Article

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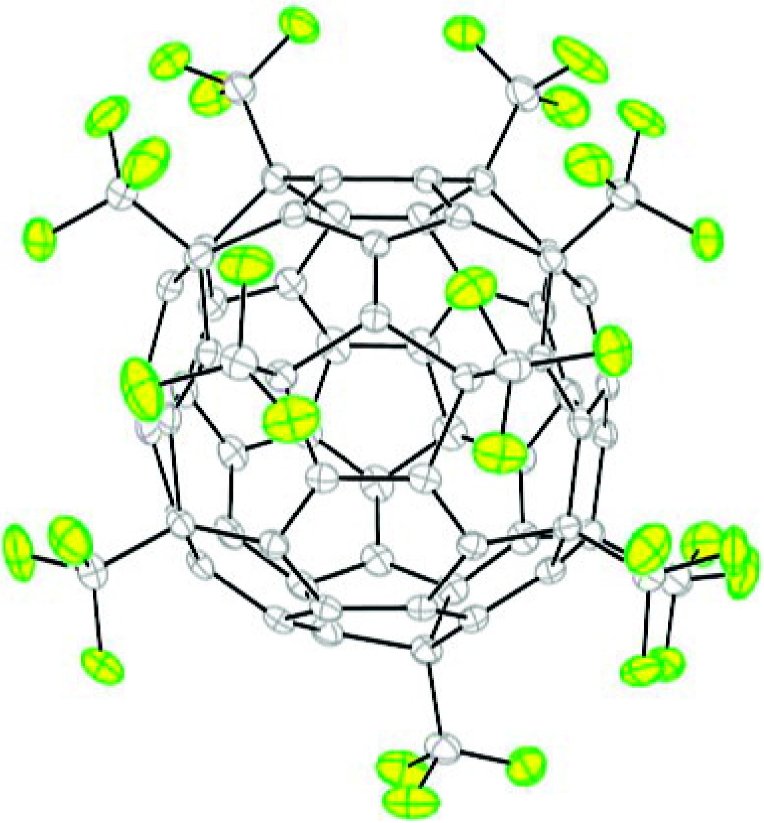
J. Am. Chem. Soc., **2005**, 127 (23), 8362-8375• DOI: 10.1021/ja050305j • Publication Date (Web): 21 May 2005



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Published on Web 05/21/2005

Synthesis, Structure, and ^{19}F NMR Spectra of 1,3,7,10,14,17,23,28,31,40-$C_{60}(CF_3)_{10}$

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Abstract: A significant improvement in the selectivity of fullerene trifluoromethylation reactions was achieved. Reaction of trifluoroiodomethane with [60]fullerene at 460 °C and [70]fullerene at 470 °C in a flow reactor led to isolation of cold-zone-condensed mixtures of $C_{60}(CF_3)_n$ and $C_{70}(CF_3)_n$ compounds with narrow composition ranges: $6 \leq n \leq 12$ for $C_{60}(CF_3)_n$ and $8 \leq n \leq 14$ for $C_{70}(CF_3)_n$. The predominant products in the C_{60} reaction, an estimated 40+ mol % of the cold-zone condensate, were three isomers of $C_{60}(CF_3)_{10}$. Two of these were purified by two-stage HPLC to 80+% isomeric purity. The third isomer was purified by three-stage HPLC to 95% isomeric purity. Thirteen milligrams of this orange−brown compound was isolated (5% overall yield based on C_{60}), and its C_1-symmetric structure was determined to be 1,3,7,10,14,17,23,28,31,40-$C_{60}(CF_3)_{10}$ by X-ray crystallography. The CF_3 groups are either *meta* or *para* to one another on a *p-m-p-p-p-m-p-m-p* ribbon of edge-sharing $C_6(CF_3)_2$ hexagons (each pair of adjacent hexagons shares a common CF_3 group). The selectivity of the C_{70} reaction was even higher. The predominant product was a single $C_{70}(CF_3)_{10}$ isomer representing >40 mol % of the cold-zone condensate. Single-stage HPLC led to the isolation of 12 mg of this brown compound in 95% isomeric purity (27% overall yield based on converted C_{70}). The new compounds were characterized by EI or S_8-MALDI mass spectrometry and 2D-COSY ^{19}F NMR spectroscopy. The NMR data demonstrate that through-space coupling via direct overlap of fluorine orbitals is the predominant contribution to J_{FF} values in these and most other fullerene$(CF_3)_n$ compounds.

Introduction

An important but synthetically challenging class of fullerene derivatives are those in which *n* independent substituents form σ bonds to *n* cage carbon atoms. Compounds such as $C_{60}X_n$ (X = H, F, Cl, Br, R, Ar, and/or R_F) are rarely prepared with high yield *and* with high compositional and isomeric purity. This is especially true for syntheses that involve radical additions, which are, in general, difficult to control.[1,2] The situation is even more complicated with analogous σ derivatives of lower-symmetry higher fullerenes. In addition to any useful and/or interesting chemical or physical properties the products might have, their importance includes what the product distributions in reaction mixtures reveal about fullerene reactivity patterns, even if it has not yet been ascertained whether the reaction is under thermodynamic or kinetic control.

Accordingly, reaction conditions and purification schemes leading to the isolation of three or fewer isomers of a given (fullerene)X_n composition are rare, and syntheses that lead to unambiguous characterization by single-crystal X-ray diffraction are fewer still. As far as C_{60} derivatives are concerned, examples include C_s-$C_{60}Br_6$,[3,4] C_{2v}-$C_{60}Br_8$,[3,4] T_h-$C_{60}Br_{24}$,[4,5] C_{3v}-$C_{60}F_{18}$,[6,7] T-$C_{60}F_{36}$,[8] C_1-$C_{60}F_{36}$,[9] D_3- and S_6-$C_{60}F_{48}$ (disordered solid solution in single crystals),[10] $C_{60}F_{18}O$ (disordered),[11] C_5-TlC_{60}-

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10.1021/ja050305j CCC: $30.25 © 2005 American Chemical Society

Ph$_5$,[12] C_s-C_{60}(9-fluorenyl)$_4$,[13] 1,6,9,18- and 1,6,11,18-$C_{60}(CH_2Ph)_4$,[14] C_{3v}-$C_{60}F_{15}(CBr(CO_2Et)_2)_3$,[15] and C_1- and C_s-$C_{60}F_{17}CF_3$ (disordered solid solution in single crystals).[16] We have excluded from this discussion the elegant and extensive work on cycloadditions to fullerenes, which generate two (or four) $C_{cage}-X$ σ bonds, not just one, for each independent X group added.[2]

Progress has been particularly slow, for example, for chlorofullerenes, which are not amenable to routine NMR characterization and which fragment extensively under most mass spectrometric conditions.[17] However, even in the case of fluorofullerenes and trifluoromethylfullerenes, for which ^{19}F NMR spectroscopy has proven to be invaluable for structure elucidation,[18,19] ambiguities can arise. The structurally characterized compound $C_{60}F_{17}CF_3$ was originally misidentified as $C_{60}F_{18}CF_2$ based on its ^{19}F NMR spectrum.[20] A more recent example involves the structures of purified C_1 isomers of $C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$, which were prepared using high-temperature reactions of C_{60} and $AgCF_3CO_2$.[21−24] On the basis of 2D ^{19}F NMR data and DFT calculations, we proposed the structures in Figure 1 having the CF_3 groups on ribbons of edge-sharing *meta*-$C_6(CF_3)_2$ or *para*-$C_6(CF_3)_2$ hexagons.[21,22] On the basis of an analysis of ^{19}F coupling constants, Taylor and co-workers proposed the structures in Figure 1 having CF_3 groups on contiguous cage carbon atoms (i.e., a series of 1,2 additions, with more than two CF_3 groups on some hexagons and pentagons).[23,24] They have also proposed that the majority of $C_{70}(CF_3)_n$ derivatives they have isolated contain CF_3 groups on contiguous cage carbon atoms.[23,25]

We now report the high-temperature trifluoromethylation of C_{60} and C_{70} with gaseous CF_3I. Among the products isolated and characterized by ^{19}F NMR spectroscopy is a C_1-symmetric isomer of $C_{60}(CF_3)_{10}$ that has been unambiguously characterized by X-ray crystallography. The structure, shown in Figure 2, and an analysis of its 1D- and 2D-COSY ^{19}F NMR spectra strongly suggest that, in general, $C_{60,70}(CF_3)_n$ derivatives prepared at high temperature have CF_3 groups arranged in *meta* or *para* positions on a ribbon of edge-sharing hexagons. Furthermore, with a precise structure in hand, an analysis of the J_{FF} NMR coupling constants supports the earlier conclusion[21,22] that through-space $^{19}F-^{19}F$ coupling is significant in trifluoromethylfullerenes and possibly in fluorofullerenes as well.

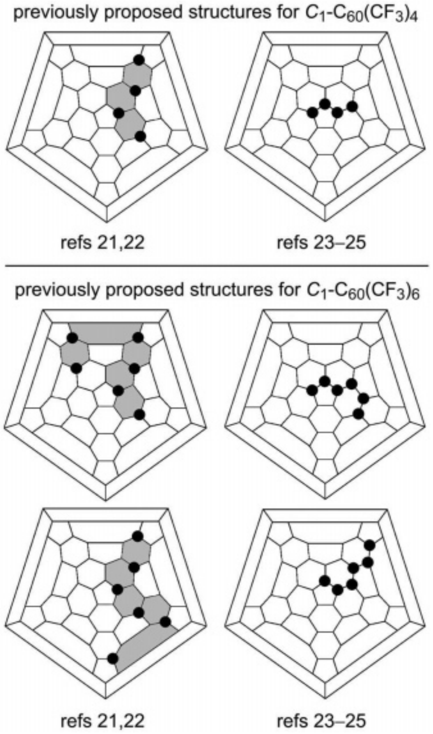

Figure 1. Schlegel diagrams for the structures of C_1-$C_{60}(CF_3)_4$ and C_1-$C_{60}(CF_3)_6$ proposed in refs 21−25. The black circles represent fullerene carbon atoms to which the CF_3 groups are attached.

Experimental Section

The compounds C_{60} (99.9+% Super Gold Grade, Hoechst) and CF_3I (99%, Sigma-Aldrich) were used as received, and C_{70} was purified to 99+ mol % by HPLC from fullerenes extracted with toluene from soot prepared by the arc-discharge method.[26] Hexane and toluene were HPLC grade. Benzene-d_6 (Cambridge) and hexafluorobenzene (Sigma-Aldrich) were dried over an appropriate drying agent and vacuum distilled.

Preparation and Isolation of Isomers $C_{60}(CF_3)_{10}$-1, $C_{60}(CF_3)_{10}$-2, and $C_{60}(CF_3)_{10}$-3. Finely ground C_{60} (150 mg, 0.208 mmol) was placed in a 0.8 cm i.d. glass tube connected to a gas handling system at one end and a mineral oil bubbler at the other. The portion of the tube containing C_{60} was placed in a 5 cm long tube furnace. After purging the sample with argon, it was heated to 460 °C and treated with 12 sccm of gaseous CF_3I (ca. 0.05 mmol min^{-1}) for 2 h (CAUTION: CF_3I decomposes in air above 300 °C and produces toxic HF, COF_2, and I_2; handle only in a well-ventilated fume hood). Orange−brown $C_{60}(CF_3)_n$ compounds and purple I_2 condensed inside the tube approximately 1 cm outside of both ends of the furnace (i.e., in the cold zones). A 40 mg portion of C_{60} was recovered unchanged from the hot zone. Iodine was removed under a flow of argon with mild heating (≤100 °C), and the orange−brown condensate (116 mg) was purified by HPLC (20 mm i.d. × 250 mm Cosmosil Buckyprep column, Nacalai Tesque, Inc.;

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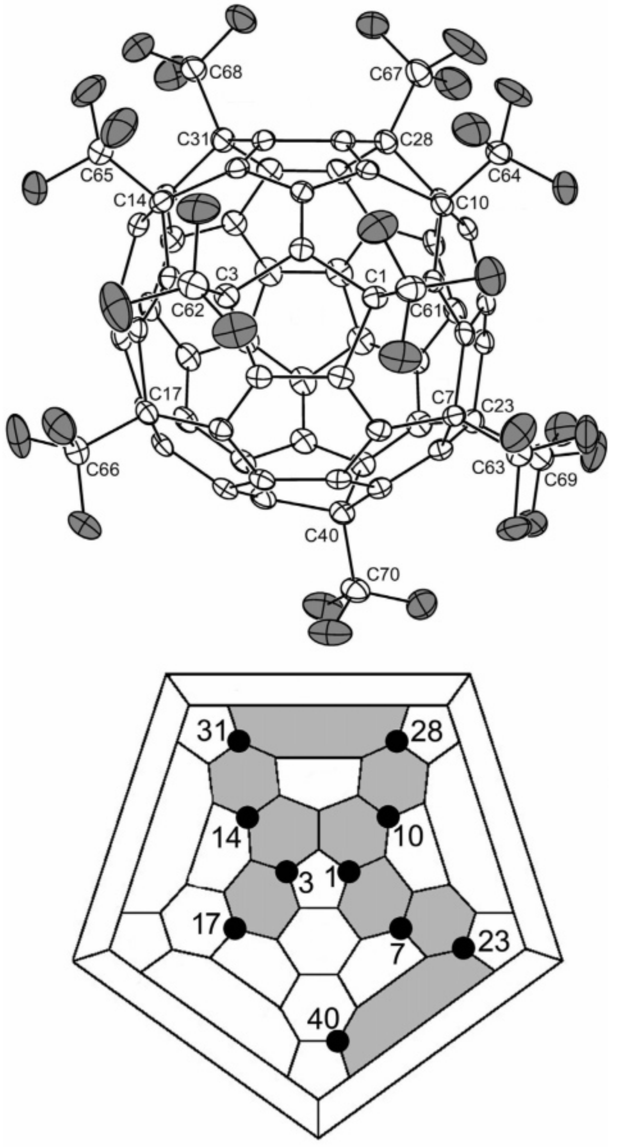

Figure 2. Structure of one enantiomorph of 1,3,7,10,17,23,28,31,40-C_{60}-$(CF_3)_{10}$ (50% anisotropic probability ellipsoids for all atoms; no disorder). The estimated standard deviations for all C−F distances and for nearly all C−C distances are ±0.003 Å. The ribbon of edge-sharing $C_6(CF_3)_2$ hexagons is highlighted in gray in the Schlegel diagram.

300 nm UV detector; 18 mL min^{-1} eluent flow rate) as follows. In the first stage, 1.8 mL injections were eluted with toluene to give eight fractions. In the second stage, 1.8 mL injections of each fraction were eluted with 20/80 (v/v) toluene/hexane. One fraction contained primarily two isomers of $C_{60}(CF_3)_{10}$, which were separated as narrow cuts and isolated by solvent evaporation (80+ mol % purity; 10(1) mg each; 3−4% overall yield each based on converted C_{60}). Another fraction contained primarily a third isomer of $C_{60}(CF_3)_{10}$. A third HPLC purification stage of this fraction using 20/80 toluene/hexane consisted of collecting a cut from 15.2 to 16.8 min. This contained 13(1) mg of 95+ mol % pure $C_{60}(CF_3)_{10}$-3 (ca. 5% overall yield based on converted C_{60}).

Preparation and Isolation of $C_{70}(CF_3)_{10}$-1. This compound was prepared using the same procedure as above except that C_{70} was used (40 mg, 0.046 mmol), the temperature was 470 °C, and the reaction time was 1 h. A 16 mg portion of C_{70} was recovered unchanged from the hot zone. The brown cold-zone condensate (35 mg) was purified by a one-stage HPLC procedure (same column and parameters as above) using 20/80 toluene/hexane as the eluent. A cut from 16.7 to 18.5 min resulted in the isolation of 12(1) mg of 95+ mol % pure, brown, microcrystalline $C_{70}(CF_3)_{10}$-1 (27% overall yield based on converted C_{70}).

Table 1. Crystal Data and Structure Refinement for $C_{60}(CF_3)_{10}$-3

formula, formula weight	$C_{70}F_{30}$, 1410.70
crystal system, space group, Z	triclinic, $P\bar{1}$, 2
color of crystal	orange−brown
unit cell dimensions	$a = 12.1433(7)$ Å
	$b = 12.3153(7)$ Å
	$c = 15.6682(9)$ Å
	$\alpha = 82.2470(10)°$
	$\beta = 86.6060(10)°$
	$\gamma = 81.9760(10)°$
temperature	173(2) K
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0529$, $wR_2 = 0.1292$
goodness-of-fit on F^2	1.037

Spectroscopic Characterization. Matrix-assisted laser desorption−ionization time-of-flight 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 or toluene/hexane 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. Electron-ionization (EI) mass spectra were recorded with a Fisons VG Quattro single quadrupole mass spectrometer. Samples were loaded into glass capillaries which were heated to 400 °C. The desorbed molecules were ionized with 20 eV electrons. Samples for ^{19}F NMR spectroscopy were benzene-d_6 solutions at room temperature and were recorded using a Bruker INOVA-400 spectrometer operating at 376.5 MHz (C_6F_6 internal standard, δ −169.9).

Structure of 1,3,7,10,14,17,23,28,31,40-$C_{60}(CF_3)_{10}$ ($C_{60}(CF_3)_{10}$-3). X-ray diffraction data from a single crystal grown by evaporation from a saturated benzene solution were recorded using a Bruker SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator). Selected details related to the crystallographic experiments are listed in Table 1. Unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections. Intensities were integrated from a series of frames (ω rotation) covering more than a hemisphere of reciprocal space. An empirical absorption correction was applied by using SADABS.[27]

The structure was solved by using direct methods and was refined (on F^2, using all data) by a full-matrix, weighted least-squares process. All carbon and fluorine atoms were refined by using anisotropic atomic displacement parameters. Standard Bruker instrument control, data reduction, and integration (SAINT) software were employed, and Bruker SHELXTL[28] software was used for structure solution, refinement, and graphics.

Results and Discussion

Synthesis of $C_{60,70}(CF_3)_n$. (a) Background and Strategy. Radical additions to fullerenes are difficult to control, especially when four or more independent X substituents[29] are added. Mixtures of fullerene(X)$_n$ compositions with a range of n values are typically formed (n is an even integer except as noted).[2] For example, the first fluorinations of C_{60} and C_{70} with F_2 produced mixtures such as $C_{60}F_{34-44}$[30] and $C_{70}F_{46-54}$.[31] Selectiv-

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ity was only achieved after screening many fluorinating agents, stoichiometries, and reaction temperatures.[18,32] Similarly, optimization of bromination and chlorination reaction conditions led to the isolation of purified, selectively halogenated derivatives such as $C_{60}Cl_6$, $C_{60}Br_6$, $C_{60}Br_8$, $C_{60}Br_{24}$, and $C_{70}Br_{10}$.[3,5,33,34]

There have been two reports in the literature describing the fluorination of fullerenes,[16,35] one describing an attempt to fluorinate fullerenes,[36] and one describing the fluorination of an azafullerene[37] that resulted in the unintentional preparation of trace amounts of fullerene derivatives containing one or more CF_3 groups. The intentional addition of n independent perfluoroalkyl groups to fullerenes to give isolable products has been studied since 1993 (cycloadditions of C_2F_4 to fullerenes[38] are excluded from this discussion). Fagan and co-workers at DuPont reported that the photolysis or thermolysis of C_{60} and R_FI in organic solvents led to mixtures of products with compositions such as $C_{60}(C_6F_{13})_nH_m$ when R_FI was $C_6F_{13}I$ and the solvent was 1,2,4-$C_6H_3Cl_3$ ($n + m$ even, $n = 6-12$) and $C_{60}(CF_3)_n$ when R_FI was CF_3I and the solvent was hexafluorobenzene ($n = 4-14$).[39] In 2002, Shinohara and co-workers reported the production of La@$C_{82}(C_8F_{17})_2$ by photolysis of a toluene solution of 0.85 mg of La@C_{82} and 1.8 equiv of $C_8F_{17}I$ followed by a multi-stage HPLC purification,[40] and we just reported the synthesis of two C_1 isomers of Y@$C_{82}(CF_3)_5$ using the $AgCF_3CO_2$ method described below.[41] Some or all of these reactions may involve the stepwise addition of perfluoroalkyl radicals to the fullerene.

In 2001, we reported[42] (and subsequently patented[43]) the solid-state trifluoromethylation of C_{60} and a C_{60}/C_{70} mixture with the metal trifluoroacetates $AgCF_3CO_2$ ($T_{rxn} = 300$ °C) and (Cr,Cu,Pd)$(CF_3CO_2)_2$ ($T_{rxn} = 350-400$ °C). In the case of $AgCF_3CO_2$, the range of n values was 2−22 for $C_{60}(CF_3)_n$ and 6−22 for $C_{70}(CF_3)_n$. In 2003, we found that a two-stage sublimation of the $AgCF_3CO_2$ reaction products, first at 380 °C to remove the more volatile components with $n \geq 12$ followed by sublimation of the residue at 500 °C, resulted in a sublimate with a narrow range of $C_{60}(CF_3)_n$ compounds with $n = 2-10$ (primarily 2−6).[21] The high T sublimation greatly simplified subsequent HPLC purification.[21] Taylor and co-workers separated into fractions, by extensive HPLC processing,[23−25] many of the products they prepared using our 2001 synthetic method.[42] Some fractions contained single isomers of single compositions.[23−25]

We are pursuing three strategies to improve the selectivity of C_{60} trifluoromethylation reactions. The first is to exhaustively trifluoromethylate C_{60} with a large excess of trifluoromethylating reagent, possibly producing a composition such as $C_{60}(CF_3)_{24}$ that might resist further addition of CF_3 groups. The second strategy (similar to the one employed by Shinohara[40]) is to limit the stoichiometric ratio of trifluoromethylating reagent to C_{60}. The third strategy, an example of which is the subject of this paper (and which was also applied to C_{70} trifluoromethylation), is to continuously remove a narrow range of compositions from the reaction zone as they are formed. In principle, this can be accomplished by selective extraction into an immiscible phase, selective precipitation from a solution, selective crystallization from a melt, or selective distillation or sublimation of a limited number of products at a given temperature. Selective sublimation seemed to be the natural choice for C_{60} trifluoromethylations because our previous work showed that (i) $C_{60}(CF_3)_n$ derivatives can be sublimed without decomposition at temperatures as high as 500 °C, (ii) derivatives with higher n values sublime at temperatures lower than that of derivatives with lower n values, and (iii) derivatives with $n = 2-10$ sublime under vacuum only at temperatures well above 380 °C.[21] This suggested that solid-state trifluoromethylation reactions of C_{60} at temperatures between 400 and 500 °C might be suitable, but that would exclude most trifluoroacetate salts since they decompose at lower temperatures (e.g., $AgCF_3CO_2$ decomposes at 230 °C and $Cr(CF_3CO_2)_2$ at 310 °C[42]). Ideally, a *gaseous* reagent that generates trifluoromethyl radicals at a constant rate when heated would flow through a tube containing solid C_{60} heated to 400−500 °C. Products with low n values would sublime out of the hot zone before they could react further, in a way that is analogous to the Knudsen cell-derived selective syntheses of $C_{60}F_{18}$ and $C_{60}F_{36}$.[18,32] This variation of the third strategy did in fact result in the production of a ca. 40% yield (based on converted C_{60}) of a mixture of isomers of a single composition, $C_{60}(CF_3)_{10}$, and a ca. 27% yield of a *single* isomer of $C_{70}(CF_3)_{10}$ (based on converted C_{70}).

(b) Reactions of C_{60} with CF_3I Vapor at 200−480 °C. (i) Experiments in Berlin. Samples of C_{60} (35−50 mg, 0.049−0.069 mmol) in a nickel boat within a glass tube were heated under an argon atmosphere to either 200, 460, or 480 °C in a temperature-programmable tube furnace. Once the set temperature was reached, CF_3I vapor at 1 atm was allowed to flow through the reaction tube for about 2 h (the flow rate was not precisely controlled but was approximately 5 sccm (ca. 0.02 mmol min^{-1})). In the 460 and 480 °C experiments, purple I_2 and orange−brown $C_{60}(CF_3)_n$ condensed in the glass tube outside of the hot zone (i.e., outside of the furnace) as soon as CF_3I had filled the tube. Iodine condensed further from the hot zone than did the fullerene products. Both I_2 and $C_{60}(CF_3)_n$ condensed at the outlet and inlet sides of the hot zone (more

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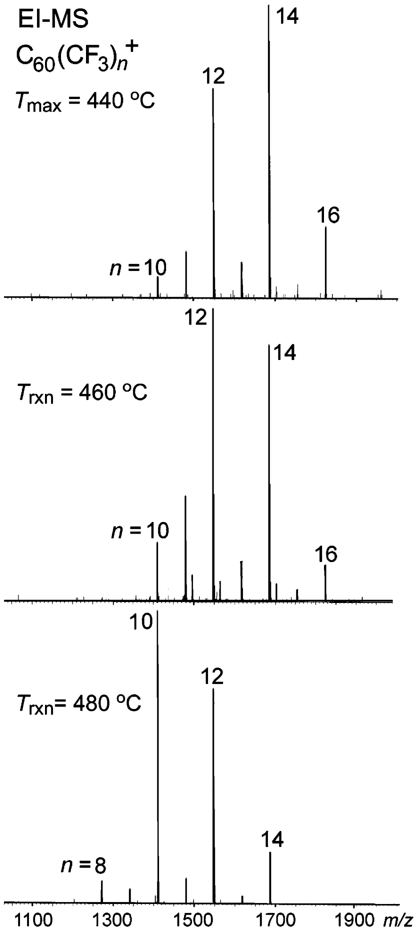

Figure 3. Electron-impact-ionization (20 eV) mass spectra of the products of the Berlin $C_{60} + CF_3I$ experiments. Lower *n* values are favored at higher temperatures because the products sublime out of the hot zone as they are formed.

appeared to condense on the outlet side), probably because the flow rate was low.

In the lowest temperature experiment, no I_2 or fullerene derivative sublimate was observed in the cold zone at 200 °C. With CF_3I continuing to flow through the reactor, the temperature was increased to 420 °C during 2.5 h (ca. 1.5 °C min^{-1}). At 300 °C, I_2 formation was apparent, indicating thermal degradation of CF_3I (this is consistent with the thermolysis of CF_3I in air[44]), but no orange−brown fullerene product was observed in the cold zones until the temperature had reached 400 °C. Since $C_{60}(CF_3)_n$ compounds with low *n* values do not sublime readily below 400 °C, it is not known at this time if such products had formed before the temperature had reached 400 °C. The temperature was held at 420 °C for 2 h and then at 440 °C for 30 min.

In each experiment, the orange−brown mixture of $C_{60}(CF_3)_n$ compounds that had condensed in the cold zone was collected in air, and I_2 was removed under a flow of argon at temperatures ≤100 °C. Electron-impact-ionization mass spectra (20 eV) of the crude mixtures of condensed products are shown in Figure 3. The molecular ions $C_{60}(CF_3)_n^+$ (n = 8, 10, 12, 14, 16) are the dominant species, with smaller amounts of some closed-shell fragment ions $C_{60}(CF_3)_{n-1}^+$. (In the 460 °C product mixture, small amounts of some $C_{60}(CF_3)_nO^+$ and $C_{60}(CF_3)_{n-1}O^+$ ions from oxide contaminants are visible, as well.)

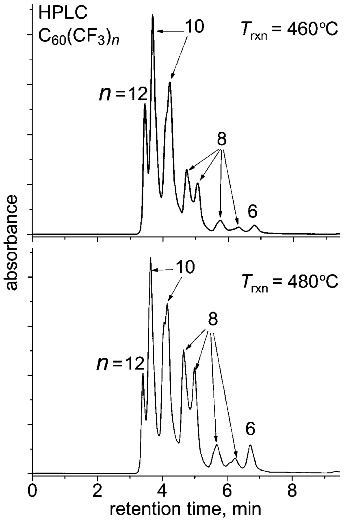

Figure 4. HPLC chromatograms of the crude cold-zone-condensed C_{60}/CF_3I reaction products from the Karlsruhe experiments. Peak assignments are based on mass spectrometric analysis of selected fractions.

The results clearly show that lower *n* values are favored at higher reaction temperatures, demonstrating the efficacy of the strategy discussed above. For example, an observable amount of $C_{60}(CF_3)_8$ was formed at 480 °C but not at lower temperatures, and no observable amount of $C_{60}(CF_3)_{16}$ was formed at 480 °C. Most striking is that $C_{60}(CF_3)_{10}$ went from being a minor component of the reaction mixture at temperatures ≤460 °C to being the predominant product at 480 °C under these conditions.

(ii) Experiments in Karlsruhe. Experiments at 460 and 480 °C were repeated in Karlsruhe, but some of the reaction conditions were different. Larger amounts of C_{60} were used (>100 mg). The C_{60} was finely ground immediately prior to the reaction, and it was placed directly in the glass tube, not in a nickel boat, in the hot zone. Furthermore, the flow rate of CF_3I was greater, ca. 12 sccm (0.5 mmol min^{-1}). Additionally, the distance between the center of the hot zone (where the C_{60} samples were located) to the cold zone where fullerene products began to condense was much shorter (4.5 cm) than in the Berlin experiments (26 cm) because a much smaller furnace was used in Karlsruhe. For these reasons, the relative amounts of $C_{60}(CF_3)_n$ products were not the same as in the Berlin experiments.

Nevertheless, the same 20 °C change in reaction temperature produced the same trend in the distribution of products, as evidenced by the HPLC traces of the crude mixtures of cold-zone-condensed products shown in Figure 4. In the 480 °C sample, there is clearly more $C_{60}(CF_3)_6$, more $C_{60}(CF_3)_8$, and less $C_{60}(CF_3)_{12}$ relative to $C_{60}(CF_3)_{10}$ than at 460 °C. In ongoing work, we are attempting to optimize the parameters of temperature, CF_3I flow rate, presence or absence of a buffer gas, C_{60} particle size, and diameter and length of the hot zone to further improve the selectivity.

The stoichiometric trifluoromethylation of C_{60} by CF_3I at high temperature can be represented by reaction 1.

$$C_{60}(s) + n\,CF_3I(g) \xrightarrow{\Delta} C_{60}(CF_3)_n(g) + n/2\,I_2(g) \qquad (1)$$

We know very little about what mechanism or mechanisms might be operable under our reaction conditions at the present

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time. It is known that CF_3I undergoes simple thermolysis to I atoms and CF_3 radicals.[45] The rate of reaction 2 at 460 °C and 1 atm can be estimated from literature data to be high enough to cause scission of the C−I bond in each CF_3I molecule more than once during its residence time in the hot zone.[45]

$$CF_3I(g) \rightarrow CF_3(g) + I(g) \tag{2}$$

Therefore, it is certainly possible that CF_3 radicals add to C_{60} one by one. It is also known that CF_3I dissociates to M−CF_3 and M−I groups on many metal surfaces,[46,47] and in some cases, including nickel,[46] CF_3 radicals can desorb from the metal surface at temperatures as low as 43 °C. However, many other pathways are possible. For example, CF_3I adds across the C=C bonds of olefins at temperatures ≥200 °C.[48] In addition, although the 7.51 eV ionization energy of the gas-phase C_{60} molecule[49] is much larger than the 1.89 eV electron affinity of the CF_3 radical,[50] the work function of solid C_{60} is only 4.7 eV,[51] very similar to the 4.6 eV work function of highly oriented pyrolytic graphite (HOPG),[52] and CF_3^- carbanions are known to form when CF_3^+ cations (and presumably CF_3 radicals) are scattered from the surface of HOPG.[53] Therefore, it is premature to rule out any mechanism involving concerted additions of CF_3I to form $C_{60}(CF_3)_nI_n$ intermediates, nucleophilic addition of ions formed by scattering from surfaces (including the surface of a particle of C_{60}), electron-transfer reactions, or a myriad of other possible elementary steps.

(c) Synthesis of $C_{60}(CF_3)_{10}$ Isomers 1−3. The orange−brown condensate from the 460 °C Karlsruhe reaction was separated into fractions by HPLC, first using toluene and then using 20/80 v/v toluene/hexane, as shown in Figure 5. Mass spectra of each fraction (not shown) led to the HPLC peak assignments in Figures 4 and 5. Toluene fraction 2 contained primarily two isomers of $C_{60}(CF_3)_{10}$. These isomers, $C_{60}(CF_3)_{10}$-1 and $C_{60}(CF_3)_{10}$-2, coeluted in toluene but were separated and collected as separate fractions in toluene/hexane for NMR analysis.

Toluene fraction 3 contained a mixture of a third isomer of $C_{60}(CF_3)_{10}$, $C_{60}(CF_3)_{10}$-3, and a smaller, but comparable, amount of $C_{60}(CF_3)_{10}O$. These too were separated in 20/80 (v/v) toluene/hexane by HPLC (not shown). The toluene/hexane fraction containing $C_{60}(CF_3)_{10}$-3 was chromatographed a third time, again in toluene/hexane, to give the bottom HPLC trace in Figure 5. From this sample, a cut of the $C_{60}(CF_3)_{10}$-3 peak from 15.2 to 16.8 min was collected. Evaporation of solvent left 13(1) mg of solvent-free, microcrystalline, highly pure $C_{60}(CF_3)_{10}$-3, which was used to obtain the S_8-MALDI mass spectrum shown in Figure 5, for NMR analysis, and for growing single crystals for X-ray crystallography. This represents a 5 mol % yield based on converted C_{60}. Although this may seem like a modest yield, only five other *highly purified*, *single isomer* C_{60} derivatives with more than six independent substituents have higher isolated yields, namely, C_{3v}-$C_{60}H_{18}$,[54] C_{3v}-$C_{60}F_{18}$,[55] C_3-$C_{60}F_{36}$,[56] T-$C_{60}F_{36}$,[56] C_{2v}-$C_{60}Br_8$,[3] and T_h-$C_{60}Br_{24}$.[5]

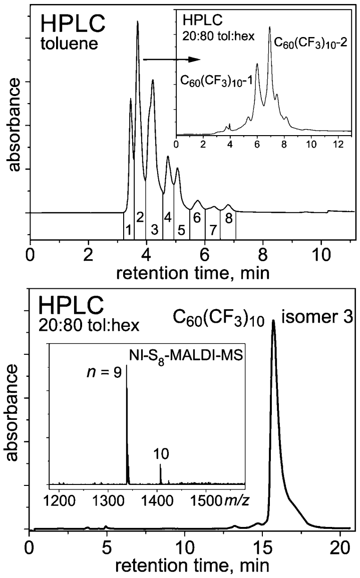

Figure 5. (Top) First-stage HPLC chromatogram of the crude cold-zone-condensed C_{60}/CF_3I reaction products from the Karlsruhe synthesis at 460 °C. The inset shows the second-stage chromatogram of first-stage toluene fraction 2. (Bottom) Third-stage HPLC purification of first-stage toluene fraction 3. The inset shows the negative-ion S_8-MALDI mass spectrum of the 13 mg sample of $C_{60}(CF_3)_{10}$-3 that was isolated by taking a cut of the third-stage purification from 15.2 to 16.8 min.

Toluene fractions 2 and 3 represent 62% of the mixture of products of the 460 °C Karlsruhe synthesis by integration of the HPLC peaks (Figure 5, top). Since fullerene derivatives with fewer substituents tend to be more highly colored, this may be an underestimate. If an intentionally overestimated 33% of the combined integrals for toluene fractions 2 and 3 are due to oxide impurities and/or other isomers of $C_{60}(CF_3)_{10}$, then the 460 °C Karlsruhe reaction conditions produced 40+ mol % of three isomers of the single composition $C_{60}(CF_3)_{10}$. It seems reasonable to expect that by optimizing the conditions to target a particular composition, 10 or more milligrams of a variety of purified, single-isomer $C_{60}(CF_3)_n$ derivatives will be isolated in the near future. This may also be true for other fullerene-$(CF_3)_n$ derivatives that are stable at the temperatures required for this selective synthesis strategy.

(d) Synthesis of $C_{70}(CF_3)_{10}$-1. The most selective trifluoromethylation reaction found in this study was a 1 h reaction between C_{70} and gaseous CF_3I at 470 °C using the Karlsruhe reaction conditions. The reaction products that condensed in the cold zone consisted of a small amount of $C_{70}(CF_3)_8$, a single isomer of $C_{70}(CF_3)_{10}$ ($C_{70}(CF_3)_{10}$-1; >40 mol %), and a mixture of $C_{70}(CF_3)_{12}$ and $C_{70}(CF_3)_{14}$ (we have not yet determined the

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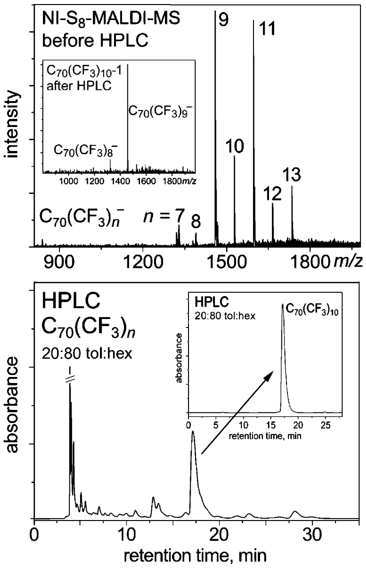

Figure 6. HPLC chromatograms and negative-ion S$_8$-MALDI mass spectra of the crude cold-zone-condensed C$_{70}$/CF$_3$I reaction products and the 12 mg purified sample of C$_{70}$(CF$_3$)$_{10}$-1 that was isolated by taking a cut of the single HPLC purification step from 16.7 to 18.5 min.

number of isomers of C$_{70}$(CF$_3$)$_8$, C$_{70}$(CF$_3$)$_{12}$, and C$_{70}$(CF$_3$)$_{14}$ present). An HPLC trace of the reaction mixture and an HPLC trace and MALDI mass spectra of the crude product and purified C$_{70}$(CF$_3$)$_{10}$-1 are shown in Figure 6. Twelve milligrams of 95+ mol % pure C$_{70}$(CF$_3$)$_{10}$-1 was isolated, which represents a 27% yield based on converted C$_{70}$ (as with the isomers of C$_{60}$(CF$_3$)$_{10}$ isolated in this study, the purity of C$_{70}$(CF$_3$)$_{10}$-1 was established by ^{19}F NMR and mass spectroscopy analyses). Significantly, the purification of this compound was accomplished with a one-stage HPLC procedure.

Structure of 1,3,7,10,14,17,23,28,31,40-C$_{60}$(CF$_3$)$_{10}$ (C$_{60}$(CF$_3$)$_{10}$-3). (a) General Comments. The asymmetric molecule, shown in Figure 2, crystallized in $P\bar{1}$ with a pair of enantiomers in the unit cell. There are no molecules of benzene (the solvent of crystallization) in the lattice. The decakis(trifluoromethyl)-[60]fullerene molecule consists of an intact C$_{60}$ cage with 10 CF$_3$ groups attached to carbon atoms C1, C3, C7, C10, C14, C17, C23, C28, C31, and C40 (this numbering scheme conforms to IUPAC and Chemical Abstracts Service recommendations;[29,57] these CF$_3$ groups will be referred to as CF$_3$-1, CF$_3$-3, CF$_3$-7, etc.). Given the tendency of many fullerenes and their derivatives to exhibit disorder in the solid state, as well as the general tendency of trifluoromethyl groups to exhibit disorder and/or extreme thermal motion about their F$_3$C−C bonds, the structure is remarkably well behaved and exhibits no apparent disorder of any kind. This fact, combined with the high quality of both the crystals and the data set recorded, makes this structure one of the most precise fullerene structures reported to date from the standpoint of individual interatomic distances and angles. The estimated standard deviation (esd) for each of the C−F, C···F, and F···F interatomic distances, and for nearly all of the cage C−C bond distances, is ±0.003 Å. The Schlegel diagrams in Figure 7 show the complete numbering scheme, all of the cage C−C distances to the nearest 0.01 Å, and the placement of C=C double bonds (1.36−1.40 Å). Selected interatomic distances and angles are listed in Table 2. The distortions of the fullerene cage from the pseudo-spherical shape of C$_{60}$ are described in detail in the Supporting Information.

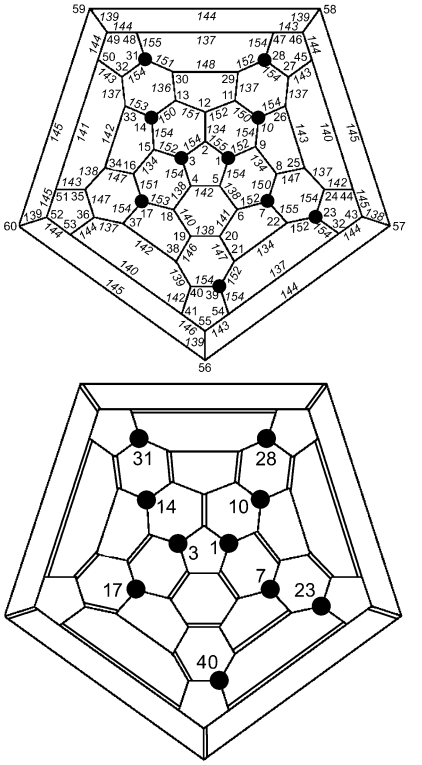

Figure 7. Schlegel diagrams for C$_{60}$(CF$_3$)$_{10}$-3 (the black circles represent fullerene carbon atoms to which the CF$_3$ groups are attached). For simplicity, fullerene C−C bond distances are shown in picometers (pm) and have been rounded off to the nearest pm (0.01 Å). Three times the estimated standard deviation (3σ) for C53−C54, C49−C59, C43−C57, C41−C55, C56−C60, C58−C59, and C57−C58 is 0.012 Å, and 3σ for all other C−C distances is 0.009 Å. The bottom Schlegel diagram shows the placement of double bonds.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for C$_{60}$(CF$_3$)$_{10}$-3[a]

C1−C61	1.565(3)	C3−C62	1.552(3)
C7−C63	1.536(3)	C10−C64	1.534(3)
C14−C65	1.542(3)	C17−C66	1.533(3)
C28−C68	1.528(3)	C31−C69	1.541(3)
C23−C67	1.539(3)	C40−C70	1.535(3)
F611···F621	2.857(3)	F612···F621	2.731(3)
F621···F612	2.961(3)	F622···F651	2.581(3)
F623···F661	2.653(3)	F611···F641	2.992(3)
F612···F633	2.961(3)	F613···F641	2.785(3)
F613···F642	2.973(3)	F613···F633	2.877(3)
F652···F691	2.568(3)	F643···F681	2.541(3)
F632···F673	2.574(3)	F692···F683	2.560(3)
F671···F703	2.640(3)	C61···C62	3.608(3)
C61···C63	4.142(3)	C61···C64	3.736(3)
C62···C65	3.809(3)	C62···C66	4.343(3)
C64···C68	4.331(3)	C65···C69	4.354(3)
C67···C70	4.397(3)	C68···C69	4.346(3)
C−F	1.312(3)−1.342(3)	F−C−F	106.3(2)-108.1(2)
C−C−F	109.6(2)−113.1(2)	C−C−C$_{CF3}$	110.3(2)-116.3(2)

[a] See Figure 7 for individual cage C−C distances.

Of the more than 300 structures of C$_{60}$, its molecular complexes, and its derivatives reported by the end of 2003,[58] only a few exhibit no disorder *and* have this level of precision for cage C−C bond distances. These include the xylene solvate of C$_{60}$F$_{18}$ (±0.002−0.003 Å),[7] C$_{60}$·Pt(OEP)·2C$_6$H$_6$ (±0.002−0.003 Å),[59] a C$_{60}$-diphenylaminofluorene dyad (±0.003−0.004

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Å),[60] and $C_{60}Br_6 \cdot 0.5C_6H_5Cl \cdot 0.5Br_2$ (±0.004 Å; the C_6H_5Cl molecule, but not the bromofullerene, is disordered about an inversion center).[4] Much more typical for ordered C_{60} derivatives are the cage C−C esd's found in structures such as $(C_{60})_2$(6,13-diphenylpentacene)$\cdot 4.5CS_2$ (±0.005−0.007 Å; some of the CS_2 molecules are disordered),[61] $C_{60}F_{15}(CBr(CO_2Et)_2)_3 \cdot C_6H_5Me$ (±0.007 Å),[15] $C_{60}(CH_2C_6H_5)_4$ (±0.007−0.008 Å),[14] C_{60}-(fluorenyl)$_4$ (±0.008 Å),[13] Pd((η^5-$C_{60}Me_5$)(η^3-C_3H_5)$\cdot CS_2$ (±0.01),[62] $C_{60} \cdot$Co(OEP)$\cdot CHCl_3$ (±0.012 Å),[63] $C_{60}Br_{24} \cdot 2Br_2$ (±0.012−0.014 Å),[4] and Tl($C_{60}Ph_5$)$\cdot$2.5THF (±0.02 Å).[12]

(b) Lattice Packing. The distorted cubic closest packing of the molecules in the lattice and an intermolecular interaction involving only carbon atoms are shown in Figures S-4 through S-6 in the Supporting Information. The distances between a C_{60} centroid and the centroids of its 12 nearest neighbor molecules vary from 10.17 to 14.17 Å (all but one of these distances fall in the narrower range of 10.17−12.57 Å). There are 33 intermolecular F···F contacts of ≤3.15 Å to a given molecule of $C_{60}(CF_3)_{10}$ (all but seven are ≤3.00 Å; see Figure S-7). Figure S-8 shows the only intermolecular $\pi-\pi$ interaction for each molecule, involving inversion-center-related hexagons (hex···hex = 3.59 Å; cf. the 3.35 Å interplanar separation in graphite). The centroid−centroid distance between these two molecules is 10.17 Å, the shortest of all 12 nearest-neighbor centroid−centroid distances, which can be compared with the 9.94 Å distance in solvent-free C_{60} at 110 K[64] and the 9.81 Å distance in $(C_{60})_2$(6,13-diphenylpentacene) at 90 K, in which the two fullerenes are forced into an orientation so that carbon atoms of two nearly parallel eclipsed pentagons make C···C contacts of 3.07−3.49 Å.[61]

(c) The CF_3 Groups. Bond distances and angles within the CF_3 groups are normal. The C−F distances range from 1.312(3) to 1.342(3) Å, but 24 out of the 30 are between 1.325(3) and 1.336(3) Å. The F−C−F angles vary from 106.3(2) to 108.1(2)°. The sp^3-sp^3 C−C distances between the CF_3 carbon atoms and the cage vary from 1.528(3) to 1.565(3) Å (the two longest, involving the most crowded CF_3 groups, are 1.565(3) Å for C1−C61 and 1.552(3) Å for C3−C62; the others are 1.542(3) Å or shorter).

The 10 CF_3 groups are arranged on a ribbon of nine edge-sharing hexagons, so that the two CF_3 groups on each hexagon are either *meta* (*m*) or *para* (*p*) to one another (see Figure 2). The CF_3 groups CF_3-17 and CF_3-40 are the termini of the chain of 10 CF_3 groups. Starting with CF_3-17, the arrangement on the ribbon of hexagons is *p-m-p-p-p-m-p-m-p*. The ribbon includes a *m-p-p-p-m* closed loop of five hexagons that bear the CF_3 groups on C1, C10, C28, C31, C14, and C3. The CF_3 groups are essentially (although not rigorously) confined to one hemisphere of C_{60}. With pentagons as the poles, the equator of C_{60} is defined by a circle that bisects 10 6,6-junctions so that the 20 carbon atoms of these junctions form a zigzag belt around the fullerene. Four CF_3 groups are bonded to four of these 20 atoms (C23, C28, C31, and C40). The other six CF_3 groups are bonded to carbon atoms in one of the hemispheres (C1, C3, C7, C10, C14, and C17). This results in the other hemisphere being virtually undistorted from a hemisphere of unsubstituted C_{60} (see Figure S-9 for more details about the undistorted hemisphere).

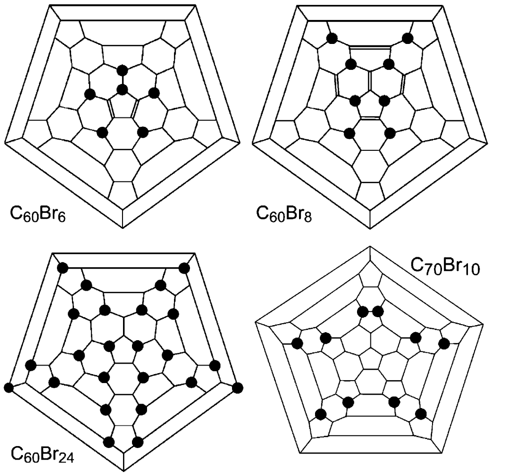

Figure 8. Schlegel diagrams for $C_{60}Br_6$, $C_{60}Br_8$, and $C_{70}Br_{10}$. Only the double bonds within pentagons are shown in the upper two diagrams.

The *m-p-p-p-m* closed loop of hexagons results in CF_3-1 and CF_3-3 being attached to the same pentagon. As far as we are aware, this is the first reported structure of any fullerene derivative with two or more independent substituents larger than bromine atoms (see below) on a given pentagon. There are, however, four bromofullerene structures with pairs of bromine atoms on pentagons, $C_{60}Br_8$ (two pairs),[3,4] $C_{60}Br_{24}$ (all pairs),[4,5] $C_{70}Br_{10}$ (one pair),[65] and $C_{78}Br_{18}$ (disordered solid solution of two different C_{2v} isomers, one with two pairs and one with four pairs),[66] the first three of which are shown as Schlegel diagrams in Figure 8. In the case of $C_{70}Br_{10}$, the pair of bromine atoms on the same pentagon are on adjacent carbon atoms in that pentagon.[65] The compound $C_{60}Br_6$,[3,4] also shown in Figure 8, has a pair of bromine atoms on two contiguous carbon atoms (a hex−hex junction) but does not have two bromine atoms on the same pentagon.

The steric demands of CF_3 groups may, in general, preclude stable structures with two or more CF_3 groups on contiguous carbon atoms. There is little doubt that a CF_3 group is sterically more demanding than a bromine atom, and bromine atoms on contiguous C_{60} cage carbon atoms have only been observed for $C_{60}Br_6$ and then only for one pair of the six bromine atoms. The van der Waals radii of bromine and iodine atoms are 1.85 and 1.98 Å;[67] the effective radii of Br, I, and CF_3 determined by Sternhell et al. from rotational barriers in 6-aryl-1,1,5-trimethylindans are 1.84 ± 0.04, 1.97 ± 0.06, and 2.2 ± 0.1 Å, respectively.[68] Charton's maximum and minimum effective radii for the CF_3 group are 2.74 and 2.11 Å, respectively;[69] the molar volumes at 25 °C of 1,4-$C_6H_4Br_2$, 1,4-$C_6H_4(CF_3)$Br, and 1,4-

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$C_6H_4(CF_3)_2$ are 128, 140, and 155 mL mol^{-1},[70] and the molar volumes at 25 °C of C_6H_5Br, C_6H_5I, and $C_6H_5CF_3$ are 105, 112, and 123 mL mol^{-1}, respectively.[70]

The steric bulk of a CF_3 group is not a sphere centered at the CF_3 carbon atom but a 3-fold-indented cylinder with a height equal to twice the van der Waals radius of a fluorine atom (i.e., 2 × 1.47 Å)[67] centered at the centroid of the three fluorine atoms (F_3) and with a maximum diameter equal to ca. 2.71 Å (1.47 + 1.24 Å, the nominal centroid···F distance). For the CF_3 groups in $C_{60}(CF_3)_{10}$-3, each F_3 centroid lies essentially along the $C_{cage}-CF_3$ vector, 0.48−0.49 Å away from the CF_3 carbon atom (the $C_{cage}-C(F_3)\cdots$centroid angles are all between 170.0(2) and 179.4(2)°). The $C_{cage}\cdots$centroid distances are 2.01−2.06 Å, which coincidentally are about the same as the C−Br distances of 1.990(3)−1.999(3) Å in $C_{60}Br_6$.[3,4] The Br···Br distance between the two bromine atoms on contiguous carbon atoms in $C_{60}Br_6$ is 3.23 Å, which is fully 1 Å shorter than twice the Charton minimum radius of 2.1 Å for CF_3. (For comparison, the distances between *meta* and *para* pairs of bromine atoms in $C_{60}Br_6$ are 4.02−4.05 and 4.40−4.98 Å, respectively, and the distances between *meta* and *para* pairs of F_3 centroids in $C_{60}(CF_3)_{10}$-3 are 4.05−4.36 and 4.46−4.76 Å, respectively.) Although it is also true that the *ortho* bromine atoms in $C_{60}Br_6$ are closer than twice the bromine van der Waals radius, the difference is only ca. 0.5 Å and bromine atoms are more polarizable than fluorine atoms. Therefore, we conclude that fullerene structures with CF_3 groups on adjacent cage carbon atoms will be the exception, not the rule,[23−25] at least on those fullerene surfaces that have curvatures similar to C_{60}. One exception that might be anticipated is 1,6,9,12,15,18-$C_{60}(CF_3)_6$ (i.e., the skew pentagonal pyramidal structure exhibited by $C_{60}Br_6$). Previously published DFT calculations predicted that this isomer is only 14.4 kJ mol^{-1} less stable than the most stable isomer with no remote pairs of CF_3 groups, the asymmetric molecule *p-p-p-m-p*-$C_{60}(CF_3)_6$.[22]

Note that the bromination reactions that produced $C_{60}Br_6$, $C_{60}Br_8$, $C_{60}Br_{24}$, $C_{70}Br_{10}$, and $C_{78}Br_{18}$ were carried out at room temperature.[3,5,34,66] It is unlikely that facile rearrangement of the C−Br bonds can occur rapidly at this temperature, so these structures probably represent kinetically favored structures if not thermodynamically stable ones. Therefore, regardless of the specific mechanism(s) for bromination of C_{60}, C_{70}, and C_{78}, it seems much more likely that it involves, *in general*, a series of *para* additions than *ortho* additions, and the same is almost certainly true for the addition of larger CF_3 radicals to C_{60} and higher fullerenes at high temperature. The fact remains that, with the two exceptions just noted, (fullerene)X_n compounds with bulky X substituents that have been unambiguously structurally characterized by single-crystal X-ray diffraction have bromine atoms,[3,5,65,66] phenyl groups,[12] fluorenyl groups,[13] or CF_3 groups (this work) that are *para* or *meta* to one another on a ribbon or a loop[12] of edge-sharing hexagons.

Significantly, the structure of $C_{60}(CF_3)_{10}$-3 contains substructures along the ribbon that are identical to the proposed *p-m-p* and *p-p-p* structures of C_1-$C_{60}(CF_3)_4$ and the proposed *p-m-p-m-p* and *p-p-p-m-p* structures of C_1-$C_{60}(CF_3)_6$ from our previous work (three of these four structures are shown on the left side of Figure 1; the *p-p-p* structure proposed for C_s-$C_{60}(CF_3)_4$ has CF_3 groups on C10, C14, C28, and C31).[21,22] In fact, there are three *p-m-p*-$(CF_3)_4$ fragments that are part of the $C_{60}(CF_3)_{10}$ structure, not just the one shown in Figure 1. Furthermore, *p-p-p*-$C_{60}(CF_3)_4$ and *p-m-p*-$C_{60}(CF_3)_4$ are substructures of the two proposed C_1 isomers of $C_{60}(CF_3)_6$. These observations, added to the fact that the reaction/purification temperatures used to prepare $C_{60}(CF_3)_{10}$-3 in this work and the two isomers each of $C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$ in our previous work[21,22] were ≥460 °C (high enough, presumably, to cause isomerization to stable arrangements), suggest that many, if not most, fullerene$(CF_3)_n$ compounds prepared at temperatures ≥460 °C will be found to contain variations of linked *p-p-p*-$C_{18}(CF_3)_4$ and *p-m-p*-$C_{18}(CF_3)_4$ fragments, and that structures with *p-m-m*-$C_{18}(CF_3)_4$ or *m-m-m*-$C_{18}(CF_3)_4$ fragments, or with terminal *m*-$C_6(CF_3)_2$ fragments, will be much less common, if they are observed at all. (In the foregoing description, *meta* and *para* refer only to edge-sharing adjacent hexagons that share a single CF_3 group. Therefore, the adjacent hexagons that contain CF_3-1, -3, -10, and -14 are not, by this definition, a *m-m* fragment; a true *m-m* fragment would comprise three CF_3 groups, not four. Furthermore, the same four CF_3 groups do not constitute a *m-m-m* fragment, also by definition, because the central polygon is a pentagon, not a hexagon.) Table 3 contains the results of our previous DFT calculations and those of Clare and Kepert[71] on the relative heats of formation of three stable $C_{60}X_4$ derivatives (X = F, Cl, CH_3, Br, CF_3, and *t*-C_4H_9). Except for X = F, the first three structures shown represent the three most stable structures. As the substituents become larger, the *p-p-p* and *p-m-p* isomers are stabilized relative to the structure with an *ortho* pair of substituents (which happens to be one of the two most stable structures found for $C_{60}F_4$). Note also that the *p-p-m* isomer of $C_{60}(CF_3)_4$ is particularly unstable.

(d) Intramolecular F···F Contacts. Figure 9 shows the 15 intramolecular F···F contacts shorter than 3.00 Å in $C_{60}(CF_3)_{10}$-3, which range from 2.541(3) to 2.992(3) Å (see Table 2; the next shortest intramolecular F···F contacts are 3.34 and 3.56 Å). Interestingly, the three F···F contacts for CF_3-1 and CF_3-3, which are closer than any other pair of CF_3 groups (C61···C62 = 3.608(3) Å), are relatively long at 2.731(3)−2.961(3) Å, and the shortest F···F contact in $C_{60}(CF_3)_{10}$-3 is for a pair of *para* CF_3 groups (F643···F681 = 2.541(3) Å; C64···C68 = 4.331(3) Å). For comparison, consider the structures of the trifluoromethylated alcohols shown in Figure 10 (these two structures will also be discussed in the NMR section below).[72,73] The F···F contacts shown in Figure 10 range from 2.51 to 2.58 Å, and the relevant $F_3C\cdots CF_3$ distances range from 3.37 to 3.71 Å.

(e) The Fullerene Carbon−Carbon Bonds. The 90 C−C bond distances in the C_{60} core of $C_{60}(CF_3)_{10}$-3 are shown in Figure 7 and graphically in Figure S-10 (Supporting Information). The small esd's for these distances allow five distinct regions to be recognized in the hemisphere containing the 10 CF_3 groups instead of the two distinct regions in the relatively undisturbed corannulene portion of the molecule, short 6,6-junctions and long 5,6-junctions (as in one of the most precise structures of the parent C_{60} molecule[59]).

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(70) Densities at 25 °C were taken from www.sigmaaldrich.com.

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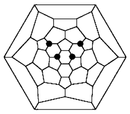
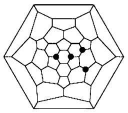
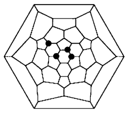
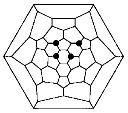
Table 3. DFT Predicted Relative Enthalpies of Formation (kJ mol^{-1}) for Selected $C_{60}X_4$ Derivatives[a]

X	isomer			
	1,6,15,18[b,c]	1,6,11,18[c,d]	1,6,9,18[d]	1,6,15,18[e]
				
	p-*p*-*p*	*p*-*m*-*p*	*p*-*p*-*o*	*p*-*p*-***m***
F	6.9	16.5	0	—
Cl	0	6.9	9.7	—
Br	0	6.7	11.0	—
CH_3	0	4.4	8.5	—
CF_3	0	8.2	36.3	>50
t-C_4H_9	0	22.6	177	—

[a] Data are from refs 71a,b, except for CF_3 values, which are from refs 21 and 22. [b] Observed in the X-ray structure of C_{60}(9-fluorenyl)$_4$ (ref 13). [c] One of two patterns observed in the X-ray structure of $C_{60}(CF_3)_{10}$-3 (this work). [d] One of two patterns observed in the X-ray structures of two electrochemically generated isomers of $C_{60}(CH_2Ph)_4$ (ref 14; an older numbering scheme was used in this reference so that the IUPAC 1,6,11,18-isomer of $C_{60}(CH_2Ph)_4$ was originally reported as 1,4,10,24-$C_{60}(CH_2Ph)_4$, and the IUPAC 1,6,9,18-isomer was originally reported as 1,2,4,15-$C_{60}(CH_2Ph)_4$). [e] No X-ray structure of any $C_{60}X_n$ molecule has been observed with a terminal *m*-C_6X_2 pair of substituents.

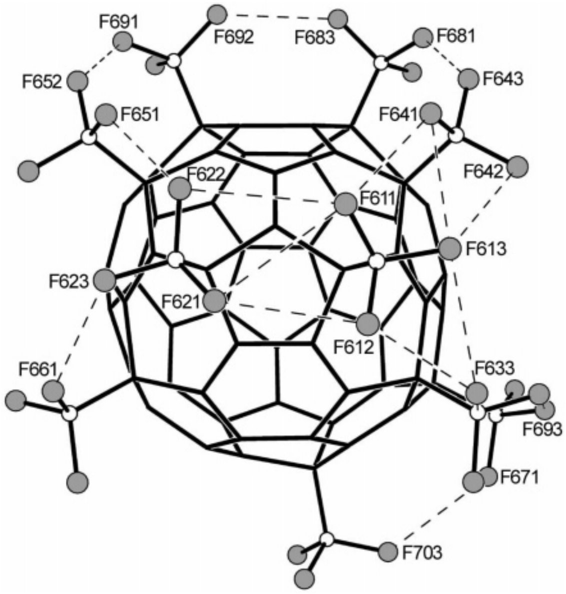


Figure 9. The 15 intramolecular F···F contacts from 2.541 to 2.992 Å in $C_{60}(CF_3)_{10}$-3. Only the fluorine atoms (gray) and the CF_3 carbon atoms (white) are shown as spheres (arbitrary size) for clarity. The individual F···F distances are listed in Table 2.

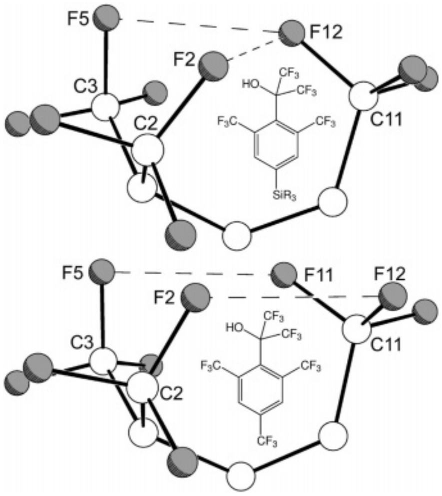


Figure 10. Intramolecular F···F contacts in two trifluoromethylated alcohols from ref 72 (top: F5···F12, 2.58 Å; F2···F12, 2.51 Å; C3···C11, 3.66 Å; C2···C11, 3.40 Å; R = *i*-Pr) and ref 73 (bottom: F5···F11, 2.58 Å; F2···F12, 2.58 Å; C3···C11, 3.71 Å; C2···C11, 3.38 Å). The unlabeled gray spheres are fluorine atoms, and the unlabeled white spheres are carbon atoms.

Fluorine-19 NMR Spectra. The 1D and 2D-COSY spectra for $C_{60}(CF_3)_{10}$-3 are shown in Figures 11 and 12, and the data are listed in Table 4 (also listed are data for $C_{60}(CF_3)_{10}$-1, $C_{60}(CF_3)_{10}$-2, *C*$_1$-$C_{60}(CF_3)_4$,[21] *C*$_1$-$C_{60}(CF_3)_6$,[21] and $C_{70}(CF_3)_{10}$-1). The 2D-COSY spectrum of $C_{60}(CF_3)_{10}$-3, along with the X-ray structure, led to the unambiguous assignment of the 10 CF_3 multiplets. The chemical shifts for the two terminal CF_3 groups are more shielded than those with two nearest-neighbor CF_3 groups. Furthermore, CF_3-1 and CF_3-3 are the most deshielded (multiplets **a** and **b**, which are accidentally isochronous). This is opposite to what was observed for the three types of fluorine atoms in $C_{60}F_{18}$, which have one, two, or three fluorine atom nearest neighbors on contiguous cage carbon atoms.[74]

The J_{FF} values for $C_{60}(CF_3)_{10}$-3 vary from 8.4 to 16 Hz and give rise to quartets for the two terminal CF_3 groups and to multiplets for the other eight CF_3 groups (the uncertainties in the J_{FF} values for $C_{60}(CF_3)_{10}$-3 and the other $C_{60/70}(CF_3)_n$ compounds discussed here are ±0.2 Hz for terminal CF_3 groups and ±1 Hz for other CF_3 groups). Some of these multiplets resemble septets, indicating that the two J_{FF} values for that CF_3 group and its two nearest-neighbor CF_3 groups are equal or nearly equal (e.g., multiplets **c** and **f**). When the two J_{FF} values are unequal, the multiplets take on their true nature as quartets of quartets (e.g., multiplets **g** and **h**). The J_{FF} coupling between CF_3-1 and CF_3-3 cannot be observed because their multiplets are accidentally isochronous. No splittings other than those

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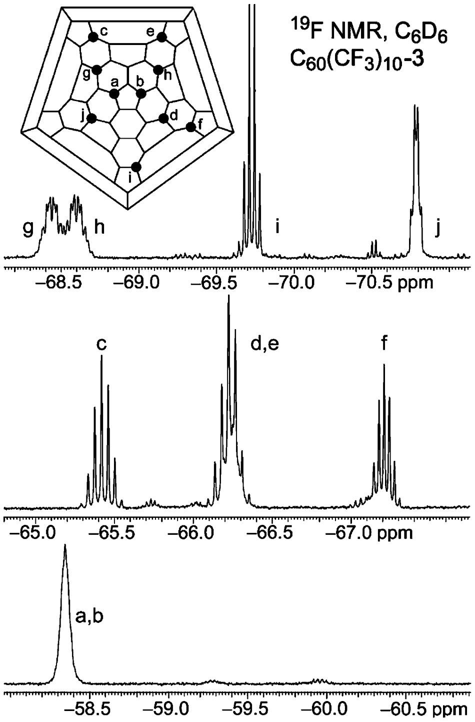

Figure 11. The 376 MHz ^{19}F NMR spectrum of $C_{60}(CF_3)_{10}$-3 (benzene-d_6, 25 °C, C_6F_6 internal standard (δ −164.9)).

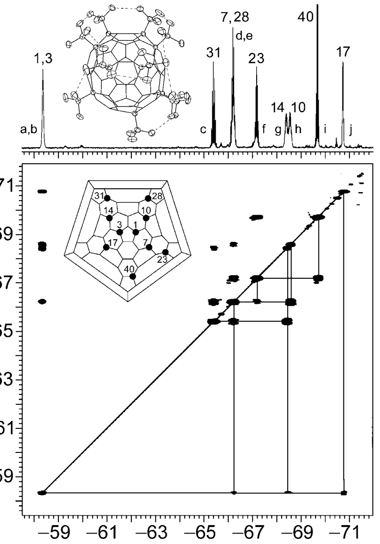

Figure 12. The ^{19}F−^{19}F COSY NMR spectrum of $C_{60}(CF_3)_{10}$-3 (benzene-d_6, 25 °C, C_6F_6 internal standard (δ −164.9)).

involving J_{FF} coupling to nearest-neighbor CF_3 groups were observed for any of the compounds listed in Table 4.

As in our previous work on C_1-$C_{60}(CF_3)_4$ and C_1-$C_{60}(CF_3)_6$,[21] we propose that through-space F−F coupling is the largest contribution to the observed J_{FF} values in $C_{60}(CF_3)_{10}$-3. Some might argue that the term "through-space coupling" is a misnomer since true through-space coupling involving zero orbital overlap (e.g., dipolar coupling) is not observed in liquid NMR spectra. Nevertheless, NMR spectroscopists have used the term for more than 40 years to describe 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.[75] It is now widely accepted that significant J coupling between proximate fluorine nuclei (i.e., $\leq$3.2 Å apart) that are separated by four or more bonds (i.e., $^{>3}J_{FF}$) is *predominantly* mediated through space (as just defined) and not through the network of covalent bonds that separate the fluorine atoms[76−82] (or for metal complexes with C−F bonds, through the network of bonds that includes metal−ligand bonds[83]). Perhaps the most compelling case is the 17 ± 2 Hz $^{398}J_{FF}$ coupling observed[84] 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).[78]

The fluorine atoms on nearest-neighbor CF_3 groups in $C_{60}(CF_3)_{10}$-3 are separated by either six (*meta*) or seven bonds (*para*). In the $^6J_{FF}$ cases, one of the intervening carbon atoms has sp^2 hybridization, while in the $^7J_{FF}$ cases, there are two equivalent pathways containing a different C=C double bond. An estimate can be made of the magnitude, but not the sign, of the through-bond contribution to $^6J_{FF}$ for a pair of CF_3 groups by examining the ^{19}F NMR data for the fluoro alcohols shown in Figure 10.[72,73] In both compounds, hydrogen bonding between the OH group and one of the *ortho* CF_3 groups resulted in slow rotation about the (HO)C−C(arene) bond. The magnitude of the $^6J_{FF}$ coupling between the hydrogen-bonded CF_3 group and the geminal CF_3 groups (two intervening sp^2 carbon atoms), which can only be through bonds, is ≤2 Hz, whereas $^6J_{FF}$ for the other *ortho* CF_3 group and the geminal CF_3 groups is 15 Hz. Therefore, the through-space contribution to the latter $^6J_{FF}$ value is probably between 13 or 17 Hz.

To estimate the likely intramolecular F···F contacts in solution so that we can compare the coupling-constant data with recent theoretical and experimental work on through-space J_{FF} coupling, we will assume that the solid-state conformations of the CF_3 groups other than CF_3-1 and CF_3-3 are maintained to a significant degree in solution. An obvious proviso is that each fluorine atom assumes each of the three positions for its CF_3 group one-third of the time. The conformations of CF_3-1, -3, -7, -17, -23, and -40 are shown in Figure 13 along with other fragments of the $C_{60}(CF_3)_{10}$-3 structure relevant to this discussion. The three fluorine atoms on CF_3-7, CF_3-17, CF_3-23, and CF_3-40 are staggered with respect to the three cage carbon atoms attached to C7, C17, C23, and C40, respectively. The same is true for the four remaining CF_3 groups not shown in Figure 13. The conformations of the unique pair of CF_3 groups on the same pentagon are revealing; CF_3-1 is almost perfectly eclipsed, and CF_3-3 exhibits a conformation between staggered and eclipsed. This is probably due to F···F steric interactions that require one

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Table 4. Fluorine-19 NMR Data[a]

compound	multiplet/−δ/res. nos. of COSY correlations/J_{FF}, Hz/location of CF_3 on C_{60}									
$C_{60}(CF_3)_{10}$-3	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**
−δ	58.3	58.3	65.4	66.8	66.8	67.2	68.4	68.6	69.7[b]	70.8[b]
COSY	**d**,**h**	**g**,**j**	**e**,**g**	**a**,**e**	**c**,**d**	**d**,**i**	**b**,**c**	**a**,**e**	**f**	**b**
J_{FF}	(9)[c,d]	(8.4), (9)[c,d]	16	*e*	(16)[d]	12−13	9, 16	9, 16	12.8	8.4
C_{60} location	C1	C3	C31	C7	C28	C23	C14	C10	C40	C17
$C_{60}(CF_3)_{10}$-2	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**
−δ	64.0	64.9	65.5	66.8	67.0	67.0	67.2	67.9	68.7[b]	70.0[b]
COSY	**d**,**g**	**c**,**g**	**b**,**f**	**a**,**e**	**d**,**i**	**c**,**h**	**a**,**b**	**f**,**j**	**h**	**e**
J_{FF}	12	12−13	13	12	12−13	12−13	12	14−15	14.2	12.6
$C_{60}(CF_3)_{10}$-1	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**
−δ	64.0	65.9	66.2	67.3	67.8	67.2[b]	70.0	70.0[b]	70.4[b]	71.1[b]
COSY	**c**,**d**	**c**,**h**	**a**,**b**	**a**,**e**	**d**,**g**	**j**	**e**,**i**	**b**	**g**	**f**
J_{FF}	12−13	12−13	12	12	15−16	13.7[f]	12−13	12.4	12.7	13.9[f]
C_1-$C_{60}(CF_3)_4$[g]	**a**	**b**	**c**	**d**						
−δ	67.1	67.3	69.7[b]	71.3[b]						
COSY	**b**,**d**	**a**,**c**	**b**	**a**						
J_{FF}	12−13	14	14.2	12.2						
C_1-$C_{60}(CF_3)_6$[g]	**a**	**b**	**c**	**d**	**e**	**f**				
−δ	66.0	67.2	67.4	68.2	69.2[b]	71.5[b]				
COSY	**c**,**f**	**c**,**d**	**a**,**b**	**d**,**e**	**d**	**a**				
J_{FF}	11−12	15	13	14−15	14.0	11.4				
$C_{70}(CF_3)_{10}$-1	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**
−δ	59.2	61.5	62.1	62.2	62.4	62.8	63.4	64.3	67.6[b]	70.7[b]
COSY	**c**,**g**	**e**,**f**	**a**,**h**	**e**,**i**	**b**,**d**	**b**,**g**	**a**,**f**	**c**,**j**	**d**	**h**
J_{FF}	11, 16	13−14	14−15	15−16	13−14	13−14	11, 16	10, 14	15.9	10.3

[a] All data are from this work, unless otherwise noted; benzene-d_6 solutions at 25 °C; C_6F_6 internal standard (δ −164.9). Coupling constants are known to ±0.2 Hz for terminal CF_3 quartets. Resonances for other CF_3 groups are multiplets; J_{FF} values for the ones that are apparent (but not true) septets are ±1 Hz. Data for impurity peaks are not included. [b] Terminal CF_3 group. [c] J_{FF} values in parentheses were not observed in these multiplets but were taken from the COSY-correlated multiplets. [d] The J_{FF} value for CF_3-1/CF_3-3 does not result in observable splittings because their multiplets are accidentally isochronous. [e] The dash denotes that the J_{FF} value could not be determined due to the complexity of the multiplet. [f] These values are the same to within experimental error. [g] Data from ref 21 (toluene-d_8).

of these most-crowded CF_3 groups to be eclipsed if the other is staggered or partially staggered, despite the fact that an eclipsed geometry results in three relatively short F⋯C_{cage} contacts of 2.6−2.7 Å (in contrast, the F⋯C_{cage} contacts for staggered CF_3-7 are ≥2.85 Å). The eclipsed geometry of CF_3-1 results in intramolecular F⋯F distances to CF_3-7 and CF_3-10 that are the longest in the molecule, 2.79−3.00 Å. In contrast, the shortest F⋯F distances that involve partially staggered CF_3-3 are 2.653 Å (F623⋯F661 to CF_3-17; see Figure 13) and 2.581 Å (to CF_3-14).

There are two observations that can be understood only if CF_3-1 and CF_3-3 exhibit the eclipsed conformation ca. 50% of the time. First, despite the different solid-state F⋯F distances to their nearest-neighbor CF_3 groups just noted, the J_{FF} values for CF_3-1/CF_3-10 and CF_3-3/CF_3-14 are both 9 Hz, suggesting equal time-averaged F⋯F distances in solution. Second, despite the same solid-state distances for F623⋯F661 and F671⋯F703 and the same trapezoidal geometry of their respective pairs of C−F bonds shown in Figure 13, the J_{FF} values for CF_3-3/CF_3-17 (8.4 Hz) and CF_3-23/CF_3-40 (12.8 Hz) are significantly different. This suggests that the time-averaged F⋯F distances for CF_3-3/CF_3-17 and CF_3-23/CF_3-40 are significantly different in solution even though they are the same in the solid state. Therefore, the average conformation of CF_3-3 in solution undoubtedly includes a significant contribution of the eclipsed conformation.

Consider the three structure fragments in Figure 13 that show pairs of CF_3 groups on a given hexagon. Each pair exhibits one relatively short F⋯F contact (2.57 Å for the *meta* pair and 2.64 or 2.65 Å for the *para* pairs). All other F⋯F distances between the pairs are ≥3.60 Å, distances for which through-space J_{FF} values are calculated to be ca. 0 Hz.[76,78,79] Since the three fluorine atoms of each CF_3 have the same δ value, pairs of fluorine atoms on neighboring CF_3 groups are in position to experience through-space coupling with one another only one-ninth of the time. Therefore, the through-space component of the observed *time-averaged* J_{FF} values in Table 4 are 9 times smaller than the through-space contribution to J_{FF} for a specific pair of fluorine atoms on a given pair of neighboring CF_3 groups. If we make the simplifying assumption that the values in Table 4 are entirely due to through-space coupling, then the magnitude of the nonzero through-space components of the time-averaged J_{FF} values for CF_3 groups other than CF_3-1 and CF_3-3 varies from 81 ± 9 to 144 ± 9 Hz.

With the above assumptions regarding F⋯F distances in solution in mind, the observed range of individual through-space J_{FF} values of 81−144 Hz is consistent with recent theoretical and experimental results on the magnitude of through-space J_{FF} coupling. Several groups have calculated the F⋯F distance dependence of J_{FF} for the rectangular $(HF)_2$ system having parallel H−F bonds, equal F⋯F and H⋯H distances, and C_{2v} symmetry.[76,78,79] In this orientation, the J_{FF} ranges reported by different groups were 18−32 Hz at 3.0 Å,[76,78,79] 60−80 Hz at 2.7 Å,[76,79] 85−120 Hz at 2.6 Å,[76,79] and 116−170 Hz at 2.5 Å.[76,79] In one study, the J_{FF} value at 2.6 Å changed from 120 to 320 Hz depending on the relative orientation of the two HF molecules.[76] Calculations involving two C−F bonds have given comparable magnitude coupling constants at comparable F⋯F distances,[76,78,79,81,85] and experimental J_{FF} values of 37−99 Hz have been reported for F⋯F distances that are between 2.5 and

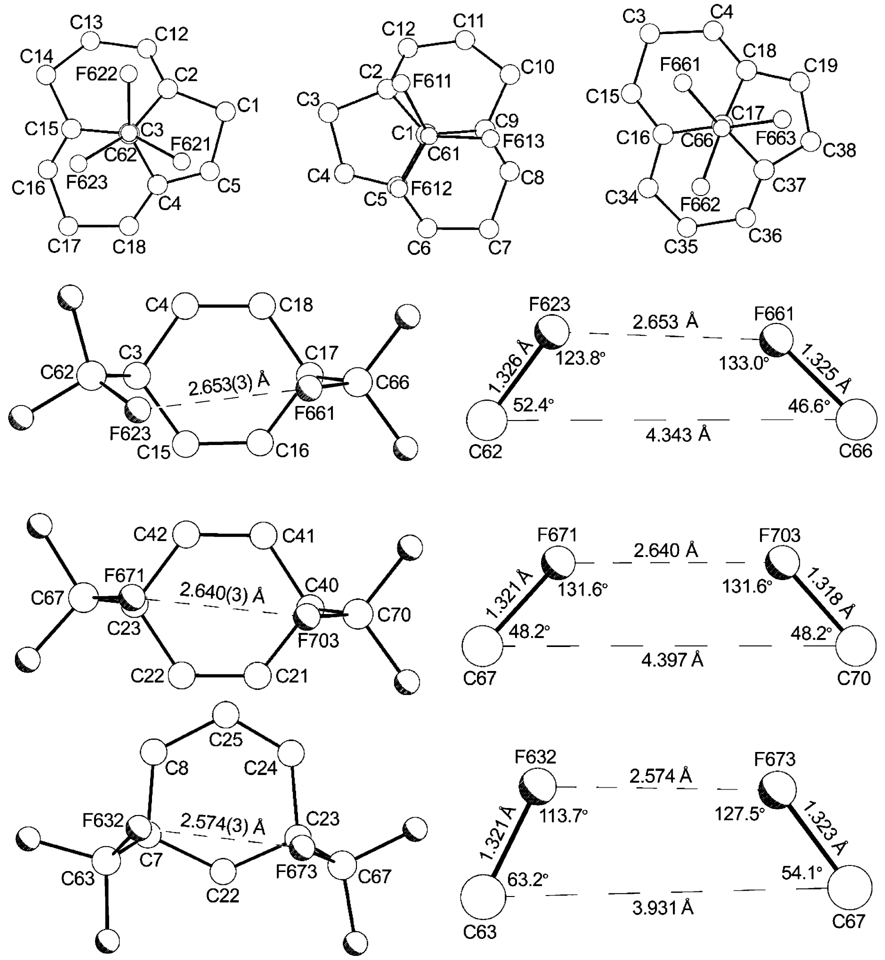

Figure 13. Fragments of the structure of $C_{60}(CF_3)_{10}$-3. In each of the three fragments at the top, the plane of the page represents the plane of the three cage carbon atoms attached to C3, C1, or C17 (from left to right). In the trapezoid drawings, the four atoms shown are coplanar to within 0.15 (top), 0.05 (middle), and 0.09 Å (bottom).

2.7 Å.[80,86] A relevant system involving CF_3 groups is *cis*-Pd-(2,4,6-$C_6H_2(CF_3)_3)_2$(L−L′), in which pairs of *ortho* CF_3 groups on different tris(trifluoromethyl)mesityl ligands are proximate and exhibit time-averaged through-space J_{FF} couplings of 7.5−10 Hz depending on the nature of the unsymmetric chelating L−L′ ligand.[82] Considering that the F•••F distances in the related compound with the symmetric chelate 2,2′-biquinoline are 2.707(7) and 2.750(7) Å,[82] slightly longer than the 2.541(3)−2.653(3) Å distances in $C_{60}(CF_3)_{10}$-3 that do not involve CF_3-1 and CF_3-3, the fact that those coupling constants are slightly smaller than the 12−16 Hz J_{FF} values for $C_{60}(CF_3)_{10}$-3 is not unexpected. Interestingly, one of the C−F•••F−C fragments in *cis*-Pd(2,4,6-$C_6H_2(CF_3)_3)_2$(2,2′-biquinoline) is a trapezoid very similar to those in Figure 13. As far as we are aware, no one has yet calculated J_{FF} values for a trapezoidal arrangement of two C−F bonds. It will be interesting to see what the predicted values of J_{FF} will be for this geometry at F•••F distances between 2.55 and 2.75 Å.

The 1D ^{19}F NMR spectra of $C_{60}(CF_3)_{10}$-1 and $C_{60}(CF_3)_{10}$-2 are compared with the spectrum of $C_{60}(CF_3)_{10}$-3 in Figure 14 (δ and J_{FF} values are listed in Table 4; 2D NMR spectra are available in Supporting Information). Both compounds clearly have C_1 symmetry. The similarity in all respects to the 1D and 2D spectra of $C_{60}(CF_3)_{10}$-3 strongly suggests that these compounds too have pairs of CF_3 groups in *meta* and/or *para* positions on the fullerene hexagons. In the case of $C_{60}(CF_3)_{10}$-2, the data are consistent with a ribbon of nine edge-sharing

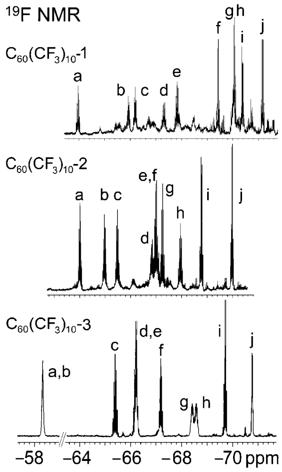

Figure 14. Fluorine-19 NMR spectra of the three isomers of $C_{60}(CF_3)_{10}$ (376.5 MHz, benzene-d_6, 25 °C, C_6F_6 internal standard (δ −164.9)). Multiplets a and b in the spectrum of $C_{60}(CF_3)_{10}$-3 are accidentally isochronous.

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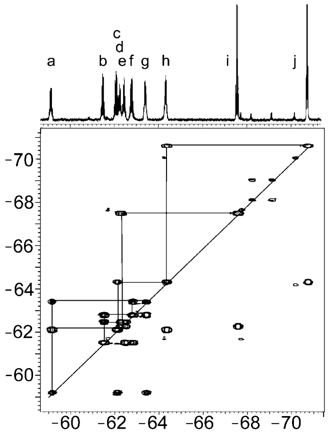

Figure 15. 1D- and 2D-COSY ^{19}F NMR spectra of $C_{70}(CF_3)_{10}$-1 (376.5 MHz, benzene-d_6, 25 °C, C_6F_6 internal standard (δ −164.9)).

hexagons (there are two terminal CF_3 groups that give rise to quartets **i** and **j**). In the case of $C_{60}(CF_3)_{10}$-1, the data are consistent with a ribbon of eight edge-sharing hexagons and an isolated *para*-$(CF_3)_2$ hexagon (there are four terminal CF_3 groups that give rise to quartets **f**, **h**, **i**, and **j**, and quartets **f** and **j** are correlated only with one another). In neither case is there evidence for a pair of CF_3 groups occupying the same pentagon, as in $C_{60}(CF_3)_{10}$-3.

The 1D and 2D spectra for $C_{70}(CF_3)_{10}$-1 are shown in Figure 15, and the data are listed in Table 4. The data are entirely consistent with a ribbon of nine hexagons but without a $C_5(CF_3)_2$ pentagon (i.e., a ribbon probably similar to that for $C_{60}(CF_3)_{10}$-2). It is surprising that $C_{70}(CF_3)_{10}$-1 is asymmetric. The compound $C_{70}Br_{10}$ is known to have C_s symmetry, with bromine atoms occupying the relatively flat equator of C_{70} (see Figure 8).[65] That structure, predicted to be the most stable for this molecule,[87] has two bromine atoms on adjacent cage carbon atoms, so it is not surprising that $C_{70}(CF_3)_{10}$-1 does not adopt this structure. What is surprising is that the second most stable structure predicted for $C_{70}Br_{10}$ has C_2 symmetry with a sterically unencumbered all-*para* ribbon on nine edge-sharing hexagons. The unambiguous asymmetry of $C_{70}(CF_3)_{10}$-1 and the fact that it was prepared at 470 °C suggests that there may be C_1 isomers of some $C_{70}X_{10}$ compounds that are especially stable and that until now have not been considered by fullerene theorists. Note that C_s-$C_{70}Br_{10}$ was prepared at room temperature.[65] Therefore, it is possible that it represents a kinetic product and not the most stable isomer.

The NMR data for C_1-$C_{60}(CF_3)_4$ and C_1-$C_{60}(CF_3)_6$ are also listed in Table 4.[21] The similarity of their δ and J_{FF} values to those of $C_{60}(CF_3)_{10}$-3 is striking. Neither compound has a closed-loop of edge-sharing hexagons. Nevertheless, both compounds have different J_{FF} values for the two terminal CF_3 group quartets (12.2 and 14.2 Hz for C_1-$C_{60}(CF_3)_4$, 11.4 and 14.0 Hz for C_1-$C_{60}(CF_3)_6$), as does $C_{60}(CF_3)_{10}$-2. Furthermore, all of the single isomer fractions of $C_{60}(CF_3)_n$ and $C_{70}(CF_3)_n$ isolated by Taylor and co-workers have δ and J_{FF} values in chloroform-*d* solution in the same ranges (for $C_{60}(CF_3)_n$, $-58.0 \geq \delta \geq -69.9$, 11.3 Hz $\leq J_{FF} \leq$ 14.5 Hz; for $C_{70}(CF_3)_n$, $-60.9 \geq \delta \geq -70.4$, 9.1 Hz $\leq J_{FF} \leq$ 17.6 Hz[23−25]) as structurally characterized $C_{60}(CF_3)_{10}$-3, the DFT-predicted structures of C_1-$C_{60}(CF_3)_4$ and C_1-$C_{60}(CF_3)_6$, and the other compounds in Table 4. In their most recent paper,[25] these authors stated that "in general [1,4 addition of CF_3 groups] does not account for the large coupling constant variations", a conclusion that is disproven by the structure and NMR spectrum of $C_{60}(CF_3)_{10}$-3. There can now be little doubt that most $C_{60,70}(CF_3)_n$ compounds prepared to date have structures based on a ribbon of edge-sharing hexagons with *p*-*m*-*p* and/or *p*-*p*-*p* segments, some of which may also have isolated *para*-$C_6(CF_3)_2$ hexagons. The one exception may be an isomer of $C_{60}(CF_3)_6$ with the skew pentagonal pyramid structure of $C_{60}Br_6$ (see Figure 8).

Conclusions

A significant improvement in the selectivity of fullerene trifluoromethylation reactions was achieved by using a stream of CF_3I flowing through a hot tube containing either C_{60} or C_{70}. The predominant products in the C_{60} reaction, an estimated 40+ mol % of the cold-zone condensate, were three isomers of $C_{60}(CF_3)_{10}$ that were purified by two- or three-stage HPLC. The selectivity of the C_{70} reaction was even higher. The predominant product was a single $C_{70}(CF_3)_{10}$ isomer representing ca. >40 mol % of the cold-zone condensate (27% overall yield based on converted C_{70}). One of the $C_{60}(CF_3)_{10}$ isomers was purified to 95+% purity, and its C_1-symmetric structure was determined to be 1,3,7,10,14,17,23,28,31,40-$C_{60}(CF_3)_{10}$ by X-ray crystallography. The CF_3 groups are either *meta* or *para* to one another on a *p*-*m*-*p*-*p*-*p*-*m*-*p*-*m*-*p* ribbon of edge-sharing $C_6(CF_3)_2$ hexagons. With this structure in hand, the ^{19}F NMR data, especially the observed, variable $^{6,7}J_{FF}$ values of 8.4(2)−16(1) Hz, clearly demonstrate that through-space coupling via direct overlap of fluorine atom orbitals is the predominant contribution to J_{FF} values in these and probably most other fullerene$(CF_3)_n$ compounds. Previous structural assignments of $C_{60,70}(CF_3)_n$ derivatives that were based on predominantly through-bond coupling[23−25] should be reconsidered.

Acknowledgment. This work was supported by the U.S. NSF (CHE-9905482), the Volkswagen Foundation (I-77/855), the Russian Foundation for Basic Research (Project No. 05-03-33051-a), and an AvH Foundation Freidrich Bessel Award (to O.V.B.). We thank Prof. D. W. Grainger for the use of his HPLC equipment, and Prof. M. M. Kappes for his generous support.

Supporting Information Available: Complete ref 80 and additional figures and tables of X-ray parameters and results for $C_{60}(CF_3)_{10}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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