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Article

Variable-Temperature F NMR and Theoretical Study of 1,9- and 1,7-CF(CF) and *C*- and *C*-CF(CF): Hindered CF Rotation and Through-Space *J* Coupling

Ivan E. Kareev, Gustavo Santiso Quiones, Igor V. Kuvychko, Pavel A. Khavrel, Ilya N. Ioffe,
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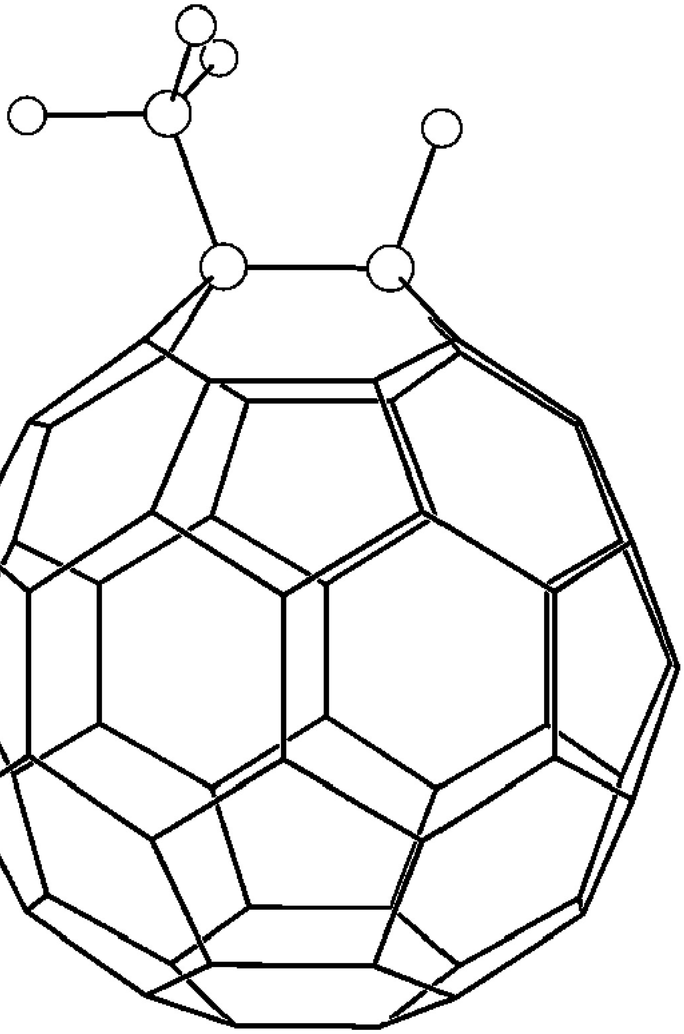

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ARTICLES

Variable-Temperature ^{19}F NMR and Theoretical Study of 1,9- and 1,7-$C_{60}F(CF_3)$ and C_s- and C_1-$C_{60}F_{17}(CF_3)$: Hindered CF_3 Rotation and Through-Space J_{FF} Coupling

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Abstract: Milligram amounts of the new compounds 1,9- and 1,7-$C_{60}F(CF_3)$ (ca. 85:15 mixture of isomers) and $C_{60}F_3(CF_3)$ were isolated from a high-temperature C_{60}/K_2PtF_6 reaction mixture and purified to 98 mol % compositional purity by two-dimensional high-performance liquid chromatography using Buckyprep and Buckyclutcher columns. The previously observed compounds $C_{60}F_5(CF_3)$ and $C_{60}F_7(CF_3)$ were also purified to 90+ mol % for the first time. Variable-temperature ^{19}F NMR spectra of the mixture of $C_{60}F(CF_3)$ isomers and the previously reported mixture of C_s- and C_1-$C_{60}F_{17}(CF_3)$ isomers demonstrate for the first time that fullerene$(F)_n(CF_3)_m$ derivatives with adjacent F and CF_3 substituents exhibit slow-exchange limit hindered CF_3 rotation spectra at -40 ± 10 °C. The experimental and density functional theory (DFT) predicted $\Delta H^{\ddagger}$ values for CF_3 rotation in 1,9-$C_{60}F(CF_3)$ are 46.8(7) and 46 kJ mol^{-1}, respectively. The DFT-predicted $\Delta H^{\ddagger}$ values for 1,7-$C_{60}F(CF_3)$, C_s-$C_{60}F_{17}(CF_3)$, and C_1-$C_{60}F_{17}(CF_3)$ are 20, 44, and 54 kJ mol^{-1}, respectively. The $^{\geq 4}J_{FF}$ values from the slow-exchange-limit ^{19}F spectra, which vary from ca. 0 to 48(1) Hz, show that the dominant nuclear spin−spin coupling mechanism is through-space coupling (i.e., direct overlap of fluorine atom lone-pair orbitals) rather than coupling through the σ-bond framework. The $^{2}J_{FF}$ values within the CF_3 groups vary from 107(1) to 126(1) Hz. Collectively, the NMR data provide an unambiguous set of $^{\geq 4}J_{FF}$ values for three different compounds that can be correlated with DFT-predicted or X-ray diffraction derived distances and angles *and* an unambiguous set of $^{2}J_{FF}$ values that can serve as an internal standard for all future J_{FF} calculations.

Introduction

We have been interested in the synthesis, characterization, and properties of fullerene$(X)_n$ derivatives with electron-withdrawing substituents for more than a decade (X = F, Cl, Br, CF_3).[1,2] Recent examples of compounds we have isolated and structurally characterized by X-ray crystallography or by ^{19}F NMR spectroscopy with corroborating density functional theory (DFT) calculations include C_{2v}-$C_{70}Br_{10}$,[2] C_1-Y@C_{82}-$(CF_3)_5$,[3] D_{5d}-$C_{60}F_{20}$,[4,5] T_h-$C_{60}F_{24}$,[6] C_{2v}-$C_{60}F_2$,[7,8] and C_{2v}-C_{60}-$(CF_3)_2$.[9,10] The latter two compounds are especially interesting because they demonstrate the interplay of offsetting steric and electronic effects in determining the most stable isomers in fullerene$(X)_n$ compounds. DFT calculations indicate that the

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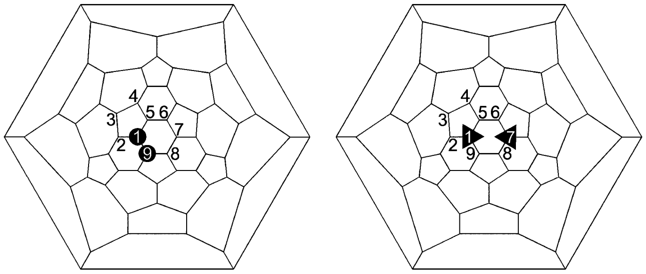

Figure 1. Schlegel diagrams of the most stable isomers of $C_{60}F_2$ (left) and $C_{60}(CF_3)_2$ (right). The isomer 1,9-$C_{60}F_2$ is predicted (DFT $\Delta H_f°$ values) to be 29.7 kJ mol^{-1} more stable than 1,7-$C_{60}F_2$.[8] Because of steric repulsion, however, the isomer 1,7-$C_{60}(CF_3)_2$ is predicted to be 34.7 kJ mol^{-1} more stable than 1,9-$C_{60}(CF_3)_2$.[9,10] The numbering scheme used is the one approved by the IUPAC[11] and the Chemical Abstracts Service.[12]

most stable isomer of $C_{60}F_2$ has fluorine atoms on the adjacent carbon atoms of a hex−hex junction (i.e., 1,9-$C_{60}F_2$)[8] but that the most stable isomer of $C_{60}(CF_3)_2$ has CF_3 groups on a *p*-C_6-$(CF_3)_2$ hexagon (i.e., 1,7-$C_{60}(CF_3)_2$),[9,10] as shown in Figure 1.[11,12] This suggested that the 1,9 and 1,7 isomers of the previously unknown composition $C_{60}F(CF_3)$ might have comparable stability.

We now report the isolation of 1,9- and 1,7-$C_{60}F(CF_3)$ from a high-temperature C_{60}/K_2PtF_6 reaction mixture. Variable-temperature ^{19}F NMR spectra show that the CF_3 group in the 1,9-isomer undergoes significantly slower rotation than the CF_3 group in the less hindered 1,7-isomer. Low-temperature ^{19}F NMR spectra of the previously reported mixture of C_s and C_1 isomers of $C_{60}F_{17}(CF_3)$, for which CF_3 resonances had not been observed at 25 °C,[13] show that restricted rotation of fullerene CF_3 groups adjacent to fullerene C−F moieties may be a general phenomenon in the growing class of fullerene$(F)_n(CF_3)_m$ compounds. Furthermore, an analysis of ^{19}F $^{\geq 4}J_{FF}$ values in the slow-exchange-limit spectra of 1,9-$C_{60}F(CF_3)$, and the two isomers of $C_{60}F_{17}(CF_3)$ show that the dominant coupling mechanism is through-space coupling (i.e., direct overlap of fluorine atom lone-pair orbitals) rather than through-bond coupling.

Experimental Section

Reagents and Solvents. The compound C_{60} (99.9% Term USA) was used as received. The compound K_2PtF_6 was obtained by treating K_2PtCl_6 with fluorine at 350 °C as previously described [Caution: F_2 is extremely hazardous and should be handled only by trained personnel].[14] Toluene was high-performance liquid chromatography (HPLC) grade. Benzene-*d*$_6$ (Cambridge), chlorobenzene, trichlorofluoromethane, and hexafluorobenzene (Sigma-Aldrich) were dried over activated 4-Å molecular sieves and vacuum distilled.

Reaction of C_{60} with K_2PtF_6. A finely ground mixture of C_{60} (0.70 g, 0.97 mmol) and K_2PtF_6 (2.31 g, 5.97 mmol) was heated at 450 °C for 6 h under dynamic vacuum. The sublimed crude product mixture (0.763 g) was dissolved in toluene, filtered through a 0.45-μm filter in order to remove insoluble inorganic byproducts, and processed by HPLC as follows.

Isolation of $C_{60}F_n(CF_3)$ ($n = 1, 3, 5, 7$). A two-stage chromatographic procedure was developed. At the first separation stage, a Cosmosil Buckyprep column (20 mm inside diameter (i.d.) × 250 mm, Nacalai Tesque Inc.) (1.8-mL injections, 18 mL/min flow rate, toluene eluent) was used, affording initial isolation of the fraction eluting between 8.5 and 13.5 min. This fraction was composed of three peaks: A, B, and C eluting at 8.8, 11, and 12.5 min, respectively. Matrix-assisted laser desorption ionization mass spectroscopy (MALDI-MS) analysis revealed that peaks B and C contained $C_{60}O$ and $C_{60}F_2$, respectively, whereas peak A was composed of the two compounds C_{60} and $C_{60}F(CF_3)$. The latter composition has not been previously observed. The Cosmosil Buckyprep column proved to be ineffective for the separation of $C_{60}F(CF_3)$ from the significant amount of C_{60} that was present. However, a second HPLC purification stage using a Regis BuckyClutcher column (20 mm i.d. × 250 mm, Regis Chemical Co.; 0.6-mL injections, 12 mL/min flow rate, toluene eluent) afforded a satisfactory separation of the two compositions. The $C_{60}F(CF_3)$ fraction eluted at 6.2 min, and 3−4-mg batches of 98% pure $C_{60}F(CF_3)$ were collected (the purity was established by subsequent HPLC and MALDI-MS analysis). The $C_{60}F(CF_3)$ fraction proved to be a mixture of 1,9-$C_{60}F(CF_3)$ and 1,7-$C_{60}F(CF_3)$. Both of these isomers and the composition $C_{60}F_3(CF_3)$ are new compounds.

Isolation of $C_{60}F_{17}(CF_3)$ (Mixture of Isomers). At the first, Cosmosil Buckyprep stage (20 mm i.d. × 250 mm, Nacalai Tesque Inc.) (18-mL injections, 1.8 mL/min flow rate, toluene eluent), a fraction eluting between 30 and 41 min was collected. At the second, Regis Buckyclutcher stage (20 mm i.d. × 250 mm, Regis Chemical Company; 1.2-mL injections, 12 mL/min flow rate, toluene eluent), a major fraction eluting at 9.5 min and containing 7−8 mg of the single composition $C_{60}F_{17}(CF_3)$ was collected (the compositional purity was demonstrated by subsequent MALDI-MS analysis). The shape of the 9.5-min HPLC peak suggested the presence of two approximately equal intensity components, which we concluded were the known C_s and C_1 isomers of $C_{60}F_{17}(CF_3)$.[13] It was not necessary to separate the two isomers for this study, but in principle their separation could probably be achieved by using a toluene−heptane eluent instead of neat toluene.

Spectroscopic Methods. MALDI mass spectra were recorded using a Voyager-DE PRO Workstation (Applied Biosystems). Sulfur was used as the matrix material. It was mixed with the sample in toluene immediately prior to deposition on the target. Nitrogen laser pulses of 337-nm wavelength, 0.5-ns duration, and 3-Hz frequency were used to desorb the species into the gas phase. The negative or positive ions formed were detected in reflectron mode. Samples for ^{19}F NMR spectroscopy were chlorobenzene or toluene-*d*$_8$ solutions and were recorded using a JEOL JNM-LA 400 (Berlin; $CFCl_3$ internal standard, δ 0) or a Bruker INOVA-400 spectrometer (Fort Collins; C_6F_6 internal standard, δ −164.9) operating at 376 MHz.

X-ray Crystallography. Cube-shaped crystals of the mixture of 1,9- and 1,7-$C_{60}F(CF_3)$ were formed by slow evaporation of solvent from a toluene solution. A black crystal that was 0.05 mm diameter was examined by X-ray diffraction at the Berlin Electron Synchrotron Radiation source BESSY at −120 °C (the X-ray wavelength was 0.900 Å). Refinement of 800 reflections showed the crystals to be cubic with $a = 22.699(3)$ Å. The extinctions were clearly consistent with the space group $I2_13$ (No. 199). By assumption that $Z = 12$ (i.e., 15 Å^3/atom), there is a 6-fold or greater disorder of the molecules in the lattice. No reasonable solution for the crystal structure could be obtained.

DFT Calculations. Predicted molecular structures, relative $\Delta H_f°$ values, and ^{19}F NMR chemical shifts[15,16] were determined with the PRIRODA package[17] using the GGA functional of Perdew, Burke, and Ernzerhof (PBE)[18] and the TZ2P {6,1,1,1,1,1/4,1,1/1,1} basis set. The ^{19}F isotropic magnetic shielding constants were calculated for the four molecules that are the subject of this paper and for a set of

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experimentally characterized reference compounds including fluorofullerenes[1] and small molecules containing CF_3 groups such as perfluorocarbons and perfluorinated ethers and ketones.[16] Effective 1D rotational potentials were used to model the internal rotations of the CF_3 groups. For a given CF_3 group, this potential was calculated for a series of fixed conformations by optimizing the remaining molecular degrees of freedom. The determination of rotational eigenstates for the potential thus obtained allowed the derivation of a temperature-dependent conformational probability−density distribution, which was further convoluted with the calculated conformational dependence of the isotropic shielding to give the average shielding constant for a given temperature (the program TORSIO[15] was used for numerical integration of the Schrödinger equation). For moderate temperatures and rotational barriers above 15 kJ mol^{-1}, this procedure, although generally preferable, rarely gave a shielding constant significantly different than simple averaging over three frozen equilibrium conformations of the CF_3 group. Linear regression of experimental δ values vs calculated shielding constants for the reference molecules provided relevant scaling and offset parameters (different sets of parameters were established for CF_3 fluorine atoms and for fullerene-cage C−F fluorine atoms).

Results and Discussion

Preparation and Isolation of $C_{60}F(CF_3)$ and $C_{60}F_3(CF_3)$. The high-temperature reaction of a finely ground mixture of C_{60} and K_2PtF_6, first reported in 1996,[19] can be optimized to produce a 60−70% isolated yield of 90+% compositionally pure $C_{60}F_{18}$.[20] The remainder of the mixture of products has been shown to contain unreacted C_{60} and small amounts of dozens of other fluorofullerenes and fluorofullerene derivatives. Those that have been purified by HPLC using Cosmosil Buckyprep columns and isolated, generally in milligram or sub-milligram amounts, as a reasonably pure single compound or a mixture of two compounds include $C_{60}F_2$ and $C_{60}F_2O$,[7] $C_{60}F_4$, $C_{60}F_6$, and $C_{60}F_8$,[21] and $C_{60}F_{17}(CF_3)$.[13]

We recently reported the use of a Regis Buckyclutcher HPLC column, routinely used for the purification of endohedral metallofullerenes,[22] to separate the compound $C_{60}F_{20}$[4] from impurities that coeluted with it in a Buckyprep column, including $C_{60}F_{12}$, $C_{60}F_{14}$, and $C_{60}F_{20}O$.[5] This successful two-dimensional Buckyprep/Buckyclutcher HPLC procedure has now been applied to the reaction products of a 450 °C reaction of C_{60} and K_2PtF_6. A plot of Buckyprep vs Buckyclutcher retention times for selected compounds is shown in Figure 2. Three new compounds, $C_{60}F(CF_3)$ (two isomers) and $C_{60}F_3(CF_3)$, have been isolated, and the previously observed compounds $C_{60}F_5(CF_3)$ and $C_{60}F_7(CF_3)$[21] have been isolated in 90+ mol % compositional purity for the first time.

The crude reaction product contained mostly $C_{60}F_{18}$ and unreacted C_{60}. It was prepurified by HPLC using a Buckyprep column. An 8.8−11.3-min fraction was then purified by the two-dimensional Buckyprep/Buckyclutcher procedure, as shown in Figure 3. A narrow cut of the Buckyclutcher separation centered at 6.2 min was rechromatographed two more times using the Buckyclutcher column to afford 3−4 mg batches of a mixture of two isomers of $C_{60}F(CF_3)$, both of which are new compounds. A combination of subsequent HPLC analysis, S_8-MALDI mass spectra (shown in Figure 4), and an ^{19}F NMR spectrum (vide infra) demonstrated that the compositional purity of this mixture of isomers was ca. 98 mol %. The HPLC traces in Figure 3 clearly show why these compounds had not been previously identified, let alone separated, from the much larger amount of unreacted C_{60} using only a Buckyprep HPLC column.

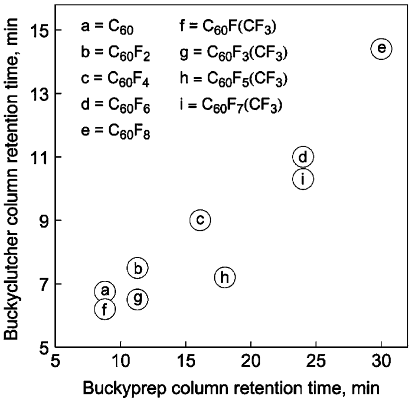

Figure 2. HPLC retention times for C_{60}, $C_{60}F_n$ derivatives ($n = 2, 4, 6, 8$), and $C_{60}F_n(CF_3)$ derivatives ($n = 1, 3, 5, 7$). The Buckyclutcher and Buckyprep column eluent rates were 12 and 18 mL toluene/min, respectively.

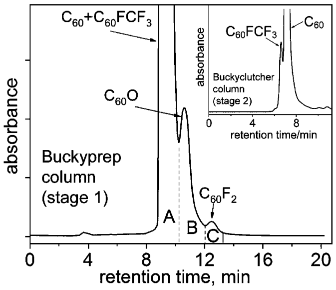

Figure 3. HPLC traces for the separations of $C_{60}F(CF_3)$ (mixture of isomers) from the 450 °C C_{60}/K_2PtF_6 reaction products. The Buckyprep and Buckyclutcher column eluent rates were 18 and 12 mL toluene/min, respectively.

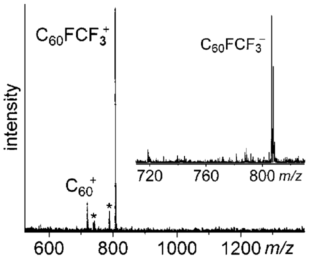

Figure 4. Positive- and negative-ion S_8-MALDI mass spectra of purified $C_{60}F(CF_3)$. The peaks marked with asterisks are due to the closed-shell fragment ions $C_{60}CF_3^+$ and $C_{60}F^+$.

Similar Buckyprep/Buckyclutcher fractions yielded highly purified sub-milligram amounts of the new compound $C_{60}F_3(CF_3)$ and the compounds $C_{60}F_5(CF_3)$ and $C_{60}F_7(CF_3)$, which had only been previously observed as impurities in batches of $C_{60}F_4$ and $C_{60}F_6$, respectively.[21] The negative-ion S_8-MALDI mass spectrum of purified $C_{60}F_3(CF_3)$ is shown in Figure 5. At the present time, an insufficient amount of $C_{60}F_3(CF_3)$ is available for a meaningful NMR analysis. Mass spectra of purified $C_{60}F_5(CF_3)$ and $C_{60}F_7(CF_3)$ are available as Supporting Information.

Isomers of $C_{60}F(CF_3)$. The DFT-predicted relative $\Delta H_f°$ values for various 1,9- and 1,7-$C_{60}XY$ isomers are listed in Table

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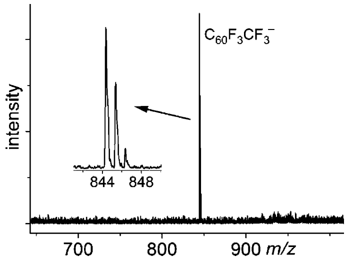
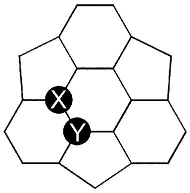
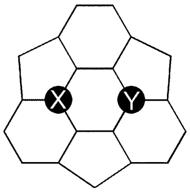


Figure 5. Negative-ion S_8-MALDI mass spectrum of purified $C_{60}F_3(CF_3)$.

Table 1. DFT-Determined Relative Enthalpies of Formation for Isomers of $C_{60}XY$

X,Y	$\Delta H_f°$(1,9-C_{60}XY), kJ mol^{-1} 	$\Delta H_f°$(1,7-C_{60}XY), kJ mol^{-1} 	ref
F,CF_3	0.0	9.8	this work
F,F	0.0	29.7	8
CF_3,CF_3	34.7	0.0	9, 10
CH_3,CH_3	0.0	3.4	8
H,H	0.0	30.9	8
Cl,Cl	1.3	0.0	8
Br,Br	2.4	0.0	8

1.[8−10] The two most stable structures for X = Y = H, F, Cl, Br, CH_3, or CF_3 were also found to be the two most stable structures for $C_{60}F(CF_3)$. Furthermore, as expected, the 1,9 and 1,7 isomers of $C_{60}F(CF_3)$ are close in energy, with the former being 9.8 kJ mol^{-1} more stable than the latter. The new data are entirely consistent with earlier conclusions[8−10] that steric factors should play a major role in determining the relative amounts of 1,9- and 1,7-$C_{60}X_2$ isomers, at least when their formation is under thermodynamic control. The predicted equilibrium geometries of 1,9-$C_{60}F(CF_3)$ and 1,7-$C_{60}F(CF_3)$ have their respective CF_3 groups in a staggered conformation with respect to the three cage C−C bonds that radiate from the sp^3 cage carbon atom bearing the CF_3 group.

The prediction of two stable isomers of $C_{60}F(CF_3)$ that are similar in energy is supported by the ^{19}F NMR data. The −40 °C spectrum of the currently inseparable mixture of two principal $C_{60}F(CF_3)$ isomers dissolved in chlorobenzene is shown in Figure 6, along with fragments of their DFT-predicted structures. The spectrum of proposed isomer 1,7-$C_{60}F(CF_3)$ consists of two singlets in a 3:1 intensity ratio at δ −69.9 and −122.6, respectively. The lack of observable $^6J_{FF}$ coupling between the C−F and C−CF_3 fluorine atoms is consistent with the large number of intervening bonds and with the predicted 3.48-Å closest-approach distance of the two types of fluorine atoms, since through-space $^{>4}J_{FF}$ coupling has not been observed or predicted for F···F distances significantly longer than 3 Å.[23−28] The spectrum of proposed isomer 1,9-$C_{60}F(CF_3)$ consists of a triplet (intensity (int.) 1, F_B, δ −57.2, $^2J_{AB}$ = 113(1) Hz), a doublet of doublets (int. 2, F_A, δ −63.9, $^4J_{AX}$ = 43(1) Hz, $^2J_{AB}$ = 113(1) Hz), and a triplet (int. 1, F_X, δ −139.3, $^4J_{AX}$ = 43(1) Hz). For comparison, the DFT-calculated δ values are −72 and −127 for 1,7-$C_{60}F(CF_3)$ and −57, −65, and −146 for 1,9-$C_{60}F(CF_3)$.

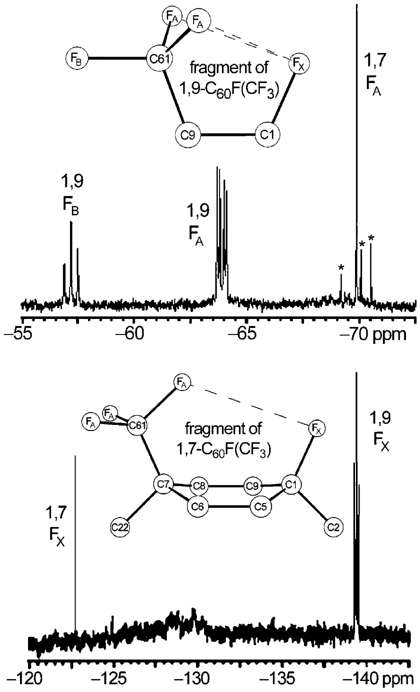


Figure 6. The −40 °C ^{19}F NMR spectrum of a mixture of 1,9- and 1,7-$C_{60}F(CF_3)$ (376 MHz, chlorobenzene, $\delta(CFCl_3)$ = 0). Also shown are drawings of fragments of the structures of the two isomers based on the DFT calculations. The F_A···F_X distances are 2.65 and 3.48 Å, respectively, in the 1,9 and 1,7 isomers. The peaks marked with asterisks are due to unidentified impurities.

The relative integrated intensities indicate that the 1,9-$C_{60}F(CF_3)$/1,7-$C_{60}F(CF_3)$ mol ratio is approximately 85/15 or 5.6. If the formation of these two isomers is under thermodynamic control at the reaction temperature, 450 °C, and this is by no means certain, a K_{eq} value of 5.6 for the transformation 1,7-$C_{60}F(CF_3) \rightleftharpoons$ 1,9-$C_{60}F(CF_3)$ would yield a $\Delta\Delta G_f$ value of −10.4 kJ mol^{-1} at 450 °C and a $\Delta\Delta H_f$ value of −14.5 kJ mol^{-1} when the statistical factor favoring the 1,7 isomer is taken into account. The latter value is in good agreement with the DFT $\Delta\Delta H_f°$ value of −9.8 kJ mol^{-1} listed in Table 1.

Hindered CF_3 Rotation. (a) 1,9-$C_{60}F(CF_3)$. The portion of the −40 °C NMR spectrum assigned to 1,9-$C_{60}F(CF_3)$ clearly indicates slow rotation of the CF_3 group in this isomer (the coupling of F_X to two CF_3 fluorine atoms instead of one further demonstrates the staggered conformation of the CF_3 group). The DFT $\Delta\Delta H_f°$ value for the eclipsed conformation of 1,9-$C_{60}F(CF_3)$ relative to its staggered conformation, which can be assumed to be the barrier height for CF_3 rotation, is 46 kJ mol^{-1}. For comparison, the eclipsed conformation of 1,7-$C_{60}F(CF_3)$ is only 20 kJ mol^{-1} less stable than its staggered conformation,

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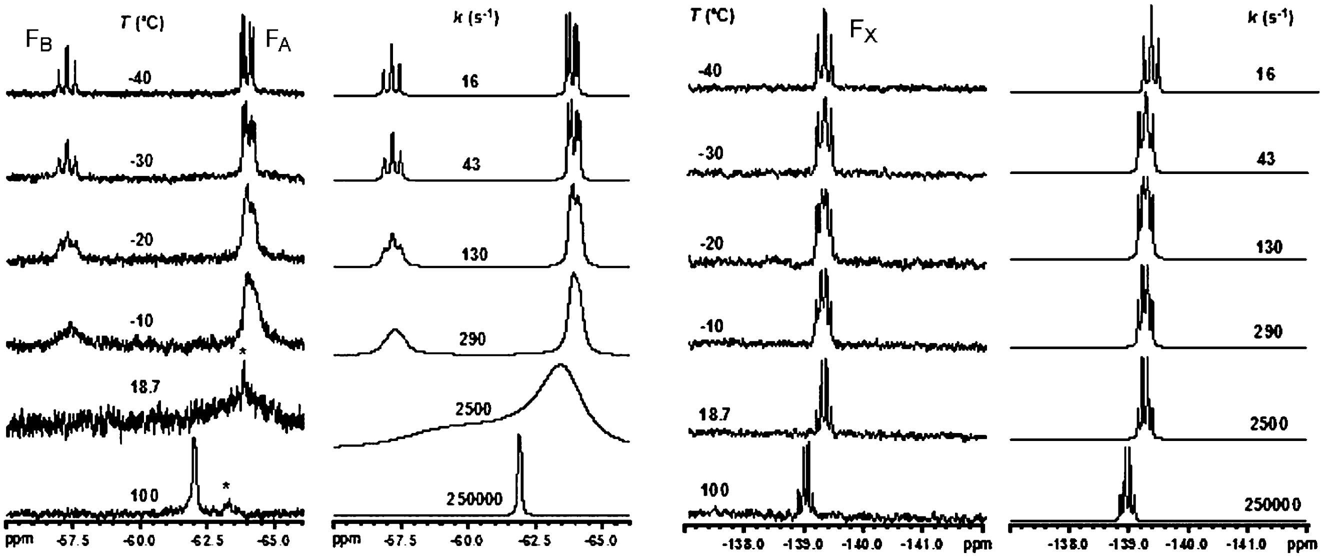

Figure 7. Variable temperature ^{19}F NMR spectra of 1,9-$C_{60}F(CF_3)$ (376 MHz, chlorobenzene, $\delta(CFCl_3) = 0$). The simulated spectra (program *gNMR*) show the first-order rate constant, *k*, for rotation of the CF_3 group between its three degenerate staggered conformations. The *k* value for 100 °C is only approximate. The peak marked with an asterisk is due to an unidentified impurity.

in harmony with the fast-exchange-limit spectrum observed for this isomer at −40 °C.

Variable-temperature ^{19}F NMR spectra of the 1,9-$C_{60}F(CF_3)$ component of the mixture of isomers are shown in Figure 7. Significantly, the CF_3 resonance at room temperature was extremely broad and could easily have been missed if it were not for the fact that its presence was indicated by mass spectrometry as well as by the 1:3:3:1 quartet observed at room temperature for the cage C−F fluorine atom. In the fast-exchange-limit spectrum at 100 °C, the CF_3 resonance was a poorly resolved doublet, the cage C−F resonance was a quartet, and the $^4J_{FF}$ value was 30(1) Hz. Since an upper limit of 3 Hz can be placed on $^4J_{BX}$ in 1,9-$C_{60}F(CF_3)$ at −40 °C (i.e., no coupling was observed), the weighted average of $^4J_{AX}$ and $^4J_{BX}$ should be ca. 29−30 Hz. The spectra were simulated using the program *gNMR* v. 5.0.1.0,[29] giving the first-order rate constant, *k*, for rotation of the CF_3 group between its three equivalent staggered conformations at each temperature. An Eyring plot of ln(*k*/T) vs 1000 K/*T* was linear with an R^2 value of 0.999 (see Supporting Information). From this plot, the activation parameters $\Delta H^{\ddagger} = 46.8(7)$ kJ mol^{-1} and $\Delta S\ddagger = -19(3)$ J mol^{-1} K^{-1} were derived (the latter value was calculated assuming that the transmission coefficient is 1.0). The experimental $\Delta H^{\ddagger}$ is the same as the DFT-predicted barrier height discussed above, 46 kJ mol^{-1}.

(b) C_s- and C_1-$C_{60}F_{17}(CF_3)$. These compounds were isolated and structurally characterized as a disordered solid solution by X-ray crystallography in 2000.[13] Schlegel diagrams and fragments of their structures, including the results of new DFT calculations, are shown in Figure 8. Note that the CF_3 group is adjacent to one fullerene C−F moiety in the C_s isomer and to two C−F moieties in the C_1 isomer. Note also that the CF_3 group in the C_s isomer is almost perfectly staggered with respect to the cage C−C bonds, but the CF_3 group in the C_1 isomer is rotated a few degrees from the staggered conformation. Interestingly, it was reported that resonances due to the CF_3 groups were missing in ^{19}F NMR spectra at 20 °C,[13] a fact that caused this pair of compounds to be misidentified as $C_{60}F_{18}(CF_2)$ in the original report of their synthesis and isolation.[30] The variable-temperature NMR spectra of 1,9-$C_{60}F(CF_3)$ suggested to us that other fullerene(F)$_n$(CF$_3$)$_m$ derivatives with adjacent F and CF_3 substituents might, in general, exhibit hindered CF_3 group rotation, and for this reason, we recorded variable-temperature ^{19}F NMR spectra of a freshly prepared ca. 50:50 mixture of C_s- and C_1-$C_{60}F_{17}(CF_3)$.

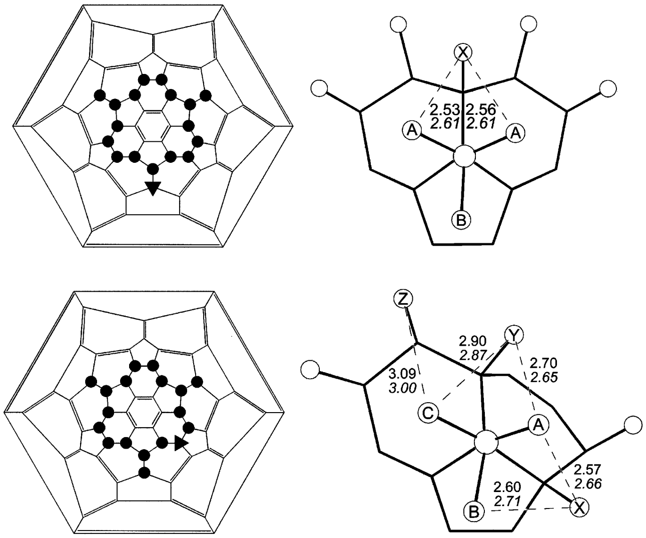

Figure 8. Schlegel diagrams and fragments of the structures of C_s-$C_{60}F_{17}$-(CF_3) (top) and C_1-$C_{60}F_{17}(CF_3)$ (bottom). The black circles and triangles in the Schlegel diagrams denote fullerene C−F and C−CF_3 moieties, respectively. The letters in the fragment drawings refer to the NMR assignments. For each F···F distance shown (Å), the upper value was calculated using the CIF file deposited with ref 13 (the esds range from 0.004 to 0.006 Å), and the lower, italicized value was calculated at the DFT level of theory.

At 80 °C, the highest temperature used, a broad near-fast-exchange limit 32-Hz doublet was observed for the C_s isomer CF_3 group at δ −64.8 (not shown). A rotationally averaged doublet of doublets was not observed for the C_1 isomer CF_3

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Table 2. ^{19}F NMR δ and J_{FF} values for the CF_3 groups in 1,9- and 1,7-$C_{60}F(CF_3)$ and in C_s- and C_1-$C_{60}F_{17}(CF_3)$[a]

compd	temp, °C	F atom	δ_{obsd}	δ_{calc}[b]	$^nJ_{FF}$ values, Hz[c]
1,9-$C_{60}F(CF_3)$	100	A,B	−59.9		$1/3((2 \times {}^2J_{AX}) + {}^2J_{BX}) = 30$
	−40	A	−63.8	−65	$^2J_{AB} = 113(1)$; $^4J_{AX} = 43$
		B	−57.2	−57	$^2J_{AB} = 113(1)$; $^4J_{BX} \leq 3$
1,7-$C_{60}F(CF_3)$	-40	A	−69.9	−72	$^6J_{AX} \leq 3$
C_s-$C_{60}F_{17}(CF_3)$	80	A,B	−64.8		$1/3((2 \times {}^2J_{AX}) + {}^2J_{BX}) = 32$
	−50	A	−67.0	−66	$^2J_{AB} = 113$; $^4J_{AX} = 48$
		B	−60.5	−56	$^2J_{AB} = 113$; $^4J_{BX} \leq 2$
C_1-$C_{60}F_{17}(CF_3)$	−30	A	−68.8	−68	$^2J_{AB} = 107$; $^2J_{AC} = 113$; $^4J_{AX} = 25$; $^4J_{AY} = 19$
		B	−60.4	−57	$^2J_{AB} = 107$; $^2J_{BC} = 126$; $^4J_{BX} = 27$
		C	−63.2	−s62	$^2J_{AC} = 113$; $^2J_{BC} = 126$; $^4J_{CY} = 5$ Hz; $^5J_{CZ} = 5$ Hz

[a] Spectra for 1,9- and 1,7-$C_{60}F(CF_3)$ were recorded using a chlorobenzene solution (δ(int. C_6F_6) = −164.9). Spectra for C_s- and C_1-$C_{60}F_{17}(CF_3)$ were recorded using a toluene solution. The F-atom labels are the same as those used in Figures 6 and 8. The δ values for cage C−F fluorine atoms in the two isomers of $C_{60}F_{17}(CF_3)$ were the same as those reported in refs 13 and 30. [b] Chemical shifts calculated at the DFT level of theory. [c] All coupling constants are ±1 Hz.

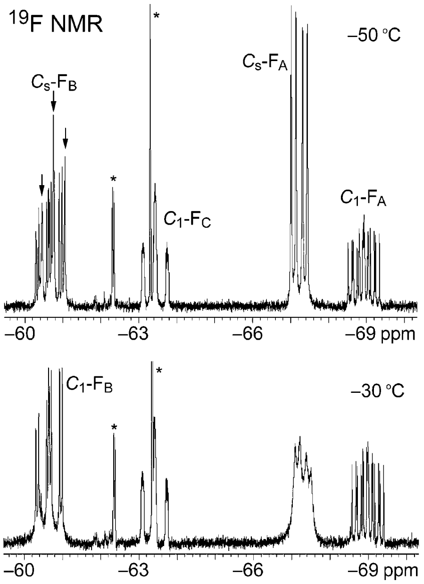

Figure 9. The CF_3 region of 376.4 MHz ^{19}F NMR spectra of a ca. 1:1 mixture of C_1- and C_s-$C_{60}F_{17}(CF_3)$ at −50 and −30 °C (toluene-d_8, C_6F_6 internal standard (δ −164.9)). Resonances marked with asterisks are due to one or more unidentified impurities.

group at any temperature. At −30 °C, separate multiplets were observed for each of the CF_3 fluorine atoms in the C_1 isomer, as shown in Figure 9, but the slow-exchange limit had not yet been reached for the C_s isomer. At −50 °C, the slow-exchange limit CF_3 subspectrum was also observed for the C_s isomer, as also shown in Figure 9. Chemical shifts and J_{FF} values for the CF_3 portions of the spectra are listed in Table 2, which also includes the corresponding values for 1,9-$C_{60}F(CF_3)$, the δ values for 1,7-$C_{60}F(CF_3)$, and the DFT-calculated δ values for all four compounds.

The slow-exchange spectrum of C_s-$C_{60}F_{17}(CF_3)$ at −50 °C is virtually congruent with the slow-exchange limit spectrum of 1,9-$C_{60}F(CF_3)$: $J_{AB} = 113(1)$ Hz and $J_{BX} \approx 0$ Hz in both cases; J_{AX} is 43(1) Hz for 1,9-$C_{60}F(CF_3)$ and 48(1) Hz for C_s-$C_{60}F_{17}(CF_3)$; and $\delta_B - \delta_A$ is 6.6 ppm for 1,9-$C_{60}F(CF_3)$ and 6.5 ppm for C_s-$C_{60}F_{17}(CF_3)$. Furthermore, the DFT-predicted barriers to CF_3 rotation are 46 kJ mol^{-1} for 1,9-$C_{60}F(CF_3)$ and 44 kJ mol^{-1} for C_s-$C_{60}F_{17}(CF_3)$. Even though the structure of C_s-$C_{60}F_{17}(CF_3)$[13] is severely distorted from the spheroidal shape of C_{60} and (presumably) 1,9-$C_{60}F(CF_3)$, the DFT $F_A \cdots F_X$ distances are 2.65 Å in 1,9-$C_{60}F(CF_3)$ and 2.61 Å in C_s-$C_{60}F_{17}(CF_3)$. All of this suggests that ^{19}F NMR $\Delta\delta$ and J_{FF} values for CF_3 groups in fullerene(F)$_n$(CF_3)$_m$ derivatives may depend primarily on the geometry of the F−C−C−CF_3 molecular fragment and not on global electronic and steric factors. This hypothesis will be examined further as additional compositionally pure fullerene(F)$_n$(CF_3)$_m$ derivatives become available.

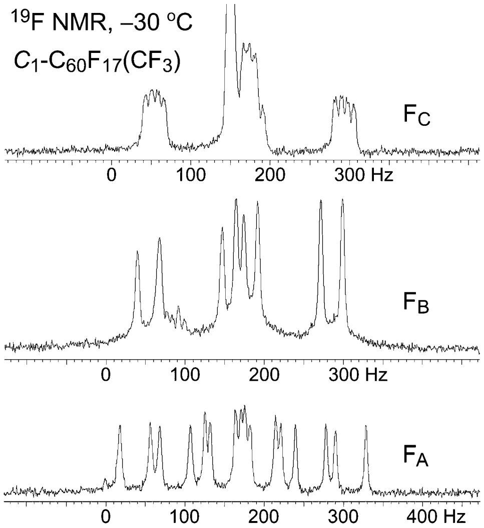

Figure 10. Expansions of selected multiplets in the CF_3 region of 376.4 MHz ^{19}F NMR spectra of a ca. 1:1 mixture of C_1- and C_s-$C_{60}F_{17}(CF_3)$ (toluene-d_8, −30 °C, C_6F_6 int. std. (δ −164.9)). Only the C_1−F_A, −F_B, and −F_C multiplets are shown.

The slow-exchange limit spectrum of C_1-$C_{60}F_{17}(CF_3)$ was very well resolved at −30 °C, as shown in Figure 10, even though the δ values for F_B in both isomers are nearly isochronous. This is due to the fact that the $\delta(F_B)$ multiplet for C_s-$C_{60}F_{17}(CF_3)$ was significantly broadened at −30 °C and only became sharp at −50 °C, which is in harmony with the significantly larger DFT $\Delta H^{\ddagger}$ for the C_1 isomer, 54 kJ mol^{-1}, relative to the $\Delta H^{\ddagger}$ value for the C_s isomer, 44 kJ mol^{-1}. The assignment of the three multiplets due to the three CF_3 fluorine atoms is based on the DFT-calculated chemical shifts (see Table 2) as well as an analysis of the through-space J_{FF} values (see below). The F_A multiplet is a doublet of doublets of doublets of doublets, and all 16 peaks are discernible in Figure 10. The F_C multiplet also exhibits coupling to four different fluorine atoms, but the 16 peaks are not as well resolved because two of the J_{FF} values are only 5 Hz. The F_B multiplet is a doublet of doublets of doublets, and all eight peaks were observed.

Table 3. ^{19}F NMR Parameters for Selected Compounds Containing Slow-Exchange Limit CF_3 Groups

compd	$^2J_{FF}$, Hz	temp, °C^a	$\Delta H‡$, kJ mol^{-1} ^{b}	$\Delta\delta$, ppm	ref
1,9-$C_{60}F(CF_3)$	113	−40	46.8(7) [46]^c	6.6	this work
C_s-$C_{60}F_{17}(CF_3)$	113	−50	[44]^c	6.5	this work
C_1-$C_{60}F_{17}(CF_3)$	107, 113, 126	−25	[54]^c	2.8, 5.6	this work
gauche 1,2-$C_2Cl_4(CF_3)_2$	105, 116, 124	−150	ca. 33^d	3.7, 8.7	31
$(SF_5)_2CHCF_3$	115	−60	44.7	11.5	32
1-R-2,6-$(CF_3)_2$-4-$C_6H_2SiR'_3$)^e	124	−96	7.2	23	
CF_3CFCl_2	115	−170	23(1)	4.7	33
CF_3CHCl_2	113	−173	22(1)	11.2	33
$CF_3CCl_2CF_3$	108	−140^f	21^g	2.3	34
CF_3CF_2I	97	−150^f	21^g	13.0	34
$PCH_3(CF_3)_2(OMe)_2$^{h}	112	−120	2.7	35	
$CF_3CPh_2(2\text{-}C_6H_4NH_2)$	125, 127^i	−60	4.1^i	36	
Ni($Br_8(CF_3)_4$-TPP)^j	114	+5^f	47^k	13.1	37
MeOCPh(CF_3)COCl	109, 113, 114	−128	34(1)	4.4, 4.8	38
1,4-$(OMe)_2$-9-CF_3-triptycene	137	+150	>105	1.2	47

^{a} Temperature at which a slow-exchange limit spectrum was obtained unless otherwise noted. ^{b} Enthalpy of activation for CF_3 rotation. ^{c} The value in square brackets was calculated at the DFT level of theory. ^{d} Estimated value obtained by choosing an approximate coalescence temperature. ^{e} R = $C(CF_3)_2OH$; R′ = *i*-Pr. ^{f} Coalescence temperature. ^{g} Errors for $\Delta H‡$ values were not given in this study, but a minimum estimate based on the published Eyring plots is ±4 kJ mol^{-1}. ^{h} Axial CF_3 groups. ^{i} ABC spin system with rapid interconversion of F_A and F_B via aryl group reorientation (i.e., racemization) even at the lowest temperature studied; $^2J_{AB}$ could not be observed due to rapid racemization; in this case $\Delta\delta$ is the difference between $\delta(F_C)$ and the average of $\delta(F_A)$ and $\delta(F_B)$. ^{j} $Br_8(CF_3)_4$-TPP = 2,3,7,8,−12,13,17,18-Br_8-5,10,15,20-$(CF_3)_4$-tetraphenylporphyrinate(2-) dianion. ^{k} $\Delta G‡$ value at the coalescence temperature.

Portions of the ^{19}F NMR spectra that include the resonances for the 17 cage C−F fluorine atoms are not shown because they have been previously published.[13,30]

In previous reports of their synthesis, a ca. 2:1 mixture of C_s- and C_1-$C_{60}F_{17}(CF_3)$, respectively,[13,30] was observed. In this work, a ca. 1:1 mixture was isolated. In any event, the difference in ΔG_f values for these two compounds must be small. Our DFT $\Delta\Delta H_f°$ value for the two isomers is 8.4 kJ mol^{-1}, with the C_s isomer more stable. The $\Delta\Delta G_f$ value at the reaction temperature would be expected to be about half this value due to a statistical factor favoring the formation of the C_1 isomer.

(c) Comparison with Other Examples of Hindered CF_3 Rotation. Of the thousands of known compounds containing CF_3 groups, before this work only 27 of them were reported to exhibit slow-exchange-limit ^{19}F NMR spectra, and all but two of these required temperatures that ranged from −60 °C to −190 °C.[23,24,31−38] Representative compounds are listed in Table 3 (see Supporting Information for a complete list of all compounds). The 113-Hz $^2J_{AB}$ value exhibited by 1,9-$C_{60}F(CF_3)$ and C_s-$C_{60}F_{17}(CF_3)$ is in the middle of the 97−137-Hz range for the previously reported compounds, while the 105−126-Hz range of $^2J_{FF}$ values for C_1-$C_{60}F_{17}(CF_3)$ spans a significant portion of the previous range. The asymmetric isomer C_1-$C_{60}F_{17}$-(CF_3) is only the seventh example of an $F_AF_BF_C$ CF_3 group for which all three $^2J_{FF}$ values can be observed. Except for two triptycene derivatives, C_1-$C_{60}F_{17}(CF_3)$ has the highest enthalpy of activation for CF_3 rotation, 54 kJ mol^{-1}, of the 30 compounds studied to date.

Through-Space J_{FF} Coupling. As in our previous work with C_1-$C_{60}(CF_3)_4$,[9] C_1-$C_{60}(CF_3)_6$,[9] and C_1-$C_{60}(CF_3)_{10}$,[39] we propose that through-space F···F coupling is the largest contribution to the observed $^4J_{FF}$ and $^5J_{FF}$ values in 1,9-$C_{60}F(CF_3)$, C_s-$C_{60}F_{17}$-(CF_3), and C_1-$C_{60}F_{17}(CF_3)$. The term "through-space coupling" is defined here as Fermi contact coupling (FCC) by direct overlap of fluorine atom orbitals (primarily lone-pair orbitals) as opposed to FCC through the σ framework of a molecule, a definition that has been used by NMR spectroscopists for more than 40 years.[40] It is now widely accepted that significant J coupling between proximate fluorine nuclei (i.e., ≤3.2 Å apart) that are separated by four or more bonds (i.e., $^{\geq 4}J_{FF}$) is mediated predominantly through space (as just defined) and not through the network of covalent bonds that separate the fluorine atoms.[25,26,28,41−44] The most convincing case is the 17 ± 2 Hz $^{398}J_{FF}$ coupling observed[45] for the fluorine atoms on 6-fluorotryptophan residues (Trp5 and Trp133) in a dihydrofolate reductase−NADPH−MTX protein complex, which Oldfield and co-workers later showed was mediated entirely by through-space coupling (F···F = 2.98 Å).[25]

Experimental and theoretical studies have shown that 37−99 Hz $^{\geq 4}J_{FF}$ values can occur when two C−F bonds are oriented so that the F···F distance is between 2.7 and 2.5 Å.[25−27,42,44,46] Given that the magnitude of the J_{FF} through-space component is known to depend on the relative orientations of the C−F bonds, the five $^4J_{FF}$ values observed for 1,9-$C_{60}F(CF_3)$, C_s-$C_{60}F_{17}(CF_3)$, and C_1-$C_{60}F_{17}(CF_3)$ with F···F distances between 2.61 and 2.71 Å, which range from 19 to 48 Hz, are consistent

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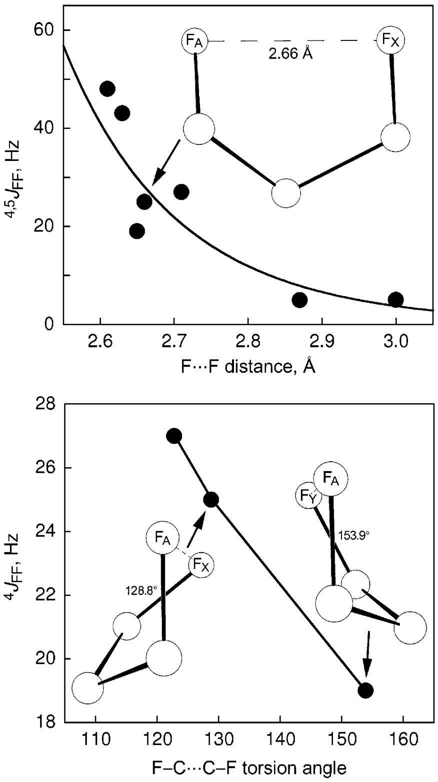

Figure 11. Plots of $^{\geq 4}J_{FF}$ vs F···F distance and selected $^{\geq 4}J_{FF}$ values (F···F = 2.65−2.71 Å) vs FC···CF torsion angle for 1,9-$C_{60}F(CF_3)$, *C_s*-$C_{60}F_{17}(CF_3)$, and *C_1*-$C_{60}F_{17}(CF_3)$. The distances and angles are from DFT calculations, but those for *C_s*-$C_{60}F_{17}(CF_3)$ and *C_1*-$C_{60}F_{17}(CF_3)$ are also very similar to the corresponding values from the disordered structure of a mixture of these two isomers of $C_{60}F_{17}(CF_3)$.

with predominantly through-space coupling. A plot of F···F distance vs $^{4,5}J_{FF}$ for these three compounds is displayed in Figure 11, which also shows some of the relative orientations of the pairs of C−F bonds as well as the F−C···C−F torsion angle dependence for the 19, 25, and 27 Hz $^{4}J_{FF}$ values that correspond to F···F distances of 2.65, 2.66, and 2.71 A, respectively. In addition to a possible torsional angle dependence, through-space J_{FF} coupling in general will probably be found to be sensitive to the "tilt angles" of the two C−F bonds, as illustrated in Figure 12. The pairs of C−F bonds shown for *C_1*-$C_{60}F_{17}(CF_3)$ and *C_1*-$C_{60}(CF_3)_{10}$ have nearly identical F···F distances and F−C···C−F torsion angles, but they have significantly different tilt angles. The F−C···C−F framework in *C_1*-$C_{60}F_{17}(CF_3)$ is a parallelogram, and $^{4}J_{FF}$ is 19(1) Hz. In contrast, the F−C···C−F framework in *C_1*-$C_{60}(CF_3)_{10}$ is a trapezoid and $^{7}J_{FF}$ is nearly four times larger, 75(2) Hz (i.e., 9 × 8.4(2) Hz).[39]

A more complete analysis of the coupling constants in 1,9-$C_{60}F(CF_3)$, *C_s*-$C_{60}F_{17}(CF_3)$, and *C_1*-$C_{60}F_{17}(CF_3)$ will be postponed until the J_{FF} values reported in this paper have been calculated at the highest appropriate level of theory[16,26−28,41,42] (at which time additional results for related compounds may also be available). Here we will conclude by pointing out why the J_{FF} results listed in Table 2 are unique as well as significant as far as the theory of through-space nuclear spin−spin coupling is concerned. First, the majority of experimental $^{\geq 4}J_{FF}$ values for which through-space coupling is thought to be the major component involve fluorine atoms attached to sp^2-hybridized carbon atoms, whereas all of the $^{\geq 4}J_{FF}$ values in Table 2 involve carbon atoms that are sp^3 hybridized. More importantly, the slow-exchange limit spectra have provided an unambiguous set of $^{\geq 4}J_{FF}$ values for three different compounds that can be correlated with DFT-predicted or X-ray diffraction derived distances and angles *and* an unambiguous set of $^{2}J_{FF}$ values that can serve as an internal standard for future J_{FF} calculations. Furthermore, *C_1*-$C_{60}F_{17}(CF_3)$ alone exhibits *six* $^{4}J_{FF}$ values (including $^{4}J_{BY} = {}^{4}J_{CX} \approx 0$) that range from ca. 0 to 27 Hz for *nearly identical sets* of F−C−C−F σ-bond arrays (albeit with different torsion angles), which strongly suggests that any contributions to J_{FF} through the σ framework must be small. Finally, the possible conformations of 1,9-$C_{60}F(CF_3)$, *C_s*-$C_{60}F_{17}(CF_3)$, and *C_1*-$C_{60}F_{17}(CF_3)$ *in solution*, where the J_{FF} values were determined, depend only on a specific C−C single bond rotational degree of freedom involving two otherwise rigid moieties (i.e., $F_3C{-}C_{60}F_n$) and are therefore more reliably known than solution conformations of many compounds that exhibit nonzero $^{\geq 4}J_{FF}$ values *and* that involve pairs of C−F bonds connected by an array of σ bonds.

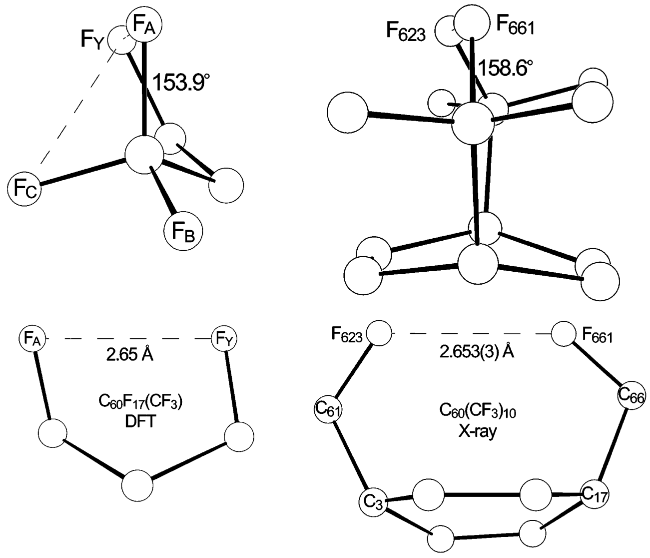

Figure 12. Similarities and differences for selected pairs of C−F bonds in the structures of C_1-$C_{60}F_{17}(CF_3)$ (left) and 1,3,7,10,14,17,23,28,31,40-$C_{60}(CF_3)_{10}$ (right). The ^{19}F $^{4}J_{AY}$ and $^{7}J_{FF}$ values involving F_{623} and F_{661} are 19(1) and 75(2) Hz, respectively.

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Supporting Information Available: Total energies and Cartesian coordinates from DFT study of 1,9- and 1,7-$C_{60}F(CF_3)$ and *C_s*- and *C_1*-$C_{60}F_{17}(CF_3)$, complete ref 42, MALDI mass spectra of $C_{60}F_5(CF_3)$ and $C_{60}F_7(CF_3)$, the Eyring plot for 1,9-$C_{60}(F_3)$, and a complete list of ^{19}F NMR parameters for compounds with slow-exchange limit CF_3 groups (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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