Thermodynamic Properties (ΔH_f(298), S(298), and $C_p(T)$ (300 $\leq T \leq$ 1500)) of Fluorinated Propanes

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Thermodynamic properties ($\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$ (300 $\leq T$/K $\leq$ 1500)), frequencies, geometries, and internal rotational barriers for 1-fluoropropane, 1,1-difluoropropane, 1,1,1-trifluoropropane, 1,2-difluoropropane, 1,1,2-trifluoropropane, 1,1,2,2-tetrafluoropropane, 1,1,1,2-tetrafluoropropane, and 1,1,1,2,2-pentafluoropropane are calculated using ab initio methods. Enthalpies of formation ($\Delta H_f°_{298}$ in kcal/mol) for the above eight compounds are estimated using the G2MP2 composite calculation method and isodesmic reactions. Entropies ($S°_{298}$ in cal mol^{-1} K^{-1}) and heat capacities ($C_p(T)$ in cal mol^{-1} K^{-1}) are estimated using HF/6-31G(d) determined frequencies and MP2(full)/6-31G(d) determined geometries. $\Delta H_f°_{298}$ for the above compounds are −67.37, −123.66, −183.09, −109.75, −164.68, −216.38, −221.57, and −271.14 kcal/mol, respectively. Rotational barriers are determined, and hindered internal rotational contributions for $S°_{298}$ and $C_p(T)$ are calculated using the rigid rotor harmonic oscillator approximation with direct integration over energy levels of the intramolecular rotation potential energy curve.

Introduction

Chlorofluorocarbons (CFCs) are being replaced by hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons(HCFCs) because of their noneffects or less adverse effects on the stratospheric ozone layer. Examples includes HFC-134a (CH_2FCF_3), a replacement for CFC-12 (CF_2Cl_2) in domestic refrigeration and automobile air conditioning units,[1] and HFC-227ea (CF_3CFHCF_3), a replacement for Halon 1301 (CF3Br) as fire suppressants[2,3] and for CFC114 (CF_2ClCF_2Cl) as refrigerant.[3]

A number of theoretical and experimental studies on thermodynamic properties ($\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$ (300 $\leq T$/K $\leq$ 1500)), frequencies, and internal rotational barrier for fluorinated ethane compounds have been reported.[4−13] However, literature data on the estimation of thermodynamic properties for fluorinated propane compounds are limited to 1-fluoropropane, 2-fluoropropane, and 2,2-difluoropropane.[4,5]

Method

1. Enthalpies of Formation ($\Delta H_f°_{298}$) Calculations. $\Delta H_f°_{298}$ values are estimated using the total energies obtained by the G2MP2 composite ab initio calculation method[14] and isodesmic reactions. All ab initio calculations are performed using the Gaussian94[15] system of programs. ZPVE's and thermal corrections to 298.15 K are obtained with scaled frequencies, 0.8929, as widely used in theoretical thermochemical calculation[16] for frequencies determined at the HF/6-31G(d) level of theory. The general isodesmic reaction to calculate $\Delta H_f°_{298}$ of fluorinated propanes is

$$CH_{(3-x)}F_xCH_{(2-y)}F_yCH_{(3-z)}F_z + CH_3CH_3 \rightarrow CH_3CH_{(2-y)}F_yCH_3 + CH_{(3-x)}F_xCH_{(3-z)}F_z \quad (1)$$

where

$$1 \leq x \leq 3$$

$$0 \leq y \leq 2$$

$$0 \leq z \leq 3$$

The method of isodesmic reactions relies on the similarity of the bonding environment in the reactants and products that leads to cancellation of systematic errors in the ab initio MO calculations.[16] The basic requirement of the isodesmic reaction is bond type conservation, where the number of each formal chemical bond type is conserved in the reaction. An isodesmic reaction will lead to more accurate results if groups are conserved in the reaction scheme.[17] This results because interactions of next-nearest-neighbor atoms in reactants and products are conserved in addition to bond types.

Since $\Delta H_f°_{298}$ for CH_3CH_3, $CH_3CH_2CH_3$, and $CH_{(3-x)}F_xCH_{(3-z)}F_z$ are well-known[4−6] and values for CH_3CFHCH_3 and $CH_3CF_2CH_3$ are reported,[5] the remaining compounds, $CH_{(3-x)}F_xCH_{(2-y)}F_yCH_{(3-z)}F_z$, in reaction 1 can be accurately estimated from the calculated $\Delta H_{rxn}°_{298}$. For example, 1-fluoropropane is estimated by the isodesmic reaction

$$CH_2FCH_2CH_3 + CH_3CH_3 \rightarrow CH_3CH_2CH_3 + CH_2FCH_3 \quad (2)$$

G2MP2 composite calculations are performed for all four compounds in reaction 2, and the enthalpy of reaction ($\Delta H_{rxn}°_{298}$) is calculated. Evaluated literature data for $\Delta H_f°_{298}$ on CH_3CH_3, $CH_3CH_2CH_3$, and CFH_2CH_3 and $\Delta H_{rxn}°_{298}$ are used to calculate

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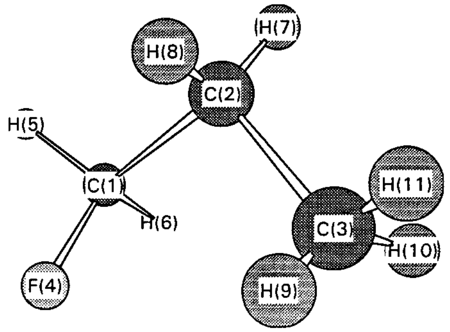
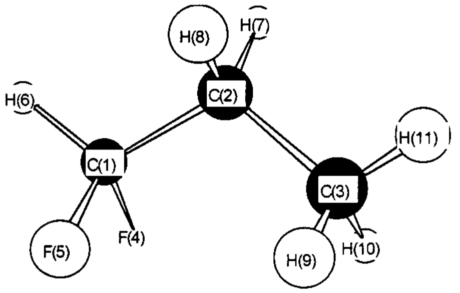


Bond Length	Å
C1-C2	1.511
C2-C3	1.523
C1-F4	1.401
C1-H5	1.094
C1-H6	1.095
C2-H7	1.097
C2-H8	1.095
C3-H9	1.091
C3-H10	1.094
C3-H11	1.093
Bond Angle	Degree
∠C1C2C3	112.2
∠F4C1C2	109.3
∠H5C1C2	111.9
∠H6C1C2	111.3
∠H7C2C1	108.2
∠H8C2C1	108.4
∠H9C3C2	110.2
∠H10C3C2	110.9
∠H11C3C2	111.2
Dihedral Angle	Degree[a]
∠F4C1C2C3	+59.9

[a] +: Clockwise, -: Counter clockwise. The direction of dihedral angle observation is C1 → C2.

Figure 1. MP2(full)/6-31G(d) determined geometry of 1-fluoropropane.

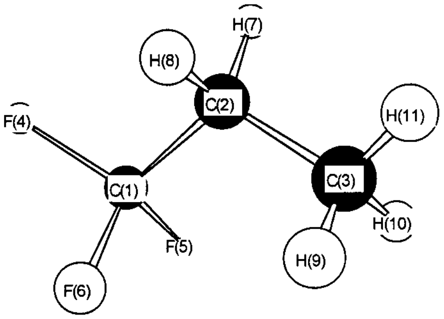


Bond Length	Å
C1-C2	1.504
C2-C3	1.524
C1-F4	1.375
C1-F5	1.375
C1-H6	1.094
C2-H7	1.095
C2-H8	1.095
C3-H9	1.091
C3-H10	1.091
C3-H11	1.092
Bond Angle	Degree
∠C1C2C3	112.2
∠F4C1C2	110.0
∠F5C1C2	110.0
∠H6C1C2	114.3
∠H7C2C1	107.7
∠H8C2C1	107.7
∠H9C3C2	110.6
∠H10C3C2	110.6
∠H11C3C2	110.6
Dihedral Angle	Degree[a]
∠F4C1C2C3	-58.8
∠F5C1C2C3	+58.8

[a] +: Clockwise, -: Counter clockwise. The direction of dihedral angle observation is C1 → C2.

Figure 2. MP2(full)/6-31G(d) determined geometry of 1,1-difluoropropane.

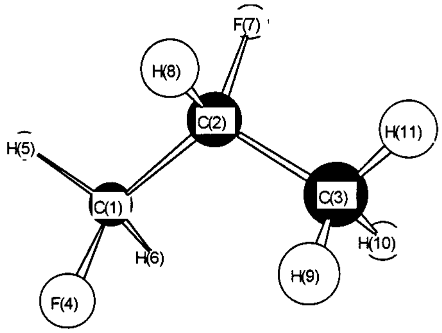
$\Delta H_f°_{298}$ of $CFH_2CH_2CH_3$. Seven additional fluorinated propanes are calculated in the same manner. We suggest this as a general isodesmic reaction scheme for estimation of monohalogenated propanes.



Bond Length	Å
C1-C2	1.500
C2-C3	1.523
C1-F4	1.353
C1-F5	1.354
C1-F6	1.354
C2-H7	1.093
C2-H8	1.093
C3-H9	1.092
C3-H10	1.092
C3-H11	1.092
Bond Angle	Degree
∠C1C2C3	112.3
∠F4C1C2	111.6
∠F5C1C2	111.8
∠F6C1C2	111.8
∠H7C2C1	106.9
∠H8C2C1	106.9
∠H9C3C2	110.7
∠H10C3C2	110.7
∠H11C3C2	110.2
Dihedral Angle	Degree[a]
∠F4C1C2C3	+180.0
∠F5C1C2C3	-60.0
∠F6C1C2C3	+60.0

[a] +: Clockwise, -: Counter clockwise. The direction of dihedral angle observation is C1 → C2.

Figure 3. MP2(full)/6-31G(d) determined geometry of 1,1,1-trifluoropropane.



Bond Length	Å
C1-C2	1.513
C2-C3	1.507
C1-F4	1.396
C1-H5	1.093
C1-H6	1.094
C2-F7	1.404
C2-H8	1.095
C3-H9	1.092
C3-H10	1.093
C3-H11	1.092
Bond Angle	Degree
∠C1C2C3	113.3
∠F4C1C2	108.4
∠H5C1C2	110.8
∠H6C1C2	110.2
∠F7C2C1	105.6
∠H8C2C1	109.6
∠H9C3C2	109.8
∠H10C3C2	109.8
∠H11C3C2	110.4
Dihedral Angle	Degree[a]
∠F4C1C2C3	+62.1
∠F4C1C2F7	-178.3

[a] +: Clockwise, -: Counter clockwise. The direction of dihedral angle observation is C1 → C2.

Figure 4. MP2(full)/6-31G(d) determined geometry of 1,2-difluoropropane.

G2MP2 calculations are performed on the most stable conformer of each compound, and the $\Delta H_f°_{298}$'s of this

TABLE 1: Vibrational Frequencies^a (in cm^{-1})

species	$CH_2FCH_2CH_3$	$CHF_2CH_2CH_3$	$CF_3CH_2CH_3$	$CH_2FCHFCH_3$	CHF_2CHFCH_3	$CHF_2CF_2CH_3$	CF_3CFHCH_3	$CF_3CF_2CH_3$
ν_1	152^b	119^b	111^b	128^b	94^b	93^b	84^b	76^b
ν_2	243^b	236^b	234^b	242^b	237^b	225^b	230^b	229^b
ν_3	337	271	244	274	262	249	244	235
ν_4	518	414	395	409	276	263	269	248
ν_5	838	541	444	475	418	389	364	360
ν_6	932	738	583	527	492	389	448	383
ν_7	1003	861	593	919	615	527	513	398
ν_8	1070	928	676	1018	738	558	588	483
ν_9	1181	1071	869	1061	917	594	629	551
ν_{10}	1233	1132	880	1191	1054	703	731	644
ν_{11}	1293	1209	1064	1233	1130	870	878	651
ν_{12}	1395	1283	1160	1268	1247	1084	1012	689
ν_{13}	1424	1289	1178	1297	1255	1097	1137	847
ν_{14}	1520	1418	1350	1379	1264	1257	1235	1033
ν_{15}	1567	1531	1350	1478	1322	1285	1273	1093
ν_{16}	1582	1556	1426	1529	1483	1354	1342	1260
ν_{17}	1626	1565	1471	1580	1522	1365	1388	1376
ν_{18}	1642	1582	1558	1589	1560	1436	1463	1381
ν_{19}	1653	1627	1576	1634	1580	1541	1512	1398
ν_{20}	1677	1645	1629	1641	1595	1574	1575	1424
ν_{21}	3201	1656	1644	1680	1635	1602	1587	1568
ν_{22}	3207	3220	1657	3219	1649	1628	1636	1584
ν_{23}	3233	3225	3225	3261	3232	1646	1648	1628
ν_{24}	3244	3258	3245	3263	3271	3244	3234	1642
ν_{25}	3266	3287	3282	3291	3303	3323	3288	3246
ν_{26}	3286	3301	3292	3303	3318	3333	3309	3327
ν_{27}	3290	3313	3304	3319	3335	3348	3318	3334

[a] Nonscaled. Frequencies are calculated at the HF/6-31G(d) level of theory. [b] Torsional frequencies. These frequencies are not included in the calculation of entropies $S°_{298}$ and heat capacities $C_p(T)$.

TABLE 2: G2MP2 Total Energies

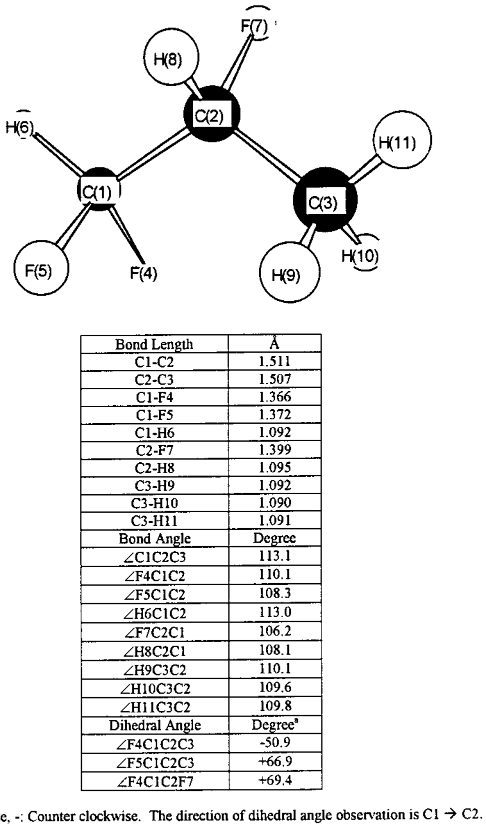
species	total energy^a	species	total energy^a
CH_3CH_3	−79.624 450	CH_3CHFCH_3	−218.006 412
CH_2FCH_3	−178.775 279	$CH_3CF_2CH_3$	−317.177 527
CHF_2CH_3	−277.942 239	CFH_2CFHCH_3	−317.152 673
CF_3CH_3	−377.116 202	$CF_2HCFHCH_3$	−416.316 634
$CH_3CH_2CH_3$	−118.847 504	$CF_2HCF_2CH_3$	−515.482 714
$CFH_2CH_2CH_3$	−217.998 301	CF_3CFHCH_3	−515.487 735
$CF_2HCH_2CH_3$	−317.165 109	$CF_3CF_2CH_3$	−614.650 639
$CF_3HCH_2CH_3$	−416.339 752		

[a] ZPVE's and thermal corrections to 298 K are included. Energies are in hartrees.

TABLE 3: Enthalpies of Formation ($\Delta H_f°_{298}$) Literature Values for Use in Isodesmic Reactions

species	$\Delta H_f°_{298}$ (kcal/mol)	species	$\Delta H_f°_{298}$ (kcal/mol)
CH_3CH_3	−20.24^a	$CH_3CH_2CH_3$	−24.82^a
CH_2FCH_3	−62.90^b	CH_3CHFCH_3	−70.15^c
CHF_2CH_3	−119.70^b	$CH_3CF_2CH_3$	−124.88^c
CF_3CH_3	−178.20^b		

[a] Reference 4. [b] Reference 6. [c] Reference 5.



Bond Length	Å
C1-C2	1.511
C2-C3	1.507
C1-F4	1.366
C1-F5	1.372
C1-H6	1.092
C2-F7	1.399
C2-H8	1.095
C3-H9	1.092
C3-H10	1.090
C3-H11	1.091
Bond Angle	**Degree**
∠C1C2C3	113.1
∠F4C1C2	110.1
∠F5C1C2	108.3
∠H6C1C2	113.0
∠F7C2C1	106.2
∠H8C2C1	108.1
∠H9C3C2	110.1
∠H10C3C2	109.6
∠H11C3C2	109.8
Dihedral Angle	**Degree^a**
∠F4C1C2C3	-50.9
∠F5C1C2C3	+66.9
∠F4C1C2F7	+69.4

[a] +: Clockwise, -: Counter clockwise. The direction of dihedral angle observation is C1 → C2.

Figure 5. MP2(full)/6-31G(d) determined geometry of 1,1,2-trifluoropropane.

conformer are calculated using isodesmic reactions. $\Delta H_f°_{298}$'s of other rotational conformers, if present, are estimated with energy differences between the lowest energy conformer at the MP2/6-31G(d) level of theory. Final $\Delta H_f°_{298}$ values are from a statistical distribution of rotational conformers.

2. Standard Entropy ($S°_{298}$) and Heat Capacities ($C_p(T)$ (300 ≤ T/K ≤ 1500)) and Hindered Rotation Contribution to Thermodynamic Parameters. Harmonic vibrational frequencies calculated at the HF6-31G(d) level of theory and the moments of inertia from molecular structures optimized at MP2(full)/6-31G(d) are used to calculate the $S°_{298}$ and $C_p(T)$'s.

Since a technique for the calculation of thermodynamic functions from hindered rotations with arbitrary potentials has been previously reported,[13,17,18] only a summary of the method is described. The technique employs expansion of the hindrance potential in a Fourier series, calculation of the Hamiltonian matrix in the basis of the wave functions of free internal rotation, and subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix. Calculated internal rotation potential barriers versus dihedral angle are represented by a

TABLE 4: Energies and Rotational Barriers

compound & rotor[a]	MP2(full)/6-31G(d)[b]	ZPVE[b] (nonscaled)	total energy[b,c]	rotational barrier height (kcal/mol)
CH$_2$F−CH$_2$CH$_3$S	−217.674 172	0.103 792	−217.581 783	0.53
CH$_2$F−CH$_2$CH$_3$S2	−217.675 105	0.103 921	−217.582 624	0.00
CH$_2$F−CH$_2$CH$_3$E	−217.667 327	0.103 941	−217.574 518	5.09
CH$_2$F−CH$_2$CH$_3$E2	−217.667 775	0.103 640	−217.575 235	4.64
CH$_2$FCH$_2$−CH$_3$S	−217.675 105	0.103 921	−217.582 808	0.00
CH$_2$FCH$_2$−CH$_3$E	−217.670 091	0.103 605	−217.577 582	3.28
CHF$_2$−CH$_2$CH$_3$S	−316.709 584	0.096 176	−316.623 959	0.01
CHF$_2$−CH$_2$CH$_3$S2	−316.709 867	0.096 312	−316.624 112	0.000
CHF$_2$−CH$_2$CH$_3$E	−316.702 319	0.096 210	−316.616 413	4.83
CHF$_2$−CH$_2$CH$_3$E2	−316.702 486	0.095 992	−316.616 774	4.60
CHF$_2$CH$_2$−CH$_3$S	−316.709 867	0.096 312	−316.624 350	0.00
CHF$_2$CH$_2$−CH$_3$E	−316.705 449	0.095 985	−316.619 744	2.89
CF$_3$−CH$_2$CH$_3$S	−415.753 761	0.087 572	−415.675 794	0.00
CF$_3$−CH$_2$CH$_3$E	−415.746 573	0.087 481	−415.668 462	4.60
CF$_3$CH$_2$−CH$_3$S	−415.753 761	0.087 572	−415.676 043	0.00
CF$_3$CH$_2$−CH$_3$E	−415.749 464	0.087 286	−415.671 526	2.83
CH$_2$F−CHFCH$_3$S	−316.692 492	0.096 040	−316.606 996	0.68
CH$_2$F−CHFCH$_3$S2	−316.693 292	0.096 211	−316.607 630	0.28
CH$_2$F−CHFCH$_3$S3	−316.693 671	0.096 155	−316.608 073	0.00
CH$_2$F−CHFCH$_3$E	−316.680 738	0.096 094	−316.594 936	8.24
CH$_2$F−CHFCH$_3$E2	−316.687 754	0.096 089	−316.601 956	3.84
CH$_2$F−CHFCH$_3$E3	−316.687 316	0.095 903	−316.601 684	4.01
CH$_2$FCHF−CH$_3$S	−316.693 671	0.096 155	−316.608 306	0.00
CH$_2$FCHF−CH$_3$E	−316.687 968	0.095 820	−316.602 411	3.55
CHF$_2$−CHFCH$_3$S	−415.722 494	0.088 335	−415.643 808	1.88
CHF$_2$−CHFCH$_3$S2	−415.725 544	0.088 400	−415.646 803	0.00
CHF$_2$−CHFCH$_3$S3	−415.724 912	0.088 424	−415.646 150	0.41
CHF$_2$−CHFCH$_3$E	−415.714 511	0.088 500	−415.635 489	7.10
CHF$_2$−CHFCH$_3$E2	−415.719 974	0.088 282	−415.641 147	3.55
CHF$_2$−CHFCH$_3$E3	−415.715 448	0.088 296	−415.636 608	6.40
CHF$_2$CHF−CH$_3$S	−415.725 544	0.088 400	−415.647 094	0.00
CHF$_2$CHF−CH$_3$E	−415.716 999	0.087 998	−415.638 426	5.44
CHF$_2$−CF$_2$CH$_3$S	−514.755 836	0.079 670	−514.684 866	2.21
CHF$_2$−CF$_2$CH$_3$S2	−514.759 360	0.079 688	−514.688 394	0.00
CHF$_2$−CF$_2$CH$_3$E	−514.746 539	0.079 732	−514.675 346	8.19
CHF$_2$−CF$_2$CH$_3$E2	−514.751 144	0.079 756	−514.679 930	5.31
CHF$_2$CF$_2$−CH$_3$S	−514.759 360	0.079 688	−514.688 664	0.00
CHF$_2$CF$_2$−CH$_3$E	−514.750 098	0.079 283	−514.679 306	5.87
CF$_3$−CHFCH$_3$S	−514.765 800	0.079 590	−514.694 906	0.00
CF$_3$−CHFCH$_3$E	−514.758 246	0.079 642	−514.687 134	4.88
CF$_3$CHF−CH$_3$S	−514.765 800	0.079 590	−514.695 201	0.00
CF$_3$CHF−CH$_3$E	−514.760 703	0.079 273	−514.689 920	3.31
CF$_3$−CF$_2$CH$_3$S	−613.796 345	0.070 823	−613.733 262	0.00
CF$_3$−CF$_2$CH$_3$E	−613.788 829	0.070 949	−613.725 478	4.88
CF$_3$CF$_2$−CH$_3$S	−613.796 345	0.070 823	−613.733 573	0.00
CF$_3$CF$_2$−CH$_3$E	−613.790 911	0.070 460	−613.727 998	3.50

[a] See Figure 9 to 16 for definition of geometric nomenclature. [b] In units of hartree. [c] Scaled ZPVE are included. The corresponding torsional frequencies are excluded.

truncated Fourier series:

$$V(\theta) = a_0 + a_1\cos(\theta) + a_2\cos(2\theta) + a_3\cos(3\theta) + b_1\sin(\theta) + b_2\sin(2\theta) + b_3\sin(3\theta) \quad (3)$$

where values of the coefficients a_i are calculated to provide the minimum and maxima of the torsional potentials with allowance of a shift of the theoretical extrema angular positions.

The Hamiltonian matrix is then truncated to the size of $2K_{\max} + 1$, where $K_{\max}$ is the maximum rotational quantum number considered. The truncated matrix (in reduced dimensionless form) is diagonalized, and the eigenvalues are used to calculate the partition function, entropy, heat capacity, etc. This is accomplished using a direct summation over the calculated energy levels according to standard expressions of statistical thermodynamics.[19]

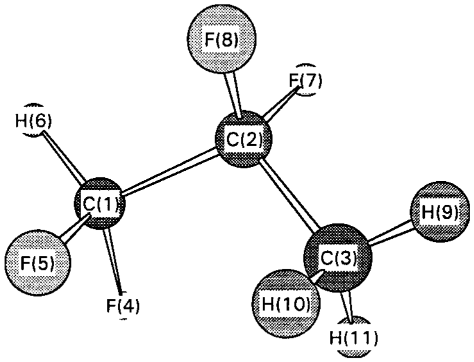
Results and Discussion

1. Geometries. Figures 1−8 present MP2(full)/6-31G(d) determined geometries. Bond lengths, bond angles for the three backbone carbons, ∠C1C2C3, bond angles between the terminal atom (either F or H) and two backbone carbons, ∠(F or H)-

TABLE 5: $\Delta H_f{}^\circ{}_{298}$ for Rotational Conformers, Weight Fraction, and Overall $\Delta H_f{}^\circ{}_{298}$ Values

compd & rotor[a]	energy (kcal/mol)	partition coefficient	final value (kcal/mol)
CH$_2$FCH$_2$CH$_3$S	−66.93	0.2901	
CH$_2$FCH$_2$CH$_3$S2	−67.46	0.7099	−67.37
CHF$_2$CH$_2$CH$_3$S	−123.66	0.4958	
CHF$_2$CH$_2$CH$_3$S2	−123.67	0.5042	−123.66
CF$_3$CH$_2$CH$_3$S	−183.09	1.0000	−183.09
CH$_2$FCHFCH$_3$S	−109.27	0.1635	
CH$_2$FCHFCH$_3$S2	−109.67	0.3212	
CH$_2$FCHFCH$_3$S3	−109.95	0.5153	−109.75
CHF$_2$CHFCH$_3$S	−162.98	0.0271	
CHF$_2$CHFCH$_3$S2	−164.86	0.6462	
CHF$_2$CHFCH$_3$S3	−164.45	0.3267	−164.68
CHF$_2$CF$_2$CH$_3$S	−214.22	0.0234	
CHF$_2$CF$_2$CH$_3$S2	−216.43	0.9766	−216.38
CF$_3$CHFCH$_3$S	−221.57	1.0000	−221.57
CF$_3$CF$_2$CH$_3$S	−271.14	1.0000	−271.14

[a] See Figures 9−16 for definition of geometric nomenclature.



Bond Length	Å
C1-C2	1.517
C2-C3	1.497
C1-F4	1.364
C1-F5	1.364
C1-H6	1.092
C2-F7	1.373
C2-F8	1.373
C3-H9	1.091
C3-H10	1.090
C3-H12	1.090
Bond Angle	Degree
∠C1C2C3	10115.4
∠F4C1C2	108.7
∠F5C1C2	108.7
∠H6C1C2	111.9
∠F7C2C1	106.4
∠F8C2C1	106.4
∠H9C3C2	108.6
∠H10C3C2	109.6
∠H11C3C2	109.6
Dihedral Angle	Degree[a]
∠F4C1C2C3	-58.9
∠F5C1C2C3	+58.9
∠F4C1C2F7	+64.0
∠F4C1C2F8	+178.1

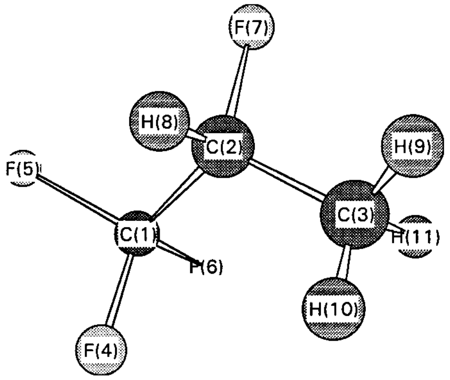
[a] +: Clockwise, -: Counter clockwise. The direction of dihedral angle observation is C1 → C2.

Figure 6. MP2(full)/6-31G(d) determined geometry of 1,1,2,2-tetrafluoropropane.

TABLE 6: Rotational Constants[a]

species	I_a	I_b	I_c
$CH_2FCH_2CH_3$	14.639	5.175	4.351
$CHF_2CH_2CH_3$	7.124	4.118	3.437
$CF_3CH_2CH_3$	5.349	2.789	2.759
$CH_2FCHFCH_3$	8.152	3.624	2.731
CHF_2CHFCH_3	4.962	2.798	2.473
$CHF_2CF_2CH_3$	3.511	2.374	2.022
CF_3CHFCH_3	3.614	2.431	1.994
$CF_3CF_2CH_3$	2.777	1.871	1.847

[a] Optimized by MP2(full)/6-31G(d). In units of gigahertz.



Bond Length	Å
C1-C2	1.513
C2-C3	1.508
C1-F4	1.353
C1-F5	1.345
C1-F6	1.346
C2-F7	1.393
C2-H8	1.094
C8-H9	1.091
C8-H10	1.091
C8-H11	1.091
Bond Angle	Degree
∠C1C2C3	112.8
∠F4C1C2	109.7
∠F5C1C2	111.3
∠F6C1C2	111.7
∠F7C2C1	106.3
∠H8C2C1	107.4
∠H9C3C2	109.3
∠H10C3C2	110.6
∠H11C3C2	109.6
Dihedral Angle	Degree[a]
∠F4C1C2F7	-177.5
∠F5C1C2F7	-58.0
∠F6C1C2F7	+62.8
∠F4C1C2C3	+62.3

[a] +: Clockwise, -: Counter clockwise. The direction of dihedral angle observation is C1 → C2.

Figure 7. MP2(full)/6-31G(d) determined geometry of 1,1,1,2-tetrafluoropropane.

TABLE 7: Coefficients of Truncated Fourier Series Representation Expansions for Internal Rotational Potentials

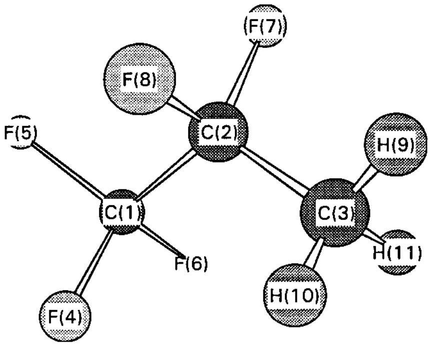
species	a_0	a_1	a_2	a_3	b_1	b_2	b_3
$CH_2F-CH_2CH_3$	2.482	−0.026	0.326	2.306	0.000	0.000	0.000
$CH_2FCH_2-CH_3$	1.640	0.000	0.000	1.640	0.000	0.000	0.000
$CHF_2-CH_2CH_3$	2.410	−0.044	−0.108	2.346	0.000	0.000	0.000
$CHF_2CH_2-CH_3$	1.445	0.000	0.000	1.445	0.000	0.000	0.000
$CF_3-CH_2CH_3$	2.301	0.000	0.000	2.301	0.000	0.000	0.000
$CF_3CH_2-CH_3$	1.417	0.000	0.000	1.417	0.000	0.000	0.000
$CH_2F-CHFCH_3$	2.841	1.599	1.281	2.523	−0.164	−0.066	0.000
$CH_2FCHF-CH_3$	1.777	0.000	0.000	1.777	0.000	0.000	0.000
$CHF_2-CHFCH_3$	3.263	0.925	0.493	2.419	−1.296	0.349	0.357
$CHF_2CHF-CH_3$	2.720	0.000	0.000	2.720	0.000	0.000	0.000
$CHF_2-CF_2CH_3$	3.892	1.733	0.202	2.361	0.000	0.000	0.000
$CHF_2CF_2-CH_3$	2.936	0.000	0.000	2.936	0.000	0.000	0.000
$CF_3-CHFCH_3$	2.439	0.000	0.000	2.439	0.000	0.000	0.000
$CF_3CHF-CH_3$	1.657	0.000	0.000	1.657	0.000	0.000	0.000
$CF_3-CF_2CH_3$	2.442	0.000	0.000	2.442	0.000	0.000	0.000
$CF_3CF_2-CH_3$	1.750	0.000	0.000	1.750	0.000	0.000	0.000

C_xC_y, and dihedral angles that show the relation between carbon and fluorine are illustrated.

Figure 1 shows the MP2(full)/6-31G(d) determined geometry of 1-fluoropropane. The methyl-F gauche conformation consistently shows lower energy than the anti gauche conformation. We evaluate this as a F−H attractive interaction between fluorine connected to C_1 and hydrogen connected to C_3, but there is no strong evidence for it. Bond lengths between fluorine connected to C_1 and hydrogens connected to C_3 (H9, H10, and H11) are 2.566, 3.294, and 3.880 Å, respectively.

The evaluated bond lengths for C_1-C_2 in 1-fluoropropane, 1,1-difluoropropane, and 1,1,1-trifluoropropane show that an increase in fluorine number at the C_1 carbon site causes a decrease in the C_1-C_2 bond length. Evaluation of the C_1-C_2 and C_2-C_3 bond lengths in 2-fluoropropane and 2,2-difluoropropane also shows that an increase of fluorine number at the C_2 carbon causes a decrease in the C_1-C_2 and C_2-C_3 bond lengths. The C_1-C_2 and C_2-C_3 bond lengths in propane, 2-fluoropropane, and 2,2-difluoropropane, for which geometries are not shown, are 1.528, 1.516, and 1.508 Å, respectively. Figures 3, 7, and 8 support this observation and show that the bond length between C_2 and C_3 decreases with an increase in number of fluorine(s) at C_2 where no fluorine is on C_3. Figures 1−3 show that the number of fluorines connected to C_1 does not significantly affect to the bond length of C_2-C_3. On the other hand, the interaction between the fluorine(s) on the C_1 with fluorine(s) and the methyl group bonded to C_2 causes an increase in the C_1-C_2 bond length.

The bond length between carbon and fluorine decreases with an increase in fluorine number on the same carbon. The bond lengths between C_1 and F are 1.401, 1.375, and 1.353 or 1.354 Å for 1-fluoropropane, 1,1-difluoropropane, and 1,1,1-trifluo-



Bond Length	Å
C1-C2	1.526
C2-C3	1.498
C1-F4	1.346
C1-F5	1.338
C1-F6	1.346
C2-F7	1.368
C2-F8	1.368
C3-H9	1.091
C3-H10	1.090
C3-H11	1.090
Bond Angle	Degree
∠C1C2C3	114.7
∠F4C1C2	110.0
∠F5C1C2	111.1
∠F6C1C2	110.0
∠F7C2C1	106.5
∠F8C2C1	106.5
∠H9C3C2	108.1
∠H10C3C2	109.8
∠H11C3C2	109.8
Dihedral Angle	Degree[a]
∠F4C1C2F7	-177.8
∠F5C1C2F7	-57.4
∠F6C1C2F7	+63.0
∠F4C1C2F8	+63.0
∠C4C1C2F3	+59.6

[a] +: Clockwise, -: Counter clockwise. The direction of dihedral angle observation is C1 → C2.

Figure 8. MP2(full)/6-31G(d) determined geometry of 1,1,1,2,2-pentafluoropropane.

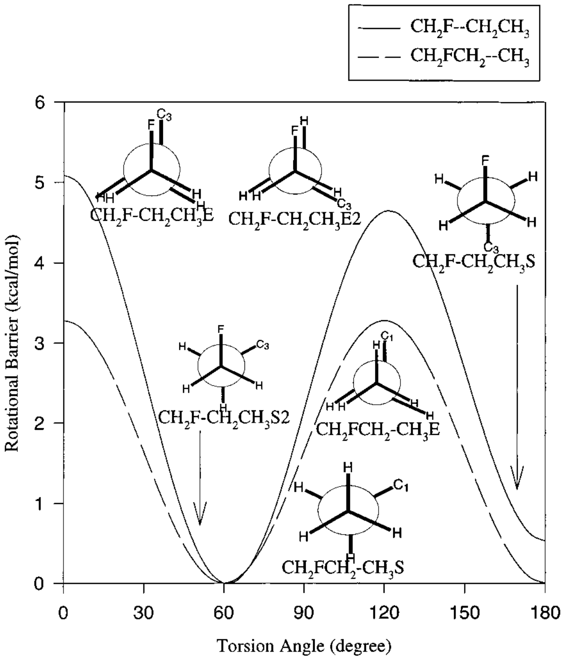


Figure 9. Potential barriers for internal rotations about C1−C2 and C2−C3 bonds of 1-fluoropropane.

ropropane, respectively. All C−H bond lengths are more than 0.01 Å longer than the normal C−H bond length in hydrocarbons.

The bond angle $\angle C_1-C_2-C_3$ is also listed in each figure. Interactions between the fluorines connected to different carbons show only slight effects on the bond angle $\angle C_1-C_2-C_3$. The interaction between the fluorines connected to the same carbon also appears to have no significant effect on the $\angle C_1-C_2-C_3$ bond angle.

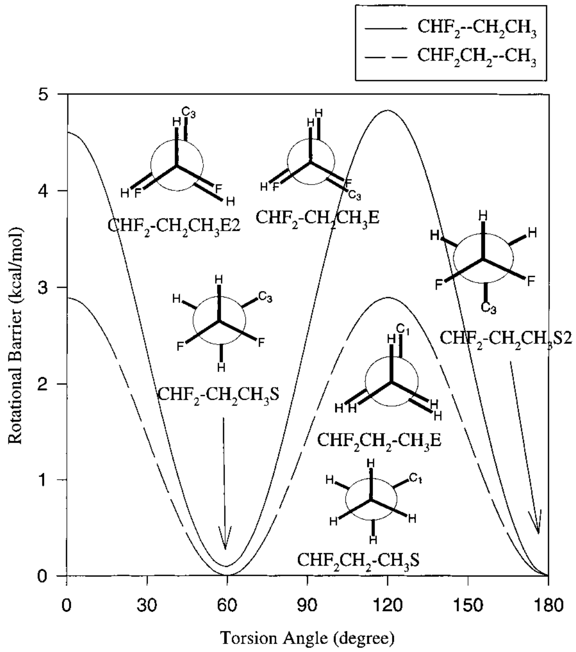


Figure 10. Potential barriers for internal rotations about C1−C2 and C2−C3 bonds of 1,1-difluoropropane.

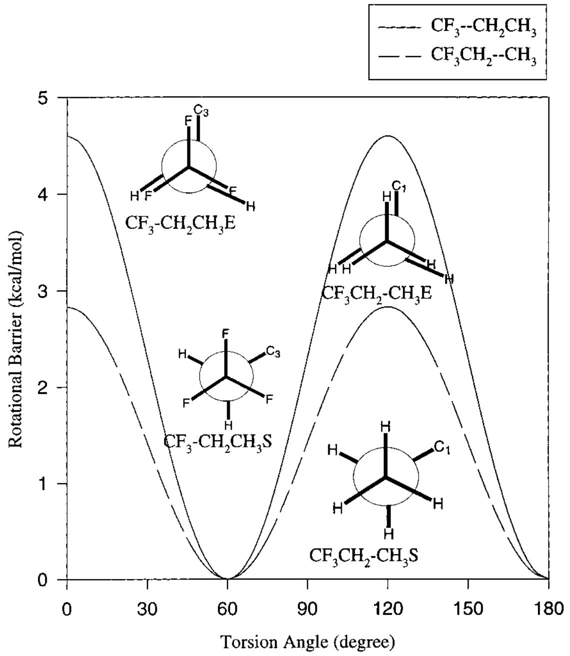


Figure 11. Potential barriers for internal rotations about C1−C2 and C2−C3 bonds of 1,1,1-trifluoropropane.

2. Frequencies. Table 1 lists the HF/6-31G(d) determined frequencies of fluorinated propane compounds: 1-fluoropropane, 1,1-difluoropropane, 1,1,1-trifluoropropane, 1,2-difluoropropane, 1,1,2-trifluoropropane, 1,1,2,2-tetrafluoropropane, 1,1,1,2-tetrafluoropropane, 1,1,1,2,2-pentafluoropropane. The first two numbers in Table 1 are torsional frequencies, which are excluded from $S°_{298}$ and $C_p(T)$ calculations. The first number is the torsional frequency for C_1 and C_2. The interaction between fluorine(s) connected to C_1 with fluorine(s) and C_3 connected to C_2 lowers the torsional frequencies. The second number is

TABLE 8: Ideal Gas-Phase Thermodynamic Properties[a]

species and symmetry no.		$H_f°_{298}$[b]	$S°_{298}$[c]	C_{p300}[c]	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
$CFH_2CH_2CH_3$	TVR[d]		63.73[g]	15.16	20.10	24.82	28.96	35.57	40.44	47.83
(3)	internal rotor 1[e]		5.38	2.41	2.45	2.43	2.35	2.11	1.87	1.48
	internal rotor 2[f]		4.28	2.13	2.19	2.10	1.96	1.70	1.51	1.26
	total	−67.37	73.39	19.70	24.74	29.35	33.27	39.38	43.82	50.57
	Frenkel et al.[h]	−67.83	72.84	19.71	24.65	29.18	33.02	39.04	43.42	
	Stull et al.[i]	−67.20	72.84	19.83	24.55	28.99	32.82	38.88	43.37	
$CHF_2CH_2CH_3$	TVR[d]		67.31	17.29	22.45	27.18	31.23	37.52	42.06	48.81
(3)	internal rotor 1[e]		5.75	2.19	2.30	2.33	2.28	2.08	1.86	1.46
	internal rotor 2[f]		4.45	2.16	2.14	2.00	1.84	1.58	1.41	1.20
	total	−123.66	77.51	21.64	26.89	31.51	35.35	41.18	45.33	51.47
$CF_3CH_2CH_3$	TVR[d]		68.43	19.97	25.33	30.01	33.90	39.78	43.91	49.92
(9)	internal rotor 1[e]		5.89	2.19	2.31	2.33	2.27	2.06	1.84	1.43
	internal rotor 2[f]		4.47	2.16	2.13	1.98	1.82	1.57	1.40	1.20
	total	−183.09	78.79	24.32	29.77	34.32	37.99	43.41	47.15	52.55
$CH_2FCHFCH_3$	TVR[d]		67.98	17.61	22.62	27.29	31.30	37.55	42.06	48.80
(3)	internal rotor 1[e]		5.58	2.50	2.44	2.35	2.23	2.01	1.83	1.51
	internal rotor 2[f]		4.18	2.10	2.20	2.15	2.03	1.77	1.57	1.30
	total	−109.75	77.74	22.21	27.26	31.79	35.56	41.33	45.46	51.61
CHF_2CHFCH_3	TVR[d]		71.27	19.75	24.96	29.63	33.56	39.51	43.70	49.79
(3)	internal rotor 1[e]		5.36	2.89	2.88	2.79	2.65	2.36	2.08	1.56
	internal rotor 2[f]		3.72	1.86	2.09	2.21	2.25	2.15	1.98	1.60
	total	−164.68	80.35	24.50	29.93	34.63	38.46	44.02	47.76	52.95
$CHF_2CF_2CH_3$	TVR[d]		74.59	22.59	27.92	32.49	36.22	41.74	45.51	50.88
(3)	internal rotor 1[e]		4.48	3.51	3.87	3.78	3.50	2.88	2.38	1.67
	internal rotor 2[f]		7.08	2.33	2.23	2.05	1.86	1.56	1.33	0.94
	total	−216.38	82.72	27.92	33.84	38.46	41.97	46.82	49.94	54.14
CF_3CHFCH_3	TVR[d]		72.14	22.41	27.82	32.43	36.20	41.75	45.54	50.92
(9)	internal rotor 1[e]		6.20	2.18	2.30	2.34	2.30	2.10	1.86	1.35
	internal rotor 2[f]		4.29	2.13	2.19	2.11	1.97	1.71	1.52	1.26
	total	−221.57	82.63	26.72	32.31	36.88	40.47	45.56	48.92	53.53
$CF_3CF_2CH_3$	TVR[d]		75.45	25.27	30.76	35.27	38.85	43.97	47.56	52.01
(9)	internal rotor 1[e]		6.38	2.19	2.30	2.34	2.30	2.09	1.82	1.26
	internal rotor 2[f]		4.23	2.11	2.20	2.14	2.02	1.76	1.56	1.29
	total	−271.14	86.06	29.57	35.26	39.75	43.17	47.82	50.94	54.56

[a] Thermodynamic properties are referenced to a standard state of an ideal gas of pure enantiometer at 1 atm. Torsional frequencies are excluded in the calculations of entropies and heat capacities. Instead, an exact contribution from hindered rotations about the C−C is included. See text. [b] In units of kcal/mol. [c] In units of cal mol^{-1} K^{-1}. [d] Sum of contributions from translations, external rotations, and vibrations. [e] Contribution from internal rotation about the C1−C2 bond. [f] Contribution from internal rotation about the C2−C3 bond. [g] Symmetry number is taken into account (−*R* ln(number of symmetry)). [h] Reference 5. [i] Reference 4.

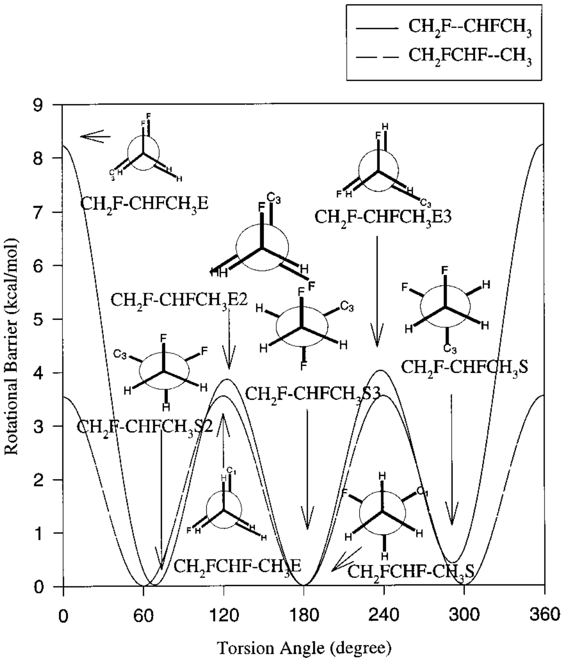


Figure 12. Potential barriers for internal rotations about C1−C2 and C2−C3 bonds of 1,2-difluoropropane.

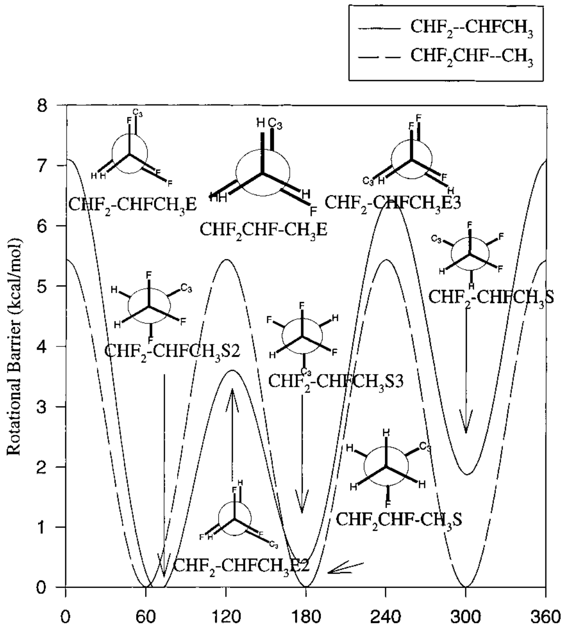


Figure 13. Potential barriers for internal rotations about C1−C2 and C2−C3 bonds of 1,1,2-trifluoropropane.

the torsional frequency for C_2 and C_3. No significant difference in frequency is observed in this C2−C3 torsion among the eight compounds; this is attributed to a lack of fluorine−fluorine or carbon−fluorine interaction between the C_2 and C_3 groups.

3. Enthalpies of Formation ($\Delta H_f°_{298}$). G2MP2 determined total energies of the lowest energy conformation for the eight compounds are listed in Table 2. The $\Delta H_f°_{298}$'s from the literature for use in isodesmic reactions are also listed in Table

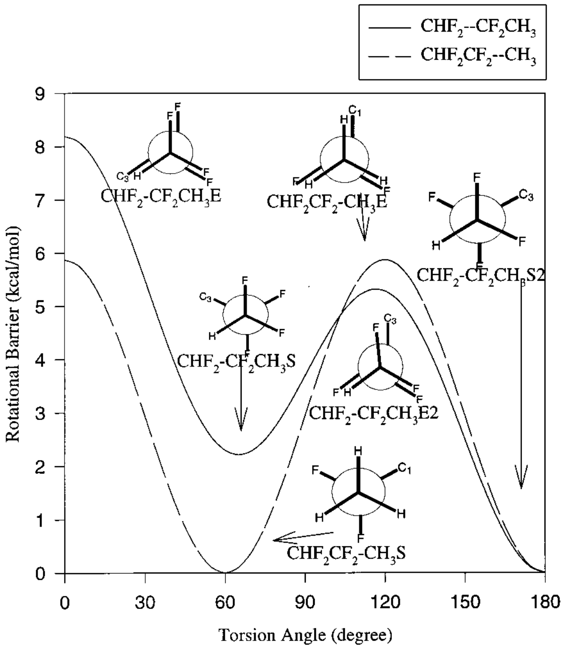


Figure 14. Potential barriers for internal rotations about C1−C2 and C2−C3 bonds of 1,1,2,2-tetrafluoropropane.

3. The $\Delta H_{\mathrm{rxn}}°_{298}$ for reaction 2 is calculated using the G2MP2 determined total energies.

$$CH_3CH_2CH_3 + CFH_2CH_3 - (CFH_2CH_2CH_3 + CH_3CH_3) = -0.02\ \mathrm{kcal/mol}$$

The $\Delta H_f°_{298}$ of 1-fluoropropane is calculated using the known $\Delta H_f°_{298}$ for ethane, propane, and fluoroethane with the calculated $\Delta H_{\mathrm{rxn}}°_{298}$. The calculation results in a value of −67.46 kcal/mol.

There are three staggered conformations in 1-fluoropropane. Two of them are F−CH_3 gauche staggered conformation and one of them is anti-gauche conformation. Gauche staggered conformation shows lower energy than anti-gauche staggered conformation as shown in Table 4 and Figure 9. $\Delta H_f°_{298}$ of higher energy conformation is estimated by adding the difference of the staggered conformation calculated at the MP2(full)/6-31G(d) level. This difference is 0.53 kcal/mol as listed in Table 4 and described below. $\Delta H_f°_{298}$ of the rotational conformers, their weight fraction, and overall $\Delta H_f°_{298}$ are listed in Table 5. Literature values[4,5] are listed in Table 8. Our result is between and in good agreement with the literature values. The $\Delta H_f°_{298}$ values of the seven remaining compounds are calculated in the same manner and listed in Table 8.

4. Rotational Barriers. Barriers for internal rotations are calculated as the difference between the total energy of each conformation and that of the global equilibrium plus the scaled ZPVE difference (see Table 4). The curves are fit by a truncated Fourier series (eq 3). Table 7 lists the coefficients of the respective Fourier series.

Figure 9 shows the calculated rotational barriers for 1-fluoropropane. Solid and broken lines in Figures 9−16 show rotational barriers for C_1−C_2 and C_2−C_3, respectively, for the eight fluoropropanes. The C−F eclipsed conformation for C_1−C_2 in 1-fluoropropane has the highest rotational barrier, which is 5.09 kcal/mol. The C−F gauche staggered conformation is more stable than C−F anti staggered conformation. Since this rotational barrier curve is symmetric with respect to zero torsion angle (∠F−C_1−C_2−C_3), it can be fit by a cosine series. The calculated rotational barrier for C_2−C_3 is 3.28 kcal/mol, and the rotational barrier curves of C_2−C_3 for all eight compounds can be fit by using only a_0 and a_3 in a truncated Fourier series.

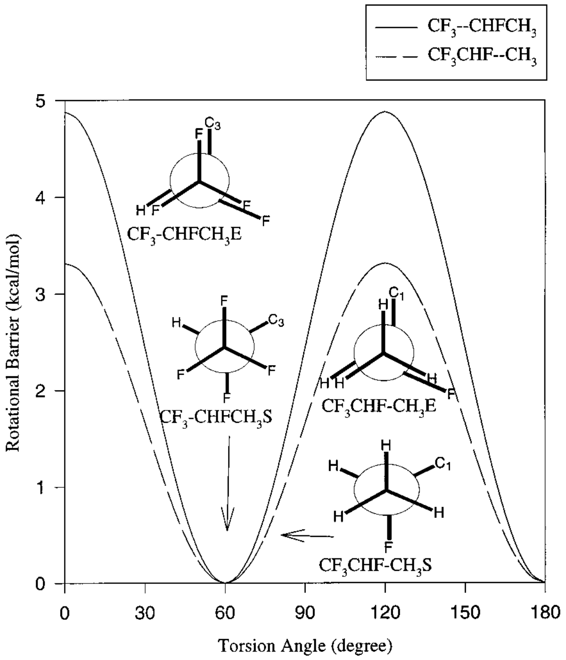


Figure 15. Potential barriers for internal rotations about C1−C2 and C2−C3 bonds of 1,1,1,2-tetrafluoropropane.

Figure 10 shows the rotational barriers for 1,1-difluoropropane. The curves are similar in form to 1-fluoropropane. The C−F eclipsed conformation has the highest rotational barrier, which is 4.83 kcal/mol. The dual C−F gauche staggered conformation is more stable than the single C−F gauche staggered conformation. The rotational barrier for C_2−C_3 is 2.89 kcal/mol.

Figure 11 shows the rotational barriers for 1,1,1-trifluoropropane. The rotational barriers are 4.60 and 2.83 kcal/mol for C_1−C_2 and C_2−C_3, respectively.

Figure 12 shows the rotational barriers for 1,2-difluoropropane. The F−F eclipsed conformation for C_1−C_2 has the highest rotational barrier, which is 8.24 kcal/mol. This rotational barrier is also the highest among the eight fluorinated propane compounds in this study. This trend is also seen in our previous study on fluorinated ethane,[13] where F−F eclipsed conformation for 1,2-difluoroethane shows the highest rotational barrier among nine fluorinated ethane compounds. The F−C gauche conformation shows the most stable conformation. The rotational barrier for C_2−C_3 is 3.55 kcal/mol.

Figure 13 shows the rotational barrier for 1,1,2-trifluoropropane. The F−C eclipsed conformation for C_1−C_2 shows a 7.10 kcal/mol rotational barrier. The single F−F, dual C−F gauche conformation is the most stable. The rotational barrier for C_2−C_3 is 5.44 kcal/mol.

Figure 14 shows the rotational barrier for 1,1,2,2-tetrafluoropropane. The dual F−F eclipsed conformation for C_1−C_2 has the highest rotational barrier, which is 8.19 kcal/mol. The dual C−F gauche conformation shows the most stable conformation. The rotational barrier for C_2−C_3 is 5.87 kcal/mol.

Figures 15 and 16 show the rotational barrier for 1,1,1,2-tetrafluoropropane and 1,1,1,2,2-pentafluoropropane, respectively. The rotational barriers are 4.88 and 3.31 kcal/mol for C_1−C_2 and C_2−C_3, respectively, for 1,1,1,2-tetrafluoropropane. The rotational barriers are 4.88 and 3.50 kcal/mol for C_1−C_2 and C_2−C_3, respectively, for 1,1,1,2,2-pentafluoropropane.

5. Standard Entropy ($S°_{298}$) and Heat Capacities ($C_p(T)$, $300 \leq T/\mathrm{K} \leq 1500$). Standard entropy ($S°_{298}$) and heat capacities

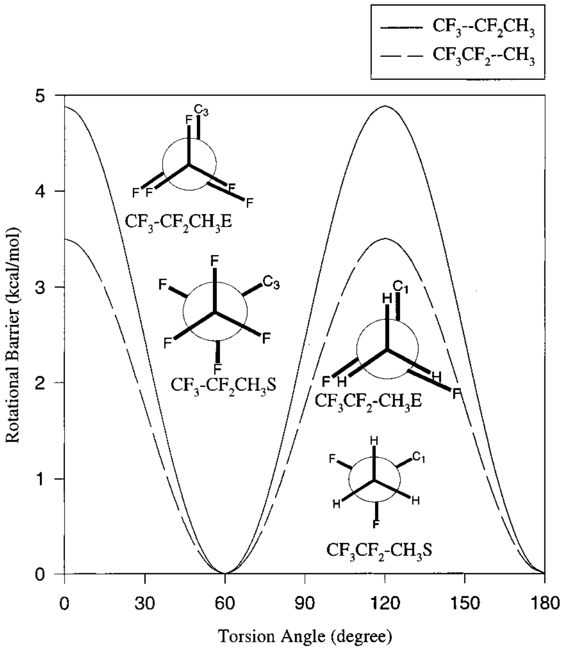


Figure 16. Potential barriers for internal rotations about C1−C2 and C2−C3 bonds of 1,1,1,2,2-pentafluoropropane.

($C_p(T)$'s, 300 ≤ T/K ≤ 1500) are listed in Table 8. TVR indicates the sum of contributions from translations, external rotations, and vibrations. Internal rotors 1 and 2 indicate contributions to $S°_{298}$ and $C_p(T)$'s from internal rotation about C_1−C_2 and C_2−C_3, respectively. Rotational constants for calculation of the contribution from internal rotations to $S°_{298}$ and $C_p(T)$'s are determined from the geometries optimized by MP2(full)/6-31G(d) level of theory and listed in Table 6. Coefficients of the truncated Fourier series representing the internal rotational potentials are tabulated in Table 7. Literature values for 1-fluoropropane are listed in Table 8.[4,5] The calculated $S°_{298}$ is 0.55 cal mol^{-1} K^{-1} higher than the literature value. The calculated $C_p(T)$'s also show 0−0.4 cal mol^{-1} K^{-1} higher values than the literature data.

Summary

Thermodynamic properties ($\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$'s (300 ≤ T/K ≤ 1500)) for 1-fluoropropane, 1,1-difluoropropane, 1,1,1-trifluoropropane, 1,2-difluoropropane, 1,1,2-trifluoropropane, 1,1,2,2-tetrafluoropropane, 1,1,1,2-tetrafluoropropane, and 1,1,1,2,2-pentafluoropropane are calculated. The $\Delta H_f°_{298}$ for the above eight compounds are estimated using the G2MP2 composite calculation methods and isodesmic reactions. Lowest energy geometries correspond to the maximum number of C−F gauche conformations. A general isodesmic reaction scheme for fluorinated propane compounds is presented and suggested for other halogenated propanes. $S°_{298}$'s and $C_p(T)$'s are estimated using scaled HF/6-31G(d) determined frequencies and MP2(full)/6-31G(d) determined geometries. Hindered internal rotational contributions for $S°_{298}$'s and $C_p(T)$'s are calculated using the rigid rotor harmonic oscillator approximation with direct integration over energy levels of the intramolecular rotation potential energy curve. Rotational barrier heights are reported for both C_1−C_2 and C_2−C_3 internal rotors. The calculated thermodynamic properties ($\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$ (300 ≤ T/K ≤ 1500)) for 1-fluoropropane are compared with literature values and shown to be in good agreement.

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