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Isolation of $C_{60}(CF_3)_n$ ($n = 2, 4, 6, 8, 10$) with high compositional purity

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Abstract

The high temperature reaction of C_{60} with silver(I) trifluoroacetate followed by 500 °C sublimation and subsequent HPLC purification has led to the isolation of the five trifluoromethyl[60]fullerenes $C_{60}(CF_3)_n$ ($n = 2, 4, 6, 8, 10$). Four of them have >90% compositional purity. Two of the compounds, $C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$, were obtained as C_1-symmetry isomers with >90% isomeric purity, and a sample of $C_{60}(CF_3)_2$ also contained ca. 15–20% of a C_s-symmetry isomer of $C_{60}(CF_3)_4$. The new compounds were characterized by IR and EI mass spectrometry (all five compounds), ^{19}F NMR spectroscopy ($C_{60}(CF_3)_2$, $C_{60}(CF_3)_4$, and $C_{60}(CF_3)_6$), and 2D COSY ^{19}F NMR spectroscopy ($C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$). Calculations at the AM1 and DFT levels of theory have led to the prediction of the most likely structures for $C_{60}(CF_3)_2$, C_1-$C_{60}(CF_3)_4$, C_s-$C_{60}(CF_3)_4$, and the two most likely structures of C_1-$C_{60}(CF_3)_6$.

Keywords: Fullerene; Trifluoromethyl; ^{19}F NMR; Mass spectrometry

There are very few reports of fullerenes with perfluoroalkyl substituents [1–6].[1] As with fluorofullerenes (FFs) [7], perfluoroalkylfullerenes (PFAFs) will have significantly enhanced electron affinities than the parent fullerene, an important property for their possible use in photovoltaic and other electronic devices. We recently reported the isolation and spectroscopic properties of a single isomer of $C_{60}(CF_3)_2$ [4] and three isomers of $C_{60}F_{17}CF_3$ [5] (the X-ray structure of $C_{60}F_{17}CF_3$, the only one of a perfluoroalkyl-containing fullerene, was also determined [5]). Both compounds were present in a complex mixture of products from the fluorination reactions of C_{60} with AgF or K_2PtF_6. No PFAF with high compositional purity[2] has been made by a deliberate attempt to perfluoroalkylate fullerenes with a perfluoroalkyl reagent. Three such attempts only resulted in complex mixtures containing $C_{60}(CF_3)_n$ compositions with $n = 2$–16 [1–3]. In addition, we previously reported that treating C_{60} with AgTFA at 300 °C resulted in a mixture of $C_{60}(CF_3)_n$ compositions with $n = 2$–22 ($TFA^- = CF_3COO^-$) [4]. In none of these four studies was the separation of individual $C_{60}(CF_3)_n$ components achieved. After this work was completed, a paper appeared reporting the isolation, characterization, and proposed structures of several $C_{60}(CF_3)_n$ derivatives [8], which were prepared using our previously reported AgTFA technique [4]. Several of the authors' conclusions concerning the likely structures of $C_{60}(CF_3)_n$ derivatives are not supported by the results reported herein.

We now report that the high temperature reaction of C_{60} with AgTFA followed by sublimation and HPLC purification leads to the isolation of the five PFAFs $C_{60}(CF_3)_n$ ($n = 2, 4, 6, 8, 10$). Four of them have >90% compositional purity. Two of the compounds, $C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$, were obtained with high isomeric purity (see footnote 2), and a sample of $C_{60}(CF_3)_2$ also contained ca. 15–20% of another isomer of $C_{60}(CF_3)_4$.

The 15 eV EI mass spectra are shown in Fig. 1 for $C_{60}(CF_3)_2$, $C_{60}(CF_3)_4$, and $C_{60}(CF_3)_6$. Similar spectra (not shown) were recorded for $C_{60}(CF_3)_8$ and $C_{60}(CF_3)_{10}$. Fluorine-19 NMR spectra are shown in Fig. 2 for $C_{60}(CF_3)_2$ and

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[1] We define PFAFs as those fullerenes with perfluoroalkyl substituents directly bonded to fullerene carbon atoms.

[2] *Compositional purity* is the mol% of molecules with a specific molecular formula in a given sample. *Isomeric purity* is the mol% of a specific isomer in a sample having a specific molecular formula.

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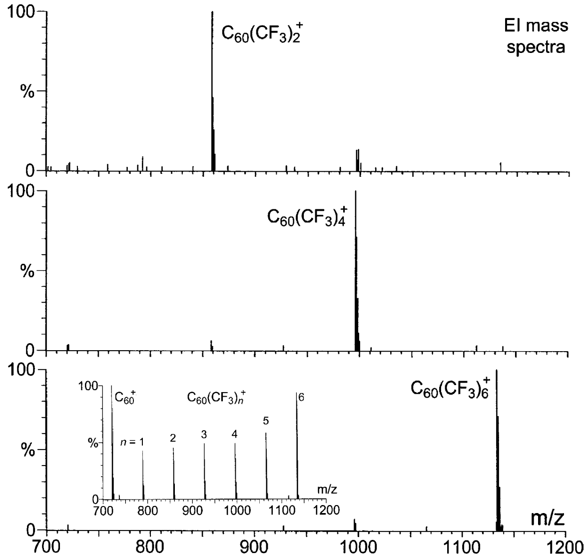

Fig. 1. Positive-ion EI mass spectra of $C_{60}(CF_3)_2$, $C_{60}(CF_3)_4$, and $C_{60}(CF_3)_6$. The ionization energy was 15 eV to suppress fragmentation. The inset is the 70 eV spectrum of the same sample of $C_{60}(CF_3)_6$.

Fig. 3 for $C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$. Two-dimensional ^{19}F NMR spectra of $C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$ are shown in Fig. 4. The IR spectra of the five compounds were similar and exhibited two strong ν(CF) bands at 1258 ± 2 and 1191 ± 2 cm^{-1}. These bands are characteristic of CF_3 groups [9].

Previously reported mass spectra of $C_{60}(CF_3)_n$ mixtures exhibited extensive fragmentation (i.e. successive CF_3 loss), as evidenced by a broad distribution of peaks for even and odd n values [1–4]. The 70 eV EI mass spectrum of $C_{60}(CF_3)_6$ (Fig. 1) illustrates this fragmentation. However, the 15 eV EI spectra are virtually free of ions due to parent-ion fragmentation. Therefore, use of the lower ionization energy allowed the compositions of the samples to be estimated: ca. 80 mol% for $C_{60}(CF_3)_2$ (with ca. 15% $C_{60}(CF_3)_4$) and >90 mol% for $C_{60}(CF_3)_n$ ($n = 4, 6, 8, 10$).

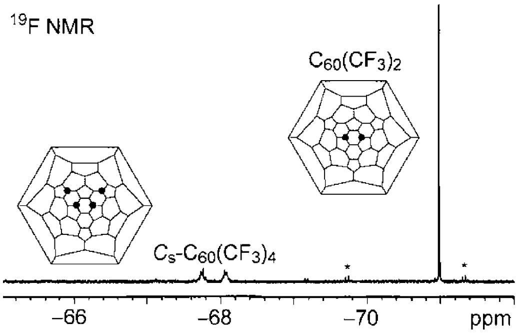

Fig. 2. 376.5 MHz ^{19}F NMR spectrum of $C_{60}(CF_3)_2$ in toluene-d_8 (δ 0 = $CFCl_3$ int. std.). The two most intense multiplets for C_1-$C_{60}(CF_3)_4$ are marked with asterisks. Two other multiplets near δ −68 are assigned to C_s-$C_{60}(CF_3)_4$. Schlegel diagrams show the proposed structures for 1,4-$C_{60}(CF_3)_2$ and C_s-$C_{60}(CF_3)_4$ (each dot represents a CF_3 group). The solid isolated from an aliquot of this sample was used to collect the EI mass spectrum labeled "$C_{60}(CF_3)_2$" in Fig. 1.

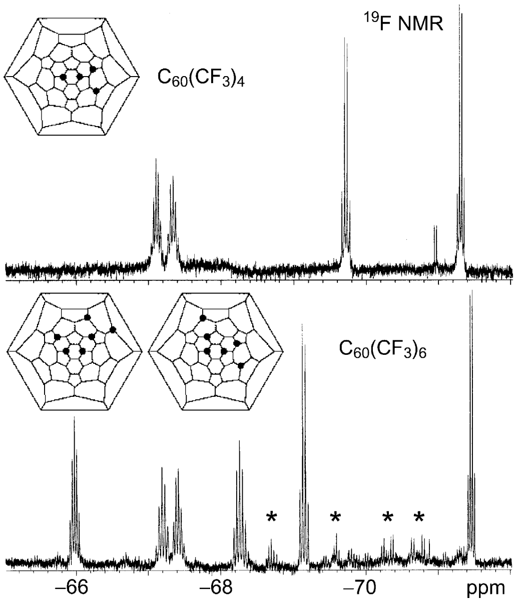

Fig. 3. 376.5 MHz ^{19}F NMR spectra of $C_{60}(CF_3)_n$ ($n = 4, 6$; toluene-d_8; δ 0 = $CFCl_3$ int. std.). The integrated intensities of the four and six main multiplets in the upper and lower spectra, respectively, are equal to within ±5%. Two small impurity peaks are at ca. δ −71 in the upper spectrum. The multiplets marked with asterisks are assigned to another isomer of $C_{60}(CF_3)_6$. Schlegel diagrams show the most likely structures of C_1-$C_{60}(CF_3)_4$ and C_1-$C_{60}(CF_3)_6$ (each dot represents a CF_3 group). Solids isolated from aliquots of these samples were used to collect the corresponding EI mass spectra in Fig. 1.

The compositional purity of $C_{60}(CF_3)_2$, $C_{60}(CF_3)_4$, and $C_{60}(CF_3)_6$ is also evident in their ^{19}F NMR spectra. The spectrum of $C_{60}(CF_3)_2$ consists of a single sharp resonance at δ −71.0, several weak resonances due to unidentified impurities, and two multiplets near δ −68. The single resonance suggests that the sample of $C_{60}(CF_3)_2$ consists of a single isomer. However, it is not possible to identify if the sample of $C_{60}(CF_3)_2$ we have isolated is the same as the $C_{60}(CF_3)_2$ isomer recently reported by Taylor and co-workers (δ −69.3) [8], because the NMR solvent used in that study was not specified. The spectrum of $C_{60}(CF_3)_4$ in Fig. 3 consists of four equal-intensity multiplets (two are 1:3:3:1 quartets) with two weak peaks near δ −71 assigned to one or more impurities. The spectrum of $C_{60}(CF_3)_6$ consists of six equal-intensity quartets or multiplets with a much less intense set of resonances that might be due to a few percent of $C_{60}(CF_3)_4$ as well as a few percent of a second isomer of $C_{60}(CF_3)_6$. The observed J_{FF} values, ca. 12–15 Hz, are consistent with through-space coupling observed in alcohols with multiple trifluoromethyl groups in close proximity [10].

The 2D COSY ^{19}F NMR spectra of $C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$, displayed in Fig. 4, show that the four and six main multiplets, respectively, are pair-wise correlated and thus belong to the same molecule. Therefore, both $C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$ are C_1-symmetry isomers each containing a "chain" of CF_3 groups that are closely spaced. Calculations at the AM1 and DFT levels of theory were used to predict the

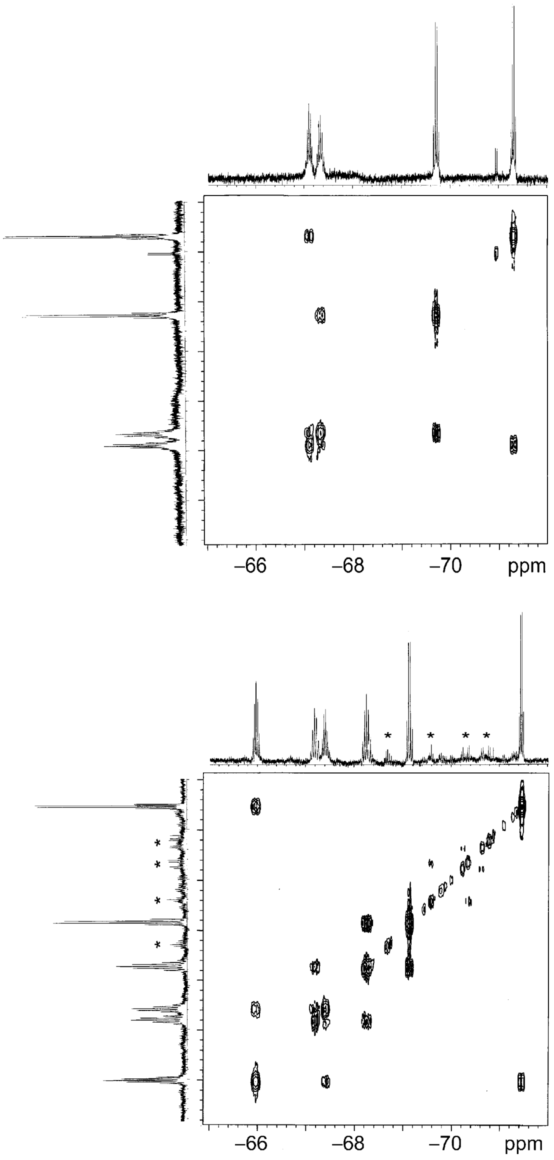

Fig. 4. 376.5 MHz ^{19}F COSY NMR spectra of C$_1$-$C_{60}(CF_3)_4$ (top) and C$_1$-$C_{60}(CF_3)_6$ (bottom) (toluene-d$_8$; δ 0 = $CFCl_3$). The integrated intensities of the four and six main multiplets in the 1D spectra are equal to within ±5%. Two small impurity peaks are at ca. δ −71 in the spectrum of C$_1$-$C_{60}(CF_3)_4$. The multiplets marked with asterisks in the spectrum of C$_1$-$C_{60}(CF_3)_6$ are assigned to another isomer of $C_{60}(CF_3)_6$.

most likely structures [11].[3] Similar calculations recently reported by Clare and Kepert for $C_{60}X_n$ (X = H, F, Cl, Br, alkyl) show that 1,4 additions to C_6 rings become energetically favored for bulky groups over 1,2 additions to a C=C bond shared by two hexagonal faces (for $n = 4$, successive 1,4 additions can lead to some 1,3 substituent dispositions) [12]. Our results predict that 1,4-$C_{60}(CF_3)_2$ is more stable than other isomers by at least 35 kJ mol^{-1}. Thus, the recently proposed [8] structure 1,2-$C_{60}(CF_3)_2$ is probably incorrect. Our results also predict that the C$_s$- and C$_1$-$C_{60}(CF_3)_4$ isomers shown in Figs. 2 and 3, respectively, are close in energy and are more stable by at least 30 kJ mol^{-1} than other isomers (these were also predicted to be the most stable isomers for $C_{60}X_4$ (X = Cl, Br, CH$_3$, *t*-Bu [12]). These two addition patterns have been proven for the C$_1$ isomer of $C_{60}(Bu)_4$ [13] and for C$_s$-C_{60}(9-fluorenyl)$_4$ [14]. The predicted stability of C$_s$-$C_{60}(CF_3)_4$ supports the assignment of the two broad multiplets in Fig. 2 to this isomer. Although C$_1$-$C_{60}(CF_3)_4$ has been isolated with >90% compositional and isomeric purity, the similar HPLC retention times of C$_s$-$C_{60}(CF_3)_4$ and 1,4-$C_{60}(CF_3)_2$ have so far prevented their separation.

Taylor and co-workers recently concluded that the various isomers of $C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$ they isolated must contain contiguous chains of CF$_3$ groups (i.e. chains of 1,2 additions) [8]. In the case of $C_{60}(CF_3)_4$, our calculations show that all possible contiguous-chain isomers are *at least* 145 kJ mol^{-1} less stable than the C$_s$-$C_{60}(CF_3)_4$ isomer shown in Fig. 2. Specifically, their proposed isomer **C** is 185 kJ mol^{-1} less stable than our proposed structure for C$_s$-$C_{60}(CF_3)_4$.

A large number of possible structures for $C_{60}(CF_3)_6$ were computationally investigated, not only those based on additions to C$_1$- or C$_s$-$C_{60}(CF_3)_4$. The two C$_1$-$C_{60}(CF_3)_6$ structures shown in Fig. 3 were found to lie lower in energy by at least 25 kJ mol^{-1} than other C$_1$-symmetry isomers of this composition. The commonly observed structure of $C_{60}X_6$ derivatives is the C$_s$ skew pentagonal pyramid [15],[4] but this $C_{60}(CF_3)_6$ structure was ca. 10 kJ mol^{-1} less stable than the C$_1$ structures. To our knowledge, $C_{60}(CF_3)_6$ is the first $C_{60}X_6$ derivative known to possess C$_1$ symmetry. The two C$_1$ isomers were previously predicted to be the most stable for C_{60}(*t*-Bu)$_6$ [12].

In ongoing work, we plan to continue characterizing the $C_{60}(CF_3)_n$ compounds we have isolated (including single-crystal X-ray diffraction experiments) and to isolate and characterize $C_{60}(CF_3)_n$ compounds with even n values between 12 and 22.

Experimental section

A mixture of C_{60} (99.9%; Term USA; 85.4 mg, 0.118 mmol) and AgTFA (Aldrich, TFA$^-$ = CF$_3$COO$^-$; 114 mg, 0.523 mmol) was ground together, placed in a glass tube which was placed in a sealed copper reactor, and heated to 280 °C for 6 h. The crude product (137.4 mg) was sublimed under dynamic vacuum at 380 °C for 6 h (1.7 mg was collected) and then at 500 °C for 33 h (50 mg was collected). A 28 mg portion of the 50 mg was dissolved in toluene and chromatographed with toluene as the eluent (HP Series 1050 HPLC; 250 mm × 10 mm Cosmosil Buckyprep column;

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[3] Geometry optimizations for a large set of possible isomers consistent with the NMR data were carried out at the AM1 level of theory. The most stable structures were reoptimized by DFT using the program PRIRODA, the TZ2P basis set and the PBE exchange-correlation function.

[4] (a) $C_{60}Br_6$, (b) $C_{60}Cl_6$.

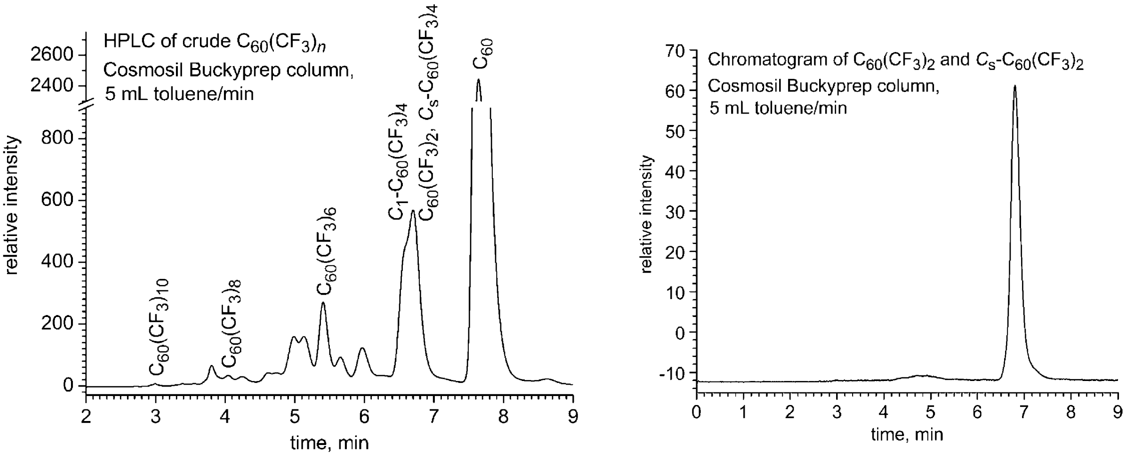

Fig. 5. HPLC traces showing the purification of $C_{60}(CF_3)_2$. This sample of $C_{60}(CF_3)_2$ still contained ca. 15% C_1-$C_{60}(CF_3)_4$.

5 ml/min flow rate). HPLC traces such as those shown in Fig. 5 were obtained. Several peaks in the chromatograph on the left are labeled with $C_{60}(CF_3)_n$ formulas determined by subsequent NMR and mass spectrometry analyses. Some isolated fractions were repurified by HPLC one, two, or three times to yield >90% compositionally pure C_1-$C_{60}(CF_3)_4$ (three times), $C_{60}(CF_3)_6$ (one time), $C_{60}(CF_3)_8$ (two times), and $C_{60}(CF_3)_{10}$ (one time). A fraction containing ca. 80 mol% $C_{60}(CF_3)_2$ and ca. 15 mol% C_s-$C_{60}(CF_3)_4$ could not be further separated. The HPLC retention times (min) were: $C_{60}(CF_3)_{10}$, 3.00; $C_{60}(CF_3)_8$, 4.05; $C_{60}(CF_3)_6$, 5.40; C_1-$C_{60}(CF_3)_4$, 6.65; $C_{60}(CF_3)_2$ and C_s-$C_{60}(CF_3)_4$, 6.90.

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