regarding dipole moments hold as for our previous study [6]. Dipole moments calculated with DFT appear to be more sensitive to basis set than do the corresponding HF and MP2 dipoles; DFT/6-31G* dipole moments are consistently too low and improve substantially with the larger TZ2P basis. MP2 dipoles also improve, but nowhere near as much; HF dipole moments often worsen as they are usually too high in any case.

The best agreement with experiment is provided by MP2/TZ2P, ACM/TZ2P and B3LYP/TZ2P. All three methods perform similarly. With the 6-31G* basis, ACM and B3LYP dipole moments are virtually the same, but with the TZ2P basis B3LYP dipoles are consistently higher than ACM. However, B3LYP/TZ2P overestimates the dipole moment to the same extent that ACM underestimates it, resulting in a very similar performance overall. The semiempirical dipole

moments are generally inferior and often do not reproduce experimentally observed trends; however this is less marked with the fluoropropenes than it was with the smaller fluorocarbons [6].

This study provides further evidence for the ability of hybrid density functionals, and the ACM functional in particular, to give consistently reliable structures, energetics and dipole moments for simple fluorocarbons. Both ACM and B3LYP are clearly better than the 'non-hybrid' density functionals, SVWN, BP and BLYP, all three of which perform overall worse than MP2.

Based on the results of this study we suggest that the experimental dipole moment of 1.85 D [36] for *trans*-1-propene may be too high, the experimental dipole moment of 0.89 D [37] for 1,1-difluoropropene is certainly too low, and the barriers to rotation in 3,3-difluoropropene of 0.8 and 1.5 kcal/mol, respectively, for the *cis-gauche* and *gauche-gauche* barriers [38], are also too low.

Appendix A

Total energies of all species examined at all levels of theory and HF/6-31G* zero point vibrational energies (ZPVE). Ab initio values are total energies in hartree (the two rows are energies with the 6-31G* and TZ2P bases, respectively); semiempirical values are heats of formation (originally in kcal/mol but converted into hartree). Relative ab initio energies (kcal/mol) reported throughout this work have been corrected using the quoted ZPVEs scaled by 0.89.

a. Semiempirical heats of formation and HF/6-31G* ZPVE

Compound	MNDO	AM1	PM3	ZPVE
Propene	0.007850	0.010389	0.010126	0.085439
Rotational TS	0.008128	0.011271	0.011197	0.084493
<i>cis</i> -1-Fluoropropene	-0.071176	-0.069632	-0.061301	0.078258
Rotational TS	-0.071332	-0.068854	-0.060812	0.077540
<i>trans</i> -1-Fluoropropene	-0.071791	-0.070263	-0.061688	0.077986
Rotational TS	-0.071537	-0.069346	-0.060555	0.077042
2-Fluoropropene	-0.065786	-0.063461	-0.061577	0.077726
Rotational TS	-0.065530	-0.062936	-0.060634	0.076744
<i>cis</i> -3-Fluoropropene	-0.063393	-0.064889	-0.054755	0.078843
<i>gauche</i> -3-Fluoropropene	-	-	-0.054522	0.078779
<i>trans</i> -3-Fluoropropene	-0.063530	-0.065408	-0.054514	0.077910
<i>cis-gauche/trans</i> rotational TS	-0.063131	-0.062713	-0.052597	0.078190
1,1-Difluoropropene	-0.149928	-0.149655	-0.142387	0.070218
Rotational TS	-0.150148	-0.148882	-0.141765	0.069517
<i>cis</i> -1,2-Difluoropropene	-0.144355	-0.141089	-0.132278	0.070221
Rotational TS	-0.144134	-0.140538	-0.131267	0.069737
<i>trans</i> -1,2-Difluoropropene	-0.142466	-0.140792	-0.129581	0.070046
Rotational TS	-0.142731	-0.140252	-0.129107	0.069636
<i>cis</i> -3,3-Difluoropropene	-0.139728	-0.145444	-0.134306	0.071104
<i>gauche</i> -3,3-Difluoropropene	-	-0.145649	-0.134714	0.071265
<i>gauche-gauche</i> Rotational TS	-0.139799	-0.143696	-0.133585	0.070860
<i>trans-gauche</i> rotational TS	-0.139323	-0.145244	-0.134153	0.070742

b. *Ab initio* energies

HF	MP2	SVWN	BP	BLYP	ACM	B3-LYP
<i>Propene</i>						
– 117.070912	– 117.458681	– 116.758968	– 117.879387	– 117.826508	– 117.865565	– 117.905217
– 117.116411	– 117.639802	– 116.819408	– 117.930573	– 117.884751	– 117.914075	– 117.958434
<i>Rotational TS</i>						
– 117.067612	– 117.455564	– 116.755263	– 117.876182	– 117.823224	– 117.862320	– 117.901899
– 117.112934	– 117.636547	– 116.815942	– 117.927530	– 117.881729	– 117.910921	– 117.955280
<i>cis-1-Fluoropropene</i>						
– 215.919805	– 216.476321	– 215.384331	– 217.105446	– 217.057528	– 217.064083	– 217.136060
– 216.009084	– 216.768017	– 215.495915	– 217.204796	– 217.166423	– 217.159132	– 217.237436
<i>Rotational TS</i>						
– 215.917738	– 216.474643	– 215.381957	– 217.103540	– 217.055555	– 217.062115	– 217.134021
– 216.007000	– 216.766289	– 215.493850	– 217.203081	– 217.164770	– 217.157307	– 217.235644
<i>trans-1-Fluoropropene</i>						
– 215.918800	– 216.475091	– 215.382987	– 217.104575	– 217.056523	– 217.063151	– 217.135009
– 216.008176	– 216.766885	– 215.494516	– 217.203905	– 217.165486	– 217.158193	– 217.236433
<i>Rotational TS</i>						
– 215.915275	– 216.471780	– 215.379103	– 217.101248	– 217.053144	– 217.059749	– 217.131552
– 216.004279	– 216.763284	– 215.490742	– 217.200600	– 217.162220	– 217.154734	– 217.232991
<i>2-Fluoropropene</i>						
– 215.925782	– 216.482084	– 215.390543	– 217.111077	– 217.063216	– 217.069905	– 217.141946
– 216.015097	– 216.773875	– 215.502050	– 217.210128	– 217.171909	– 217.164692	– 217.243112
<i>Rotational TS</i>						
– 215.921621	– 216.478247	– 215.386538	– 217.107371	– 217.059444	– 217.066079	– 217.138050
– 216.010667	– 216.769858	– 215.498304	– 217.206637	– 217.168361	– 217.161001	– 217.239369
<i>cis-3-Fluoropropene</i>						
– 215.915959	– 216.469544	– 215.372715	– 217.095373	– 217.048652	– 217.055167	– 217.128071
– 216.006743	– 216.762727	– 215.487039	– 217.197181	– 217.160076	– 217.152391	– 217.231718
<i>gauche-3-Fluoropropene</i>						
– 215.915168	– 216.468441	– 215.370086	– 217.094277	– 217.047516	– 217.053948	– 217.126856
– 216.006573	– 216.762603	– 215.485437	– 217.197060	– 217.160270	– 217.151991	– 217.231586
<i>gauche-gauche Rotational TS</i>						
– 215.912859	– 216.465807	– 215.367449	– 217.091765	– 217.044756	– 217.051597	– 217.124295
– 216.003696	– 216.759228	– 215.482484	– 217.194133	– 217.157062	– 217.149232	– 217.228593
<i>cis-gauche Rotational TS</i>						
– 215.910751	– 216.464587	– 215.365452	– 217.090187	– 217.043541	– 217.049777	– 217.122745
– 216.001800	– 216.758509	– 215.480932	– 217.192960	– 217.156229	– 217.147767	– 217.227382
<i>1,1-Difluoropropene</i>						
– 314.775465	– 315.500511	– 314.017967	– 316.338313	– 316.294282	– 316.269761	– 316.373120
– 314.906241	– 315.900877	– 314.177399	– 316.482401	– 316.450268	– 316.408108	– 316.519317
<i>Rotational TS</i>						
– 314.773398	– 315.498776	– 314.015602	– 316.336462	– 316.292342	– 316.267827	– 316.371111
– 314.904016	– 315.899050	– 314.175207	– 316.480627	– 316.448533	– 316.406201	– 316.517433
<i>cis-1,2-Difluoropropene</i>						
– 314.763916	– 315.488252	– 314.004602	– 316.326849	– 316.284013	– 316.257901	– 316.362317
– 314.897947	– 315.891182	– 314.167476	– 316.474228	– 316.443370	– 316.399563	– 316.511860
<i>Rotational TS</i>						
– 314.759310	– 315.484035	– 314.000004	– 316.322672	– 316.279829	– 316.253598	– 316.357993
– 314.892816	– 315.886474	– 314.162911	– 316.470058	– 316.439194	– 316.395178	– 316.507464
<i>trans-1,2-Difluoropropene</i>						
– 314.765543	– 315.489891	– 314.005933	– 316.327766	– 316.285204	– 316.259010	– 316.363632
– 314.897917	– 315.891261	– 314.167707	– 316.474131	– 316.443576	– 316.399515	– 316.512046
<i>Rotational TS</i>						
– 314.762321	– 315.487093	– 314.002619	– 316.324900	– 316.282296	– 316.256035	– 316.360611
– 314.894515	– 315.888262	– 314.164657	– 316.471450	– 316.440907	– 316.396663	– 316.509195
<i>cis-3,3-Difluoropropene</i>						
– 314.779707	– 315.500664	– 314.007559	– 316.331670	– 316.289950	– 316.264567	– 316.369826
– 314.912563	– 315.903291	– 314.171839	– 316.480189	– 316.451054	– 316.406709	– 316.520442
<i>gauche-3,3-Difluoropropene</i>						
– 314.779427	– 315.500661	– 314.007828	– 316.331033	– 316.289514	– 316.264219	– 316.369629
– 314.911744	– 315.902340	– 314.171304	– 316.478769	– 316.449610	– 316.405644	– 316.519322
<i>gauche-gauche Rotational TS</i>						
– 314.770593	– 315.495997	– 314.002247	– 316.326644	– 316.285100	– 316.259505	– 316.364881
– 314.906665	– 315.898330	– 314.166568	– 316.475123	– 316.446053	– 316.401521	– 316.515279
<i>cis-gauche Rotational TS</i>						
– 314.776291	– 315.497446	– 314.003780	– 316.328168	– 316.286471	– 316.261208	– 316.366492
– 314.908814	– 315.899662	– 314.167999	– 316.476433	– 316.447306	– 316.403091	– 316.516806

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