Synthesis and Conformational Studies of Methylated, Highly Branched Fluoroolefins: Gear-Meshed Conformational Isomers

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Methylated, highly branched fluoroolefins were prepared by treatment of hexafluoropropene trimers with CH_3Li and CH_3MgBr. Their structures, which included some rotational isomers, were determined by NMR and GC-MS and were further confirmed by B3LYP-GIAO calculation of NMR shieldings. Of the seven methylated fluoroolefins isolated in pure states, three were shown to be mixtures of pairs of conformational isomers. The methylated fluoroolefins containing two bulky geminal substituents such as $(CF_3)_2CF$ and $(CF_3)_2CCH_3$ showed gear-meshed conformations in which the two bulky substituents were conformationally locked.

Introduction

Fluoroolefins have been used industrially as important monomers for the preparation of engineering polymers and also as intermediates for various functional materials.[1] They have also recently been attracting attentions as the starting materials for hydrocarbon-fluorocarbon hybrid compounds, which could be useful as key compounds in fluorous chemistry.[2] The unique properties of fluoroolefins mainly derive from the electronegativity and/or the steric hindrance of fluorinated substituents. As an example, persistent perfluoroalkyl radicals, which can be prepared either by direct fluorination or by electrochemical fluorination of highly branched fluoroolefins,[3,4] are stable to oxidizing agents, acids, and bases, and in one particular case even to 100% fluorine gas. Such surprising properties and reactivities are due to the presence of highly branched perfluoroalkyl groups surrounding the radical center. Structural studies on such highly branched perfluoroalkyl compounds are therefore significant not only for study of the properties and reactivities of fluorinated compounds but also for the design of new functional fluorinated compounds.

It is well known that ^{19}F NMR measurements are informative for identification of fluorinated compounds.[5] This method is also useful for configurational and conformational studies of the perfluoroalkyl compounds, thanks to ^{19}F-^{19}F through-space couplings, the magnitudes of through-space couplings depending mainly on the nonbonding F−F distance.[6−9] For example, conformations of highly branched fluoroolefins such as hexafluoropropene dimers and trimers have been reported: thanks to the steric hindrance of the perfluoroalkyl groups, hexafluoropropene trimers have several rotational isomers at ambient temperature.[10,11] With recent development in computational chemistry, experimental ^{19}F chemical shifts have become reproducible through ab initio and DFT calculations of ^{19}F shieldings.[12−15] In addition, ab initio and DFT calculations have now become a very powerful tool for structural and conformational studies of fluorinated compounds.[16−20] These researches, however, have targeted only simple fluorinated compounds, but not complex fluorinated compounds. We recently carried out a systematic study on DFT calculations of ^{19}F shielding values of various fluoro compounds by the B3LYP-GIAO method with various basis sets; we found that the 6-31++G(d,p) basis set is quite good for estimation of the chemical shifts of rather complex fluoro compounds.[21]

We have also reported the formation of various methylated, highly branched fluoroolefins (**1**−**10**) by treatment of perfluoro(3-ethyl-2,4-dimethyl-2-pentene) (**T-3**) or perfluoro(4-methyl-3-isopropyl-2-pentene) (**T-2**) with organometallic reagents (CH_3Li and CH_3MgBr), focusing on the formation of an unusual cyclized product (**5**) and a reduced conjugated diene product (**6**).[22] Here we would like to report the full details of these reactions, with emphasis on the structural elucidation of the products **1**−**10** and additional new products (**11**, **12**). The discussion includes the gear-meshed conformations and rotational isomers of the products (**2**, **3**, **8**) that were revealed by the combination of experimental and theoretical NMR analyses by our previously reported B3LYP-GIAO method.

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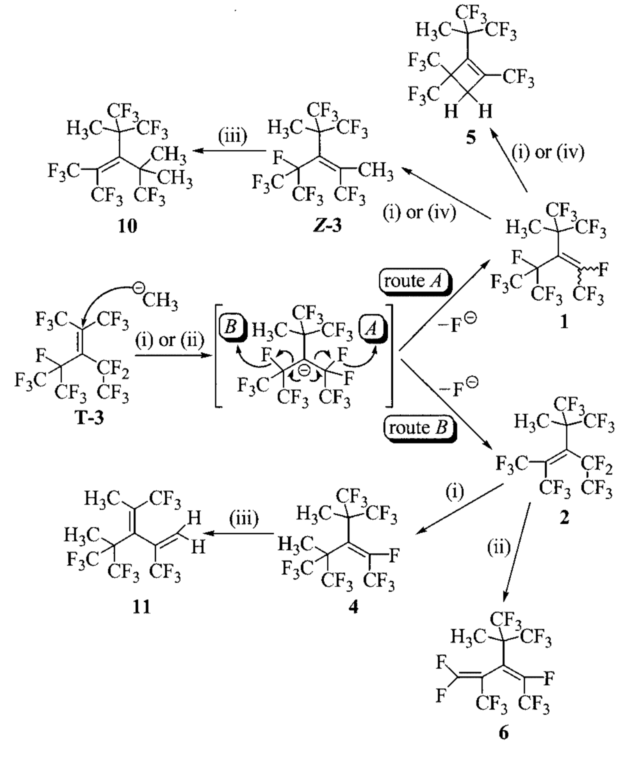
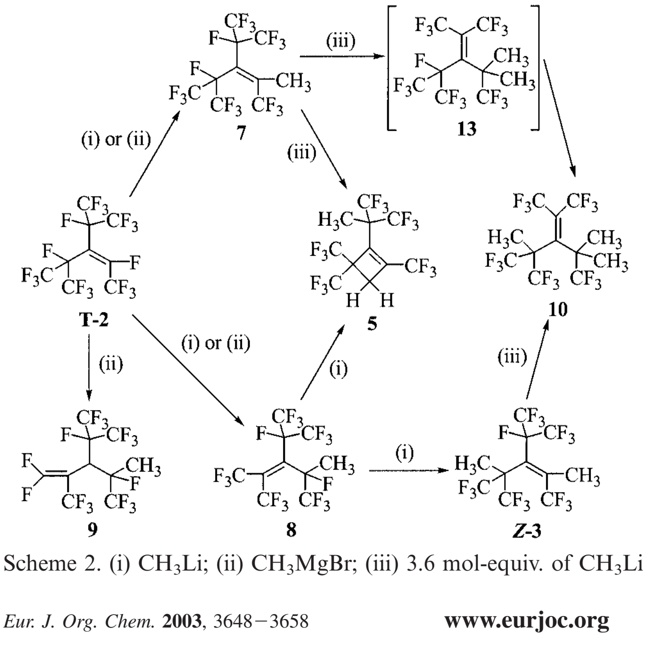
Results and Discussion

Synthetic routes to the various kinds of methylated highly branched fluoroolefins (**1**−**12**) are presented in Schemes 1 and 2. The methylated fluoroolefins **1**−**4** and **7**−**10** may have been formed by the following addition/elimination mechanism (Ad_N-E). The organometallic reagents CH_3Li and CH_3MgBr could have attacked the C=C double bond of **T-3** or **T-2**. A formed anionic intermediate would then release a fluorine atom by two elimination routes: **1** being obtained by route A, and **2** by route B. Dimethylated fluoroolefins could have been formed by a similar Ad_N-E mechanism, (*Z*)-**3** being obtained from **1** while **4** was obtained from **2** (Scheme 1). The cyclized product **5** and the reduced product **6** were reported previously,[22] and the other diene **11**, newly found this time, is discussed later. Although the $(CF_3)_2C=$ group of **T-3** is bulkier than the $(CF_3)CF=$ group of **T-2**, their reactivities towards CH_3Li or CH_3MgBr were almost the same. In contrast, nucleophilic attacks on trimers **T-2** and **T-3** occurred only at the C-2 site and not at the C-3 site with bulkier substituents such as C_2F_5 or $(CF_3)_2CF$ groups.



Scheme 1. (i) CH_3Li; (ii) CH_3MgBr; (iii) 6.0 mol-equiv. of CH_3Li; (iv) 3.6 mol-equiv. of CH_3MgBr



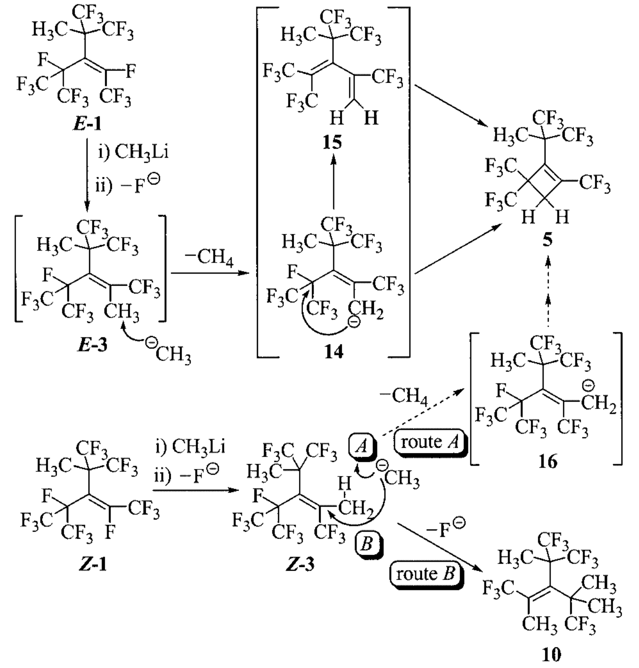
Scheme 2. (i) CH_3Li; (ii) CH_3MgBr; (iii) 3.6 mol-equiv. of CH_3Li

In the cases both of **T-3** and of **T-2**, CH_3MgBr was less reactive towards the methylated fluoroolefins, providing monomethylated fluoroolefins (**1**, **2**, **7**, **8**) without formation of dimethylated fluoroolefins except when a large amount of CH_3MgBr was used (over 3.6 mol-equiv. against **T-3**). CH_3Li, on the other hand, was more reactive towards monomethylated fluoroolefins **1** and **2**, giving dimethylated fluoroolefins [(*Z*)-**3**, **4**] with the use even of 1.2 mol-equiv. CH_3Li for **T-3**. The product distributions and yields obtained from treatment of **T-3** with various amounts of CH_3Li (1.2−6.0 mol-equiv. against **T-3**) are shown in Table 1. An increase in the amount of CH_3Li used with **T-3** from 1.2 to 2.5 mol-equiv. caused a dramatic decrease in the yields of the monomethylated products (*Z*)-**1** (from 30 to 4.6%) and **2** (from 12 to 1.9%), and a significant increase of the dimethylated, products (*Z*)-**3** (from 6.3 to 31%) and **4** (from 2.9 to 14%) instead (Entry 2). A further increase in CH_3Li from 2.5 to 4.8 mol-equiv. caused sudden drops in the yields of monomethylated (*E*)-**1** (from 35 to 4.7%) and dimethylated (*Z*)-**3** (from 31 to 5.6%), and accordingly, trimethylated fluoroolefin **10**, diene **11**, and cyclized product **5** appeared (Entry 4). Treatment of **T-3** with a large excess of CH_3Li (6.0 mol-equiv. relative to **T-3**) gave a trimethylated fluoroolefin **10** (30% yield), a cyclized one **5** (18% yield), and a polyfluoropentadiene **11** (22% yield), together with unknown high-boiling by-products (Entry 5). The circumstantial evidence from the changes in the product distributions in Entries 1−5 suggested that the methylated fluoroolefins varied in the following manners: (*Z*)-**1** → (*Z*)-**3** → **10**; **2** → **4** → **11**; (*E*)-**1** → [(*E*)-**3**] → **5** (see Scheme 1).

Table 1. Reactions of hexafluoropropene trimer **T-3** with various amounts of CH_3Li

Entry[a]	**T-3** [mmol]	CH_3Li [mmol]	Yield (%)
1	1.9	2.3	(*E*)-**1** (36), (*Z*)-**1** (30), **2** (12), (*Z*)-**3** (6.3), **4** (2.9), **T-3** (11)
2	1.9	4.8	(*E*)-**1** (35), (*Z*)-**1** (4.6), **2** (1.9), (*Z*)-**3** (31), **4** (14), **5** (6.2)
3	1.0	3.6	(*E*)-**1** (24), (*Z*)-**3** (30), **4** (16), **5** (29)
4	1.0	4.8	(*E*)-**1** (4.7), (*Z*)-**3** (5.6), **4** (6.8), **5** (32), **10** (12), **11** (11)[b][c]
5	1.0	6.0	**5** (18), **10** (30), **11** (22)[b][c]

[a] Determined by ^{19}F and ^{1}H NMR unless otherwise noted. [b] Determined by GC. [c] Unknown high-boiling by-products were also obtained.



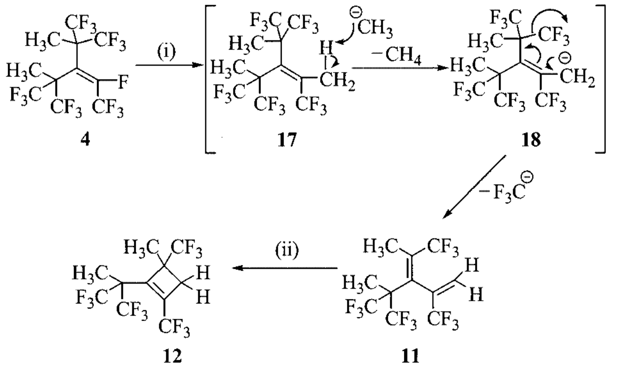
Scheme 3. Mechanisms of formation of **5** and **10**

The relationships between the methylated fluoroolefins **1**, **3**, **5**, and **10** are shown in Scheme 3.

Nucleophilic attack of CH_3Li on (*E*)-**1** provided (*E*)-**3** by fluorine atom elimination. Because the CH_3 group of (*E*)-**3** was very reactive towards excess CH_3Li, (*E*)-**3** gave **5** via two possible intermediates: anion **14** and/or diene **15**. Through a similar Ad_N-E mechanism, (*Z*)-**1** gave (*Z*)-**3**, which was less reactive than (*E*)-**3** towards CH_3Li. With addition of a large excess of CH_3Li, however, (*Z*)-**3** could react with CH_3Li by nucleophilic attack on CH_3 (route A) or on the C-2 site of the double bond (route B). The product distribution indicated that route B was dominant and (*Z*)-**3** mainly turned into **10**, because the conversion of (*Z*)-**3** into **5** via **16** by route A seems to be difficult, due to the gear-meshed conformational lock discussed in detail later.

In the case of **T-2**, an increase in the amount of CH_3Li (1.2−2.5−3.6 mol-equiv.) relative to **T-2** caused dramatic decreases in the yields of the monomethylated compounds **7** (47−25−5.3%) and **8** (20−11−0%) and a sharp increase in those of the cyclized compounds **5** (1.1−27−49%) instead. The yields of dimethylated compounds (*Z*)-**3** (2.6−4.9−0%) and trimethylated **10** (0−0−17%) from treatment of **T-2** with excess CH_3Li were somewhat lower than from treatment of **T-3** with excess CH_3Li; the formation of **5** was favorable in the reactions between **T-2** and excess CH_3Li. These product distributions suggested that the methylated fluoroolefins varied in the following manners: **7** → (**13**) → **10**; **7** → [(*E*)-**3**] → **5**; **8** → [(*E*)-**3**] → **5**; **8** → (*Z*)-**3** → **10** (see Scheme 2).

Although both mono- and dimethylated fluoroolefins **1**−**4**, **7** and **8** were isolated by preparative GC, **10** and **11** could not be purified, because of thermal decomposition during GC. The structures of **10** and **11** were therefore determined only as a mixture and their conformations could not be determined. The formation of **11** was explainable by the mechanism described in Scheme 4.



Scheme 4. A mechanism for the reaction between **T-3** and a large excess of CH_3Li; (i) CH_3Li; (ii) heat

Reaction between **4** and CH_3Li could give the trimethylated fluoroolefin **17**, which would immediately react with excess CH_3Li, to form an intermediate anion **18**. Removal of a CF_3 anion from **18** would give polyfluoropentadiene compound **11**, which would give another polyfluorocyclobutene **12** through a [2+2] cycloaddition known in the polyfluorinated diene[22] during the GC separation of the reaction mixture. Addition of CH_3 groups to a C=C double bond made the double bond less reactive towards organometallic nucleophiles, so that when a large excess of CH_3Li was used it should preferentially attack the CH_3 groups rather than the C=C double bond substituted with a CH_3 group, to give the unusual products **5** and **11**.

The methylated fluoroolefins synthesized above were identified by ^{19}F NMR, ^{1}H NMR, ^{13}C NMR, and GC-MS. The ^{19}F NMR and ^{1}H NMR chemical shifts are summarized in Table 2, while the ^{19}F NMR coupling constants are shown in Table 3. The atom numbers appearing in Tables 2−5 and in the following text are defined in Figure 1. The NMR chemical shifts of the methylated fluoroolefins were informative for assignment of the configurations of the products **1**−**12**: the CH_3 peaks (δ = 2.2−2.3 ppm) connected with the double bond (sp^2) appeared at somewhat lower fields than those connected with the sp^3-carbon atom (δ = 1.8−2.0 ppm). The ^{19}F NMR peaks of the methylated fluoroolefins also depended on their connected carbon atoms: Csp^2-F: δ = −64 to −74 ppm, Csp^3-F: δ = −138 to −167 ppm, CF_2: δ = −70 to −91 ppm, Csp^3-CF_3: δ = −63 to −73 ppm, and Csp^2-CF_3: δ = −53 to −63 ppm. The CF_2 fluorine atoms displayed a wide AB coupling pattern (ca. 280 Hz).

In ^{19}F NMR spectra of the methylated fluoroolefins, non-bond, through-space couplings were observed between F, CF_3, and bis(CF_3) groups connected with the double bond in a similar manner to those seen and previously re-

Table 2. Experimentally determined and calculated values of ^{19}F NMR and ^{1}H NMR chemical shifts of highly branched fluoroolefins

Compound[a][b]		δ(CF)/δ(CF$_2$) [ppm]					δ(CF$_3$) [ppm]		δ(CH$_3$) [ppm]	
(*E*)-**1**	atoms (couplings)	F-2 (sept, d)	F-4 (q, d)	F-1 (d)	F-5 (s)	F-*b* (d)			H-*d*	
	calcd.	−61.41	−161.14	−71.32	−77.22	−76.26			1.89	
	obsd.	−72.32	−160.70	−62.63	−70.50	−67.88			1.79	
(*Z*)-**1**	atoms (couplings)	F-2 (sept, d)	F-4 (sept, d)	F-1 (s)	F-5 (d)	F-*b* (d)			H-*d*	
	calcd.	−68.61	−165.90	−67.17	−79.70	−72.49			2.02	
	obsd.	−74.37	−166.13	−59.24	−71.97	−66.13			1.98	
2a[c]	atoms (couplings)	F-4 (AB, q)	F-4 (AB, sept)	F-1 (br. m)	F-5 (q, q)	F-*b* (m)	F-*b* (br. s)	F-*c* (br. s)	H-*d*	
	calcd.	−82.20	−92.98	−59.23	−75.84	−67.84	−74.95	−65.73	2.12	
	obsd.	−76.88	−90.02	−53.00	−70.06	−60.73	−67.36	−58.53	2.00	
2b[c]	atoms (couplings)	F-4 (AB, q)	F-4 (AB, q)	F-1 (m)	F-5 (m)	F-*b* (m)	F-*b* (br. s)	F-*c* (br. s)	H-*d*	
	calcd.	−89.23	−93.85	−64.51	−77.53	−75.80	−62.81	−65.74	2.08	
	obsd.	−82.73	−90.79	−58.02	−70.36	−66.23	−57.44	−59.75	2.00	
(*Z*)-**3a**	atoms (couplings)	F-4 (br. sept)		F-1 (sept)	F-5 (q)	F-*b* (d)			H-*d*	H-*f*
	calcd.	−152.86		−72.06	−77.75	−71.25			1.96	2.37
	obsd.	−150.93		−64.67	−70.02	−63.98			1.91	2.33
(*Z*)-**3b**	atoms (couplings)	F-4 (q)		F-1 (d)	F-5 (br. s)	F-*b* (s)			H-*d*	H-*f*
	calcd.	−151.77		−67.85	−74.66	−72.17			2.07	2.45
	obsd.	−146.23		−61.82	−68.32	−64.10			1.83	2.30
4	atoms (couplings)	F-2 (m)		F-1 (br. s)	F-5 (s)	F-*b* (d)			H-*d*	H-*e*
	calcd.	−54.70		−66.67	−70.14	−75.17			2.03	2.06
	obsd.	−64.26		−59.48	−63.03	−66.32			1.91	2.00
7	atoms (couplings)	F-4 (q)	F-*a* (sept)	F-1 (d)	F-5 (d)	F-*b* (s)			H-*f*	
	calcd.	−164.41	−162.61	−67.01	−77.55	−77.56			2.24	
	obsd.	−164.34	−163.72	−58.33	−69.71	−71.92			2.21	
8a	atoms (couplings)	F-4 (q, d)	F-*a* (m)	F-1 (br. d)	F-5 (m)	F-5 (m)	F-*b* (m)	F-*c* (m)	H-*e*	
	calcd.	−161.18	−144.24	−60.11	−78.25	−73.24	−82.23	−64.69	2.07	
	obsd.	−156.54	−138.50	−56.53	−70.35	−69.07	−72.82	−57.18	2.02	
8b	atoms (couplings)	F-4 (q, m)	F-*a* (m)	F-1 (m)	F-5 (m)	F-5 (m)	F-*b* (d, m)	F-*c* (m)	H-*e*	
	calcd.	−155.46	−146.18	−66.83	−82.41	−71.66	−78.78	−62.29	1.99	
	obsd.	−154.06	−134.90	−56.50	−73.09	−65.99	−71.41	−59.29	2.02	

[a] Calculated by B3LYP-GIAO method relative to CFCl$_3$ for ^{19}F NMR and to (CH$_3$)$_4$Si for ^{1}H NMR spectroscopy. [b] Fluorine and hydrogen atom numbers are defined as the connected carbon number in Figure 1. [c] Measured at −30 °C.

ported with hexafluoropropene dimers and trimers.[10,11] These characteristic F,F couplings are helpful for determination of the conformations of the methylated fluoroolefins (Figure 1). Two geometrical isomers of **1** were distinguished by the non-bond, through-space coupling: the isopropyl fluorine atom (F-4) was coupled with the CF$_3$ group (F-1) in the (*E*) isomer (q, $^{5}J_{\text{F-1,F-4}}$ = 58.7 Hz), and with the bis(CF$_3$) group (F-*b*) in the (*Z*) isomer (sept, $^{5}J_{\text{F-4,F-b}}$ = 37.3 Hz), while the vinylene fluorine atom (F-2) was coupled with the bis(CF$_3$) group (F-*b*) in the (*E*) isomer (sept, $^{5}J_{\text{F-2,F-b}}$ = 41.3 Hz), and with the bis(CF$_3$) group (F-5) in the (*Z*) isomer (sept, $^{5}J_{\text{F-2,F-5}}$ = 37.0 Hz) (Table 3). The ^{19}F-^{19}F homo-decoupling measurement indicated that these two fluorine atoms (F-2 and F-4) were also coupled to one another through the bond in both (*E*) and (*Z*) isomers. The conformations of **4** and **7** could also be determined by the characteristic through-space couplings (the vinylene fluorine atom of **4** and the isopropyl fluorine atoms of **7**, respectively).

In the case of **2**, the ^{19}F NMR spectra showed several broadened and combined peaks at 25 °C. We therefore measured the ^{19}F NMR spectra at various temperatures from −30 °C to 50 °C, as shown in Figure 2. The peaks broadened and eventually fused at higher temperatures (50 °C). At lower temperatures, on the other hand, the peaks sharpened and thus separated from one another, permitting the assignment of **2** as a pair of rotational isomers **2a** and **2b** at −30 °C. The methylene fluorine atoms of **2** (F-4) were useful for the determination of the conformation of each rotational isomer: among the methylene fluorine atoms of **2a** (F-4), one was coupled with the CF$_3$ group (F-1) (q, $J_{\text{F-1,F-4}}$ = 26.5 Hz) and the other was coupled with the bis(CF$_3$) group (F-*b*) (sept, $J_{\text{F-4,F-}b}$ = 28.5 Hz); among the methylene fluorine atoms of **2b** (F-4), one was coupled with the CF$_3$ group (F-1) (q, $J_{\text{F-1,F-4}}$ = 34.2 Hz) in a similar manner to **2a** while the other, however, was slightly coupled with one of the CF$_3$ groups of bis(CF$_3$) (F-*b*) (q, $J_{\text{F-4,F-}b}$ = 11.3 Hz) (Table 3). In the ^{19}F NMR spectra of (*Z*)-**3**, sets

Table 3. ^{19}F NMR coupling constants of highly branched fluoroolefins

Compound[a]	Coupling atoms		Coupling const. J [Hz]
(E)-**1**	^{4}J	F-2,F-4	9.6
	^{5}J	F-1,F-4	58.7
	^{5}J	F-2,F-b	41.3
(Z)-**1**	^{4}J	F-2,F-4	13.6
	^{5}J	F-2,F-5	37.0
	^{5}J	F-4,F-b	37.3
2a[b]	^{2}J	F-4,F-4	278.6
	^{5}J	F-1,F-4	26.5
	^{5}J	F-4,F-b	28.5
2b[b]	^{2}J	F-4,F-4	280.6
	^{5}J	F-1,F-4	34.2
	^{5}J	F-4,F-b	11.3
(Z)-**3a**	^{5}J	F-4,F-b	27.8
	^{6}J	F-1,F-5	15.5
(Z)-**3b**	^{5}J	F-1,F-4	53.8
4	^{5}J	F-2,F-b	46.9
7	^{5}J	F-1,F-4	64.2
	^{6}J	F-5,F-a	38.0
8a	^{4}J	F-4,F-a	10.7
	^{6}J	F-1,F-4	53.1
8b	^{5}J	F-4,F-b	27.4

[a] Fluorine atom numbers are defined as the connected carbon number in Figure 1. [b] Measured at −30 °C.

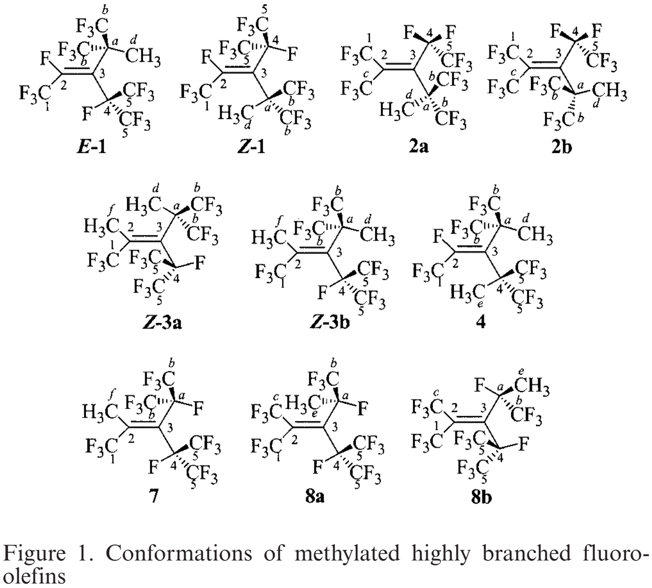

***E*-1** ***Z*-1** **2a** **2b**
***Z*-3a** ***Z*-3b** **4**
7 **8a** **8b**

Figure 1. Conformations of methylated highly branched fluoroolefins

of peaks of two rotational isomers, (Z)-**3a** and (Z)-**3b**, were observed at ambient temperature. These two rotamers were distinguishable from one another at temperatures between −30 °C and 50 °C, and the conformations of (Z)-**3a** and (Z)-**3b** were determined from the couplings with the isopropyl fluorine atom (F-4) and/or the CF$_3$ group (F-1). Although the ^{19}F NMR spectra of **8** were moderately complicated, the couplings with the isopropyl fluorine atom (F-4) and/or bis(CF$_3$) group (F-5) indicated that **8** also consisted of two rotational isomers, **8a** and **8b**. According to variable-temperature ^{19}F NMR measurements, these two rotamers, like (Z)-**3**, existed at temperatures between −30 °C and 50 °C.

Because of the presence not only of large and far-ranging couplings between ^{13}C-^{19}F nuclei but also of couplings between ^{13}C-^{1}H nuclei, the ^{13}C NMR spectra of methylated fluoroolefins were more complex if not decoupled. The chemical shifts of ^{13}C{^{19}F, ^{1}H} NMR spectra, measured under conditions for simultaneous decoupling with ^{19}F and ^{1}H nuclei, are summarized in Table 4. The ^{13}C NMR peaks appeared for CH$_3$ at $\delta = 15-24$ ppm, for C(CH$_3$)(CF$_3$) at $\delta = 56-62$ ppm, for CF(CF$_3$) at $\delta = 93-98$ ppm, for CF$_2$ at $\delta \approx 117$ ppm, for CF$_3$ at $\delta = 117-124$ ppm, for C=CF at $\delta = 154-159$ ppm, and sp^2-carbon atom except C=CF at $\delta = 112-146$ ppm.

Coupling constants of ^{13}C-^{19}F and ^{13}C-^{1}H nuclei were determined by ^{13}C{^{1}H} and ^{13}C{^{19}F} NMR spectra, respectively. These coupling constants are summarized in Table 5. The ^{13}C-^{19}F coupling constants ($^{1}J = 207-290$ Hz; $^{2}J = 27-45$ Hz) were rather larger than the ^{13}C-^{1}H coupling constants ($^{1}J = 132-135$ Hz; $^{2}J = 3.9-7.1$ Hz). In per- and polyfluoroalkyl compounds, ^{13}C NMR chemical shifts and ^{13}C-^{19}F, ^{13}C-^{1}H coupling constants were previously determined by ^{1}H and ^{19}F broadband decoupling, and further by 2D NMR measurements.[24−26] These assignments for ^{13}C NMR also support our assignments for the methylated fluoroolefins.

To confirm the structures of methylated fluoroolefins, NMR shieldings were calculated by the B3LYP-GIAO method (Tables 2 and 4), which was capable of good reproduction of the experimentally measured ^{19}F NMR chemical shifts for various perfluoro compounds with rotational isomers[27]. The geometries of possible rotational isomers **2a**−**2e** optimized by the B3LYP method with the 6-31G(d) basis set are shown in Figure 3. The rotamers **2b** and **2c** were defined by the rotation about the C3−Ca axis of **2a** and the rotamers **2d** and **2e** were defined by the rotation about the C3−C4 axis of **2a**. The calculated energy values of **2a** and **2b** were distinctly different from those of **2c**−**2e** ($\Delta E_{\mathbf{2b-2a}} = 0.80$ kcal mol^{-1}, $\Delta E_{\mathbf{2c-2a}} = 6.87$ kcal mol^{-1}, $\Delta E_{\mathbf{2d-2a}} = 5.34$ kcal mol^{-1}, $\Delta E_{\mathbf{2e-2a}} = 5.29$ kcal mol^{-1}). The projection formulas depicted in Figure 1 show that **2a** and **2b** each have only one CF$_3$ group in a *gauche* conformation to the plane defined by the double bond, while the other rotamers **2c**−**2e** each have two CF$_3$ groups in such *gauche* or near in-plane positions. This difference seems to be the cause of the energy differences between **2a**/**2b** and **2c**−**2e**. The ^{19}F chemical shift values calculated by the B3LYP-GIAO method with the 6-31++G(d,p) basis set are summarized along with the experimentally measured data (Figure 4). Although all the calculated values are at somewhat higher fields than the corresponding experimentally determined ones, there is a good consistency between **2a**

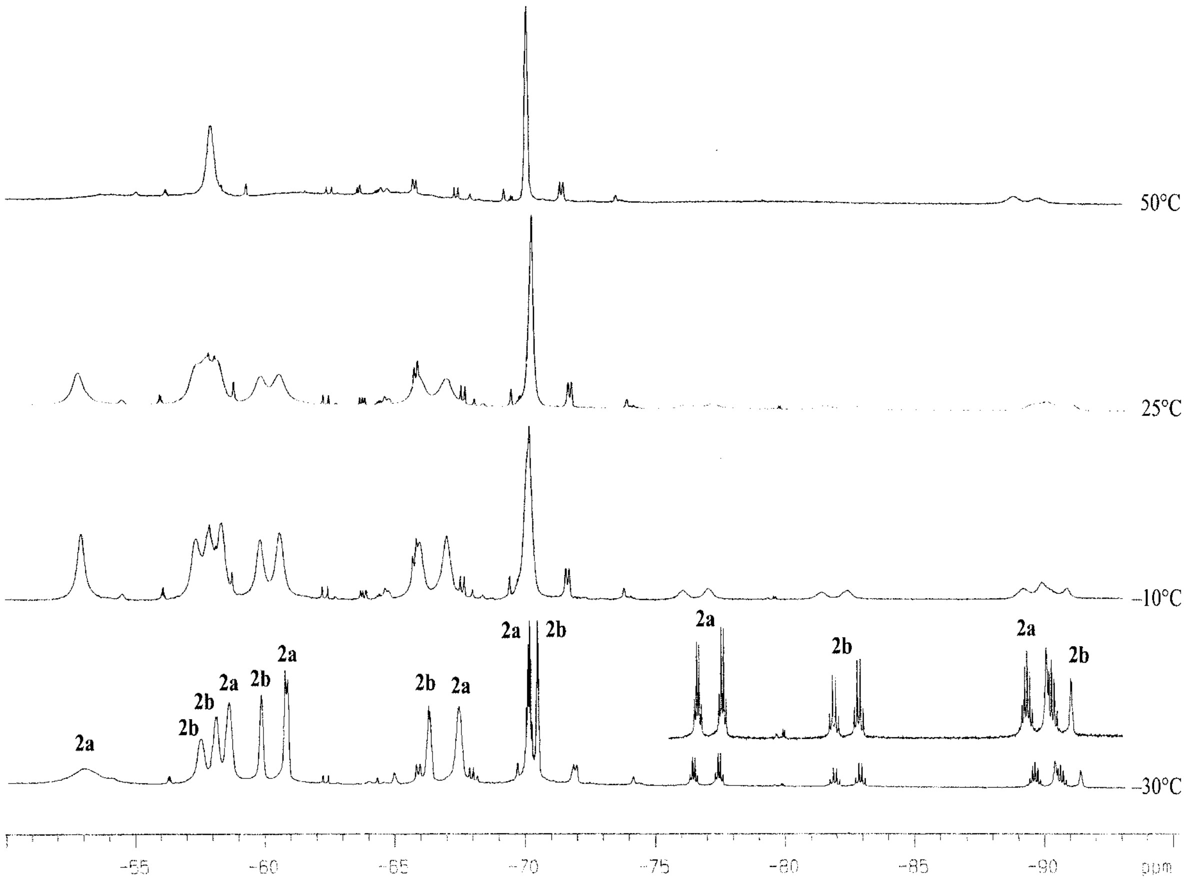


Figure 2. Variable-temperature ^{19}F NMR spectra of **2**

and **2b** on the experimentally determined and calculated chemical shifts. This consistency was not apparent from the numerical data, but very clearly visualized by the assistance of pattern recognition of chemical shift distribution in each rotamer **2a**−**2e**. It is quite clear that the chemical shift distribution patterns of **2c**−**2e** are different from those of **2a** and **2b**. The conformational structures **2a** and **2b** estimated by the coupling patterns between the CF_3 group(s) at the juxtapositions and vicinal fluorine atoms of the CF_2CF_3 group (q, $J_{F\text{-}1,F\text{-}4} = 26.5$ Hz and sept, $J_{F\text{-}4,F\text{-}b} = 28.5$ Hz for **2a** and q, $J_{F\text{-}1,F\text{-}4} = 34.2$ Hz and q, $J_{F\text{-}4,F\text{-}b} = 11.3$ Hz for **2b**) were rigorously confirmed by the DFT calculation.

Similarly to those of **2a**−**2e**, the geometries of the other methylated fluoroolefins optimized by the B3LYP method with the 6-31G(d) basis set, and their ^{19}F shieldings were calculated by the B3LYP-GIAO method with the 6-31++G(d,p) basis set. The optimized structures are presented in Figures S1 and S2 (perspective views) and Table S1 (Cartesian coordinates) (Supporting Information). The calculated NMR chemical shifts are also summarized in Tables 2 (^{19}F and ^{1}H NMR) and 4 (^{13}C NMR). The calculated ^{19}F shieldings showed good consistency with experimentally measured values: the calculated values were slightly smaller than the experimentally determined ones except for the calculated values for vinylene fluorine atoms (F-2) of (*Z*)-**1**, (*E*)-**1**, and **4**, which were larger than the experimentally measured ones. The calculated ^{1}H and ^{13}C shieldings also showed good consistency with experimentally ascertained values except in only a few cases. Although the calculated values were slightly lower than the experimentally determined values, the calculated values of sp^2-carbon atom (C-3) of (*Z*)-**3** and **4** were larger than the experimentally determined values. Since the deviation was not large and appeared at only a small number of atoms, possibly affected by π-electrons, the conformations in Figure 1, elucidated by experimental data, were considered to be supported by the DFT calculation.

Both the experimentally determined and the calculated NMR data provided considerable information relating to the configurations and conformations of the methylated fluoroolefins. Three methylated fluoroolefins [**2**, (*Z*)-**3**, **8**] were shown to consist of pairs of rotamers, whereas the other methylated fluoroolefins [(*E*)-**1**, (*Z*)-**1**, **4**, **7**] were shown to exist as single rotamers between −30 °C and 50 °C. Figure 1 indicates that methylated, highly branched fluoroolefins occupied specific conformations because of the presence of two bulky substituents [such as $(CF_3)_2CF$ and $(CF_3)_2CCH_3$] connected with C-3. The bulky CF_3 groups thus occupy positions perpendicular to the plane defined by the double bonds, F, and CH_3 groups. For steric reasons, the vinylene fluorine atom (F-2) and the CH_3 group (H-*d*) in the plane in (*E*)-**1** were tucked into the clefts between the bis(CF_3) (F-*b*) and bis(CF_3) groups (F-5), respectively, forming a gear-meshed locking structure. The

Table 4. Experimentally determined and calculated values of ^{13}C NMR chemical shifts of highly branched fluoroolefins

Compound[a][b]		$\delta(C_{sp2}F_n)$ [ppm]		$\delta(C_{sp3}F_n)$ [ppm]						$\delta(CH_3)$ (ppm)	
(*E*)-**1**	atoms	C-2	C-3	C-1	C-4	C-5	C-*a*	C-*b*		C-*d*	
	calcd.	151.03	107.69	114.77	87.31	117.66	51.88	121.35		11.47	
	obsd.	158.59	112.44	118.03	93.22	119.70	57.18	123.47		15.50	
(*Z*)-**1**	atoms	C-2	C-3	C-1	C-4	C-5	C-*a*	C-*b*		C-*d*	
	calcd.	143.59	116.48	114.29	89.59	118.21	52.84	120.41		10.84	
	obs.	154.92	116.34	117.55	95.64	120.26	56.74	122.90		16.65	
2[c]	atoms	C-2	C-3	C-1	C-4	C-5	C-*a*	C-*b*	C-*c*	C-*d*	
	calcd.	129.84	140.06	116.80	111.87	115.78	55.50	120.08	116.79	13.85	
	obs.	127.50	139.00	119.79	117.34	118.66	60.20	122.83	119.40	19.02	
(*Z*)-**3a**	atoms	C-2	C-3	C-1	C-4	C-5	C-*a*	C-*b*		C-*d*	C-*f*
	calcd.	135.72	129.76	119.97	88.57	117.47	54.52	121.74		11.50	14.88
	obs.	145.48	126.23	123.90	96.57	120.19	61.27	123.80		16.31	20.98
(*Z*)-**3b**	atoms	C-2	C-3	C-1	C-4	C-5	C-*a*	C-*b*		C-*d*	C-*f*
	calcd.	146.31	119.73	118.46	89.09	118.29	53.31	122.32		11.96	16.31
	obs.	150.55	117.32	121.93	97.35	120.32	58.84	123.85		17.95	21.57
4	atoms	C-2	C-3	C-1	C-4	C-5	C-*a*	C-*b*		C-d	C-e
	calcd.	146.97	120.55	117.86	89.44	117.45	88.78	117.67		12.61	13.74
	obs.	157.15	117.40	121.54	95.00	120.43	94.25	119.83		17.28	18.84
7	atoms	C-2	C-3	C-1	C-4	C-5	C-*a*	C-*b*		C-*f*	
	calcd.	143.50	115.66	117.86	89.44	117.45	88.78	117.67		14.61	
	obs.	147.82	123.75	121.54	95.00	120.43	94.25	119.83		20.79	
8a	atoms	C-2	C-3	C-1	C-4	C-5	C-*a*	C-*c*	C-*e*	C-*b*	
	calcd.	126.93	140.18	116.39	91.38	117.58	91.15	117.31	118.82	18.02	
	obs.	133.93	146.24	119.70	96.66	120.32	97.42	119.86	121.48	22.95	
8b	atoms	C-2	C-3	C-1	C-4	C-5	C-*a*	C-*c*	C-*e*	C-*b*	
	calcd.	124.48	139.83	116.43	90.51	116.73	92.72	117.11	119.15	15.09	
	obs.	132.70	143.90	119.62	95.65	119.45	97.46	119.75	121.57	23.13	

[a] Calculated by B3LYP-GIAO method relative to $(CH_3)_4Si$. [b] Carbon atom numbers are defined in Figure 1. [c] ^{13}C NMR shieldings are given as the weighted average of rotational isomers.

same kinds of gear-meshed structures are commonly seen in all structures except for **2**, and the pairs of rotamers, (*Z*)-**3a**/(*Z*)-**3b**, and **8a**/**8b**, arise from the directions of gears, clockwise or counterclockwise. Such a directional change may be impossible for **4** due to the presence of the two heavily substituted $(CF_3)_2CCH_3$ groups on the same sp^2-carbon atom, so **4** existed as a single rotamer. On the other hand, such a directional gear change should apparently be possible for **7**, so the reason for the single rotamer for **7** is unclear, but common features seen in the rotamers of (*Z*)-**3** and **8** suggest that the presence of at least one CF_3 group tucked into $(CF_3)_2C$ or $(CF_3)(CH_3)C$ groups is required for the existence of rotamers. The gear-meshed conformation has previously been observed in "polybulky systems" in which several bulky groups, such as isopropyl,[28−30] cyclohexyl,[31] and dimethylsilyl[32] are connected with planar sp^2 frameworks of the olefins and aromatic compounds. Such gear structures have been identified by X-ray analysis of hexaisopropylbenzene[28] and tetraisopropylethylene.[33] X-ray structures on the related perfluoroolefins derived from hexafluoropropene, 2-*p*-tolyloxy-*F*-(4-methyl-3-isopropyl-2-pentene),[34] and 5-*F*-(2-isopropyl-1,3-dimethylbut-1-enyloxy)isophthalic acid ethanol clathrate[35] have been reported. There are no 3D coordinates for the latter, as reported by H. Tomoda et al., but the former, reported by S. V. Sereda, showed a gear-meshed structure of two $(CF_3)_2CF$ groups connected with the same sp^2-carbon atom, supporting the gear-meshed structures of methylated highly branched fluoroolefins determined by the experimentally ascertained and calculated NMR investigations in this report.

Conclusion

On treatment of **T-3** and **T-2** with CH_3Li or CH_3MgBr, five monomethylated fluoroolefins [(*E*)-**1**, (*Z*)-**1**, **2**, **7**, **8**] and two dimethylated fluoroolefins [(*Z*)-**3**, **4**] were isolated in pure forms by preparative GC. The ^{19}F-^{19}F through-space coupling provided significant information regarding both the configurations and the conformations of these methylated compounds, which was supported by the NMR shielding data provided by B3LYP-GIAO calculation. Three pairs of conformational isomers about **2**, (*Z*)-**3**, and **8** were dis-

Table 5. ^{13}C NMR coupling constants of highly branched fluoroolefins

Compounds[a][b][c]		^1J [Hz]						^2J [Hz]						^3J [Hz]	
(*E*)-**1**	coupled atoms	C-1,F-1	C-2,F-2	C-4,F-4	C-5,F-5	C-*b*,F-*b*	C-*d*,H-*d*	C-1,F-2	C-2,F-1	C-4,F-5	C-5,F-4	C-*a*,F-*b*	C-*a*,H-*d*	C-4,F-2	C-3,H-*d*
	coupling const.	277.0	247.3	207.2	288.6	288.5	134.5	42.8	42.8	35.5	28.7	27.4	4.4	5.4	5.1
(*Z*)-**1**	coupled atoms	C-1,F-1	C-2,F-2	C-4,F-4	C-5,F-5	C-*b*,F-*b*	C-*d*,H-*d*	C-1,F-2	C-2,F-1	C-4,F-5	C-5,F-4	C-*a*,F-*b*	C-*a*,H-*d*	C-4,F-2	C-3,H-*d*
	coupling const.	276.9	279.0	218.6	291.1	286.5	135.0	41.4	43.3	34.7	29.2	29.3	4.1	4.5	5.0
(*Z*)-**3a**	coupled atoms	C-1,F-1	C-5,F-5	C-*b*,F-*b*	C-*d*,H-*d*	C-*f*,H-*f*		C-5,F-4	C-2,H-*f*	C-*a*,H-*d*				C-*f*,F-1	C-*b*,H-*d*
	coupling const.	280.9	288.4	288.2	134.0	132.4		30.4	7.5	3.9				6.5	3.4
(*Z*)-**3b**	coupled atoms	C-1,F-1	C-5,F-5	C-*b*,F-*b*	C-*d*,H-*d*	C-*f*,H-*f*		C-5,F-4	C-2,H-*f*	C-*a*,H-*d*				C-*f*,F-1	C-*b*,H-*d*
	coupling const.	275.5	295.6	284.8	143.2	133.0		29.1	8.1	3.9				4.6	4.2
4	coupled atoms	C-1,F-1	C-2,F-2	C-5,F-5	C-*b*,F-*b*	C-*d*,H-*d*	C-*e*,H-*e*	C-1,F-2	C-4,F-5	C-*a*,F-*b*	C-4,H-*e*	C-*a*,H-*d*		C-4,F-2	C-5,H-e
	coupling const.	278.0	323.8	286.5	288.0	134.5	134.9	44.4	28.4	27.3	4.6	5.1		3.1	5.1
7	coupled atoms	C-1,F-1	C-4,F-4	C-5,F-5	C-*a*,F-*a*	C-*b*,F-*b*	C-*f*,H-*f*	C-2,F-1	C-5,F-4	C-*b*,F-*a*	C-2,H-*f*			C-*f*,F-1	C-1,H-*f*
	coupling const.	278.0	210.5	289.6	210.2	290.1	133.0	34.7	28.2	27.3	7.1			5.2	4.3

[a] Carbon atom numbers are defined in Figure 1. [b] Fluorine and hydrogen atom numbers are defined as the connected carbon number in Figure 1. [c] ^{13}C NMR coupling constant values of **2** and **8** could not be determined because non-decoupled ^{13}C NMR spectra were very complicated.

tinguished by ^{19}F NMR spectroscopic data, while no conformational isomers were found in **1**, **4**, and **7**. Because of the steric hindrance of the substituent with two CF_3 groups, gear-meshed conformations were seen in the methylated fluoroolefins except in the case of **2**, which has C_2F_5 and $(CF_3)_2CCH_3$ groups at C-3.

Experimental Section

General Remarks: Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system fitted with a Heise-Bourdon tube gauge and a Televac thermocouple gauge. Gas chromatographic analysis was performed with a Shimadzu GC-17A instrument (column: 0.25 mm i.d. × 60 m, df = 1.5 µm NEUTA BOND-1, GL Science). Preparative gas chromatographic separation was performed with a Gasukuro Kogyo LL-75 machine (column: 4.0 m × 3/8 in, Fomblin-H 15% chromosorb PAW 80/100). ^1H and ^{13}C NMR spectra were measured with a Varian INOVA-300 spectrometer operating at 300 MHz and at 75.42 MHz, respectively, with $CDCl_3$ as the solvent. ^{19}F NMR spectra were measured with a Varian INOVA-300 spectrometer at 282.24 MHz with $CDCl_3$ as the solvent; positive δ values downfield from the internal reference, $CFCl_3$. GC-MS data were obtained with a Shimadzu QP-5000 quadrupole mass spectrometer by electron-impact ionization at 70 eV (column: 0.25 mm i.d. × 60 m, df = 1.5 µm NEUTA BOND-1, GL Science). Perfluoro(4-methyl-3-isopropyl-2-pentene) (**T-2**) and perfluoro(3-ethyl-2,4-dimethyl-2-pentene) (**T-3**) were prepared by oligomerization of a hexafluoropropene monomer in the presence of a fluoride anion and a crown ether[36] and were then separated with a spinning-band column: **T-2** was of 90−95% purity, contaminated by **T-3**, while **T-3** was of 100% purity. Methyllithium was used as a complex with lithium bromide in 1.5 M ethereal solution, manufactured by Aldrich Chemical Co., Inc. Methylmagnesium bromide was used as 3.0 M ethereal solution manufactured by Tokyo Kasei Kogyo Co., Ltd. Anhydrous diethyl ether was obtained by distillation under argon and dried with sodium metal. Other reagents were obtained from commercial sources and were used without further purification. The reactions with methyllithium or methylmagnesium bromide were carried out under argon and anhydrous conditions.

Synthesis of Monomethylated Fluoroolefins (*E*)-1, (*Z*)-1, and 2: An ethereal solution of CH_3MgBr (3.0 M, 0.4 mL) was added dropwise to a suspension of **T-3** (0.87 g, 1.9 mmol) in diethyl ether (10 mL), cooled with ice. After the mixture had been stirred at 0 °C for 5 h, the resulting white suspension was trap-to-trap-distilled with the aid of a vacuum line system (1 Torr) at ambient temperature. Crude products (1.69 g) included **1** [(*Z*)/(*E*) = 2.5] in 39% yield, **2** in 23% yield, and 31% recovery of **T-3**, determined by ^{19}F and ^1H NMR spectroscopy. Pure (*Z*)-**1**, (*E*)-**1**, and **2** were obtained by preparative GC (column temperature: 70 °C) and were used for ^{13}C NMR and variable-temperature ^{19}F NMR measurement.

(*E*)-1: MS (EI, 70 eV): *m*/*z* (%) = 357 (1.9) [$M^+ - CF_3 - HF$], 289 (2.4), 269 (5.2), 263 (7.6), 164 (7.4), 119 (6.5), 95 (5.9), 77 (5.1), 69 (100), 65 (31), 51 (15).

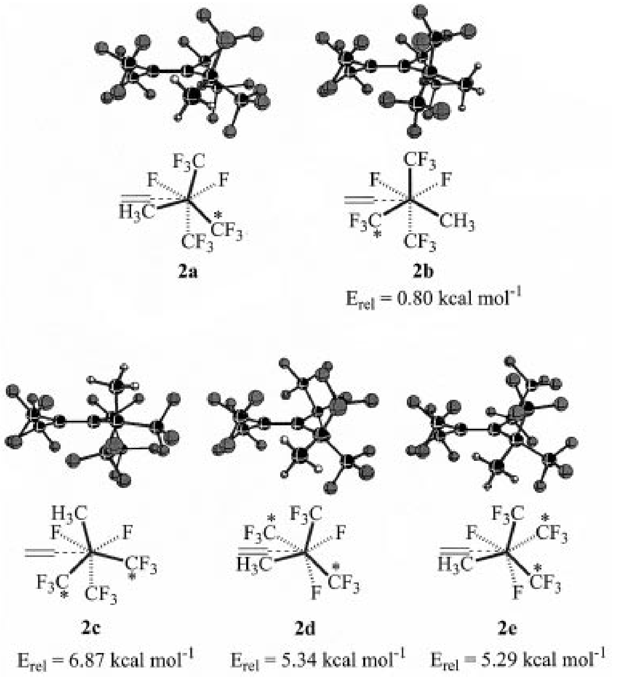


Figure 3. Possible rotational isomers of **2** [the upper figures are perspective views of the molecules **2a**−**2e** and the lower ones are projection formulas viewing the molecules **2a**−**2e** down from C-*a* to C-4 by placing the eyes on the plane defined by the double bond, C-*a*, C-4; the double bond on the plane of the paper and dotted line, representing the bonds between sp^2-carbon atom and C-*a* or C-4, are toward us or away from us out of the plane of the paper; the bold and broken lines are above and below the plane of paper, respectively; the asterisked CF_3 groups are gauche to the double bond plane or near the plane (for details, see the text)] and their relative energies based on **2a**

(*Z*)-1: MS (EI, 70 eV): *m*/*z* (%) = 357 (1.9) [M$^+$ − CF_3 − HF], 289 (2.5), 269 (4.9), 263 (4.1), 164 (7.7), 119 (6.0), 95 (6.0), 77 (6.0), 69 (100), 65 (32), 51 (14).

2: MS (EI, 70 eV): *m*/*z* (%) = 357 (1.1) [M$^+$ − CF_3 − HF], 289 (2.7), 269 (3.8), 263 (8.9), 164 (6.2), 119 (5.3), 69 (100), 65 (23), 51 (8.5).

Synthesis of Monomethylated Fluoroolefins 7 and 8: An ethereal solution of CH_3MgBr (3.0 M, 0.6 mL) was added dropwise to a suspension of **T-2** (0.68 g, 1.5 mmol) in diethyl ether (5 mL), cooled with ice. After the mixture had been stirred at 0 °C for 5 h, the resulting white suspension was trap-to-trap-distilled with the aid of a vacuum line system (1 Torr) at ambient temperature. Crude products (0.52 g) included **7** in 22% yield and **8** in 40% yield, with formation of **9** in 9.2% yield as an isomeric by-product of **8**, determined by ^{19}F and ^{1}H NMR spectroscopy. Pure **7** and **8** were obtained by preparative GC (column temperature: 70 °C) and were used for ^{13}C NMR and variable-temperature ^{19}F NMR measurement.

7: MS (EI, 70 eV): *m*/*z* (%) = 407 (2.9) [M$^+$ − H − 2 F], 377 (3.3) [M$^+$ − CF_3], 357 (1.9) [M$^+$ − CF_3-HF], 319 (4.9), 181 (5.1), 69 (100), 65 (34), 51 (27).

8: MS (EI, 70 eV): *m*/*z* (%) = 407 (2.5) [M$^+$ − H − 2 F], 225 (8.7), 119 (5.5), 69 (100), 51 (30).

Compound **9** was identified as a mixture of two rotational isomers **9a** and **9b**.

9: MS (EI, 70 eV): *m*/*z* (%) = 357 (3.0) [M$^+$ − CF_3 − HF,], 331 (17), 181 (68), 115 (18), 69 (100), 65 (34), 51 (27). **9a**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.96 (m, CH_3) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −52.9 (br. s, 1 F, $CF_3C{=}C\mathit{F}_2$), −54.7 (t m, *J* = 31.8, 3 F, $\mathit{CF_3}C{=}CF_2$), −60.8 (q, *J* = 31.8, 1 F, $CF_3C{=}C\mathit{F}_2$), −68.8

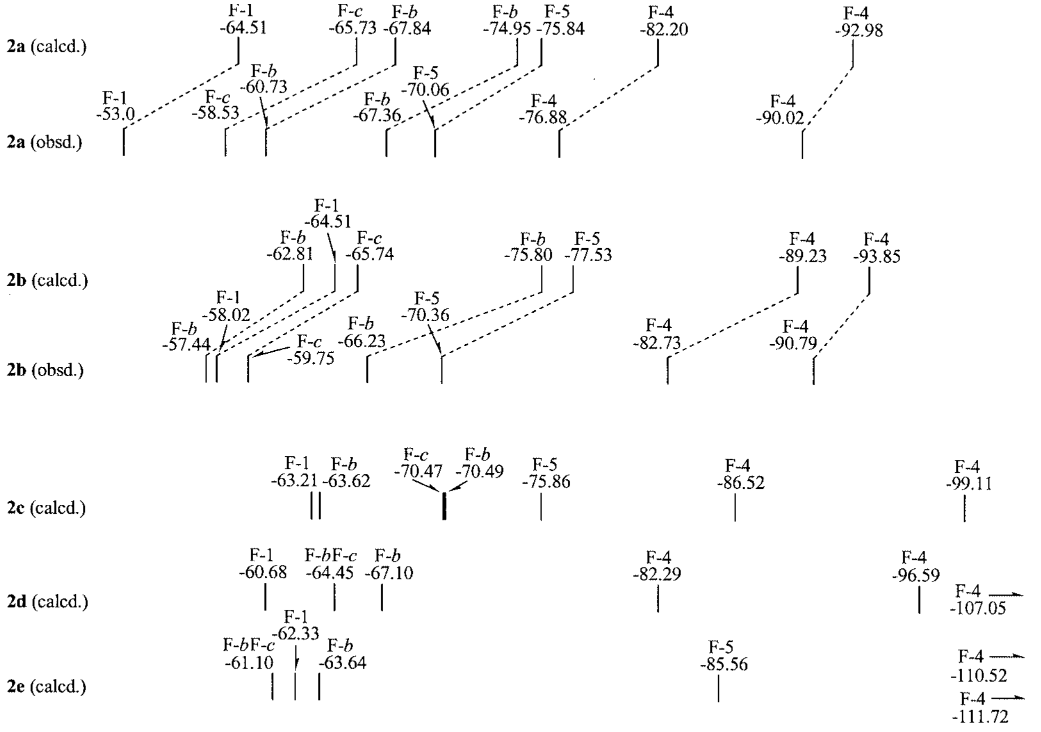


Figure 4. Comparison diagram between calculated and experimentally determined ^{19}F chemical shifts of **2**

[s, 3 F, $\mathrm{CF}(\mathit{CF}_3)_2$], −72.0 [s, 3 F, $\mathrm{CF}(\mathit{CF}_3)_2$], −76.4 [s, 3 F, $\mathrm{CF}(\mathit{CF}_3)(\mathrm{CH}_3)$], −149.7 [s, 1 F, $\mathrm{C}\mathit{F}(\mathrm{CF}_3)(\mathrm{CH}_3)$], −172.5 [s, 1 F, $\mathrm{C}\mathit{F}(\mathrm{CF}_3)_2$], −174.9 (m, 1 F, 3-F) ppm. **9b**: ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.89$ (m, CH_3) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): $\delta = -55.9$ (m, 3 F, $\mathit{CF}_3\mathrm{C{=}CF}_2$), −57.0 (m, 1 F, $\mathrm{CF_3C{=}C}\mathit{F}_2$), −64.3 (d, $J = 108.4$, 1 F, $\mathrm{CF_3C{=}C}\mathit{F}_2$), −69.1 [s, 3 F, $\mathrm{CF}(\mathit{CF}_3)_2$], −70.9 [s, 3 F, $\mathrm{CF}(\mathit{CF}_3)_2$], −77.0 [d, $J = 23.4$, 3 F, $\mathrm{CF}(\mathit{CF}_3)(\mathrm{CH}_3)$], −163.4 [m, 1 F, $\mathrm{C}\mathit{F}(\mathrm{CF}_3)(\mathrm{CH}_3)$], −172.7 (d, $J = 108.4$, 1 F, 3-F), −174.0 [s, 1 F, $\mathrm{C}\mathit{F}(\mathrm{CF}_3)_2$] ppm.

Synthesis of Dimethylated Fluoroolefins (*Z*)-3 and 4: An ethereal solution of $CH_3Li/LiBr$ (1.5 M, 2.4 mL) was added dropwise to a suspension of **T-3** (0.45 g, 1.0 mmol) in diethyl ether (5 mL), cooled with ice. After the mixture had been stirred at 0 °C for 5 h, the resulting white suspension was trap-to-trap-distilled with the aid of a vacuum line system (1 Torr) at 50 °C. Crude products (0.47 g) included (*Z*)-**3** in 30% yield, **4** in 16% yield, (*Z*)-**1** in 24% yield, and **5** in 29% yield, determined by ^{19}F and ^1H NMR spectroscopy. Pure (*Z*)-**3** and **4** were obtained by preparative GC (column temperature: 90 °C) and were used for ^{13}C NMR and variable-temperature ^{19}F NMR measurement.

(*Z*)-3: MS (EI, 70 eV): *m*/*z* (%) = 383 (2.1) [$M^+ - 3\,F - 2\,H$], 353 (6.8) [$M^+ - CF_3 - HF$], 333 (7.5), 313 (7.6), 283 (5.1), 263 (7.3), 245 (5.8), 225 (11), 213 (6.7), 195 (5.7), 189 (7.3), 163 (7.1), 146 (10), 145 (19), 127 (5.6), 119 (6.9), 113 (6.5), 95 (11), 77 (17), 69 (100), 65 (57), 51 (38).

4: MS (EI, 70 eV): *m*/*z* (%) = 353 (2.2) [$M^+ - CF_3 - HF$], 145 (11), 95 (6.3), 77 (11), 69 (100), 51 (18).

Treatment of T-3 with a Large Excess of Methyllithium. Formation of 11 and 12: An ethereal solution of $CH_3Li/LiBr$ (1.5 M, 3.2 mL) was added dropwise to a suspension of **T-3** (0.46 g, 1.0 mmol) in diethyl ether (5 mL), cooled with ice. After the mixture had been stirred at 0 °C for 5 h, the resulting white suspension was trap-to-trap-distilled with the aid of a vacuum line system (1 Torr) at 70 °C. Crude products (0.41 g) included **10** in 30% yield, **11** in 22% yield, **5** in 18% yield, and unknown high-boiling by-products. Separation of **10** and **11** by preparative GC (column temperature: 140 °C) was unsuccessful, due to the thermal decomposition of **11**. Another polyfluorocyclobutene compound **12** was obtained in 17% yield by the thermal decomposition of **11**.

10: ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.66$ [s, 3 H, $C(CF_3)_2(CH_3)$], 1.81 [s, 6 H, $C(CF_3)(CH_3)_2$] ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): $\delta = -60.5$ [m, 3 F, $C(CF_3)(CH_3)_2$], −64.9 [m, 6 F, $C{=}C(CF_3)_2$], −70.5 [m, 6 F, $C(CF_3)_2(CH_3)$] ppm. MS (EI, 70 eV): *m*/*z* (%) = 418 (7.9) [$M^+ - F - H$], 399 (7.9) [$M^+ - 2\,F - H$], 349 (8.2) [$C_{11}H_8F_{11}{}^+$], 253 (100) [$C_8H_5F_8{}^+$], 233 (18), 203 (21), 183(20), 163 (12), 145 (22), 95 (10), 77 (19), 69 (60), 65 (83), 51 (30).

11: ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.67$ [s, 3 H, $C(CF_3)_2(CH_3)$], 2.16 [s, 3 H, $C{=}C(CF_3)(CH_3)$], 5.55 (s, 1 H, $CF_3C{=}CH_2$), 6.07 (s, 1 H, $CF_3C{=}CH_2$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): $\delta = -61.5$ [s, 3 F, $C{=}C(CF_3)(CH_3)$], −64.2 [m, 3 F, $C(CF_3)_2(CH_3)$], −64.9 [m, 3 F, $C(CF_3)_2(CH_3)$], −67.5 (m, 3 F, $CF_3C{=}CH_2$) ppm. MS (EI, 70 eV): *m*/*z* (%) = 368 (4.3) [M^+], 329 (2.5) [$M^+ - 2\,F - H$], 299 (30), 203 (11), 183 (11), 145 (18), 110 (100), 95 (39), 90 (10), 77 (16), 69 (31), 65 (63), 51 (22).

12: ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.51$ [s, 3 H, $C(CF_3)_2(CH_3)$], 1.71 [s, 3 H, $C(CF_3)(CH_3)$], 2.39 (AB, $J = 15.0$, 1 H, $-CH_2-$), 2.39 (AB, $J = 15.0$, 1 H, $-CH_2-$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): $\delta = -63.5$ (m, 3 F, CF_3), −70.3 [br. s, 3 F, $C{=}C(CF_3)(CH_3)$], −70.7 [m, 3 F, $C(CF_3)_2(CH_3)$], −74.7 [m, 3 F, $C(CF_3)_2(CH_3)$] ppm. MS (EI, 70 eV): *m*/*z* (%) = 368 (7.1) [M^+], 349 (2.8) [$M^+ - F$], 329 (5.6) [$M^+ - 2\,F - H$], 299 (41), 203 (13), 183 (12), 163 (11), 145 (18), 110 (100), 95 (40), 90 (17), 77 (16), 75 (10), 69 (41), 65 (59), 51 (19).

Computational Methods: Density functional theory (DFT) calculations were performed by use of the GAUSSIAN98 program package.[37] All geometries were optimized at the B3LYP hybrid functional[38−40] with the 6-31G(d) basis set. Isotropic NMR shielding tensors were calculated at the B3LYP level by use of the gauge-independent atomic orbital (GIAO) method[41−44] with the 6-31++G(d, p) basis set. The chemical shifts (δ) were calculated from the shielding (σ), by $\delta = \sigma_{\mathrm{ref}} - \sigma$, where σ_{ref} is the shielding of $CFCl_3$ in ^{19}F NMR ($\sigma_{\mathrm{ref}} = 179.1618$ ppm) calculated by the same method. Similarly, the calculated shieldings of $(CH_3)_4Si$ are used as σ_{ref} values in ^1H NMR ($\sigma_{\mathrm{ref}} = 31.6517$ ppm) and ^{13}C NMR ($\sigma_{\mathrm{ref}} = 182.4602$ ppm), respectively.

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[1] R. E. Banks, *Organofluorine Chemicals and Their Industrial Application*, Ellis Horwood Ltd., London, **1979**; R. E. Banks, *Preparation, Properties, and Industrial Applications of Organofluorine Compounds*, Ellis Horwood Ltd., London, **1982**.

[2] D. P. Curran, *Angew. Chem. Int. Ed.* **1998**, *37*, 1174−1196; J. A. Gladysz, D. P. Curran, *Teterahedron* **2002**, *58*, 3823−3825.

[3] K. V. Scherer, T. Ono, K. Yamanouchi, R. Fernandez, P. Henderson, *J. Am. Chem. Soc.* **1985**, *107*, 718−719.

[4] T. Ono, H. Fukaya, M. Nishida, N. Terasawa, T. Abe, *Chem. Commun.* **1996**, 1579−1580.

[5] C. H. Dungan, J. R. Van Wazer, *Compilation of Report F19 NMR Chemical Shifts*, John Wiley & Sons, Inc., New York, **1970**.

[6] A. D. Buckingham, J. E. Cordle, *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 994−1004.

[7] J. Hilton, L. H. Sutclfe, *Specrochim. Acta A* **1976**, *32*, 201−213.

[8] V. I. Bakhmutov, M. V. Galakhov, E. I. Fedin, *Magn. Reson. Chem.* **1985**, *23*, 971−972.

[9] L. Ernst, K. Ibrom, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1881−1882.

[10] F. Cavagna, C. Schumann, *J. Magn. Reson.* **1976**, *22*, 333−344.

[11] C. Schumann, F. Cavagna, *J. Magn. Reson.* **1975**, *18*, 172−184.

[12] K. B. Wiberg, J. D. Hammer, K. W. Zilm, J. R. Cheesenman, T. A. Keith, *J. Phys. Chem. A* **1998**, *102*, 8766−8773.

[13] K. B. Wiberg, K. W. Zilm, *J. Org. Chem.* **2001**, *66*, 2809−2817.

[14] T. Tamura, J. Irisawa, *J. Fluorine Chem.* **1999**, *99*, 157−160.

[15] T. Tamura, J. Irisawa, K. Ohnishi, *J. Fluorine Chem.* **2000**, *102*, 205−210.

[16] F. Trautner, S. Reinemann, R. Minkwitz, H. Oberhammer, *J. Am. Chem. Soc.* **2000**, *122*, 4193−4196.

[17] C. Leibold, J. Foropoulos, H. M. Marsden, J. M. Shreeve, H. Oberhammer, *Inorg. Chem.* **2002**, *41*, 6125−6128.

[18] R. J. Abraham, C. F. Tormena, R. Rittner, *J. Chem. Soc., Perkin Trans. 2* **2001**, 815−820.

[19] D. Federsel, A. Herrmann, D. Christen, S. Sander, H. Willner, H. Oberhammer, *J. Mol. Struct.* **2001**, *567−568*, 127−136.

[20] M. R. Helal, Y. A. Yousef, A. T. Afaneh, *J. Comput. Chem.* **2002**, *23*, 966−976.

[21] H. Fukaya, T. Ono, *J. Comput. Chem.*, in press.

[22] M. Nishida, T. Ono, *J. Fluorine Chem.* **2003**, *120*, 93−96.

[23] M. Nishida, Y. Hayakawa, M. Matsui, K. Shibata, H. Muramatsu, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3494−3496.

[24] A. Foris, *Magn. Resn. Chem.* **2001**, *39*, 386−398.

[25] A. A. Ribeiro, M. J. Glen, *J. Magn. Reson. A* **1994**, *107*, 158−166.

[26] A. A. Ribeiro, *J. Fluorine Chem.* **1997**, *83*, 61−66.

[27] As well as by ^{19}F NMR spectroscopy, the two rotational isomers of **2** were also indistinguishable by ^{13}C NMR at ambient temperature. The ^{13}C shieldings of **2** were therefore calculated as the weighted average of **2a** and **2b**, the populations of which were estimated from the Boltzmann equation at 298 K by use of $\Delta E_{\mathbf{2b}-\mathbf{2a}}$.

[28] J. Siegel, A. Gutiérrez, W. B. Schweizer, O. Ermer, K. Mislow, *J. Am. Chem. Soc.* **1986**, *108*, 1569−1575.

[29] O. Ermer, *Angew. Chem. Int. Ed. Engl.* **1983**, *222*, 998−999.

[30] U. Berg, C. Roussel, *J. Am. Chem. Soc.* **1980**, *102*, 7848−7853.

[31] I. Columbus, S. E. Biali, *J. Org. Chem.* **1994**, *59*, 3402−3407.

[32] I. I. Schuster, W. Weissensteiner, K. Mislow, *J. Am. Chem. Soc.* **1986**, *108*, 6661−6663.

[33] G. Casalone, T. Pilati, M. Simonetta, *Tetrahedron Lett.* **1980**, *21*, 2345−2348.

[34] S. V. Sereda, L. L. Gervits, M. Yu. Antipin, K. N. Makarov, Y. T. Struchkov, *Zh. Strukt. Khim.* **1989**, *30*, 199−200.

[35] H. Tomoda, F. Nemoto, H. Ohyanishiguchi, N. Yamamoto, T. Taga, *Chem. Lett.* **1987**, 661−664.

[36] W. Dmowski, W. T. Flowers, R. N. Haszeldine, *J. Fluorine Chem.* **1977**, *9*, 94−95.

[37] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *GAUSSIAN98, Revision A.7*, Gaussian, Inc., Pittsburgh, PA, **1998**.

[38] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[39] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785−789.

[40] B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200−206.

[41] R. McWeeny, *Phys. Rev.* **1962**, *126*, 1028−1034.

[42] R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789−807.

[43] K. Wolinski, A. J. Sadlej, *Mol. Phys.* **1980**, *41*, 1419−1430.

[44] K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251−8260.

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