

DISSERTATION

FLUORINE-CONTAINING FULLERENES AND ENDOMETALLOFULLERENES:
SYNTHESIS, STRUCTURE, AND SPECTROSCOPIC CHARACTERIZATION

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ABSTRACT

FLUORINE-CONTAINING FULLERENES AND ENDOMETALLOFULLERENES: SYNTHESIS, STRUCTURE, AND SPECTROSCOPIC CHARACTERIZATION

Many new members of a relatively new class of exohedral fullerene derivatives with fluorine-containing electron-withdrawing groups have been prepared and studied by spectroscopic methods and X-ray crystallography. The fluorination and/or perfluoroalkylation reactions were performed with C_{60} , C_{70} , the higher hollow fullerenes C_{60+m} ($m = 14, 16, 18, 20$, and 22), the endohedral metallofullerene $Sc_3N@C_{80}-I_h(7)$, and the azafullerene dimer $(C_{59}N)_2$. Several efficient synthetic methods have been developed for perfluoroalkylation, which involved high-temperature reactions with $AgCF_3CO_2$ and with thermally or photochemically activated reactions with R_FI reagents ($R_F = CF_3$, C_2F_5 , $n-C_3F_7$, $i-C_3F_7$, $n-C_4F_9$, and $n-C_6F_{13}$). Structural studies of the $C_{60}(R_F)_n$ and $C_{70}(R_F)_n$ products demonstrated that variation of the size and structure of the R_F radical led to the formation of derivatives with unprecedented addition patterns and hence unprecedented properties. Many of these derivatives were shown to have superior electron-accepting properties. Trifluoromethylation of a sample of insoluble hollow higher fullerenes resulted in the structural characterization of several new dodecakis(trifluoromethyl)fullerene compounds, and this led to the first experimental observation of

fullerenes $C_{74}-D_{3h}$ and $C_{78}-D_{3h}(5)$. In the case of trifluoromethylation of $(C_{59}N)_2$, a strong effect of the heteroatom on the addition patterns of the products was discovered. The first X-ray crystal structure of a single regioisomer of $C_{59}N(CF_3)_5$, as well as spectroscopic studies of $C_{59}N(CF_3)_{7,9,11}$, revealed unexpected addition patterns which resemble that of $C_s-C_{60}X_6$ derivatives. The isolation and characterization of seventeen $Sc_3N@C_{80-I_h}(CF_3)_n$ (even $n = 2-16$) compounds, including the X-ray structures of $Sc_3N@C_{80-I_h(7)}(CF_3)_{10}$, $Sc_3N@C_{80-I_h(7)}(CF_3)_{12}$, $Sc_3N@C_{80-I_h(7)}(CF_3)_{14}$, and $Sc_3N@C_{80-I_h(7)}(CF_3)_{16}$, have demonstrated for the first time a strong mutual effect of (i) the presence of the Sc_3N cluster on the addition pattern and (ii) the addition pattern on the position of and structure of the Sc_3N cluster.

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CHAPTER 1. FLUORINATION OF C₆₀ WITH A_xMF_y FLUORINATING AGENTS (A = ALKALI METAL; M = 3d METAL)

Introduction

Synthesis and study of new fluorinated fullerenes (FFs) attract a lot of attention due to their potential practical applications in energy storage, low-dielectric materials, bioengineering, medicine, and components of LED devices.¹⁻⁶ However, a selective synthesis that leads to the preparation at least 85+ mol% of a single isomer is known only for three compounds: C₆₀F₁₈, C₆₀F₃₆, and C₆₀F₄₈.⁷⁻⁹ Thus, the development of synthetic methods for the selective preparation of FFs remains a largely unsolved problem. Metal fluorides, which have been used as fluorinating agents (FAs) in fullerene chemistry since 1995, have several advantages for the preparation of FFs.¹⁰ In contrast to direct fluorination or the use of XeF₂ (or KrF₂), metal fluorides are easy and safer to handle.¹¹ In addition, a degree of fluorination (i.e., the value of n in the C₆₀F _{n} products) can be controlled by varying the oxidation state of the metal or by adding alkali metal fluorides, (i.e., by using a mechanical mixture of AF and MF _{x} or a ternary salt A _{x} MF _{y} (A = alkali metal; M = 3d metal)). In general, it was found that use of ternary alkali-metal fluorides can lead to formation of C₆₀F _{n} with lower range of n values compared to the corresponding binary metal fluorides.¹² Previously, it was demonstrated that, for example, the use of the ternary metal fluoride KMnF₄ led to the formation and isolation of C₆₀F₈.¹² The main goal of the present work was the synthesis, isolation, and characterization of C₆₀F _{n} compounds with $n < 18$ which are usually obtained with a very

small yield and therefore, their properties, such as relative thermal stabilities, ionization energies, electron affinities or oxidation and reduction potentials are not very well studied to date. The compounds with $n < 18$ can be more useful synthons for further selective substitution reactions than the derivatives with $n \geq 18$ due to a greater number of sterically accessible C–F bonds. For example, it was previously shown that $C_{60}F_{18}$ can be selectively trisubstituted at the three least-sterically hindered C–F bonds.¹³

Fluorination reactions of C_{60} under a variety of the experimental conditions, selective synthesis of the composition $C_{60}F_{44}$, an effective FA for the preparation of $C_{60}F_n$ with $n < 18$, and a non-chromatographic purification of $C_{60}F_{20}$, which allowed for the confirmation of its unique Saturn-like molecular structure by X-ray crystallography, will be discussed in this chapter. Most of ternary salts (e.g., $KCrF_6$, $RbCrF_6$, $CsCrF_6$, $LiCoF_4$, K_2NiF_6 , $LiMnF_4$, $CsMnF_4$ or Cs_2CuF_6) in this work were used for fullerene fluorination for the first time. This work has already been published.¹⁴

1.1. Experimental Section

1.1.1. Reagents and Solvents. C_{60} (99.5%, TERM USA), hexafluorobenzene (Sigma-Aldrich), and heptane or toluene for HPLC analysis (Sigma-Aldrich) were used as received. All metal fluorides were prepared using known or modified procedures (described below) by Dr. Z. Mazej (Jožef Stefan Institute, Ljubljana, Slovenia) and were handled in an inert-atmosphere glovebox.

$KCrF_6$ and $CsCrF_6$. These compounds were prepared by photochemical reactions of KF/CrF_3 or CsF/CrF_3 mixtures with elemental F_2 in anhydrous HF at ambient temperature.¹⁵

LiMnF₄, KMnF₄, and CsMnF₄. Anhydrous HF was condensed into an FEP tube containing a mixture of AF (A = Li, K, Cs) and MnF₂, and F₂ was slowly added at 25 °C until the conversion of MnF₂ to MnF₃ was complete. In each case, all volatiles were removed under vacuum leaving a homogeneous equimolar mixture of the solids MnF₃ and LiF, KHF₂ or CsF·*n*HF, respectively, which were then heated under vacuum in a nickel or platinum boat at 490–500 °C for several hours.

Cs₂CuF₆. This compound was prepared by static fluorination of a 2:1 mol:mol CsCl:CuCl mixture with elemental F₂ (45 bar) in a 100 mL nickel autoclave heated to 350 °C for 17 days.¹⁶

LiCoF₄. This compound was prepared by static fluorination of a LiF/CoF₂ mixture with elemental F₂ (10 bar) in a 100 mL nickel autoclave heated at 417 °C for 5 days.¹⁷

K₃CoF₆. This compound was prepared by a modification of the method originally reported by Klemm and Hoppe.¹⁸ It was synthesized by step-by-step fluorination of K₃Co(CN)₆ in a 100 mL nickel autoclave. First, 800 mL of 1/20 F₂/Ar was used (1–3 bar each time, 70 °C, 15 min; after each addition the reaction vessel was cooled to 25 °C and volatiles pumped away), followed by 800 mL of 1/10 F₂/Ar, 800 mL of 1/1 F₂/Ar, and finally elemental F₂ (2 bar, 300 °C, 12 h). The powder XRD pattern of the isolated light-blue solid matched the literature XRD pattern of isostructural K₃FeF₆ (cubic unit cell).¹⁹

1.1.2. Synthesis of Fluorinated Fullerenes. In a typical experiment, a mixture of C₆₀ and one of the ternary salts was ground in an inert atmosphere glove box. The mixture was loaded into a nickel boat, which was placed in a quartz tube. The tube was evacuated and heated for a given temperature for a given amount of time (see Table 1.1

for details). The volatile FFs were sublimed out from the hot zone and condensed on the inner wall of the quartz tube outside of the furnace. The sublimate was collected and analyzed by HPLC (10 × 250 mm Buckyprep Cosmosil column) and the spectroscopic techniques (listed below).

1.1.3. X-ray Crystallography. Crystals (colorless plates) of D_{5d} -C₆₀F₂₀ compound were grown by slow evaporation of a saturated benzene solution. The diffraction-quality single crystal (0.023 × 0.028 × 0.067 mm) was mounted in paratone oil on a glass fiber rod. X-ray diffraction data were collected at ChemMatCARS (CARS = Consortium for Advanced Radiation Sources) sector 15-B at the Advanced Photon Source of Argonne National Laboratory. The data set was collected at 120 K using a diamond (111) crystal monochromator at a wavelength of 0.41328 Å. Data were recorded using a Bruker CCD (charge-coupled device) detector. Absorption and other corrections were applied by using SADABS.²⁰ The structures were solved using direct methods and refined (on F^2 , using all data) by a full-matrix, weighted least-squares process. Standard Bruker control and integration software (APEX II) was employed, and Bruker SHELXTL²¹ software was used for structure solution, refinement, and graphics.

There are two halves of D_{5d} -C₆₀F₂₀ independent molecules in the asymmetric unit in which neither carbon cage nor fluorine atom disorder was observed. Selected details related to this crystallographic experiment are listed in Table 1.2.

1.1.4. Theoretical Calculations. DFT calculations were performed by Dr. A. A. Popov (Leibniz Institute for Solid State and Materials Research, Dresden, Germany). Optimization of the molecular structure of C₆₀F₂₀ was performed at the B3LYP/6-311G(2d) level with the use of Firefly/PC GAMESS package.²²

1.1.5. Spectroscopic Measurements. Fluorine-19 NMR spectra were recorded using a Bruker INOVA-400 spectrometer operating at 376.48 MHz (C_6F_6 was used as an internal standard ($\delta = -164.9$). Negative-ion atmospheric-pressure chemical-ionization (NI-APCI) mass spectra were recorded using a Therm Quest Finnigan LCQ-DUO spectrometer.

1.2 Results and Discussion

The reactions of C_{60} with MF_x and A_xMF_y (A-alkali metal, M-high valent 3d metal) were performed under different experimental conditions. Stoichiometric ratios, reaction times, and temperatures were varied as listed in Table 1.1. Based on the fluorinating ability, FAs can be roughly divided into two groups: those which produced $C_{60}F_n$ ($n > 36$) and $C_{60}F_n$ ($n \leq 36$). The first group includes ternary metal fluorides containing Cr(V), Ni(IV), and Cu(IV), and the second one consists of ternary salts containing Mn(III) and Co(III). FAs of the first group produced $C_{60}F_n$ ($n = 42, 44, 46$; Figures 1.3–1.5). The selective synthesis of the $C_{60}F_{44}$ composition was achieved by using Cs_2CuF_6 as well as a binary fluoride, AgF_2 , which was earlier used for this purpose. (Figure 1.1) In Figure 1.2, the ^{19}F NMR spectrum shows that several $C_{60}F_{44}$ isomers are probably present.

It is known that CoF_3 is more active than MnF_3 .^{12,23,24} Herein, it was confirmed that using MnF_3 as a fluorinating agent, $C_{60}F_{36}$ and $C_{60}F_{18}/C_{60}F_{20}$ compounds were produced as major and minor components in the reaction mixture, respectively. The reaction of C_{60}/CoF_3 under the same experimental conditions led to the formation of primarily $C_{60}F_{38}$, as shown in Figure 1.6. It was also found that $LiCoF_4$ is a stronger FA

than LiMnF_4 . However, K_3CoF_6 and K_3MnF_6 fluorinating abilities cannot be compared because these FAs did not produce any FFs.

Previously, it was shown that the effective synthesis of FFs with low number of fluorine atoms (fewer than 20) is difficult to develop.^{9,12} The high temperature range (470–500 °C) required for synthesis of FFs with low fluorination degree leads to the sublimation of C_{60} itself which significantly decreases the conversion of C_{60} into FF products. Only one particular isomer of $\text{C}_{3v}\text{-C}_{60}\text{F}_{18}$ can be synthesized with a high yield.⁷ In the present work, it was found that LiMnF_4 is a more efficient FA for the production of FFs with $n = 2, 4, 6, 8$, and 20 compared to other FAs listed in Table 1.1. Although fluorinated products are still formed in small amounts in comparison with $\text{C}_{60}\text{F}_{18}$. The results in Table 1.1 show that the distribution of products in the reaction mixture is strongly dependent on the C_{60}/FA mole ratio. For instance, it was shown that the preparation of $\text{C}_{60}\text{F}_{2-8}$ and $\text{C}_{60}\text{F}_{20}$, the fluorination reaction had to be carried out at 470 °C for 3 h and the optimum $\text{LiMnF}_4/\text{C}_{60}$ molar ratio is 20. Despite the fact that these conditions are optimal for the synthesis of compounds with a low degree of fluorination, the overall C_{60} conversion was low (ca. 25 %). Notably, a significant amount of $\text{C}_{60}\text{F}_{20}$ was found in the samples. Due to the low solubility of $\text{C}_{60}\text{F}_{20}$, a non-chromatographic fractional crystallization method was developed for the isolation of this compound, which had been previously used for the purification of $\text{C}_3\text{-C}_{60}\text{F}_{36}$.²⁵ For this purpose, a sample which contained $\text{C}_{60}\text{F}_{18}$, $\text{C}_{60}\text{F}_{36}$, $\text{C}_{60}\text{F}_{2-8}$, and $\text{C}_{60}\text{F}_{20}$ was dissolved in benzene. Slow evaporation of the solvent led to the formation of $\text{C}_{60}\text{F}_{20} \cdot 2\text{C}_6\text{H}_6$ well-cut colorless crystals were be easily isolated from the solution for X-ray diffraction analysis.

The structure of the $C_{60}F_{20}$ molecule confirms its D_{5d} symmetry, which was earlier predicted by theoretical calculations based on spectroscopic studies (Figure 1.8).²⁶ D_{5d} - $C_{60}F_{20}$ has two corannulene-like fragments formed by type *a*, *b*, *c*, and *d* C–C bonds on the top and bottom of the molecule which are isolated from each other by a continuous loop of twenty $C(sp^3)$ atoms to which fluorine atoms are attached. This equatorial location of halogen atoms gave a recognizable name, Saturnene, for this type of molecule. The closest analogue known in the fullerene literature is the molecule D_{5d} - $C_{50}Cl_{10}$, which also has two corannulene-like fragments separated by the belt of ten chlorine atoms on the equator.²⁷

There are seven different types of C–C bonds in D_{5d} - $C_{60}F_{20}$ molecule (Table 1.3). Comparison of the corannulene X-ray structure with the corannulene-liked fragments in $C_{60}F_{20}$ and $C_{50}Cl_{10}$ shows that the C–C bonds are similar, as shown in the Table 1.3 (the ranges for four bond types overlap with each other). At the same time, the “bowls” (distance between centroid formed by five carbon atoms of central pentagon and another centroid of 15 carbon atoms located on the edge of corannulene molecule) of the corannulene-like fragments of $C_{60}F_{20}$ and $C_{50}Cl_{10}$ are deeper (1.5 Å)²⁷ than corannulene itself (0.86 Å, Figure 1.7).²⁸ In addition, the experimental values for C–C and C–F bonds are in a good agreement with the theoretical ones. The type *f* are the longest C–C bonds (1.654(5)–1.659(5) Å), similar to those in D_3 - $C_{60}F_{48}$ (1.627(7) Å)²⁹ and C_{3v} - $C_{60}F_{18}$ (1.672(4) Å).³⁰ In the case of $C_{50}Cl_{10}$, type *f* bonds (1.586(5)–1.588(5)²⁷ Å) are significantly shorter due to their being pentagon-pentagon junctions instead of pentagon-hexagon junctions as in $C_{60}F_{20}$. The angles formed by the pentagon plane and the nearest carbon atoms are also similar for corannulene (58°)²⁸, $C_{60}F_{20}$ (61°), and $C_{50}Cl_{10}$ (60°)²⁷.

As shown in Table 1.4, the experimentally determined angles in the $C_{60}F_{20}$ molecule are very close to the DFT predicted ones. In addition, the $\angle \mathbf{ef}$ in corannulene are very similar ($103.4(4)$ – $105.1(2)^\circ$) to those in $C_{60}F_{20}$ ($102.8(3)$ – $103.4(3)^\circ$).

The unit-cell packing, which is idealized body centered cubic, is shown in Figure 1.9. The fullerene centroid...centroid distances between the center and the corners of the centrosymmetric triclinic cell, which approximates a cube, are 11.09–11.36 Å. The centroid...centroid distances along the crystallographic a axes (perpendicular to the page in Figure 1.9) are 12.47 Å. The fullerenes pack with C_6H_6 molecules centered on four of the six unit-cell faces. Thus, each $C_{60}F_{20}$ molecule is encapsulated into a “cage” formed by four benzene molecules, which probable prevents rotational disorder (Figure 1.10). The absence of cage and F atom disorder results in this being a precise structure. Standard errors (σ) are 0.003–0.004 Å and 0.004–0.005 Å for C–C and C–F bonds, respectively. The perpendicular distance between the least squares C_6 planes of the benzene molecules and the least-squares plane of the closest fullerene hexagon is 3.336(5) Å. The closest F...F distances between $C_{60}F_{20}$ molecules are 2.709(5) Å and 2.831(5) Å. The tight packing of the fullerene and solvent molecules may be responsible for the very low solubility of this compound in organic solvents.

1.3. Summary and Conclusions

The new reactions of C_{60} with ternary metal fluorides studied in the present work showed that some of these metal fluorides the latter ones can be used for the preparation of $C_{60}F_n$ fluorofullerenes with a wide range of even n values, from 2 to 48. For the selective synthesis of $C_{60}F_{44}$ (mixture of isomers), optimal experimental conditions were

achieved using K_2NiF_6 or Cs_2CuF_6 , either of which can be used as an alternative to AgF_2 . For the production of low-substituted FFs with $n = 2, 4, 6, 8$, and 20 , it was demonstrated that LiMnF_4 is the most effective fluorinating agent used in this work. Thus, a new fluorinating agent could be added to KMnF_4 or K_2PtF_6 , which were previously to be effective for the preparation of C_{60}F_n compounds with even $n < 18$. A new non-chromatographic method, based on different solubilities of C_{60}F_n compounds, were developed for the isolation and purification of the elusive compound $D_{5d}\text{-C}_{60}\text{F}_{20}$, which resulted in the isolation of this particular isomer from a mixture of different FFs. The growth of single $\text{C}_{60}\text{F}_{20}$ crystals suitable for X-ray diffraction led to the verification of its previously proposed Saturn-like structure. The absence of positional disorder due to the encapsulation of the $D_{5d}\text{-C}_{60}\text{F}_{20}$ molecule into a cage made by four solvent molecules resulted in a highly precise crystal structure with low standard errors.

Table 1.1. Fluorinating agents (FAs), reaction conditions, and products of C₆₀ fluorination.

fluorinating agent (FA)	FA/C ₆₀ mol ratio	reaction temperature, °C	reaction time, h	major products, C ₆₀ F _n ^[a]	minor products, C ₆₀ F _n ^[a,b]
KCrF ₆	46	270	6.5	46 , 44	42, 48
RbCrF ₆	46	270	4	46 , 44	42, 48
CsCrF ₆	46	270	10	44 , 46	42, 48
MnF ₃	40	420	10	36	18, 20
LiMnF ₄	10	470	3	18	2–8, 20, 36
LiMnF ₄	20	470	3.5	18 , 36	2–8
LiMnF ₄	30	470	10	36 , 18	2–8
LiMnF ₄	40	470	3.5	36 , 18	2–8
KMnF ₄	40	470	3.5	36, 18	2–8, 20
CsMnF ₄	10	470	3	no FFs	no FFs
CoF ₃	40	420	10	38 , 40	36
LiCoF ₄	40	432	8.5	36 , 38	
LiCoF ₄	15	480	7	36 , 18	2–8, 20
LiCoF ₄	40	480	7	36 , 38	
K ₂ NiF ₆	46	380	10	44	46, 42
Cs ₂ CuF ₆	50	330	10	44	

^[a] The more abundant product is listed first; product ratios were determined using APCI mass spectrometry. ^[b] 2–8 = 2, 4, 6, 8.

Table 1.2. Crystal data and structure refinement parameters for C₆₀F₂₀.

	C ₆₀ F ₂₀ ·2 C ₆ H ₆
molecular formula	C ₆₀ F ₂₀ ·2 (C ₆ H ₆)
formula weight	1256.82
crystal system	Triclinic
space group	$P\bar{1}$
Z	2
color of crystal	colorless
unit cell dimensions	
a , Å	12.4647(9)
b , Å	13.2404(9)
c , Å	13.2742(9)
α , deg	90.465(2)
β , deg	90.655(2)
γ , deg	91.403(2)
temperature, K	120(2)
final R indices	$R_1 = 0.0548$
$[I > 2\sigma(I)]$	$wR_2 = 0.1304$
goodness-of-fit on F^2	1.080

Table 1.3. Comparison of bond lengths in C₆₀F₂₀, C₅₀Cl₁₀, and C₂₀H₁₀ X-ray structure DFT-predicted C₆₀F₂₀ structure.^a

bond type, Å	C ₆₀ F ₂₀ (X-ray: this work)	C ₆₀ F ₂₀ (DFT calcs. ²⁶)	C ₅₀ Cl ₁₀ ²⁷	C ₂₀ H ₁₀ ²⁸
a	1.426(4)–1.435(4)	1.433	1.420(4)–1.434(4)	1.415(2)–1.416(2)
b	1.392(4)–1.398(4)	1.399	1.409(3)–1.423(3)	1.376(2)–1.379(2)
c	1.419(4)–1.437(4)	1.427	1.406(6)–1.430(5)	1.442(2)–1.447(2)
d	1.363(5)–1.365(5)	1.378	1.374(7)–1.391(6)	1.378(2)–1.381(2)
e	1.504(5)–1.520(4)	1.507	1.519(5)–1.55(1)	–
f	1.654(5)–1.659(5)	1.670	1.586(5)–1.588(5) ^b	–
g	1.551(4)–1.561(5)	1.570	–	–
C–Hal (F, Cl)	1.380(3)–1.396(3)	1.387	1.738(5)–1.921(6)	–

^a See Figure 1.8 for a key to the bond types.

^b pentagon-pentagon junction

Table 1.4. Comparison of bond angles in the DFT-predicted and X-ray determined structures.^a

angle	C ₆₀ F ₂₀ X-ray structure, deg	C ₆₀ F ₂₀ DFT calculations, deg ²⁶
∠ef	102.8(3)–103.4(3)	102.7
∠eg	110.8(3)–111.5(3)	111.0
∠fg	118.4(3)–119.5(3)	118.7

^aSee Figure 1.8 for a key to the bond types.

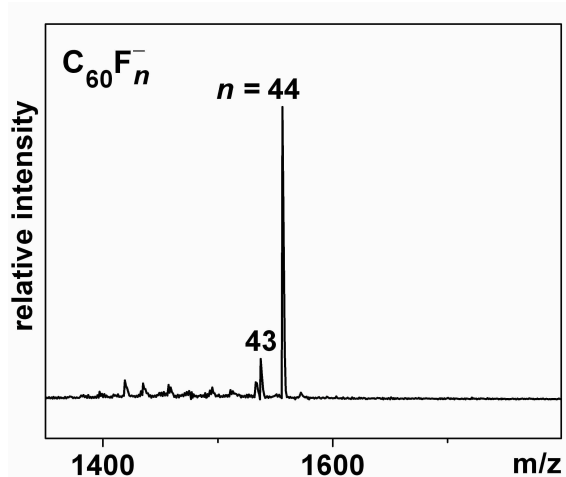


Figure 1.1. NI-APCI mass spectrum of crude mixture of $C_{60}F_n$ products from the reaction of AgF_2 with C_{60} (340 °C, 4 h).

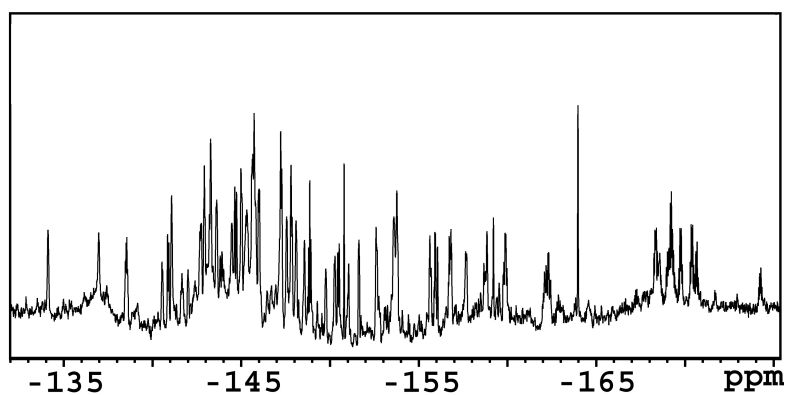


Figure 1.2. Fluorine-19 NMR spectrum of crude mixture of $C_{60}F_n$ products from the reaction of AgF_2 with C_{60} (340 °C, 4 h).

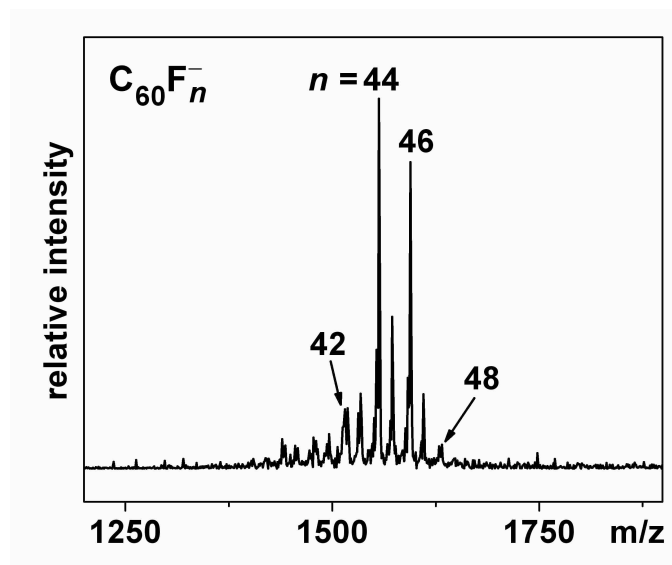


Figure 1.3. NI-APCI mass spectrum of crude mixture of $C_{60}F_n$ products from the reaction of $CsCrF_6$ with C_{60} (270 °C, 10 h).

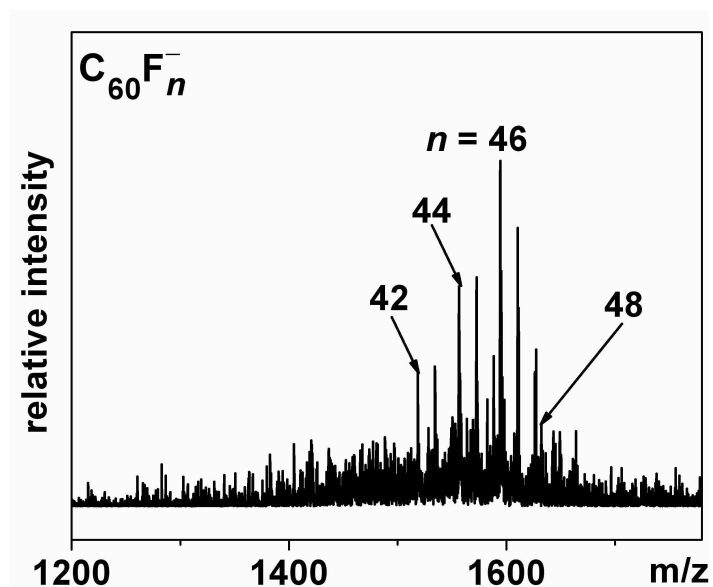


Figure 1.4. NI-APCI mass spectrum of crude mixture of $C_{60}F_n$ products from the reaction of $KCrF_6$ with C_{60} (270 °C, 6.5 h).

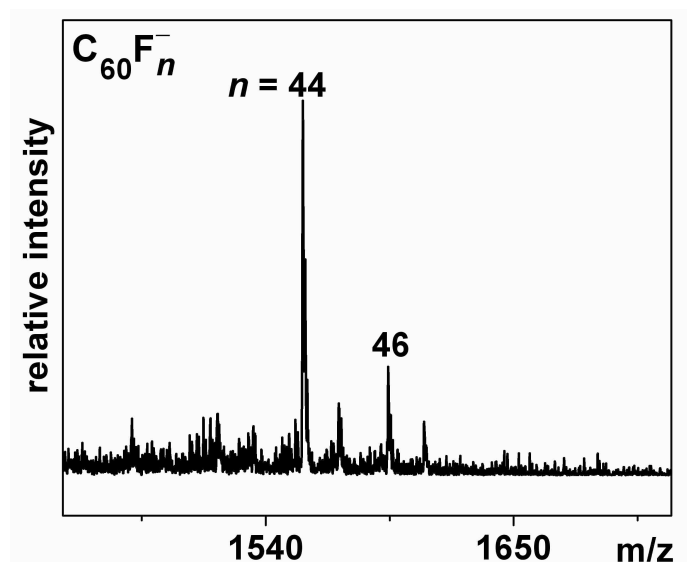


Figure 1.5. NI-APCI mass spectrum of the crude mixture of $C_{60}F_n$ products from the reaction of K_2NiF_6 with C_{60} (380 °C, 10 h).

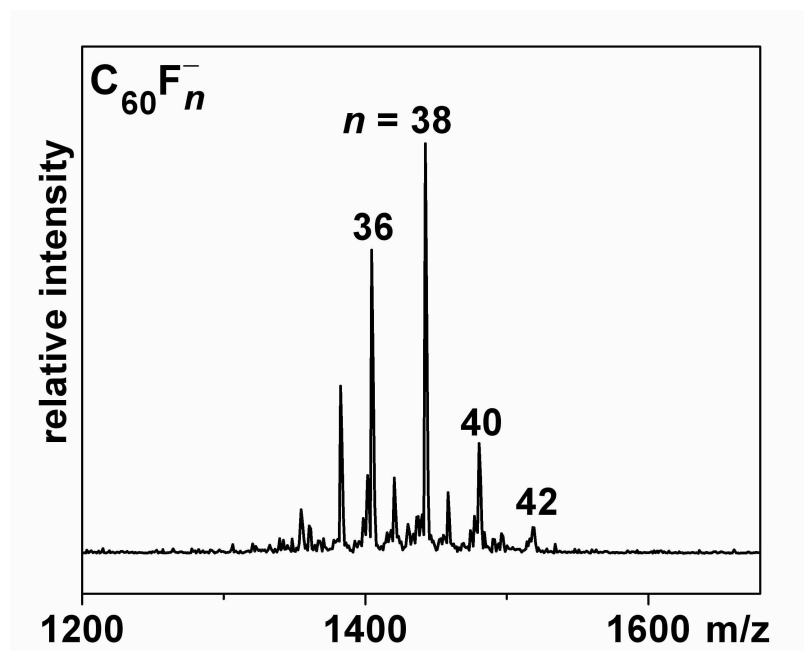


Figure 1.6. NI-APCI mass spectrum of the crude mixture of $C_{60}F_n$ products from the reaction of CoF_3 with C_{60} (420 °C, 10 h).

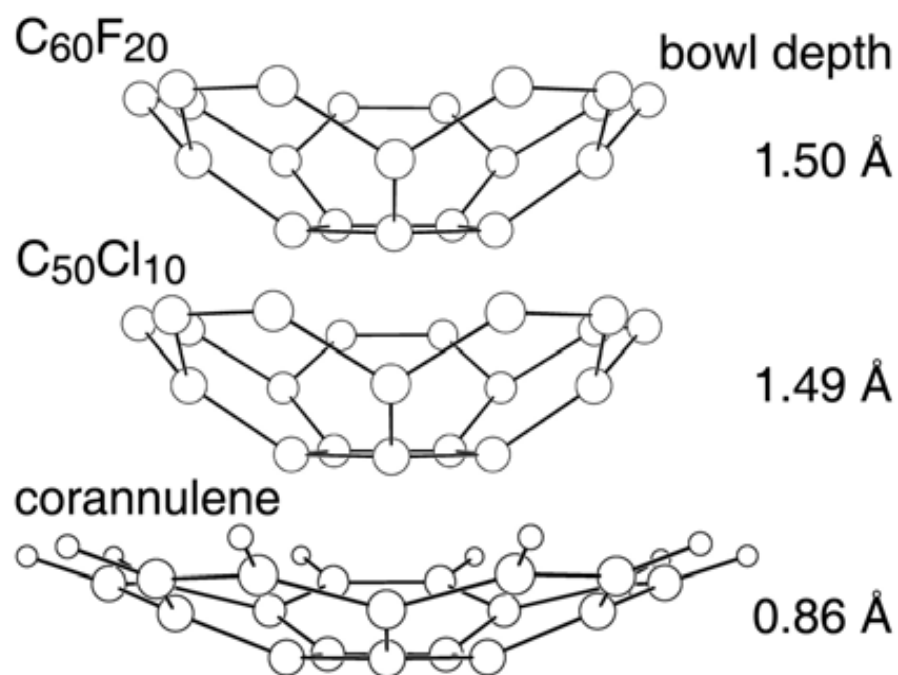


Figure 1.7. Drawings of the X-ray structure of corannulene (C₂₀H₁₀) and the corannulene-like fragments in C₆₀F₂₀ and C₅₀Cl₁₀. The bowl depth is defined as the perpendicular distance between the least-squares plane of the 10 rim C atoms and the least-squares plane of the 5 base C atoms.

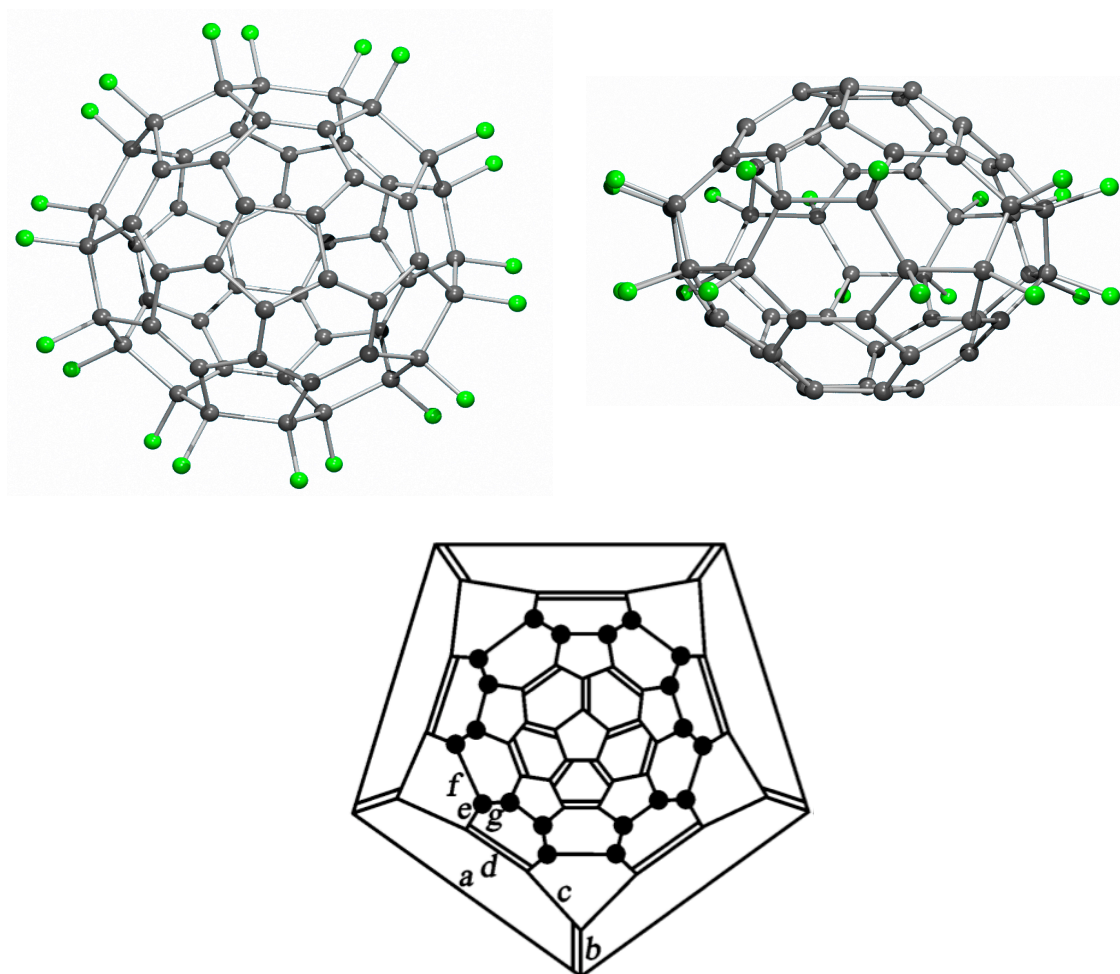


Figure 1.8. Two views of the D_{5d} - $C_{60}F_{20}$ molecule (top) and its Schlegel diagram (bottom). The various bond types (**a–f**) are discussed in the text.

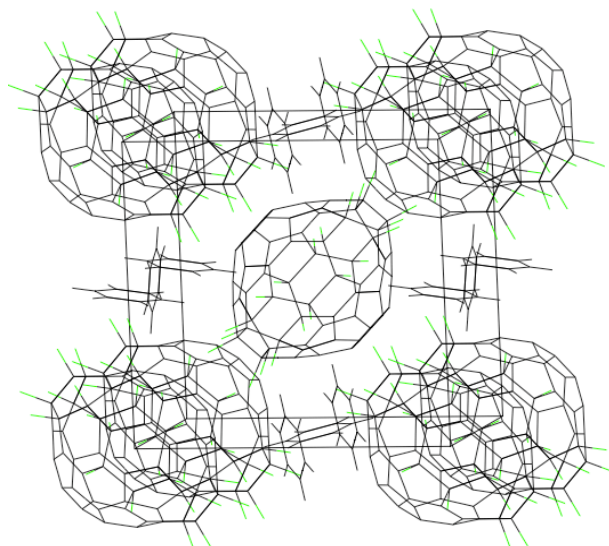


Figure 1.9. The packing of $C_{60}F_{20}$ and C_6H_6 molecules in $C_{60}F_{20} \cdot 2C_6H_6$. Consideration of $C_{60}F_{20}$ molecule as one spherical unit allowed us to describe the packing of $C_{60}F_{20}$ molecules as distorted body centered cubic lattice. The fullerene centroid...centroid distances between the center and the corners of the cell are 11.09–11.36 Å.

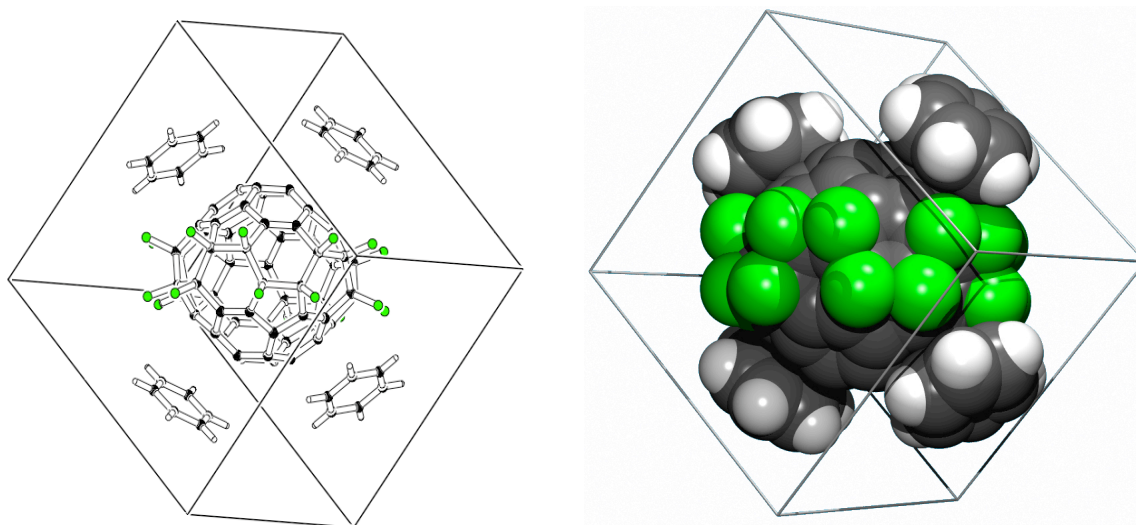


Figure 1.10. D_{5d} - $C_{60}F_{20}$ molecule encapsulated into a “cage” made by four benzene molecules. The tight solvent cage the rotational disorder. The tight unit cell packing may also explain the very low solubility of $C_{60}F_{20}$ compound in organic solvents.

CHAPTER 2. HIGH-TEMPERATURE AND PHOTOCHEMICAL SYNTHESSES OF C₆₀ AND C₇₀ FULLERENE DERIVATIVES WITH LINEAR PERFLUOROALKYL CHAINS

Introduction

Considerable interest in extending the family of fullerene(R_F)_n compounds beyond trifluoromethylfullerenes (TMFs) is driven by several factors. These compounds may potentially be used as materials with strong electron accepting properties for various practical applications. It has been recently proven that fullerene(CF₃)_n compounds exhibit a wide range of $E_{1/2}$ values (for C₆₀(CF₃)_n compounds the range is over 750 mV), and most TMFs are better electron acceptors than parent fullerenes.^{31,32} Similarly strong electron accepting properties can also be predicted for other fullerene(R_F)_n derivatives, since electron-withdrawing character of the longer-chain R_F radicals is very close to or higher than that of CF₃. Furthermore, it was discovered that the redox properties are linked to the addition patterns of fullerene(CF₃)_n derivatives, so that within one composition, say, six isomers of C₆₀(CF₃)₁₀, $E_{1/2}$ varies by 500 mV.³² Such remarkable variability in redox properties, in combination with superb thermal stability, good solubility in various organic solvents, stability in air and upon exposure to moisture or aggressive chemical environment, makes this class of compounds excellent candidates for practical applications in electronic devices and for energy conversion.

From a fundamental point of view, TMFs have already provided an unprecedented wealth of information on fullerene addition patterns, not only for C₆₀ and C₇₀^{31,32} but also for higher fullerenes^{33,34} and endometallofullerenes.³⁵⁻³⁷ Due to the ease with which fullerene(CF₃)_n compounds form well-ordered single crystals by simple solvent evaporation, more than 70 X-ray-determined structures are now known.^{31-33,38-50} Even when TMFs do not form suitable crystals for crystallography, ¹⁹F NMR spectroscopy coupled with DFT calculations serves as a very valuable tool for addition-pattern elucidation.^{33,39} In addition, 2D and/or variable-temperature NMR experiments may allow the conformations of various R_F chains to be precisely determined, and "through-space" Fermi-contact *J*_{FF} coupling constant and chemical-shift analyses will contribute new knowledge to the field of ¹⁹F NMR spectroscopy.^{33,39}

Before starting to prepare PFAFs (perfluoroalkylfullerenes) other than TMFs, it was hypothesized that replacing CF₃ groups with larger R_F addends could lead to variations in the addition patterns of the observed products. By varying gradually the size and the structure of the R_F groups, while keeping the number of R_F groups constant, one could gain insight into the effect of the R_F steric requirements on fullerene addition patterns. Indeed, very first results on the X-ray structures of C₆₀(C₂F₅)₆⁵¹ and C₆₀(*i*-C₃F₇)₆⁵² revealed new fullerene addition patterns that were not seen in C₆₀(CF₃)₆ isomers, and later reports of X-ray structures of C_{60/70}(C₂F₅)_n and C₇₀(*n*-C₃F₇)_n isomers provided further examples of new structures.⁵³⁻⁵⁶ A closely related question that will be addressed in this work concerns determination of the highest possible degree of addition for various R_F groups on a given fullerene. It might be found that the longer the R_F chain, the lower the maximum value of *n*, with TMFs having the largest *n* values for a given fullerene cage.

However, it is not clear that the R_F chain length will dramatically affect the maximum *n* values for R_F groups longer than C₂F₅, since the steric bulk of the CF₂ moiety directly attached to the cage is the same for various length R_F groups. It is also worthwhile examining whether PFAFs with maximum *n* values will lead to the formation of *fewer* geometric isomers, and hence higher selectivity, than with smaller *n* values, especially under high temperature conditions. Finally, findings on the fundamental aspects of reactions of perfluoroalkyl radicals with fullerenes may lead to a better understanding of one of the most common types of derivatizations in fullerene chemistry, namely radical addition reactions.

Thus, in this chapter, extensive experimental studies of fullerene perfluoroalkylation reactions, involving linear-chain R_F radicals, and the products of those reactions are discussed. These studies involved synthesis, isolation, spectroscopic characterization, structural studies, and electrochemical measurements for the selected compounds. This work has been accepted for publication and is now in press.⁵⁷

2.1. Experimental Section

2.1.1. Reagents and Solvents. The reagents and solvents CF₃I (Apollo Scientific, 98%), C₂F₅I (Sigma-Aldrich, 97%), *n*-C₃F₇I (Sigma-Aldrich, 98%), *n*-C₄F₉I (Sigma-Aldrich, 98%), *n*-C₆F₁₃I (Sigma-Aldrich, 99%), C₆₀ (Term USA), C₇₀ (Term USA), Cu powder (Sigma-Aldrich, ~40 mesh, 99.5%) chloroform-*d* and toluene-*d*₈ (Cambridge Isotopes), hexafluorobenzene (Sigma-Aldrich), and heptane or toluene for HPLC purification (Sigma-Aldrich) were used as received. 1,2-dichlorobenzene (Sigma-Aldrich, ACS grade) was distilled over CaH₂ and stored in the glovebox. Tetrabutylammonium

tetrafluoroborate ($\text{N}(n\text{-Bu})_4\text{BF}_4$ (Fluka, puriss. grade) was stored in the glove box after drying under vacuum at 70 °C for 24 h.

2.1.2. Synthesis.

2.1.2.1. Photochemical Reactions. In a typical UV-vis experiment, a finely ground C_{60} (50 mg, 0.007 mmol) and hexafluorobenzene (0.5 mL) were placed in the thin glass ampoule (I.D. = 5 mm). After condensation of CF_3I (1.5 mL, 6.2 mmol), the glass ampoule was sealed. The tubes with the samples were exposed to UV radiation (450 W Hg lamp) at room temperature during 48 h or 7 days.

2.1.2.2. Reactions in a Hot Flow Tube

$\text{C}_{60}(\text{C}_n\text{F}_{2n+1})_n$, $n = 1, 3, 4, 6$ and $\text{C}_{70}(\text{C}_n\text{F}_{2n+1})_n$, $n = 2, 3, 4$. In a typical experiment, finely ground C_{60} (or C_{70}) (100 mg, 0.139 (or 0.119) mmol) was placed in a 0.8-cm I.D. quartz tube connected to a gas handling system at one end and a mineral-oil bubbler at the other (Table 2.1). The portion of the tube containing C_{60} (or C_{70}) was placed in a 40-cm long tube furnace. The perfluoroalkylating agents which were used in this work have a wide range of the boiling temperatures. Therefore, to perform the perfluoroalkylation reactions at high temperatures, several different methods of $\text{R}_\text{F}\text{I}$ introduction to the system were used. CF_3I and $\text{C}_2\text{F}_5\text{I}$ were introduced directly from the gas cylinders at room temperature. [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.] In the reaction between C_{60} (or C_{70}) and $n\text{-C}_3\text{F}_7\text{I}$ (b.p. = 40 °C) or $i\text{-C}_3\text{F}_7\text{I}$ (b.p. = 39 °C), nitrogen was used as a carrier gas and bubbled through liquid $\text{C}_3\text{F}_7\text{I}$ (both isomers) at room temperature. In the case of $n\text{-C}_4\text{F}_9\text{I}$ (b.p. = 67 °C) and $n\text{-C}_6\text{F}_{13}\text{I}$ (b.p. = 117 °C),

nitrogen was bubbled through the perfluoroalkylating agents at 65 °C and 113 °C, respectively.

After purging the apparatus with argon or flow of perfluoroalkylating agent, C₆₀ (or C₇₀) was heated to 320–500 °C. [CAUTION: The perfluoroalkylating reagents used in this work decompose in air above 300 °C and produce toxic HF, COF₂, and I₂; handle only in a well-ventilated fume hood.] Orange-brown products and purple I₂ condensed inside the tube (in the cold zones). After the reaction, the obtained product (together with iodine) was washed from the tube using hexane (or toluene) followed by evaporation of the solvent and iodine at room temperature.

Two reactions of C₆₀(C₇₀) with CF₃I were performed at 500 °C during 2 and 12 hours, while other parameters such as the length of the quartz tube, flow rate of CF₃I, amount of the C₆₀ were the same. Two nearly identical HPLC traces of the products from both experiments, shown in Figure 2.1. To examine reproducibility of C₆₀/CF₃I reactions (520 °C, 3 h), two experiments were performed, HPLC results are shown in Figure 2.2.

2.1.2.3. Reactions in Sealed Ampoules. In a typical experiment, finely ground C₆₀(C₇₀) was placed in a glass ampoule, the ampoule was evacuated, R_FI was then added, and the ampoule was sealed. In some cases, fine copper powder was added as a promoter. The reactions were carried out at 320–550 °C during 24–48 h (Table 2.1). After the reaction, formed iodine and an excess of the unreacted perfluoroalkylating agent were removed under vacuum. In the reactions between C₆₀ and CF₃I, the conditions (amounts of the reagents, time and temperature) described in the paper⁴⁰ were followed as precisely as possible. The reaction between C₆₀ (20 mg, 0.028 mmol) and an excess of *n*-C₃F₇I was carried out in a sealed-ampoule at 290 °C for 24 h (Table 2.1).

2.1.3. Isolation and Purification. Isolation and purification of perfluoroalkylated compounds were performed by HPLC (high pressure liquid chromatography) method using Cosmosil Buckyprep column (Nacalai Tesque Inc., 10 mm I.D. $\times$ 250 mm) at 300 nm UV detection. $C_{70}(C_2F_5)_2$ was isolated and characterized by ^{19}F NMR, UV-vis spectroscopies, and DFT calculations.⁵⁸ Two isomers of $C_{70}(C_2F_5)_4$ were isolated from the high-temperature flow tube reaction product and purified in 20:80 toluene/heptane eluent at 5 mL min⁻¹ ($C_{70}(C_2F_5)_4$ -I) and 60:40 (v:v) toluene/heptane eluent at 5 mL min⁻¹ ($C_{70}(C_2F_5)_4$ -II), and their retention times were 24.6 and 12.8 min, respectively. The $C_{70}(C_2F_5)_{10}$ isomer (**70-10-8- C_2F_5**) eluted at 5.8 min was isolated and purified from 400 °C- and 430 °C-product using 20:80 (v:v) toluene/heptane mixture as an eluent. The addition patterns which are unambiguously determined (X-ray crystallography or ^{19}F NMR spectroscopy) are assigned a consecutive number for a given composition of PFAF. For example, the eight isomer $C_{70}(C_2F_5)_{10}$ will be denoted as **70-10-8- C_2F_5** . The first number, **70**, denotes the fullerene cage, the second number, **10**, is number of R_F groups, the third number, **8**, is an arbitrary isomer number denoting the specific addition pattern, and finally the type of R_F group, C_2F_5 in this case, is shown. If two PFAF molecules with the same number of different R_F groups have the same addition pattern, then they will have the same isomer number.

2.1.4. X-ray Crystallography. Crystals of $C_{70}(C_2F_5)_{12}$ were grown by slow evaporation from saturated perfluoroheptane solution. A diffraction-quality single crystal (0.175 $\times$ 0.192 $\times$ 0.215 mm) was mounted in paratone oil on a glass fiber glued to a small copper pin. The data set was collected at 120 K using a diamond (111) crystal monochromator, a wavelength of 0.41328 Å, and a Bruker CCD detector at

ChemMatCARS Sector 15-B at the Advanced Photon Source at Argonne National Laboratory (CARS = Consortium for Advanced Radiation Sources).

Single crystals of $C_{70}(C_2F_5)_{10}$ ($0.031 \times 0.041 \times 0.103$ mm) were grown from saturated heptane solution. The crystals were mounted in paratone oil on a MiTeGen $10\ \mu\text{m}$ loop. The data set was collected at 100 K using a silicon (111) crystal monochromator on a D8 goniostat equipped with a Bruker APEXII CCD detector at Beamline 11.3.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory using synchrotron radiation tuned to $\lambda = 0.7749\ \text{\AA}$.

For a suitable crystal of $C_{60}(C_2F_5)_{10}$ ($0.250 \times 0.130 \times 0.050$ mm), data were collected with a Bruker SMART diffractometer (Mo-K α , $\lambda = 0.71073\ \text{\AA}$; graphite monochromator; $T = 100(2)$ K).

For all structures, absorption and other corrections were applied using SADABS.²⁰ The structures were solved using direct methods and refined (on F^2 , using all data) by a full-matrix, weighted least squares process. Standard Bruker control and integration software (APEX II) was employed, and Bruker SHELXTL²¹ software was used for structure solution, refinement, and graphics.

2.1.5. Spectroscopic Measurements. Fluorine-19 NMR spectra were recorded using a Bruker INOVA-400 spectrometer operating at 376.48 MHz (C_6F_6 was used as an internal standard ($\delta = -164.9$). Negative-ion atmospheric-pressure chemical-ionization (NI-APCI) mass spectra were recorded using a Therm Quest Finnigan LCQ-DUO spectrometer. An Agilent Technologies Model 6210 TOF spectrometer was used to record negative-ion atmospheric-pressure-photo-ionization (NI-APPI) mass spectra. Electronic absorption spectra of hexane or perfluorohexane solutions of the $C_{70}(C_2F_5)_n$

solutions were recorded using Varian Cary 500 Scan UV-Vis-NIR spectrophotometer. The electrochemical studies were performed by a graduate student James B. Whittaker (CSU) and Dr. A. A. Popov (Leibniz Institute for Solid State and Materials Research, Dresden, Germany). Cyclic voltammetry experiments were carried out in the inert atmosphere in the glove box (water and oxygen content below 1 ppm) in a single-compartment electrochemical cell. The electrolyte solution was 0.1 M N(*n*-Bu)₄BF₄ in *o*-dichlorobenzene. The working electrode was a platinum wire (0.5 mm diameter). A platinum wire (0.5 mm diameter) and a silver wire (0.5 mm diameter, Alfa Aesar Premion, 99.99%) served as the counter electrode and quasi-reference electrode, respectively. The potentials were measured relative to Fe(Cp*)₂⁺⁰ and Fe(Cp)₂⁺⁰ potentials. The experiments were controlled by a PAR 263 potentiostat/galvanostat.

2.2. Results and Discussion

2.2.1. Synthesis, Characterization, and Isolation. Table 2.1 summarizes the reaction conditions and compositions of the perfluoroalkylated C₆₀ obtained in this study and in the literature. In general, the perfluoroalkylation of fullerenes is not a selective process: in most cases products represent complex mixtures of compounds which vary not only in molecular composition but also in the addition patterns within a given composition. Therefore, common analytical methods such as elemental chemical analysis, IR spectroscopy or mass spectrometry are not sufficient for characterization of the composition of PFAFs, when used alone or in their combinations. The crude reaction products described in this Chapter have been characterized systematically by an array of the spectroscopic methods such as APCI/APPI/EI mass spectrometry, ¹⁹F NMR, and

HPLC, the latter with the use of several eluents of varying polarity. As it has been demonstrated recently in the study on chlorofullerenes,⁵⁹ only combination of the above methods of analysis may provide most reliable information on the composition of the products of polyadditions to fullerenes. Yet, as it was shown in this study, for some products, especially for highly substituted PFAFs, these methods were not sufficient either, since (i) capabilities of the used chromatographic technique reached their limits in separations and (ii) due to complexity of the ^{19}F NMR spectral features of PFAFs it became difficult (if not impossible) to get reliable information on the isomeric compositions. In more favorable cases, ^{19}F NMR was successfully used for isolated fractions to determine the number of isomers or to identify the dominant isomer in the product and to determine its symmetry. PFAFs compounds which were isolated as pure isomers were analyzed by ^{19}F NMR, HPLC and mass spectrometry, and these samples were also characterized by cyclic voltammetry, and by X-ray crystallography, when good-quality single crystals were obtained. These data will be described below along with the detailed description of the separation procedures by HPLC. Such detailed approach to characterization allows one to unambiguously identify these compounds in the future studies of PFAFs when larger amounts of the samples are available and new approaches to their purifications are developed.

2.2.1.1. Perfluoroethylation of C_{70} . Previously, a highly selective, high-yield synthesis of a single isomer of $\text{C}_{70}(\text{CF}_3)_{10}$ was achieved under specific set of reaction conditions while using CF_3I as a trifluoromethylating agent.³¹ Predominant formation of the single isomer of $\text{C}_{70}(\text{CF}_3)_8$ was also reported (though with very moderate yield) when different set of conditions, including a different trifluoromethylating agent, (AgCF_3CO_2)

was applied.⁶⁰ It was hypothesized that it could also be possible to develop techniques for selective preparation of $C_{70}(C_2F_5)_n$ compounds by carefully tuning reaction parameters.

Prior reports on the synthesis of perfluoroethylated C_{70} derivatives, however, provided no evidence for high selectivity in these reactions. In the first study, Fagan and co-workers obtained $C_{70}(C_2F_5)_n$ ($n = 10, 12, 14, 16$) derivatives using $C_2F_5-C(O)O-O(O)C-C_2F_5$ as a perfluoroethylating agent (in Freon-113 at 25 °C).⁶¹ In the second study, reactions between C_{70} and C_2F_5I in sealed glass ampoules (180–360 °C) were used to produce $C_{70}(C_2F_5)_n$ ($n = 8, 10, 12$) compounds, and in all cases complex mixtures with multiple isomers were formed.^{53,54}

Flow-tube reactions of C_{70} with C_2F_5I were studied in this work at 320–460 °C. (Figure 2.3, data for 460 °C not shown). The use of temperatures lower than 300 °C or higher than 460 °C yielded very little product. The range of $C_{70}(C_2F_5)_n$ compositions obtained at 320–430 °C was unexpectedly narrow—mostly $C_{70}(C_2F_5)_n$ derivatives with $n = 10$ and 12. The trend of decreasing n with the increase in temperature was similar to the one observed previously for the trifluoromethyl derivatives of C_{60} and C_{70} ,^{38,60} although the range of the compositions was much more narrow than for TMFs. Carrying reactions at 300 or 320 °C gave $C_{70}(C_2F_5)_{12}$ as the dominant composition; the reaction at 430 °C produced $C_{70}(C_2F_5)_{10}$ as the main product (Figure 2.3). It was observed that relative content of one isomer of $C_{70}(C_2F_5)_{10}$ (**70-10-8- C_2F_5**) with retention time 5.8 min (in 20:80 (v:v) toluene/heptane eluent at 5 mL min⁻¹ flow rate) gradually increased with the reaction temperature and reached its maximal content in the product formed at 430 °C (Figure 2.4). This isomer was isolated and characterized spectroscopically and by X-ray crystallography (see below and Figure 2.5).

From the crude reaction products obtained at 400 °C, it has also been isolated and characterized three minor components, $C_{70}(C_2F_5)_2$ (one isomer) and $C_{70}(C_2F_5)_4$ (two isomers, Figures 2.6 and 2.7). The ^{19}F NMR and NI-APCI mass spectra of purified $C_{70}(C_2F_5)_2$ are shown in Figure 2.8. The mass spectrum shows the parent ion $C_{70}(C_2F_5)_2^-$ (m/z 1078) and the cyano-adduct $C_{70}(C_2F_5)_2(CN)^-$ (m/z 1104). In the positive-ion mode (not shown), the protonated species $C_{70}(C_2F_5)_2H^+$ were observed. Proton- and cyanide-adducts are frequently observed in APCI mass spectra of acetonitrile solutions of fullerene(R_F) $_n$ derivatives, especially for low n -values. The ^{19}F NMR spectrum exhibits two singlets in the CF_3 region and a complex, second-order pattern in the CF_2 region. The two singlets indicate that the compound has C_1 symmetry [$^3J_{FF}$ values in C_2F_5 groups are generally small and frequently not observed.⁴⁰ Based on ^{19}F NMR and UV-vis spectra and DFT calculations, it was shown that purified $C_{70}(C_2F_5)_2$ is almost certainly the asymmetric isomer 7,24- $C_{70}(C_2F_5)_2$.⁵⁸

The ^{19}F NMR spectrum of $C_{70}(C_2F_5)_4$ -I has four narrow resonances at δ -79.68, -80.05, -80.30, and -80.52 due to fluorine atoms of the four magnetically inequivalent CF_3 groups and a group of peaks in the $-\delta$ region 110–120 due to $F(CF_2)$ atoms (Figure 2.6). This ^{19}F NMR spectrum is reminiscent of the spectra of other non-symmetric fullerene(C_2F_5) $_n$ compounds (e.g., the structurally characterized p,p,p - $C_{60}(C_2F_5)_6$ has six sharp resonances (6 CF_3 groups) in the $-\delta$ 78–82 region⁵¹).

It was then attempted to produce larger amounts of the $C_{70}(C_2F_5)_4$ and other compounds with low degree of substitution by increasing the reaction temperature. However, further increase in temperature to 460 °C did not result in the shift towards the species with lower n values, as was expected based on the analogy with

trifluoromethylation process. Instead, a drastic drop in the yield was observed and partial fragmentation of C_2F_5I caused by high temperature led to the generation of CF_3 radicals followed by the formation of the fullerene(CF_3) $_n$ derivatives (even n ranging between 4 and 10).

Perfluoroethylation in the sealed glass ampoule at 400 °C resulted in the crude product which mostly contain $C_{70}(C_2F_5)_{10}$ as shown in Figure 2.9. Up to 95% ion intensity in the NI-APPI mass spectrum was due to $C_{70}(C_2F_5)_{10}$ suggesting highly selective process. However, analysis of the ^{19}F NMR spectrum and HPLC trace (recorded in 20:80 (v:v)-toluene/heptanes eluent) proved that multiple isomers were present in the product. When copper powder was added as a promoter, the reaction yielded products with $n(C_2F_5) = 10$ and 12, the latter being more abundant composition. HPLC analysis of the crude products from both reactions performed in toluene and then in pure heptane showed us that the main products elute at very short retention times, which made further chromatographic processing unproductive. Such situation led to impossibility of isolation and characterization of the main products of these reactions. Similar result was obtained by Troyanov and *et al.* for the sealed-ampoule synthesis of $C_{70}(C_2F_5)_{10}$ at 350, 360, and 400 °C.^{53,54} Though several minor isomers of $C_{70}(C_2F_5)_{8,10}$ were isolated and characterized by X-ray crystallography,⁵³ the most abundant $C_{70}(C_2F_5)_{10}$ isomers (2.7–3.25 min retention time) were not characterized at all.

The possibility of exhaustive perfluoroethylation of C_{70} has also been explored. To achieve maximum degree of addition, the crude product, $C_{70}(C_2F_5)_{10-12}$ obtained in 400 °C-reaction was treated again with C_2F_5I at 300 °C for four hours in the flow tube. The composition has not practically changed after such treatment (Figure 2.10). In

contrast, similar experiments performed with $C_{70}(CF_3)_{10}$ (> 90% single isomer) at 300 °C in the flow tube resulted in its partial conversion into $C_{70}(CF_3)_{12-16}$. This approach can be elaborated further to achieve even higher degree of substitution and a higher conversion of $C_{70}(CF_3)_{10}$. The experiments with crude trifluoromethylated products of C_{60} performed under similar conditions yielded even deeper trifluoromethylation than in case of C_{70} , (i.e., mass spectral data indicated the presence of $C_{60}(CF_3)_n$ ($n = 14-23$, Figure 2.11)). Notably, a high degree of trifluoromethylation can be achieved in the UV-initiated reactions of C_{60} with CF_3I in C_6F_6 at room temperature (Figure 2.12). When a crude trifluoromethylated $C_{60}(CF_3)_n$ ($n = 8, 10, 12$) product dissolved in C_6F_6 was irradiated with UV light for 24 h at room temperature, a significantly smaller shift in composition was observed (i.e., the maximum addition of 16 CF_3 groups was achieved (Figure 2.11)).

These data demonstrate that the difference in size between CF_3 and C_2F_5 radicals plays more important role for the highly substituted derivatives: it appears that formation of the stable compounds with more than 14 C_2F_5 groups to C_{70} is unfavorable under the conditions studied in this work. It is feasible that the higher steric strain in $C_{70}(C_2F_5)_{n>12}$ can result in the lower thermal stability, which may explain that Fagan et al. who prepared $C_{70}(C_2F_5)_n$ at room temperature, were able to achieve the addition of as many C_2F_5 groups as 16.⁶¹

2.2.1.2. Preparation of $C_{2m}(R_F)_n$ with $R_F = C_3F_7$, C_4F_9 , and C_6F_{13} . Fagan and co-workers⁶¹ reported that the reaction between C_{60} and perfluorohexyl iodide in 1,2,4 trichlorobenzene at 200 °C led to the formation of the compound with ten C_6F_{13} groups as a major component in the reaction mixture. Furthermore, even for longer chain R_F radicals such as $C_{12}F_{25}$ this composition was dominant.^{61,62} Figure 2.13 presents the EI

(electron ionization) mass spectra of the products obtained in this work using reactions of C_{60} with $R_F I$, where $R_F = n-C_3F_7$, $n-C_4F_9$, and $n-C_6F_{13}$. All reactions were performed at 320 or 350 °C in a flow tube in the presence of copper powder (Table 2.1). Notably, all three products have very similar compositional distribution, i.e. $C_{60}(R_F)_{10}$ is the predominant species (Figure 2.13). Very similar result was obtained for the reaction between C_{60} and $n-C_3F_7I$ (290 °C, 24 h) in the sealed ampoule.

Fullerene C_{70} mixed with Cu powder and $n-C_3F_7I$ were reacted at 350–380 °C for 7 hours in the flow tube, the product with predominant composition $C_{70}(n-C_3F_7)_{10}$ was obtained. Use of lower temperature and longer time of the reaction between C_{70} and $n-C_3F_7I$ in a sealed-ampoule procedure by the authors⁵⁶ yielded a mixture of $C_{70}(n-C_3F_7)_n$ (even $n = 2-10$) with $n = 8$ being dominant composition. All these results clearly indicate that $n = 10$ is the highest substitution degree in fullerene(R_F)_{*n*} with $R_F > C_3F_7$.

As expected, PFAFs with $R_F > C_2F_5$ are much harder to separate than their perfluoroethyl- and TMF analogues. The tendency of decreasing retention times as the size of R_F increases (for a given composition) has been noted before⁵⁸ and observed in the present study. For example, under similar HPLC conditions, $C_{70}(n-C_3F_7)_{10}$ isomers elute at 2.7–3.5 min whereas retention times of $C_{70}(C_2F_5)_{10}$ are 2.7–7.0 min.^{53,56} In case of $C_{70}(n-C_3F_7)_8$ and $C_{70}(C_2F_5)_8$ isomers, the respective ranges of retention times are 3.5–13 min and 7–42 min in pure heptane, respectively.^{54,56} This situation makes the use of the HPLC method in the current configuration (Cosmosil Buckyprep column and heptane as the non-polar solvent) very challenging. It was found that under these conditions it is practically impossible to achieve separation of the isomers of fullerene(R_F)_{*n*>10} for linear R_F groups longer than C_2F_5 .

Physical properties of fullerene(R_F) $_n$ with longer chains are markedly different from those of trifluoromethyl derivatives. First, their solubility in hexane or toluene is significantly lower, while solubility in perfluorinated solvents is very high, especially, in case of fullerene(C_6F_{13}) $_n$. Secondly, the volatility is lower than that of TMFs; it was also observed melting of the crude $C_{60}(CF_3)_n$ ($n = 8, 10$) mixtures at 400 °C and melting of $C_{60}(C_2F_5)_n$ mixtures at 290 °C, which has not being reported for other polyadducts of fullerenes. Such versatility in the properties of PFAFs expands the options for processing of these potentially important electron acceptor materials in the future applications.

2.2.1.3. On Selectivity of Perfluoroalkylation Reactions. Selective one-step preparation of a single-isomer of any PFAF could not be achieved under any conditions examined. It was possible, however, in several cases to prepare products with one predominant composition. In particular, a high compositional purity for fullerene(R_F) $_{10}$ was obtained in the reaction of C_{70} and C_2F_5I and in reactions between C_{60} and R_FI ($R_F = n-C_3F_7$, $n-C_4F_9$, and $n-C_6F_{13}$). However, in all these cases subsequent HPLC and ^{19}F NMR analysis demonstrated presence of many isomers. Trifluoromethylation of C_{60} , C_{70} , and higher fullerenes is also not selective reaction, except for one case, when a single isomer of $C_{1-C_{70}}(CF_3)_{10}$ was prepared with high yield and high isomeric purity using a long-flow-tube reactor.³¹ In 2006, it was reported that reaction of C_{60} and CF_3I in a sealed ampoule at 440 °C yielded $S_6-C_{60}(CF_3)_{12}$ with high compositional and isomeric purity.⁴⁰ This result was very different from the reaction at 440 °C in the long flow-tube.³³ The latter reaction yielded a mixture of products $C_{60}(CF_3)_n$ with $n = 10, 12, 14$. Among many different isomers with composition $C_{60}(CF_3)_{12}$ isolated from this mixture (at least five were identified by ^{19}F NMR spectroscopy), it was also $S_6-C_{60}(CF_3)_{12}$, which was

identified both by X-ray crystallography and ^{19}F NMR spectroscopy.³³ This isomer was not nearly a dominant product in the crude reaction product. Though the conditions of the experiments were clearly different (e.g., pressure of CF_3I in the sealed ampoule was 5 bar,⁴⁰ while in a flow tube it was 1 atm) such a drastic difference in the relative abundances of the products was puzzling. In addition, conclusions by authors⁴⁰ on the remarkable compositional and isomeric purity were only based on the X-ray crystallography performed for a single crystal, which is not a reliable method for characterization of the purity of the bulk samples of fullerene derivatives.⁵⁹ Therefore, the reaction described in the paper⁴⁰ was repeated in our labs. Conditions of the synthesis were reproduced as close as possible to the procedure described in the paper⁴⁰, and then crude products were carefully analyzed by ^{19}F NMR, HPLC, and APCI mass spectrometry methods. While mass spectrometry data may provide only qualitative data on the molecular composition, ^{19}F NMR spectroscopy allows one to estimate quantitatively the content of a specific $\text{C}_{60}(\text{CF}_3)_n$ isomer in the product mixture, provided that its peaks do not overlap with those of the other compounds. In order to have representative data for the whole bulk crude product, the crude solid sample was homogenized, and then 1–2 mg of the solid was completely dissolved in CDCl_3 . Its ^{19}F NMR spectrum is shown in Figure 2.14. Estimation of the relative content of $S_6\text{-C}_{60}(\text{CF}_3)_{12}$ was relatively easy since due to high symmetry it has a very characteristic two-line spectrum ($\delta -66.1(\text{m}, \text{CF}_3)$ and $-67.3(\text{m}, \text{CF}_3)$), each peak representing six CF_3 groups. (the inset in Figure 7 shows ^{19}F NMR of pure sample of $S_6\text{-C}_{60}(\text{CF}_3)_{12}$). Because of the high symmetry, its presence seems indeed very striking in the ^{19}F NMR spectrum of the crude sample; however, according to the peaks integration, $S_6\text{-C}_{60}(\text{CF}_3)_{12}$

constitutes *ca.* 20% of total intensity. It was then repeated this synthesis four more times keeping the same temperature, time, amounts of the reagents as in reference,⁴⁰ and varying the size or geometry (or both) of the glass ampoule, and the rate of heating of reaction mixture, which are also important parameters but were not specifically described in reference.⁴⁰ In all four new experiments, the result was very similar to the first reaction, and again – very different from the results reported in reference.⁴⁰ The typical HPLC traces of the crude products obtained with toluene or heptane as eluents are given in Figure 2.14, along with its NI-APCI mass spectrum. The latter shows the presence of the species with 10, 12, 14, and even 16 CF₃ groups. The HPLC trace recorded with heptane as an eluent clearly demonstrates the presence of multiple products – in full agreement with the ¹⁹F NMR result described above (Figure 2.14). Results of the several experiments in the sealed ampoule at 440 °C for 48 hours consistently showed that this reaction yields a mixture of C₆₀(CF₃)_{*n*}, where *n* = 12, 14, and 16. The *S*₆-C₆₀(CF₃)₁₂ compound is presented in this mixture in the amounts of at most 20–25 mol % of the overall mixture of trifluoromethylated products. In contrast to the reported earlier extremely low solubility of *S*₆-C₆₀(CF₃)₁₂ in organic solvents,⁴⁰ it was possible to perform its purification using HPLC method with toluene and heptane as eluents and also record its ¹⁹F NMR spectra both in CDCl₃ and C₆D₆.³³ It was also observed that dry crystals of the purified *S*₆-C₆₀(CF₃)₁₂ re-dissolve in organic solutions at much slower rate than before its purification and crystallization, but it is a common feature for many other purified fullerene(CF₃)_{*n*} compounds. After an ¹⁹F NMR solution spectrum of *S*₆-C₆₀(CF₃)₁₂ was published,³³ the authors⁴⁰ partially addressed controversy about solubility and provided more detail on the synthetic procedure: “the selective formation of C₆₀(CF₃)₁₂ (*S*₆ isomer)

was observed *in some cases* (italicized by us) in the hot zone when clogging of the narrow middle section of the ampoule with crystalline iodine effectively blocked supply of gaseous CF_3I for further trifluoromethylation”.⁴⁴ This remark helps one to realize that the necessary condition for selectivity of the reaction is “clogging” of the reaction vessel, otherwise applying the right temperature, reagent amounts and time of reaction in the sealed glass tube *will not result in the selective synthesis*, as was demonstrated in the experiments. Clogging of the ampoule can hardly be controlled or easily reproduced; therefore, more experimental work is needed to develop (if possible) a fully reproducible method for the selective preparation of a highly symmetric $S_6\text{-C}_{60}(\text{CF}_3)_{12}$ in practically significant amounts.

2.2.2. Electrochemical Studies. Preliminary electrochemical studies of some isolated perfluoroethylated C_{60} and C_{70} compounds were performed by the graduate student James B. Whittaker and Dr. Alexey A. Popov. Presently, it is not possible to carry out a comprehensive study of electrochemical properties of fullerene(C_2F_5)_n compounds that would be parallel in depth and quality to the earlier study of fullerene(CF_3)_n compounds.^{31,32} Most fullerene(C_2F_5)_n compounds for which molecular structures are known were available to us either in insufficient quantities or low purity (or both) due to low selectivity of the synthetic procedures and challenging chromatographic separations. Therefore, the goal here was to determine if it would be worthwhile to direct future efforts into studies of electrochemical properties of PFAFs. First, it was examined if the suggestion that PFAFs with the same addition pattern but different R_F groups would have similar redox properties. It was recently demonstrated in Strauss group that it is the case for 7,24- $\text{C}_{70}(\text{CF}_3)_2$ and 7,24- $\text{C}_{70}(\text{C}_2\text{F}_5)_2$: their $E_{1/2}$ values were measured as 0.26 and 0.28

V vs. $C_{70}^{0/-}$, respectively.⁵⁸ In this study, the first peak potentials for two isomers of $C_{60}(C_2F_5)_{10}$, which presumably have the same addition patterns as those of two of $C_{60}(CF_3)_{10}$ isomers (**60-10-6-CF₃** and **60-10-1-CF₃**) were estimated as 0.44 and 0.68 V *cf.* $E_{1/2}(\text{60-10-6-CF}_3) = 0.33 \text{ V}$ and $E_{1/2}(\text{60-10-1-CF}_3) = 0.57 \text{ V}$ vs. $C_{60}^{0/-}$.³² Electrochemical study was done for the mixture of isomers of $C_{70}(C_2F_5)_{10}$, from which one of the isomers, **70-10-8-C₂F₅**, was characterized by single-crystal X-ray diffraction (see below). While it is not possible yet to assign the observed peaks to the isomers with definitive structures, it is clear that at least one of the $C_{70}(C_2F_5)_{10}$ isomers has its first reduction potential 0.60 V more positive than C_{60} and C_{70} . For comparison, DFT calculated LUMO energy of the isomer **70-10-8-C₂F₅**, -4.947 eV, is 0.63 eV lower than the value for C_{70} (-4.315 eV). Preliminary cyclic voltammetry measurements for two isomers of $C_{60}(C_2F_5)_6$ ($E_{1/2} = 0.28$ and 0.43 V) and an isomer of $C_{60}(C_2F_5)_8$ ($E_{1/2} = 0.34 \text{ V}$) indicate that this class of PFAFs may provide as rich collection of new acceptor materials with variable redox properties as TMFs.

2.2.3. Structural Studies. Many dozens of TMFs have been carefully studied by X-ray crystallography.^{31,32,38} In many cases, predictions of the most probable addition patterns for trifluoromethylated derivatives were based on the analysis of the ^{19}F NMR spectra and DFT calculations. In all cases reported to date, these predictions were proven to be correct by the subsequent X-ray crystallography.^{32,38}

Structural characterization of perfluoroalkylated fullerenes with $R_F = C_mF_{2m+1}$ substituents where $m > 1$ represents a more challenging task. Three main factors contribute to this. First, a smaller compositional range of fullerene(R_F)_{*n*} ($n < 12$) than TMFs can be subjected to isolation and purification using currently developed HPLC

procedures. Consequently, fewer highly substituted compounds can be available in the pure form for structural studies. For example, as noted above, none of the crude mixtures of fullerene(R_F) $_n$ with $n-R_F = C_4F_9$ or C_6F_{13} could be separated into pure compounds, only four out of dozens compounds in the crude $C_{70}(n-C_3F_7)_n$ were characterized, while $C_{60/70}(C_2F_5)_n$ compounds with $n \geq 12$ were found practically inseparable. Even for $C_{70}(C_2F_5)_n$ with $n = 8, 10$ only a few minor isomers were isolated from crude mixtures, while the most abundant isomers were inseparable, leaving a large gap in knowledge and understanding of the most favorable addition patterns for these PFAFs. The only class of PFAFs (not counting TMFs) which has been satisfactorily studied to date is $C_{60}(C_2F_5)_n$ with $n = 6, 8$, and 10 (Figure 2.15).

The second problem is higher complexity of the ^{19}F NMR spectra of PFAFs than those of TMFs. Their interpretation and particularly obtaining structural information is far more difficult, therefore one cannot rely on the NMR as a complement to X-ray crystallography for structural determinations. For instance, for $C_{60}(C_2F_5)_{6,8}$ compounds, a typical ^{19}F NMR spectrum contains a group of narrow resonances assigned to the CF_3 groups at $(-\delta)$ 78–82, and a group of complex peaks in the CF_2 region at $(-\delta)$ 112–116.⁵¹ The ^{19}F NMR method remains very useful and highly sensitive for evaluation of the purity of PFAFs or determination of molecular symmetry, but it cannot provide compelling information on the addition patterns at this time. As the PFAFs include larger and larger R_F radicals they become more and more challenging for computational studies as well. Finally, even if one succeeds in growing suitable for crystallography single crystals, more complications arise in solving their structures due to challenging modeling of rotational disorder of long perfluoroalkyl chains.⁶³ Thus, it was concluded that at

present the most complete set of structural data for PFAFs is that of $C_{60}(C_2F_5)_{6,8,10}$. For all other PFAFs, only fragmentary information is available, which does not allow one to discuss in-depth or make conclusions about preferred structures for a given R_F . Available structural data on PFAFs from the literature and present new data on the X-ray structures for several PFAFs will be discussed below.

2.2.3.1. Addition Patterns in $C_{60}(C_2F_5)_n$. These PFAFs are formed predominantly with n values of 8–12, both in the flow-tube and sealed ampoule syntheses. The HPLC traces of crude products from both syntheses and determined that relative isomeric distributions are very close (Figure 2.16). Several X-ray structures of $C_{60}(C_2F_5)_8$ and $C_{60}(C_2F_5)_6$ have been determined previously.^{51,55} In this work the addition pattern for three isomers of $C_{60}(C_2F_5)_8$ (**60-8-1- C_2F_5** , **60-8-3- C_2F_5** , and **60-8-7- C_2F_5**) and one isomer of $C_{60}(C_2F_5)_{10}$ (**60-10-6- C_2F_5**) using X-ray crystallography have been determined. The X-ray structure for the latter compound is determined more accurately than previously published in reference⁵⁵. The Schlegel diagrams of the $C_{60}(C_2F_5)_8$ and $C_{60}(C_2F_5)_6$ isomers with the known structures are presented in Figure 2.15 and Table 2.2. The compounds **60-8-1- C_2F_5** , **60-8-3- C_2F_5** , and **60-10-6- C_2F_5** have the same addition patterns as their TMF counterparts.³² The isomer **60-8-1- C_2F_5** is the first example of the fullerene(C_2F_5) $_n$ in which all eight C_2F_5 groups form a single p^3mpmp ribbon. In the Strauss group, the X-ray structure of **60-8-6- C_2F_5** with the p^3mp ribbon containing six C_2F_5 groups (which constitutes the addition pattern of isomer **60-6-1- CF_3** ³²) and a pair of C_2F_5 groups on an isolated hexagon was published. The formation of these isomers as abundant products (as well as **60-8-3- C_2F_5** , **60-8-8- C_2F_5** , **60-8-9- C_2F_5** , and **60-8-10- C_2F_5**) demonstrates that the steric strain introduced in these structures due to larger size

of C_2F_5 groups than CF_3 does not affect significantly distribution of the most favorable addition patterns; even additions of C_2F_5 groups in *meta* positions appear in these structures. It is therefore not surprising that one of the isomers of $\text{C}_{60}(\text{C}_2\text{F}_5)_{10}$, **60-10-6- C_2F_5** , has the same addition pattern as the trifluoromethyl derivative **60-10-6- CF_3** ³², its ten addends are arranged in *pmp*- and *p³mp* ribbons. The second isomer of $\text{C}_{60}(\text{C}_2\text{F}_5)_{10}$, **60-10-7- C_2F_5** , which crystal structure was determined in reference⁵⁵ has a pair of C_2F_5 groups on the isolated *p*- $\text{C}_6(\text{CF}_3)_2$ hexagon and a *pmpmpmp* ribbon, the latter is also a pattern of **60-8-4- CF_3** .³² As shown in Figure 2.17, **60-10-7- C_2F_5** addition pattern can be obtained from **60-8-4- CF_3** by the addition of two C_2F_5 groups (two red dots) to the 42 and 56 carbon atoms which form an isolated *p*- $\text{C}_6(\text{CF}_3)_2$ hexagon.

2.2.3.2. X-ray Structure of $\text{C}_{60}(\text{C}_2\text{F}_5)_{10}$. Table 2.3 lists the experimental data on the X-ray structure of the isomer of $\text{C}_{60}(\text{C}_2\text{F}_5)_{10}$ (**60-10-6- C_2F_5**). It repeats the addition pattern reported earlier for **60-10-6- CF_3** .^{32,55} At present, X-ray crystal structures are known only for two isomers of $\text{C}_{60}(\text{C}_2\text{F}_5)_{10}$, and the crystal lattices of both isomers do not contain solvent molecules.⁵⁵ In Figure 2.17, the distances for the closest neighbors in three different layers of both isomers are shown. Each $\text{C}_{60}(\text{C}_2\text{F}_5)_{10}$ molecule has six nearest neighbors in the same layer, three in the layer above, and three in the layer below. The *ABCABC* stacking of the close-packed layers of $\text{C}_{60}(\text{C}_2\text{F}_5)_{10}$ molecules can be considered as distorted cubic close-packed (*ccp*). In contrast, molecules of **60-10-6- CF_3** form a distorted hexagonal close-packed (*hcp*) lattice despite the absence of solvent molecules in the crystal lattice and an identical addition pattern (Figure 2.18 shows that each $\text{C}_{60}(\text{CF}_3)_{10}$ molecule has six neighbors in the same layer, three in the layer above, and three the layer below. Other known isomers of $\text{C}_{60}(\text{CF}_3)_{10}$ (e.g., **60-10-3- CF_3** (Figure

2.19³⁸) and **60-10-4-CF₃** (Figure 2.20)), which crystallize without solvent molecules in the lattice, form distorted *ccp* packing arrangements.

2.2.3.3. Addition Patterns in C₇₀(C₂F₅)_n. In contrast to the C₆₀(C₂F₅)_n crude products, from which it was possible to isolate and characterize almost all main components, both in this work and earlier,^{51,55} the most abundant products in the crude C₇₀(C₂F₅)_n mixtures have not been isolated despite the attempts. Recent reports by Tamm and co-workers described synthesis of C₇₀(C₂F₅)_n in the sealed ampoule.^{53,54} The HPLC separation of the crude resulted in the identification of at least 17 different fractions as various C₇₀(C₂F₅)₁₀ isomers, several minor components were successfully isolated and studied by X-ray method,⁵³ while the most dominant products contained in the fraction eluting 2–9 min in pure hexane were not characterized at all. Therefore, it remains unknown how many isomers of C₇₀(C₂F₅)₁₀ constitute the most abundant fraction and what addition patterns are favored under the reported experimental conditions. The Schlegel diagrams of the nine isomers of C₇₀(C₂F₅)₁₀ determined by X-ray analysis are shown in Table 2.4. Some C₇₀(C₂F₅)_n compounds have the same addition pattern as C₇₀(CF₃)_n derivatives. For example, in the structures of **70-10-1-C₂F₅** and **70-8-1-C₂F₅** addends have the same locations as in TMFs **70-10-1-CF₃** and **70-8-1-CF₃**, respectively. In addition, several isomers of C₇₀(C₂F₅)₈ and C₇₀(C₂F₅)₁₀ contain addition patterns of **70-6-2-CF₃** and **70-4-1-CF₃** as sub-patterns.

Interestingly, similarities in the addition patterns of perfluoroethyl- and trifluoromethylated compounds were also recently demonstrated for the C₇₈(2) fullerene.⁶⁴ The difference between *p*⁵,*p*,*p*-C₇₈(C₂F₅)₁₀⁶⁴ and *p*⁹-C₇₈(CF₃)₁₀³⁹ was found only in the position of two C₂F₅ groups. The latter compound forms one long *p*⁹ ribbon,

while in the former compound this ribbon is broken into a shorter ribbon p^7 and two isolated *para*-C₆(C₂F₅)₂ hexagons.

In this work, significantly improved data for the crystal structure of **70-10-8-C₂F₅** isomer were obtained, and the first structure of an isomer of C₇₀(C₂F₅)₁₂, **70-12-5-C₂F₅**, which is described below, was determined.

2.2.3.4. X-ray Structure of C₇₀(C₂F₅)₁₀. The crystals of **70-10-8-C₂F₅** (Figure 2.21) have a tendency to grow as non-merohedral twins from various solvents. The first data set was collected on a Bruker Kappa APEX II CCD diffractometer at 100 K. The original structural model, which did not take into account twinning, was of very low quality, and close to the result reported for the same compound (which also crystallized in the same space group) by Troyanov and co-workers (Table 2.5).⁵⁵ After detailed analysis of the obtained data, two twin domains were assigned, and final refinement against twinned data resulted in the significant improvement of the original model (Table 2.5). The second data set for these crystals was collected at Advanced Light Source, Berkeley National Laboratory using synchrotron radiation which allowed us to use a smaller (0.031 × 0.041 × 0.103 mm) and better-quality non-twinned single crystal. Data collection and structure solution parameters are listed in Table 2.3.

The molecule of **70-10-8-C₂F₅** has one p^5 ribbon and four C₂F₅ groups attached to two isolated *para*-C₆(C₂F₅)₂ hexagons. Thus, six C₂F₅ groups form a ribbon on the equator and the four of them attach to the reactive sites on the two poles of the C₇₀ molecule. This addition pattern also contains the p^3,p substructure of **70-6-2-CF₃**.

There are no solvent molecules in the crystal lattice of C₂- p^5,p,p -C₇₀(C₂F₅)₁₀ structure. C₇₀(C₂F₅)₁₀ molecules form complex puckered layers as shown in Figure 11.

The distance between two mean planes of the closest layers is 13.79 Å, and in one layer the neighboring molecules are arranged at 10.440, 10.889, and 12.485 Å from each other, as shown in Figure 10. The analysis of the four $C_{70}(C_2F_5)_{10}$ crystal structures which crystallize without solvent in the lattice showed that fullerene molecules in **70-10-9- C_2F_5** , **70-10-11- C_2F_5** , **70-10-13- C_2F_5** , and **70-10-15- C_2F_5** isomers^{53,54} (as shown in Figures 2.22, 2.23, 2.24, and 2.25, respectively) form layers as in the case of **70-10-8- C_2F_5** . In addition, the stacking of the *ABAB* packed layers of $C_{70}(C_2F_5)_{10}$ molecules in the **70-10-11- C_2F_5** isomer⁵³ can be considered as a distorted *hcp* arrangement (Figure 2.23).

2.2.3.5. X-ray Structure of $C_{70}(C_2F_5)_{12}$. In the first experimentally determined molecular structure of C_{70} with 12 C_2F_5 addends (**70-12-5- C_2F_5** ; IUPAC lowest locants = 1,4,23,25,27,31,38,44,47,51,55,68), substituents form a unique addition pattern which contains four C_2F_5 groups on the two isolated *para*- $C_6(C_2F_5)_2$ hexagons, three C_2F_5 groups form a short *pm* ribbon, and five groups form a *mp³m* loop, which can be considered as a part of a common skew pentagonal-pyramid (SPP) addition pattern. In this case an isolated butadiene moiety is formed, as shown in Figure 2.21. Table 2.6 shows a comparison of the C–C distances in the central pentagon of the SPP fragments in four perfluoroalkylated derivatives. Each type of the following C–C bonds has similar values of C–C distances in all four structures, at $\pm 3\sigma$ level of confidence: **a**, **d** (double bonds) and **e**, **f** (single bonds). At the same time, **b** and **c** C–C bonds are the same in the structures of $C_{60}(C_2F_5)_4O^{65}$ and $C_{60}(CF_3)_4O^{65}$ (at $\pm 3\sigma$ level of confidence) but significantly different from **70-12-5- C_2F_5** and **60-10-4- CF_3** . Remarkably, the structure of **70-12-5- C_2F_5** does not have any kind of disorder, in contrast to **70-10-8- C_2F_5** , in which four C_2F_5 groups are disordered due to the rotation of either the CF_3 or both of the CF_3

and CF₂ moieties around C–C single bonds. The absence of rotational disorder is unusual in case of perfluoroalkylated derivatives, especially in the case of longer linear R_F chains.⁵³ The comparison of addition patterns for the known isomers of C₇₀(C₂F₅)₁₀^{53,54} with C₇₀(C₂F₅)₁₂ isomer shows that the latter cannot be obtained by simple addition of two C₂F₅ groups to any of the reported C₇₀(C₂F₅)₁₀ isomers.

There are no solvent molecules in the crystal lattice of C₇₀(C₂F₅)₁₂ molecule. As shown in Figure 2.21, C₇₀(C₂F₅)₁₂ molecules form puckered layers. The closest F··F distance between C₇₀(C₂F₅)₁₂ molecules is 2.571(3) Å. The distance between two mean planes is 11.47 Å which is close to the value observed in the molecular packing of C₇₀(C₂F₅)₁₀ (see above). One C₇₀(C₂F₅)₁₂ molecule inside the layer is surrounded by six others, and the distances between the neighboring molecules are 12.970, 14.347, and 14.387 Å as shown in Figure 2.21.

2.2.3.6. Addition Patterns in C₇₀(n-C₃F₇)_n. As mentioned above, the main components in the C₆₀₍₇₀₎(n-C₃F₇)_n reaction mixtures prepared in this work were not separable by existing HPLC procedures. Out of at least two dozens of different components revealed by the HPLC analysis of the crude C₇₀(n-C₃F₇)_n product, only four minor fractions which contained C₇₀(n-C₃F₇)₈ isomers were characterized by X-ray crystallography by others.⁵⁶ The addition patterns of all four C₇₀(n-C₃F₇)₈ isomers repeat those of C₇₀(C₂F₅)₈ compounds (Table 2.2).

2.3. Summary and Conclusions

In this work, several high-temperature synthetic procedures for the preparation of air- and thermally stable PFAFs with linear perfluoroalkyl chains have been developed.

These reactions occur at high temperatures and with good-to-quantitative fullerene conversion. Systematic studies of the effect of reaction conditions (temperature, time, effect of catalyst, etc.) on the product composition allowed us to find specific conditions for preparation of the products with a narrow composition. For example, procedures for several $(C_{60(70)}/R_F)I$ ($R_F = C_3F_7$, C_4F_9 , and C_6F_{13}) systems, in which fullerene(R_F)₁₀ was the major component in the reaction mixture have been developed. It was demonstrated that isomers of fullerene(R_F) _{$m > 10$} are practically inseparable by HPLC method while using Cosmosil Buckyprep column and pure heptane as an eluent because of the general tendency for longer- R_F chain derivatives to have shorter retention times in comparison with trifluoromethylated analogs. Furthermore, these results and literature data⁵⁵ indicate that even in case of fullerene(R_F)₁₀ isomers, only a small fraction of isomers is subject to HPLC purifications, leaving the most abundant isomers yet to be isolated and characterized in the future, when appropriate separation techniques are found. In the present work, $C_{70}(C_2F_5)_{12}$, the first C_{70} - based PFAF other than CF_3 with $n(R_F) > 10$ was isolated using fractional crystallization. Determination of its X-ray structure revealed an unprecedented addition pattern, which is not a product of subsequent R_F addition to any of the known isomers of $C_{70}(C_2F_5)_{10}$. PFAFs with a low number of addends (e.g., $C_{70}(C_2F_5)_4$ or $C_{70}(C_2F_5)_2$) which are usually well separable were only found as the minor products in the reaction mixtures. Presently, no synthetic methods exist that afford PFAFs with low substitution degree.

It was shown that the maximum degree of addition for trifluoromethylated derivatives was 22–23 CF_3 groups per cage; in contrast, perfluoroethylation (both for C_{60}

and C₇₀) results in the maximal addition of 14 groups, while for larger R_Fs the highest addition value was 10.

Based on the results of the present work, two routes for the future development of long-chain perfluoroalkyl fullerene chemistry can be proposed. The first direction is the search for new methods or optimization of the known synthetic techniques for preparation of the compounds with a low degree of substitution. These compounds can be easily separated by existing HPLC methods and can potentially become important alternatives for trifluoromethylated derivatives including their use for further derivatizations. Another direction is the exploration of the new separation techniques which would allow one to isolate highly substituted perfluoroalkyl fullerenes, which are easy to prepare in high yields as mixtures but difficult to purify with the currently used chromatographic approach.

Finally, the electrochemical data for the selected PFAFs demonstrate that they exhibit strong electron accepting properties, reversible reductions in solution, their redox properties vary with the addition patterns, which indicates that they have potential to develop into a new and promising class of organic electron acceptor materials.

Table 2.1. Perfluoroalkylating agents, reaction conditions, and products of C₆₀ perfluoroalkylation.

R _F in R _F I	T _{rxn} , °C	t, h	reactor/solvent/ promoter	MS data on C ₆₀ (R _F) _n		refs.
				<i>n</i>	<i>n</i> _{max}	
C₂F₅	200	24	SA/C ₆ F ₆	10–16	14	⁶¹
	320	4	FT/Cu	10–14	12	⁵¹
	380–440	40–70	SA	6–10	8	⁵⁵
	400	2–4	FT/Cu	6–10	8	this work
	420–440	–	SA	8–10	8	⁵¹
	440	–	SA	6, 8		⁵¹
	430	2–4	FT/Cu	4–8	6	⁵¹
	460	2–4	FT/Cu	2	8	this work
	500	2–4	FT/Cu	2 (CF ₃)	8	this work
<i>n</i>-C₃F₇	290	24	SA	4–12	10	this work
	350	7	FT/Cu	10, 12	10	this work
	380	6	FT/Cu	8, 10	10	this work
<i>n</i>-C₄F₉	350	4	FT/Cu	8–10	10	this work
<i>n</i>-C₆F₁₃	200	24	SA/1,2,4-C ₆ H ₃ Cl ₃	6–12	10	⁶²
	340	5.5	FT/Cu	8–10	10	this work
<i>n</i>-C₁₂F₂₅	200	24	SA	6–12	10	⁶²

SA – sealed ampoule; FT – flow tube; *n*_{max} – most abundant *n* in C₆₀(R_F)_n

Table 2.2. Comparison of the $C_{60}(C_2F_5)_n$ and $C_{70}(C_nF_{2n+1})_n$, $n = 2, 3$ addition patterns with known addition patterns for trifluoromethylated derivatives.

$C_{60}(C_2F_5)_n$			
compound	abbreviation	same addition pattern ^{f,e}	related trifluoromethylated structures ^f
1,6,11,16,18,24,27,36- $C_{60}(C_2F_5)_8$ ^a	60-8-1-C_2F_5	60-8-1-CF_3	
1,6,11,18,24,27,53,56- $C_{60}(C_2F_5)_8$ ^{a,b}	60-8-3-C_2F_5	60-8-3-CF_3	
1,6,11,18,24,27,32,35- $C_{60}(C_2F_5)_8$ ^c	60-8-6-C_2F_5		1,6,11,18,24,27- $C_{60}(CF_3)_6$ (60-6-1-CF_3)
1,6,11,18,24,27,36,39- $C_{60}(C_2F_5)_8$ ^{a,b}	60-8-7-C_2F_5		1,6,11,16,18,24,27,36- $C_{60}(C_2F_5)_8$ (60-8-1-CF_3)
1,6,11,18,24,27,41,57- $C_{60}(C_2F_5)_8$ ^b	60-8-8-C_2F_5		1,6,11,18,24,27- $C_{60}(CF_3)_6$ (60-6-1-CF_3)
1,6,11,18,24,27,51,59- $C_{60}(C_2F_5)_8$ ^b	60-8-9-C_2F_5		1,6,11,18,24,27- $C_{60}(CF_3)_6$ (60-6-1-CF_3)
1,6,11,18,24,27,33,51,54,60- $C_{60}(C_2F_5)_{10}$ ^{a,b}	60-10-6-C_2F_5	60-10-6-CF_3	
1,6,11,16,18,28,31,36,42,56- $C_{60}(C_2F_5)_{10}$ ^b	60-10-7-C_2F_5		1,6,11,16,18,28,31,36- $C_{60}(CF_3)_8$ (60-8-4-CF_3)
$C_{70}(C_nF_{2n+1})_n$, $n = 2, 3$			
1,4,10,19,25,41,49,60,66,69- $C_{70}(C_2F_5)_{10}$ ^d	70-10-1-C_2F_5	70-10-1-CF_3	
1,4,11,19,31,41,46,55,62,67- $C_{70}(C_2F_5)_{10}$ ^{a,d}	70-10-8-C_2F_5		1,4,11,19,31,41- $C_{70}(CF_3)_6$ (70-6-2-CF_3)
1,4,11,19,23,31,44,55,57,67- $C_{70}(C_2F_5)_{10}$ ^d	70-10-9-C_2F_5		1,4,11,19,31,41- $C_{70}(CF_3)_6$ (70-6-2-CF_3)
1,4,11,19,31,41,51,64- $C_{70}(C_2F_5)_8$ ^e	70-8-1-C_2F_5	70-8-1-CF_3	
7,15,24,34,44,47,53,56- $C_{70}(C_2F_5)_8$ ^e			7,24,44,47- $C_{70}(CF_3)_4$ (70-4-1-CF_3)
7,17,24,36,44,47,53,56- $C_{70}(C_2F_5)_8$ ^e	70-8-3-C_2F_5	70-8-3-C_3F_7	7,24,44,47- $C_{70}(CF_3)_4$ (70-4-1-CF_3)
7,17,24,36,44,47,53,56- $C_{70}(n-C_3F_7)_8$ ^f	70-8-3-C_3F_7	70-8-3-C_2F_5	
7,15,24,34,44,47,53,56- $C_{70}(n-C_3F_7)_8$ ^f	70-8-4-C_3F_7	70-8-4-C_2F_5	
1,4,23,28,36,44,46,57- $C_{70}(n-C_3F_7)_8$ ^f	70-8-5-C_3F_7	70-8-5-C_2F_5	
1,4,23,28,34,44,46,52- $C_{70}(n-C_3F_7)_8$ ^f	70-8-6-C_3F_7	70-8-6-C_2F_5	

^a X-ray crystal structure determined in this work; ^b X-ray crystal structure determined in ref.³⁵; ^c X-ray crystal structure determined in ref.⁶⁶; ^d X-ray crystal structure determined in ref.³⁶; ^e X-ray crystal structure determined in ref.³⁹; ^f addition patterns discussed in ref.⁵⁹.

Table 2.3. Crystallographic data for **70-12-5-C₂F₅**, **70-10-8-C₂F₅**, and **60-10-6-C₂F₅**.

	C ₇₀ (C ₂ F ₅) ₁₂	C ₇₀ (C ₂ F ₅) ₁₀	C ₆₀ (C ₂ F ₅) ₁₀
molecular formula	C ₉₄ F ₆₀	C ₉₀ F ₅₀	C ₈₀ F ₅₀
formula weight	2268.94	2030.90	1910.80
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	4	4	4
color of crystal	red	brown	brown
unit cell dimensions			
<i>a</i> , Å	14.3871(11)	19.5072(6)	17.9226(7)
<i>b</i> , Å	22.2798(16)	16.3789(4)	16.7522(6)
<i>c</i> , Å	23.3969(16)	20.8066(6)	20.3122(9)
<i>α</i> , deg	90	90	90
<i>β</i> , deg	103.890(2)	98.356(2)	98.988(1)
<i>γ</i> , deg	90	90	90
temperature, K	120(2)	100(2)	100(2)
final <i>R</i> indices	<i>R</i> ₁ = 0.0499	<i>R</i> ₁ = 0.0665	<i>R</i> ₁ = 0.0667
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> ₂ = 0.1410	<i>wR</i> ₂ = 0.1943	<i>wR</i> ₂ = 0.2141
goodness-of-fit on <i>F</i> ²	1.019	1.032	1.048

Table 2.4. IUPAC numbering and Schlegel diagrams of the $C_{70}(C_2F_5)_{10}$ isomers known from X-ray structures

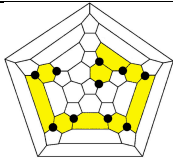
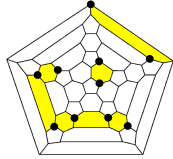
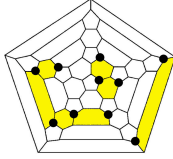
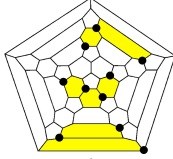
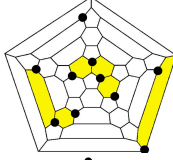
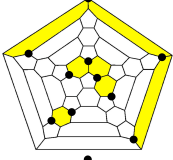
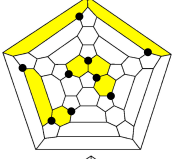
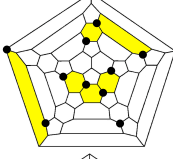
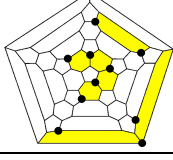
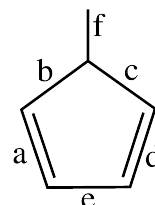
compound ^{53,54}	abbreviations	Schlegel diagrams
1,4,10,19,25,41,49,60,66,69- $C_{70}(C_2F_5)_{10}$ -I	70-10-1-C_2F_5	
1,4,11,19,31,41,46,55,62,67- $C_{70}(C_2F_5)_{10}$ -VII	70-10-8-C_2F_5	
1,4,11,19,23,31,44,55,57,67- $C_{70}(C_2F_5)_{10}$ -IV	70-10-9-C_2F_5	
1,4,11,33,38,46,53,55,62,64- $C_{70}(C_2F_5)_{10}$ -II	70-10-10-C_2F_5	
1,4,11,24,33, 38,43,48,53,55- $C_{70}(C_2F_5)_{10}$ -III	70-10-11-C_2F_5	
1,4,23,28,33,38,44,46,53,55- $C_{70}(C_2F_5)_{10}$ -V	70-10-12-C_2F_5	
1,4,11,33,38,46,48,53,55,62- $C_{70}(C_2F_5)_{10}$ -VI	70-10-13-C_2F_5	
1,4,11,24,33,38,43,53,55,64- $C_{70}(C_2F_5)_{10}$ -VIII	70-10-14-C_2F_5	
1,11,16,18,33,46,48,54,62,68- $C_{70}(C_2F_5)_{10}$ -IX	70-10-15-C_2F_5	

Table 2.5. Comparison of structural models of **70-10-8-C₂F₅** isomer.

	ref. ⁵³	before twin refinement	after twin refinement
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a , Å	19.465(1)	19.504(1)	19.507(1)
b , Å	16.290(1)	16.413(1)	16.413(1)
c , Å	20.626(3)	20.864(2)	20.857(1)
β , deg	98.860(4)	98.246(5)	98.237(3)
Z	4	4	4
volume, Å ³	6462(1)	6609.1(6)	6609.1(6)
$d(\text{calc})$, g cm ⁻³	2.087	2.041	2.041
data/parameters	5701/912	9502/1243	19805/1320
R_1 [$I \geq 2\sigma(I)$]/ wR_2 (all)	0.153/0.355	0.173/0.474	0.078/0.203
$\Delta\rho$ (max/min), e Å ⁻³	0.616/−0.556	3.59/−1.37	1.73/−0.68
e.s.d. (C–C, C–F), Å	0.017–0.030	0.019–0.020	0.007–0.008

Table 2.6. X-ray C–C bond distances in the cyclopentadiene pentagon in the structures of **70-12-5-C₂F₅**, C₆₀(C₂F₅)₄O, C₆₀(CF₃)₄O, and **60-10-4**.

bond type, Å	C ₇₀ (C ₂ F ₅) ₁₂ this work	C ₆₀ (C ₂ F ₅) ₄ O ⁶⁵	C ₆₀ (CF ₃) ₄ O ⁶⁵	C ₆₀ (CF ₃) ₁₀ ³²
a	1.354(4)	1.358(7)	1.342(5)	1.347(3)
b	1.542(4)	1.481(7)	1.482(5)	1.534(3)
c	1.545(3)	1.476(4)	1.481(5)	1.530(3)
d	1.343(4)	1.361(7)	1.353(5)	1.344(3)
e	1.479(4)	1.496(7)	1.480(5)	1.481(3)
f	1.506(4)	1.511(7)	1.488(6)	1.508(3)



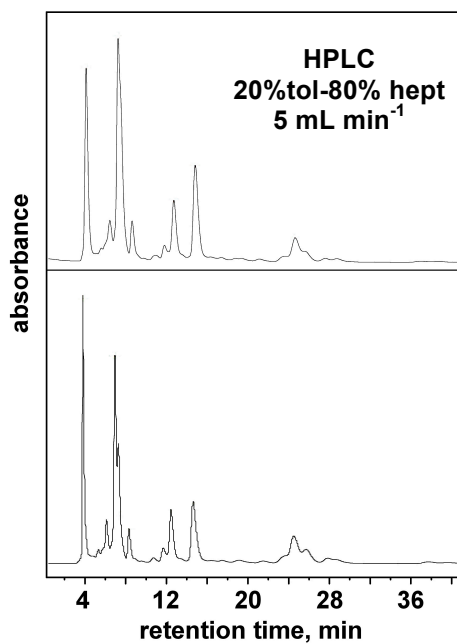


Figure 2.1. HPLC traces of the products obtained in the C_{60}/CF_3I reaction at 500 °C during 12 (top) and 2 hours (bottom).

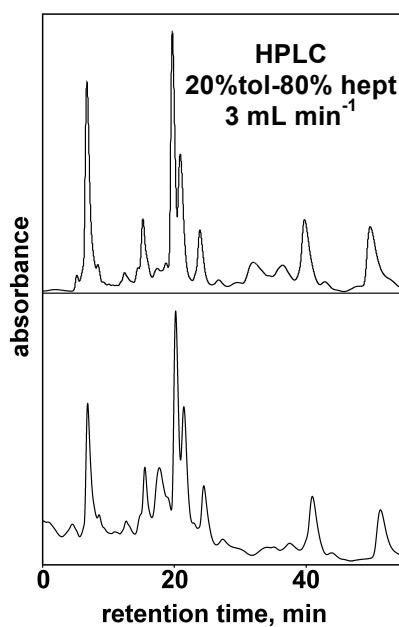


Figure 2.2. HPLC traces of the products obtained in the two identical reactions of C_{60} with CF_3I at 520 °C (3 hours).

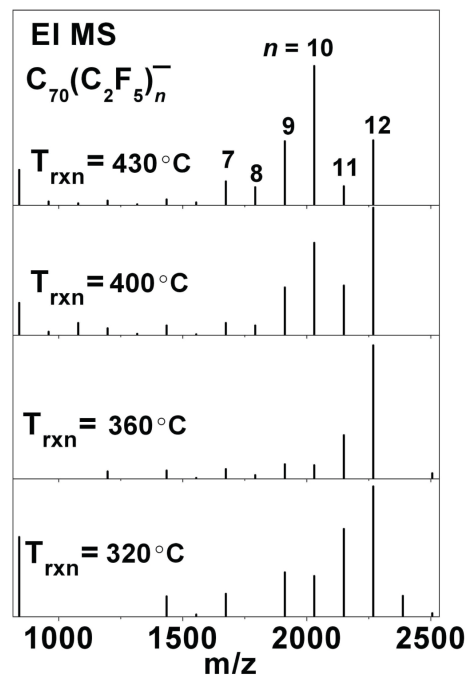


Figure 2.3. EI mass spectra of the crude products obtained in the C_{70}/C_2F_5I reactions at 320–430 °C.

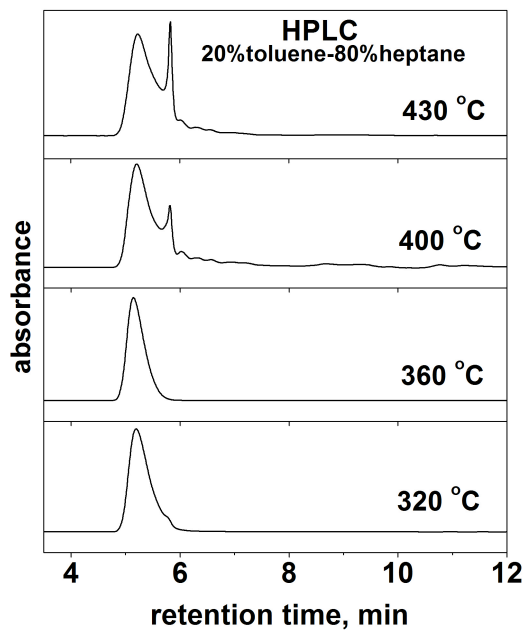


Figure 2.4. HPLC traces of the crude, cold-zone condensed products of the reactions of C_{70} with C_2F_5I at different temperatures.

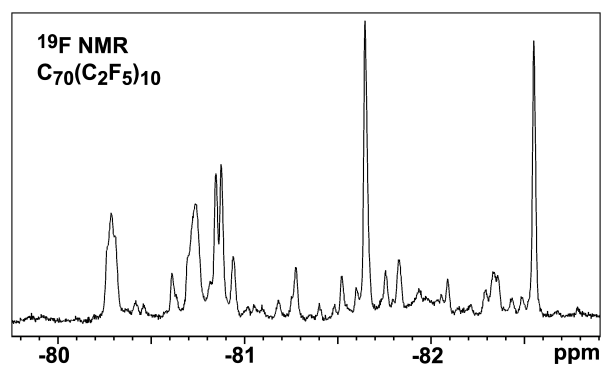


Figure 2.5. Fluorine-19 NMR spectrum of **70-10-8-C₂F₅** (chloroform-*d*, 376.5 MHz)

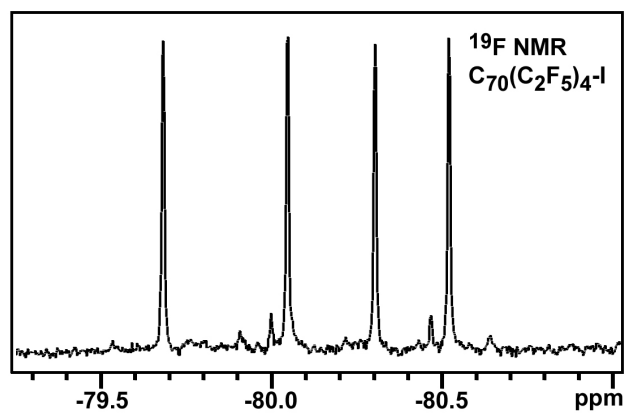


Figure 2.6. Fluorine-19 NMR spectrum of C₇₀(C₂F₅)₄-I, (toluene-*d*⁸, 376.5 MHz)

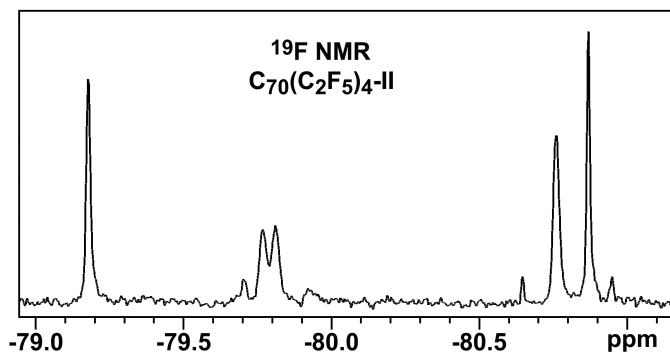


Figure 2.7. Fluorine-19 NMR spectrum of C₇₀(C₂F₅)₄-II, (toluene-*d*⁸, 376.5 MHz)

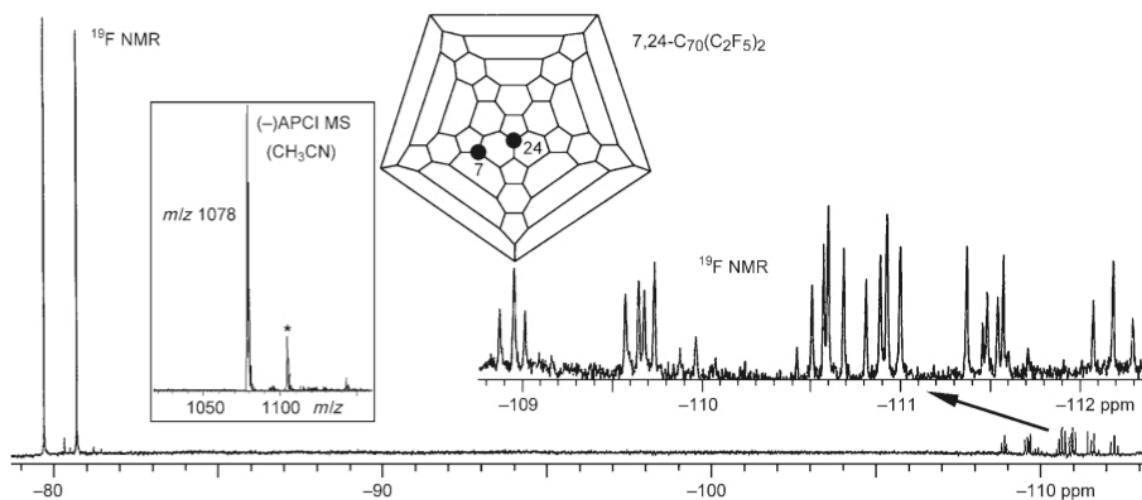


Figure 2.8. The ^{19}F NMR spectrum of HPLC-purified $7,24\text{-C}_{70}(\text{C}_2\text{F}_5)_2$ (376.5 MHz, toluene- d^8 , 25 °C, C_6F_6 int. std. (δ -164.9 ppm)). The CF_3 region near δ -80 exhibits a sharp singlet for each of the two unique CF_3 groups. The CF_2 region δ -108 to -113 is also shown expanded for clarity (middle, right). The inset (middle, left) shows the negative-ion APCI mass spectrum of the purified sample; the asterisk denotes a peak at 1104 Da due to a cyano-adduct of the compound. A numbering scheme (top, center) is shown for clarity.

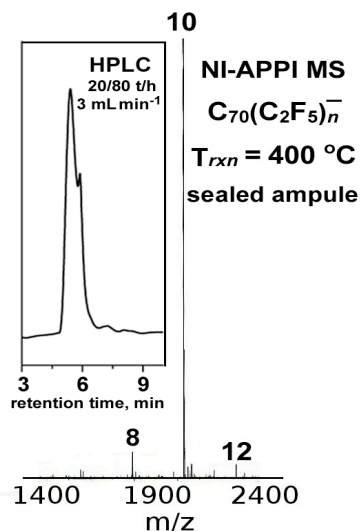


Figure 2.9. NI-APPI mass spectrum and HPLC trace (20:80 (v:v) toluene/heptane eluent) of the $\text{C}_{70}(\text{C}_2\text{F}_5)_n$ ($n = 8, 10, 12$) products prepared at 400 °C in a sealed glass ampoule for 24 h.

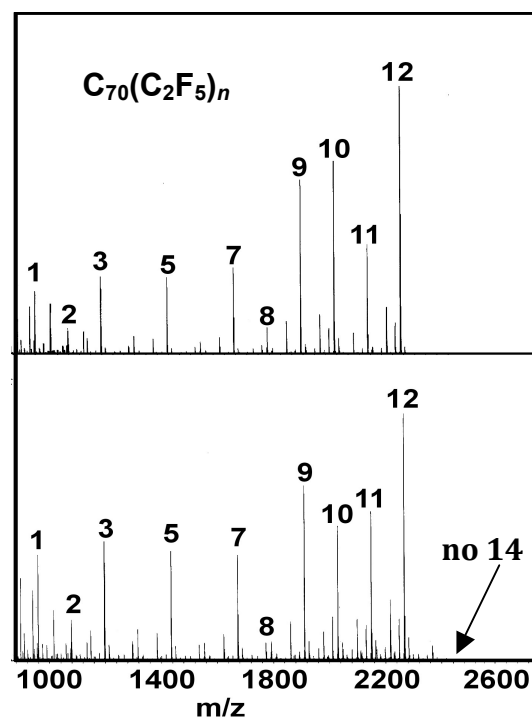


Figure 2.10. The EI mass spectra of the products of two reactions:
 (top) $C_{70} + C_2F_5I$ at 400 °C (6 h); (bottom) $C_{70}(C_2F_5)_n + C_2F_5I$ at 300 °C (4 h).

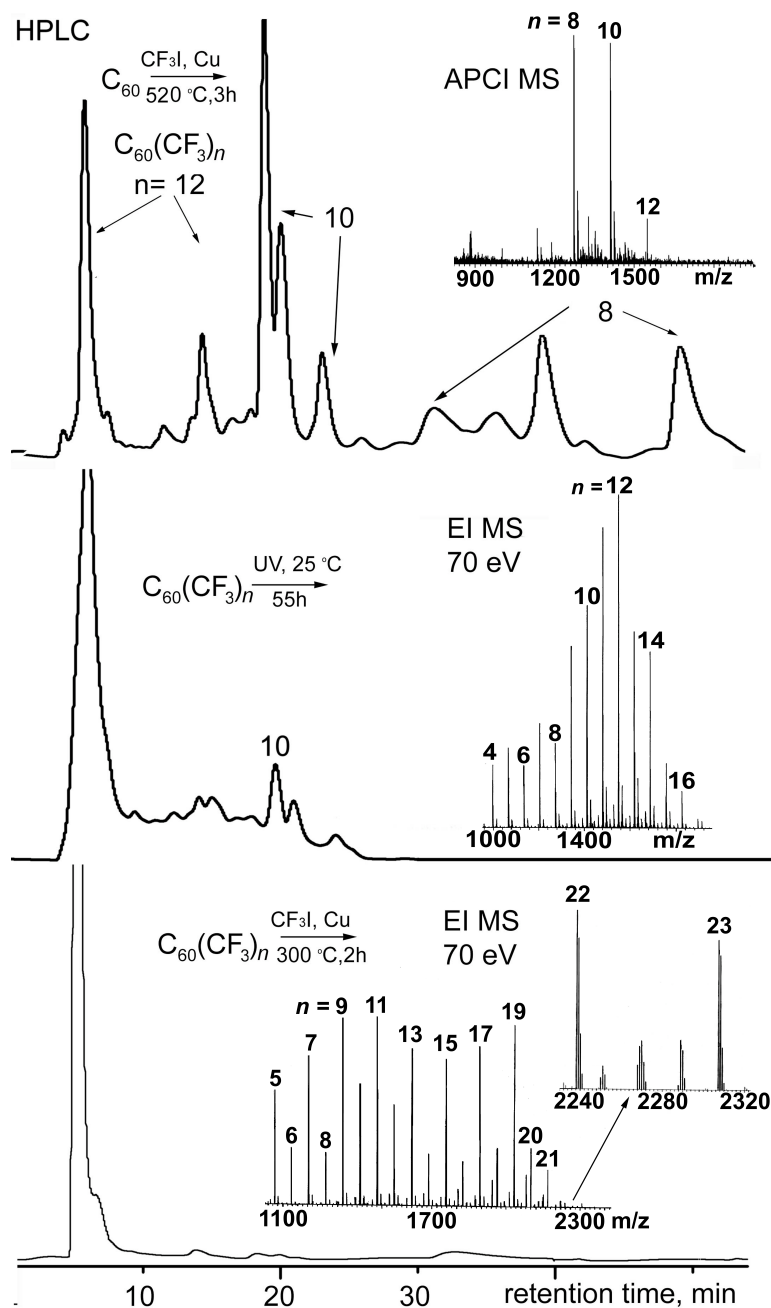


Figure 2.11. (top) HPLC trace and APCI mass spectrum of the C_{60}/CF_3I reaction at $520^\circ C$ for 3 h; (middle) HPLC trace and EI mass spectrum (70 eV) of the product of trifluoromethylation of $C_{60}(CF_3)_n$ ($n = 8, 10, 12$) under UV irradiation at room temperature; (bottom) HPLC trace and EI mass spectrum (70 eV) of the product of $C_{60}(CF_3)_n$ ($n = 8, 10, 12$) trifluoromethylation at $300^\circ C$ in a hot tube.

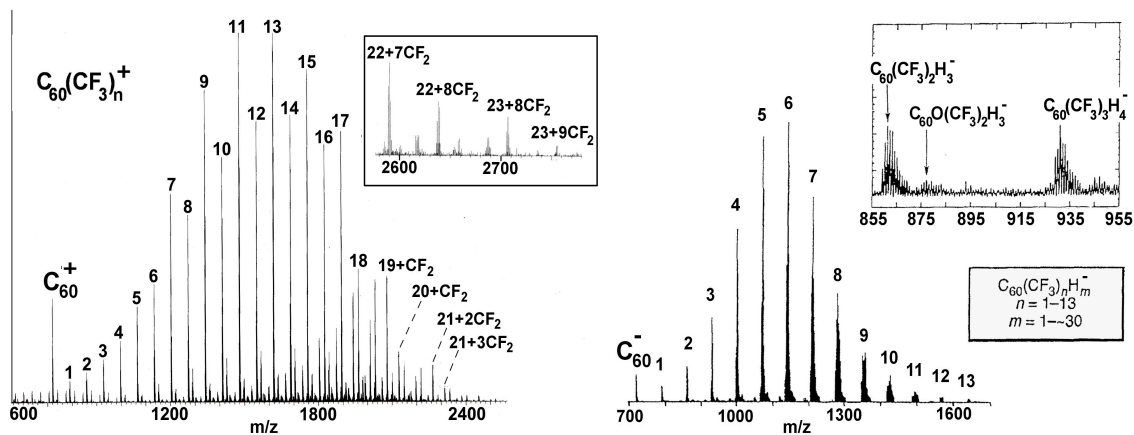


Figure 2.12. EI mass spectrum (70 eV) of the product of the reaction of C_{60} with CF_3I under UV irradiation in hexafluorobenzene (left) and electron capture mass spectrum of the product of the UV reaction of C_{60} with CF_3I in benzene solution.⁶⁵ (right)

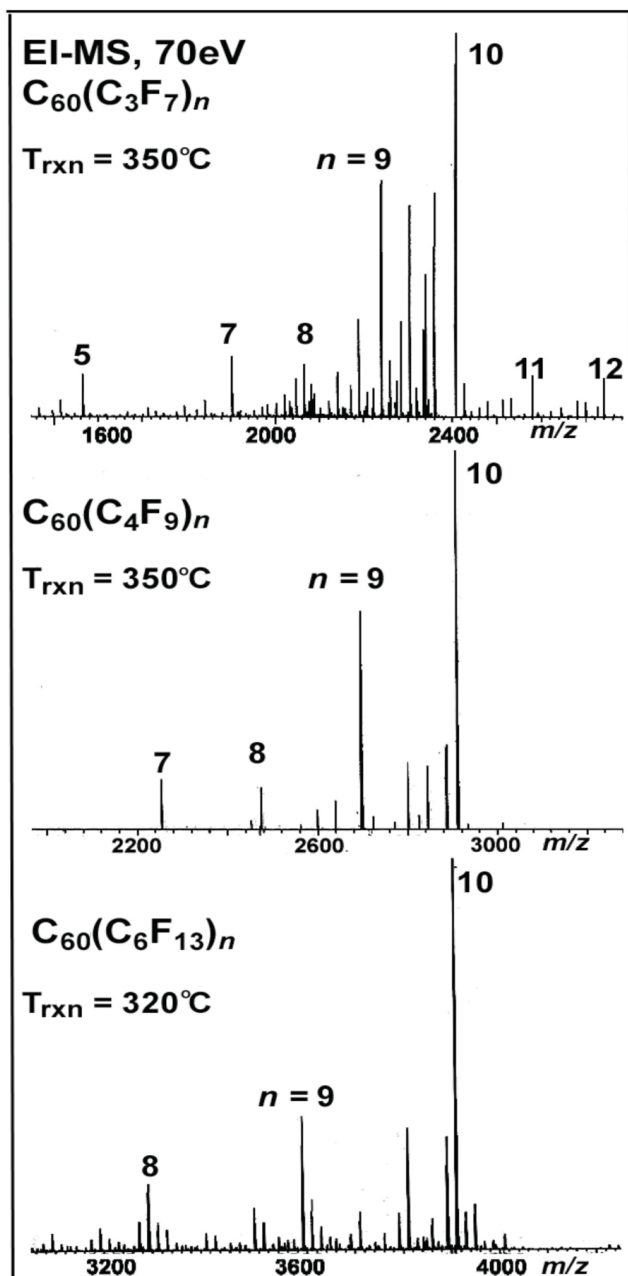


Figure 2.13. EI mass spectra of the products obtained in the reactions of C_{60} and $n-C_3F_7I$ at $350^\circ C$ for 7 h (top), $n-C_4F_9I$ at $350^\circ C$ for 4 h (middle), and $n-C_6F_{13}I$ at $350^\circ C$ for 5.5 h (bottom).

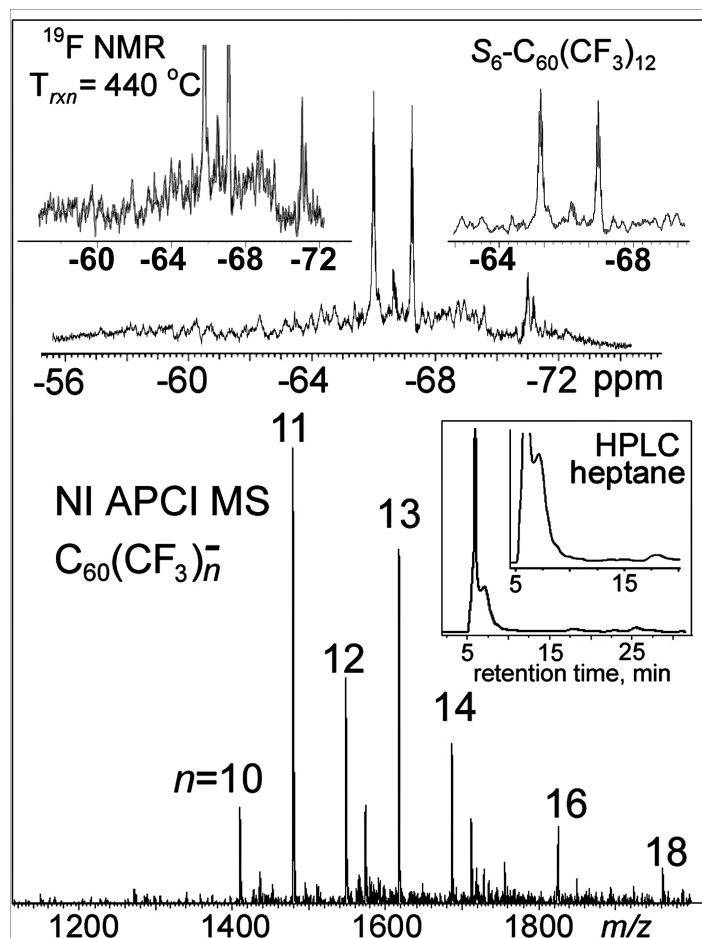


Figure 2.14. (top) Fluorine-19 NMR spectrum of the $\text{C}_{60}(\text{CF}_3)_n$ product obtained at 440 °C for 48 h in a sealed ampoule (the inset on the left is an expansion). The inset on the right shows ^{19}F NMR spectrum of the purified $\text{S}_6\text{-C}_{60}(\text{CF}_3)_{12}$. (bottom) NI-APCI MASS SPECTRUM of the same product and (inset) its HPLC trace (100% heptane, 3 mL min $^{-1}$ flow rate).

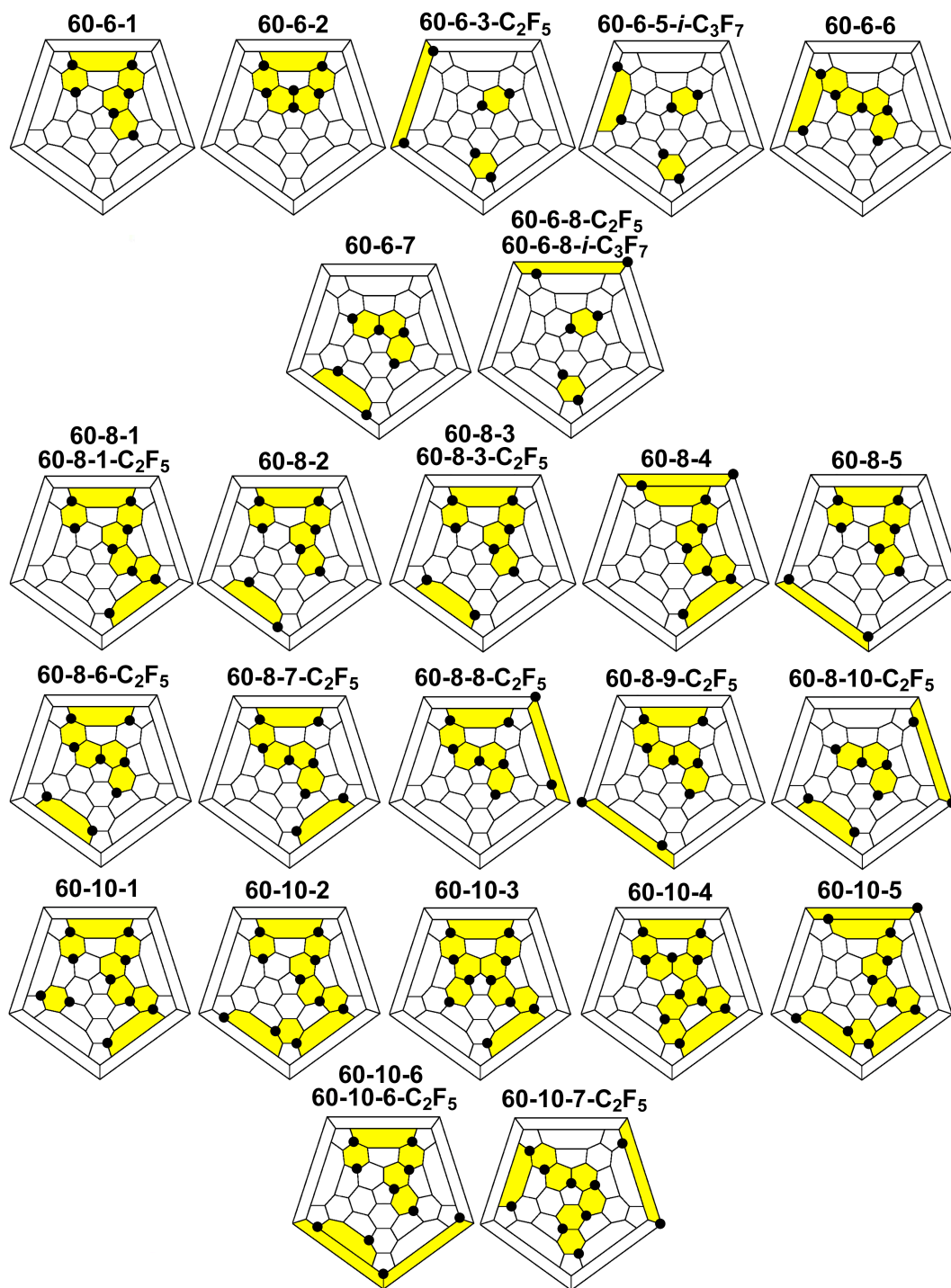


Figure 2.15. Schlegel diagrams of isomers of $C_{60}(CF_3)_{6,8,10}$ and $C_{60}(C_2F_5)_{6,8,10}$ with the known structures (X-ray crystallography or ^{19}F NMR spectroscopy). Black dots represent the addition site of R_F group. Yellow-filled hexagons represent hexagons with added R_F groups.

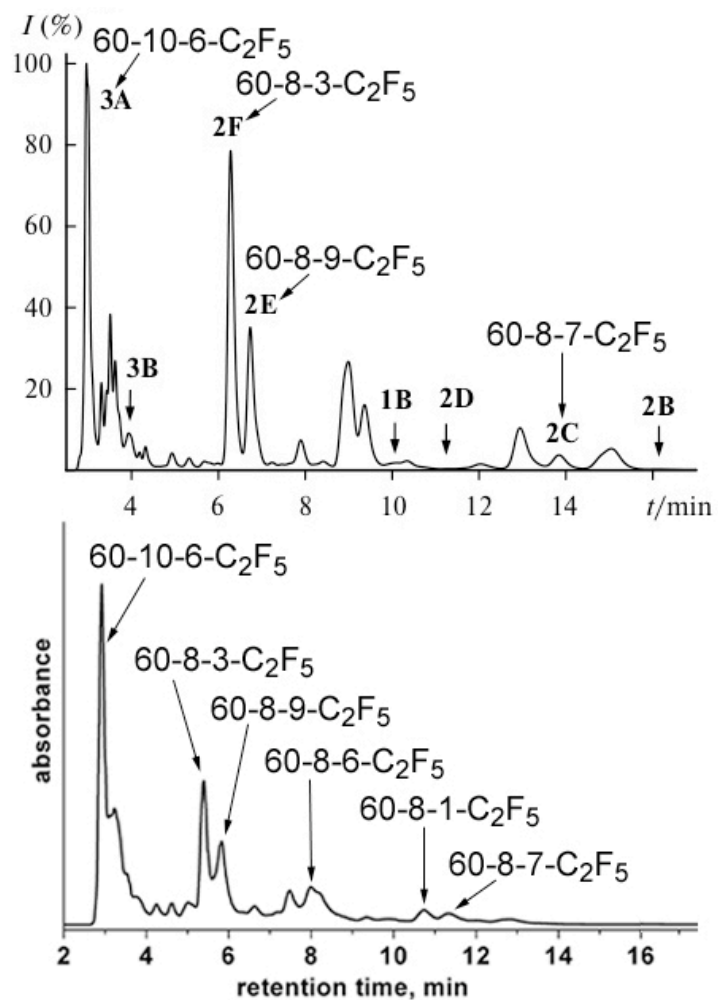


Figure 2.16. HPLC traces of the $C_{60}(C_2F_5)_n$ ($n = 6, 8, 10$) products obtained in C_{60}/C_2F_5I reactions at 380–390 °C (top,⁵³) and in the present work at 400 °C (bottom).

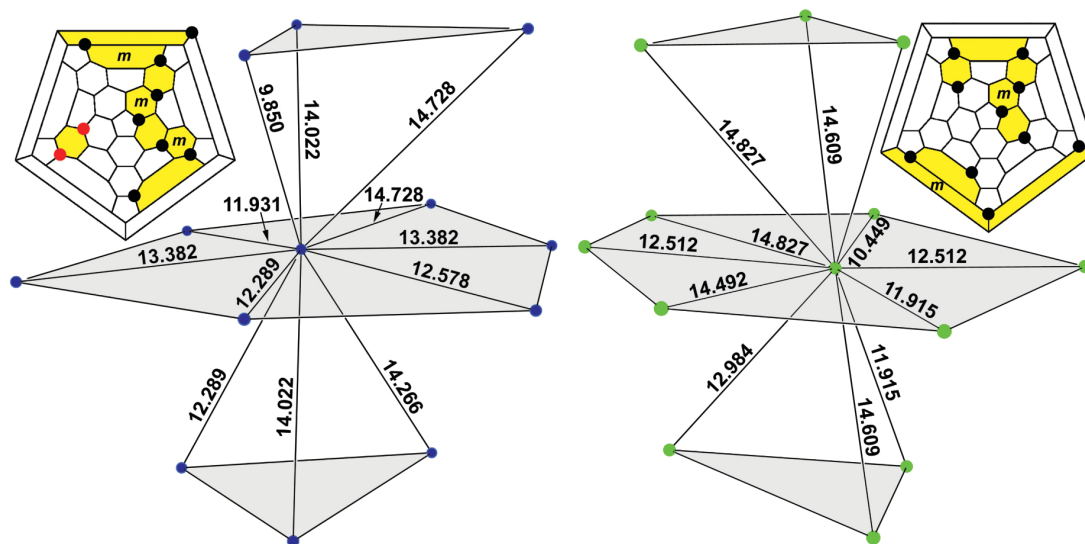


Figure 2.17. Schlegel diagrams and packing of **60-10-7-C₂F₅** (left) and **60-10-6-C₂F₅** (right) isomers. On the Schlegel diagram of **60-10-7-C₂F₅** black dots represent the addition pattern of **60-8-4** isomer as a sub-pattern. For both isomers, each C₆₀(C₂F₅)₁₀ molecule is surrounded by six molecules in one layer and by three ones in the top and bottom layers which leads to formation of distorted cubic close packing. The distances between neighboring molecules are shown. The blue and green dots on the picture represent centroids of C₆₀(C₂F₅)₁₀ molecules.

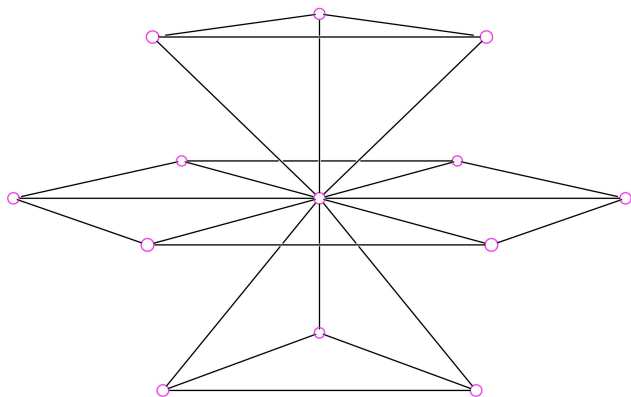


Figure 2.18. **60-10-6** molecules form hexagonal closed packed lattice. One $C_{60}(CF_3)_{10}$ molecule has six neighbors in the same layer, three ones in the layer above and three molecules the layer below.⁶⁷ The pink dots on the picture represent centroids of **60-10-6** molecules.

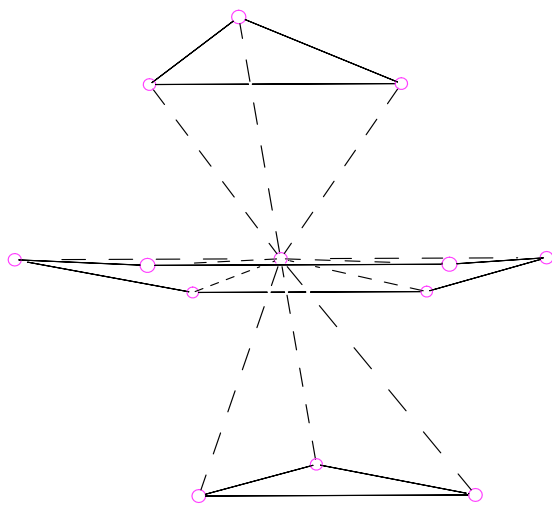


Figure 2.19. Each **60-10-3** molecule is surrounded by six molecules in one layer and by three ones in the top and bottom layers which leads to formation of distorted cubic close packing.³⁸ The pink dots on the picture represent centroids of **60-10-3** molecules.

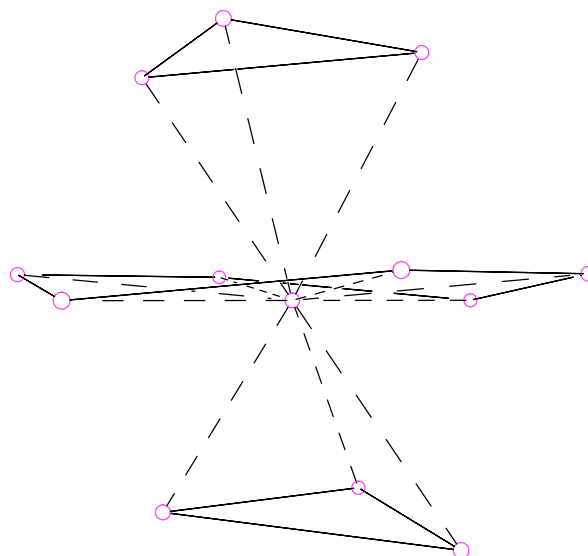


Figure 2.20. Each $C_{60}(C_2F_5)_{10}$ (**60-10-4**) molecule is surrounded by six molecules in one layer and by three ones in the top and bottom layers which leads to formation of distorted cubic close packing.⁵⁰ The pink dots on the picture represent centroids of **60-10-4** molecules.

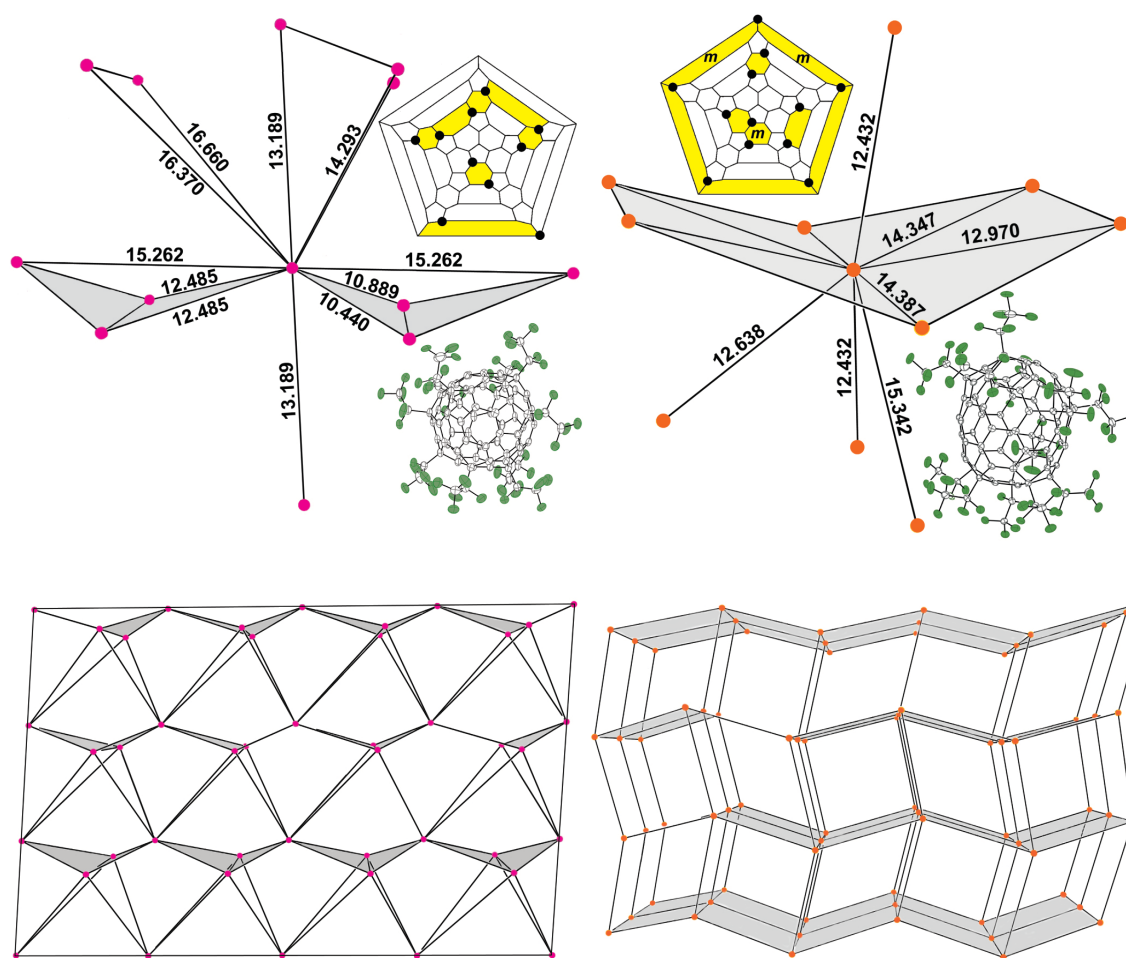


Figure 2.21. (top) Crystal packing diagrams, Schlegel diagrams, and X-ray crystal structures (50 % probability ellipsoids) of **70-10-8-C₂F₅** (left) and **70-12-5-C₂F₅** (right) isomers. The distances between fullerene cage centroids of the neighboring molecules are shown. (bottom) C₇₀(C₂F₅)₁₀ (left) and C₇₀(C₂F₅)₁₂ (right) molecules form puckered layers. The pink and orange dots are the centroids of the fullerene cages in **70-10-8-C₂F₅** (left) and **70-12-5-C₂F₅** (right) structures, respectively.

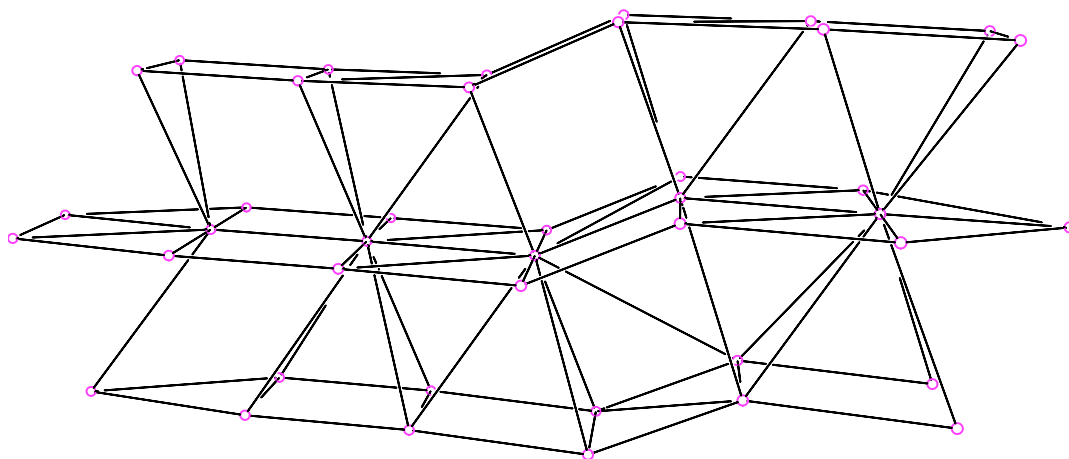


Figure 2.22. **70-10-9- C_2F_5** molecules (isomer IV in ref.⁵³) form pucker layers. The pink dots are the centroids of **70-10-9- C_2F_5** molecules.

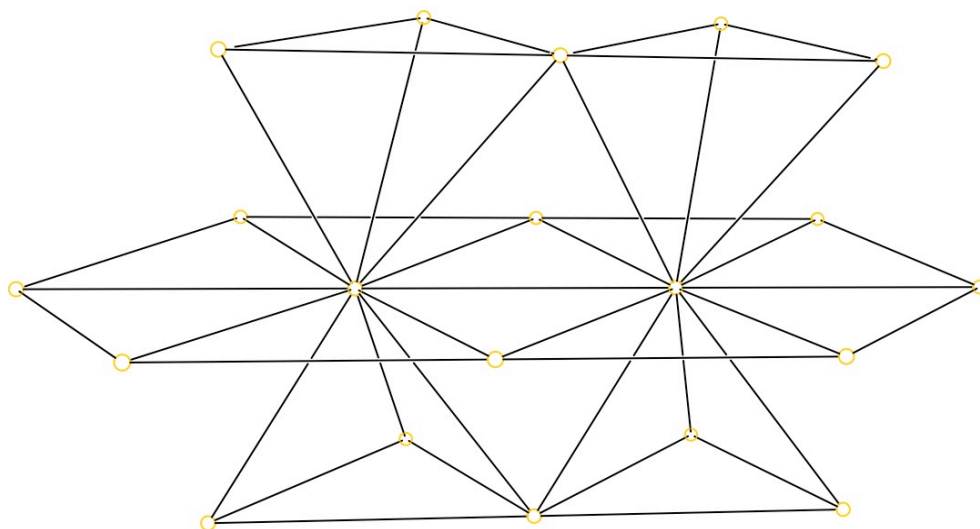


Figure 2.23. A distorted hexagonal closed packing is formed by stacking of the *ABAB* packed layers of **70-10-11- C_2F_5** molecules (isomer III in ref.⁵³). The yellow dots are the centroids of **70-10-11- C_2F_5** molecules

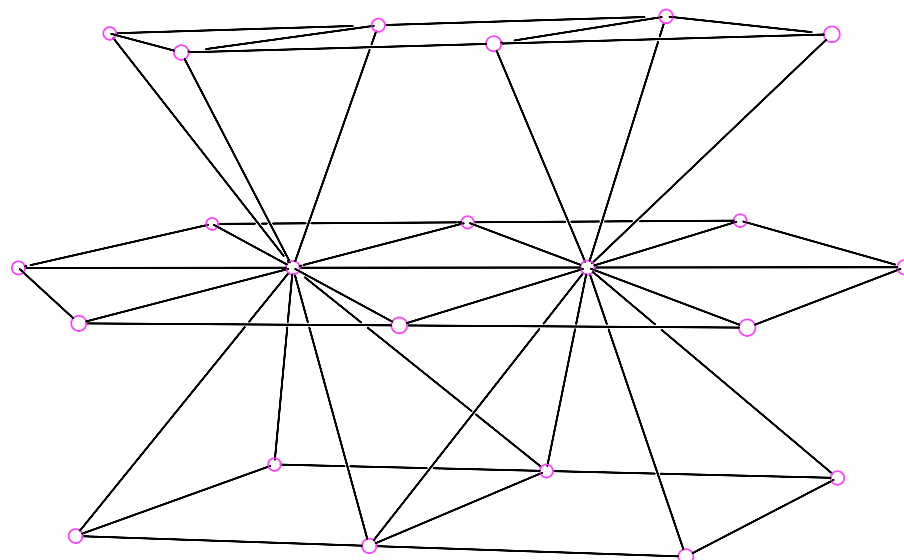


Figure 2.24. 70-10-13-C₂F₅ molecules (isomer VI in ref.⁵³) form layers. The pink dots are the centroids of 70-10-13-C₂F₅ molecules.

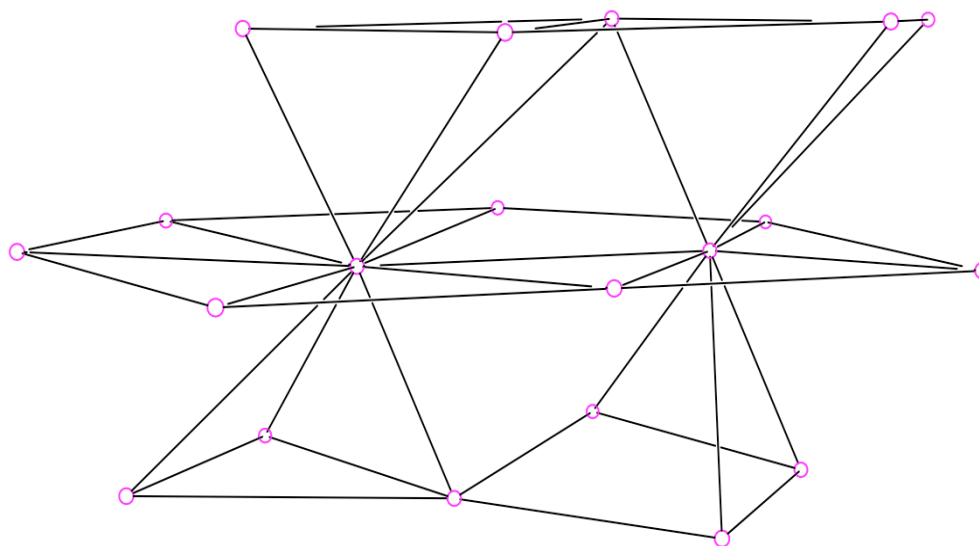


Figure 2.25. 70-10-15-C₂F₅ molecules (isomer IX in ref.⁵⁴) form puckered layers. The pink dots are the centroids of 70-10-15-C₂F₅ molecules.

CHAPTER 3. SYNTHESIS, STRUCTURES AND ELECTROCHEMICAL PROPERTIES OF PERFLUOROISOPROPYLFULLERENES

Introduction

Fullerene acceptor materials play increasingly important role in organic molecular electronics.⁶⁸ One of the active areas of research is the development of new components for organic photovoltaics. The need for more efficient small-gap polymers and new fullerene-based electron acceptors with the wide range of electronic properties has recently driven activity of synthetic and physical organic chemists in this field.^{68,69} Based on the studies of over forty TMF compounds it was shown that their redox properties are mainly determined by their addition patterns rather than by the number of addends.³²

It is well known that perfluoroalkyl iodides, which are easily cleaved by light or heat with following formation of perfluoroalkyl radicals, can be used for the preparation of fullerene(R_F)_n compounds.^{34,38,51} The increase in steric bulk of the perfluoroalkyl groups may lead to formation of very stable radicals, as was observed in case of the Scherer radical, which possesses an incredible stability is due to the steric effects.^{70,71} The bulkiness of the attacking radicals may also have a great influence on the rate of addition which was confirmed by the kinetic studies of the reaction between β -methylstyrene and a number of perfluoroalkylated radicals such as CF_3 , C_2F_5 , $n-C_3F_7$, $i-C_3F_7$, and $t-C_4F_9$.⁷¹ It was shown that the smallest steric effect was observed for CF_3 radicals, while it became greater for long and branched ones.⁷¹ In case of fullerene perfluoroalkylation, the

replacement of CF_3 by a larger attacking radical (e.g., $i\text{-C}_3\text{F}_7$) is expected to result in the formation of fundamentally new addition patterns due to the different steric requirements of the bulkier group. The X-ray crystal structure of $\text{C}_{60}(i\text{-C}_3\text{F}_6)_6$ demonstrated that the use of the bulkier $i\text{-C}_3\text{F}_6$ group resulted in a different addition pattern than observed in either isomer of $\text{C}_{60}(\text{CF}_3)_6$.⁵² Thus, the main goal of this work was the development of synthetic techniques for the preparation of fullerene($i\text{-C}_3\text{F}_7$)_n compounds and their isolation, and characterization, including the study of their electron-accepting properties.

In this chapter, a new group of thermally and chemically stable exohedral fullerene derivatives, fullerene($i\text{-C}_3\text{F}_7$)_n, that possess superior electron acceptor properties than C_{60} and even many recently studied trifluoromethylfullerenes (TMFs) will be discussed. The comparison of different synthetic procedures for synthesis of fullerene($i\text{-C}_3\text{F}_7$)_n derivatives and discussion of the obtained $\text{C}_s\text{-C}_{60}(i\text{-C}_3\text{F}_6)_2$, $\text{C}_2\text{-C}_{60}(i\text{-C}_3\text{F}_6)_4$, $\text{C}_1\text{-C}_{60}(i\text{-C}_3\text{F}_6)_4$, $\text{C}_1\text{-C}_{60}(i\text{-C}_3\text{F}_6)_6$, $\text{C}_3\text{-C}_{60}(i\text{-C}_3\text{F}_6)_6$, and $\text{C}_s\text{-C}_{60}(\text{CF}_3)_2(i\text{-C}_3\text{F}_6)_2$ X-ray crystal structures will be given in detail. This work has been accepted for publication and is now in press.⁷²

3.1. Experimental Section

3.1.1. Reagent and solvents. The reagents and solvents $i\text{-C}_3\text{F}_7\text{I}$ (Apollo Scientific, 98% or SynQuest, 97%), C_{60} and C_{70} (Term USA), hexafluorobenzene (Sigma-Aldrich), heptane and toluene for HPLC purification (Sigma-Aldrich), chloroform-*d* (Chembridge Isotopes) were used as received.

3.1.2. Synthesis of $\text{C}_{60}(i\text{-C}_3\text{F}_7)_n$ and $\text{C}_{70}(i\text{-C}_3\text{F}_7)_n$ derivatives. Three methods of preparation of $\text{C}_{60}(i\text{-C}_3\text{F}_7)_n$ and $\text{C}_{70}(i\text{-C}_3\text{F}_7)_n$ derivatives were developed in this work

which include reactions under UV-vis irradiation, in a hot flow tube, and in a sealed glass ampoule (see Tables 3.1 and 3.2).

In typical UV-vis experiments, a finely ground C_{60} or C_{70} (5–30 mg, 0.007–0.042 or 0.006–0.036 mmol), $i\text{-}C_3F_7I$ (0.5 mL, 6.2 mmol), and toluene (0.5 mL) or hexafluorobenzene (0.5 mL) were placed in the thin glass tube (I.D. = 5 mm). The tubes with the samples were exposed under UV-vis radiation at room temperature during 21 h or 7 days.

In the reactions, which were performed in a heated quartz tube, C_{60} (or C_{70}) (50–100 mg, 0.069–0.139 mmol (or 0.060–0.119 mmol)) was mixed with the fine copper powder (500 mg, 7.87 mmol). Nitrogen gas was bubbled through the liquid perfluoroalkylating agent ($i\text{-}C_3F_7I$) which was delivered to the hot reaction zone (320–500 °C). The reaction time was varied from 2 to 9 hours (see Table 3.1).

The syntheses in the sealed glass ampoules were carried out at 290–416 °C during 24 h in which 20–50 mg (0.028–0.069 mmol) of C_{60} and 1 mL (12.4 mmol) $i\text{-}C_3F_7I$ were used (see Table 3.1).

The preparation of $C_{60}(n\text{-}C_3F_7)_n$ and $C_{70}(n\text{-}C_3F_7)_n$ compounds was performed in a hot flow tube and sealed glass ampoules. In typical experiment in a hot flow tube, 50–100 mg (0.069–0.139 mmol) of C_{60} and 100 mg of C_{70} (0.119 mmol) were used. $n\text{-}C_3F_7I$ was delivered in the hot reaction zone (350–380 °C) using the same procedure as in case of $i\text{-}C_3F_7I$. The reaction time was varied from 7 to 13 hours. Details of the experiments are given in Table 3.2.

3.1.3. Isolation of $C_{60}(i\text{-}C_3F_7)_n$ and $C_{60}(i\text{-}C_3F_7)_n(CF_3)_m$ Derivatives. $C_{60}(i\text{-}C_3F_7)_n$ products was purified by HPLC (10 mm i.d. × 250 mm long Cosmosil Buckyprep

column (Nacalai Tesque, Inc.), 300 nm UV detector). First, separation of the $C_{60}(i-C_3F_7)_n$ crude samples obtained in a sealed glass ampoule (290 °C) was done in toluene as an eluent at 5 mL min⁻¹ flow rate. Three different fractions 2.9 min (**I**), 3.6 min (**II**), 5.6 min (**III**), and 6.3 min (**IV**) were isolated. Subsequent purification of **III** and **IV** fractions using 100% toluene as an eluent at 5 mL min⁻¹ flow rate resulted in the isolation of pure $C_{60}(i-C_3F_7)_2$ (5 min) and $C_{60}(i-C_3F_7)(CF_3)$ (5.8 min) compounds. The mixture of 10:90 (v:v) toluene/heptanes was used as eluent to perform the further purification of **I** and **II** fractions. As a result, three pure fractions (retention times shown in parenthesis) such as $C_{60}(i-C_3F_7)_4$ (8.5 min), $C_{60}(i-C_3F_7)_4$ (11.2 min), and **60-4-5-C₃F₇** (11.8 min) were isolated from fractions **I** and **II**. The rest of fractions **I** and **II** were finally purified in 100% heptane (at 5 mL min⁻¹ flow rate) to yield the following pure isomers: $C_{60}(i-C_3F_7)_6$ (3.4 min), **60-6-9-C₃F₇** (4.5 min), $C_{60}(i-C_3F_7)_6$ (5.0 min), **60-6-5-C₃F₇** (5.8 min), $C_{60}(i-C_3F_7)_4$ (13.7 min from 8.5 min using 10:90 toluene/heptane as the eluent), **60-4-4-C₃F₇** (17.3 min), $C_{60}(i-C_3F_7)_4$ (21.5 min), and **60-4-5-C₃F₇** (23 min).

Two isomers of $C_{60}(i-C_3F_7)_2(CF_3)_2$ were isolated from the sample that was obtained in a hot flow tube at 320 °C. First purification was performed in 100% toluene at 5 mL min⁻¹ flow rate with following isolation of 3.5 min fraction. For the second step, a toluene/heptane mixture (60:40 (v:v)) was used as the eluent, which allowed for the isolation of two isomers that eluted at 5.7 min and 7.0 min.

3.1.4. X-ray Crystallography. X-ray diffraction data from crystals of $C_s-C_{60}(i-C_3F_7)_2$ (**60-2-1-C₃F₇**) were collected at 150 K on a D8 goniostat equipped with a Bruker APEXII CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to $\lambda = 0.7749$ Å. The

series of 3 s data frames measured at 0.2° increments of ω were collected to calculate a unit cell. For data collection frames were measured for a duration of 3 s at 0.3° intervals of ω with a maximum 2θ value of $\sim 60^\circ$. Two superimposed C_{60} cage orientations were found for $C_s-C_{60}(i-C_3F_7)_2$. The main cage orientation was located after several cycles of refinement. The minor one was treated as a rigid group with the same geometry as a major one. These orientations refined to fractional occupancies of 83% and 17%, as shown in Figure 3.4. The minor component is related to the major one by a mirror plane which contains two C1–C201 and C1A–C201A bonds. Notably, this symmetry operation does not move the C1–C2–C2A–C1A–C9A–C9 hexagon with the attached $i-C_3F_7$ groups. The displacement parameters of the overlapping atoms in both cages were constrained to be equal.

X-ray diffraction data from crystals of $C_2-C_{60}(i-C_3F_7)_4$ (**60-4-4- C_3F_7**) and $C_1-C_{60}(i-C_3F_7)_4$ (**60-4-5- C_3F_7**) (grown by slow evaporation from a saturated toluene and benzene solution, respectively) were recorded on a Bruker Kappa APEX II CCD diffractometer employing Mo $K\alpha$ radiation (graphite monochromator). The rotational disorder of two $i-C_3F_7$ groups in **60-4-4- C_3F_7** structures was successfully modeled. The site-occupancy factors of the two modeled orientations for the $i-C_3F_7$ groups in **60-4-4- C_3F_7** structure attached to the C28 and C31 were 89/11% and 58/42%, respectively.

In the structure of **60-4-5- C_3F_7** , the site occupancy factors for the four disordered $i-C_3F_7$ groups which attach to C1, C7, C36, and C39 cage carbon atoms are 88/12%, 81/19%, 85/15%, and 89/11%, respectively. In addition, the two C_{60} cage orientations have been refined to have fractional occupancies 86% and 14%.

The crystals of $C_1-C_{60}(C_3F_7)_6$ (**60-6-9- C_3F_7**), $C_s-C_{60}(CF_3)_2(i-C_3F_7)_2$, and $C_s-C_{60}(CF_3)_4O$ compounds were grown by slow evaporation of the saturated toluene solutions. The diffraction-quality single crystal was mounted in paratone oil on a glass fiber rod glued to a small copper wire. X-ray diffraction data were collected at ChemMatCARS (CARS = Consortium for Advanced Radiation Sources) sector 15-B at the Advanced Photon Source (Argonne National Laboratory). The data set was collected at 100 K using a diamond (111) crystal monochromator at a wavelength of 0.4428 Å. Data were recorded using a Bruker CCD (charge-coupled device) detector. Absorption and other corrections were applied by using SADABS.²⁰ The site-occupancy factors of the two modeled orientations for the one disordered $i-C_3F_7$ group in **60-6-9- C_3F_7** structure were 86% and 0.14%.

The brown crystals of $C_s-C_{60}(CF_3)_2(i-C_3F_7)_2$, $C_3-C_{60}(C_3F_7)_6$ (**60-6-5- C_3F_7**), and $C_s-C_{60}(CF_3)_4O$ compound were grown from saturated heptane/toluene solution. The X-ray diffraction data were recorded on a Bruker Kappa APEX II CCD diffractometer employing Mo K α radiation (graphite monochromator).

All structures were solved by using direct methods and 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 control and integration software (APEX II) was employed, and Bruker SHELXTL²¹ software was used for structure solution, refinement, and graphics. Selected details related to the crystallographic experiments are listed in Tables 3.4 and 3.5.

3.1.5. Spectroscopic Measurements. Atmospheric-pressure chemical-ionization (APCI) and atmospheric pressure photo-ionization (APPI) mass spectra were recorded

using a ThermQuest Finnagan LCQ-DUO spectrometer (acetonitrile eluent, 0.3 mL·min⁻¹ flow rate) and Agilent Technologies Model 6210 TOF with APPI spectrometer. In latter case, flow injection was done using acetonitrile which contained 1% toluene. Samples for ¹⁹F NMR spectroscopy were chloroform-*d* solutions containing a small amount of hexafluorobenzene as an internal standard (δ -164.9). Spectra were recorded using a Varian INOVA-unity 400 spectrometer operating at 367.45 MHz.

Electrochemical measurements were performed by graduate student James B. Whitaker (CSU) and/or Dr. Alexey A. Popov (Institute for Solid State Research, Dresden, Germany). Cyclic voltammetry was carried out in a glovebox (water and oxygen content below 1 ppm) in one-compartment electrochemical cell. The electrolyte solution was 0.1 M N(*n*-Bu)₄BF₄ (TBABF₄) in *o*-dichlorobenzene. Platinum wire, platinum wire loop and a silver wire served as working, counter, and pseudo-reference electrodes, respectively. The potentials were measured relative to the Fe(Cp)₂⁺⁰ or Fe(Cp*)₂⁺⁰ couples (i.e., either Fe(Cp)₂ or Fe(Cp*)₂ was added as an internal standard at the end of the voltammetric measurements) using a PAR 273 potentiostat/galvanostat.

3.1.6. Theoretical Calculations. Dr. A. A. Popov performed DFT calculations using PBE functional and TZ2P-quality basis set implemented by the PRIRODA package, as previously described.⁷³

3.2. Results and Discussion

3.2.1. Synthesis and Isolation. The reactions of C₆₀ or C₇₀ and *i*-C₃F₇I (*n*-C₃F₇I) were studied under different conditions which included photolytic and thermal methods of producing of iso-heptafluoropropyl radicals which lead to the formation of the

brownish-orange powders. Syntheses were carried out in a hot flow tube (320–500 °C), sealed glass ampoules (290–390 °C), and glass tubes (room temperature, UV-vis irradiation).

3.2.1.1. Hot Flow Tube Reactions. Perfluoroalkylation reactions of C_{60} and C_{70} were carried out in a hot flow tube at 320–500 °C during 2–10 hours (Tables 3.1 and 3.2). It is interesting to note that the two experiments of C_{60} using $i\text{-C}_3\text{F}_7\text{I}$ at 500 °C did not lead to any product formation. At the same time, as known from the previous studies³⁸, reactions of C_{2m} fullerenes ($m = 30\text{--}45$) using CF_3I at high temperatures (400–550 °C) in the same hot tube led to a good yield of trifluoromethylated products. For instance, trifluoromethylation of C_{60} at 500 °C led to a successful formation of $C_{60}(\text{CF}_3)_n$ derivatives ($n = 8, 10$, and 12 ; see Chapter 2).

Decreasing the $C_{60}/i\text{-C}_3\text{F}_7\text{I}$ reaction temperature to 450–480 °C led to the formation of the $C_{60}(\text{CF}_3)_n(i\text{-C}_3\text{F}_7)_m$ and $C_{60}(\text{CF}_3)_n$ derivatives listed in Table 3.1. Therefore, synthesis in this temperature range led to a decomposition of the $i\text{-C}_3\text{F}_7$ radicals with concomitant formation of CF_3 radicals and their subsequent addition to the fullerene cage.

The experiments were performed at 320 and 380 °C and yielded $C_{60}(i\text{-C}_3\text{F}_7)_n$ ($n = 6\text{--}12$) compounds, in which the most abundant ones had six and ten substituents according to mass spectrometry data. However, a significant temperature decrease did not allow us to eliminate by-products which contained CF_3 and $i\text{-C}_3\text{F}_7$ (or CF_3) groups on the carbon cage (Table 3.1). In case of C_{70} , the synthesis with $i\text{-C}_3\text{F}_7\text{I}$ at 320 °C led to formation of $C_{70}(i\text{-C}_3\text{F}_7)_n$ derivatives ($n = 8$ and 10), $C_{70}(i\text{-C}_3\text{F}_7)_{10}$ was the most abundant one among them according to mass spectral data.

For comparison with *iso*-heptafluoropropylation, the reactions of C₆₀ and C₇₀ with *n*-C₃F₇I were carried out under similar conditions at 350–380 °C. According to the mass spectral data, the C₆₀ or C₇₀ perfluoroalkylated derivatives that were formed contained up to 12 *n*-C₃F₇ groups. The most abundant negative ions in the mass spectra were C₆₀(*n*-C₃F₇)₁₀[−] and C₇₀(*n*-C₃F₇)₁₀[−].

In summary, in the reactions of C₆₀ and C₇₀ with *i*-C₃F₇I as well as *n*-C₃F₇I in a hot flow tube a use of the appropriate temperature range is a key parameter for the successful product formation. It was found that the temperature range, at which fullerene(*i*-C₃F₇)_{*n*} compounds are formed, is relatively lower in case of C₆₀/*i*-C₃F₇I system in comparison with trifluoromethylation reactions. Increase of the reaction temperature usually led to decrease of the number of attached substituents and, in some cases, degradation of *i*-C₃F₇ radicals with following formation of the compounds containing CF₃ and *i*-C₃F₇ groups.

3.2.1.2. Sealed Glass Ampoule Reactions. Based on the experience obtained in the studies of the reactions in a hot flow tube, a lower temperature range (290–390 °C) was chosen for the series of C₆₀/*i*-C₃F₇I and C₆₀/*n*-C₃F₇I syntheses in sealed glass ampoules (see Tables 3.1 and 3.2). The C₆₀/*i*-C₃F₇I reactions were carried out at 290–390 °C which led to formation of C₆₀(*i*-C₃F₇)_{*n*} where *n* varied from 2 to 8 according to MS analysis. For example, in the reaction at 290 °C no more than eight substituents were observed, and the main products contained 2, 4, 6, and 8 *i*-C₃F₇ groups according to MS and HPLC analyses (see Figure 3.1). The attempts to increase the reaction temperature above 300 °C led to a significant decrease of the yield of C₆₀(*i*-C₃F₇)_{*n*} derivatives, and finally, at 390 °C no product formation was observed (see Table 3.1). Thus, in a closed

system, such as a sealed glass ampoule, the temperature above which no product was formed, is approximately 110 °C lower than in the hot flow tube reactions. In contrast to the reaction of C₆₀ with *i*-C₃F₇I, in the C₆₀/*n*-C₃F₇I synthesis at 290 °C, a narrow product distribution was observed (Figure 3.2). According to APPI mass spectrometry and HPLC analysis, only one major product with 10 *n*-C₃F₇ groups was obtained but ¹⁹F NMR data showed several products, possibly, due to different C₆₀(*i*-C₃F₇)₁₀ isomers. A great number of different products was recently observed in the reaction of C₇₀ with *n*-C₃F₇I, which was carried out at 300–310 °C during 90 h.⁵⁶ In these C₇₀(*n*-C₃F₇)_{*n*} derivatives, where *n* varied from 2 to 10, the compounds with 8 substituents prevailed in the reaction mixture. According to HPLC and MALDI MS data, 16 different isomers of C₇₀(*i*-C₃F₇)₈ were observed in the crude sample, the four structures of which were determined by X-ray crystallography.⁵⁶

In the experiments described above, in which the homolysis of C–I bond was performed by heating, a fine copper powder was added to the reaction mixture. The idea of using a copper powder as a thermal activator for C–I bond was based on very well known process for the alkyl halides where the R–X (X = Cl, Br, and I) bond absorbed on the metal surface (Al, Fe, Co, Ni, Cu, Ru, Pd, Ag, W, and Pt) can be broken easily by thermal activation and resulted in the formation of propyl fragments and iodine atoms.^{74,75} In the present work there were two control experiments in glass sealed ampoules (290 °C) under the same reaction conditions with and without the presence of copper in the C₆₀/*i*-C₃F₇I reaction. It was shown that in the case of the absence of copper powder, yield of perfluoroalkylated fullerenes was significantly lower compared to the

$C_{60}/i\text{-C}_3\text{F}_7\text{I}$ reaction in which copper was added to the reaction mixture. This fact confirmed that copper takes an active part in the formation of $i\text{-C}_3\text{F}_7$ radicals.

In summary, the reactions of C_{60} with $i\text{-C}_3\text{F}_7\text{I}$ performed in glass ampoules have two main advantages in comparison to the syntheses in a hot flow tube. First of all, due to low temperature range, less degradation of $i\text{-C}_3\text{F}_7$ radicals and therefore, smaller amounts of by-products were observed. Second, in comparison with the reactions in a hot flow tube, a formation of the lower substituted $C_{60}(i\text{-C}_3\text{F}_7)_n$ products (even $n = 2\text{--}8$) in a sealed glass ampoule led to use existing HPLC procedures for separation and purification of the obtained derivatives.

3.2.1.3. UV Reactions at Room Temperature. Perfluoroalkyl iodides $C_n\text{F}_{2n+1}\text{I}$ ($n = 1, 3$) dissociate to form perfluoroalkyl and iodine radicals under UV irradiation.^{76,77} The preparation of perfluoroalkylated fullerenes using photodissociation at room temperature may allow one to avoid the formation of byproducts with two different radicals (i.e., CF_3 and $i\text{-C}_3\text{F}_7$) on the fullerene cage, which was observed in some of the high temperature reactions. Furthermore, different isomers with new addition patterns can be formed in comparison with the ones observed in flow tube or ampoule reactions. In addition, a UV-induced reaction may lead to a very high yield of the products which was demonstrated in the example of reaction between $n\text{-C}_3\text{F}_7\text{I}$ and electron-deficient olefins.^{71,78}

A synthesis of $C_{60}(i\text{-C}_3\text{F}_7)_n$ and $C_{70}(i\text{-C}_3\text{F}_7)_n$ compounds under UV irradiation was performed in the thin glass NMR tubes at room temperature. The brownish-orange product was obtained, and the maximum number of substituents per cage was 12 in case of $C_{60}(i\text{-C}_3\text{F}_7)_n$ and $C_{70}(i\text{-C}_3\text{F}_7)_n$ derivatives (Table 3.1 and 3.2). Despite the fact that UV-

induced reactions allowed us to eliminate the radical decomposition, the yield of the products was extremely low. The reason for this may be that the photoinitiated process can require extensive photolysis time.^{78,79} For instance, for the reactions of C_2F_5I or C_3F_7I with acetylenes or olefins under UV-light the duration of the syntheses ranges from hours to days or even weeks.^{71,78} Therefore, to increase the yield in our case, the exposure time was increased from 48 h to 7 days. Two experiments, in which reaction time was extended to 7 days, were performed. The main difference between them was an addition of the fine copper powder in one of the glass tubes, which was successfully used in thermally-induced reactions. Although according to the APPI MS data, the maximum number of the attached $i-C_3F_7$ groups in both cases (with and without copper in the reaction mixture) was 12, the yield of $C_{60}(i-C_3F_7)_n$ derivatives was significantly increased in the case of the reaction with the addition of the copper powder. Thus, it was shown that similar to the high temperature syntheses, copper plays an important role as a promoter for the formation of $i-C_3F_7$ radicals in the UV-vis perfluoroalkylation reactions.

3.2.2. Isolation and Purification of $C_{60}(i-C_3F_7)_n$ Compounds. It is known that usually the perfluoroalkylated fullerenes (PFAFs) with a high degree of substitution have lower retention time in HPLC trace in comparison with PFAFs a low degree of substitution.³² This fact was previously demonstrated by the example of HPLC separation of CF_3 and C_2F_5 compounds. The use of a bulky substituent, such as $i-C_3F_7$ group, also led to a decrease of the retention times in comparison with the trifluoromethylated derivatives with the same number of substituents on the fullerene cage. For example, different $C_{60}(i-C_3F_7)_4$ isomers have 2.9–3.6 min retention times but at the same time, $C_{60}(CF_3)_4$ compounds are eluted in toluene (at 5 mL min^{-1} flow rate) at 6 min under the

same separation conditions. The $C_{60}(i-C_3F_7)_6$ derivatives obtained in this work are eluted at 2.9 min in toluene. In contrast, trifluoromethylated compounds with six CF_3 groups have approximate retention time from 4 to 6 min under the same experimental conditions. Thus, $C_{60}(i-C_3F_7)_n$ derivatives with high degree of substitution should have a very short retention and therefore, a multi-step HPLC procedure should be used for their separation (see Section 1.3.1 for more detail).

The main products obtained in a hot flow tube at 320–480 °C or glass tube under UV irradiation at room temperature had from six to ten $i-C_3F_7$ groups per cage (see Table 3.1). Thus, a crude mixture contains the derivatives with a high degree of substitution and therefore, further purification of the obtained compounds was not possible using the existing HPLC method. Use of temperature-composition dependence observed for trifluoromethylation reaction where increase of the temperature led to formation of lower substituted fullerenes and therefore, a simplification of HPLC procedure failed in the case of $C_{60}/i-C_3F_7$ system. As described above, a significant increase of the reaction temperature led to a lower yield of the products. In addition, the presence of the $C_{60}(CF_3)_n$ derivatives in the reaction mixture due to degradation of $i-C_3F_7$ radicals also led to a complication of the HPLC separation. The only two pure $C_{60}(i-C_3F_7)_2(CF_3)_2$ isomers with a low number of substituents were successfully isolated from the reaction mixture obtained at 320 °C and characterized by ^{19}F NMR spectroscopy (see Figures 3.18 and 3.19). In contrast to the reactions in a hot flow tube, no more than eight substituents per cage were observed in the sealed glass ampoules (290 °C). This led to significant simplification of HPLC procedure due to fewer compounds with longer retention times in comparison with flow system product. Thus, eight pure $C_{60}(i-C_3F_7)_n$ (with $n = 2, 4$, and 6)

and one $C_{60}(i-C_3F_7)(CF_3)$ compounds were isolated. The compounds with two substituents such as $C_{60}(i-C_3F_7)_2$ and $C_{60}(i-C_3F_7)(CF_3)$ were isolated and purified using toluene as an eluent. The derivatives with four and six $i-C_3F_7$ groups underwent purification in a toluene/heptane mixture (60:40) mixture and subsequently in pure heptane. According to the HPLC data, the most abundant derivative in the crude reaction mixture was $C_{60}(i-C_3F_7)_2$. Among four isolated $C_{60}(i-C_3F_7)_4$ isomers, the two major isomers, **60-4-5- C_3F_7** and an $C_{60}(i-C_3F_7)_4$ isomer with an unknown addition pattern (retention time = 21.5 min), and two minor isomers, **60-4-4- C_3F_7** and another $C_{60}(i-C_3F_7)_4$ isomer with an unknown addition pattern (retention time = 13.7 min) were observed. In the case of three pure $C_{60}(i-C_3F_7)_6$ isomers, there were two major isomers with unknown addition patterns, one with a retention time of 3.4 min and one with a retention time of 5.0 min, and one minor isomer, **60-6-5- C_3F_7** . All of the purified $C_{60}(i-C_3F_7)_4$ and $C_{60}(i-C_3F_7)_6$ compounds were analyzed by ^{19}F NMR spectroscopy (see Figures 3.5, 3.6, 3.9, 3.10, 3.13, 3.14–3.19). The crystal structures of **60-2-1- C_3F_7** , **60-4-4- C_3F_7** , **60-4-5- C_3F_7** , **60-6-5- C_3F_7** , and **60-6-9- C_3F_7** derivatives will be discussed below.

3.2.3. Crystallographic Studies. The addition patterns of five compounds, **60-2-1- C_3F_7** , **60-4-4- C_3F_7** , **60-4-5- C_3F_7** , **60-6-9- C_3F_7** , and $C_{60}(CF_3)_2(i-C_3F_7)_2$, were determined by X-ray crystallography (see Figure 3.3–3.8, 3.12).

3.2.3.1. 1,7- C_s - $C_{60}(i-C_3F_7)_2$ (60-2-1- C_3F_7**).** In the **60-2-1- C_3F_7** structure, the two $i-C_3F_7$ groups attach in *para* position to C1 and C7 carbon atoms and repeat the addition pattern of C_s - $C_{60}(CF_3)_2$ compound.³² In Figure 3.4, the positional disorder of the fullerene cage observed in the case of the C_s - $C_{60}(i-C_3F_7)_2$ crystal structure is shown. Two orientations of the C_{60} cage with fractional occupancies 83% and 17% were found and

properly modeled. The major component of the fullerene cage is related to the minor one by a mirror plane. The molecules of **60-2-1-C₃F₇** pack in columns along *a* axis and they are arranged in off-set head-to-tail manner, as shown in Figure 3.4.

3.2.3.2. 1,7,28,31-C₂-C₆₀(*i*-C₃F₇)₄ (60-4-4-C₃F₇) and 1,7,36,39-C₁-C₆₀(*i*-C₃F₇)₄ (60-4-5-C₃F₇). Only three addition patterns are known for C₆₀(CF₃)₄ compounds with four R_F groups. In two of them, the four CF₃ groups form *pmp* and *p*³ ribbons.^{65,80} In the third one,⁶⁶ the trifluoromethyl groups add to C1, C7, C16, and C36 (**60-4-2-CF₃**, with two isolated *p*-C₆(CF₃)₂ hexagons). There is no structural information for C₆₀(C₂F₅)₄ derivatives to date.

New **60-4-4-C₃F₇** and **60-4-5-C₃F₇** crystal structures determined in the present work are the first examples of the perfluoroisopropylated C₆₀ derivatives with four groups. They demonstrate that in both cases, four *i*-C₃F₇ groups do not form ribbons and attach to the two isolated hexagons (see Figures 3.3 and 3.5). In the case of **60-4-4-C₃F₇** structure, four substituents attach to C1, C7, C28, and C31 carbon atoms. Such addend arrangement results in C₂ symmetry of the addition pattern which is also demonstrated by ¹⁹F NMR spectrum in which four resonances ($-\delta$ 71–74 ppm) were assigned to eight CF₃ groups (see Figure 3.5). In the nonsymmetric **60-4-5-C₃F₇** isomer, four *i*-C₃F₇ groups are attached to C1, C7, C36, and C39. Due to the absence of elements of symmetry, eight resonances observed in the ¹⁹F NMR spectrum between δ -71 and -74 ppm were assigned to eight CF₃ groups as shown in Figure 3.5.

3.2.3.3. 1,7,16,36,43,46-C₁-C₆₀(*i*-C₃F₇)₆ (60-6-9-C₃F₇) and 1,7,16,30,36,47-C₃-C₆₀(*i*-C₃F₇)₆ (60-6-5-C₃F₇). In contrast to perfluoroalkylated C₆₀ compounds with four groups, the pool of addition patterns known for C₆₀(R_F)₆ derivatives is more

diverse.^{51,55,80,81} The addition patterns of two isomers of $C_1-C_{60}(i-C_3F_7)_6$ (**60-6-3- C_3F_7** and **60-6-8- C_3F_7**), determined by Troyanov and co-workers⁸² and two others, $C_1-C_{60}(i-C_3F_7)_6$ and $C_3-C_{60}(i-C_3F_7)_6$ (**60-6-5- C_3F_7** and **60-6-9- C_3F_7**), determined in this work, demonstrated that six $i-C_3F_7$ groups have a tendency to arrange themselves on isolated $p-C_6(i-C_3F_7)_2$ hexagons, as in case of the $C_{60}(i-C_3F_7)_4$ compounds (see Figures 3.3, 3.7, and 3.8).

The **60-6-5- C_3F_7** molecule has idealized C_3 symmetry (but the molecule has no crystallographically imposed symmetry) with perfluoroisopropyl groups arranged on three isolated $p-C_6(i-C_3F_7)_2$ hexagons, with the addends attached to C1, C7, C16, C30, C36, and C47, as shown in Figures 3.7 and 3.11. The three F $\cdots$ F distances range from 2.616(3) to 2.657(3) Å and the three F–C $\cdots$ C–F torsion angles range from 51.9(3)° to 56.4(3)° (see Figure 3.6). In contrast, the F $\cdots$ F distance and F–C $\cdots$ C–F torsion angle for the isolated $p-C_6(CF_3)_2$ hexagon in 1,6,11,18,24,27,52,55- $C_{60}(CF_3)_8$ are 2.695(3) Å and 3.4(2)°, respectively.⁵² The differences are due in part to the different lengths of the fluoromethine C–F bonds (these range from 1.372 (4) to 1.378 (4) in $C_{60}(i-C_3F_7)_6$) and trifluoromethyl C–F bonds (these range from 1.304(3) to 1.347(3) Å, and average 1.328(1) Å, in 1,6,11,18,24,27,52,55- $C_{60}(CF_3)_8$) and range from 1.318(4) to 1.353(4) Å, and average 1.333(1) Å, in $C_{60}(i-C_3F_7)_6$). The compound **60-6-3- C_3F_7** ,⁸² in which the addends attach to C1, C7, C16, C36, C46, and C49, has an addition pattern similar to **60-6-5- C_3F_7** . The difference between them is the position of only two $i-C_3F_7$ groups, as shown in Figure 3.11. In the structure of **60-6-5- C_3F_7** , two $i-C_3F_7$ groups are attached to C30 and C47 instead of to C46 and C49 in **60-6-3- C_3F_7** (see Figure 3.11). The three

intramolecular F...F distances in **60-6-3-C₃F₇** range from 2.450(3) to 2.691(3) Å and the three F–C...C–F torsion angles are 7.2(1), 22.3(1), and 61.3(1)°.

In the nonsymmetrical isomers **60-6-8-C₃F₇** and **60-6-9-C₃F₇**, the addends are attached to C1, C7, C16, C36, C45, and C57 and to C1, C7, C16, C36, C43, and C46, respectively (see Figures 3.3 and 3.8). There are three intramolecular F...F contacts in **60-6-8-C₃F₇** and **60-6-9-C₃F₇** between pairs of perfluoroisopropyl groups that share the same hexagon that range from 2.545(3) to 2.647(3) Å and from 2.546(2) to 2.726(2) Å, respectively. The F–C...C–F torsion angles for the isolated hexagons in **60-6-8-C₃F₇** and **60-6-9-C₃F₇** are 53.82(2), 57.61(2), and 63.56(2)° and 23.03(2), 65.83(2), and 47.24(2)°, respectively.

The addition patterns observed for **60-6-5-C₃F₇**, **60-6-8-C₃F₇**, and **60-6-9-C₃F₇** compounds have a **60-4-2-CF₃** sub-structure known for 1,7,16,36-C₆₀(CF₃)₄. Notably, **60-6-3-C₃F₇** and **60-6-8-C₃F₇** have perfluoroethyl analogs: two C₆₀(C₂F₅)₆ isomers with exactly the same addition patterns.^{51,55} The intermolecular F...F distance in **60-6-3-C₂F₅** are in a range similar to that in **60-6-3-C₃F₇**: from 2.518(3) to 2.689 Å, and three torsion angles are 22.34(2), 44.97(2), and 59.46(2)°. In the structure of **60-6-8-C₂F₅**, the three F...F distances are 2.455, 2.562, and 2.651 Å, and torsion angles varied from 27.94 to 43.15°.

In summary, five crystal structures determined in the present work show that the bulky *i*-C₃F₇ groups attach only to the isolated hexagons in *para* position and, in contrast to CF₃ and C₂F₅ substituents, do not form loops or ribbons on a fullerene cage. For the C₆₀(*i*-C₃F₇)₈ compound⁸², eight substituents keep the same tendency.

3.2.3.4. C_s - $C_{60}(CF_3)_2(i-C_3F_7)_2$. The addition pattern of C_s - $C_{60}(CF_3)_2(i-C_3F_7)_2$ consists of a ribbon of four edge-shared $C_2(R_F)_2$ hexagons. Two CF_3 groups attach to C1 and C7 carbon atoms (black triangles on Schlegel diagram, Figure 3.3) and form addition pattern known for X-ray crystal structure of C_s - $C_{60}(CF_3)_2$ ^{66,80} and C_s - $C_{60}(i-C_3F_7)_2$ (see above). The attachment of two $i-C_3F_7$ groups to C11 and C24 (black dots on the Schlegel diagram, Figure 3.3) results in a continuous *para-para-para* **60-4-3- CF_3** addition pattern. The same arrangement of the R_F substituents (CF_3) groups was previously observed for C_s - $C_{60}(CF_3)_4O$ and C_s - $C_{60}(C_2F_5)_4O$ derivatives.⁶⁵ Addition of oxygen atom to the reactive C26–C27 bond in the latter structures led to formation a very stable skew-pentagonal-pyramid addition pattern.⁶⁵ Notably, it is very difficult to obtain the p^3 - $C_{60}(CF_3)_4$ crystal structure without impurity of p^3 - $C_{60}(CF_3)_4O$. In the present work, the structure of p^3 - $C_{60}(CF_3)_4$ was determined by X-ray crystallography which contains only 11% of C_s - $C_{60}(CF_3)_4O$ (Figure 3.12). Surprisingly, formation of the epoxide was not observed in case of the $C_{60}(CF_3)_2(i-C_3F_7)_2$ compound which may be explained by partial shielding and hence possible protection of the C26–C27 bond due to bulkiness of two $i-C_3F_7$ groups. (Figure 3.12).

3.2.4. Electrochemical Studies. Previous electrochemical studies of a wide range of trifluoromethylated fullerenes demonstrated that the redox properties of fullerene(CF_3)_n derivatives are linked to their addition patterns.³² It was found that the addition pattern of trifluoromethylated fullerenes directs the shift of the first reduction potential versus $C_{60}^{0/-}$ value. In fullerene(CF_3)_n derivatives, the LUMO is always anchored to double bonds in pentagons (DBIP) with two sp^2 neighbors (i.e., non-terminal double bonds in pentagons, *nt*-DBIPs). When two *nt*-DBIPs were conjugated in one

pentagon (i.e., in a fulvene-like LUMO), higher shifts were observed in comparison to isomers with only one *nt*-DBIP (i.e., an acenaphthalene-like LUMO). To reveal the effect of the addition pattern and, in particular, of the relative position of *nt*-DBIPs on the electron-accepting properties of fullerene(*i*-C₃F₇)_{*n*} compounds, PBE/TZ2P-predicted LUMO energies and adiabatic electron affinities (EAs) of all structurally characterized derivatives were calculated by Dr. Alexey A. Popov.

Figure 3.3 lists changes of LUMO energies and EA values of the derivatives in comparison to those of unmodified C₆₀. The effect of the addition pattern can be clearly seen by comparing the values for different isomers. For instance, Δ LUMO for **60-4-4-C₃F₇**, -0.41 eV, is 0.11 eV larger than that for **60-4-5-C₃F₇**, which agrees well with the fact that *nt*-DBIPs are close to each other in the former and are further apart in the latter. Note that the Δ LUMO for **60-4-1-CF₃** with only one *nt*-DBIP is -0.33 eV, which is quite close to the value found for **60-4-5-C₃F₇**. The largest Δ LUMO among **60-6** isomers, -0.52 eV for **60-6-8-C₃F₇**, is also found for the structure with the nearest position of *nt*-DBIPs. For comparison, Δ LUMO for **60-6-1-CF₃** with *p*³*mp* addition pattern and fulvene-shape LUMO is -0.48 eV. Thus, even though one *nt*-DBIP has a weaker effect on Δ LUMO than the effect of two conjugated *nt*-DBIPs in a fulvene fragment, by combining three *nt*-DBIPs in a fortuitous arrangement it is possible to obtain a stronger electron acceptor. This is especially well illustrated by **60-8-11-C₃F₇**, in which the special arrangement of four *nt*-DBIPs results in a record-high Δ LUMO value, -0.87 eV, which can be compared to the values for **60-8-1-CF₃** and **60-8-5-CF₃**, -0.53 and -0.70 eV, respectively. Thus, the observed trends in $\Delta E(\text{LUMO})$ values indicate that the electron accepting properties of fullerene(*i*-C₃F₇)_{*n*} derivatives can be as high as, and in some cases

higher than, for fullerene(CF₃)_n derivatives with the same *n* value but with different addition patterns.

To support this conclusion, the cyclic voltammetry studies of a series of fullerene(*i*-C₃F₇)_n compounds isolated in this work were performed by Dr. Alexey A. Popov and James B. Whitaker. For most of these derivatives, at least two reversible reduction steps at moderate scan rates were observed. The *E*_{1/2} values listed in Table 3.3 show that for compounds with two, four, or six *i*-C₃F₇ groups, the increase in first reduction potentials vs. C₆₀^{0/-} can be as high as 0.43 V.

3.3. Summary and Conclusions

In this work several techniques, which include thermal and photochemical cleavage of C–I bond, were developed for the preparation of C₆₀(₇₀)(*i*-C₃F₇)_n derivatives. It was found that the temperature range, which was mainly determined by product formation and degradation of *i*-C₃F₇ radicals, is relatively lower in case of C₆₀/*i*-C₃F₇I system compared to trifluoromethylation reactions. Systematic studies of the experimental conditions led to the preparation of a wide range of C₆₀(*i*-C₃F₇)_n compounds (even *n* = 2–8), which were separated by HPLC and characterized by ¹⁹F NMR spectroscopy and X-ray crystallography. It was shown that degradation of *i*-C₃F₇ radicals led to the formation of mixed perfluoroalkyl derivatives which contain two different R_F groups (i.e., C₆₀(*i*-C₃F₇)(CF₃) (one isomer) and C₆₀(*i*-C₃F₇)₂(CF₃)₂ (three isomers) were isolated and characterized). Six crystal structures, for C₆₀(*i*-C₃F₇)₂, C₂-C₆₀(*i*-C₃F₇)₄·0.5C₇H₈, C₁-C₆₀(*i*-C₃F₇)₄·C₆H₆, C₁-C₆₀(*i*-C₃F₇)₆, C₃-C₆₀(*i*-C₃F₇)₆, and C_s-C₆₀(*i*-C₃F₇)₂(CF₃)₂, were determined by X-ray crystallography, four of which have unique addition patterns which have never been observed for any fullerene derivative. Based on

the crystallographic data reported in this dissertation and from the recent literature, the general tendency is that derivatives with 2, 4, 6, or 8 bulky $i\text{-C}_3\text{F}_7$ groups only exhibit addition patterns with isolated $p\text{-C}_6(i\text{-C}_3\text{F}_7)_2$ hexagons. Furthermore, in addition to thermal stability, solubility, and stability in air which are very useful physicochemical properties for the further practical applications, fullerene($i\text{-C}_3\text{F}_7$) $_n$ derivatives also exhibit a uniquely wide range of reduction potentials for a given composition. The relationship between the addition patterns in the fullerene derivatives and their electron accepting properties has been substantiated due to the new findings on the correlations between the positions of nt -DBIPs and first reduction potentials. A good correlation between the DFT-calculated LUMO energies and $E_{1/2}$ potentials provide further validation of our theoretical approach and allows for tentative predictions of reduction potentials for new fullerene addition patterns.

Table 3.1. Reaction conditions and products of C₆₀ and C₇₀ perfluoroalkylation using *i*-C₃F₇I.

fullerene, mg	$n(i\text{-C}_3\text{F}_7\text{I})/$ $n(\text{fullerene})$	reactor type/ T_{rxn} , °C	reaction time	solvent or promoter	MS data $\text{C}_{60}(i\text{-C}_3\text{F}_7)_k(\text{CF}_3)_m$		
					k	k_{max}	m
C ₆₀							
30	68	UV/25	21 h	C ₆ F ₆	4–10	6	–
5	507	UV/25	48 h	C ₆ H ₆	8–10	8	–
10	152	UV/25	7 days	C ₆ F ₆	4–12	10	–
10	152	UV/ 25	7 days	C ₆ F ₆ /Cu	4–12	6	–
40	63	Amp./290	24 h	Cu	1–8	6	1
50	31	Amp./316	24 h	Cu	1–6	2	1
20	38	Amp./319	24 h	–	1–6	2	{1;1}
20	38	Amp./390	24 h	Cu	no product		
100	excess	Flow/320	4 h	Cu	6,8	6	
100	excess	Flow/380	9 h	Cu	6–12	10	10–12
50	excess	Flow/480	5 h	Cu	6–10	6	8–10
60	excess	Flow/500	2–4 h	Cu	no product		
C ₇₀							
100	excess	Flow/320	10.5 h	Cu	8–10	10	–
23	53	Amp./416	24 h	Cu	no product		
5	592	UV/ 25	48 h	C ₆ F ₆	10– 12	10	–

Table 3.2. Reaction conditions and products of C₆₀ and C₇₀ perfluoroalkylation using *n*-C₃F₇I.

fullerene, mg	n(<i>n</i> -C ₃ F ₇ I)/ n(fullerene)	reactor type/T _{rxn} , °C	reaction time	solvent or promoter	MS data		
					C ₆₀ (<i>n</i> -C ₃ F ₇) _{<i>k</i>} (CF ₃) _{<i>m</i>}		
					<i>k</i>	<i>k</i> _{max}	<i>m</i>
C ₆₀							
21	84	Amp./290	24 h	Cu	6–12	10	–
50	excess	Flow/350	7 h	Cu	8–12	10	–
100	excess	Flow/380	7 h	Cu	8–12	10	–
C ₇₀							
100	excess	Flow/380	13 h	Cu	4–12	10	–

Table 3.4. Crystal data and structure refinement for $C_{60}(i-C_3F_7)_2$, $C_2-C_{60}(i-C_3F_7)_4 \cdot 0.5C_7H_8$, $C_1-C_{60}(i-C_3F_7)_4 \cdot C_6H_6$, and $C_1-C_{60}(i-C_3F_7)_6$.

	$C_{60}(i-C_3F_7)_2$	$C_{60}(i-C_3F_7)_4 \cdot 0.5C_7H_8$	$C_{60}(i-C_3F_7)_4 \cdot C_6H_6$	$C_{60}(i-C_3F_7)_6$
molecular formula	$C_{66}F_{14}$	$C_{75.5}H_4F_{28}$	$C_{78}H_6F_{28}$	$C_{78}F_{42}$
formula weight	1058.66	1442.79	1474.83	1734.78
crystal system	orthorhombic	monoclinic	triclinic	triclinic
space group	$Pnma$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	4	4	2	2
color	red-brown	red	brown	brown
unit cell				
a , Å	19.622(4)	22.645(4)	10.0294(4)	10.2212(6)
b , Å	17.836(3)	10.1528(17)	12.1981(5)	13.6183(8)
c , Å	10.009(2)	23.011(4)	23.011(4)	21.9933(9)
α , deg	90	90	75.600(2)	80.248(2)
β , deg	90	115.435(8)	81.858(2)	87.129(2)
γ , deg	90	90	75.199(2)	71.128(2)
temperature, K	150(2)	100(2)	100(2)	100(2)
final R	$R_1 = 0.0399$	$R_1 = 0.0643$	$R_1 = 0.0671$	$R_1 = 0.0598$
indices	$wR_2 = 0.115$	$wR_2 = 0.1759$	$wR_2 = 0.2005$	$wR_2 = 0.1625$
goodness-of-fit on F^2	1.024	1.058	1.008	1.046

Table 3.5. Crystal data and structure refinement for $C_8-C_{60}(i-C_3F_7)_2(CF_3)_2$, $C_3-C_{60}(i-C_3F_7)_6$, and $C_8-C_{60}(i-C_3F_7)_4O \cdot 0.5C_8H_{10}$.

	$C_{60}(i-C_3F_7)_2(CF_3)_2$	$C_{60}(i-C_3F_7)_6$	$C_{60}(i-C_3F_7)_4O \cdot 0.5C_8H_{10}$
molecular formula	$C_{68}F_{20}$	$C_{78}F_{42}$	$C_{72}F_{28}O_{0.11}$
formula weight	1196.68	1734.78	1051.40
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/m$	$P2_1/n$	$C2/c$
Z	2	4	8
color of crystals	brown	brown	brown
unit cell			
a , Å	9.9096(13)	13.5877(3)	39.500(5)
b , Å	19.959(2)	31.1809(7)	10.1407(14)
c , Å	10.3595(14)	13.7240 (3)	20.1901(19)
α , deg	90	90	90
β , deg	109.141(3)	106.873(1)	113.254(4)
γ , deg	90	90	90
temperature, K	100(2)	100(2)	100(2)
final R indices	$R_1 = 0.0532$	$R_1 = 0.0520$	$R_1 = 0.0612$
$[I > 2\sigma(I)]$	$wR_2 = 0.1484$	$wR_2 = 0.1330$	$wR_2 = 0.1641$
goodness-of-fit on	1.070	1.010	1.061

Table 3.3. Reversible $E_{1/2}$ values for fullerene(*i*-C₃F₇)_{*n*} derivatives (even *n* = 2–6).

compound	relative $E_{1/2}$ [V] vs. fullerene ^{0/-} {V vs. Fe(Cp) ₂ ⁺⁰ }			
	0/- couple	-2/- couple	2-/3- couple	3-/4- couple
C ₆₀	0.00	-0.39	-0.85	-1.32
60-2-1-C₃F₇	0.13	-0.29	-0.81	-1.25
60-4-3-C₃F₇	0.23	-0.22	-0.80	—
60-4-4-C₃F₇	0.32	-0.32	-0.80	—
60-4-5-C₃F₇	0.20	-0.26	-0.78	—
60-6-3-C₃F₇	0.30	-0.23	-0.79	—
60-6-5-C₃F₇	0.23	-0.25	-0.80	—
60-6-8-C₃F₇	0.43	-0.17	-0.86	—

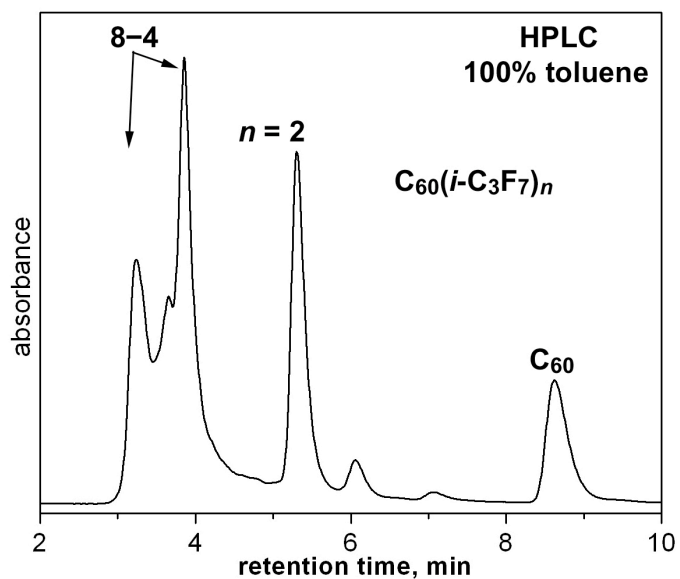


Figure 3.1. HPLC trace of the crude $C_{60}(i-C_3F_7)_n$ (even $n = 2-8$) product obtained in the sealed glass ampoule at 290 °C for 24 h.

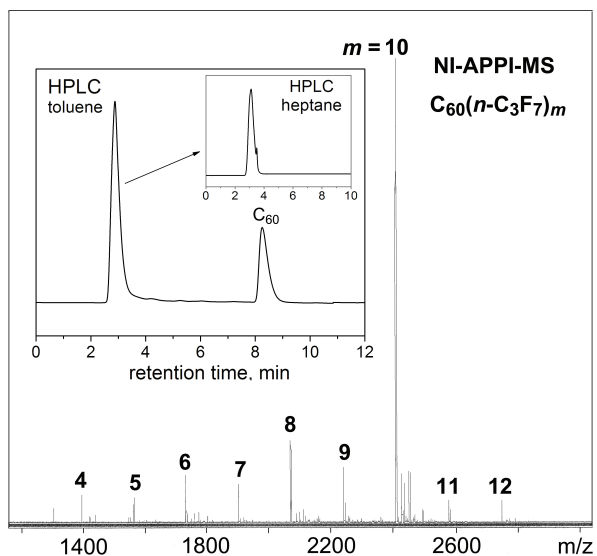


Figure 3.2. HPLC trace of the crude $C_{60}(n-C_3F_7)_m$ ($m = 4-12$) product obtained in the sealed glass ampoule at 290 °C for 24 h.

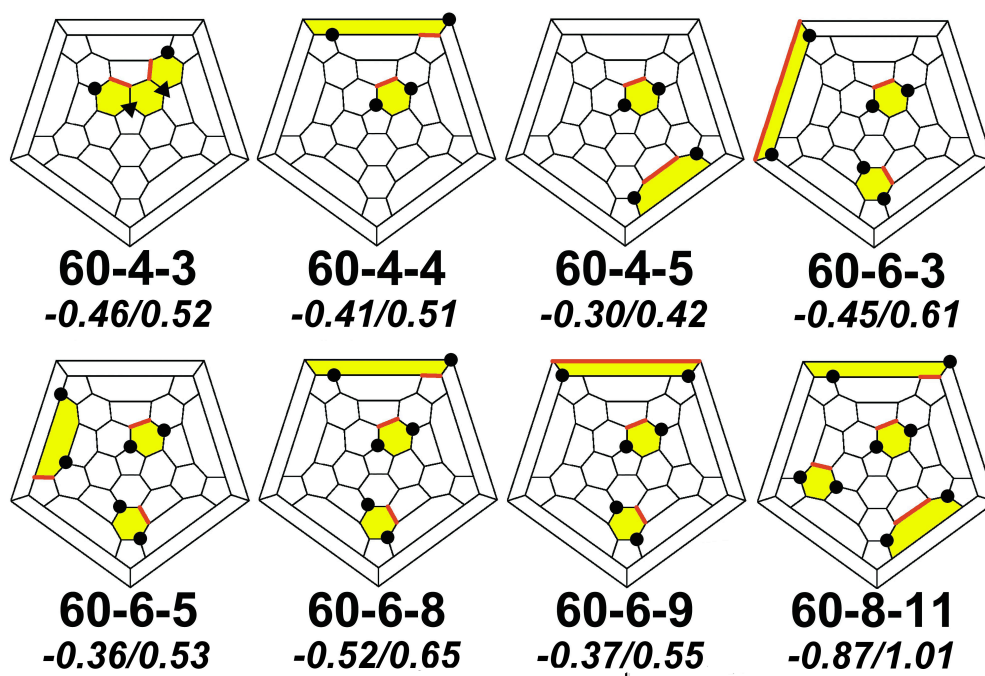


Figure 3.3. Schlegel diagrams for fullerene(*i*-C₃F₇)_{*n*} isomers with the X-ray determined structures/addition patterns. Dark circles denote *i*-C₃F₇ groups, solid triangles – CF₃ groups, and red solid lines show *nt*-DBIPs. The DFT-calculated $\Delta E(\text{LUMO})/\Delta E_A$ values (vs. fullerene) are given for each isomer.

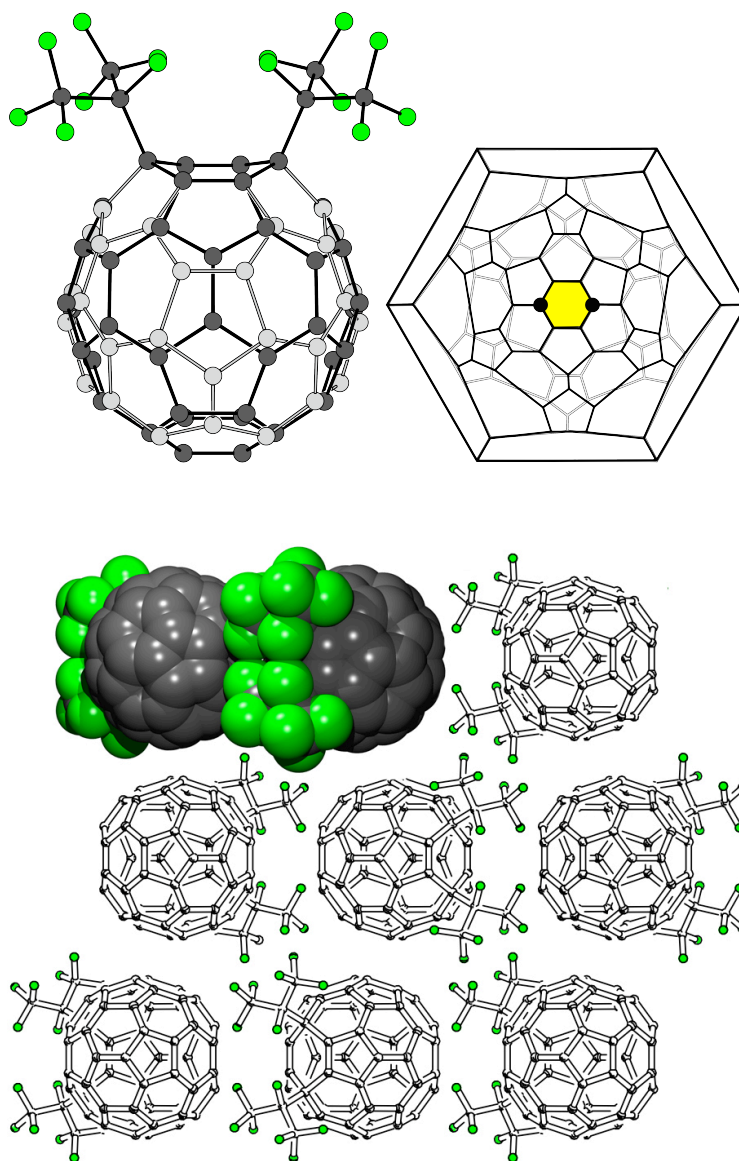


Figure 3.4. The Schlegel diagram (top), crystal structure (top), and packing of $C_{60}(i-C_3F_7)_2$ molecules (bottom) are shown. The grey and black fullerene cages on the Schlegel diagram and molecular structure relate to two modeled orientations of C_{60} cage. The presence of the mirror plane and the absence of the two-fold axis in the molecular structure lead to two possible orientations of C_{60} cage with exactly the same positions of the $i-C_3F_7$ groups.

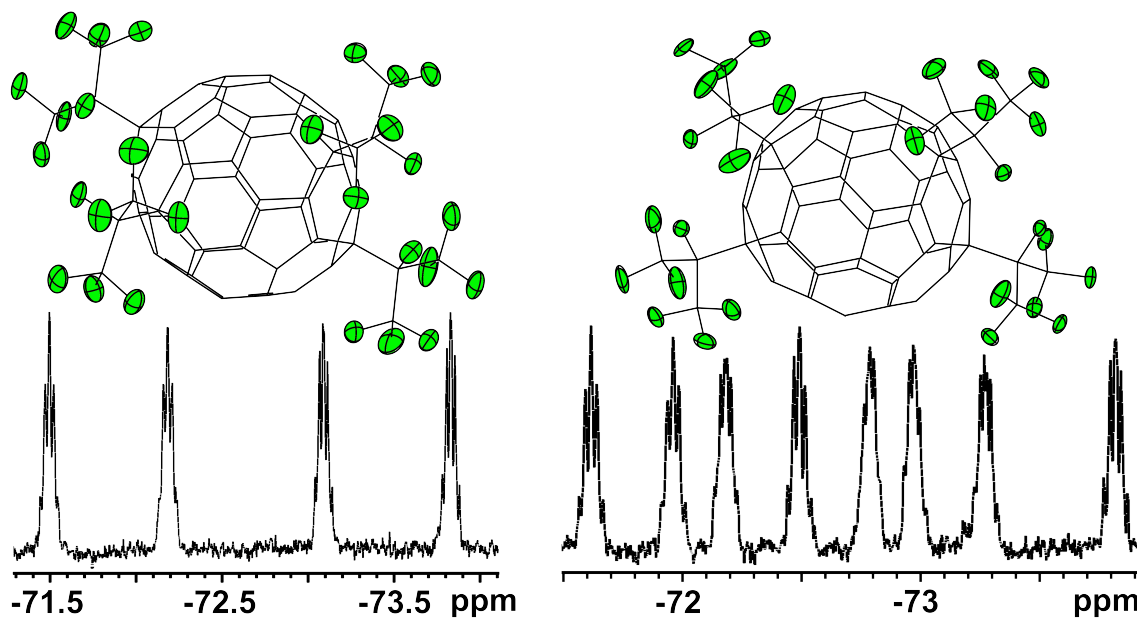


Figure 3.5. The crystal structures (50% anisotropic probability ellipsoids for all atoms) and ^{19}F NMR spectra of **60-4-4** (left) and **60-4-5** (right) compounds.

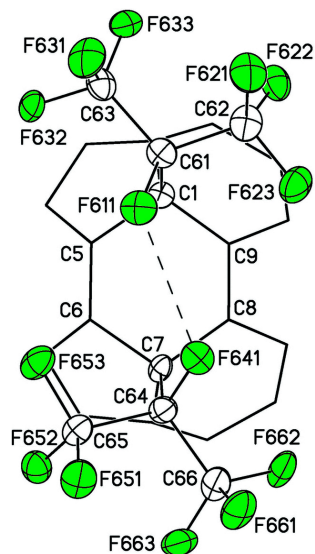


Figure 3.6. A portion of the structure of **60-6-5** showing one of the three *para*- $\text{C}_6(\text{C}_6(\text{i-C}_3\text{F}_7)_2)$ hexagons. The F611...F641 distance is 2.653 (3) Å and the F611-C61...C64-F641 torsion angle is 56.4(3)°.

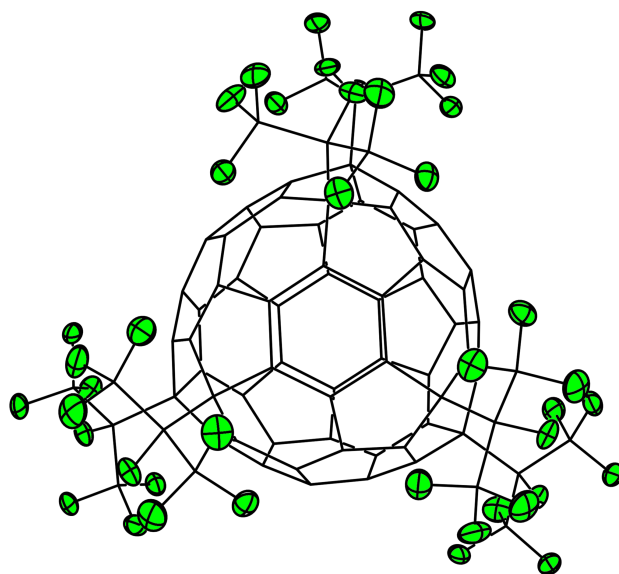


Figure 3.7. X-ray crystal structure of **60-6-5** (50% anisotropic probability ellipsoids for all atoms).

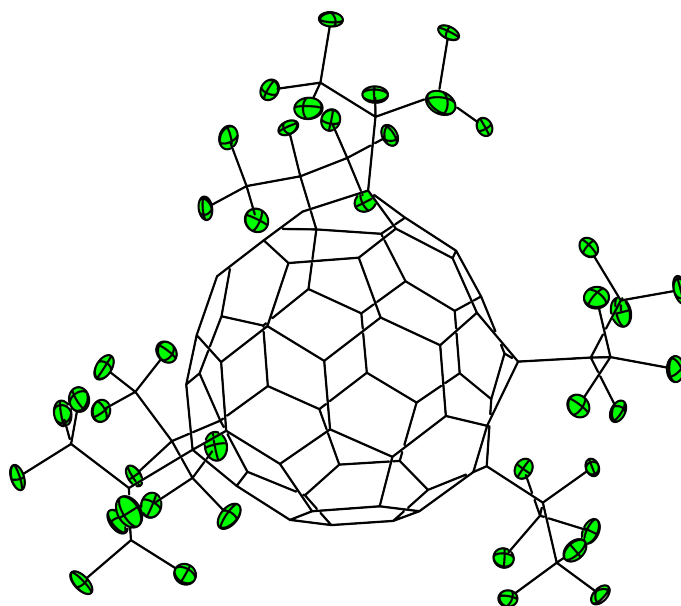


Figure 3.8. X-ray crystal structure of **60-6-9** (50% anisotropic probability ellipsoids for all atoms).

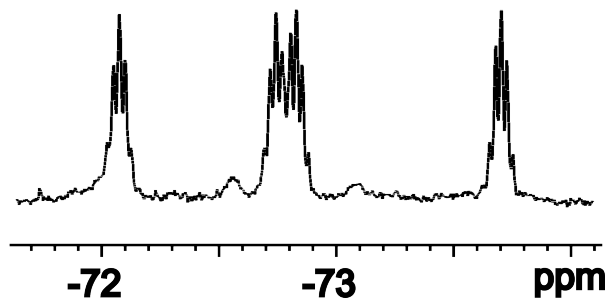


Figure 3.9. Fluorine-19 NMR of **60-6-5** in chloroform-*d*, 376.5 MHz.

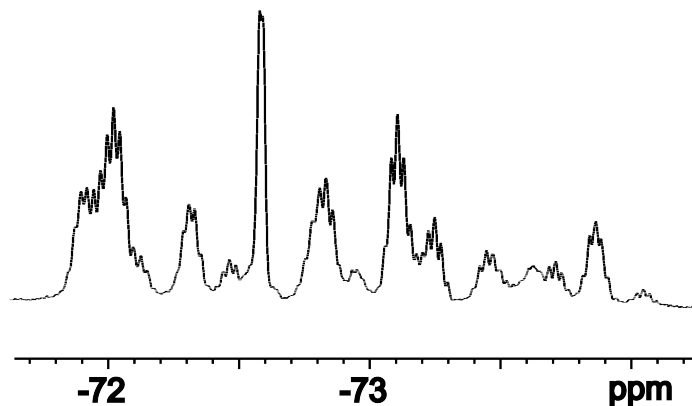


Figure 3.10. Fluorine-19 NMR of **60-6-9** in chloroform-*d*, 376.5 MHz.

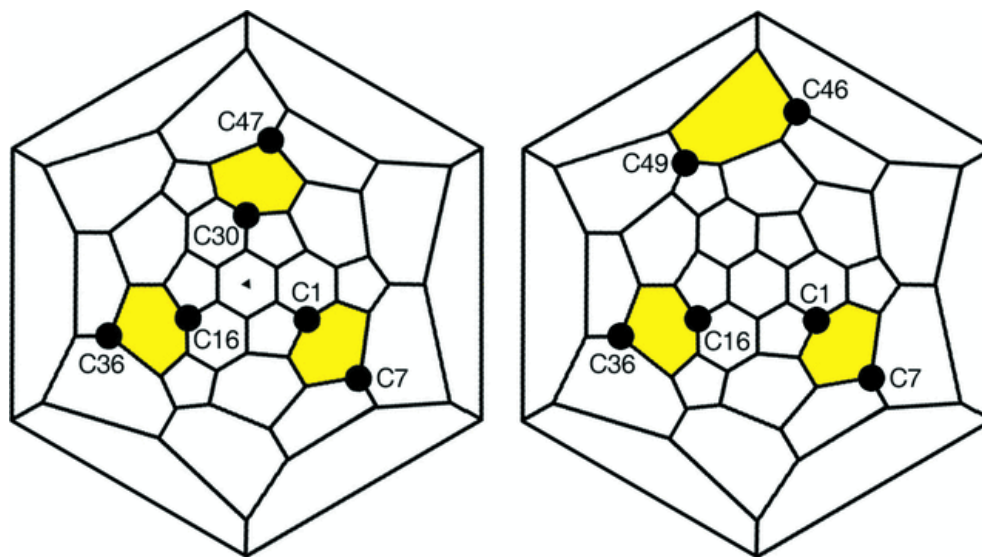


Figure 3.11. Schlegel diagrams of 1,7,16,30,36,47- $C_{60}(i-C_3F_7)_6$ (left) and 1,7,16,36,46,49- $C_{60}(C_2F_5)_6$ (right).⁵¹ The small triangle in the center denotes the molecular C_3 axis.

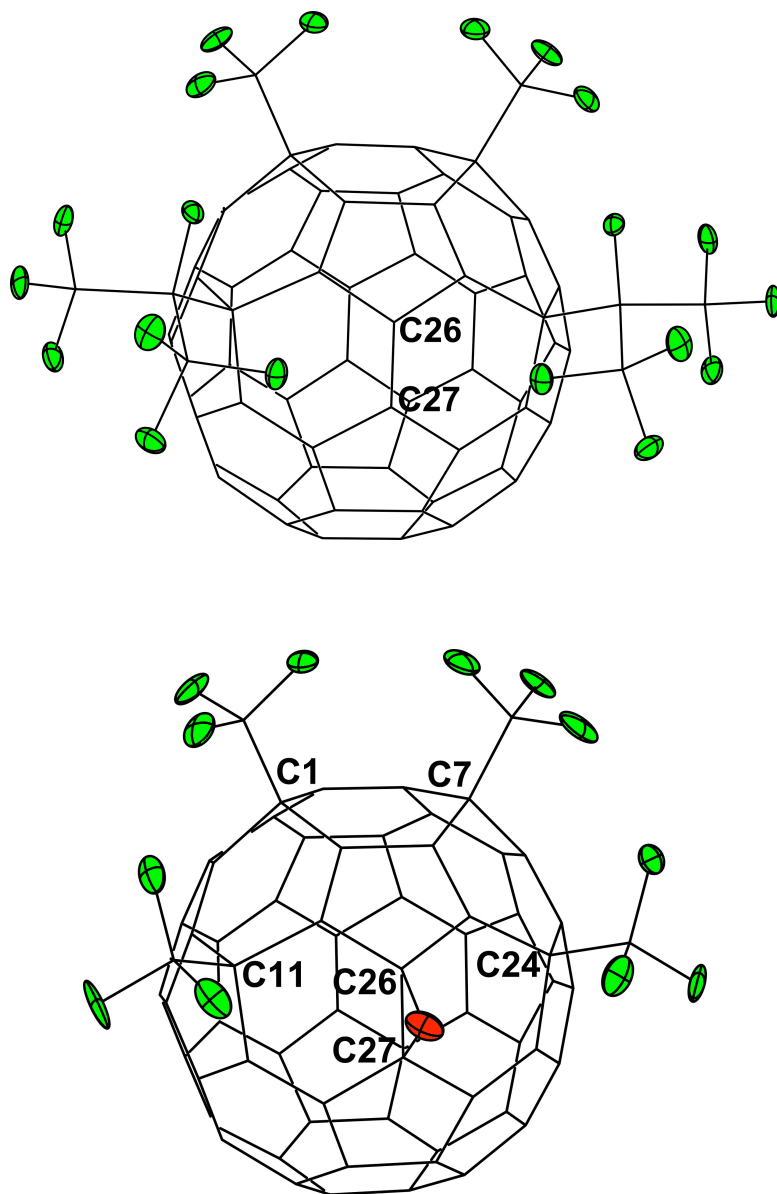


Figure 3.12. X-ray crystal structures of C₆₀(*i*-C₃F₇)₂(CF₃)₂ (top) and of C₆₀(CF₃)₄O (bottom) (50% anisotropic probability ellipsoids for all atoms).

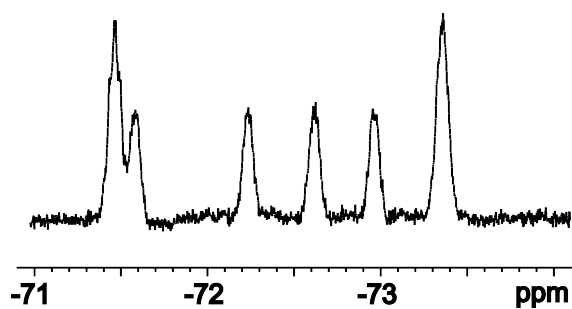


Figure 3.13. Fluorine-19 NMR of $C_{60}(i-C_3F_7)_4$ (r.t. 13.7 min) in chloroform-*d*, 376.5 MHz.

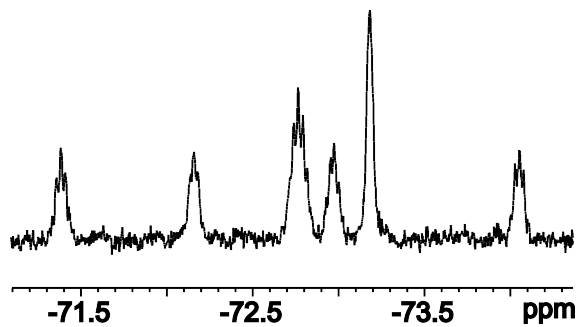


Figure 3.14 Fluorine-19 NMR of $C_{60}(i-C_3F_7)_4$ (r.t. 21.5 min) in chloroform-*d*, 376.5 MHz.

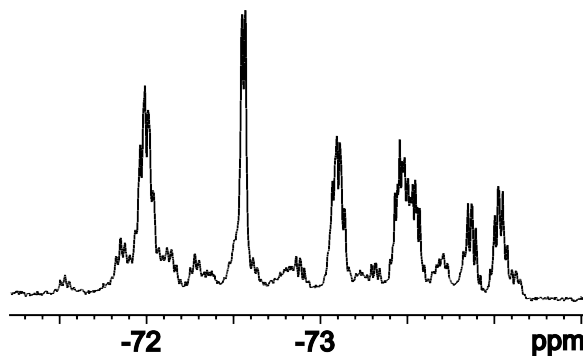


Figure 3.15. Fluorine-19 NMR of $C_{60}(i-C_3F_7)_6$ (r.t. 5.0 min) in chloroform-*d*, 376.5 MHz.

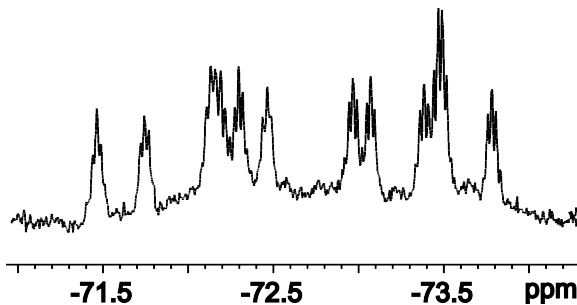


Figure 3.16. Fluorine-19 NMR of $C_{60}(i-C_3F_7)_6$ (r.t. 3.4 min) in chloroform-*d*, 376.5 MHz.

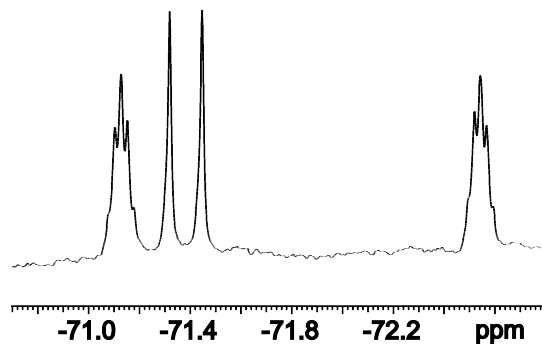


Figure 3.17. Fluorine-19 NMR of $C_{60}(i-C_3F_7)(CF_3)$ in chloroform-*d*, 376.5 MHz.

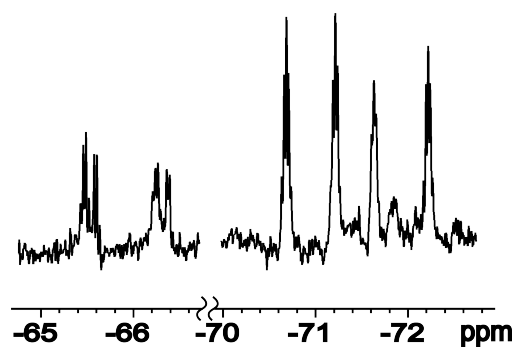


Figure 3.18. Fluorine-19 NMR of $C_{60}(i-C_3F_7)_2(CF_3)_2$ (r.t. 5.7 min) in chloroform-*d*, 376.5 MHz.

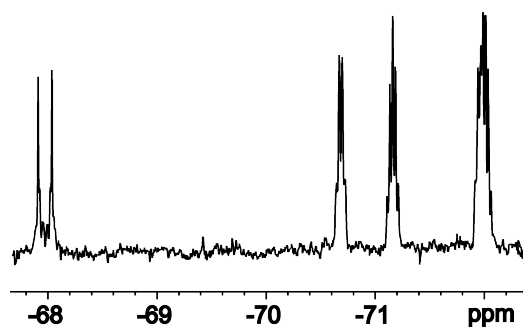


Figure 3.19. Fluorine-19 NMR of $C_{60}(i-C_3F_7)_2(CF_3)_2$ (r.t. 7.0 min) in chloroform-*d*, 376.5 MHz.

CHAPTER 4. TRIFLUOROMETHYLATED $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))$ COMPOUNDS: SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, AND X-RAY CRYSTALLOGRAPHIC STUDIES

Introduction

Metallic nitride fullerenes (MNFs),^{83,84} which are a subset of endohedral metallofullerenes (EMFs), have been the focus of intense research for the past decade.⁸⁵ This is in part because (i) they possess unusual structures^{83,84,86,87} and physicochemical properties,⁸⁸ (ii) their exohedral derivatives may find use in medical applications such as MRI and as X-ray contrast agents,^{89,90} and (iii) recent breakthroughs in their synthesis and purification have made them available in larger quantities.⁹¹⁻⁹⁴ The several factors such as presence and the nature of metal cluster inside of fullerene and size and/or symmetry of the carbon cage can influence chemical reactivity of endohedral metallofullerenes. One of the examples that demonstrates the influence of the nature of the metal in the internal trimetallic nitride cluster on chemical reactivity is the result of the study of Bingel reaction reported by Echegoyen and co-workers: they achieved cycloaddition to $\text{Y}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))$, and, at the same time, an attempt to derivatize $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))$ did not lead to any product formation.^{95,96} The control of the regioselectivity of the cycloaddition reactions by the trimetallic nitride cluster was also observed.⁹⁵ It was shown that in the case of $\text{Sc}_3\text{N}@\text{C}_{80}$, the cycloaddition occurred to a [5,6] double bond ring junction while cycloaddition reactions with $\text{Y}_3\text{N}@\text{C}_{80}$ led to the addition to the double bond at a [6,6] ring junction.⁹⁵ Higher chemical reactivity in

comparison with $\text{Sc}_3\text{N}@\text{C}_{80}\text{-}I_h(7)$ was also observed for a fullerene with different carbon cage – C_{78} (D_{3h} isomer) around the same metallic cluster – Sc_3N . It was shown that $\text{Sc}_3\text{N}@\text{C}_{78}\text{-}D_{3h}$ has a high regioselectivity in Bingel-Hirsch cyclopropanation, although under the same reaction conditions the attempts of $\text{Sc}_3\text{N}@\text{C}_{80}\text{-}I_h(7)$ derivatization did not lead to any product formation.⁹⁷ The selective formation of bisadduct in case of $\text{Sc}_3\text{N}@\text{C}_{78}\text{-}D_{3h}$ was explained by direct control of the second reaction site by Sc_3N inside of the fullerene cage. In addition, there are some publications^{86,92,97} which demonstrate that D_{5h} cage isomers of some endohedral metallofullerenes (e.g., $\text{Sc}_3\text{N}@\text{C}_{80}$ or $\text{Lu}_3\text{N}@\text{C}_{80}$) exhibit higher reactivity in the cycloaddition reaction in comparison with the I_h isomers with the same metal cluster inside. The principle of isolation of $\text{Sc}_3\text{N}@\text{C}_{80}\text{-}I_h(7)$ in SAFA⁹¹ or Dorn process⁸³ is based on its lower chemical activity than empty fullerenes and other MNFs.

Up to date, the only two examples of perfluoroalkylation reactions of endometallofullerenes are known from literature data.^{35,98} One of them includes the reaction (dynamic vacuum, 400 °C) between $\text{Y}@\text{C}_{82}$ -enriched DMF extract and silver (I) trifluoroacetate (AgTFA).³⁵ This study demonstrated that (i) AgTFA is an efficient reagent for synthesis of the perfluoroalkylated $\text{Y}@\text{C}_{82}$ derivatives, (ii) the compounds $\text{Y}@\text{C}_{82}(\text{CF}_3)_n$ with odd number of the substituents on a fullerene cage were formed in these reactions, and (iii) a selective preparation of $\text{Y}@\text{C}_{82}(\text{CF}_3)_5$ compound can be achieved at 400 °C for 10 h. Another example of endohedral-fullerene perfluoroalkylation is a photochemical reaction of $\text{La}@\text{C}_{82}$ with perfluorooctyl iodide which led to isolation of seven isomers of $\text{La}@\text{C}_{82}(\text{C}_8\text{F}_{17})_2$ using a combination of fluoruous biphasic technique and HPLC chromatography.⁹⁸

In this Chapter, the reactions of $\text{Sc}_3\text{N}@C_{80}$ with AgCF_3CO_2 and CF_3I will be described. For the first time 17 new highly soluble $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_n$ (even $n = 2\text{--}16$) derivatives, were isolated and characterized. The X-ray structures of four derivatives with 10, 12, 14, and 16 CF_3 substituents, $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{10}$, $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{12}$, $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{14}$, and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{16}$ were determined. These compounds and their molecular structures are significant for the following five reasons: (i) $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{10}$, $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{12}$, and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{14}$ exhibit neither cage nor endohedral atom disorder, a situation rarely observed in EMF X-ray structures^{86,87} including the MNF $\text{Sc}_3\text{N}@C_{80}$ ^{83,84} and its exohedral derivatives⁹⁹⁻¹⁰²; (ii) they are the first X-ray structures of any EMF with more than four cage $\text{C}(\text{sp}^3)$ atoms; they are rare examples of fullerene(X)_n derivatives with one or more X groups on triple hexagon junctions (i.e., with sp^3 THJs)^{97,103-105}; (iii) the addition pattern of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{16}$ includes two isolated cyclopentadienyl(1–) rings; (iv) the structures are precise enough that a meaningful analysis of interatomic distances and angles can be performed and correlated with computational results at the DFT level of theory; (v) the Sc_3N clusters in these structures are more distorted from 3-fold symmetry than in any other MNF X-ray structure published to date, and the distortions are clearly caused by the pattern of cage $\text{C}(\text{sp}^3)$ atoms in these compounds. Part of this work has been published.^{36,37}

4.1. Experimental Section

4.1.1 Reagents and Solvents. The reagents and solvents: AgCF_3CO_2 (Aldrich, 99.99+%), benzyl bromide (Aldrich, 98%), carbon disulfide (Alfa Aesar, 99.8%, HPLC grade), copper powder (Sigma-Aldrich, ~ 40 mesh, 99.5 %), CoF_3 (Sigma-Aldrich),

MnF₃ (Sigma-Aldrich), CF₃I (Apollo Scientific, 98%), *i*-C₃F₇I (Apollo Scientific, 98% and SynQuest, 97%), hexafluorobenzene (Sigma-Aldrich), 1,2-dichlorobenzene (Sigma-Aldrich, 99%, anhydrous), chloroform-*d* (Cambridge Isotopes), and heptane and toluene for HPLC purification (Sigma-Aldrich) were used as received. The Sc₃N@C₈₀-*I*_h(7) and Er₃N@C₈₀-*I*_h were prepared according the method described in literature.⁹¹ KMnF₄ was prepared by Dr. Mazej as described previously.¹⁴ Synthesis of K₂PtF₆ was performed using established procedure.¹⁰⁶

4.1.2. Preparation of Sc₃N@C₈₀(CF₃)_{*n*} Derivatives. In a typical reaction, a 100-mg crude extract which contains 12% Sc₃N@C₈₀ (*D*_{5h} and *I*_h isomers), 62% C₆₀, and 26% C₇₀ was loaded in a quartz flow tube and treated with a stream of CF₃I gas at 430–530 °C for 1.5–4 h [CAUTION: CF₃I decomposes in air above 300 °C and produces toxic HF, COF₂, and I₂; handle only in a well-ventilated fume hood].. In the several reactions, which were carried out at 482, 500, and 530 °C, the copper powder was used as a promoter. After the reaction was stopped and iodine removed from the system, the product was removed from the tube by washing with hexane, then with toluene, and finally with *o*-dichlorobenzene.

The reaction of Sc₃N@C₈₀-*I*_h(7) with AgCF₃CO₂ was carried out in the glass tube (0.4 cm I.D., 10.5 cm length) which was incorporated into metal copper container (0.6 cm I.D., 11.5 cm length) closed from both ends. In a typical experiment, Sc₃N@C₈₀-*I*_h(7) (10 mg, 0.01 mmol) was mixed with silver trifluoroacetate (110 mg, 0.5 mmol) and the mixture was loaded into a glass tube. Internal glass tube was used to avoid surface contact and possible exchange reaction between Cu and AgCF₃CO₂. The reactor was placed in a 45-cm long tube furnace (8 cm I.D.). The reactions of Sc₃N@C₈₀-*I*_h(7) with

AgCF₃CO₂ were carried out at 350 °C for 2.5 h. Heating was performed under dynamic vacuum. The black-brown Sc₃N@C₈₀-I_h(CF₃)_n products, part of which condensed in a glass tube end, were collected using organic solvents which allow us to separate insoluble products of the AgCF₃CO₂ decomposition. For the isolation of the obtained trifluoromethylated Sc₃N@C₈₀-I_h(7) derivatives, three-step extraction scheme was used in which hexane, toluene, and *o*-dichlorobenzene were used consequently. The replacement of the solvent by the next one (e.g., hexane by toluene) was done when after exhaustive extraction which means that almost all soluble scandium-containing products have been already extracted in this particular solvent. As a result of the three-step extraction 7 mg of the combined Sc₃N@C₈₀-I_h(7)(CF₃)_n products (after removing unreacted starting material) were isolated from one 10-mg preparation. The crude product was analyzed by HPLC and mass-spectrometry.

The obtained Sc₃N@C₈₀-I_h(CF₃)_n reaction products have been used for the further study of the trifluoromethylation reaction. The products of the reaction from the first cycle were ground with the “fresh” portion of silver (I) trifluoroacetate (110 mg, 0.5 mmol) and then the synthesis was continued under similar conditions (350 °C for 2.5 h) using the same reactor. After the second cycle, the black brown Sc₃N@C₈₀-I_h(7)(CF₃)_n products were extracted using the same three-step scheme. The HPLC chromatograms (eluent-toluene, flow rate- 5 mL min⁻¹) of the crude samples from different washes are shown on Figure 4.2.

4.1.3. Separation of Sc₃N@C₈₀-I_h(7)(CF₃)_n. The Sc₃N@C₈₀-I_h(CF₃)_n products obtained from the reaction of Sc₃N@C₈₀ (crude extract contained 12% Sc₃N@C₈₀ (D_{5h} and I_h isomers) with CF₃I were separated and purified by HPLC (10 mm

I.D. $\times$ 250 mm long Cosmosil Buckyprep column (Nacalai Tesque, Inc.), 300 nm UV detector). The fractions which were isolated using toluene as an HPLC eluent were subjected to further purification using 20:80 (v:v) toluene:heptane mixture. Thus, the $\text{Sc}_3\text{N}@C_{80}$ compounds with 10 (retention time (r.t.) 6 min), 12 (r.t. 3.2 min) trifluoromethyl groups were purified using 20:80 (v:v) toluene:heptane mixture at 5 mL min^{-1} flow rate.

The separation of the $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_n$ crude samples obtained from $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{)}/\text{AgCF}_3\text{CO}_2$ reactions was done in toluene as an eluent at 5 mL min^{-1} flow rate. Six different fractions 2.9–4.0 (**Ia**) and 4.0–8.0 min (**Ib**), 8.0–9.3 min (**II**), 9.3–23.0 min (**III**), 23.0–27.0 (**IV**), and unreacted $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{)}$ (31.0–35.5 min) were isolated. The second stage of purification of **II**, **III**, and **IV** using 100% toluene as an eluent at 5 mL min^{-1} flow rate resulted in the isolation (retention times shown in parenthesis) of six pure fractions such as **10-1** (8.0 min), **8-1** (12.8 min), **8-2** (9.0 min), **4-1** (14.9 min), **4-2** (17.32 min), and **2** (23 min). The abundant **10-1**, **4-1**, and **2** isomers were isolated with 98+% purity. The purity of the isolated compounds was estimated based on HPLC, MS, and ^{19}F NMR data. In addition, two fractions of different $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_8$ isomers such as **8-3**, **8-4** (12.1 min) and **8-1**, **8-5** (13.1 min) were isolated from toluene fraction **III** using toluene as an eluent at 5 mL min^{-1} flow rate. The fraction **Ia** from toluene with retention time 4.0–8.0 min was eluted in heptane to separate **16-1** (3.9 min) and **14-1** (5.9 min) at 7 mL min^{-1} flow rate. Following purification of **16-1** (5.2 min), **16-2** (10.5 min), **14-1** (8.0 min), and **14-3** (15.0 min) in the same eluent at 5 min^{-1} flow rate. The purification of the most abundant **16-1** and **14-1** isomers resulted in to 80+% and 90+% of the compositional and isomeric purity, respectively. The **12-1**, **12-2**, **12-3**, and **12-4**

isomers were also isolated from the toluene fraction **Ia** and **Ib** with subsequent purification in 30:70 toluene/heptane and 10:90 toluene/heptane eluents. Subsequent isolation and purification of **12-1** was done at 3 and 5 mL min⁻¹ flow rate using 30:70 toluene/heptane eluent, and the retention times were 17.7 and 10.7 min, respectively. The purity of **12-1** isomer after three-step purification was 85+%. The **12-2** isomer was isolated from toluene fraction **I** with 4.2 min retention time (5 mL min⁻¹ flow rate) with subsequent purification in 30:70 toluene/heptane eluent at 7 mL min⁻¹ flow rate (retention time 21 min) and then at 5 mL min⁻¹ flow rate (retention time was 33 min). The use of this purification scheme resulted to 80+% of **12-2** isomer. The **12-3** isomer was finally isolated and purified in 10:90 toluene/heptane eluent at 5 mL min⁻¹ flow rate. The isolation and purification of **12-4** was carried out in 30:70 toluene/heptane mixture at 5 and 3 mL min⁻¹ flow rate, and retention times were 12.8 and 20.8 min, respectively. From toluene fraction **II** the **10-2** isomer was separated with subsequent purification in 60:40 toluene/heptane at 5 mL min⁻¹ flow rate led to isolation of **10-2** (17.9 min) with 70+% purity.

4.1.4. Fluorination of Sc₃N@C₈₀-I_h(7). Fluorination experiments of Sc₃N@C₈₀-I_h were carried out in a glass tube at 350–550 °C under dynamic vacuum as it was described earlier for preparation of C₆₀F_n derivatives. The reaction of Sc₃N@C₈₀-I_h (3 mg, 0.003 mmol) with K₂PtF₆ (10.5 mg, 0.03 mmol) were ground together and heated at 380–550 °C for 3h. For fluorination with manganese trifluoride, two experiments using 50 mg (0.45 mmol) and 217 mg (1.9 mmol) of MnF₃ per 5 mg (0.005 mmol) of Sc₃N@C₈₀-I_h(7) were performed at 350–450 and 350 °C for 5 and 6 h, respectively. The reaction of KMnF₄ (100 mg, 0.59 mmol) with Sc₃N@C₈₀-I_h (9 mg,

0.008 mmol) was carried out at 520 °C for 4 h. Cobalt trifluoride (46.5 mg, 0.40 mmol) and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))$ (10 mg, 0.01 mmol) was heated at 420 °C for 6 h.

4.1.5. Trifluoromethylation of $\text{Er}_3\text{N}@\text{C}_{80}$. Trifluoromethylation of $\text{Er}_3\text{N}@\text{C}_{80}$ was carried out in a glass sealed ampoule (E.D. = 6 mm, length = 20 cm)). The starting material mainly contains $\text{Er}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))$ but also small amounts of $\text{Er}_2@\text{C}_{2n}$ compounds. In the sealed-ampoule experiment, 6 mg (0.004 mmol) of $\text{Er}_3\text{N}@\text{C}_{80}$ and 0.5 mL (5.3 mmol) of CF_3I were heated at 432 °C for 48 h. The brown products were analyzed using EI mass-spectrometry.

4.1.6. Photochemical Reaction of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{10}$ with $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$. A mixture of **10-1** (1 mg, 0.0006 mmol) and $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ (1.6 mg, 0.009 mmol) dissolved in 2 mL of deoxygenated toluene was irradiated without cooling for 1 h which led to change the color of the solution from green to dark brown. The obtained very well soluble in toluene brown products, were subjected to HPLC and NI-APPI MS analyses.

4.1.7. X-ray Crystallography. The crystals of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{10}$ (**10-1**) (brown rhombs, $0.009 \times 0.055 \times 0.088$ mm) and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h)(\text{CF}_3)_{12}$ (**12-1**) (brown prisms, $0.013 \times 0.020 \times 0.029$ mm) were grown by slow evaporation of the saturated *p*-xylene and carbon disulfide, respectively.

In the case of **10-1** and **12-1** X-ray crystal structures, the diffraction-quality single crystals were mounted in a paratone oil on a glass fiber rods glued to a small copper wire. X-ray diffraction data were collected at ChemMatCARS (CARS = Consortium for Advanced Radiation Sources) sector 15-B at the Advanced Photon Source (Argonne National Laboratory). The data sets were collected at 100(2)–120(2) K using a diamond (111) crystal monochromator, a wavelength of 0.4132 Å and a Bruker CCD detector. The

asymmetric unit of **10-1** and **12-1** structures contains only one MNF molecule; neither the carbon cage nor the Sc₃N cluster is disordered. In these structures, four of the CF₃ groups exhibit rotational disorder. The site-occupancy factors of the two modeled orientations for the trifluoromethyl groups attached to the C3, C17, C28, and C47 in **10-1** were 62/48%, 59/41%, 41/59%, and 51/49%, respectively; to the C24, C28, C51, and C70 in **12-1** were 79/21%, 84/16%, 90/10%, and 90/10%, respectively; Parameters of fluorine atoms in the major and minor disordered parts were refined anisotropically. Relevant experimental parameters are listed in Table 4.2.

Crystals (0.014 × 0.062 × 0.074 mm) of Sc₃N@C₈₀-I_h(7)(CF₃)₁₄ (**14-1**) were grown by slow evaporation of a saturated *p*-xylene solution. Relevant experimental parameters are listed in Table 4.2. A diffraction-quality single crystal was mounted in paratone oil on a glass fiber glued to a small copper pin. X-ray diffraction data were collected at ChemMatCARS Sector 15-B at the Advanced Photon Source at Argonne National Laboratory (CARS) Center for Advanced Radiation Sources). The data set was collected at 100 K using a diamond (111) crystal monochromator, a wavelength of 0.4428 Å, and a Bruker CCD detector with 1 s counting per frame. Unit-cell parameters were refined by least-squares using 9908 reflections. There is one molecule of Sc₃N@C₈₀(CF₃)₁₄ in the asymmetric unit; neither the carbon cage nor the Sc₃N cluster is disordered. Four of the CF₃ groups exhibit rotational disorder. The site-occupancy factors of the two modeled orientations for the trifluoromethyl groups that include C103, C104, C117, and C165 were 49/51%, 48/52%, 51/49%, and 89/11%, respectively. All of the F atoms in the major and minor disordered parts were refined anisotropically.

A diffraction-quality single crystal of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))\text{(CF}_3\text{)}_{16}$ (**16-1**) ($0.040 \times 0.040 \times 0.060$ mm) compound was mounted in paratone oil on a MiTeGen 10 μm loop. The data set was collected at 100 K using a silicon (111) crystal monochromator on a D8 goniostat equipped with a Bruker APEXII CCD detector at Beamline 11.3.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory using synchrotron radiation tuned to $\lambda = 0.7749$ Å. There is one molecule of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))\text{(CF}_3\text{)}_{16}$ in the asymmetric unit; neither the carbon cage nor the CF_3 groups are disordered. One Sc atom in Sc_3N cluster is disordered among two positions, Sc3A and Sc3B, with site-occupancy factors 43(2)% and 57(2)%, respectively. The major and minor disordered parts of Sc3 atom were refined anisotropically. Relevant experimental parameters are listed in Table 4.2.

Absorption and other corrections were applied by using SADABS.²⁰ The structures were solved using direct methods and refined (on F^2 , using all data) by a full-matrix, weighted least squares process. Standard Bruker control and integration software (APEX II) was employed, and Bruker SHELXTL²¹ software was used for structure solution, refinement, and graphics.

4.1.8. Spectroscopic Measurements. Atmospheric-pressure chemical-ionization (APCI) and atmospheric pressure photo-ionization (APPI) mass spectra were recorded using a ThermQuest Finnigan LCQ-DUO spectrometer (acetonitrile eluent, $0.3 \text{ mL} \cdot \text{min}^{-1}$ flow rate) and Agilent Technologies Model 6210 TOF with APPI spectrometer. In latter case, flow injection was done using acetonitrile which contained 1% toluene. Samples for ^{19}F NMR spectroscopy were chloroform-*d* solutions containing a small amount of hexafluorobenzene as an internal standard ($\delta = -164.9$). Spectra were recorded using a

Varian INOVA-unity 400 spectrometer operating at 367.45 MHz. UV-vis spectra were recorded using Varian CARY 500 Scan UV-vis-NIR spectrometer.

4.1.9. Theoretical Calculations. Dr. A. A. Popov (Leibniz Institute for Solid State and Materials Research, Dresden, Germany) performed DFT calculations using PBE functional and TZ2P-quality basis set implemented by the PRIRODA package.⁷³

4.2. Results and Discussion

4.2.1. Synthesis of $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_n$ Derivatives. In the preliminary trifluoromethylation reactions, a crude extract which contains 12% $\text{Sc}_3\text{N}@\text{C}_{80}$ (D_{5h} and I_h isomers), 62% C_{60} , and 26% C_{70} , according to the HPLC data, was used. A wide range of parameters was varied to establish the optimal experimental conditions for synthesis of trifluoromethylated $\text{Sc}_3\text{N}@\text{C}_{80}$ derivatives. The experiments were carried out in a flow tube reactor at 430–530 °C for 1.5–4 h in the presence (or in the absence) of the copper powder as a promoter. Use of the reaction temperature above 530 °C (and up to 760 °C) did not lead to the formation of $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_n$ derivatives. The hollow fullerene $(\text{CF}_3)_n$ obtained in these reactions sublimed out from the hot zone and condensed in the cold part of the reactor. According to the EI MS data, the obtained $\text{C}_{60}(\text{CF}_3)_n$ compounds contain 2–20 CF_3 groups per fullerene cage.

Less volatile $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_n$ products as well as unreacted $\text{Sc}_3\text{N}@\text{C}_{80}$ remained in the hot reaction zone. The extraction of the trifluoromethylated MNFs was performed using hexane and then toluene as solvents to isolate $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_n$ with $n = 4$ –14 according to the EI MS analysis. Preliminary HPLC separation of the extracted derivatives demonstrated that the $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_n$ compounds with $n = 8, 10$, and 12

could be isolated. Washing with *o*-dichlorobenzene led to the extraction of $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_2$ and unreacted $\text{Sc}_3\text{N}@\text{C}_{80}$. Two $\text{Sc}_3\text{N}@(\text{C}_{80}-I_h(7))(\text{CF}_3)_2$ (**2-1**) and $\text{Sc}_3\text{N}@(\text{C}_{80}-D_{5h}(6))(\text{CF}_3)_2$ compounds were isolated and characterized by ^{19}F NMR, UV-vis, and APCI MS spectroscopies (Figures 4.1 and 4.13). Thus, it can be concluded that both D_{5h} and I_h isomers of $\text{Sc}_3\text{N}@\text{C}_{80}$ react with CF_3 radicals at essentially the same rate at high temperatures (430–530 °C) despite less reactivity of $\text{Sc}_3\text{N}@(\text{C}_{80}-I_h(7))$ which was previously observed in cycloaddition reactions.

Another trifluoromethylating agent in the reactions with $\text{Sc}_3\text{N}@(\text{C}_{80}-I_h)$ was AgCF_3CO_2 (AgTFA). Previous study of the $\text{Y}@\text{C}_{82}$ trifluoromethylation indicated that use of AgTFA resulted in a selective formation of $\text{Y}@\text{C}_{82}(\text{CF}_3)_5$.³⁵ The reactions of $\text{Sc}_3\text{N}@(\text{C}_{80}-I_h(7))$ with AgTFA were carried out in a glass open tube at 350 °C for 2.5 h as described earlier.³⁵ It is interesting to note that increase of the reaction temperature up to 450 °C led to a drastic drop in the yield of $\text{Sc}_3\text{N}@(\text{C}_{80}-I_h)(\text{CF}_3)_n$ compounds, possibly because of thermal degradation of the products and/or $\text{Sc}_3\text{N}@\text{C}_{80}$. For the isolation of trifluoromethylated MNF compounds, the three-step extraction procedure has been used. First, the products were washed off using hexane which allowed us to extract mainly $\text{Sc}_3\text{N}@(\text{C}_{80}-I_h(7))(\text{CF}_3)_{10-18}$. The toluene fraction contained a wider range of the obtained products $\text{Sc}_3\text{N}@(\text{C}_{80}-I_h)(\text{CF}_3)_n$ where n varied from 2 to 18. (Figure 4.2) In Figure 4.3, NI-APPI mass spectra and HPLC trace of the crude product are shown. According to the mass spectral data, the main components in the reaction mixture contain 12 and 14 CF_3 groups. In the last stage, *o*-dichlorobenzene was used for complete extraction, and in that case, the main components were **2-1** and unreacted $\text{Sc}_3\text{N}@(\text{C}_{80}-I_h(7))$. (Figure 4.2) Thus, the $\text{Sc}_3\text{N}@(\text{C}_{80}-I_h(7))(\text{CF}_3)_n$ compounds with even $n = 10-18$ have a very good solubility

in aliphatic solvents (heptane or hexane) as well as in aromatic ones. The derivatives with a low number of CF₃ groups ($n = 2, 4$) have low solubility in aliphatic solvents but they are very well soluble in aromatic solvents (benzene, toluene or *o*-dichlorobenzene), in contrast to underivatized EMFs which have a notoriously low solubility in the common organic solvents.

A maximum degree of substitution observed in Sc₃N@C₈₀-I_h(7) trifluoromethylation is 18 CF₃ groups per fullerene cage. Therefore, 22.5% of the cage carbon atoms are sp³ hybridized carbons. In contrast, the attachment of 22 trifluoromethyl groups to the hollow C₆₀ fullerene was observed in similar reactions (see Chapter 2), which corresponds to the transformation of 37% sp² carbon cage atoms into sp³ ones. Thus, despite the larger C₈₀ cage, a lower number of CF₃ groups was added to Sc₃N@C₈₀-I_h(7) compared to the C₆₀ cage. Possible reasons will be explained later in the text. To achieve the higher degree of trifluoromethylation, the obtained Sc₃N@C₈₀-I_h(CF₃)_{*n*} (even $n = 2-18$) compounds were treated again with the “fresh” excess of AgTFA (~1:138 ratio) at the same temperature. Surprisingly, the NI-APPI mass spectrum and HPLC trace of the crude mixture after such treatment showed only a small shift of the composition towards the higher trifluoromethylated compounds. Mass spectral data demonstrate that the second cycle of trifluoromethylation led to the formation of Sc₃N@C₈₀-I_h(7)(CF₃)_{*n*} with $n = 14$ and 16 as the main components in the crude reaction mixture. The maximum number of CF₃ groups attached to the fullerene cage only shifted slightly to 20.

Therefore, maximum occupancy of the fullerene-cage surface achieved in these reactions was only 25%. In contrast, a maximum number of CF₃ groups attached to C₆₀ is

23 per fullerene, and therefore, 38% of sp^2 carbons became sp^3 ones. Thus, trifluoromethylation of MNF with the large ($C_{80-I_h(7)}$) cage led to the addition of fewer substituents than in case of hollow C_{60} fullerene. In case of the cycloaddition reactions, Dorn and co-workers observed the addition of 8 and 10 addends to $Sc_3N@C_{80-I_h(7)}$ or $Lu_3N@C_{80-I_h(7)}$ which relates to of 20% and 25% of sp^3 hybridized carbons on the fullerene cage, respectively. Thus, observed percentage of sp^3 carbons on the cage obtained in trifluoromethylation reactions is approximately the same as observed for cycloaddition of $Sc_3N@C_{80-I_h(7)}$. Interestingly, trifluoromethylation of monometallofullerene $Y@C_{82}$ (DMF extract) with excess of AgTFA (> 1:25 fullerene/AgTFA ratio, 400 °C, 10 h) resulted in the selective formation of TMFs with only five CF_3 groups per cage.³⁵

4.2.2. Separation of $Sc_3N@C_{80-I_h(7)}(CF_3)_n$ Derivatives. It is known that on the Cosmosil Buckyprep column retention times usually increase for the fullerenes with larger cage size.³³ For the same size-cage, the endohedral fullerenes have longer retention times than hollow fullerenes.⁹¹ The same trend was observed in the case of trifluoromethylated MNFs. For example, $Sc_3N@C_{80-I_h(7)}(CF_3)_2$ (**2-1**) has significantly longer retention time (27 min) than $C_{60}(CF_3)_2$ (7.1 min). Thus, both factors (the large C_{80} cage and the presence of the Sc_3N cluster inside the fullerene cage) contribute favorably towards more efficient HPLC separation of the $Sc_3N@C_{80-I_h(7)}(CF_3)_n$ compounds with the use of Buckyprep HPLC column.

Another aspect that facilitated the HPLC processing is different solubility of the obtained $Sc_3N@C_{80-I_h(7)}(CF_3)_n$ derivatives in different solvents. The compounds with high n values have good solubility in the aliphatic solvents, while the compounds with

low n values are practically not soluble in hexane. Therefore, three-stage extraction was applied to the crude mixture. First, extraction was done with hexane (see above) which allowed us to isolate the $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_n$ compounds with $n > 10$. They were subjected to the HPLC separation using heptane/toluene (70:30 or 90:10) mixtures with high content of heptane or 100% heptane as eluents. The second extraction was done with 100% toluene, and the last one – with *o*-DCB which extracted mostly unreacted $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$ and $n = 2$. Significant decrease of solubility observed for low trifluoromethylated species required use of *o*-dichlorobenzene for the extraction of $n = 2$ and the starting material. Isolation of **2-1** and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$ was done using 100% toluene; because of the sufficient differences in retention times a higher flow rate could be applied. Therefore, a multiple-step extraction allowed us to choose the optimal separation conditions for the compounds with different n values. In addition, the absence of by-products such as hydrogen- or oxygen-containing species resulted in the much simpler compositions of the product of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}/\text{AgTFA}$ reactions, in contrast to the earlier reported $\text{C}_{60}(\text{C}_{70})/\text{AgTFA}$ experiments (300–340 °C, 1–3 h) which showed the formation to numerous $\text{C}_{60/70}(\text{CF}_3)_n\text{H}$ compounds which had very close retention times to the ones of $\text{C}_{60(70)}(\text{CF}_3)_n$ compounds.⁶⁶ This led to the significant simplification of HPLC procedures used for the separation and purification of the obtained $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_n$ derivatives. For, example, one stage of the HPLC separation with the use 100% toluene as an eluent was sufficient for the isolation of six isomers (**2**, **4-1**, **4-2**, **8-1**, **8-2**, and **10-1**; see detailed in the Experimental Section and Figures 4.4 and 4.5). The most abundant **2-1** and **10-1** isomers were isolated with 98+% purity.

The $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_{12}$ isomers (**12-1**, **12-2**, **12-3**, and **12-4**) were purified in a two-stage procedure, involving a use of 30:70 (v:v) toluene:heptane and 10:90 (v:v) toluene:heptane eluents (Figure 4.6). Highly substituted derivatives such as **16-1**, **14-1**, and **14-2** were isolated using 100% heptane. NI-APPI MS analysis was mostly used to determine the compositional purity of the isolated fraction and compositional distribution in the crude samples. Recently, it was shown that NI-APPI is a sensitive ionization method for mass spectrometric detection of natural electrophores such as fullerenes and fluorinated derivatives (e.g., perfluoropentane, hexafluorobenzene, perfluorotributylamine or perfluoromethyldiamantane).¹⁰⁷ In addition, for some compounds APPI MS analysis is more sensitive, offers less ion suppression, and generates much more reproducible signals than APCI, especially at low mobile-phase flow rate.¹⁰⁸ In Figures 4.7–4.10, NI-ESI, NI-APCI, and NI-APPI mass spectra of the purified $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_{12}$ (**12-2** isomer) are shown which demonstrate that NI-APPI method led to formation of the high intensity $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_{12}^-$ molecular ion, less fragmentation, and almost no formation of adducts with solvent compared to NI-ESI and NI-APCI mass spectrometry. Thus, NI-APPI technique gives the reliable results for the detection and compositional purity determination of the $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_n$ compounds.

After the HPLC separation of the crude trifluoromethylated products and MS analysis of the isolated fractions were completed, it was found that $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_n$ derivatives with 4, 6, and 8 CF_3 groups were formed in very small quantities. According to the HPLC analysis of the toluene extract, the total amount of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_n$ compounds with $n = 4, 6, 8$ were comparable with the amount of only one isomer of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_2$ (**2-1**) and their total peak area in HPLC trace is

approximately half of the **10-1** peak area, assuming that the compounds have similar absorption coefficients. For instance, the fractions containing trifluoromethylated $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$ derivatives with six CF_3 groups were so small that they could be characterized only by mass-spectrometry. At the same time, we were able to isolate $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_4$ (**4-1** and **4-2** isomers) and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_8$ (**8-1**, **8-2**, **8-3**, **8-4**, and **8-5** isomers) and then characterized by ^{19}F NMR spectroscopy and mass-spectrometry.

4.2.3. Other Reactions. To study steric effect of the substituent, on the polyaddition to $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$, the addition of the small F atom and bulky *i*- C_3F_7 groups to $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$ was attempted. The previous theoretical and experimental studies of $\text{Sc}_3\text{N}@\text{C}_{80}$ fluorination reactions predicted the formation highly substituted $\text{Sc}_3\text{N}@\text{C}_{80}\text{F}_n$ ($n = 42\text{--}64$) compounds with major component which contains 52 fluorine atoms.¹⁰⁹ In the case of perfluoroalkylation reactions, studies involving $\text{C}_{60}/i\text{-C}_3\text{F}_7\text{I}$ reactions demonstrated that overall addition degree to fullerene is lower than in case of trifluoromethylation (see Chapter 3 for more details). Importantly, different addition patterns compared to trifluoromethylated analogs were observed for the hollow fullerene(*i*- C_3F_7)_{*n*}.

4.2.3.1. Fluorination. Fluorination of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$ was performed under dynamic vacuum at 380–550 °C for 2–6 h using K_2PtF_6 , MnF_3 , CoF_3 , and KMnF_4 as fluorinating agents (FAs). The ratio of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}/\text{FA}$ was varied from 1:10 to 1:388. (see Experimental Section) Although similar experimental conditions were used for successful preparation of $\text{C}_{60(70)}\text{F}_n$ compounds, formation of fluorinated $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$ derivatives was not observed.

4.2.3.2. $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{)}/i\text{-C}_3\text{F}_7\text{I}$ Reaction. The photochemical experiment of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{)}$ with $i\text{-C}_3\text{F}_7\text{I}$ was carried out in a quartz ampoule at room temperature for 47 hours. The addition up to 12 bulky $i\text{-C}_3\text{F}_7$ radicals to $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))$ cage was observed, in contrast to their trifluoromethylated analogs for which maximum degree of substitution (see above) was 18 CF_3 groups per fullerene cage.

However, for the $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(i\text{-C}_3\text{F}_7)_n$ derivatives, a significant decrease of retention time (Figure 4.11) was observed which resulted in a complex HPLC trace and impossibility of their separation using existing chromatographic techniques. The similar tendency was previously described for the hollow fullerenes with long perfluoroalkyl chains. There is only one other example in the literature which reported EMF perfluoroalkylation. Shinohara and co-workers reported that use of 1.8 equivalents of $\text{C}_8\text{F}_{17}\text{I}$ with monometallofullerene $\text{La}@\text{(C}_{82}\text{-C}_s\text{)}$ under UV-vis irradiation resulted in the addition of two perfluoroalkyl C_8F_{17} groups per EMF cage and the isolation of seven isomers of *bis*-derivative.⁹⁸ Thus, our experiments of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))$ with $i\text{-C}_3\text{F}_7\text{I}$ confirm that photochemical cleavage of C–I bonds leads to the effective formation of perfluoroalkyl radicals with following preparation of perfluoroalkylated EMFs.

4.2.3.3. Reaction of $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{)}(\text{CF}_3)_n$ with $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$. The isolated $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{)}(\text{CF}_3)_n$ compounds were used as precursors for the further derivatization, which was demonstrated on the example of **10-1** and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{)}(\text{CF}_3)_{14}$ compounds. A photochemical reaction of **10-1** with excess of benzyl bromide (16.8 equivalents) was carried out in a quartz ampoule at room temperature, and 2 mL of deoxygenated toluene were used as a reaction medium. After 1 h under UV irradiation, the reaction solution changed the color from green to dark brown, and there was no unreacted starting material

in the crude mixture according to the HPLC analysis. As a result, the addition of six benzyl group to **10-1** was observed based on the APPI mass spectral data (Figure 4.12). A similar one-hour-photochemical reaction of the unmodified $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$ (or $\text{Lu}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$) with the large excess of $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ (1000 equivalents) led to the formation and isolation of the derivatives with only two benzyl groups.

Thus, in the benzylation reactions, trifluoromethylated $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h)$ compounds exhibit a higher reactivity compared to the naked $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$.

4.2.3.4. Trifluoromethylation of $\text{Er}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}$. Trifluoromethylation of $\text{Er}_3\text{N}@\text{C}_{80}$ sample was carried out in a glass sealed ampoule at 432 °C for 48 h using CF_3I as a trifluoromethylating agent. The sample of $\text{Er}_3\text{N}@\text{C}_{80}$ mainly contains I_h isomer but the small amounts of $\text{Er}_3\text{N}@\text{(C}_{80}\text{-D}_{5h}\text{(6))}$ and $\text{Er}_2@\text{C}_{2n}$ were also observed in the HPLC trace of the starting material. The trifluoromethylated compounds obtained from this reaction was analyzed by mass-spectrometry. NI-EI MS analysis showed that the trifluoromethylation of the minor components in the starting material such as $\text{Er}_2@\text{C}_{84}$, $\text{Er}_2@\text{C}_{88}$, and $\text{Er}_2@\text{C}_{90}$ occurred. Thus, $\text{Er}_2@\text{C}_{88}(\text{CF}_3)_{15}$, $\text{Er}_2@\text{C}_{88}(\text{CF}_3)_{17}$, $\text{Er}_2@\text{C}_{84}(\text{CF}_3)_{19}$, $\text{Er}_2@\text{C}_{88}(\text{CF}_3)_{19}$, and $\text{Er}_2@\text{C}_{90}(\text{CF}_3)_{19}$ species were detected by mass-spectrometry.

4.2.4. Addition Patterns of the $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_n$ (even $n = 2-16$) Derivatives.

$\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_2$ and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-D}_{5h}\text{(6))}(\text{CF}_3)_2$. Fluorine-19 NMR spectrum of the $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}(\text{CF}_3)_2$ compound isolated from $\text{Sc}_3\text{N}@\text{C}_{80}/\text{CF}_3\text{I}$ or $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{(7))}/\text{AgCF}_3\text{CO}_2$ reactions contains a singlet at $\delta -71.4$, indicating either symmetry-related CF_3 groups or CF_3 groups rendered chemical-shift equivalent by rapid reorientation of the Sc_3N cluster inside the cage (Figure 4.13). Fluorine-19 NMR

spectrum of the mixture of two *bis*-derivatives isolated from the reaction of the extract $\text{Sc}_3\text{N}@\text{C}_{80}$ (mixture of D_{5h} and I_h cage isomers) and CF_3I contains two singlets, at δ -71.4 (rel. int. 7) and -73.3 (rel. int. 1). It is virtually certain that the compound with δ -73.3 belongs to $\text{Sc}_3\text{N}@(\text{C}_{80}\text{-}D_{5h}(6))$. The DFT calculations were performed for more than 20 isomers of $\text{Sc}_3\text{N}@(\text{C}_{80}\text{-}I_h(7))(\text{CF}_3)_2$, in which different cluster positions were chosen as starting points for geometry optimization. The two most stable optimized structures each have two of the three Sc atoms bonded to the cage C atom that is *para* to each of the cage $\text{C}(\text{CF}_3)$ atoms, as shown in Figure 4.13. This results in a p^3 ribbon of edge sharing hexagons with the sequence $\text{C}(\text{Sc})\cdots\text{C}(\text{CF}_3)\cdots\text{C}(\text{CF}_3)\cdots\text{C}(\text{Sc})$. The two lowest energy isomers differ only in the position of the third Sc atom, and the DFT-calculated energy difference between them is less than 2 kJ mol^{-1} . Both isomers were slightly distorted ideal C_2 symmetry in that the Sc atom farthest from the CF_3 groups is displaced from the center of its closest hexagon toward one of the 5/6 junctions. Thus, on the NMR time scale, this Sc atom would undergo rapid reorientation with respect to the C atoms of its hexagon, resulting in the apparent molecular C_2 symmetry and chemical-shift equivalent CF_3 groups. Other DFT-optimized structures in which only one Sc atom is bonded to a cage C atom *para* to a CF_3 group are $13\text{--}21\text{ kJ mol}^{-1}$ less stable than the first two; all other isomers are $26\text{--}65\text{ kJ mol}^{-1}$ higher in energy. These results reveal a significant difference between $\text{Sc}_3\text{N}@(\text{C}_{80}\text{-}I_h(7))(\text{CF}_3)_2$ and $\text{Sc}_3\text{N}@(\text{C}_{80}\text{-}I_h(7))$. Variable-temperature ^{45}Sc NMR spectroscopy and DFT calculations have shown that the Sc_3N cluster effectively undergoes free rotation in $\text{Sc}_3\text{N}@(\text{C}_{80}\text{-}I_h)$.^{83,110} Therefore, either 1,2 additions (i.e., cycloadditions to a cage C–C bond) or 1,4 additions (i.e., *para* addition of CF_3 groups to a hexagon) can substantially affect dynamics of the cluster. There is only

one way to add two CF₃ groups to *para* positions of a Sc₃N@C₈₀-D_{5h}(6)) hexagon so that the CF₃ groups are symmetry related. By analogy to the DFT results for the I_h cage isomer, we suggest that two of the three Sc atoms are coordinated to cage carbon atoms that are *para* to the sp³ C(CF₃) atoms in Sc₃N@C₈₀-D_{5h}(6))(CF₃)₂, as shown in Figure 4.13. Figure 4.13 also shows the UV-vis-NIR absorption spectra of the pure Sc₃N@C₈₀-I_h(7))(CF₃)₂ and the mixture of Sc₃N@C₈₀-I_h(7))(CF₃)₂ and Sc₃N@C₈₀-D_{5h}(6))(CF₃)₂. The lowest-energy transition of Sc₃N@C₈₀-I_h(7))(CF₃)₂ occurs at 920 nm (1.35 eV), a significantly longer wavelength than the 735 nm (1.69 eV) value for the parent Sc₃N@C₈₀-I_h(7)).¹¹¹ A shoulder at 772 nm (1.62 eV) is assigned to the lowest-energy transition of Sc₃N@C₈₀-D_{5h}(6))(CF₃)₂, which almost coincides with the 780 nm (1.59 eV) value for the parent Sc₃N@C₈₀-D_{5h}(6)).¹¹¹ Therefore, the addition of two CF₃ groups results in a 0.34 eV decrease in the Sc₃N@C₈₀-I_h) optical gap and a small increase of 0.03 eV in the Sc₃N@C₈₀-D_{5h}(6)) optical gap.

Sc₃N@C₈₀-I_h(7))(CF₃)₄ (4-1). The ¹⁹F NMR pattern of the Sc₃N@C₈₀(CF₃)₄ with four equal-intensity quartets suggests that in this C₁-symmetric compound two pairs of neighboring CF₃ groups are far apart from each other and each CF₃ group exhibits the splitting only due to the interaction with the CF₃ group in the shared hexagon or pentagon. DFT calculations revealed that there are three isomers of Sc₃N@C₈₀(CF₃)₄ within 10 kJ mol⁻¹ range; one of them has C_s symmetry, and two isomers are non-symmetric ones. The lowest energy isomer has 1,7,31,52 addition pattern with C_s symmetry and comparably small HOMO-LUMO gap, 0.94 eV, while the virtually isoenergetic C₁-1,7,32,51-Sc₃N@C₈₀(CF₃)₄ has the gap of 1.10 eV, the highest among lowest energy isomers. The C₂-1,7,52,72-Sc₃N@C₈₀(CF₃)₄ isomer with comparable

HOMO-LUMO gap, 1.12 eV, is 14.3 kJ mol⁻¹ less stable. Based on its low relative energy, the highest gap and C₁ symmetry, which is compatible with ¹⁹F NMR spectrum, it was proposed that Sc₃N@C₈₀(CF₃)₄ has *p,p*-1,7,32,51 addition pattern (Figure 4.14). Two other stable C₁ isomers are 1,7,54,70-Sc₃N@C₈₀(CF₃)₄ ($\Delta E = 8.5$ kJ mol⁻¹, gap 0.99 eV) and 1,7,14,35-Sc₃N@C₈₀(CF₃)₄ ($\Delta E = 14.4$ kJ mol⁻¹, gap 0.96 eV). The isomers with low relative energy and small gaps (below 1.0 eV) are also probably formed but are more reactive and hence are faster converted to the products with the larger number of added CF₃ groups. Note that the HOMO-LUMO gap of the proposed Sc₃N@C₈₀(CF₃)₄ isomer is 0.1 eV smaller than that gap of Sc₃N@C₈₀(CF₃)₂, which agrees with the experimental UV-vis spectra of these compounds (Figure 4.21).

Sc₃N@C₈₀-I_h(7)(CF₃)₈ (8-1). Based on the ¹⁹F NMR spectrum (see Figure 4.20), the addition pattern of **8-1** compound should contain a ribbon of eight CF₃ groups. Figure 4.15 shows the Schlegel diagrams of the most stable **8-1** isomer according to the DFT calculations. It has two conformers with slightly different position of Sc₃N cluster (they are different in energy by only 2.8 kJ mol⁻¹) and is 38 kJ mol⁻¹ more stable than any other isomers with different CF₃ addition patterns. Specific peculiarity of this isomer is that CF₃ ribbon forms two semi-isolated benzene rings, and Sc atoms are coordinated to the cage atoms in the close vicinity of the carbon atoms that would be C-sp³ if the rings were fully isolated.

Sc₃N@C₈₀-I_h(7)(CF₃)₈ (8-2). The ¹⁹F NMR spectrum of **8-2** (Figure 4.15, Table 4.1) shows that this compound has one isolated CF₃ group and two ribbons formed by the remaining seven CF₃ groups (this implies either “5+2” or “4+3” combination of ribbons). Based on the close resemblance of the ¹⁹F NMR spectra of **8-2** and **10-1** (which structure

is known from X-ray crystallographic data and will be described in detail below), it was suggested that (i) isolated CF₃ group is added to triple-hexagon junction (THJ) since its $-\delta(\text{F})$ value is 80.9 ppm, and that (ii) addition pattern of **8-2** can be obtained from the addition pattern of **10-1** by removal of two CF₃ groups. These two suggestions lead to six “4+3+1” (a ribbon of four CF₃ groups + a ribbon of three CF₃ groups + an isolated CF₃ group) and six “5+2+1” possible isomers of **8-2**. All 12 isomers were studied by DFT calculations. From these structures the “5+2+1” isomer shown in Figure 4.15 has the HOMO-LUMO gap of 1.15 eV and is 13.5 kJ mol⁻¹ more stable than the proposed structure of **8-1**. All other Sc₃N@C₈₀-I_h(7)(CF₃)₈ isomers are less stable by 22 kJ mol⁻¹ or more.

Sc₃N@C₈₀-I_h(7)(CF₃)₁₀ (10-1). Fluorine-19 NMR spectrum of **10-1** contains one singlet, two quartets, and seven multiplets (Figure 4.15, Table 4.1). Based on the spectroscopic data, it was suggested that the addition pattern of this compound has a ribbon of nine CF₃ groups and one isolated CF₃ group (“9+1”). According to the DFT calculations the Schlegel diagram of the most stable isomer of **10-1** (40 kJ/mol more stable than all other isomers) is shown in Figure 4.16. The proposed addition pattern of **10-1** isomer was later confirmed by X-ray crystallographic studies that will be described in detail in section 4.2.5.1 of this Chapter.

Sc₃N@C₈₀-I_h(7)(CF₃)₁₂ (12-1). Fluorine-19 NMR spectrum of **12-1** with one singlet, two quartets and nine multiplets indicates (Figure 4.15, Table 4.1) that this compound has the “11+1” addition pattern. Based on the close resemblance of the ¹⁹F NMR spectra of **12-1** and **10-1**, it was suggested that (i) isolated CF₃ group is added to THJ since its $-\delta$ value is 78.0 ppm, and that (ii) addition pattern of **12-1** can be obtained

from the addition pattern of **10-1** by addition of two CF₃ groups either to one end of the ribbon, or by addition of one group to each end of the ribbon (Figure 4.15, Table 4.1). There are 23 isomers of this sort, of them 9 have one CF₃ group attached to THJs as a part of the ribbon (in addition to the isolated CF₃ group). The structure with the lowest energy (26 kJ mol⁻¹ more stable than the second most stable isomer) has the gap of 1.24 eV and is proposed to be a structure of **12-1**. Thus, **12-1** can be obtained from **10-1** by the addition of a pair of CF₃ groups to C54 and C70 (Figure 4.17). The proposed addition pattern **12-1** based on the spectroscopic data and DFT calculations was later confirmed by X-ray crystallography. X-ray crystal structure of **12-1** will be discussed in detail in section 4.2.5.2 of this Chapter.

Sc₃N@C₈₀-I_h(7)(CF₃)₁₂ (12-2). Fluorine-19 NMR spectrum of **12-2** with two quartets and 10 multiplets indicates that the addition pattern has the ribbon of 12 CF₃ groups (Figure 4.15, Table 4.1). All possible isomers of **12-2** formed by removal of two CF₃ groups from either **14-1** or **14-3** were studied by DFT calculations. The lowest energy structure obtained this way is 16 kJ mol⁻¹ less stable than **12-1** and has relatively large HOMO-LUMO gap of 1.24 eV (Figure 4.18). This isomer is based on **14-3**, while the lowest energy isomer based on **14-1** is 28.2 kJ mol⁻¹ less stable and has the gap of 0.95 eV.

Sc₃N@C₈₀-I_h(7)(CF₃)₁₂ (14-1). Fluorine-19 NMR spectrum of **14-1** exhibits two quartets and 12 multiplets, shows that the addition pattern of this compound has the ribbon of 14 CF₃ groups (Figure 4.19, Table 4.1). The strongly shifted singlet is observed as in the spectra of **8-2** (δ -80.8), **10-1** (δ -78.9), and **12-1** (δ -78.0), which is assigned to the isolated CF₃ group attached to THJ (Table 4.1). In the ¹⁹F NMR spectrum of **14-2** this

singlet is split into a quartet ($\delta -80.2$, Table 4.1). This indicates that THJ-bonded CF_3 group is present in **14-2** and it is one of the terminal groups. In addition, it was suggested that the structure of **14-2** results from the addition of four groups to **10-1**. One group is added to *meta* or *para* position in the THJ- CF_3 containing hexagon, so that THJ-bonded CF_3 group becomes terminal. Three other groups should be added to the opposite end of the ribbon so that the ribbon of 14 CF_3 groups is formed. This leads to more than 100 possible isomers, which were studied by the DFT calculations. The isomer shown in Figure 4.19 has the lowest energy (40 kJ mol^{-1} more stable than all other isomers) and the largest HOMO-LUMO gap (1.36 eV). This structure is 4 kJ mol^{-1} less stable than **14-3** isomer characterized by X-ray crystallography. Based on the high stability and large HOMO-LUMO gap of this structure, it was suggested that it is the most probable addition pattern of **14-1**.

The **4-2**, **8-5**, **10-2**, **12-3**, **12-4**, and **16-1** were isolated and purified only in small amounts which were enough only for spectroscopic characterization of these compounds (Figures 4.20, 4.22–4.29). The structural analysis of these isomers required synthesis and isolation of these particular isomers in larger quantities and probably it will be a subject for a future work.

4.2.5. X-ray structural Studies. Use of a slow solvent evaporation method led to the formation of the $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{10} \cdot 1.5\text{C}_8\text{H}_{10}$ and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{12} \cdot \text{CS}_2$ single crystals suitable for X-ray diffraction. The small size ($9\text{--}88 \text{ }\mu\text{m}$) of the obtained crystals required the use of synchrotron radiation to perform crystallographic studies which allowed us to determine **10-1** and **12-1** structures with high precision.

4.2.5.1. 1,3,7,17,24,28,39,47,51,62-Sc₃N@C₈₀-I_h(CF₃)₁₀ (10-1). X-ray structural data for **10-1** confirmed the addition pattern that was predicted based on the ¹⁹F NMR spectroscopy and DFT calculations (see above, Figure 4.16). It consists of one isolated CF₃ group and an “S-shaped” ribbon of six edge-sharing *para*-C₆(CF₃)₂ hexagons and two 1,3-C₅(CF₃)₂ pentagons (Figure 4.16). Addition of electron-withdrawing trifluoromethyl groups creates electron-deficient regions on a fullerene cage. The trimetallic nitride cluster has formally 6+ charge and, therefore, it tends to “coordinate” to the remaining electron-rich C–C bonds. Increase of the number of CF₃ groups on the cage leads to decrease in the number of such bonds. X-ray structure of **10-1** demonstrates that an addition of ten trifluoromethyl groups results in one Sc₃N orientation which is significantly more stable than alternative orientations. In addition, CF₃ group attachment leads to the distortion of the cluster from the idealized *D*_{3h} symmetry which was previously observed in the crystal structures of **14-3** and **16-2** isomers. Figure 4.35 shows that one Sc1–N–Sc3 angle in **10-1** is 119.2(2)° (still close to 120° in the underivatized Sc₃N@C₈₀-I_h(7)) but Sc2–N–Sc3 and Sc1–N–Sc2 are 105.5(2)° and 135.3(2)°, respectively. The distance between nitrogen atom and a centroid of Sc atoms is 0.170 Å. Despite the angular distortion, Sc₃N cluster is still planar within 0.016 Å, and Sc–N bond lengths are 2.005(4) Å, 2.031(4) Å, and 2.031(4) Å which are close to Sc–N distances (1.993(1)–2.053(1) Å) in the unmodified Sc₃N@C₈₀-I_h(7). Each scandium atom coordinates to two C–C bonds on the cage: Sc1⋯C12–C13 and Sc1⋯C13–C31 distances are 2.174(5) Å and 2.205(5) Å; Sc2⋯C22–C43 and Sc2⋯C42–C43 distances are 2.158(5) Å and 2.196(5) Å; Sc3⋯C76–C80 and Sc2⋯C74–C76 distances are 2.152(5) Å and 2.171(5) Å, respectively (Figures 4.38–4.41). The Sc–C distances from Sc1, Sc2, and Sc3

to the closest cage carbon atoms C13, C43, and C74 are 2.275(5) Å, 2.264(5) Å, and 2.254(5) Å, respectively (Figures 4.37, 4.39–4.41). The centroid of all cage carbons is shifted 0.257(5) Å from the centroid of three scandium atoms and 0.089 Å from nitrogen atom, respectively, as shown in Figure 4.51 (Table 4.3).

4.2.5.2. 1,3,7,17,24,28,39,47,51,54,62,70-Sc₃N@C₈₀-I_h(7)(CF₃)₁₂ (12-1). X-ray crystallographic studies proved that the determined **10-1** addition pattern is a sub-pattern of **12-1** structure, and the latter one is different by the presence of two more CF₃ groups attached to C54 and C70 carbon atoms (Figure 4.16 and 4.17). The **12-1** addition pattern contains a ribbon, made of seven edge-sharing *para*-C₆(CF₃)₂ hexagons and three 1,3-C₅(CF₃)₂ pentagons, and one isolated CF₃ group attached to THJ (Figure 4.17). As in the case of **10-1**, only one Sc₃N orientation is observed, and the trimetallic nitride cluster is planar within 0.008 Å. The geometrical parameters of Sc₃N, such as Sc–N–Sc angles and Sc–N bond lengths are very similar to those in **10-1** structure. One of the Sc1–N–Sc3 angles is still close to 120° (119.4(2)°), and Sc2–N–Sc3 and Sc1–N–Sc2 are 105.2(2)° and 135.4(2)°, respectively (Figure 4.35). The Sc–N bond lengths are 2.002(4) Å, 2.038(4) Å, and 2.045(4) Å (Figure 4.36). In addition, Sc atoms coordinate to exactly the same C–C bonds as observed in **10-1** crystal structure. The distances from Sc1 to C12–C13 and C13–C31 bonds are 2.183(3) Å and 2.194(3) Å; from Sc2 to two close C22–C43 and C42–C43 bonds are 2.147(3) Å and 2.203(3) Å; Sc3 to two close C76–C80 and C74–C76 bonds are 2.147(3) Å and 2.170(3) Å, respectively (Figures 4.42–4.44). The Sc–C distances from Sc1, Sc2, and Sc3 to the closest cage carbon atoms C13, C43, and C76 are 2.278(3) Å, 2.267(3) Å, and 2.246(3) Å, respectively (Figures 4.37, 4.42–4.44). The shift of the cage-carbon-atom centroid is 0.256(3) Å relative to the centroid of Sc atoms and

0.089 Å to nitrogen atom (Figures 4.51). The Sc–N distance between the scandium-atom centroid and nitrogen atom is 0.168(3) Å (Figures 4.51 and Table 4.3).

4.2.5.3. 1,3,7,17,28,39,41,45,47,51,54,62,65,70-Sc₃N@(C₈₀-I_h(7))(CF₃)₁₄ (**14-3**).

The CF₃ groups in **14-3** are attached to 14 cage C(sp³) atoms that form a continuous ribbon of edge-sharing *para*- and *meta*-C₆(CF₃)₂ hexagons and 1,3-C₅(CF₃)₂ pentagons (each shared edge is a cage C(sp³)–C(sp²) bond) (Figure 4.30). Four CF₃ groups, on C1, C3, C17, and C65, exhibit two-fold rotational disorder. The C1, C3, and C17 CF₃ groups are ca. 50% staggered and ca. 50% eclipsed with respect to the three cage C–C bonds that radiate from the cage C atom to which they are attached, and the C65 CF₃ group is 88.6(4)% staggered and 11.4(4)% eclipsed. Ignoring these disordered CF₃ groups, the range of F⋯F contacts shorter than 3 Å between CF₃ groups that share the same hexagon or pentagon is 2.591(5)–2.791(5) Å. This range is normal for CF₃ derivatives of hollow higher fullerenes.^{34,39}

Four of the CF₃ groups in **14-3** are attached to C₈₀ THJs C41, C45, C62, and C65. This is unprecedented (Figure 4.30). Before this work, no fullerene derivative of any kind had been found with more than two sp³ THJs, probably because (i) sp² THJs are the least pyramidal cage C atoms in empty underivatized higher fullerenes,¹¹² and the release of angle strain at more pyramidal sites is part of the driving force for exohedral functionalization at those particular sites,¹¹² and (ii) no EMF with more than four cage C(sp³) atoms had been structurally characterized. However, the degree-of-pyramidalization in underivatized EMFs is more complicated than in empty underivatized higher fullerenes because some EMF sp² THJs are more pyramidal than some of the cage C(sp²) atoms that make up the EMF pentagons. There are X-ray structures of two

cycloadducts of MNFs that have one sp^3 THJ each, $Sc_3N@C_{78-D_{3h}(5)}((CH_2)_2NCPH_3)^{97}$ and $Sc_3N@C_{80}((CH_2)_2NCPH_3)^{103}$. The former compound appears to be the stable isomer of this composition; the latter compound isomerizes in solution to a more stable isomer with no sp^3 THJs.¹⁰³ In addition, the bis-cycloadduct $Sc_3N@C_{78-D_{3h}(5)}(C(CO_2Et)_2)_2$ is believed to have two sp^3 THJs.¹¹³

DFT calculations, summarized in Figure 4.31, show that the 1,3,7,17,28,39,41,45,47,51,54,62,65,70 isomer **14-3**, with four sp^3 THJs, is more stable than several hypothetical isomers without sp^3 THJs, viz. isomers 3, 5, 7, and 8. However, if the Sc_3N^{6+} cluster is removed from **14-3**, the remaining hexaanion 1,3,7,17,28,39,41,45,47,51,54,62,65,70- $C_{80}(CF_3)_{14}^{6-}$ is far less stable than $C_{80}(CF_3)_{14}^{6-}$ isomers 3 and 5. Therefore, the presence of the metal cluster appears to stabilize the formation of the four sp^3 THJs in **14-3**. It is probably due to the formation of sp^3 THJs tends to localize negative charge in pentagons to which one or more metal atoms are bonded. For example, the four sp^3 THJs in **14-3** are bonded to a common pentagon, and this is the same pentagon that interacts strongly with Sc2 through C43, the closest cage C atom to Sc2, and C42 and C44, the third and fourth closest cage C atoms to Sc2 (Sc2–C42 = 2.408(4) Å and Sc2–C44 = 2.408(3) Å). The evidence that this pentagon has become more "electron-rich" relative to the same pentagon in the precursor $Sc_3N@C_{80}$ is two-fold: (i) the C42–C63, C44–C63, and C63–C64 distances in **14-3** are ca. 1.41 Å whereas they are ca. 1.44 Å in (DFT-optimized) $Sc_3N@C_{80}$ (Figure 4.32); and (ii) Sc2 has moved from being closest to C23 and C24 in $Sc_3N@C_{80}$ to being closest to C22 and C43 in **14-3**, even though this has caused the Sc1–N–Sc2 bond angle to undergo a significant distortion from 120° in $Sc_3N@C_{80}$ to 136.7(1)° in **14-3** (Figure 4.35). In

addition, note that sp^3 THJs C62 and C65 are also bonded to the pentagon that interacts with Sc3, and C–C distances within that pentagon have also been shortened relative to $Sc_3N@C_{80}$.

4.2.5.4. 2,4,10,16,20,23,25,34,46,53,57,62,65,68,71,74- $Sc_3N@(C_{80}-I_h(7))(CF_3)_{16}$ (16-2). The CF_3 groups in **16-2**, none of which is disordered, are attached to 16 cage $C(sp^3)$ atoms, half of which are sp^3 THJs (C34, C53, C57, C62, C65, C68, C71, and C74, Figure 4.33). (The range of F...F distances for **16-2** is 2.527(2)–2.900(2) Å.) In this compound, the localization of negative charge in pentagons reaches the maximum extent. The eight sp^3 THJs form a double loop of edge-sharing $p-C_6(CF_3)_2$ hexagons, and each loop of five $p-C_6(CF_3)_2$ hexagons surrounds an isolated pentagon composed of $C(sp^2)$ atoms (i.e., the pentagons are isolated in that their π systems are not in conjugation with the rest of the fullerene π system or with each other; the $p-C_6(CF_3)_2$ hexagon that includes C71 and C74 is common to both loops). Isolated $C(sp^2)_5^-$ pentagons with *six* π electrons in fullerene derivatives (i.e., in $C_{60}X_5^-$ anionic moieties) are aromatic and can coordinate to *exohedral* metal atoms in η^5 Cp-like fashion.¹¹⁴ However, in **16-2** the isolated pentagons coordinate to an *endohedral* metal atom, Sc3.

Formally, each isolated pentagon has received one of the two electrons that Sc3 donates to the C_{80} cage to become a six-electron aromatic $C(sp^2)_5^-$ pentagon. The Sc3 atom appears to be η^2 bonded to both isolated pentagons simultaneously, although not equally, and this inequality leads to the observed disorder in the position of Sc3 (Sc3a (43(2)% occupancy) and Sc3b (57(2)% occupancy) are 0.455(3) Å apart). In the structure of $Sc(\eta^5-Cp^*)_2(CH_2CMe_3)$, the ranges of Sc–C(Cp) and C(Cp*)–C(Cp*) distances are 2.482(4)–2.541(4) Å and 1.403(5)–1.423(5) Å, respectively.¹¹⁵ In **16-2**, the ranges of

Sc3a/b–C and C–C distances involving the isolated pentagons are 2.20(5)–2.92(9) Å and 1.401(2)–1.441(2) Å, respectively (the longest C–C bond in each of the isolated C(sp²)₅[−] pentagon is the one that is closest to Sc3, C72–C73 and C76–C80; note that the range of all C(sp²)–C(sp²) distances in **16-2** is 1.344(2)–1.470(2) Å). Another indication of the aromatic, electron-rich nature of the isolated pentagons is that C72–C73 and C76–C80 are significantly shorter than C13–C31 (1.461(2) Å) and C42–C43 (1.459(2) Å), which are η² bonded to Sc1 and Sc2, respectively, and are not part of isolated aromatic C(sp²)₅[−] pentagons (see Figure 4.34). Interestingly, the distances between Sc3a or Sc3b and the centroids of their respective isolated pentagons are ca. 2.28 Å, only 0.07 Å longer than the corresponding distances in Sc(η⁵-Cp*)₂(CH₂CMe₃) (ca. 2.21 Å).¹¹⁵

In accordance with the X-ray structure of **16-2**, our DFT calculations show that there are two conformational isomers of **16-2** that differ only in the position of Sc3 (the calculated Sc3a⋯Sc3b distance is 0.457 Å). The predicted energy difference between these conformers is 0.78 kJ mol^{−1} and is reduced to 0.36 kJ mol^{−1} if zero-point vibrational energy (ZPVE) is taken into account. It was also located the transition state between the conformers, and found it to be only 1.36 kJ mol^{−1} above the lower energy structure (0.69 kJ mol^{−1} if ZPVE is also considered; to ensure that this transition state corresponds to the true energy barrier between the conformers, intrinsic-reaction-coordinate calculations were carried out following the normal mode with an imaginary frequency in both directions). With such a low energy barrier to interconversion, the disorder found in the position of Sc3 is almost certainly a true equilibrium at 100 K, the temperature of the X-ray data collection. An equilibrium quotient of 1.3(1) can be calculated for the conformational equilibrium {Sc3a-conformer} ⇌ {Sc3b-conformer} (i.e., 57(2) ÷

43(2) = 1.3(1)). At 100 K, this corresponds to an energy difference of 0.26(2) kJ mol⁻¹, in excellent agreement with the DFT predicted value of 0.36 kJ mol⁻¹. This is the first time that an experimentally observed disorder in M₃N cluster conformations in an MNF has been shown by theory to be due to two or more energy minima, each with a full set of non-imaginary frequencies, and that the transition between the minima has a low barrier.

4.2.5.5. Geometry and Location of Sc₃N Cluster in 10-1, 12-1, 14-3, and 16-2

Structures. The X-ray crystal structures of **10-1** and **12-1** have a similar addition pattern with **14-3** (a modified “S-ribbon”). In contrast, **16-2** addition pattern is significantly different (see above). It contains CF₃ groups arranged in the double loop of the edge-sharing *p*-C₆(CF₃)₂ hexagons, which leads to the formation of two isolated pentagons coordinating to Sc₃ atom. There are two conformational isomers of **16-2** that differ only in the position of Sc₃ atom, and therefore, in the X-ray structure we observed that Sc₃ metal atom is disordered among two positions (see above, Figure 4.33). Thus, we have prepared and structurally characterized a set of four Sc₃N@C₈₀-I_h(7)) polyadducts which allow for in-depth analysis of the dynamic of Sc₃N cluster inside the fullerene cage and study of the correlation between its geometrical parameters, the number of substituents, and their addition patterns.

The correlation between Sc–N–Sc angles and a number of the substituents for the known Sc₃N@C₈₀-I_h(7)) crystal structures is plotted in Figure 4.35. It reveals that the increase of CF₃ group number on the fullerene sphere leads to a significant distortion of Sc₃N cluster from three-fold symmetry. The Sc–N–Sc angles in the cluster of the naked Sc₃N@C₈₀ cage are very close to 120° (118.5(1)°, 119.6(1)°, and 120.7(1)°). The presence of two substituents or cycloadduct on the Sc₃N@C₈₀ cage starts to deviate Sc–

N–Sc angles from 120°, and the observed range for the $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))\text{X}_2$ is 113.6(3)–125.9(3)° (Figure 4.35). For the compounds with 10 or 12 CF_3 groups two Sc–N–Sc angles became significantly different from 120° (105° and 135°). The maximum angle distortion is achieved in the **16-2** structure in which the Sc–N–Sc angles are 102.2(2)°, 107.1(1)°, and 150.5(1)°. At the same time, Sc_3N cluster is still planar in all structures. There are three different Sc–N bond lengths observed for the naked $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))$ crystal structure as shown in Figure 4.36. Addition of 10 CF_3 groups leads to two Sc–N bonds with an identical length (2.031(4) Å). The same tendency observed in **12-1** and **14-3** structures in which two Sc–N bonds have very close values of the bond lengths. In **16-1**, Sc–N distances are in the narrower range (2.0027(13)–2.013(2) Å) compared to 1.997(3)–2.051(3) Å observed for **10-1**, **12-1**, and **14-3** structures as shown in Figure 4.36. Thus, we can conclude that in the highly substituted $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_n$ compounds, the deviation of trimetallic nitride cluster from the idealized D_{3h} symmetry occurs mainly due to distortion of Sc–N–Sc angles.

The same cluster orientation inside the fullerene cage was observed in **10-1**, **12-1**, and **14-3** crystal structures. Figures 4.37 and 4.39–4.50 show that one of the Sc atoms is always close to C76, C43, and C13 cage carbons in three structures. The distances from each Sc atom to the closest C–C bond are also similar for three structures: the distances from Sc1 to C12–C13 and C13–C31 bonds are 2.174(5)–2.183(3) Å and 2.194(3)–2.205(5) Å; from Sc2 to C22–C43 and C42–C43 bonds are 2.147(3)–2.158(5) and 2.189(5)–2.203(3) Å; from Sc3 to C76–C80 and C74–C76 bonds are 2.147(3)–2.152(5) Å and 2.170(3)–2.171(5) Å, respectively, as shown in Figure 4.38. The minor change in the position of Sc2 atom, which is closer to C22–C43 (2.148(4) Å) bond and equidistant

to two C42–C43 and C43–C44 bonds (2.189(4) Å), was observed in structure **14-3** (Figure 4.46). In contrast, Sc2 atom in **10-1** and **12-1** structures coordinates only to two C22–C43 and C42–C43 bonds (Figures 4.40 and 4.43). In **16-1**, Sc₃N cluster changes its location, and three scandium atoms become close to the C80, C73, C42, and C31 (C13) carbon atoms (Figures 4.37 and 4.48–4.50).

In Figure 4.51 the dependence of the cluster position on the number of trifluoromethyl groups is shown. The centroid of the cage carbons is considered as a center of the fullerene cage, and both the nitrogen atom and the centroid of scandium atoms represent the center of Sc₃N cluster. In the unmodified Sc₃N@C₈₀-I_h(7) cage centroids of Sc and C atoms, and N atom are on the same site. The addition of the 10 CF₃ group leads to shift of Sc₃N cluster from the center of the cage as it is demonstrated by the centroid(C)–centroid(Sc) and centroid(C)–N distances which are 0.257(5) Å and 0.089(6) Å, respectively. Further attachment of two or four CF₃ groups does not significantly affect the position of the cluster, and the centroid(C)–centroid(Sc) and centroid(C)–N distances which are 0.256(3)–284(4) Å and 0.089(6)–0.115(5) Å, respectively (Table 4.2). In contrast, in **16-2** structure the centroid of cage carbons is shifted 0.513(3) Å from centroid of Sc atoms and 0.181(2) Å from N atom. To estimate effect of cage distortion due to formation of sp³ carbon atoms, new artificial C₈₀(I_h) cage was constructed. Carbon atoms connected to CF₃ groups were replaced by the centroids of the nearest three C atoms. The coordinates of these centroids were adjusted to achieve curvature of C₈₀(I_h) cage by moving them 0.220(5) Å in the direction from the center of the fullerene cage. It was found that the distance from the centroid(C*) of the “idealized” C₈₀(I_h) cage to the centroid(C*) of the actual distorted cage is no longer than 0.026(2) Å.

(Table 4.2) Therefore, the shift of centroid(C)–centroid(Sc)/centroid(C*)–centroid(Sc) (0.257(4)/0.243(4) Å) and centroid(C)–N/ centroid(C*)–N (0.092(6)/0.077 Å) distances in **16-2** compared to **12-1** (**10-1**) structure is almost the same as one observed between **12-1** (or **10-1**) and naked $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))$. Thus, a change of addition pattern observed in **12-1** (or **10-1** or **14-1**) structure to the one in **16-2** crystal structure affects the cluster position as strongly as addition of 12 groups to the unmodified $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h)$.

To summarize, the change of the addition pattern type leads to much more significant changes in the geometry of cluster (Sc–N–Sc angles) and location of trimetallic nitride cluster inside a $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))$ cage compared to the consecutive addition of two or four CF_3 groups .

4.2.5.6. Packing of 10-1, 12-1, 14-3, and 16-2 Molecules. The crystal lattices of **10-1**, **12-1**, and **14-3** structures contain *p*-xylene, carbon disulfide, and *p*-xylene molecules, respectively but there is no solvent incorporated into **16-2** lattice. As shown in Figure 4.52, each **10-1** molecule is surrounded by six other fullerene molecules in one layer and by three ones in the top and bottom layers which leads to formation of distorted hexagonal close packing (*hcp*). In **12-1** structure, one fullerene molecule is also surrounded by six others, but four molecules are located in the top layer, and two fullerene molecules in the bottom one. The distorted cubic close packing was observed in case of **14-3** and **16-2** crystal structures: each fullerene molecule is surrounded by six molecules in one layer, and by three ones in the top and bottom layers as shown in Figure 4.53.

In the $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h(7))(\text{CF}_3)_{12}\cdot\text{CS}_2$ structure, CS_2 molecules fill the voids in the crystal lattice, and each **12-1** molecule is surrounded by four solvent molecules.

Figures 4.54 and 4.55 demonstrate that *p*-xylene molecules form layers in $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}I_h\text{)}(\text{CF}_3)_{10}\cdot 1.5 \text{ C}_7\text{H}_8$ and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}I_h(7))(\text{CF}_3)_{14}\cdot 0.5 \text{ C}_8\text{H}_{10}$ crystal structures. Previously formation of the channels made of *p*-xylene molecules was also observed in $\text{C}_{74}(\text{CF}_3)_{12}\cdot 3\text{C}_8\text{H}_{10}$ structure. Thus, in the case of highly substituted trifluoromethylated metallofullerenes, the aromatic hydrocarbons may play an analogous role as porphyrin molecules for crystallization with naked fullerenes. Figure 4.56 demonstrates the design of the molecular assemblies in which three *p*-xylene and two $\text{Co}^{\text{II}}(\text{OEP})$ molecules surround **10-1** and C_{60} in $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}I_h(7))(\text{CF}_3)_{10}\cdot 1.5 \text{ C}_8\text{H}_{10}$ and $\text{C}_{60}\cdot 2\text{Co}^{\text{II}}(\text{OEP})\cdot \text{CHCl}_3$ ¹¹⁶ crystal structures, respectively. Thus, an effective packing due to the presence of the solvent in the crystal lattice may explain the absence of the positional cage disorder in the discussed $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}I_h(7))(\text{CF}_3)_n$ structures which is typically observed for $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}I_h)$ cycloadducts.

The closest intermolecular F $\cdots$ F distances between trifluoromethylated $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}I_h(7))$ molecules in **10-1**, **12-1**, **14-3**, and **16-2** are 2.897(4) Å (F072 $\cdots$ F623), 2.720(3) Å (F172 $\cdots$ F622), 2.695(5) Å (F511 $\cdots$ F623), and 2.550(2) Å (F162 $\cdots$ F463), respectively.

4.3. Summary and Conclusions

The results of the present work demonstrate that the MNFs $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}I_h(7))$ and $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}D_{5h}(6))$ can be readily transformed into perfluoroalkylated derivatives by using high-temperature R_F radical addition methodologies previously developed for hollow fullerenes. It was found that in the high temperature trifluoromethylation reactions both isomers (I_h and D_{5h}) of $\text{Sc}_3\text{N}@\text{C}_{80}$ exhibited very similar reactivity. In contrast, in the cycloaddition reactions $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}I_h(7))$ isomer is less reactive than $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}I_h)$.

The efficient synthetic procedure allows one to synthesize, isolate, and characterize seventeen $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-I}_h\text{)}(\text{CF}_3)_n$ ($n = 2\text{--}16$) compounds.

The analysis of the obtained X-ray crystal structures of **10-1**, **12-1**, **14-3**, and **16-2** compounds showed that the presence of the Sc_3N cluster has a strong influence on the pattern of CF_3 radical additions to $\text{Sc}_3\text{N}@\text{C}_{80}$, and that the addition pattern of exohedral substituents can have a strong influence on the geometry of the Sc_3N cluster in $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_n$ derivatives.

Table 4.1. Fluorine-19 NMR $-\delta$ and J_{FF} values for $\text{Sc}_3\text{N}@\text{(C}_{80}\text{-}I_{\text{h}}(7))\text{(CF}_3)_n$ compounds

4-1	70.5	71.3	74.2	74.5				
	q	q	q	q				
J_{FF} , Hz	17.8	17.8	17.0	17.0				
4-2	64.4	71.2						
	um	um						
J_{FF} , Hz	–,–	–,–						
8-1	61.8	62.4	65.4	66.1	66.6	67.3	74.5	74.6
	as	qq	as	qq	qq	qq	q	q
J_{FF} , Hz	14,14	11,13	12,12	13,14	10,12	10,13	13.2	10.1
8-2	60.0	62.5	69.5	70.8	71.6	75.6	80.8	
	m	um	q	q	q	q	s	
J_{FF} , Hz	–,–	–,–	19.8	16.0	15.2	12.2	–	
8-3	62.8	63.8	65.8	70.6	71.2	71.3	73.6	79.9
	um	um	m	q	q	q	q	s
J_{FF} , Hz	–,–	–,–	–,–	16.56	12.8	16.6	12.4	–

J_{FF} , Hz	–,–	–,–	–,–	16.56	12.8	16.6	12.4	–					
8-5	63.0	63.9	70.9	72.8	73.4	74.1	75.1	76.1					
	as	as	q	q	q	q	q	q					
J_{FF} , Hz	15,14	15,14	14.68	17.32	17.69	15.81	15.06	15.06					
10-1	61.2	64.5	66.1	67.1	67.5	68.0	69.2	71.9	78.9				
	um	um	um	qq	m	um	q	q	s				
J_{FF} , Hz	13.2,–	–,–	–,–	19.3,9	11,–	11,–	19.3	13.2	–				
10-2	56.6	60.1	63.6	64.7	67.1	69.3	72.5	72.6	74.6	82.7			
	um	um	um	um	um	q	q	q	q	s			
J_{FF} , Hz	–,–	–,–	–,–	–,–	–,–	9.1	8.4	11.5	13.0	–			
12-1	60.4	61.5	64.5	66.8	67.1	67.4	67.9	69.4	71.3	78.0			
	um	um	um	um	um	um	um	q	q	s			
	–,–	–,–	–,–	–,–	–,–	–,–	–,–	19.1	14.5	–			
12-2	58.7	60.2	62.7	63.6	66.1	66.8	67.2	67.7	68.1	72.0	74.5	77.3	
	as	m	um	qq	as	qq	qq	qq	as	as	q	q	
J_{FF} , Hz	11,11	12.8,14	–,–	11,13	11,11	10,13	11,14	10,12	11,11	11,12.8	12.8	12.8	

12-4	59.6	62.5	64.0	65.6	66.1	66.7	67.5	71.6	72.2	72.3	72.5	77.9				
	as	m	m	um	m	m	um	q	um	q	q	q				
J_{FF} , Hz	12,12	11,12	11,12	–,–	12,12	11,11	–,–	17.6	–,–	17.6	9.9	12.5				
14-1	58.4	62.2	64.0	64.7	65.0	66.0	66.6	67.8	68.2	69.0	73.2	73.7	80.2			
	as	um	m	um	um	as	um	qq	as	as	q	as	q			
J_{FF} , Hz	12,12	–,–	11,12	–,–	–,–	12,12	–,–	10,12	11,11	14,14	14.5	12,12	11.5			
14-2	57.1	61.5	61.7	63.0	67.1	68.7	70.0	70.7	70.9	71.4	72.0	73.1	73.4			
	um	um	um	um	um	um	um	um	um	um	um	um	um	um		
J_{FF} , Hz	–,–	–,–	–,–	–,–	–,–	–,–	–,–	–,–	–,–	–,–	–,–	–,–	–,–	–,–		
16-1	60.1	62.0	63.0	63.2	63.5	64.6	65.6	65.8	66.1	66.2	66.9	68.00	68.6	70.5	81.9	
	um	um	as	um	um	um	um	um	um	um	m	um	m	m	q	
J_{FF} , Hz	–,–	–,–	12,14	–,–	–,–	–,–	–,–	–,–	–,–	–,–	13,–	–,–	11,12	12,12	15.5	

All data from this work; chloroform-*d* solutions at 24 (± 1 °C; C₆F₆ internal standard (δ –164.9). Coupling constants are known to (0.2 Hz for terminal CF₃ quartets except when second-order effects result in a multiplet that is significantly different than a Pascal 1:3:3:1 quartet. In those cases, the J_{FF} values are ca. ± 1 Hz. Resonances for other CF₃ groups are multiplets; J_{FF} values for the ones that are apparent (but not true) septets are ± 1 Hz; J_{FF} values for multiplets deconvoluted by spectral simulation are ± 1 Hz.

Table 4.2. Crystal data and structure refinement parameters for **10-1**, **12-1**, **14-3**, and **16-2** crystal structures.

	Sc ₃ N@C ₈₀ (CF ₃) ₁₀ ·1.5 C ₈ H ₁₀ (10-1)	Sc ₃ N@C ₈₀ (CF ₃) ₁₂ ·CS ₂ (12-1)	Sc ₃ N@C ₈₀ (CF ₃) ₁₄ ·0.5 C ₈ H ₁₀ (14-3)	Sc ₃ N@C ₈₀ (CF ₃) ₁₆ (16-2)
molecular formula	C ₉₀ F ₃₀ NSc ₃ ·1.5(C ₈ H ₁₀)	C ₉₂ F ₃₆ NSc ₃ ·CS ₂	C ₉₄ F ₄₂ NSc ₃ ·0.5(C ₈ H ₁₀)	C ₉₆ F ₄₈ NSc ₃
formula weight	1959.03	2013.96	2128.91	2213.85
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i>	4	4	4	2
<i>a</i> , Å	13.2149(15)	13.2899(14)	13.618(1)	13.8756(6)
<i>b</i> , Å	20.0393(15)	38.424(5)	25.451(2)	15.3985(7)
<i>c</i> , Å	24.432(3)	13.5862(16)	19.3451(16)	16.7884(7)
<i>α</i> , deg	90	90	90	73.911(3)
<i>β</i> , deg	95.696(2)	115.789(3)	98.491(2)	88.258(3)
<i>γ</i> , deg	90	90	90	74.257(3)
temperature, K	120(2)	120(2)	100(2)	100(2)
final <i>R</i> indices	<i>R</i> ₁ = 0.0674	<i>R</i> ₁ = 0.0511	<i>R</i> ₁ = 0.0661	<i>R</i> ₁ = 0.0437
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> ₂ = 0.1648	<i>wR</i> ₂ = 0.1188	<i>wR</i> ₂ = 0.1894	<i>wR</i> ₂ = 0.1253
goodness-of-fit on <i>F</i> ²	1.103	1.008	1.071	1.010

Table 4.3. Comparison of Sc₃N cluster position in Sc₃N@C₈₀-I_h(7), **10-1**, **12-1**, **14-3**, and **16-2** crystal structures.

	Sc ₃ N@C ₈₀ -I _h	10-1	12-1	14-3	16-2
centroid(C)–centroid(C*), Å	–	0.016(5)	0.011(3)	0.008(3)	0.026(2)
centroid(C)–N, Å	0.000(4)	0.089(6)	0.089(6)	0.115(5)	0.181(2)
centroid(C*)–N, Å	–	0.074(6)	0.079(6)	0.116(5)	0.156(2)
centroid(C)–centroid(Sc), Å	0.000(4)	0.257(5)	0.256(3)	0.284(4)	0.513(3)
centroid(C*)–centroid(Sc*), Å	–	0.243(5)	0.246(3)	0.282(4)	0.489(3)
centroid(Sc)–N, Å	0.000(2)	0.170(4)	0.168(3)	0.190(3)	0.337(2)

* data for the “idealized” C₈₀(I_h) cage (see text)

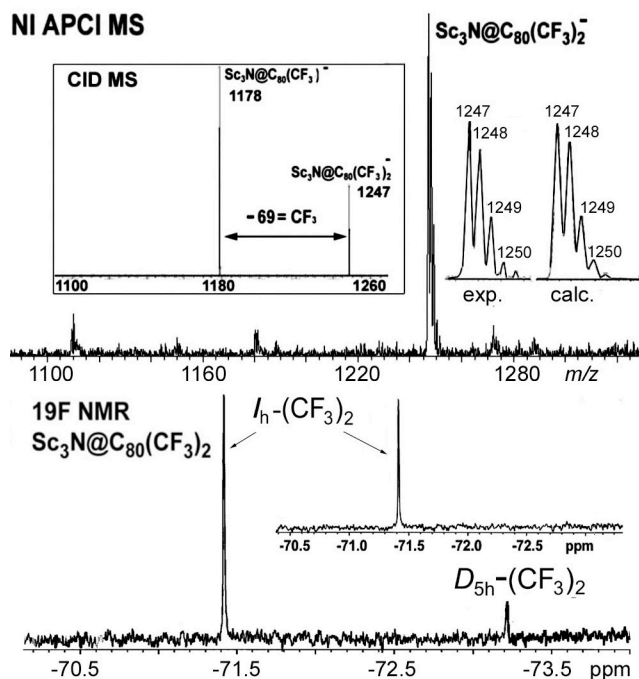


Figure 4.1. Top: Negative APCI mass spectrum of Sc₃N@C₈₀(CF₃)₂; inset (on the left): CID mass spectrum of the molecular ion (m/z 1247), dominant fragment is due to loss of CF₃; inset (on the right): theoretical and observed isotope distributions for Sc₃N@C₈₀(CF₃)₂. Bottom: Fluorine-19 NMR spectrum (CDCl₃, 376.45 MHz) of mixture of (*I_h*)- and (*D_{5h}*)- Sc₃N@C₈₀(CF₃)₂, inset: ¹⁹F NMR spectrum of the pure (*I_h*)- Sc₃N@C₈₀(CF₃)₂.

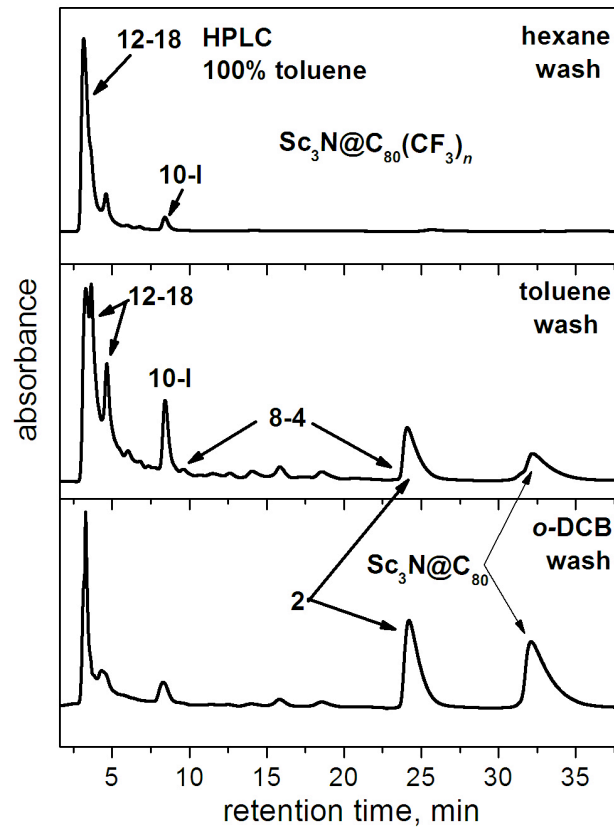


Figure 4.2. Three-step extraction scheme for isolation of black-brown $\text{Sc}_3\text{N}@\text{C}_{80}\text{-I}_h(7)(\text{CF}_3)_n$ compounds which includes a use of hexane, toluene, and *o*-dichlorobenzene as solvents.

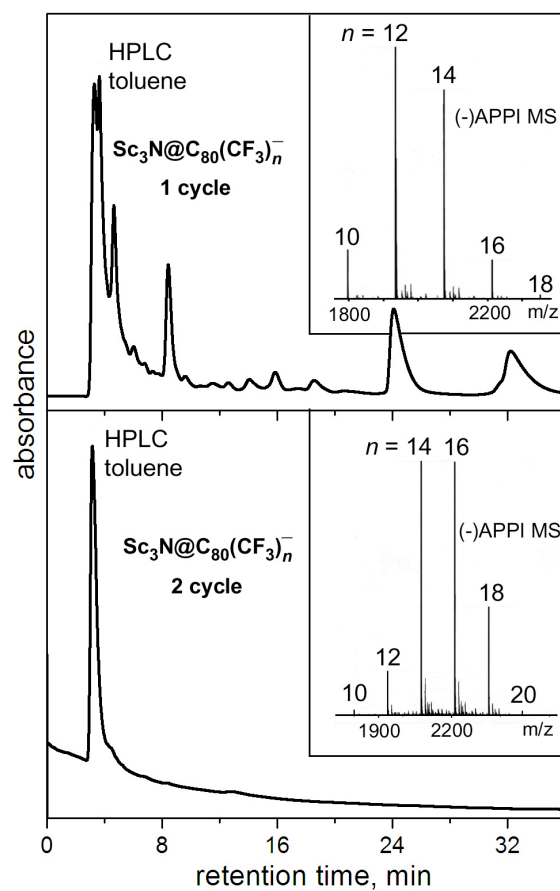


Figure 4.3. HPLC traces of crude $\text{Sc}_3\text{N}@(\text{C}_{80}\text{-}I_h(7))(\text{CF}_3)_n$ products obtained from $\text{Sc}_3\text{N}@(\text{C}_{80}\text{-}I_h)/\text{AgCF}_3\text{CO}_2$ (top) and $\text{Sc}_3\text{N}@(\text{C}_{80}\text{-}I_h(7))(\text{CF}_3)_n/\text{AgCF}_3\text{CO}_2$ ($n = 2\text{--}18$) (bottom) reactions at 350 °C for 2.5 h.

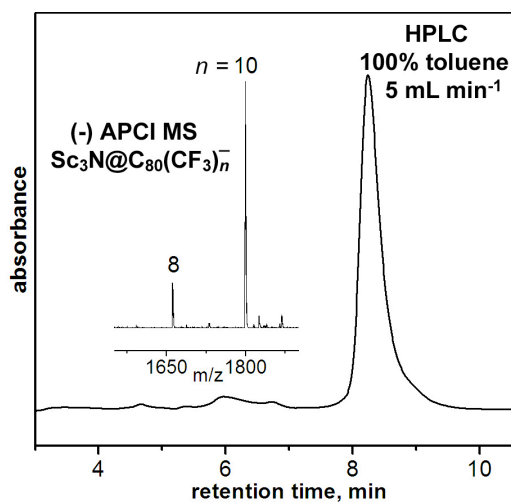


Figure 4.4. HPLC trace and NI-APCI-mass spectrum of HPLC-purified **10-1** isomer.

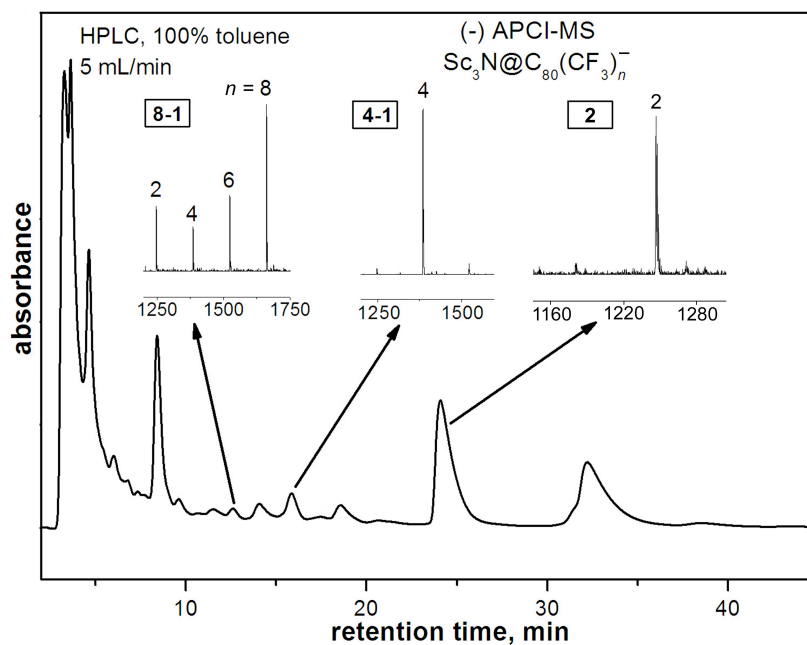


Figure 4.5. HPLC trace of the crude Sc₃N@C₈₀(CF₃)_n product (toluene wash) obtained at 350 °C for 2.5 h using AgCF₃CO₂ as a trifluoromethylating agent. The insets show NI-APCI mass spectra of the HPLC-purified **2-1**, **4-1**, and **8-1** isomers.

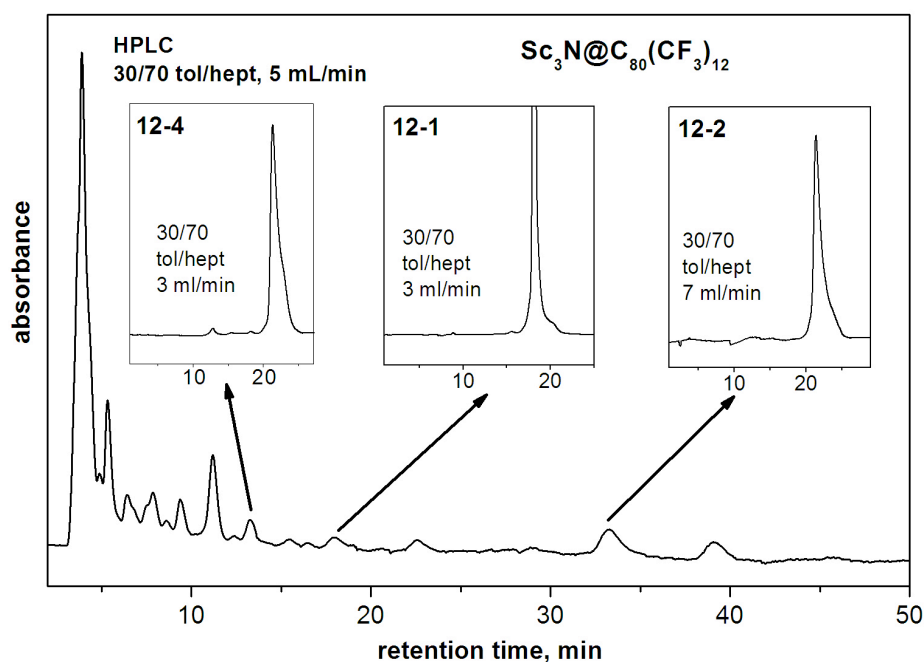


Figure 4.6. HPLC trace of the 2.9–8 min toluene fraction in 30:70 (v:v) toluene/heptane at 5 mL min⁻¹ flow rate. The insets show isolation and purification of **12-1**, **12-2**, and **12-4** isomers using 30:70 (v:v) toluene/heptane as en eluent at 7, 3, and 3 mL min⁻¹ flow rate, respectively.

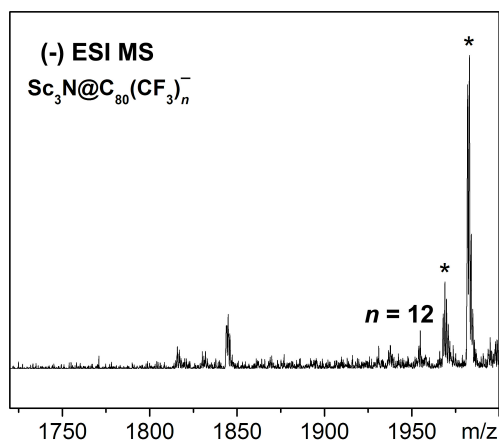


Figure 4.7. NI-ESI mass spectrum of **12-2** isomer recorded using ThermQuest Finnigan LCQ-DUO spectrometer. * – molecular ions of adducts with solvent.

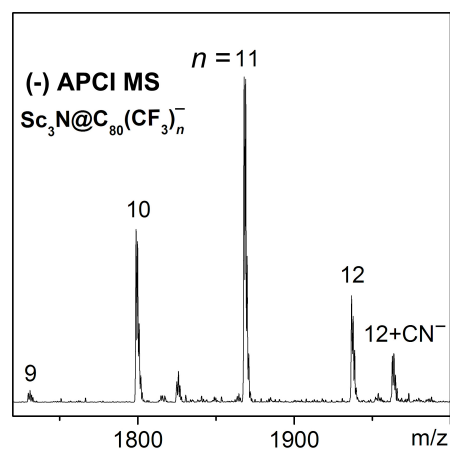


Figure 4.8. NI-APCI mass spectrum of **12-2** isomer recorded using ThermQuest Finnigan LCQ-DUO spectrometer.

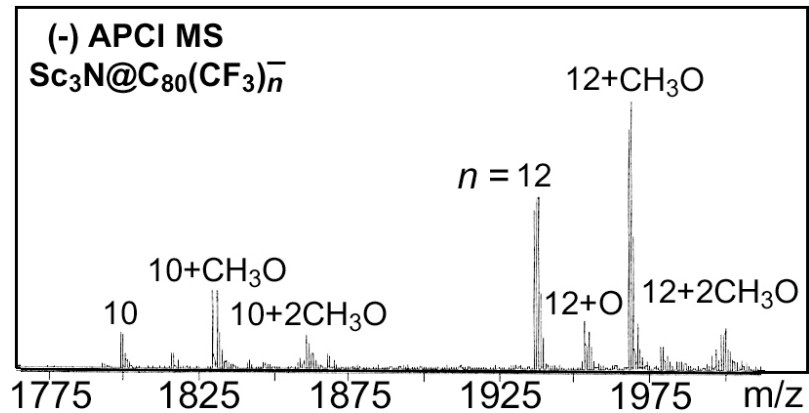


Figure 4.9. NI-APCI MS spectrum of **12-2** isomer recorded using Agilent Technologies Model 6210 TOF spectrometer.

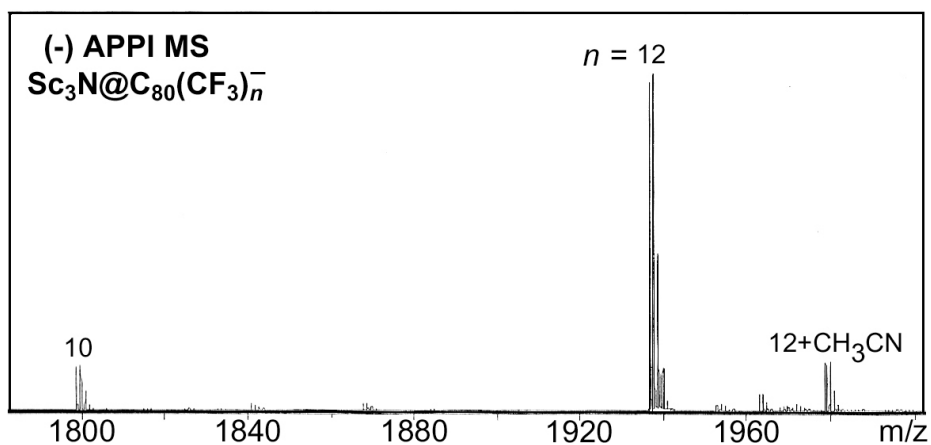


Figure 4.10. NI-APPI MS spectrum of **12-2** isomer recorded using Agilent Technologies Model 6210 TOF spectrometer.

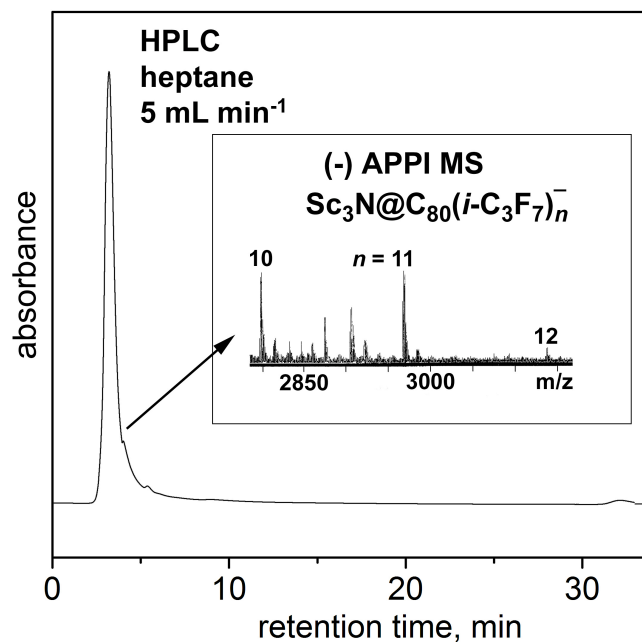


Figure 4.11. HPLC trace and NI-APPI-MS spectrum of the crude $\text{Sc}_3\text{N@}(\text{C}_{80}\text{-I}_h(7))(\text{i-C}_3\text{F}_7)_n$ obtained from the reaction of $\text{Sc}_3\text{N@}(\text{C}_{80}\text{-I}_h)$ with $\text{i-C}_3\text{F}_7\text{I}$ under UV-vis irradiation at room temperature for 47 h.

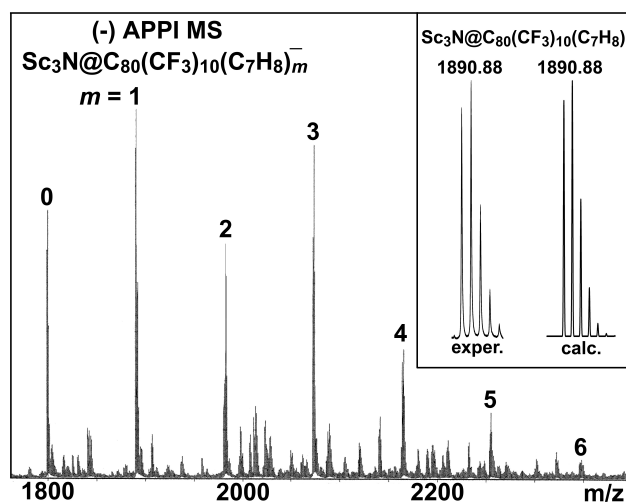


Figure 4.12. NI-APPI-MS spectrum of the crude $\text{Sc}_3\text{N@}(\text{C}_{80}\text{-I}_h(7))(\text{CF}_3)_{10}(\text{C}_7\text{H}_7)_m$ ($m = 1\text{--}6$) obtained from the reaction of $\text{Sc}_3\text{N@}(\text{C}_{80}\text{-I}_h(7))(\text{CF}_3)_{10}$ with $\text{C}_7\text{H}_7\text{Br}$ under UV-vis irradiation at room temperature for 40 min. The inset shows the experimental and theoretical isotopic distribution of $\text{Sc}_3\text{N@}(\text{C}_{80}\text{-I}_h(7))(\text{CF}_3)_{10}(\text{C}_7\text{H}_7)$ ion.

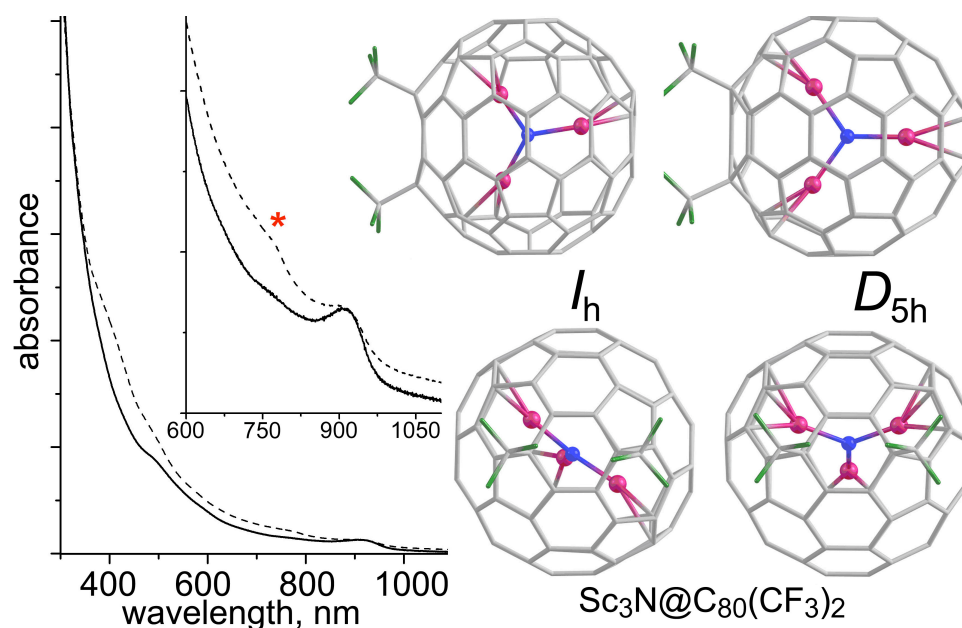


Figure 4.13. UV-Vis absorption spectra of $\text{Sc}_3\text{N}@\text{C}_{80-I_h(7)}(\text{CF}_3)_2$ in toluene (black line) and the mixture of $\text{Sc}_3\text{N}@\text{C}_{80-I_h(7)}$ - and $\text{Sc}_3\text{N}@\text{C}_{80-D_{5h}(6)}(\text{CF}_3)_2$ (dashed line). The asterisk in the inset denotes the band assigned to the lowest energy transition in $\text{Sc}_3\text{N}@\text{C}_{80-D_{5h}(6)}(\text{CF}_3)_2$. Two views of the DFT-optimized most stable isomers of $\text{Sc}_3\text{N}@\text{C}_{80-I_h(7)}(\text{CF}_3)_2$ and $\text{Sc}_3\text{N}@\text{C}_{80-D_{5h}(6)}(\text{CF}_3)_2$.

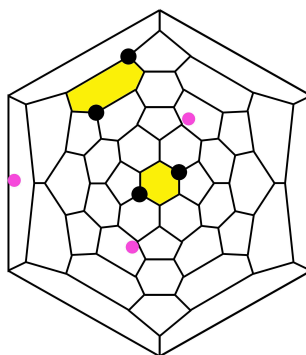


Figure 4.14. The Schlegel diagram of $1,7,32,54\text{-Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_4$ (4-1) compound.

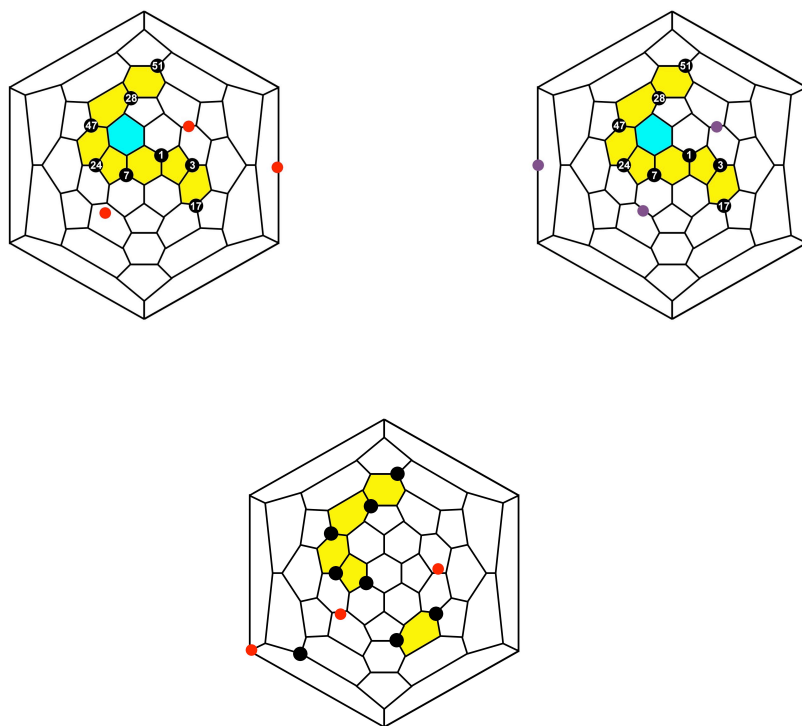


Figure 4.15. The Schlegel diagrams of the two conformers of the most stable **8-1** isomer (top) and the most stable **8-2** isomer (top).

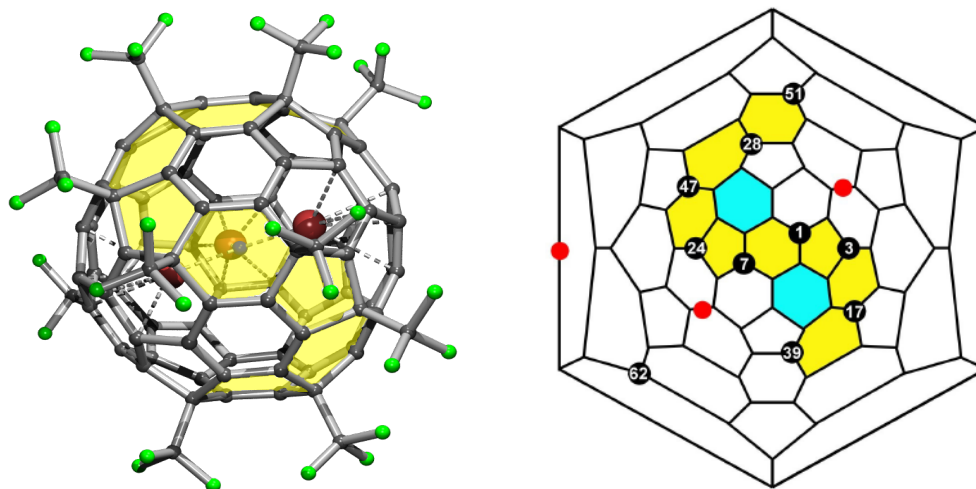


Figure 4.16. X-ray crystal structure (left) and Schlegel diagram (right) of **10-1**.

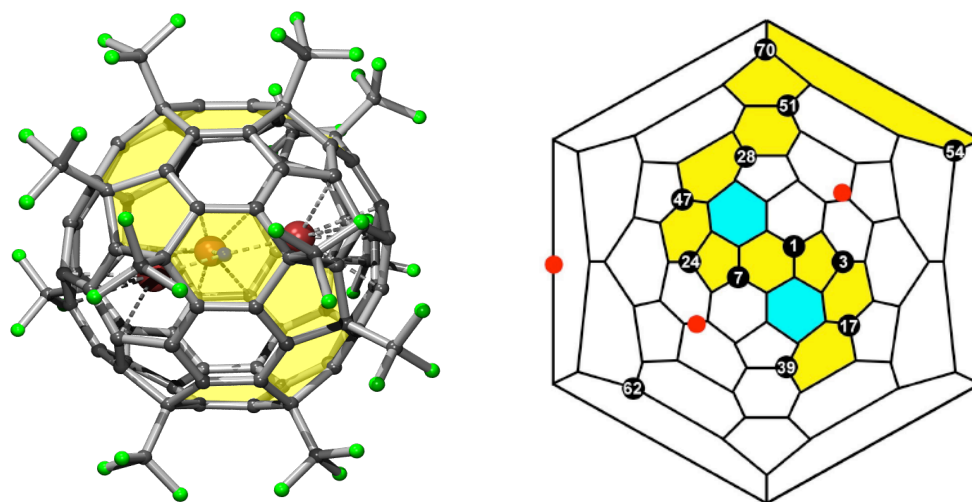


Figure 4.17. X-ray crystal structure (left) and Schlegel diagram (right) of **12-1**.

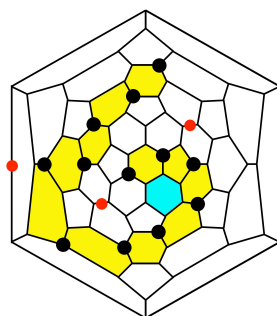


Figure 4.18. The Schlegel diagram of the most stable **12-2** isomer.

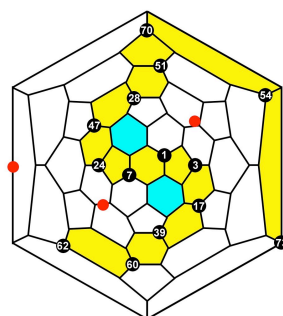


Figure 4.19. The Schlegel diagram of the most stable **14-1** isomer.

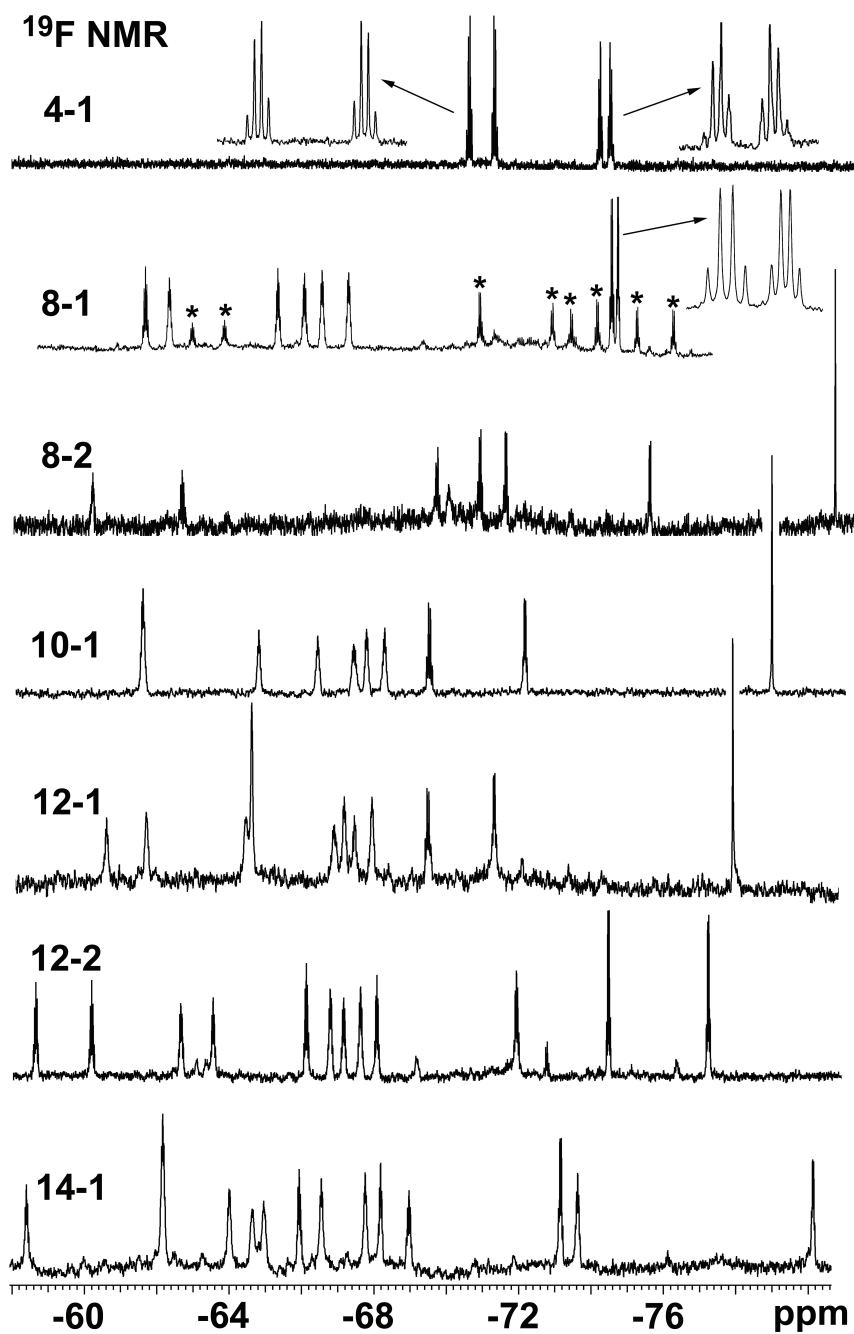


Figure 4.20. Fluorine-19 NMR spectra of 4-1, 8-1, 8-2, 10-1, 12-1, 12-2, and 14-1 (chloroform-*d*, 376,48 MHz, internal standard (δ -164.9)). The multiplets labeled with asterisks relate to the ^{19}F NMR spectrum of 8-5 compound.

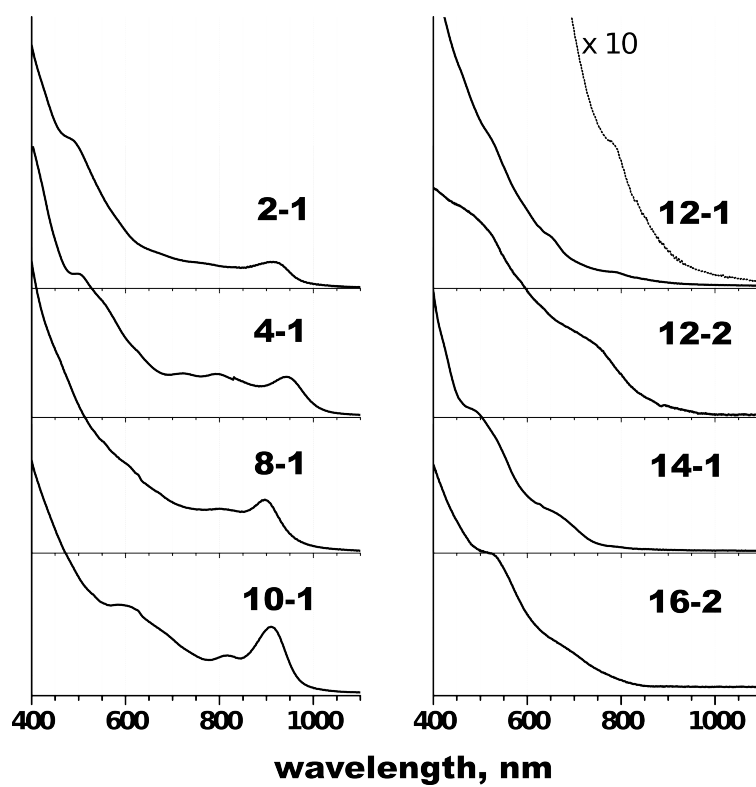


Figure 4.21. UV-vis spectra of 2-1, 4-1, 8-1, 10-1, 12-1, 12-2, 14-1, and 16-2 compounds in toluene.

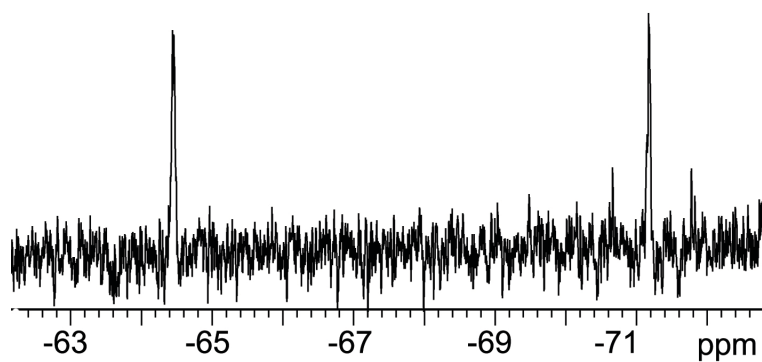


Figure 4.22. Fluorine-19 NMR spectrum of 4-2 isomer in chloroform-*d*.

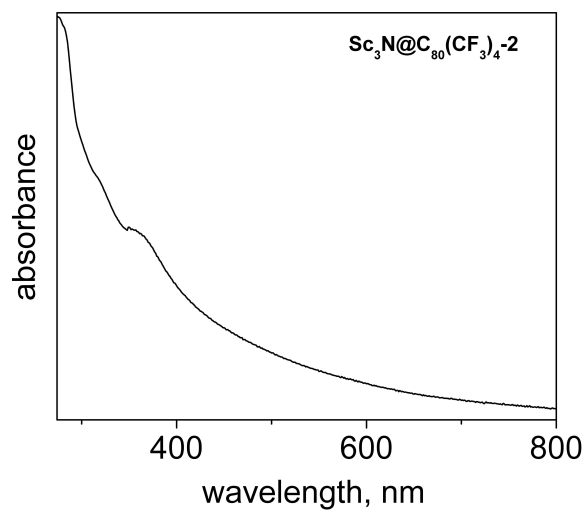


Figure 4.23. UV-vis spectrum of **4-2** isomer in chloroform.

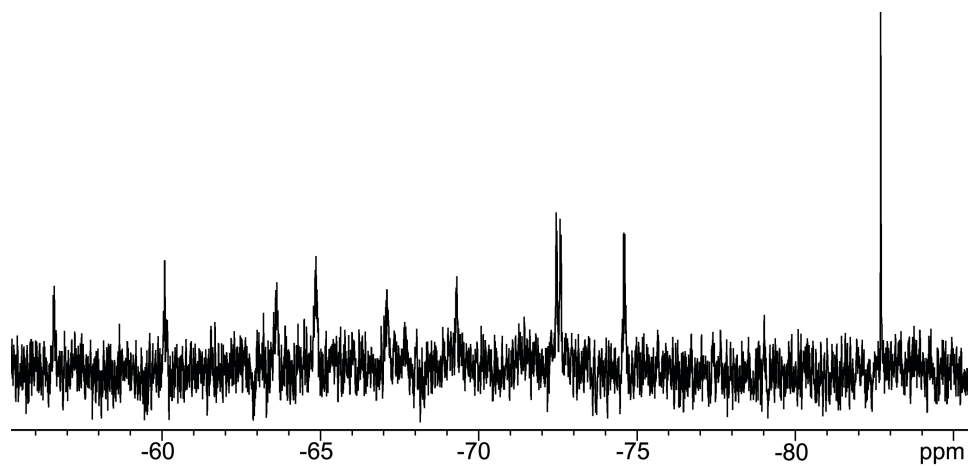


Figure 4.24. Fluorine-19 NMR spectrum of **10-2** isomer in chloroform-*d*.

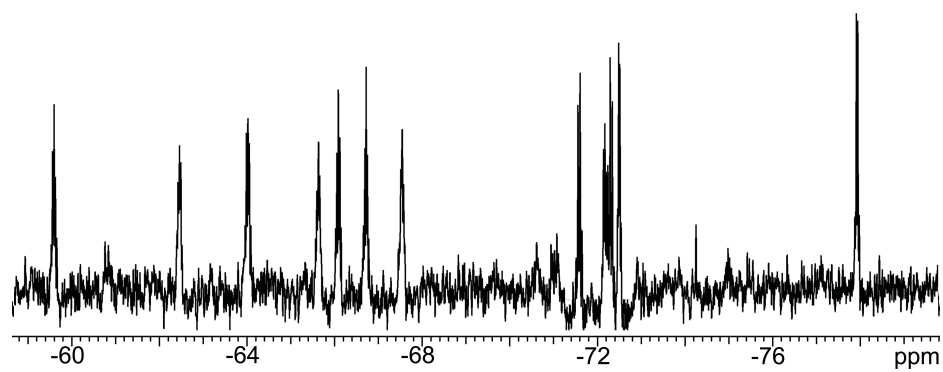


Figure 4.25. Fluorine-19 NMR spectrum of **12-4** isomer in chloroform-*d*.

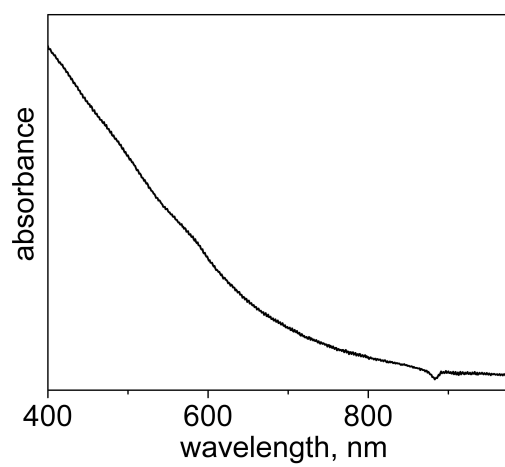


Figure 4.26. UV-vis spectrum of **12-4** isomer in chloroform.

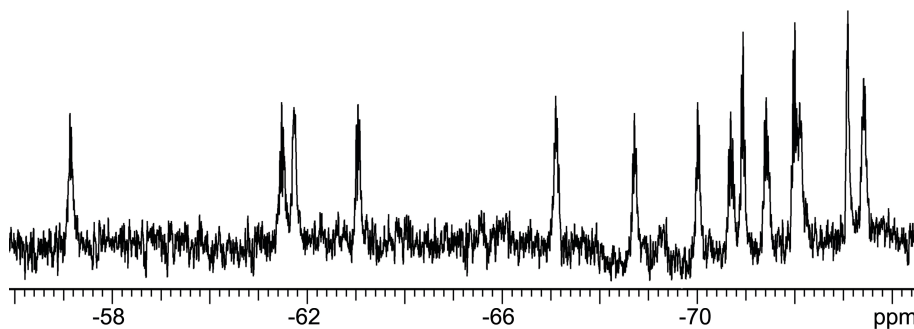


Figure 4.27. Fluorine-19 NMR spectrum of **14-2** isomer in chloroform-*d*.

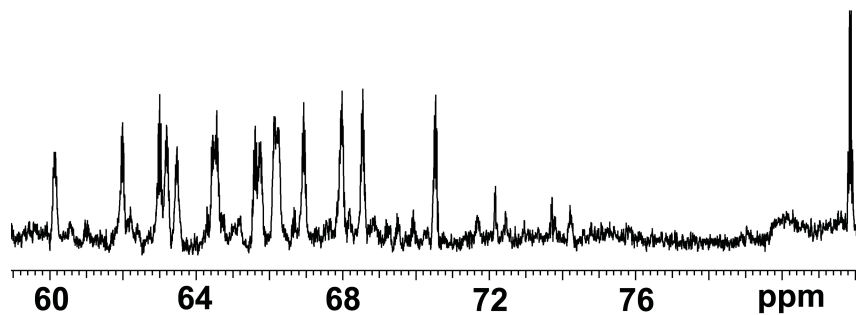


Figure 4.28. Fluorine-19 NMR spectrum of **16-1** isomer in chloroform-*d*.

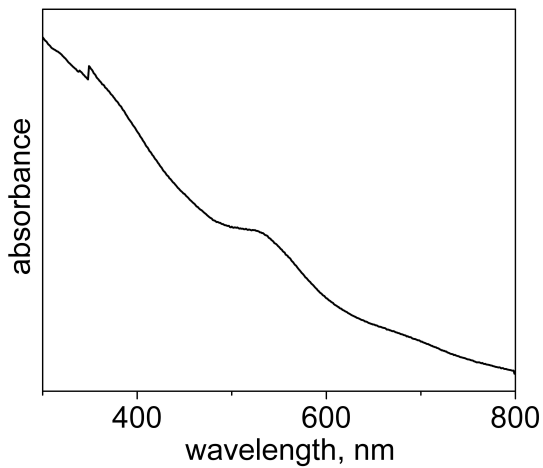


Figure 4.29. UV-vis spectrum of **16-1** isomer in chloroform.

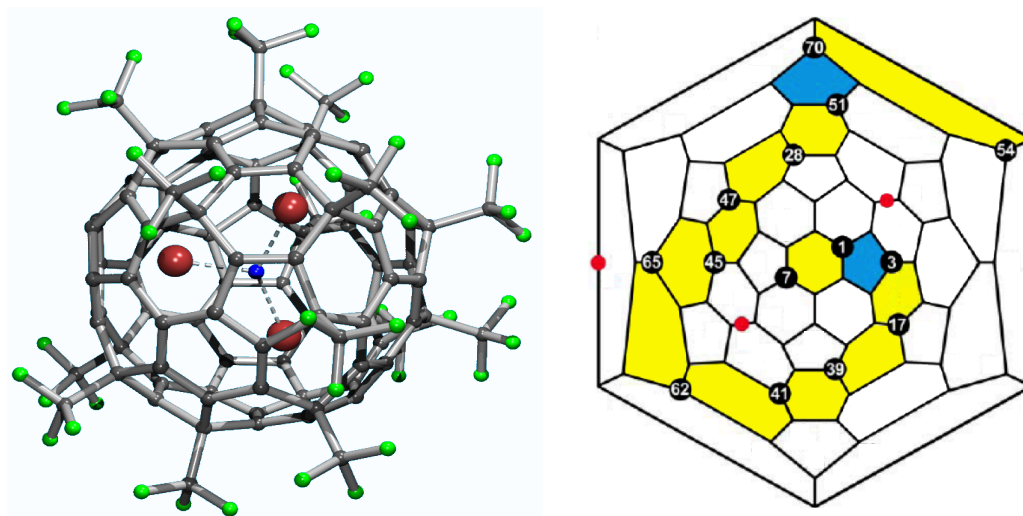


Figure 4.30. X-ray crystal structure (left) and Schlegel diagram (right) of **14-3**.

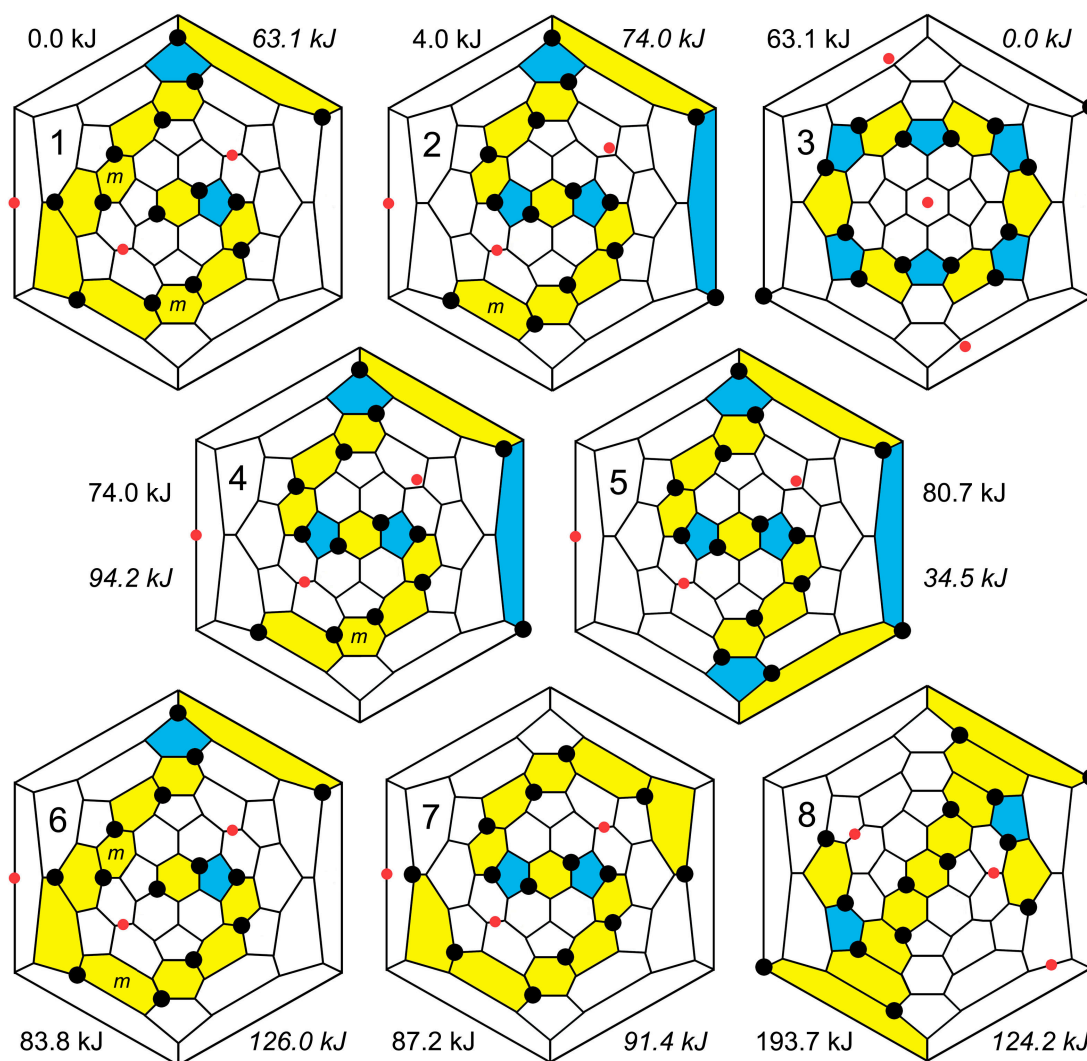


Figure 4.31. Schlegel diagrams for **14-3** (labeled 1, upper left) and seven hypothetical isomers of $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_{14}$. The black circles indicate the cage $\text{C}(\text{sp}^3)$ atoms bonded to the CF_3 groups, *para*- and *meta*- $\text{C}_6(\text{CF}_3)_2$ hexagons are highlighted in yellow, 1,3- $\text{C}_5(\text{CF}_3)_2$ pentagons are highlighted in blue, and the Sc atoms are indicated by small red circles. DFT-predicted relative energies are shown for the compounds (regular font) and for the $\text{C}_{80}(\text{CF}_3)_{14}^{6-}$ hexaanion with the same addition pattern (italic font). Note that isomers 3, 5, 7, and 8 do not have sp^3 THJs.

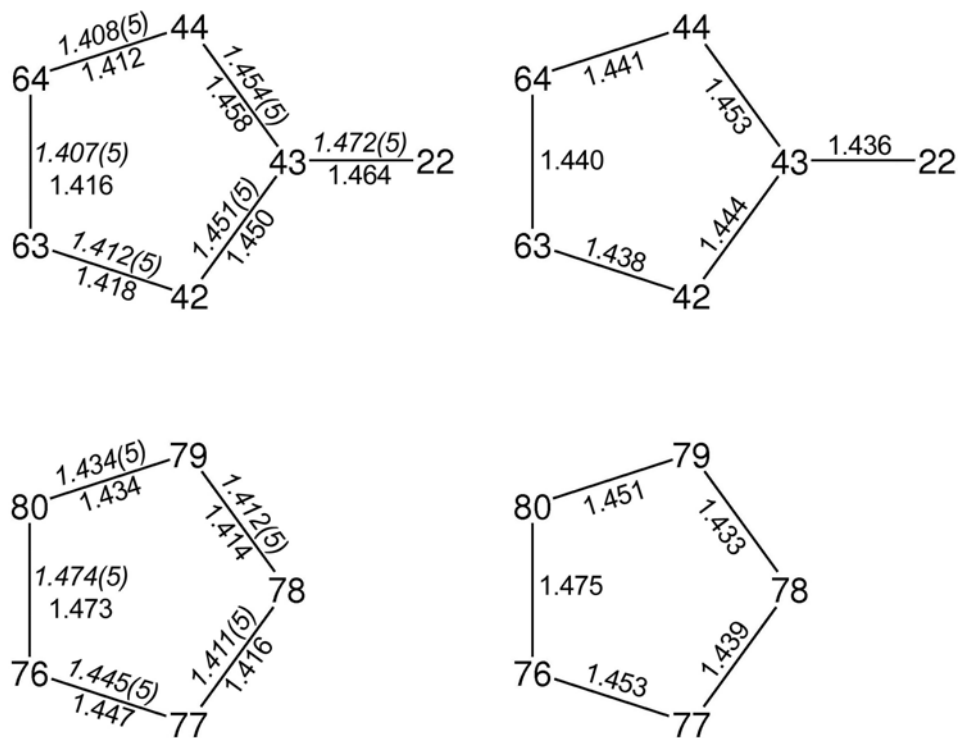


Figure 4.32. Comparison of the X-ray and DFT-predicted cage C–C distances in Å for two pentagons in **14-3** (left) and in DFT-optimized $\text{Sc}_3\text{N@C}_{80}$ (right).

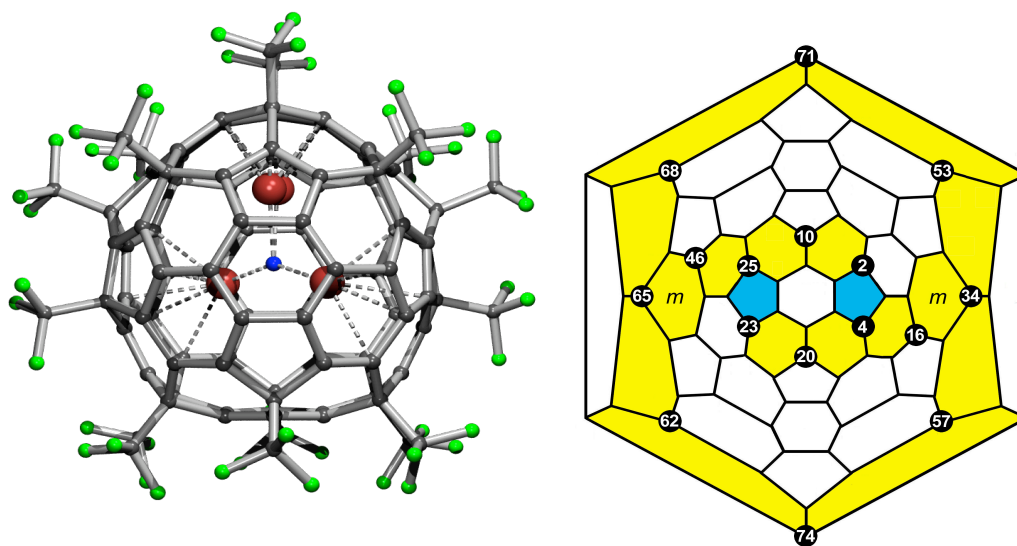


Figure 4.33. X-ray crystal structure (left) and Schlegel diagram (right) of **16-2**.

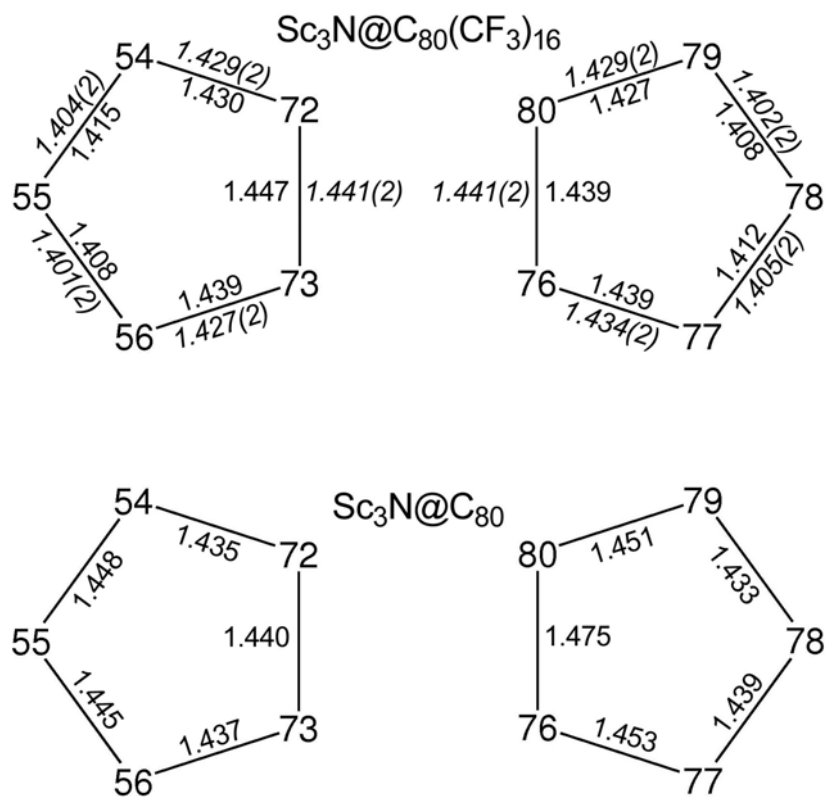


Figure 4.34. Comparison of X-ray and DFT-predicted cage C–C distances in Å for two pentagons in **16-2** (top) and in DFT-optimized $\text{Sc}_3\text{N@C}_{80}$ (bottom).

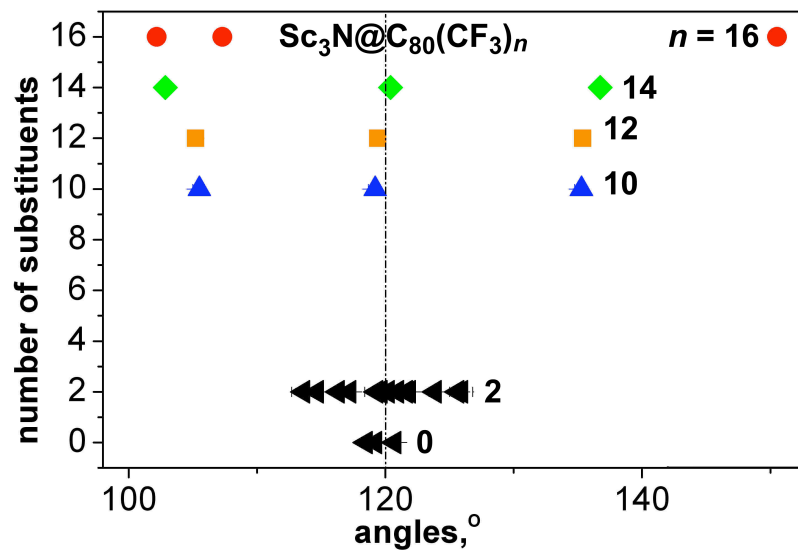


Figure 4.35. Dependence of Sc-N-Sc angles in Sc_3N cluster on the number of substituents on the $\text{Sc}_3\text{N}@C_{80}$ cage. Literature data for $\text{Sc}_3\text{N}@C_{80}\text{X}_2$ include the X-ray structures not only with two independent groups on the cage but also with one cycloadduct attached to $\text{Sc}_3\text{N}@C_{80}$.

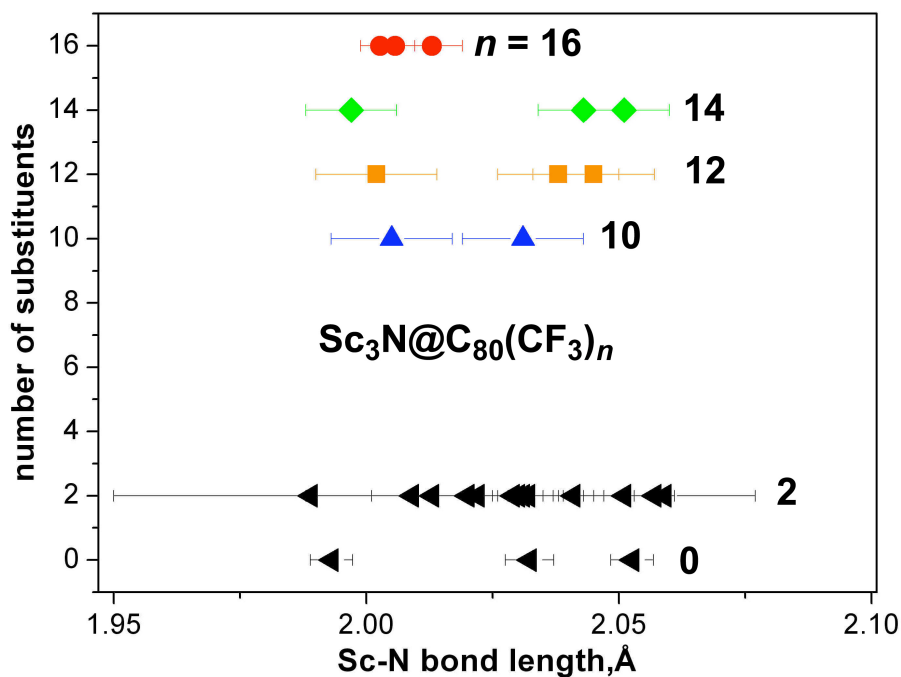


Figure 4.36. Dependence of Sc-N bond length in Sc_3N cluster on number of substituents on the $\text{Sc}_3\text{N}@C_{80}$ cage. Literature data for $\text{Sc}_3\text{N}@C_{80}\text{X}_2$ include the X-ray structures not only with two independent groups on the cage but also with one cycloadduct attached to $\text{Sc}_3\text{N}@C_{80}$.

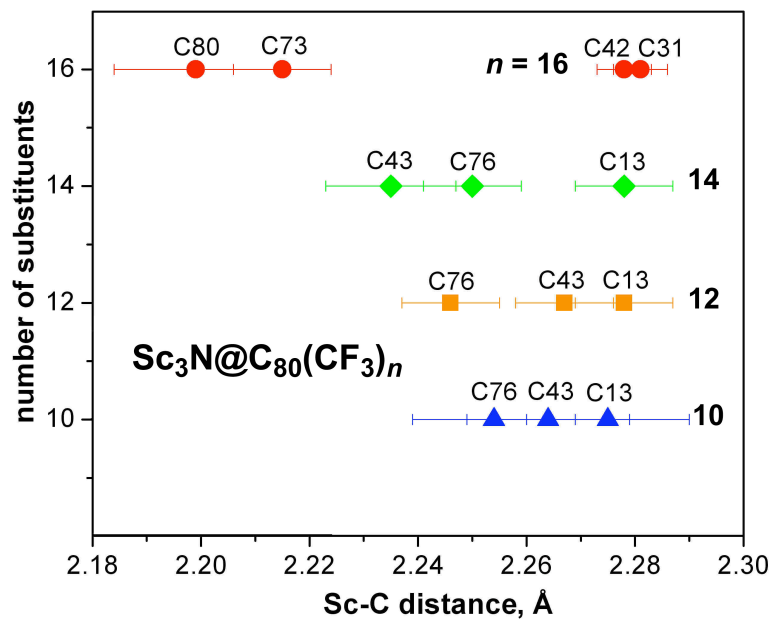


Figure 4.37. Dependence of the shortest Sc-C distances on the number of the substituents. The numbers of the closest cage carbon atoms are shown above the labels.

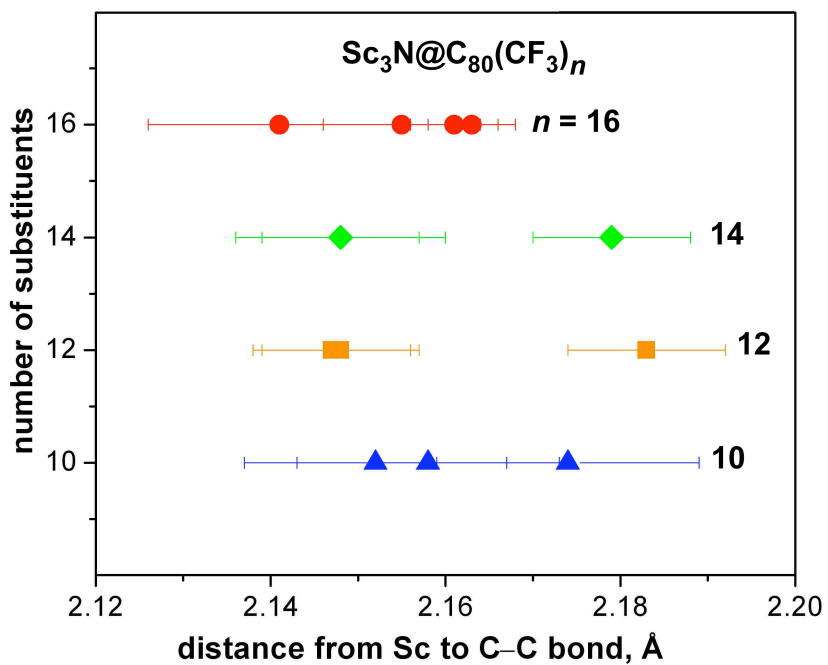


Figure 4.38. Dependence of the distances from Sc atom to the closest C-C cage bond on the number of CF_3 groups.

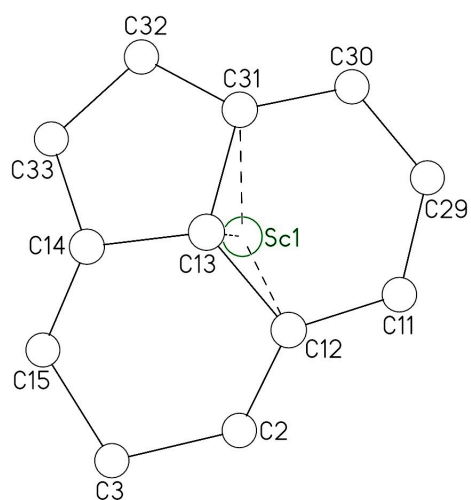


Figure 4.39. The distance between Sc1 and the closest C13 cage carbon atom in **10-1** structure is 2.275(5) Å. The distances from Sc1 to two close C12–C13 and C13–C31 bonds are 2.174(5) Å and 2.205(5) Å, respectively.

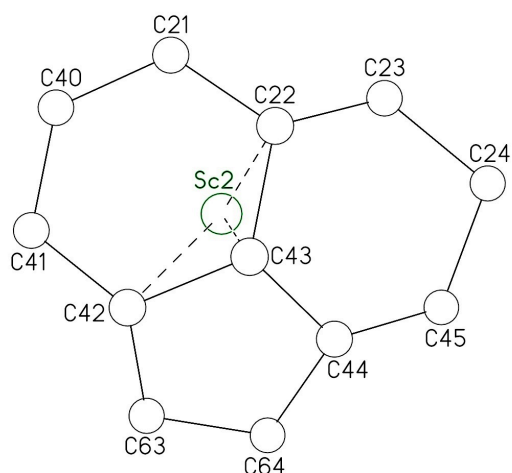


Figure 4.40. The distance between Sc2 and the closest C43 cage carbon atom in **10-1** structure is 2.264(5) Å. The distances from Sc2 to two close C22–C43 and C42–C43 bonds are 2.158(5) Å and 2.196(5) Å, respectively.

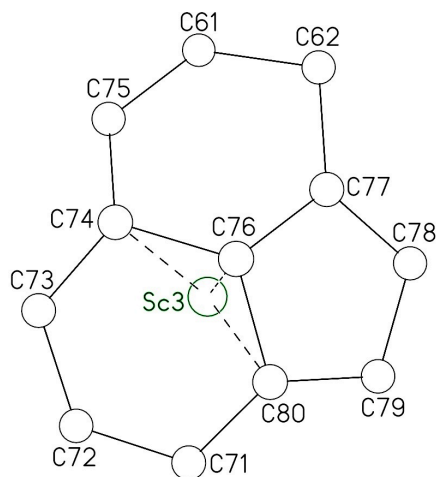


Figure 4.41. The distance between Sc3 and the closest C74 cage carbon atom in **10-1** structure is 2.254(5) Å. The distances from Sc3 to two close C76–C80 and C74–C76 bonds are 2.152(5) Å and 2.171(5) Å, respectively.

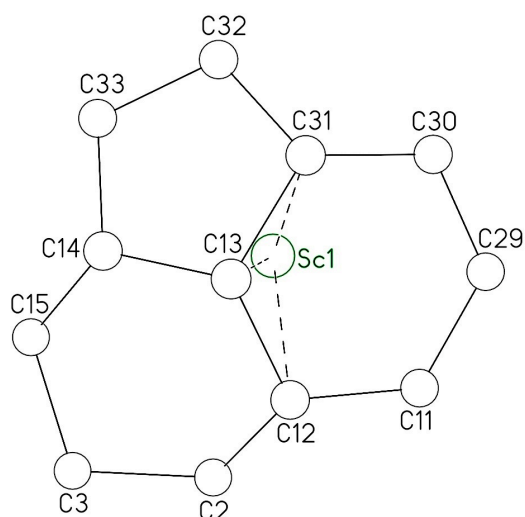


Figure 4.42. The distance between Sc1 and the closest C13 cage carbon atom in **12-1** structure is 2.278(3) Å. The distances from Sc1 to two close C12–C13 and C13–C31 bonds are 2.183(3) Å and 2.194(3) Å, respectively.

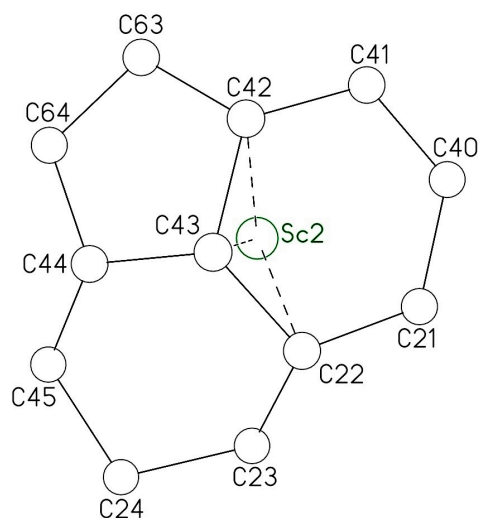


Figure 4.43. The distance between Sc2 and the closest C43 cage carbon atom in **12-1** structure is 2.267(3) Å. The distances from Sc2 to two close C22–C43 and C42–C43 bonds are 2.147(3) Å and 2.203(3) Å, respectively.

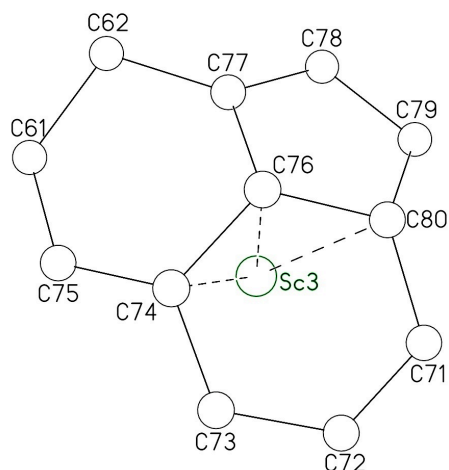


Figure 4.44. The distance between Sc3 and the closest C76 cage carbon atom in **12-1** structure is 2.246(3) Å. The distances from Sc3 to two close C76–C80 and C74–C76 bonds are 2.147(3) Å and 2.170(3) Å, respectively.

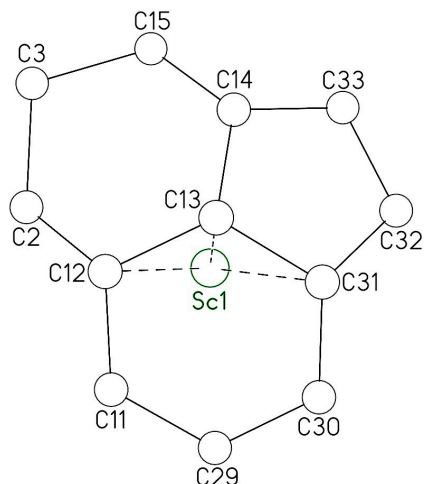


Figure 4.45. The distance between Sc1 and the closest C13 cage carbon atom in **14-3** structure is 2.278(3) Å. The distances from Sc1 to two close C12–C13 and C13–C31 bonds are 2.179(3) Å and 2.200(3) Å, respectively.

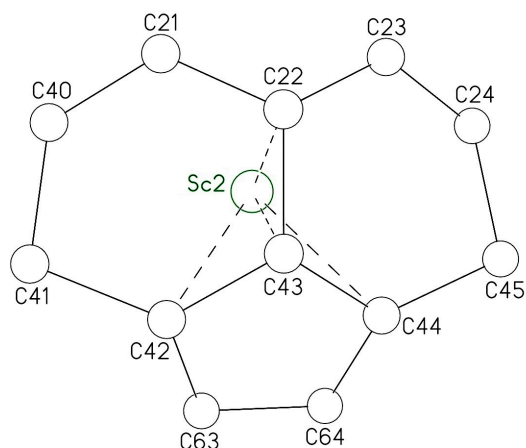


Figure 4.46. The distance between Sc2 and the closest C43 cage carbon atom in **14-3** structure is 2.235(4) Å. The distances from Sc2 to two close C22–C43, C42–C43, and C43–C44, bonds are 2.148(4) Å, 2.189(4) Å, and 2.189(4) Å, respectively.

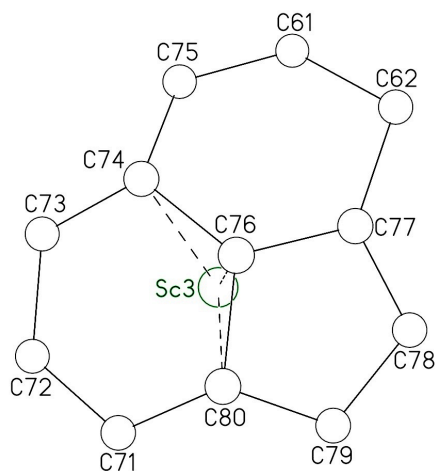


Figure 4.47. The distance between Sc3 and the closest C76 cage carbon atom in **14-3** structure is 2.250(3) Å. The distances from Sc3 to two close C76–C80 and C74–C76 bonds are 2.147(3) Å and 2.170(3) Å, respectively.

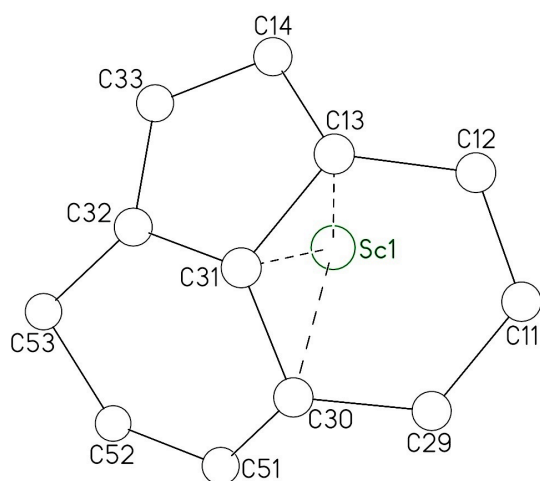


Figure 4.48. The distance between Sc1 and the closest C31 cage carbon atom in **16-2** structure is 2.281(2) Å. The distances from Sc1 to two close C13–C31 and C30–C31 bonds are 2.163(2) Å and 2.220(2) Å, respectively.

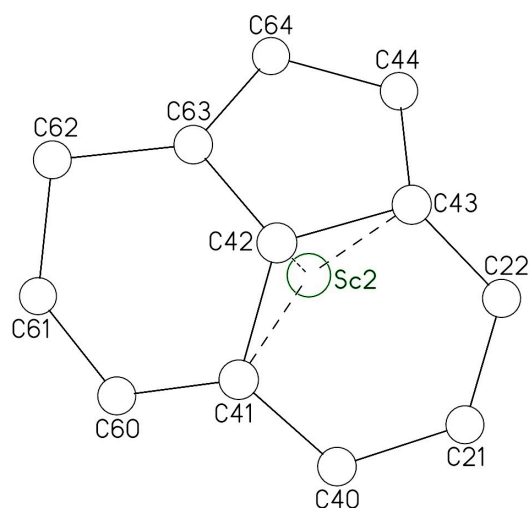


Figure 4.49. The distance between Sc2 and the closest C42 cage carbon atom in **16-2** structure is 2.278(2) Å. The distances from Sc2 to two close C42–C43 and C41–C42 bonds are 2.161(2) Å and 2.218(2) Å, respectively.

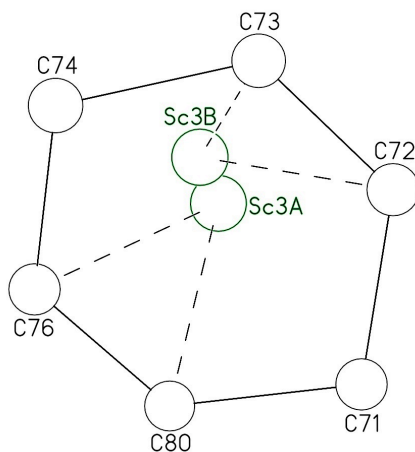


Figure 4.50. Sc3 atom in Sc₃N cluster is disordered among two positions, Sc3A and Sc3B, with site-occupancy factors 43(2)% and 57(2)%, respectively. The distance between Sc3a and the closest C80 cage carbon atom in **16-2** structure is 2.199(5) Å. The distances from Sc3a to close C76–C80 bond is 2.141(5) Å. The distance between Sc3b and the closest C73 cage carbon atom in Sc₃N@C₈₀(CF₃)₁₆ structure is 2.215(3) Å. The distances from Sc3a to close C72–C73 bond is 2.155(3) Å.

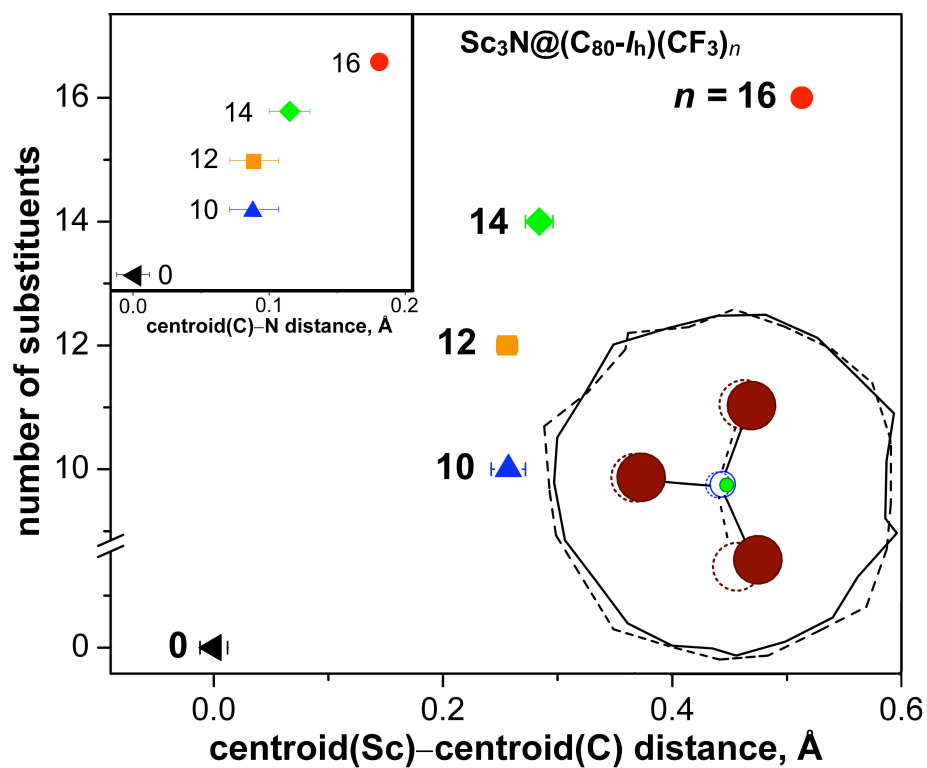


Figure 4.51. Dependence of the distance from cage-carbon-atom to centroid of Sc atoms in Sc₃N cluster on the number of CF₃ groups. The inset (left) shows the dependence of the distance from nitrogen atom to scandium-atom centroid on number of CF₃ groups. The inset (right) demonstrates the shift of the Sc₃N cluster in **16-2** (the dashed line) compared to one in **10-1** (the solid line). Centroids of **16-2** and **10-1** carbon cages are superimposed (green dot).

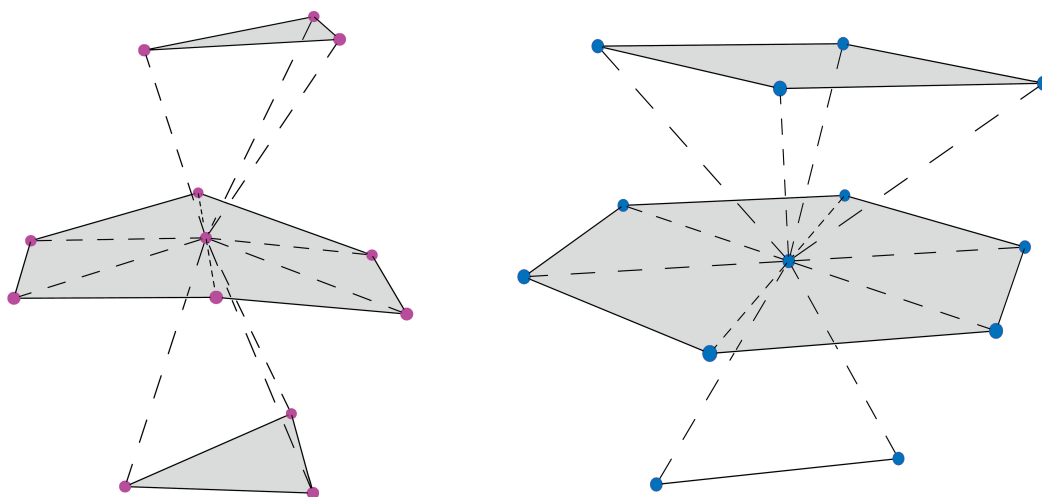


Figure 4.52. (left) Each **10-1** molecule is surrounded by six molecules in one layer and by three ones in the top and bottom layers which leads to formation of distorted *hcp*. (right) In one layer the **12-1** molecule is surrounded by six others. Four ones are located in the top layer, and two **12-1** molecules in the bottom. The purple and blue dots represent centroids of $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_{10}$ and $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_{12}$ molecules, respectively.

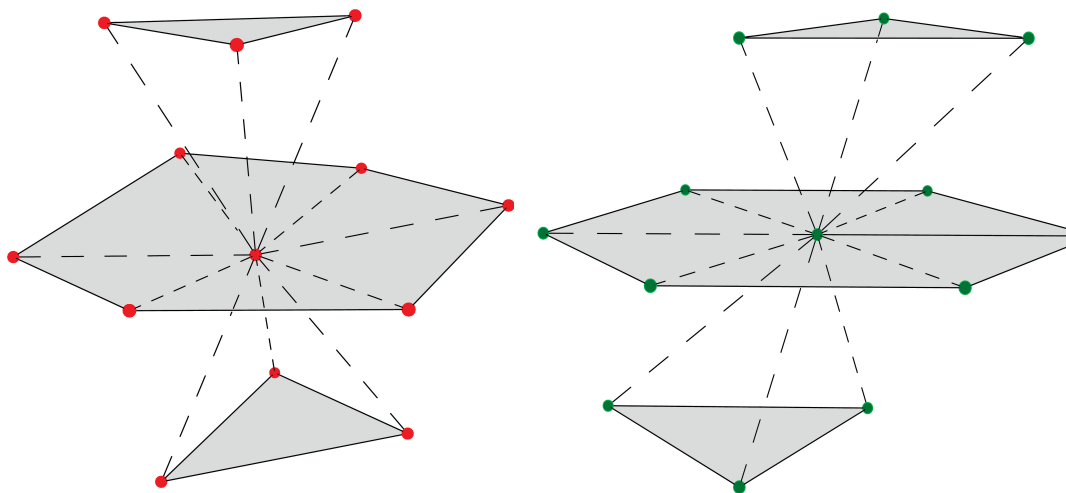


Figure 4.53. For **14-3** and **16-2** structures, each fullerene molecule is surrounded by six molecules in one layer and by three ones in the top and bottom layers which leads to formation of distorted *ccp*. The red and green dots represent centroids of $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_{14}$ and $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_{16}$ molecules, respectively.

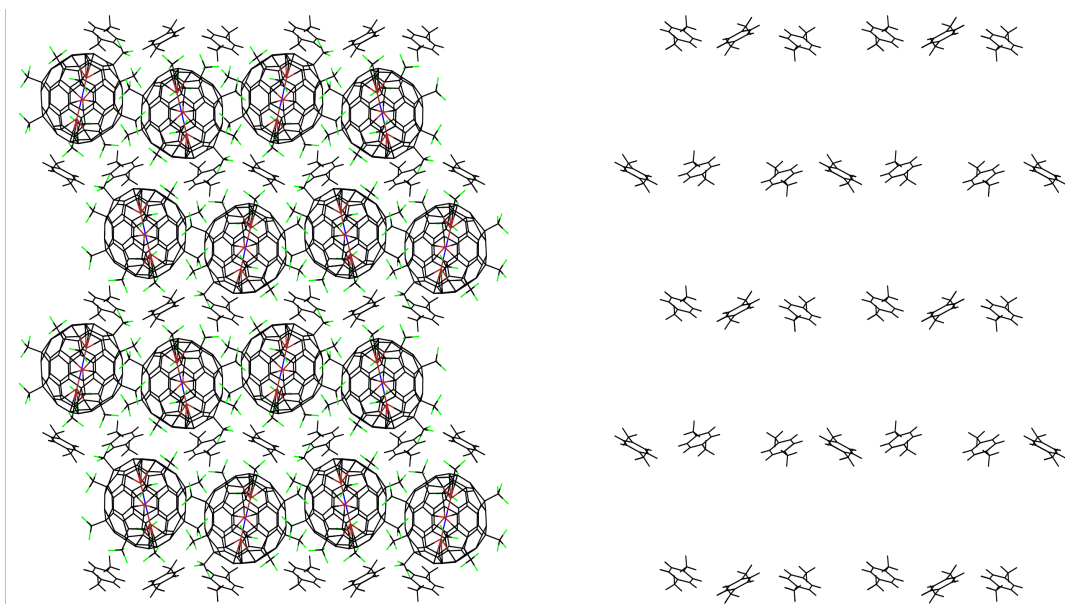


Figure 4.54. (left) Packing of **10-1** molecules in the crystal lattice. (right) The *p*-xylene molecules form layers. Each **10-1** molecule is locked by three solvent molecules.

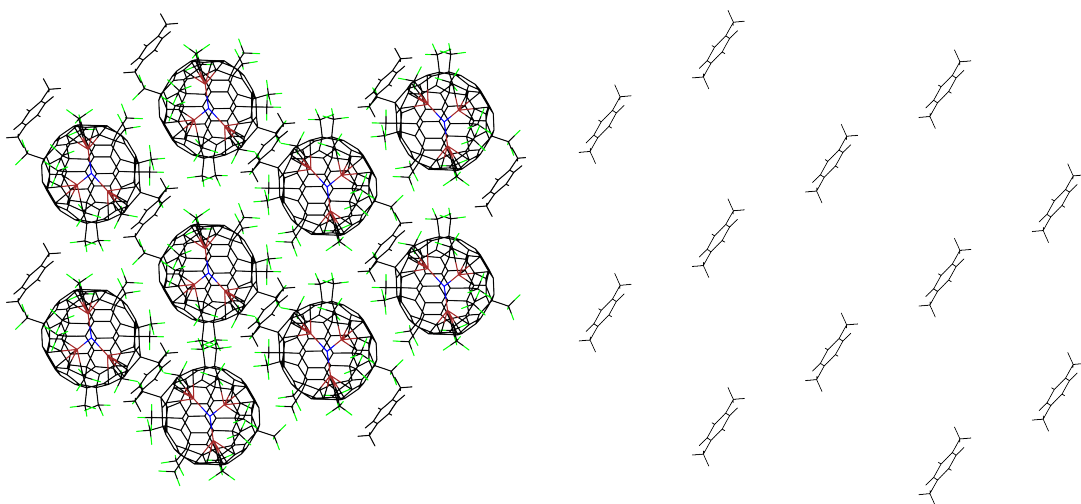


Figure 4.55. (left) Packing of **14-3** molecules in the crystal lattice. (right) The *p*-xylene molecules form layers which may prevent the rotational disorder of fullerene cage.

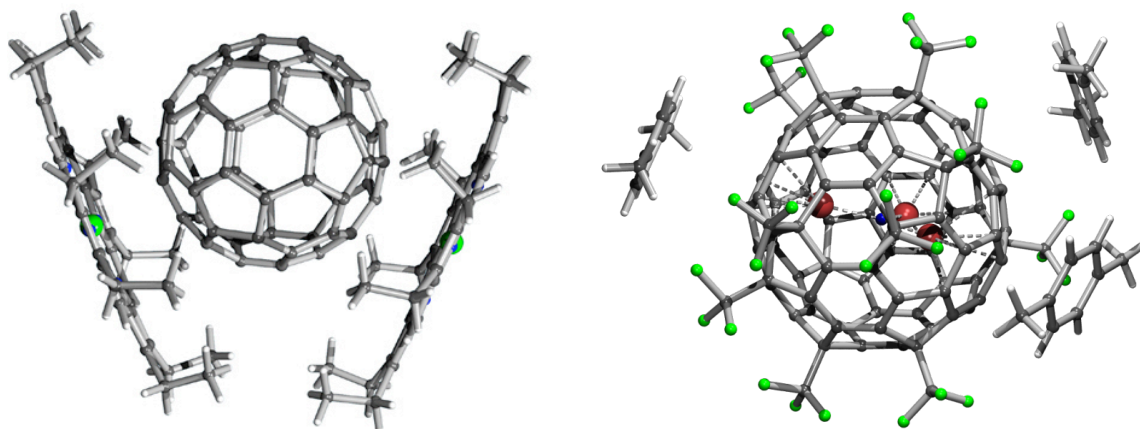


Figure 4.56. (left) Structure of $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$, C_{60} molecules are surrounded by porphyrin molecules. (right) Structure of $Sc_3N@C_{80}(CF_3)_{10} \cdot 1.5 C_8H_{10}$. $Sc_3N@C_{80}(CF_3)_{10}$ is surrounded by *p*-xylene molecules. Both structures were determined by X-ray diffraction.

CHAPTER 5. TRIFLUOROMETHYL DERIVATIVES OF INSOLUBLE HOLLOW HIGHER FULLERENES

Introduction

The hollow (i.e., nonendohedral) fullerenes^{117,118} range in size from C_{20} to cages with over 400 carbon atoms.^{119,120} The first two decades of hollow fullerene research were focused almost exclusively on soluble hollow fullerenes, especially with respect to exohedral derivatization.^{118,121,122} However, it was generally believed that a considerable number of insoluble hollow higher fullerenes (HHFs) were also present in the soots. Their insolubility had been attributed to their covalently linked polymeric nature.^{123,124}

In 1993, Yeretdzian and co-workers reported that the yield of insoluble C_{74} in soots was similar to the yields of soluble HHFs C_{2n} with $2n > 74$ and that C_{74} was sufficiently stable to be sublimed.¹²⁵ In 1998, Diener and Alford demonstrated that insoluble HHFs include C_{2n} isomers with all values of $2n$ from 74 to 104.¹²⁴ A sample of C_{74} -enriched insoluble HHFs was subsequently fluorinated to yield $D_3-C_{74}F_{38}$, the first derivative of the $C_{74}-D_{3h}$ cage.¹²⁶

Fullerene $(CF_3)_n$ derivatives are more stable at higher temperatures than any other class of exohedral fullerene derivatives reported to date.^{32,38,47,65,127} For this reason, and because fullerene $(CF_3)_n$ derivatives are stable in organic solvents and can exhibit nearly fragmentation-free mass spectra,⁶⁰ trifluoromethylation seemed like the most appropriate way to produce a series of derivatized insoluble HHFs for detailed study.

In the present chapter, the high-temperature trifluoromethylation of a mixture of many insoluble HHFs, which resulted in the preparation of one or two relatively abundant isomers of the six compositions $C_{2n}(CF_3)_{12}$, $2n = 74, 76, 78, 80, 82$, and 84 , will be discussed. Four of the compounds are derivatives of four hollow fullerene cages that have not been previously observed. The first two X-ray crystal structures of the exohedral derivatives of insoluble HHFs were determined. This work has already been published.^{33,34}

5.1. Experimental Section

5.1.1. Reagent and Solvents. Fullerene-containing soot was generated using the direct current arc-discharge of graphite rods by Dr. M. Diener and Dr. B. Bolskar from TDA company.^{33,124} The reagents and solvents: CF_3I (Apollo Scientific, 98%), Cu powder (Sigma-Aldrich, ~ 40 mesh, 99.5%) chloroform-*d* and benzene-*d*⁶ (Cambridge Isotopes), hexafluorobenzene (Sigma-Aldrich), and heptane or toluene for HPLC purification (Sigma-Aldrich) were used as received.

5.1.2. Synthesis of $HHF(CF_3)_n$ Compounds. In a typical trifluoromethylation reaction, a sample of insoluble HHFs was mixed with copper powder and heated at $500^\circ C$ for 5 h in the presence of gaseous CF_3I using a hot flow tube as a reactor. [CAUTION: CF_3I decomposes in air above $300^\circ C$ and produces toxic HF, COF_2 , and I_2 ; handle only in a well-ventilated fume hood.] There were four separate syntheses under the same experimental conditions for the preparation of $HHF(CF_3)_{12}$ derivatives. The amounts of HHFs and copper powder used in the four separate preparations were ($\{HHF \text{ mass in mg} : Cu \text{ mass in mg}\}$): $\{22:180\}$, $\{45:280\}$, $\{45:280\}$, and $\{74:562\}$. The volatile products,

which condensed in a narrow zone near the 25 °C end of the reaction tube, were collected and, after I₂ was removed under vacuum, processed by HPLC (10 mm I.D. × 250 mm long Cosmosil Buckyprep column (Nacalai Tesque, Inc.), 300 nm UV detector, toluene or heptane eluent, 5 mL min⁻¹ flow rate). A combination of HPLC traces and NMR and mass spectra showed that 120 mg of fullerene(CF₃)₁₂ compounds that condensed in the cold zone of the reaction tube contained ca. 25% of C₂-C₇₄(CF₃)₁₂ (ca. 30 mg), 3-5% of C₂-C₇₈(CF₃)₁₂, C₂-C₈₂(CF₃)₁₂ (2 isomers), C₁-C₇₈(CF₃)₁₂, C₂-C₇₆(CF₃)₁₂, C₈-C₈₀(CF₃)₁₂, and smaller amounts of other C_{2n}(CF₃)₁₂ (2n = 60, 70, 86, 88, 90, 92, 94, and 96).

5.1.3. X-ray Crystallography. Yellow crystals of C₂-p¹¹-(C₇₄-D_{3h})(CF₃)₁₂ compound were grown from saturated *p*-xylene solution. The X-ray diffraction data were recorded on a Bruker Kappa APEX II CCD diffractometer employing Mo Kα radiation (graphite monochromator) at 100 K, and the structure was initially solved by Brian Newell using a partial data set.

Single crystals of C₂-p¹¹-(C₇₄-D_{3h}(5))(CF₃)₁₂ suitable for X-ray diffraction were grown from *p*-xylene solution. The data set was collected and the crystal structure was solved by Prof. K. Seppelt from the Free University (Berlin, Germany). Table 5.3 contains selected crystallographic experimental parameters and refinement results. The structure of this compound proved to be difficult to refine satisfactorily. Two data sets were obtained for crystals from different crystallization batches, and both data sets yielded the same overall structure for the fullerene molecule. However, standard refinement in each case led to physically unreasonable atomic displacement parameters for some atoms of the fullerene cage and chemically unreasonable electron density in parts of the solvent-occupied regions of the structure. The best residual indices were

obtained from a model for which the program SQUEEZE¹²⁸ was used to fill the disordered solvent regions; this model for $C_2-p^{11}-(C_{78}-D_{3h})(CF_3)_{12}$ is reported here.

Two $C_2-p^{11}-(C_{74}-D_{3h})(CF_3)_{12}$ and $C_2-p^{11}-(C_{78}-D_{3h})(CF_3)_{12}$ structures were solved by using direct methods and 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 control and integration software (APEX II) was employed, and Bruker SHELXTL²¹ software was used for structure solution, refinement, and graphics. Selected details related to the crystallographic experiments are listed in Table 5.3.

5.1.4. Spectroscopic Measurements. Atmospheric-pressure chemical-ionization (APCI) mass spectra were recorded using a ThermQuest Finnagan LCQ-DUO spectrometer (acetonitrile eluent, 0.3 mL min⁻¹ flow rate) and Agilent Technologies Model 6210 TOF with APPI spectrometer. In the latter case, flow injection was done using acetonitrile which contained 1% toluene. Samples for ¹⁹F NMR spectroscopy were chloroform-*d* solutions containing a small amount of hexafluorobenzene as an internal standard ($\delta = -164.9$). Spectra were recorded using a Varian INOVA-unity 400 spectrometer operating at 367.45 MHz. 2D-COSY ¹⁹F NMR spectra were recorded by Dr. I. V. Kuvychko.

5.1.5. Theoretical Calculations. Dr. A. A. Popov performed DFT calculations (Leibniz Institute for Solid State and Materials Research, Dresden, Germany) using PBE functional and TZ2P-quality basis set implemented by the PRIRODA package.⁷³

5.2. Results and Discussion

Trifluoromethyl groups are sterically more demanding than CH₃, Br, or even Ph substituents.^{129,130} For this reason, a main requirement for varying of the experimental conditions was a preparation of HHF(CF₃)₁₂ derivatives, anticipating that they would have one CF₃ group per pentagon. This restriction would severely limit the number of possible isomers, greatly simplifying structure elucidation. This was indeed the case. The reaction conditions described in the Experimental Section led to seven relatively abundant HHF(CF₃)₁₂ single isomers that could be purified to varying extents (e.g., one to 50% purity and one in excess of 97% purity) and characterized by APCI mass spectrometry and ¹⁹F NMR spectroscopy. The NI-APCI mass spectra of HPLC-purified samples of the single isomers of C₂-C₇₄(CF₃)₁₂, C_s-C₇₆(CF₃)₁₂, C₁-C₇₈(CF₃)₁₂, and C_s-C₈₀(CF₃)₁₂, of C₂-C₈₂(CF₃)₁₂-2, and of a mixture of at least two isomers of C₈₄(CF₃)₁₂ are shown in Figure 5.1. The mass spectra of C₂-C₇₈(CF₃)₁₂ and C₂-C₈₂(CF₃)₁₂-1 (not shown) were similar to those of C₁-C₇₈(CF₃)₁₂ and C₂-C₈₂(CF₃)₁₂-2. Fluorine-19 NMR spectra of seven of the new compounds are shown in Figure 5.7 (the amounts of individual isomers of C₈₄(CF₃)₁₂ present in the mixture are insufficient for detailed NMR study at this time). In addition, spectra of S₆-C₆₀(CF₃)₁₂ and an isomer of C₁-C₇₀(CF₃)₁₂ are included for comparison. Contrary to the literature report,⁴⁰ it was found that S₆-C₆₀(CF₃)₁₂ is soluble in benzene-*d*⁶ (See Chapter 2 for more details). The structural principles observed for previously reported fullerene(CF₃)_{*n*} addition patterns and their associated ¹⁹F NMR spectra, plus new DFT-predicted relative Δ*H*_f[°] values, HOMO-LUMO gaps, and other geometric principles, were used to determine the most likely structures for four of the

seven new compounds (see below). The structures of two $C_2-C_{74}(CF_3)_{12}$ and $C_2-C_{78}(CF_3)_{12}$ compounds were determined by X-ray crystallography.

The following structural/geometrical principles were used:

1. Addition patterns are ribbons or loops of edge-sharing *m*- and *p*- $C_6(CF_3)_2$ hexagons. An isolated *p*- $C_6(CF_3)_2$ hexagon can be also added.^{32,50,65,67,131}
2. Ribbons always end with a *p*- $C_6(CF_3)_2$ hexagon, never with a *m*- $C_6(CF_3)_2$ hexagon, and always end with a p^3 or *pmp* sequence, never with an *mpp* sequence.^{65,132}
3. CF_3 groups that have eclipsed or nearly eclipsed conformations with respect to the cage have $-\delta(^{19}F)$ values less than 60 (Figure 5.2).^{38,60}
4. J_{FF} coupling is only observed between CF_3 groups sharing the same hexagon, because the coupling is predominantly mediated through space by the overlap of F atom lone pairs.^{31,35,38,41}
5. For numbers of the substituents less than or equal to 12, two CF_3 groups are rarely on adjacent cage carbon atoms (exceptions are $C_{60}(CF_3)_6-2^{65}$ and $C_{60}(CF_3)_{12-3}^{32,43}$) or on the same pentagon (exceptions are $C_{70}(CF_3)_{12-4}^{31}$, $C_{60}(CF_3)_{12-2}^{41}$ and $C_{60}(CF_3)_{12-4}^{127}$).
6. For numbers of perfluoroalkyl radicals less than or equal to 18, R_F groups are not attached to triple-hexagon junctions (THJs), because these are the least pyramidalized of fullerene sp^2 carbon atoms and they resist further pyramidalization that occurs when an exohedral substituent is added (see Chapter 4 for more details).¹¹⁰ For example, perfluoroalkylated derivatives of HHF fullerenes with 18 or fewer substituents have no sp^3 THJ, including $C_{78}(C_2F_5)_{10}$,⁶⁴ $C_{82}(CF_3)_{12}$,¹³³ $C_{82}(CF_3)_{18}$,¹³³ $C_{84}(C_2F_5)_{12}$,¹³⁴ $C_{84}(CF_3)_{16}$,¹³⁴ $C_{84}(CF_3)_{12}$,¹³⁴

$C_{86}(CF_3)_{16}$,¹³⁵ $C_{86}(CF_3)_{18}$,¹³⁵ $C_{88}(CF_3)_{18}$,¹³⁶ $C_{92}(CF_3)_{16}$,¹³⁶ and $C_{96}(C_2F_5)_{12}$.¹³⁷ Only one trifluoromethyl derivative with 20 CF_3 group, $C_{94}(CF_3)_{20}$, has two CF_3 groups attached to THJs.¹³⁷

7. The other geometric principles are as follows and are based on the fact that six of the seven compounds possess either C_s , C_2 , or C_i symmetry (see below). The key to C_s symmetry for fullerene(CF_3)₁₂ derivatives is the availability of pentagons on the symmetry plane. Given that such a pentagon is present, the only possibility is shown in Figure 5.3. Otherwise, C_s symmetry would require two CF_3 groups on one pentagon, and that is a violation of one of the six structural principles for fullerene(CF_3)_n derivatives. Therefore, one single intensity NMR multiplet is required for each pentagon on the symmetry plane. The key to C_2 symmetry for fullerene(CF_3)₁₂ derivatives with a single ribbon of 12 CF_3 groups is the presence of a p - $C_6(CF_3)_2$ hexagon in the middle of the ribbon that lies on the C_2 axis, as shown in Figure 5.4 (the carbon atoms at the top and bottom of this type of hexagon are THJs in all higher fullerenes). For a C_2 derivative with a double ribbon, an exhaustive search of possible isomers is necessary because there is no simple geometric rule that can be used.
8. Finally, very few of the IPR cages for C_{74} - C_{82} have a center of symmetry. Only a single loop of 12 CF_3 groups, two loops of six CF_3 groups, or two ribbons of six CF_3 groups are compatible with C_i symmetry. The isomer of $C_{82}(CF_3)_{12}$ that exhibits two quartets (see below), which must have two ribbons of six CF_3 groups, would be a candidate for C_i symmetry except for the fact that none of the

nine IPR C_{82} cages possesses a center of symmetry. Therefore, C_i symmetry will not be considered further for the compounds isolated in this work.

C_2 - $C_{74}(\text{CF}_3)_{12}$. The only IPR isomer of C_{74} has D_{3h} symmetry and is not soluble in organic solvents.^{117,124} The ^{19}F NMR spectrum of C_2 - $C_{74}(\text{CF}_3)_{12}$ consists of five multiplets plus one simple quartet, all of equal intensity (Figures 5.8, Table 5.1). This requires a single ribbon of 11 edge-sharing $\text{C}_6(\text{CF}_3)_2$ hexagons and overall C_2 or C_s symmetry. Thirty-two isomers are topologically consistent with the NMR multiplet pattern, but only the C_2 isomer shown as a Schlegel diagram in Figure 5.7, which was proven by X-ray diffraction (see below), and is consistent with all of the structural and geometric principles listed above. In addition, the other 31 isomers have AM1 energies at least 199 kJ mol^{-1} higher than C_2 - $C_{74}(\text{CF}_3)_{12}$, underscoring the instability of isomers with substituents on THJs. Significantly, it can be prepared in ca. 25 mg batches with 97+% purity.

The X-ray crystal structure of C_2 - $C_{74}(\text{CF}_3)_{12}$ is shown in Figure 5.5. The $C_{74}(\text{CF}_3)_{12}$ molecule has crystallographic C_2 symmetry. The C_2 axis is the only remaining symmetry element of the original D_{3h} cage after the 12 CF_3 groups have been added to give a ribbon of 11 $\text{C}(sp^3)\text{-C}(sp^2)$ edge-sharing $p\text{-C}_6(\text{CF}_2)_2$ hexagons (see Schlegel diagram in Figure 5.7). The esd's for individual cage C-C distances range from 0.0017 to 0.0020 Å (Table 5.2). A plot in Figure 5.6 shows the agreement between the cage C-C distances of the X-ray and DFT structures. A network of $\text{F}\cdots\text{F}$ contacts between hexagon-sharing CF_3 groups range in distance from 2.6322(17) to 2.8785(14) Å. Tables 5.1 and 5.2 list $\text{F}\cdots\text{F}$ distances, $\text{F}_3\text{C}\cdots\text{CF}_3$ distances between hexagon-sharing CF_3 groups, and $\text{F-C}\cdots\text{C-C}$ torsion angles from the X-ray and the DFT structures. The latter parameter

indicates the conformation of each CF₃ group with respect to the fullerene cage. The X-ray and DFT-optimized structures of C₂-C₇₄(CF₃)₁₂ both show that the pair of CF₃ groups that are fourth from either end of the p^{11} ribbon is the only pair that are fully eclipsed with respect to the fullerene cage. The significance is that F-C $\cdots$ C-C torsion angles in fullerene(CF)₃ structures appear to be correlated with chemical shift in ¹⁹F NMR. It was found that $-\delta$ values < 60 indicate that CF₃ groups have eclipsed or nearly eclipsed conformations (see structural principle #3).³² For example, the multiplet for the CF₃ groups attached to C37 and C27 has $-\delta = 55.2$ (CF₃ groups # 79 and # 81 in the DFT predicted structure, Table 5.1) which correlates to the value of the torsion angles which are 0.8(1)° (F783-C78 $\cdots$ C37-C38) and 0.9(1)° (F782-C78 $\cdots$ C27-C28) (Table 5.1).

Packing of C₂-C₇₄(CF₃)₁₂ molecules is shown in Figure 5.6. The solvent molecules (*p*-xylene) form channels which may be responsible for the absence of the positional disorder of the C₇₄(CF₃)₁₂ molecules, and thus leading to determination of the C-C and C-F bond lengths with high precision.

C₂-C₇₈(CF₃)₁₂. There are five IPR isomers of C₇₈,¹¹⁷ three of which are known to be soluble: C₇₈-D₃(1); C₇₈-C_{2v}(2); and C₇₈-C_{2v}(3).¹³⁸⁻¹⁴⁰ Troyanov and co-workers recently determined the crystal structure of the perfluoroethylated (C₇₈-C_{2v}(2))(C₂F₅)₁₀ derivative.⁶⁴ The C₂-C₇₈(CF₃)₁₂ compound obtained in the present work is the first exohedral derivative of the hollow C₇₈-D_{3h}(5) fullerene, which was initially predicted by DFT calculations (Table 5.4) and then confirmed by X-ray crystallography (Figure 5.8). Despite the refinement problems for this structure (see Experimental Section), there is no doubt that the molecular structure consists of a C₇₈-D_{3h} cage with 12 CF₃ groups forming a ribbon of 11 *p*-C₆(CF₃)₂ hexagons (see Schlegel diagram in Figure 5.8). The p^{11} ribbon

is not even approximately C_2 symmetric with respect to the CF_3 conformations. For example, in the X-ray structure the CF_3 groups attached to C23 and C46 have $F-C\cdots C-C$ torsion angles of 15.58° and 51.88° (average 33.78°), and the CF_3 groups attached to C32 and C58 have torsion angles of 28.08° and 17.38° (average 22.78°). The latter pair of CF_3 groups has the smallest average torsion angle for any pair in this compound. Accordingly, none of the ^{19}F NMR multiplets for $C_2-C_{78}(CF_3)_{12}$ have $-\delta$ values below 60. Thus, none of the torsion angles has a value close to 0° in contrast to the torsion angles observed in the $C_2-C_{78}(CF_3)_{12}$ structure (see above).

$C_2-C_{82}(CF_3)_{12}$ -1. There are nine IPR isomers of C_{82} .¹¹⁷ The predominant soluble isomer, which has been characterized by ^{13}C NMR spectroscopy, is $C_{82}-C_2(3)$.^{138,141} Recently, the crystal structures of $(C_{82}-C_2(3))(CF_3)_{12}$ and $(C_{82}-C_2(3))(CF_3)_{18}$ compounds were determined by Troyanov and co-workers.¹³³

The ^{19}F NMR spectrum of $C_2-C_{82}(CF_3)_{12}$ consists of six equal-intensity apparent septets or unresolved multiplets, as well as one quartet (Figure 5.7 and Table 5.5). It is comparable with the spectra of $C_2-C_{74}(CF_3)_{12}$ and $C_2-C_{78}(CF_3)_{12}$ and therefore requires a single C_2 or C_s ribbon (none of the IPR C_{82} cages has an inversion center). Only three of the nine IPR cages can have C_2 or C_s ribbons that are consistent with six equal-intensity multiplets including one quartet, and these are $C_{82}-C_2(1)$, $C_{82}-C_2(5)$ (two isomers), and $C_{82}-C_{2v}(9)$. The DFT-predicted remaining $p^{11}-(C_{82}-C_2(5))(CF_3)_{12}$ isomer has HOMO-LUMO gap of 1.80 eV. Notably, all of the isolated compounds are yellow to red-orange in color, and therefore it was assumed that any isomer of the new compositions should have a DFT-predicted gap of at least 1.0 eV. For instance, the electronic spectrum of a dichloromethane solution of $C_2-C_{74}(CF_3)_{12}$, which is yellow in color, has weak bands at

430 nm (2.88 eV) and 400 nm and an intense band at 280 nm, and the DFT predicted HOMO-LUMO gap for $C_2-C_{74}(CF_3)_{12}$ is 2.17 eV.

Two of the multiplets in the ^{19}F NMR spectrum of the $C_2-C_{82}(CF_3)_{12}$ compound have $-\delta$ values below 60 (Table 5.5). Therefore, the DFT-optimized structure of $C_2-p^{11}-(C_{82}-C_2(5))(CF_3)_{12}$ contains two pairs of CF_3 groups which are nearly eclipsed. The two calculated C–F $\cdots$ C–C torsion angles are 6° for one pair and 14° for the other one.

The $C_{82}-C_2(5)$ cage isomer is predicted to have a ΔH_f° value of +30.1 kJ mol $^{-1}$ relative to $C_{82}-C_2(3)$, which is the most stable IPR C_{82} cage.¹⁴¹ No exohedral derivatives of hollow $C_{82}-C_2(5)$ have been reported to date. Therefore, the compound $C_2-p^{11}-(C_{82}-C_2(5))(CF_3)_{12}$ provides the first experimental evidence for the presence of the hollow fullerene $C_{82}-C_2(5)$ in arc-discharge soots.

$C_2-C_{82}(CF_3)_{12}$ -2. Like the ^{19}F NMR spectra of $C_2-C_{74}(CF_3)_{12}$, $C_2-C_{78}(CF_3)_{12}$, and $C_2-C_{82}(CF_3)_{12}$ -1, the spectrum of $C_2-C_{82}(CF_3)_{12}$ -2 consists of six equal-intensity apparent septets or unresolved multiplets (see Table 5.6). Two of the multiplets are quartets, and this requires two symmetry-related ribbons of six CF_3 groups each in addition to overall C_2 or C_s symmetry. According to DFT calculations, of all possible isomers of all nine C_{82} cages, only the isomer $C_2-p^5,p^5-(C_{82}-C_2(3))(CF_3)_{12}$ is consistent with the structural/geometric principles above and the NMR data and has a HOMO-LUMO gap > 1 eV (its predicted gap is 2.08 eV). The 2D-COSY spectrum showed that the third CF_3 group from one end of each ribbon should be eclipsed or nearly eclipsed (i.e., the $-\delta$ value for a multiplet is 55.7, Table 5.6). The DFT optimized structure of $C_2-p^5,p^5-(C_{82}-C_2(3))(CF_3)_{12}$ shows that $\text{tors}(C-C\cdots C-F) = 13.2^\circ$ for the third CF_3 group (CF_3 #92 and #87 in Figure 5.6) from the end of each ribbon. Thus, $C_2-p^5,p^5-(C_{82}-C_2(3))(CF_3)_{12}$ is the

most probable structure of $C_2-C_{82}(CF_3)_{12}$ -2. It is noteworthy that all of the soluble fullerene $C_{82}-C_2(3)$ was not extracted out of the sublimed fraction of the arc-discharge soot with *o*-dichlorobenzene. This may be because the polymeric network of insoluble fullerenes physically traps some soluble cages or because the polymeric network may include some soluble cages (including small amounts of C_{60} and C_{70}) covalently linked to the more reactive small- or zero-gap cages. The reason why $C_{82}-C_2(3)$ appears to be the most abundant soluble higher fullerene in the mixture of “insoluble” fullerenes used to prepare compounds is not clear at this time.

$C_1-C_{78}(CF_3)_{12}$. The ^{19}F NMR spectrum of $C_1-C_{78}(CF_3)_{12}$ consists of 12 equal-intensity multiplets including four quartets: δ -56.2 (*m*); -59.0 (*u.m.*); -62.5 (*u.m.*); -63.5 (*as*, 15.0 Hz); -64.3 (*u.m.*); -64.4 (*u.m.*); -65.1 (*as*, 15.0 Hz); -66.1 (*u.m.*); -68.4 (*q*, 16.0 Hz); -68.8 (*q*, 16.0 Hz); -70.4 (*q*, 16.0 Hz); -72.2 (*q*, 6.0 Hz) (Figure 5.7). It requires overall C_1 symmetry and either a ribbon of 10 CF_3 groups plus an isolated *p*- $C_6(CF_3)_2$ hexagon, a ribbon of eight plus a ribbon of four, or two ribbons of six. It is also possible that stable CF_3 derivatives of HHFs can have ribbons with an odd number of CF_3 groups. To narrow down these possibilities, a selective decoupling experiment showed that none of the quartets was coupled to another quartet, ruling out a ribbon of 10 CF_3 groups plus an isolated hexagon. Note that the quartets with the highest $-\delta$ values in the spectrum of $C_1-C_{70}(CF_3)_{12}$ are coupled to one another, and this compound, in contrast to $C_1-C_{78}(CF_3)_{12}$, is known to have an isolated hexagon.⁴⁵ The spectrum of $C_1-C_{78}(CF_3)_{12}$ also exhibits a less intense set of multiplets (10 are clearly discernible), suggesting that a second, less abundant C_1 isomer of this composition may also be present. In order to determine which of the five C_{78} cages of $C_1-C_{78}(CF_3)_{12}$ is present, the structure will have

to be determined by X-ray diffraction. Without at least one element of symmetry, there are too many possibilities to consider at this time.

C_s - $C_{76}(CF_3)_{12}$. The two IPR isomers of [76]fullerene are $C_{76}-D_2(1)$ and $C_{76}-T_d(2)$,¹¹⁷ and only the soluble D_2 empty cage was known to exist before this work.¹⁴² Recently, Troyanov and co-workers determined the $C_{76}Cl_{24}$ structure of a non-IPR isomer of C_{76} fullerene (C_2 -symmetric isomer 18917 of C_{76}).¹⁴³ The ^{19}F NMR spectrum of C_s - $C_{76}(CF_3)_{12}$ (which is only ca. 50% pure at this time) consists of three double-intensity apparent septets, two single-intensity apparent septets, an unresolved double-intensity multiplet (a broad singlet), and a double-intensity quartet (Figure 5.7). Two single intensity multiplets are not possible for overall C_2 symmetry because no HHF isomer has two cage carbon atoms on a C_2 axis. Therefore, this derivative must have C_s symmetry. The remaining pattern of septets, with no quartets, can only be due to a loop of edge-sharing $C_6(CF_3)_2$ hexagons (note that the spectrum of S_6 - $C_{60}(CF_3)_{12}$ consists only of apparent septets, and this compound is known to have a loop of 12 CF_3 groups⁴⁰). This unique multiplet pattern is consistent with only one possible isomer, C_s -($C_{76}-T_d(2)$)(CF_3)₁₂, which has a 2.06 eV HOMO-LUMO gap. It has a loop of nine edge-sharing p - $C_6(CF_3)_2$ hexagons plus a p^2 ribbon of three CF_3 groups, demonstrating for the first time that the addition patterns of some hollow fullerene(CF_3)_{*n*} derivatives can include a ribbon of edge-sharing $C_6(CF_3)_2$ hexagons with an odd number of CF_3 groups (it was already shown that a C_2 isomer of $C_{60}(CF_3)_{10}$ has a pair of p^3m^2 loops with five CF_3 groups each⁵⁰). The DFT-optimized structure of C_s -($C_{76}-T_d(2)$)(CF_3)₁₂ (Table 5.7) is entirely consistent with the ^{19}F NMR $-\delta$ values (Table 5.7). This is the first experimental evidence for the existence of the $C_{76}-T_d(2)$ cage in arc-discharge soots.

C_s - $C_{80}(CF_3)_{12}$. There are seven IPR isomers of C_{80} ,¹¹⁷ but only $C_{80}-D_{5d}(1)$ and $C_{80}-D_2(2)$ are soluble and have been isolated and characterized.^{144,145} The ^{19}F NMR spectrum of C_s - $C_{80}(CF_3)_{12}$ is unusual for fullerene(CF_3)_n derivatives (Figure 5.7). There are four double intensity apparent septets, two single-intensity apparent septets, a sharp double-intensity singlet, and no quartets. This requires C_s symmetry with the mirror plane passing through a loop of 10 CF_3 groups as well as through an isolated p - $C_6(CF_3)_2$ hexagon (the latter giving rise to the double-intensity singlet). The only possible isomer that follows the structural and geometric principles is C_s - $p^{10}(\text{loop})_p$ -($C_{80}-C_{2v}(5)$)(CF_3)₁₂, shown as a Schlegel diagram in Figure 5.7. The C–C distances and C–F⋯C–C torsion angles for the DFT-optimized structure is listed in Table 5.8. This compound is the first exohedral derivative of hollow $C_{80}-C_{2v}(5)$ to be isolated and characterized and provides the first evidence for the existence of hollow $C_{80}-C_{2v}(5)$ in arc-discharge soots.

5.3. Summary and Conclusions

Seven new HHF derivatives $C_{2n}(CF_3)_{12}$ have been characterized by ^{19}F NMR spectroscopy, X-ray crystallography, and studied by DFT. The C_2 - $C_{78}(CF_3)_{12}$, C_2 - $C_{82}(CF_3)_{12}$ (2 isomers), C_1 - $C_{78}(CF_3)_{12}$, C_2 - $C_{76}(CF_3)_{12}$, C_s - $C_{80}(CF_3)_{12}$ compounds are the first exohedral derivatives of insoluble fullerenes which were isolated and characterized. A single most-probable isomer was determined in six of the seven cases, including derivatives of four IPR HHF cages that had not been previously observed experimentally: $C_{76}-T_d(76:2)$; $C_{78}-D_{3h}(78:5)$; $C_{80}-C_{2v}(80:5)$; and $C_{82}-C_2(82:5)$. The structures of C_2 - $C_{74}(CF_3)_{12}$ and C_2 - $C_{78}(CF_3)_{12}$ compounds determined by X-ray crystallography confirm

the molecular structures that were predicted based on spectroscopic data and DFT studies in the beginning of the present work.

Thus, the present work demonstrates that trifluoromethylation has emerged as a powerful tool for the conclusive identification of previously “unknown” fullerene cages.

Table 5.1. Torsion C–F⋯C–C angles [°], $-\delta(^{19}\text{F})$, and $^7J_{\text{FF}}$ coupling constants for $\text{C}_2\text{-C}_{74}(\text{CF}_3)_{12}$ molecule.

CF_3	C–F⋯C–C, deg	$-\delta(^{19}\text{F})$	$^7J_{\text{FF}}$, Hz
86	52.4	70.0 (q)	15.0
85	23.5	63.2 (qq)	13.0, 15.0
80	54.0	67.7 (as)	12.0
79	1.0	55.2 (as)	12.0
77	51.5	67.5 (m)	12.0
75	33.1	63.6 (m)	–
76	33.0	63.6 (m)	–
78	51.6	67.5 (m)	12.0
81	0.9	55.2 (as)	12.0
82	54.0	67.7 (as)	12.0
83	23.4	63.2 (qq)	13.0, 15.0
84	52.5	70.0 (q)	15.0

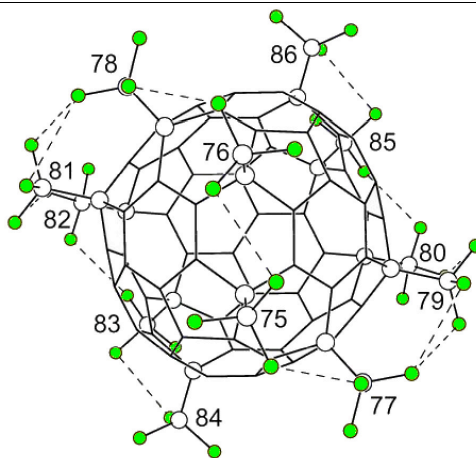


Table 5.2. Interatomic distances [$\text{\AA}$] and angles [$^\circ$] for $\text{C}_2\text{-}p^{11}\text{-(C}_{74}\text{-}D_{3h})\text{(CF}_3\text{)}_{12}$ from the X-ray structure and DFT-optimized structure.

Parameter	X-ray	DFT	CF_3 locants
F...F distance			
F751...F762	2.6325(15)	2.690	43...62
F761...F772	2.7011(16)	2.741	62...47
F771...F782	2.8785(14)	2.864	47...27
F771...F783	2.7595(15)	2.766	47...27
F781...F792	2.6823(14)	2.745	27...11
F782...F792	2.8079(14)	2.853	27...11
F791...F802	2.6223(17)	2.676	11...2
F801...F811	2.639(2)	2.685	2...5
$\text{F}_3\text{C...CF}_3$ distance			
C75...C76	3.962(2)	4.013	43...62
C76...C77	4.213(2)	4.309	62...47
C77...C78	4.024(2)	4.053	47...27
C78...C79	3.986(2)	4.042	27...11
C79...C80	4.313(2)	4.340	11...2
C80...C81	3.875(2)	3.938	2...5
F-C...C-C torsion angle			
F751-C75...C43-C60	52.0(1)	52.4	43
F762-C76...C62-C45	24.7(1)	23.4	62
F772-C77...C47-C46	47.1(1)	54.0	47
F782-C78...C27-C28	0.8(1)	0.9	27
F791-C79...C11-C10	56.4(1)	51.5	11
F802-C80...C2-C1	33.6(1)	33.0	2

Table 5.3. Crystal Data and Structure Refinement for $(C_{74}-D_{3h})(CF_3)_{12}\cdot 3C_8H_{10}$ and $(C_{78}-D_{3h})(CF_3)_{12}\cdot nC_7H_8$

formula	$(C_{74}-D_{3h})(CF_3)_{12}\cdot 3C_8H_{10}$	$(C_{78}-D_{3h})(CF_3)_{12}\cdot nC_8H_{10}$
crystal system,	monoclinic, $C2/c$, 4	triclinic, $P\bar{1}$, 2
space group, Z		
color of crystal	yellow	yellow
unit cell dimensions	$a = 25.7275(13) \text{ \AA}$	$a = 14.305(7) \text{ \AA}$
	$b = 13.3117(7) \text{ \AA}$	$b = 15.264(8) \text{ \AA}$
	$c = 23.8412(12) \text{ \AA}$	$c = 20.733(9) \text{ \AA}$
	$\beta = 109.791(3)^\circ$	$\alpha = 97.23(2)^\circ$
		$\beta = 98.96(2)8^\circ$
		$\gamma = 94.32(1)8^\circ$
temperature, K	100(1)	153(2)
$R_1 [I \geq 2\sigma(I)]/wR_2$ (all)	0.0503/0.1215	0.0734/0.218

Table 5.4. C–C distances [Å], torsion C–F⋯C–C angles [°], $-\delta(^{19}\text{F})$, and $^7J_{\text{FF}}$ coupling constants for $\text{C}_2\text{-C}_{78}(\text{CF}_3)_{12}$ molecule. DFT-predicted structure of $\text{C}_2\text{-C}_{78}(\text{CF}_3)_{12}$ is shown below.

CF_3	C⋯C, Å	C–F⋯C–C, deg	$-\delta(^{19}\text{F})$	$^7J_{\text{FF}}$, Hz
90	4.202	51.4	71.3 (q)	12.0
89	4.202, 4.096	40.8	61.9 (um)	–
88	4.096, 4.047	11.2	60.6 (um)	–
87	4.047, 4.244	59.4	65.1 (um)	–
86	4.244, 4.051	12.5	65.1 (um)	–
80	4.051, 4.152	55.7	61.0 (um)	–
85	4.193	52.0	71.3 (q)	12.0
84	4.193, 4.087	39.0	61.9 (um)	–
83	4.087, 4.028	11.5	60.6 (um)	–
82	4.028, 4.405	55.3	65.1 (um)	–
81	4.405, 4.028	57.5	65.1 (um)	–
79	4.028, 4.152	4.9	61.0 (um)	–

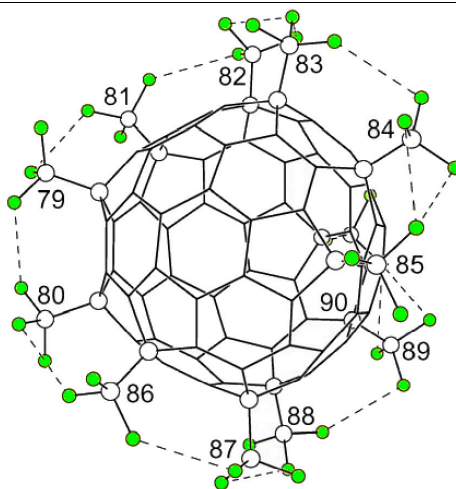


Table 5.5. C–C distances [Å], torsion C–F⋯C–C angles [°], $-\delta(^{19}\text{F})$, and $^7J_{\text{FF}}$ coupling constants for $\text{C}_2\text{-C}_{82}(\text{CF}_3)_{12}\text{-1}$ molecule. DFT-predicted structure of $\text{C}_2\text{-C}_{82}(\text{CF}_3)_{12}\text{-1}$ is shown below.

CF_3	C⋯C, Å	C–F⋯C–C, deg	$-\delta(^{19}\text{F})$	$^7J_{\text{FF}}$, Hz
93	3.967	51.6	70.5 (q)	13.0
92	3.967, 3.886	14.7	57.6 (um)	–
89	3.886, 4.393	43.1	65.7 (as)	15.0
86	4.393, 4.034	57.4	66.7 (as)	14.0
85	4.034, 4.079	6.5	55.7 (as)	14.0
83	4.079, 4.306	49.4	63.6 (um)	–
84	4.306, 4.080	49.7	63.6 (um)	–
87	4.080, 4.033	6.4	55.7 (as)	14.0
88	4.033, 4.393	57.3	66.7 (as)	14.0
90	4.393, 3.886	43.2	65.7 (as)	15.0
91	3.886, 3.967	14.7	57.6 (um)	–
94	3.967	51.6	70.5 (q)	13.0

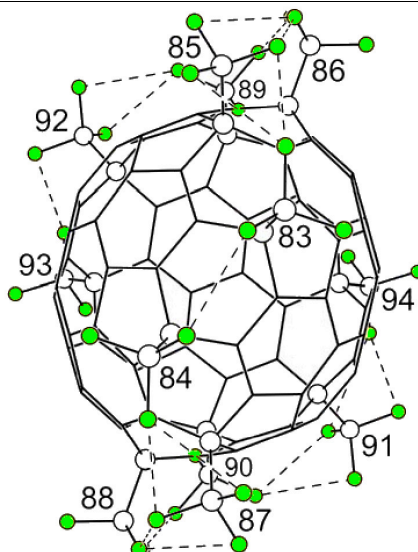


Table 5.6. C–C distances [Å], torsion C–F⋯C–C angles [°], $-\delta(^{19}\text{F})$, and $^7J_{\text{FF}}$ coupling constants for $\text{C}_2\text{-C}_{82}(\text{CF}_3)_{12}\text{-2}$ molecule. DFT-predicted structure of $\text{C}_2\text{-C}_{82}(\text{CF}_3)_{12}\text{-2}$ is shown below.

CF_3	$\text{C}\cdots\text{C}$, Å	$\text{C-F}\cdots\text{C-C}$, deg	$-\delta(^{19}\text{F})$	$^7J_{\text{FF}}$, Hz	COSY
94	4.286	53.7	71.4 (q)	16.0	f
93	4.286, 3.885	37.4	64.8 (as)	14.0	c
92	3.885, 3.919	13.2	55.7 (as)	14.0	a
91	3.919, 4.328	55.0	64.5 (as)	15.0	b
90	4.328, 4.067	19.9	65.7 (as)	16.0	d
84	4.067	55.2	70.7 (q)	17.0	e
89	4.285	53.7	71.4 (q)	16.0	f
88	4.285, 3.885	37.3	64.8 (as)	14.0	c
87	3.885, 3.919	13.2	55.7 (as)	14.0	a
86	3.919, 4.329	54.9	64.5 (as)	15.0	b
85	4.329, 4.067	20.2	65.7 (as)	16.0	d
83	4.067	55.1	70.7 (q)	17.0	e

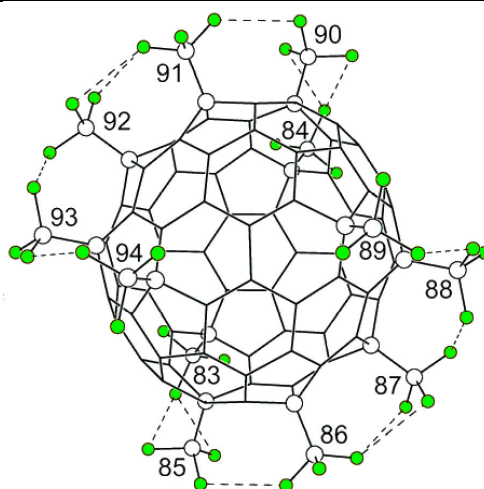


Table 5.7. C–C distances [Å], torsion C–F⋯C–C angles [°], $-\delta(^{19}\text{F})$, and $^7J_{\text{FF}}$ coupling constants for $\text{C}_s\text{-C}_{76}(\text{CF}_3)_{12}$ molecule. DFT-predicted structure of $\text{C}_s\text{-C}_{76}(\text{CF}_3)_{12}$ is shown below

CF_3	$\text{C}\cdots\text{C}$, Å	$\text{C-F}\cdots\text{C-C}$, deg	$-\delta(^{19}\text{F})$	$^7J_{\text{FF}}$, Hz
88	4.103	58.4	71.4 (q)	13.0
86	4.103, 4.103	0.0	55.9 (um)	–
87	4.103, 4.103	58.4	71.4	13.0
84	4.410, 4.046	57.5	66.8 (um)	
83	4.046, 4.042	0.2	55.8 (as)	13.0
82	4.042, 4.407	57.5	66.8 (um)	–
81	4.407, 4.046	57.3	66.8 (um)	–
80	4.046, 4.046	0.0	56.4 (as)	13.5
79	4.046, 4.407	57.4	66.8 (um)	–
78	4.407, 4.042	57.3	66.8 (um)	–
77	4.042, 4.046	0.1	55.8 (as)	13.0
85	4.046, 4.410	57.6	66.8 (um)	–

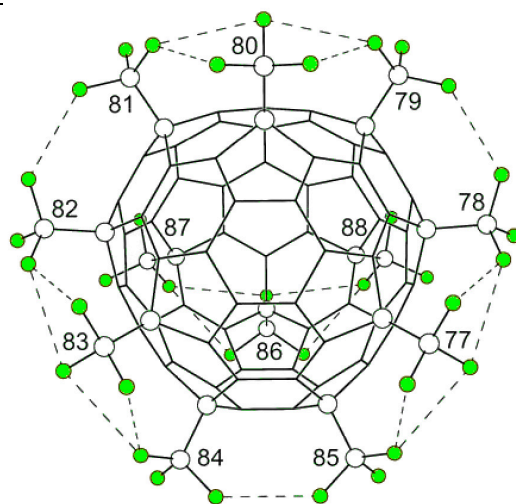
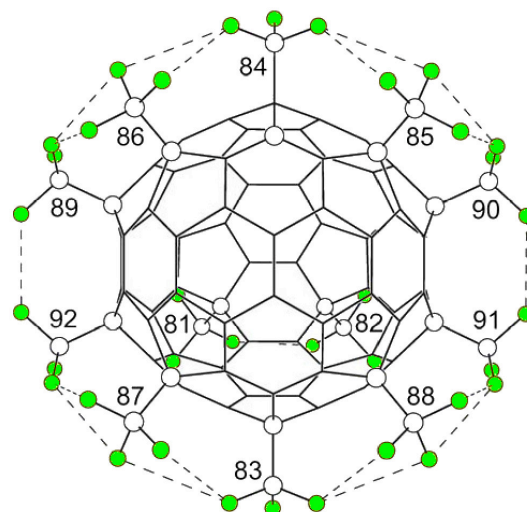


Table 5.8. C–C distances [$\text{\AA}$] and torsion C–F $\cdots$ C–C angles [$^\circ$] for C_s -C₈₀(CF₃)₁₂ molecule. DFT-predicted structure of C_s -C₈₀(CF₃)₁₂ is shown (right).

CF ₃	C–C, $\text{\AA}$	C–F $\cdots$ C–C, deg
81	4.232	57.8
83	4.232	58.9
89	4.417, 4.026	59.3
86	4.026, 4.145	4.0
84	4.145, 4.144	60.1
85	4.144, 4.021	3.9
90	4.021, 4.417	60.1
91	4.417, 4.021	59.4
88	4.021, 4.142	3.7
83	4.142, 4.142	60.1
87	4.142, 4.021	3.5
92	4.021, 4.417	59.4



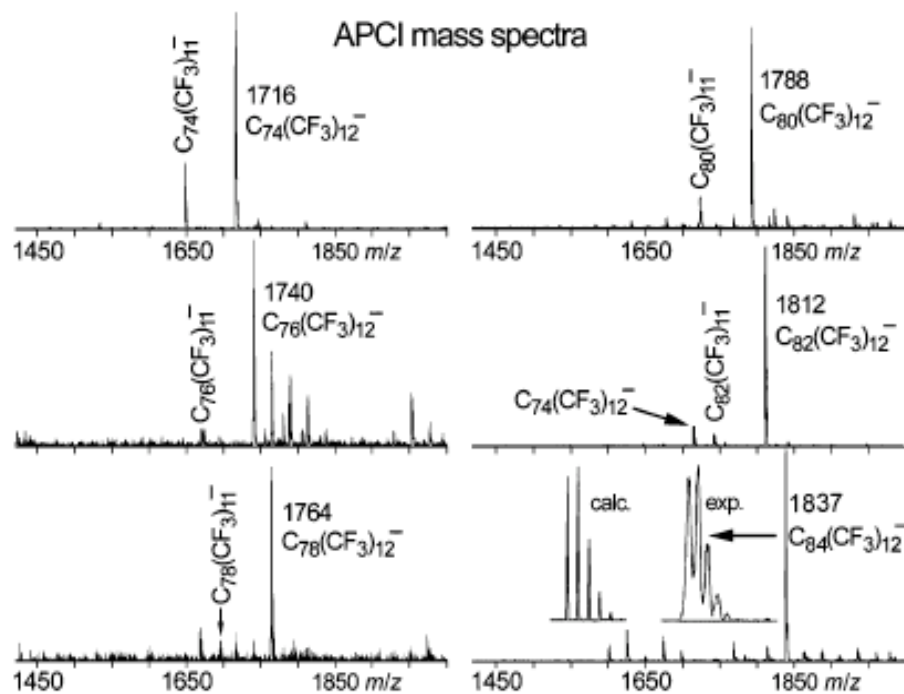


Figure 5.1. Atmospheric-pressure chemical-ionization mass spectra of C_2 - $C_{74}(\text{CF}_3)_{12}$, C_5 - $C_{76}(\text{CF}_3)_{12}$, C_1 - $C_{78}(\text{CF}_3)_{12}$, C_5 - $C_{80}(\text{CF}_3)_{12}$, C_2 - $C_{82}(\text{CF}_3)_{12-2}$, and a mixture of isomers of $C_{84}(\text{CF}_3)_{12}$. The mass spectra of C_2 - $C_{78}(\text{CF}_3)_{12}$ and C_2 - $C_{82}(\text{CF}_3)_{12-1}$ (not shown) were similar to those of C_1 - $C_{78}(\text{CF}_3)_{12}$ and C_2 - $C_{82}(\text{CF}_3)_{12-2}$, except that they exhibited lower levels of impurities.

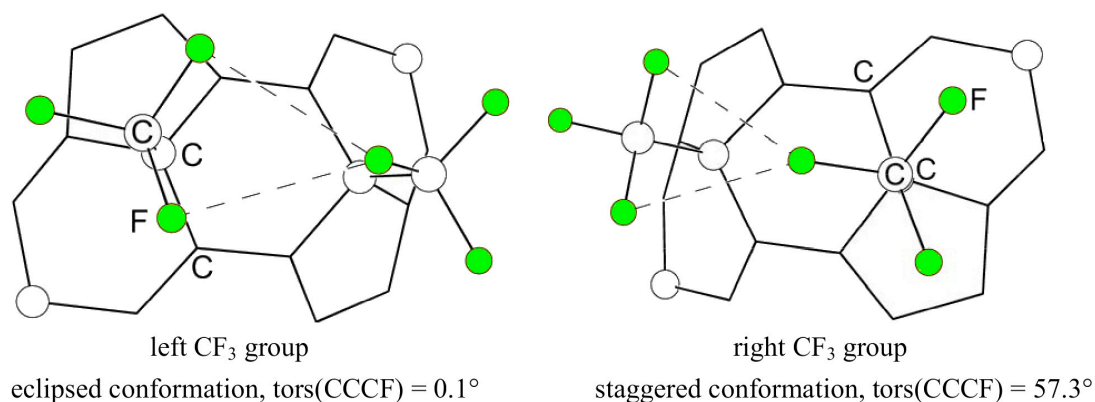


Figure 5.2. Two different conformations of CF₃ groups: eclipsed (left) are staggered (right) are shown.

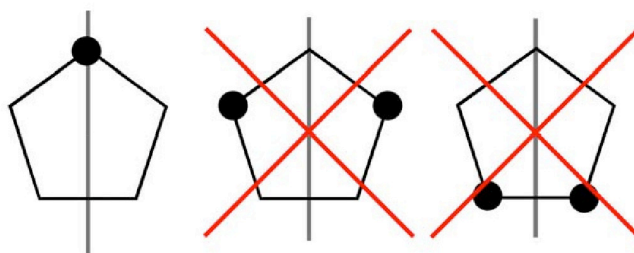


Figure 5.3. Three possible situations for attachment of substituents to fullerene pentagons that sit on a plane of symmetry. The symmetry plane is depicted as a thin vertical line. Only the situation on the left is possible for fullerene(CF₃)_n derivatives if two CF₃ groups are not on adjacent cage carbon atoms and if two CF₃ groups do not share the same pentagon.

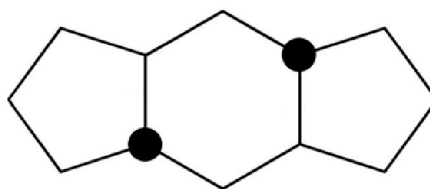


Figure 5.4. The shown situation for a pair of substituents to share a fullerene hexagon through which passes a perpendicular C₂ symmetry axis is only possible for fullerene(X)_n derivatives if the substituents are not attached to triple-hexagon junctions.

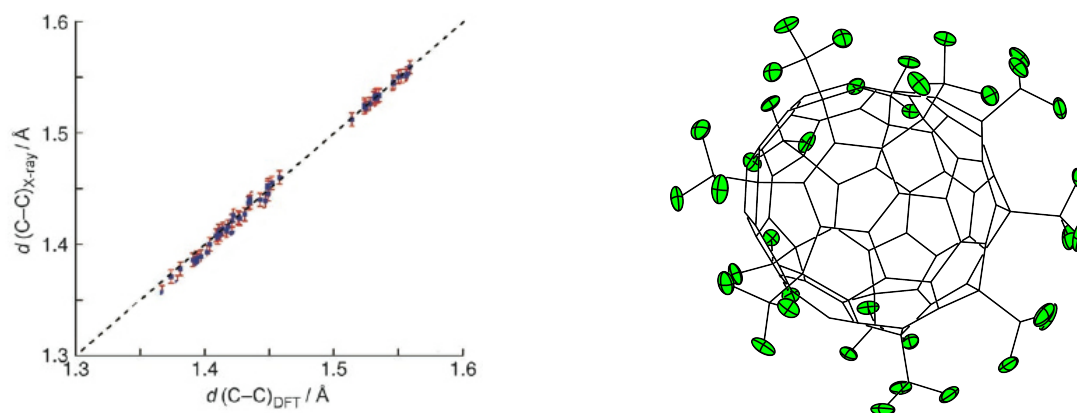


Figure 5.5. X-ray crystal structure (50% probability ellipsoids) of $\text{C}_2\text{-C}_{74}(\text{CF}_3)_{12}$ (right). The plot shows the correlation between the cage C–C distances in the X-ray structure vs. those in the DFT structure ($\pm 3\sigma$ error bars) (left).

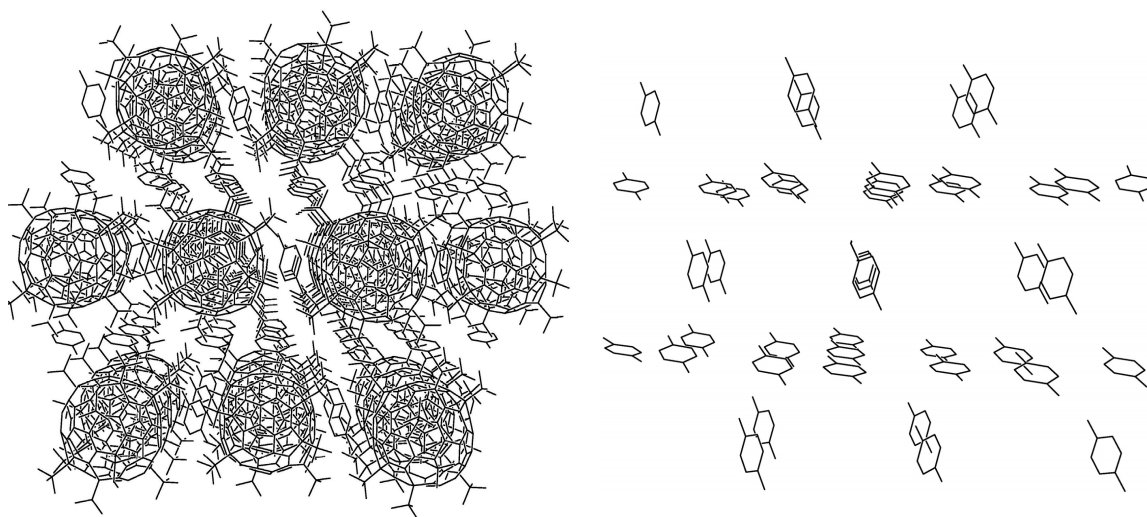


Figure 5.6. Packing of $\text{C}_2\text{-C}_{74}(\text{CF}_3)_{12}$ and p -xylene molecules (left), and packing plot showing just the p -xylene molecules (right).

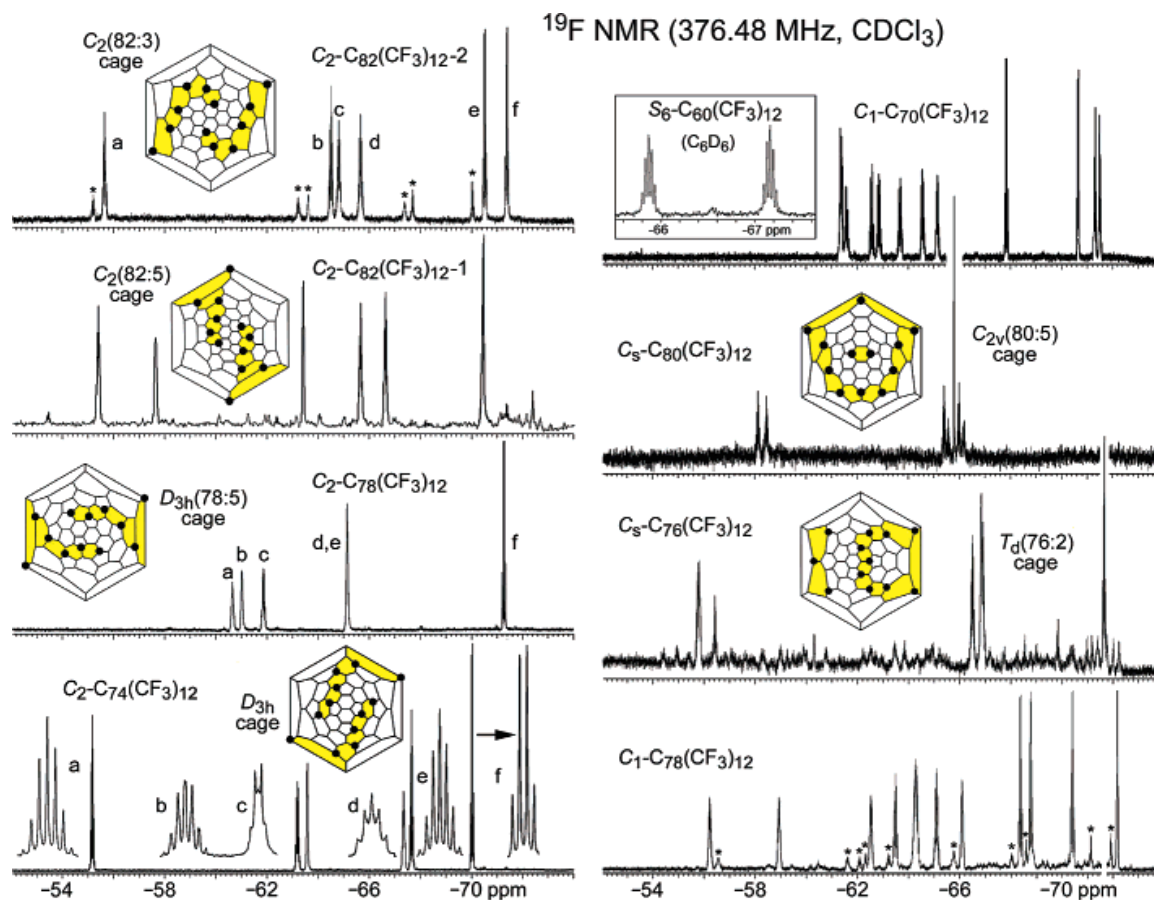


Figure 5.7. Fluorine-19 NMR spectra (chloroform- d), 25 °C, C_6F_6 internal standard (δ -164.9) of (left: bottom to top) $\text{C}_2\text{-C}_{74}(\text{CF}_3)_{12}$, $\text{C}_2\text{-C}_{78}(\text{CF}_3)_{12}$, $\text{C}_2\text{-C}_{82}(\text{CF}_3)_{12-1}$, $\text{C}_2\text{-C}_{82}(\text{CF}_3)_{12-2}$, and (right: bottom to top) $\text{C}_1\text{-C}_{78}(\text{CF}_3)_{12}$, $\text{C}_s\text{-C}_{76}(\text{CF}_3)_{12}$, $\text{C}_s\text{-C}_{80}(\text{CF}_3)_{12}$, $\text{C}_1\text{-C}_{70}(\text{CF}_3)_{12}$, and $\text{S}_6\text{-C}_{60}(\text{CF}_3)_{12}$ (benzene- d^6). The structures of these compounds are shown on Schlegel diagrams. The multiplets marked with asterisks in the spectrum of $\text{C}_2\text{-C}_{82}(\text{CF}_3)_{12-2}$ are due to a small amount of $\text{C}_2\text{-C}_{74}(\text{CF}_3)_{12}$ in the sample. The multiplets marked with asterisks in the spectrum of $\text{C}_1\text{-C}_{78}(\text{CF}_3)_{12}$ may be due to another isomer of $\text{C}_1\text{-C}_{78}(\text{CF}_3)_{12}$.

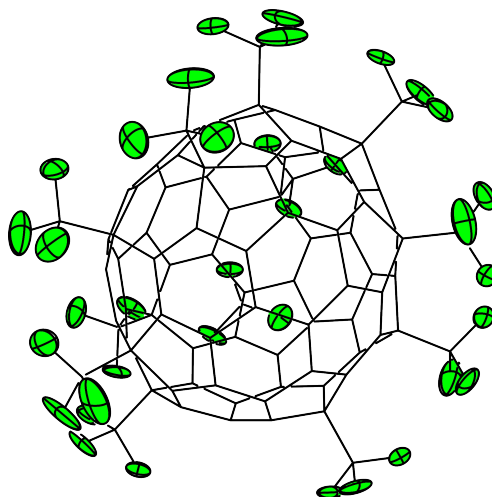


Figure 5.8. X-ray crystal structure (50% probability ellipsoids) of C₂-C₇₈(CF₃)₁₂.

**CHAPTER 6. NITROGEN-ATOM-DIRECTED PERFLUOROALKYLATION OF
9,9'-BI-1-AZA(C₆₀-I_h)[5,6]FULLERENE. SYNTHESIS, CHARACTERIZATION,
AND DFT STUDY OF C₅₉N(CF₃)_n ISOMERS (*n* = 5, 7, 9, 11), INCLUDING THE
X-RAY STRUCTURE OF 6,9,12,15,18-C₅₉N(CF₃)₅**

Introduction

Preparative syntheses of C₅₉N derivatives and (C₅₉N)₂ demonstrated that chemical modification of the all-carbon cage in fullerenes may result in the substitution of a cage-carbon atom(s) with a different element, e.g., a nitrogen atom.^{146,147} At present, heterofullerenes represent a relatively small, and yet fascinating to many, group of compounds. Only azafullerenes of C₆₀ and C₇₀ compounds are made in bulk quantities, which resulted in the development of their chemistry, as well as extensive spectroscopic studies. For the most recent and comprehensive review see reference¹⁴⁸.

There are some challenges that chemists have to deal with while studying these compounds. First, their availability is much more limited than that of parent fullerenes, since an elaborate multi-stage synthesis is required, and the yields in the known synthetic methods are not very high (e.g., 26%).^{146,147} The other problem in the studies of azafullerene derivatives is the dramatic increase in the number of possible isomers, even in the case of bisadducts, as compared to C₆₀. This complicates isolation and characterization of functionalized C₅₉N compounds significantly.

In several cases, however, a limited number of the derivatives with structures analogous to those of C_{60} was observed. For example, highly regioselective synthesis of pentamalonates of monoarylated $C_{59}N$ was achieved.¹⁴⁸ In the high-temperature fluorination of $(C_{59}N)_2$ with metal fluorides, a limited number of polyadducts with specific odd numbers of substituents ($C_{59}NF_{17}$, $C_{59}NF_{33}$, and $C_{59}NF_{35}$) were obtained.¹⁴⁹ These three compounds were characterized by ^{19}F NMR and mass spectrometry, and the conjectured structures were believed to be analogous to their C_{60} counterparts.¹⁴⁹ ICl-chlorination of the monophenyl derivative of $C_{59}N$ yielded a product, $C_{59}NCl_4Ar$,¹⁵⁰ in which substituents were arranged in a pattern known as a skew pentagonal pyramidal structure (SPP), which was earlier reported for numerous $C_{60}X_6$ compounds ($X = Br, Cl, CH_3, CF_3, Ph$).^{65,151-159} These few successful examples notwithstanding, the problems outlined above remain, and further studies of the chemistry of azafullerenes will have to address the low availability of the azafullerene substrates and enormously rich isomerism possibilities.

In the past few years, we developed methods for the high-yield, high conversion synthesis, separation and isolation of perfluoroalkylated fullerenes.^{31,32} Structures, spectroscopic and electrochemical properties have been studied in detail for C_{60} , C_{70} , some higher fullerenes, and endometallofullerenes.^{31-33,39} This type of exohedral derivatization of carbon cages was proven to have advantages as compared to other functionalizations: (i) fullerene(R_F)_n are stable thermally³⁸ and the use of high temperatures for their synthesis allows formation of a very limited number of isomers, which represent (in the majority of the cases) the thermodynamically most stable isomers (within DFT energies of 20–30 kJ mol⁻¹);³² (ii) compositions of fullerene(R_F)_n products

can be partially controlled by varying reaction conditions, which simplifies isolation of pure compounds.^{31,32,38,160} (iii) attachment of the electron-withdrawing-fluorine-containing groups improves the electron-accepting properties of the fullerenes,³² thereby facilitating negative-ion MS analysis; and (iv) this derivatization allows for the use of sensitive ^{19}F NMR spectroscopy for analysis and structural elucidation. The propensity of fullerene(R_F) $_n$ compounds to form well-ordered single crystals simplified significantly structural elucidations, and at present over 100 X-ray structures for various fullerene(R_F) $_n$ have been determined.^{33,38,39,41,45,47,48,51,52,81,133,161} Even in cases when X-ray data were not available, the combination of the detailed analysis of ^{19}F NMR data, UV-vis and Raman spectroscopy, and DFT calculations could be used to find the most probable structures for a large number of compounds.

The fundamental goal of the present work is to probe how the presence of heteroatom affects reactivity of the heterofullerene cage, and in particular, isomerism in its polyadducts.

In this study, for the first time the preparation, isolation and characterization of a series of new perfluoroalkyl derivatives of aza[60]fullerene will be discussed. Presence of the nitrogen atom in the cage creates an unusual (for fullerene chemistry) situation: firstly, the symmetry of the cage is reduced, increasing dramatically the possible number of isomers as compared to its I_h - C_{60} counterpart; secondly, since $(\text{C}_{59}\text{N})_2$ has a very low homolytic bond cleavage energy, the species which participates in chemical reactions is a radical (as a result of the unpaired electron from the N atom), and therefore products of multiple additions have an odd number of substituents. The first X-ray structure of an exohedral derivative of azafullerene, $\text{C}_{59}\text{N}(\text{CF}_3)_5$, was obtained.

6.1. Experimental Section

6.1.1. Reagents and Solvents. The reagents and solvents CF_3I (Apollo Scientific), hexafluorobenzene (Sigma-Aldrich), 1,2-dichlorobenzene (Sigma-Aldrich, 99%, anhydrous), copper powder (Sigma-Aldrich, ~ 40 mesh, 99.5%), chloroform-*d* and benzene-*d*⁶ (Cambridge Isotopes), and heptane and toluene for HPLC purification (Sigma-Aldrich) were used as received. $(\text{C}_{59}\text{N})_2$ was synthesized as described in reference¹⁴⁶.

6.1.2. Preparation and Isolation of $\text{C}_{59}\text{N}(\text{CF}_3)_n$ Compounds. The reaction of $(\text{C}_{59}\text{N})_2$ with CF_3I was carried out either in a hot flow tube³³ or in a sealed glass ampoule. In a typical flow-tube experiment, $(\text{C}_{59}\text{N})_2$ (15 mg, 0.01 mmol) was mixed with copper powder (500 mg, 7.87 mmol) and was placed in a quartz tube (0.7 cm I.D.) connected to a gas handling system at one end and a mineral-oil bubbler at the other end. The glass tube was placed in a 40-cm long furnace. The reactions of $(\text{C}_{59}\text{N})_2$ with CF_3I were carried out at 500, 520, and 530 °C for 1.5–3.5 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.] The orange volatile $\text{C}_{59}\text{N}(\text{CF}_3)_n$ products, which condensed in a narrow zone near the 25 °C end of the reaction tube, were collected by washing with solvent (hexanes) after I_2 was removed under vacuum. Under similar conditions, a control experiment involving a reaction of C_{60} (80 mg, 0.11 mmol) mixed with copper powder (290 mg, 4.57 mmol) with CF_3I was also performed at 500 °C for 3.5 h. The experiment in the glass sealed ampoule was carried out at 530 °C for 24 h, in which 10 mg (0.007 mmol) of $(\text{C}_{59}\text{N})_2$ and excess of CF_3I (0.5 mL) were used. The control reaction of C_{60} (10 mg, 0.01 mmol) with CF_3I (0.5 mL) in the sealed ampoule under the same reaction conditions was also

performed. Crude products obtained in the C_{60}/CF_3I and $(C_{59}N)_2/CF_3I$ reactions were analyzed by mass spectrometry, HPLC and ^{19}F NMR spectroscopy (Figures 6.1–6.9). Further isolation and purification of the azafullerene $(CF_3)_n$ was performed by the HPLC (high pressure liquid chromatography) method using a Cosmosil Buckyprep column (Nacalai Tesque Inc., 10 mm I.D. $\times$ 250 mm) at 300 nm UV detection. The HPLC processing involved several stages due to the complexity of the product mixture. First, isolation of four fractions in toluene (HPLC eluent) was done as shown in Figure 6.2. Fraction **IV** contained a single isomer of $C_{59}N(CF_3)_5$ as evidenced by NI-APCI mass spectrometry and ^{19}F NMR spectroscopy. It was purified to 98+% by eluting it again with toluene (retention time (r.t.) was 7.0 min at 5 mL min⁻¹ flow rate). Slow evaporation of the toluene solution of the purified sample led to the formation of red-orange crystals, one of which was used for the X-ray crystallographic study. Toluene fractions **II** and **III** contained several isomers of $C_{59}N(CF_3)_9$ and $C_{59}N(CF_3)_7$, respectively. One of the $C_{59}N(CF_3)_7$ isomers was obtained at 90+% purity using a mixture of 50:50 (v:v) toluene:heptane as eluent (14.6 min r. t. at 5 mL min⁻¹ flow rate). A single isomer of $C_{59}N(CF_3)_9$ was isolated from fraction 2 using the same eluent and purified to 98+% (10.0 min r.t. at 3 mL min⁻¹ flow rate). One pure isomer of $C_{59}N(CF_3)_{11}$ (90+% purity) was isolated from toluene fraction **I** via the subsequent HPLC separation in 10:90 (v:v) toluene:heptane as eluent (6.6 min r.t. at 5 mL min⁻¹ flow rate). In addition, several fractions were isolated from toluene fractions **II** and **III**, each containing a mixture of two isomers (or more) of the same composition, $C_{59}N(CF_3)_9$ (r.t. = 9.3 min, 50:50 (v:v) toluene:heptane, 5 mL min⁻¹ flow rate) and $C_{59}N(CF_3)_7$ (r.t. = 8.9 min, 50:50 (v:v) toluene:heptane, 3 mL min⁻¹ flow rate), respectively.

6.1.3. Reactions of $(C_{59}N)_2$ with Br_2 and $i-C_3F_7I$ and Isolation of

$C_{59}N(i-C_3F_7)_3$. In a bromination experiment, 10 mg (0.007 mmol) of $(C_{59}N)_2$ was placed in 1 mL of liquid Br_2 . Reaction was carried out at room temperature during 7 days with constant stirring. An excess of bromine was removed by evaporation. Thermogravimetric analysis (TGA) of $C_{59}NBr_n$ bromides was performed in the temperature range 25–500 °C at 3 °C min⁻¹ heating rate using a TGA-2950 instrument (Figure 6.12). For $C_{59}NBr_n/i-C_3F_7I$ reaction, 18 mg of the azafullerene bromide, 4 mg (13.5 mmol) of $i-C_3F_7I$, and 800 mg (12.6 mmol) of fine copper powder were used. For $(C_{59}N)_2/i-C_3F_7I$ reaction, 5 mg (0.003 mmol) of azafullerene $(C_{59}N)_2$, 4 mg (13.5 mmol) of $i-C_3F_7I$, and 800 mg (12.6 mmol) of fine copper powder were used. Perfluoroalkylation reactions were performed in a sealed glass ampoule at 180 °C for 22 h using 0.6 mL (5.3 mmol) of *o*-dichlorobenzene as a solvent medium. An HPLC separation of $C_{59}N(i-C_3F_7)_n$ compounds obtained from the $C_{59}NBr_n/i-C_3F_7I$ reaction was first performed in toluene at 5 mL min⁻¹ flow rate using a Cosmosil Buckyprep column (Nacalai Tesque, Inc.). Subsequent separation of the toluene fraction with retention time of 2.9–5.2 min was carried out using 30:70 (v:v) toluene/heptane mixture as an eluent at 5 mL min⁻¹ flow rate, and $C_{59}N(i-C_3F_7)_3$ (11.4 min retention time) was isolated. The final purification of $C_{59}N(i-C_3F_7)_3$ derivative was performed using 30:70 (v:v) toluene/heptane as an eluent (at 5 mL min⁻¹ flow rate, Figure 6.14).

6.1.4. X-ray Crystallography. X-ray diffraction data from a crystal of $C_{59}N(CF_3)_5$ (grown by slow evaporation from saturated toluene solution) were recorded on a Bruker Kappa APEX II CCD diffractometer employing Mo K α radiation (graphite monochromator). Selected details related to the crystallographic experiments are listed in

Table 6.2. Unit cell parameters were obtained from least-squares fits to the angular coordinates of all reflections, and intensities were integrated from a series of frames (ω and φ rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied by using SADABS.²⁰ The structure was solved by using direct methods and refined (on F^2 , using all data) by a full-matrix, weighted least squares process. All atoms were refined by using anisotropic atomic displacement parameters. Standard Bruker control and integration software (APEX II) was employed, and Bruker SHELXTL²¹ software was used for structure solution, refinement, and graphics.

6.1.5. Spectroscopic Measurements. Atmospheric-pressure chemical-ionization (APCI) mass spectra were recorded using a ThermQuest Finnigan LCQ-DUO spectrometer. ¹⁹F NMR spectra were recorded using a Bruker INOVA-400 spectrometer operating at 376.48 MHz (C₆F₆ was used as an internal standard ($\delta = -164.9$)).

6.1.6. Theoretical Calculations. Dr. A. A. Popov performed DFT calculations (Leibniz Institute for Solid State and Materials Research, Dresden, Germany) using PBE functional and a TZ2P-quality basis set implemented by the PRIRODA package.⁷³

6.2. Results and Discussion

6.2.1. Synthesis and Isolation of C₅₉N(CF₃)_{*n*} (*n* = 5, 7, 9, 11) Isomers. The first striking difference with trifluoromethylation of C₆₀ and other closed-shell fullerenes is that the reaction of dimer (C₅₉N)₂ leads to the formation of the derivatives with odd number of the substituents. Since (C₅₉N)₂ has a very low homolytic bond cleavage energy (75 kJ mol⁻¹),¹⁶² its heating produces radical species (due to unpaired electron from N atom), which then react with CF₃ radicals formed from CF₃I. No experimental evidence

is found for the presence of the trifluoromethylated dimer molecules in these reactions. In a continuous flow apparatus synthesis at 500 °C, the range of n values for $C_{59}N(CF_3)_n$ compounds was 5–15 according to NI-APCI MS data (Figure 6.1). The most abundant species have $n(CF_3) = 9$ and 11. Fragmentation due to the loss of a CF_3 group – a typical pathway in EI mass spectra of these compounds^{80,163} – is negligible in the APCI mass spectra for lower n (5–11) and increases gradually for species with higher n values. Figure 6.1 shows a NI-APCI mass spectrum of the product obtained in the sealed glass tube. It can be seen that the product distribution shifts towards higher $n(CF_3)$ values reaching $n(max) = 18$. Accordingly, the relative intensities of the high-mass ions with even n values are also much higher than those for lower n .

For comparison, Figure 6.1 also shows the NI-APCI mass spectrum and HPLC trace of the reaction product of C_{60} and CF_3I at 520 °C. First, note that the even- n ions are dominating (for $n < 14$), and second, a more narrow composition is observed for $C_{60}(CF_3)_n$ products than in the analogous reaction with $(C_{59}N)_2$.

The product of the 530 °C reaction between $(C_{59}N)_2$ and CF_3I in a continuous flow tube was first chromatographed with 100% toluene. Four main fractions were observed, as shown in Figure 6.2. Isolation and subsequent HPLC purification of these fractions gave the following compounds or mixtures of compounds: $C_{59}N(CF_3)_{11-15}$ (fraction I); $C_{59}N(CF_3)_9$ (fraction II); $C_{59}N(CF_3)_7$ (fraction III); and $C_{59}N(CF_3)_5$ (single isomer, fraction IV). Interestingly, a one-stage HPLC isolation with toluene as an eluent was sufficient for obtaining 98+% pure sample of a single isomer of $C_{59}N(CF_3)_5$ (see inset in Figure 6.2), whereas isolation of pure isomers for other compositions was much more difficult. In the end, isolation of only one isomer with satisfactory purity for each of

the following compositions: $C_{59}N(CF_3)_7$, $C_{59}N(CF_3)_9$, and two isomers of $C_{59}N(CF_3)_{11}$ was achieved. For comparison, using similar purification strategies multiple isomers of $C_{60}(CF_3)_{10}$ (6 isomers), $C_{60}(CF_3)_8$ (6 isomers), $C_{70}(CF_3)_{12}$ (4 isomers) $C_{70}(CF_3)_{10}$ (7 isomers), $C_{70}(CF_3)_8$ (2 isomers) were readily isolated. This unexpected difficulty in the HPLC processing of $C_{59}N(CF_3)_n$ may be due to much closer similarities in the structures, and consequent similar retention behavior on the HPLC column for these derivatives, than observed previously for other trifluoromethylated fullerenes. Figures 6.7–6.9 show the ^{19}F NMR spectra of the several samples (obtained from some of the most abundant fractions III and IV of the crude material) which contain either a mixture of two isomers of $C_{59}N(CF_3)_7$, a mixture of one isomer of $C_{59}N(CF_3)_7$ and one isomer of $C_{59}N(CF_3)_9$, or a mixture of two isomers of $C_{59}N(CF_3)_9$. Attempts to isolate pure compounds from these fractions using less polar eluents, which typically lead to 90+% pure $C_{60}(CF_3)_{2-10}$ derivatives, proved to be unsuccessful. Our further structural studies and theoretical calculations (see sections below) confirmed that for a given addition level the number of isomers with very similar structures and very close energies is much higher in the case of $C_{59}N$ than for C_{60} derivatives.

6.2.2. Reaction of $(C_{59}N)_2$ with $i-C_3F_7I$. Perfluoroalkylation of the $(C_{59}N)_2$ dimer using $i-C_3F_7I$ was performed in a sealed glass ampoule at 180 °C using *o*-dichlorobenzene as a reaction medium. The product was a brownish-orange material which is very soluble in organic solvents such as toluene or heptane. In Figure 6.10, the NI-APCI mass spectrum of the crude product from the $(C_{59}N)_2/i-C_3F_7I$ reaction shows the formation of $C_{59}N(i-C_3F_7)_n$ ($n = 7-11$) derivatives where $n = 8$ was the dominant species. In principle, the fullerene(R_F) $_n$ (where $R_F = C_2F_5$ or C_3F_7) with a high degree of

substitution are not possible to separate using existing HPLC methods (see Chapter 2 for more details). In addition, in the case of $C_{59}N(i-C_3F_7)_n$ derivatives the HPLC separation became more complicated due to the formation of a large number of isomers. It is known that the presence of bromine atoms on a fullerene cage can direct further addition of the fluorine atoms.¹⁶⁴ Figure 6.11 demonstrates that use of $C_{60}Br_{24}$ instead of pristine C_{60} leads to (i) a decrease in the number of fluorine atoms from the 42 observed in C_{60}/XeF_2 to 24 and (ii) formation of mainly $C_{60}F_{24}$ composition in contrast to a wide range of the products observed in the case of C_{60} fluorination. Thus, to decrease the number of $i-C_3F_7$ groups on the $C_{59}N$ cage it was decided to use azafullerene bromide as a starting material instead of the unmodified $(C_{59}N)_2$ dimer.

Bromination was performed in liquid bromine at room temperature over 7 days resulting in a bright orange product. The IR spectra of $C_{59}NBr_n$ derivatives reveals the appearance of new intense bands not observed for the pristine $(C_{59}N)_2$ compound¹⁶⁵ that were in the $700\text{--}900\text{ cm}^{-1}$ region resulting from C–Br bond formation in the IR spectra of known $C_{60}Br_n$ ($n = 6, 8, \text{ and } 24$) bromides^{151,166} (Table 6.1). In Figure 6.12, TGA curves of $C_{59}NBr_n$ and $C_{60}Br_{24}$ obtained under the same experimental conditions are shown. In contrast to $C_{60}Br_{24}$, azafullerene bromide decomposition does not occur as one sharp step, but instead is observed over a wide temperature range. The loss of mass in the $25\text{--}240\text{ }^\circ\text{C}$ temperature range corresponds to the loss of approximately 6–7 bromine atoms. Subsequent mass loss above $\sim 240\text{ }^\circ\text{C}$ corresponds to an unknown process. In addition, the IR spectrum of the solid residue which was left after the TGA experiment demonstrates the absence of the high intensifying bands that correspond to C–Br stretches as shown in Figure 6.13 and Table 6.1.

The $C_{59}NBr_n$ bromide obtained was used for further reaction with $i\text{-C}_3\text{F}_7\text{I}$ under the same experimental conditions as for the $(C_{59}N)_2/i\text{-C}_3\text{F}_7\text{I}$ reaction. Figure 6.10 shows the NI-APCI mass spectrum of the crude mixture obtained from $C_{59}NBr_n/i\text{-C}_3\text{F}_7\text{I}$ reaction. Formation of $C_{59}N(i\text{-C}_3\text{F}_7)_n$ compounds where n varied from 3 to 7 with $n = 3$ as a major component was indicated (Figure 6.10). Thus, a shift of the composition toward formation of $C_{59}N(i\text{-C}_3\text{F}_7)_n$ derivatives with a low degree of substitution was observed due to the presence of bromine atoms on the fullerene cage. Formation of $C_{59}N(i\text{-C}_3\text{F}_7)_nBr_m$ derivatives was not detected in the mass spectra probably because of an easy cleavage of C–Br bond which was also observed for C_{60} bromides.¹⁶⁴ Thus, use of the $C_{59}N$ bromide instead of naked C_{60} led to the formation of $C_{59}N(i\text{-C}_3\text{F}_7)_n$ derivatives with lower n values which can be separated using a standard HPLC procedure. The HPLC separation of the $C_{59}N(i\text{-C}_3\text{F}_7)_n$ compounds obtained from the reaction led to the isolation of $C_{59}N(i\text{-C}_3\text{F}_7)_3$ derivative, which was the main product in the reaction mixture. In Figure 6.14, the NI-APCI mass spectrum of pure $C_{59}N(i\text{-C}_3\text{F}_7)_3$ is shown. Based on ^{19}F NMR analysis, the molecular structure of $C_{59}N(i\text{-C}_3\text{F}_7)_3$ possesses a two-fold axis or a mirror plane. Further DFT calculations should be performed to predict the most stable structure of the $C_{59}N(i\text{-C}_3\text{F}_7)_3$ isomer formed.

In summary, heptaisoperfluoropropylation similar to trifluoromethylation leads to the formation of $C_{59}N$ derivatives with odd numbers of substituents. In addition, the use of the bulky $i\text{-C}_3\text{F}_7$ substituent instead of the CF_3 group resulted in a low degree of addition (11 $i\text{-C}_3\text{F}_7$ vs 19 CF_3) when excess perfluoroalkyl iodide was used. The use of brominated azafullerene as a starting material for the further $C_{59}NBr_n/i\text{-C}_3\text{F}_7\text{I}$ reaction led

to the formation of $C_{59}N$ derivatives with a lower number of *i*- C_3F_7 groups than in the case of pristine $(C_{59}N)_2$.

6.2.3. X-ray Structure of $C_{59}N(CF_3)_5$. The NI-APCI mass spectrum and ^{19}F NMR spectrum of the isolated $C_{59}N(CF_3)_5$ compound are shown in Figures 6.3 and 6.4. The addition pattern of $C_s-C_{59}N(CF_3)_5$ is related to the skew pentagonal pyramid (SPP) addition pattern^{118,167} exhibited by many $C_{60}X_6$ compounds including $C_s-C_{60}Cl_6$,^{59,154} $C_s-3C_{60}Br_6$,^{151,152} $C_s-C_{60}Me_6$,¹⁵⁹ and $C_s-C_{60}(CF_3)_6$,⁶⁵ as well as $C_s-C_{60}Me_5H$,¹⁶⁸ $C_{60}(p-t-BuC_6H_4)_5H$,¹⁶⁹ $C_{60}(m-MeC_6H_4)_5H$,¹⁶⁹ and several $C_{60}X_4O$ epoxides including $C_s-C_{60}(CF_3)_4O$,⁶⁵ $C_s-C_{60}(C_2F_5)_4O$,⁶⁵ and $C_s-C_{60}(t-BuO_2)_4O$.¹⁷⁰ It is also related to the addition pattern, $C_{60}(CF_3)_{12}$, which may be a mixture of up to three isomers (two C_2 isomers and one C_{2h} isomer), all isomers having two SPP groups of six CF_3 substituents on opposite poles of the C_{60} cage).^{32,43} In the case of the $C_{59}N(CF_3)_5$ structure, there are only five substituent and a nitrogen atom which plays the role of the “sixth substituent”. The nitrogen atom is at the apex of the {N1, C6, C9, C12, C15, C18} pyramid. The asymmetric unit contains only one molecule of $C_s-C_{59}N(CF_3)_5$, which is disordered by overlap of five molecules rotated by 72° relative to each other. As a result, the nitrogen atom is disordered among the five positions in the C1, C2, C3, C4, and C5 pentagon (Figures 6.15 and 6.16) with relative N/C occupancies of 0.16(2)/0.84(2), 0.18(2)/0.72(2), 0.31(2)/0.69(2), 0.15(2)/0.85(2), and 0.10(3)/0.90(3), respectively. The same type of disorder was observed in the $C_s-C_{60}Cl_6$ crystal structure⁵⁹ but in that case only two $C_s-C_{60}Cl_6$ molecules overlap, rotated by 72° relative to each other.

The $C_{59}N(CF_3)_5$ molecules are arranged in nearly close-packed layers parallel to the crystallographic *ab* plane, as shown in Figure 6.16. The $C_{59}N$ centroid-centroid

distances within the close-packed layer are $9.757 (\times 2)$, $10.008 (\times 2)$, and $10.248 (\times 2)$ Å. The centroids within a layer are co-planar to within 0.035 Å. The layers are stacked so that the $C_{59}N(CF_3)_5$ molecules are stacked *in register*, 10.179 Å apart, giving rise to the very unusual non-close-packed stacking arrangement AAA..., as shown in Figures 6.16 and 6.17. No structure composed of only one type of atom exhibits this structure, and it is only rarely found for binary interstitial compounds such as WC (close-packed layers of W atoms are stacked in register, AAA..., and the C atoms are in one-half of the trigonal-prismatic holes).¹⁷¹ Recently, two $C_{60}X_5H$ ($X = CH_3$, *p-t*-BuC₆H₄) structures were reported in which fullerene molecules are packed in columns. However, the packing in the $C_{60}(p\text{-}t\text{-BuC}_6\text{H}_4)_5H \cdot 3C_5H_{12}$ structure is distorted *ccp* (ABC...) with interlayer distances 13.593 and 13.753 Å (Figure 6.18). The packing in the $C_{60}X_5H \cdot C_5H_{12}$ structure can be considered to be a distorted *hcp* array (ABAB..., Figure 6.19) with a stacking period of the molecules within the zig-zag column of 10.153 Å.¹⁶⁸ The structures of $C_{60}Br_6$ ^{151,152} and $C_{60}Cl_6$ ^{59,154} exhibit two common¹⁷¹ close-packed geometries, *viz.* close-packed layers of fullerene molecules that are stacked ABAB... and ABAC..., respectively. For comparison, C_{60} crystallizes with a *ccp* structure.¹⁷²

Thus, the presence of the nitrogen atom in the $C_{59}N$ cage and therefore, an absence of the sixth substituent on a fullerene sphere in the SPP addition pattern leads to an unusual packing of $C_{59}N(CF_3)_5$ molecules with a rare AAA... arrangement.

6.2.4. Addition Patterns of $C_{59}N(CF_3)_7$, $C_{59}N(CF_3)_9$, and $C_{59}N(CF_3)_{11}$ Compounds. Fluorine-19 NMR and NI-APCI mass spectra of the isolated $C_{59}N(CF_3)_7$, $C_{59}N(CF_3)_9$, and $C_{59}N(CF_3)_{11}$ compounds are shown in Figures 6.4–6.6. The ¹⁹F NMR spectrum (in C_6D_6) of the $C_{59}N(CF_3)_7$ derivative consists of three multiplets, which

correspond to five CF₃ groups, and two quartets with the same coupling constant ($J_{\text{FF}} = 12.2$ Hz), which correspond to the two CF₃ groups on the same hexagon (Figure 6.4, Table 6.3). According to the AM1 calculations performed by Dr. A. A. Popov, the five possible structures for C₅₉N(CF₃)₇ shown in Figure 6.15 represent the most stable ones (within 1 kJ/mol) among the structures which are consistent with the experimental spectroscopic data. All of the calculated molecules have an SPP motif consisting of the five CF₃ groups which are located around the nitrogen atom, while two CF₃ groups are added separately in *para* positions with respect to each other on the same hexagon. Interestingly, in all of these structures the isolated pair of CF₃ groups is added to the most remote hexagons with respect to the SPP moiety.

The fluorine-19 NMR spectrum (in CDCl₃) of C₅₉N(CF₃)₉ consists of six multiplets and two quartets (Table 6.3). Figure 6.4 shows the correspondence between four multiplets (δ -68.0, -68.5, -69.1, and -71.5) and three multiplets (δ - 68.3, -69.0, and -72.2 ppm) in the ¹⁹F NMR spectra of the C₅₉N(CF₃)₉ and C₅₉N(CF₃)₅ compounds, respectively. In addition, the two multiplets (δ - 67.1 and -67.4) and two quartets (δ -70.3, -71.9 ppm) in the ¹⁹F NMR spectra of C₅₉N(CF₃)₉ can be considered as the slightly shifted ¹⁹F NMR spectrum of the *pmp*-C₆₀(CF₃)₄ derivative which also has two multiplets (δ -67.1 and -67.4 ppm) and two quartets (δ -69.9 and -71.5 ppm).⁸⁰ Thus, it is reasonable to suggest that the C₅₉N(CF₃)₉ compound has an addition pattern which includes the SPP motif plus a *pmp* ribbon. The theoretical calculations for the structures of C₅₉N(CF₃)₉ which are consistent with the ¹⁹F NMR data yielded three most stable structures with nearly the same relative energy (within 1 kJ mol⁻¹). The Schlegel diagrams for these structures are shown in Figure 6.15. The common fragments are the

presence of the SPP motif and a ribbon of CF₃ groups on the edge-sharing hexagons. Similarly to the structures of C₅₉N(CF₃)₇ discussed above, the *pmp* ribbon of four CF₃ groups is located on the side of the molecule which is the farthest from the SPP moiety.

The energies of the isomers of C₅₉N(CF₃)₁₁₋₁ that can be obtained from C₅₉N(CF₃)₅ by the addition of three pairs of CF₃ groups (in each pair CF₃ groups are in *para* position to each other) were computed at the AM1 level with subsequent DFT calculations for selected structures. The most stable structure that is consistent with the experimental ¹⁹F NMR spectrum in C₆D₆ (seven multiplets and two quartets with 12.2 and 16.8 Hz coupling constants, Table 6.3) is shown in Figure 6.15. It is surprising that the ribbons prefer to have one or even two common pentagons with SPP. Another surprising result is that the energy can vary by as much as 9 kJ mol⁻¹ range by varying of the nitrogen atom.

The fluorine-19 NMR spectrum (in CDCl₃) of C₅₉N(CF₃)₁₁₋₂ contains seven multiplets as shown in Figure 6.6. The correlation of three multiplets (δ -68.2, -68.7, and -72.5 ppm) with multiplets observed in the ¹⁹F NMR spectrum of the C₅₉N(CF₃)₅ derivative allows us to suggest that C₅₉N(CF₃)₁₁₋₂ should have a SPP fragment. The remaining four multiplets in the ¹⁹F NMR spectrum of C₅₉N(CF₃)₁₁₋₂ have very similar chemical shifts and intensities to the multiplets observed in the spectrum of C_s-C₆₀(CF₃)₆ (-59.9 (intensity (int.) 1), -61.4 (int. 1), -65.4 (int. 2), and -67.5 (int. 2), Figure 6.6).⁶⁵ Thus, the most probable addition pattern of C₅₉N(CF₃)₁₁₋₂ contains two SPP fragments. Further DFT calculations will be necessary to narrow down the number of the possible isomers and predict the most stable structure of C₅₉N(CF₃)₁₁₋₂.

Thus, according to the spectroscopic data and DFT calculations C₅₉N(CF₃)₇,

$C_{59}N(CF_3)_9$, and $C_{59}N(CF_3)_{11-1}$, $C_{59}N(CF_3)_{11-2}$ compounds have a common SPP motif with addition of two CF_3 groups, *pmp*-, and *pmpmp* ribbons and another SPP fragment, respectively.

6.2. Summary and Conclusions

In this work, trifluoromethylation of a total of less than 100 mg of the azafullerene $(C_{59}N)_2$ using CF_3I as a trifluoromethylating agent resulted in the preparation, isolation, spectroscopic, and structural characterization of $C_{59}N(CF_3)_n$ compounds with $n = 5, 7, 9$, and 11 . The isolated single regioisomer of $C_{59}N(CF_3)_5$, which was characterized by X-ray crystallography, became the first example of the structurally characterized exohedral derivative of azafullerene. Combination of ^{19}F NMR spectroscopy with DFT calculations allowed prediction of the most probable structure of $C_{59}N(CF_3)_7$, $C_{59}N(CF_3)_9$, and $C_{59}N(CF_3)_{11}$. Each of these has the *spp* addition pattern plus an isolated *para*- $C_6(CF_3)_2$ hexagon (for $n = 7$) or a ribbon of edge-sharing *para*- and *meta*- $C_6(CF_3)_2$ hexagons (for $n = 9$ and 11) or a second SPP pattern on the opposite pole of the molecule. These results clearly demonstrate a profound effect of the cage nitrogen atom on the addition patterns of azafullerene, which, with the exception of $C_{59}N(CF_3)_5$ and $C_{59}N(CF_3)_{11-1}$, do not have precedents in their C_{60} derivative counterparts.

The $(C_{59}N)_2/i-C_3F_7I$ reaction led to the synthesis of $C_{59}N(i-C_3F_7)_n$ (odd $n = 7-11$) compounds which can not be separated using the existing HPLC technique. In contrast, use of azafullerene bromide as a starting material led to the shift of the compositional distribution toward the derivatives with fewer substituents on a $C_{59}N$ cage. It allowed

isolation and characterization of the main $\text{C}_{59}\text{N}(i\text{-C}_3\text{F}_7)_3$ compound from the crude mixture.

Table 6.1. IR bands for C₆₀Br₆, C₆₀Br₈, C₆₀Br₂₄, C₅₉NBr_{*n*}, and (C₅₉N)₂ compounds.

	C ₆₀ Br ₆ ^a	C ₆₀ Br ₈ ^a	C ₆₀ Br ₂₄ ^a	C ₅₉ NBr _{<i>n</i>}	C ₅₉ NBr _{<i>n</i>} after TG	(C ₅₉ N) ₂ ^b
x	1473	1422	1400	1452	1421*	1574
	1421	1250	1244	1419	1363	1565
	1291	1182	1117	1335	1318	1460
	1265	1142	1050	1265	1239	1443
	1198	1086	946	1239	1185*	1423*
	1152	1047	912	1196	845	1416
	1085	963	849	1065,	820	1196
	1065	947	776	943	577*	1186*
	945	845	751	842	568*	1174
	850	820	720	826	529*	579
	829	766	606	815	524*	576*
	812	750	546	792		568*
	801	718		777		529*
	751	706		752		523*
	742	610		747		
	708	563		723		
	679	546		706		
	661	526		658		
	606	516		608		
	575			601		
	562			594		
	551			574		
	538			569		
	529			542		
	484			538		
	458			526		

^a IR spectra published in the paper^{151,166}^b IR spectra published in the paper¹⁶⁵* -common IR bands for C₅₉NBr_{*n*} and (C₅₉N)₂ compounds

Table 6.2. Crystal Data and Structure Refinement for C₅₉N(CF₃)₅.

molecular formula	C ₆₄ NF ₁₅
formula weight	1067.65
crystal system	orthorhombic
space group	<i>Pbca</i>
<i>Z</i>	2
color of crystal	red-orange
unit cell dimensions	
	$a = 20.0148(5) \text{ \AA}$
	$b = 17.3007(5) \text{ \AA}$
	$c = 20.3568(5) \text{ \AA}$
temperature, K	100(1)
final <i>R</i> indices	$R_1 = 0.0505$
[$I \geq 2\sigma(I)$]	$wR_2 = 0.1492$
goodness-of-fit on F_2	1.035

Table 6.3. Fluorine-19 NMR $-\delta$ (ppm) and J_{FF} (Hz) values for $\text{C}_{59}\text{N}(\text{CF}_3)_n$ compounds.

$\text{C}_{59}\text{N}(\text{CF}_3)_5$ (CDCl_3)									
$-\delta$	68.3	69.0	72.2						
	m	um	as						
$J_{\text{FF}}(\text{Hz})$	14, 15	12, –	16, 17						
$\text{C}_{59}\text{N}(\text{CF}_3)_7$ (CDCl_3)									
$-\delta$	67.8	68.0	68.2	68.8	71.75	72.02			
	um	um	um	um	q	as			
	–, –	–, –	–, –	–, –	12.2	16, 17			
$\text{C}_{59}\text{N}(\text{CF}_3)_9$ (CDCl_3)									
$-\delta$	67.1	67.4	68.0	68.5	69.1	70.3	71.5	71.9	
	as	as	m	m	m	q	m	q	
$J_{\text{FF}}(\text{Hz})$	12, 12	13, 13	16, 16	14, 15	15, 15	13.5	16, 16	11.4	
$\text{C}_{59}\text{N}(\text{CF}_3)_{11-1}$ (CDCl_3)									
$-\delta$	61.7	61.9	66.6	67.9	69.1	69.3	69.9	71.1	76.6
	um	um	um	um	um	um	um	um	um
$J_{\text{FF}}(\text{Hz})$	–, –	–, –	–, –	–, –	–, –	–, –	–, –	–, –	–, –
$\text{C}_{59}\text{N}(\text{CF}_3)_{11-2}$ (CDCl_3)									
$-\delta$	60.9	64.0	66.9	68.2	68.7	69.0	72.5		
	um	um	um	um	um	um	um		
$J_{\text{FF}}(\text{Hz})$	–, –	–, –	–, –	–, –	–, –	–, –	–, –		
$\text{C}_{59}\text{N}(\text{CF}_3)_7$ (C_6D_6)									
$-\delta$	66.7	67.2	67.4	67.6	70.5				
	um	um	um	q	q				
$J_{\text{FF}}(\text{Hz})$	–, –	–, –	–, –	12.2	12.2				
$\text{C}_{59}\text{N}(\text{CF}_3)_{11-1}$ (C_6D_6)									
$-\delta$	60.3	60.8	65.4	66.9	67.8	68.3	70.0	70.3	75.8
	um	um	as	as	um	um	q	q	um
$J_{\text{FF}}(\text{Hz})$	–, –	–, –	11, 11	11, 13	–, –	–, –	12.2	16.8	–, –

C₅₉N(CF₃)₁₁-2 (C₆D₆)						
$-\delta$	60.6	63.5	66.6	68.2	68.7	72.7
	um	um	um	um	um	um
	—,—	—,—	—,—	—,—	—,—	—,—

All data from this work; chloroform-*d* or benzene-*d*⁶ solutions at 24 (±1 °C; C₆F₆ internal standard (δ −164.9). Coupling constants are known to ±0.2 Hz for terminal CF₃ quartets. In those case, the J_{FF} values are ca. ±1 Hz. Resonances for other CF₃ groups are multiplets; J_{FF} values for the ones that are apparent (but not true) septets are ±1 Hz; J_{FF} values for multiplets deconvoluted by spectral simulation are ±1 Hz.

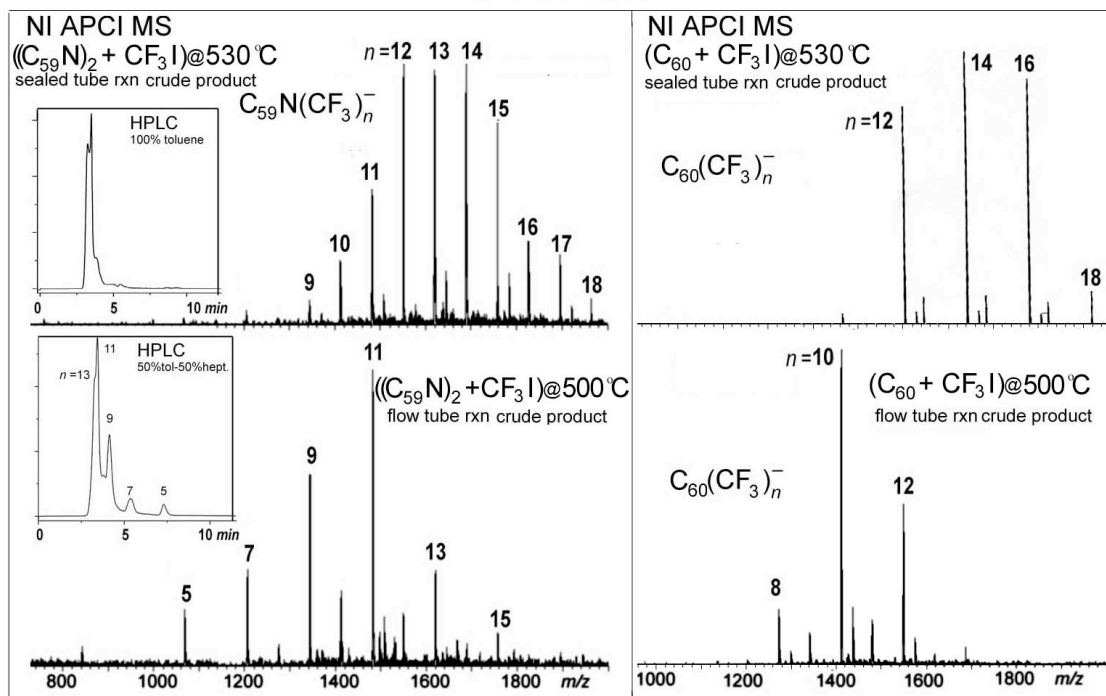


Figure 6.1. Negative-ion APCI mass spectra of the reaction $C_{59}N(CF_3)_n$ products obtained in a sealed glass ampoule at $530^\circ C$ for 24 h (top, left) and a hot flow tube at $500^\circ C$ for 3 h (bottom, left). The insets (left top and bottom) are the respective HPLC traces of the crude products, recorded with toluene as an eluent. Negative-ion APCI mass spectra of the crude products obtained in C_{60}/CF_3I reactions which were carried out in a glass sealed ampoule at $530^\circ C$ for 24 h (top, right) and in a hot flow tube at $500^\circ C$ for 3 h (bottom, right).

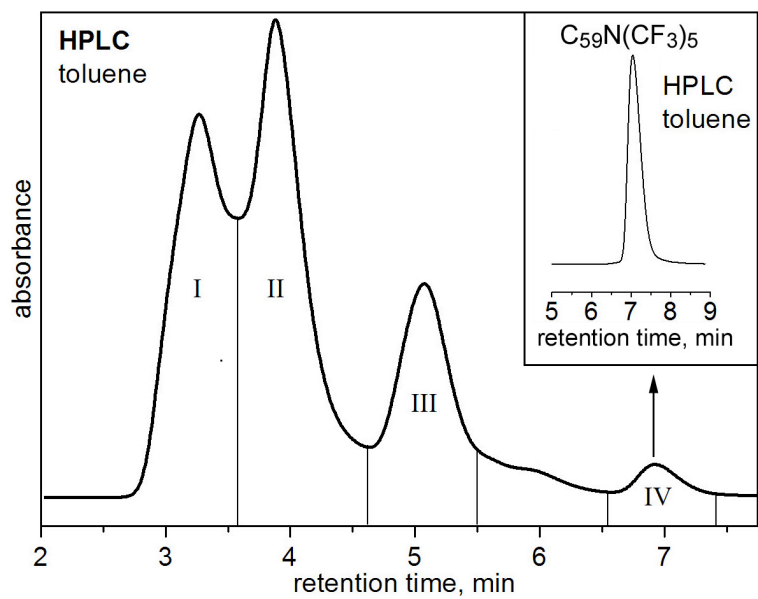


Figure 6.2. HPLC trace of the crude product obtained in the flow tube reaction of $(C_{59}N)_2$ with CF_3I at 530 °C for 3 h, toluene was used as an eluent. The inset shows the HPLC trace of a single $C_{59}N(CF_3)_5$ isomer after one-stage HPLC processing with toluene as eluent.

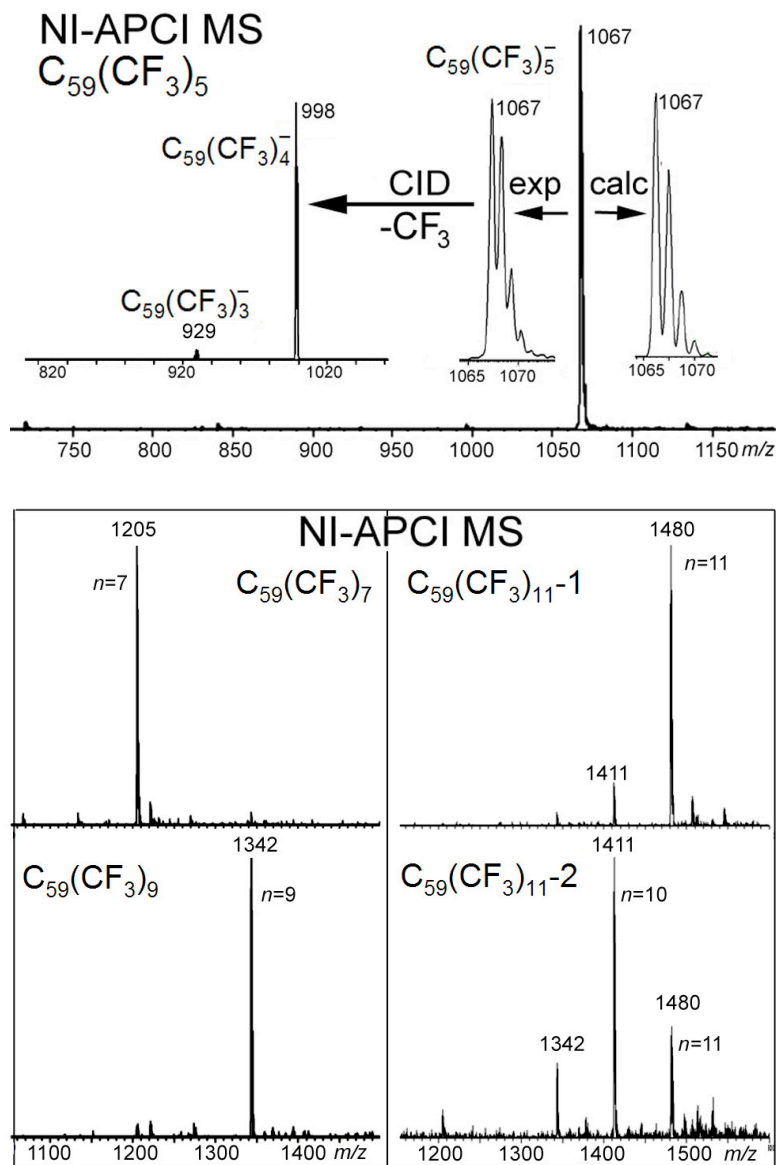


Figure 6.3. Top: Negative-ion APCI mass spectrum of the purified fraction of a single isomer of $C_{59}N(CF_3)_5$. Inset on the left shows a CID spectrum of an ion with m/z 1067, insets on the right show experimental and calculated isotope distributions for $C_{59}N(CF_3)_5$. Bottom: Negative-ion APCI mass spectra of the purified fractions of single isomers of $C_{59}N(CF_3)_7$, $C_{59}N(CF_3)_9$ and two isomers of $C_{59}N(CF_3)_{11}$. All spectra were recorded under identical conditions and using identical instrument parameters.

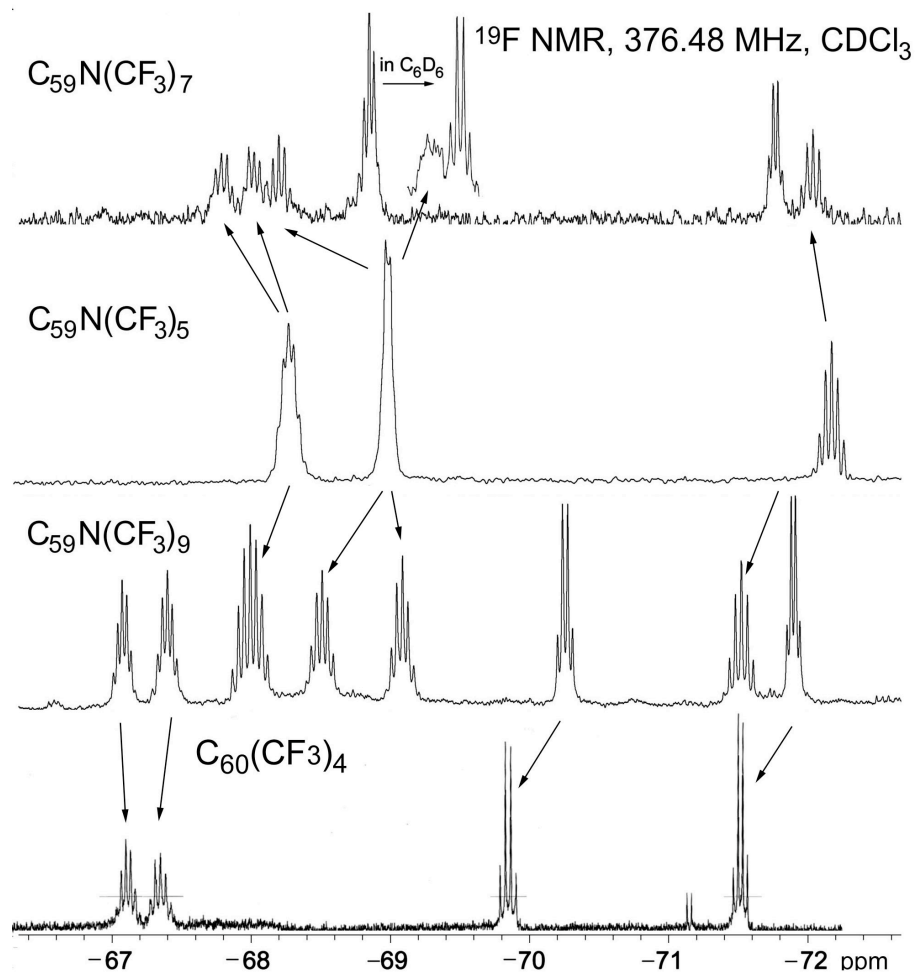


Figure 6.4. Fluorine-19 NMR spectra (from top to bottom) of $\text{C}_{59}\text{N}(\text{CF}_3)_7$, $\text{C}_{59}\text{N}(\text{CF}_3)_5$, $\text{C}_{59}\text{N}(\text{CF}_3)_9$, and $\text{C}_{60}(\text{CF}_3)_4$ (376.5 MHz; 20 °C; CDCl_3 ; C_6F_6 internal standard, δ -164.9). Inset in top spectrum shows a fragment of the spectrum recorded in C_6D_6 as a solvent.

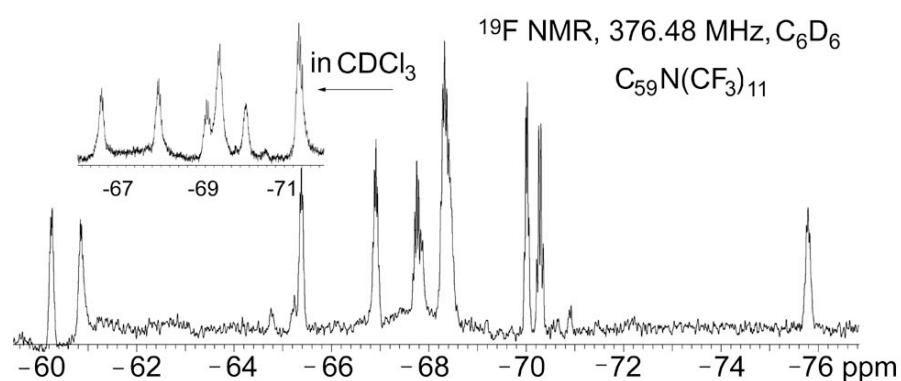


Figure 6.5. Fluorine-19 NMR spectrum of $\text{C}_{59}\text{N}(\text{CF}_3)_{11}\text{-1}$. Inset shows a fragment of the spectrum between δ -66.5 and -71.5 recorded in CDCl_3 (376.5 MHz; 20 °C; C_6D_6 ; C_6F_6 internal standard, δ -164.9)

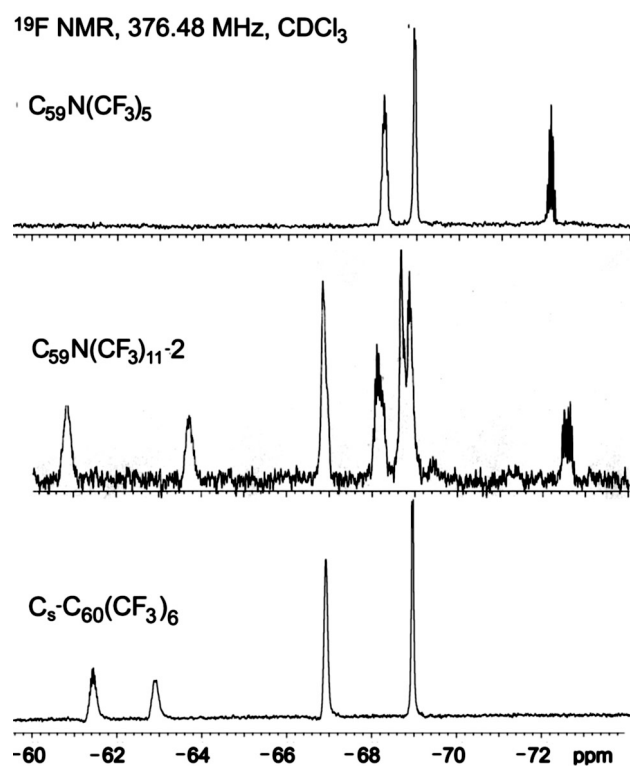


Figure 6.6. Fluorine-19 NMR spectra (from top to bottom) of $\text{C}_{59}\text{N}(\text{CF}_3)_5$, $\text{C}_{59}\text{N}(\text{CF}_3)_{11}\text{-2}$, and $\text{C}_s\text{-C}_{60}(\text{CF}_3)_6$ (376.5 MHz; 20 °C; CDCl_3 ; C_6F_6 internal standard, δ -164.9).

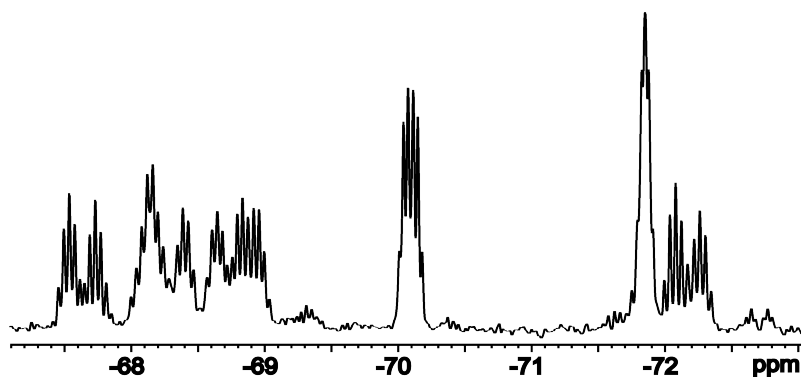


Figure 6.7. Fluorine-19 NMR spectrum of a mixture of two $C_{59}N(CF_3)_7$ (r.t. = 9.3 min, 50:50 (v:v) toluene:heptane, 5 mL min^{-1}) isomers (376.5 MHz; $20\text{ }^\circ\text{C}$; chloroform-*d*; C_6F_6 internal standard, $\delta -164.9$).

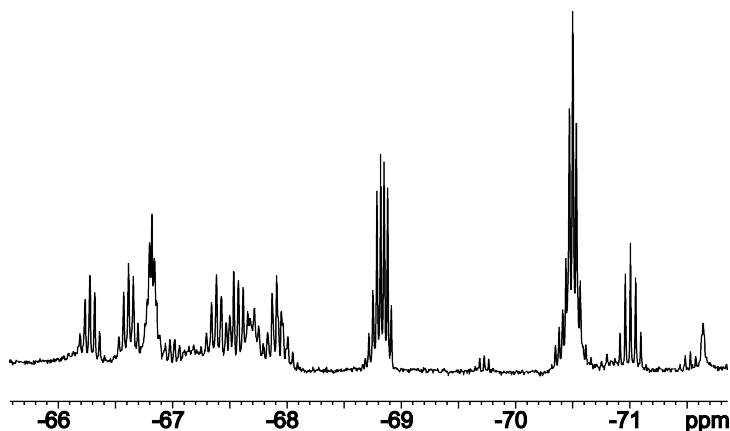


Figure 6.8. Fluorine-19 NMR spectrum of a mixture of $C_{59}N(CF_3)_7$ and $C_{59}N(CF_3)_9$ (r.t. = 10.2 min, 50:50 (v:v) toluene:heptane, 3 mL min^{-1}) isomers (376.5 MHz; $20\text{ }^\circ\text{C}$; chloroform-*d*; C_6F_6 internal standard, $\delta -164.9$).

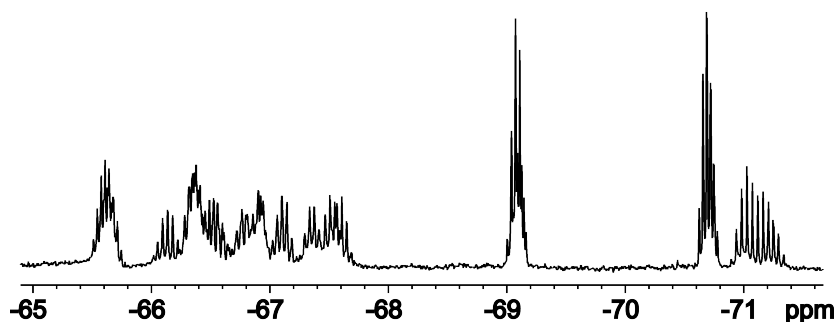


Figure 6.9. Fluorine-19 NMR spectrum of a mixture of two $C_{59}N(CF_3)_9$ (r.t. = 8.9 min, 50:50 (v:v) toluene:heptane, 3 mL min^{-1}) isomers (376.5 MHz; $20\text{ }^\circ\text{C}$; chloroform-*d*; C_6F_6 internal standard, $\delta -164.9$).

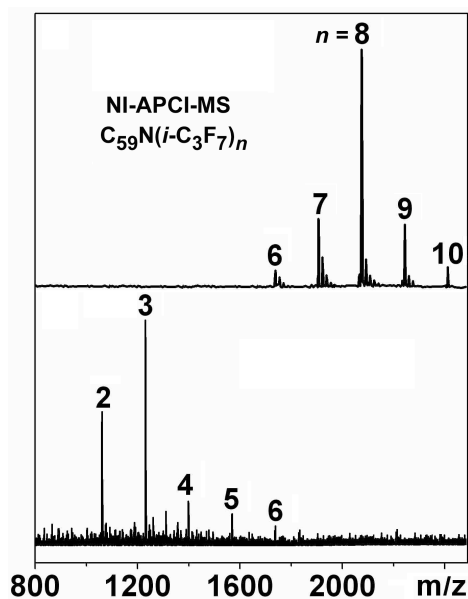


Figure 6.10. NI-APCI mass spectra of the crude product obtained in $(C_{59}N)_2/i-C_3F_7I$ (top) and $C_{59}NBr_n/i-C_3F_7I$ (bottom) reactions

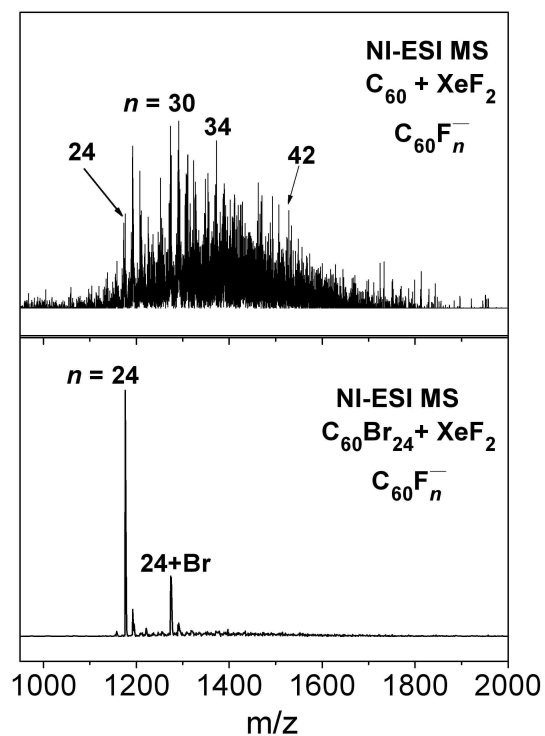


Figure 6.11. NI-ESI mass spectra of the product obtained in $C_{60}Br_{24}/XeF_2$ and C_{60}/XeF_2 reactions.¹⁶⁴

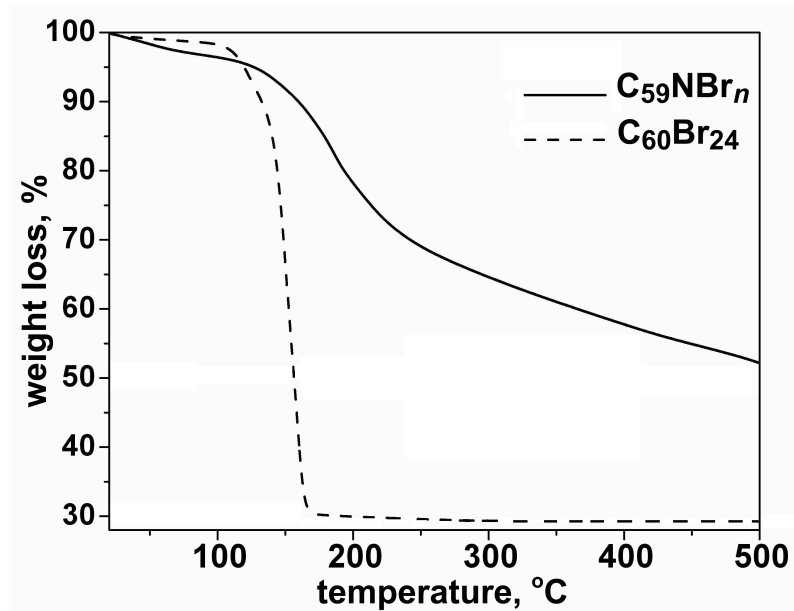


Figure 6.12. TGA analysis of $C_{59}NBr_n$ and $C_{60}Br_{24}$ bromides ($3\text{ }^{\circ}\text{C min}^{-1}$ heating rate).

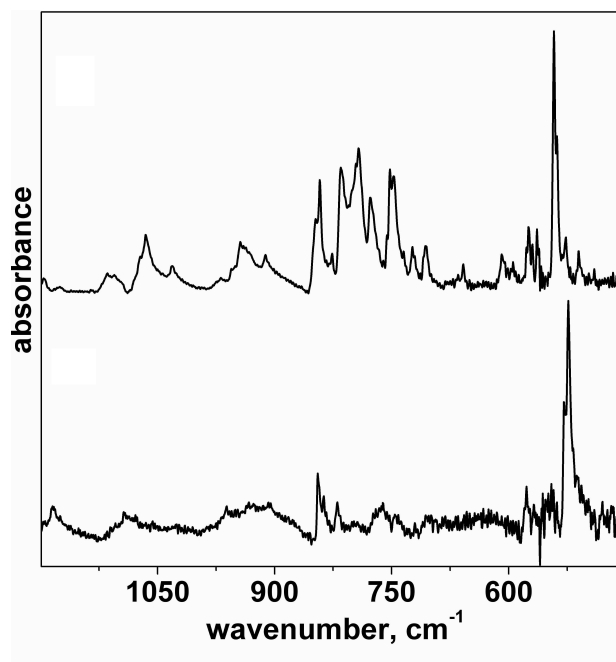


Figure 6.13. (top) IR spectrum of $C_{59}NBr_n$ bromides; (bottom) IR spectrum of $C_{59}NBr_n$ sample after TGA.

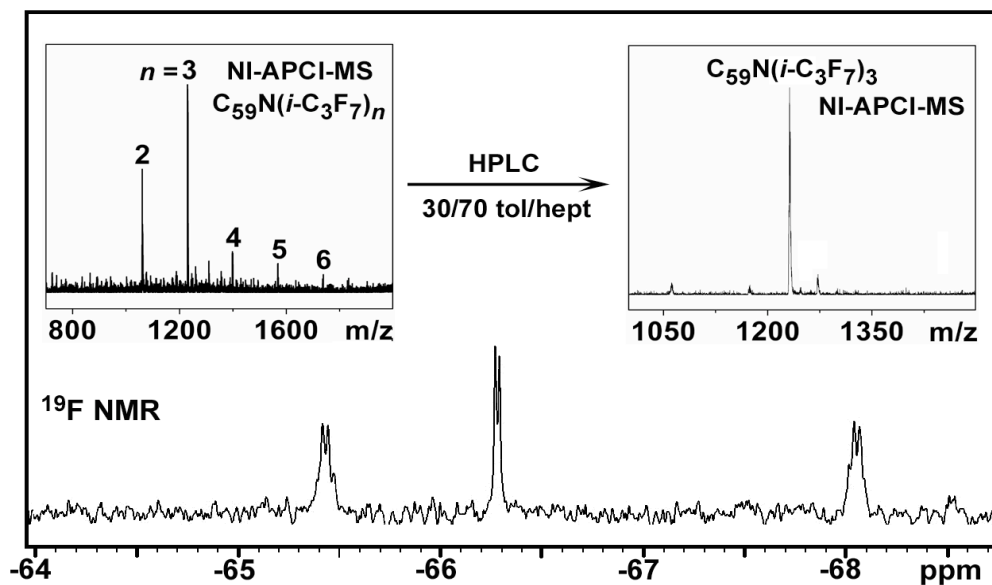


Figure 6.14. Fluorine-19 NMR and NI-APCI mass spectra (right insert) of $C_{59}N(i-C_3F_7)_3$ compound which was isolated from a crude $C_{59}N(i-C_3F_7)_n$ (odd $n = 1-7$) mixture (left insert) and purified using 30:70 (v:v) toluene/heptane mixture as an eluent.

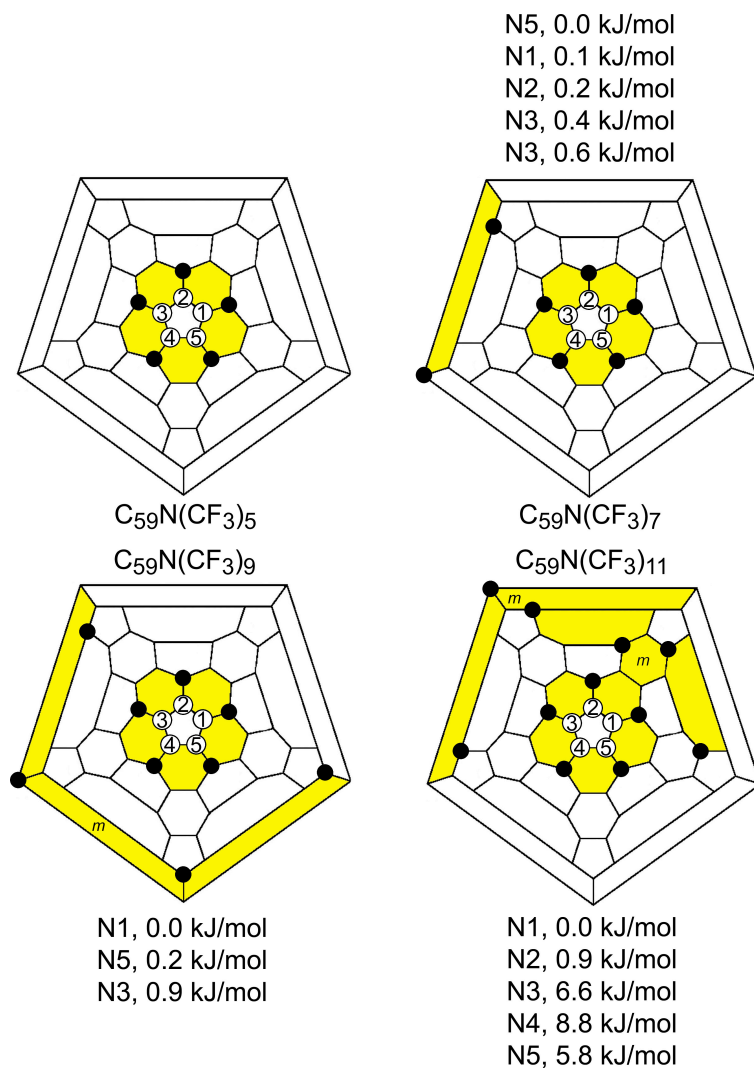


Figure 6.15. The Schlegel diagram of the most probable isomers of $C_{59}N(CF_3)_5$, $C_{59}N(CF_3)_7$, $C_{59}N(CF_3)_9$ and $C_{59}N(CF_3)_{11-1}$. The number N1 means that nitrogen atom is located on position 1 in the central pentagon.

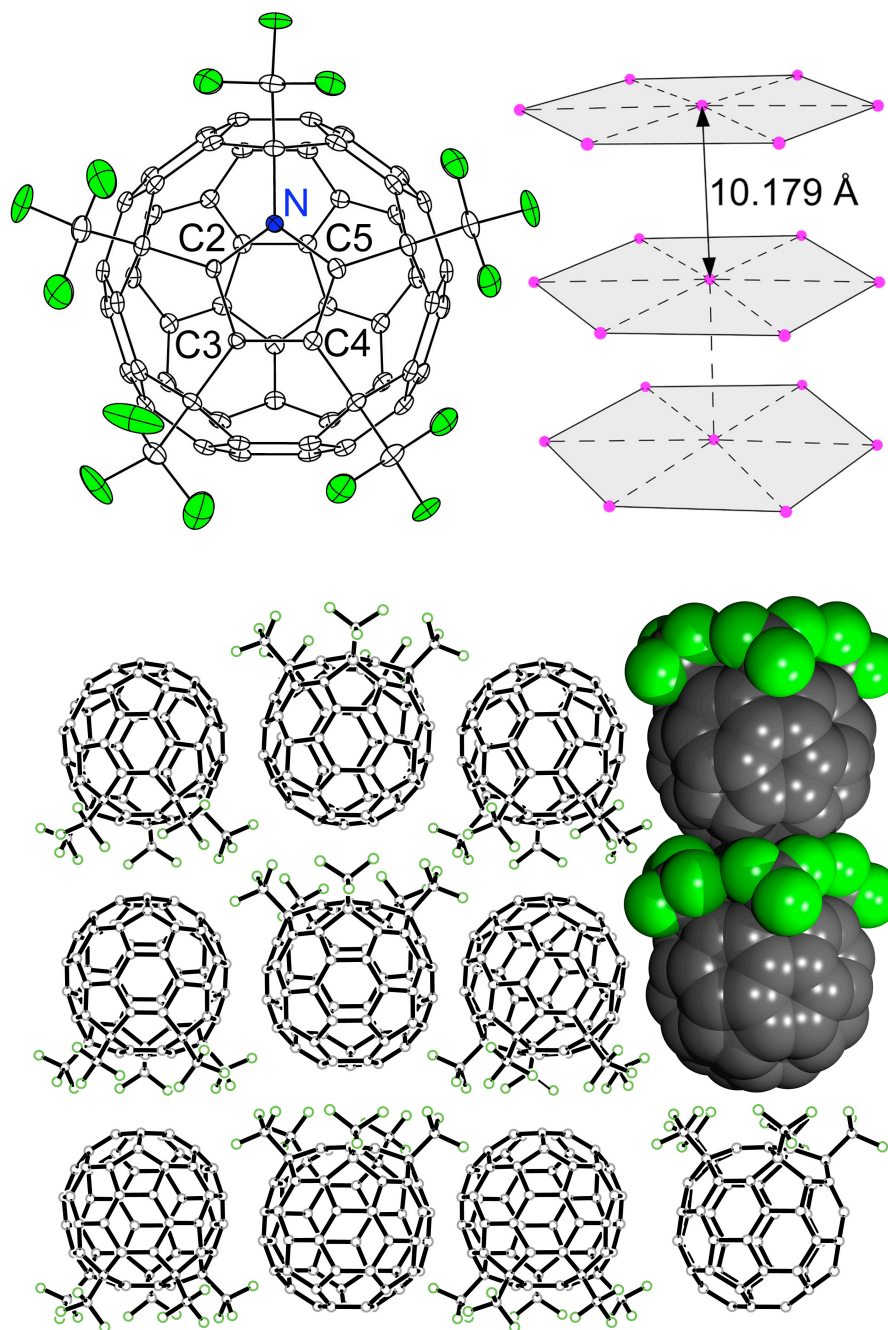


Figure 6.16. X-ray structure of $C_{59}N(CF_3)_5$ (50% probability ellipsoids). In the crystal $C_{59}N(CF_3)_5$ molecules form columns with head-to-tail orientation. The layers of the $C_{59}N(CF_3)_5$ molecules are stacked in AAA sequence and form primitive hexagonal arrays with the interlayer distance 10.179 Å. Pink dots are centroids of azafullerene molecules.

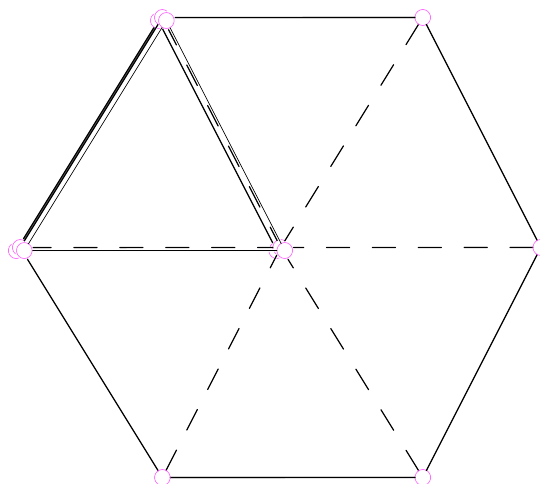


Figure 6.17. Molecular packing in $C_{59}N(CF_3)_5$ crystal structure. The pink circles are $C_{59}N$ centroids. One close-packed layer, three centroids above and three below are shown.

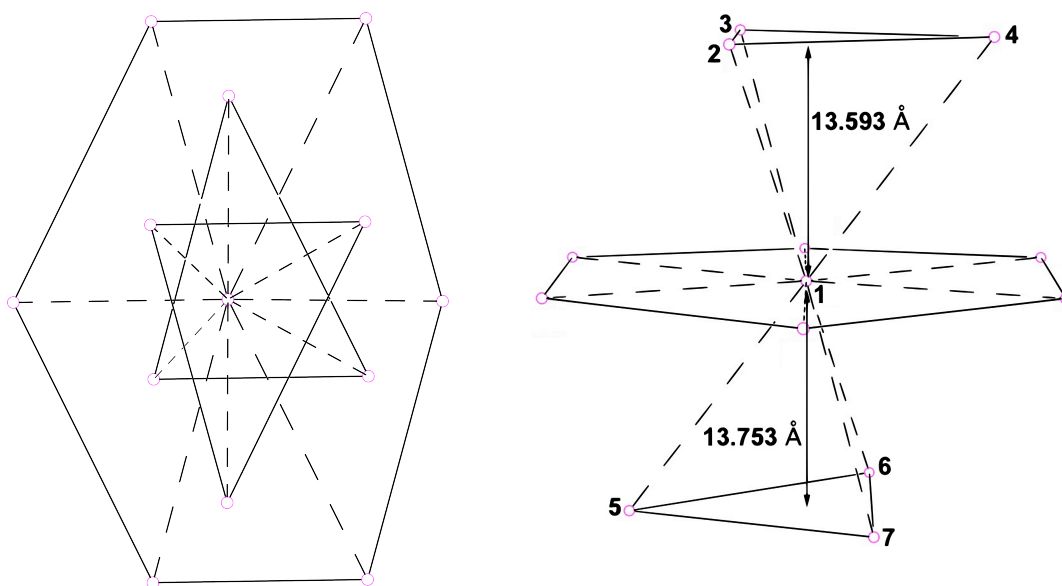


Figure 6.18. (left) Distorted cubic close packing of $C_{60}(p-t-BuC_6H_4)_5H$ molecules in $C_{60}(p-t-BuC_6H_4)_5H \cdot 3C_5H_{12}$ structure.¹⁶⁹ The pink circles are C_{60} centroids. (right) The distances between **1** centroid and centroid, which are made of **2**, **3**, and **4** ones, and centroid, which are made of **5**, **6**, and **7** ones, are 13.593 and 13.753 Å, respectively.

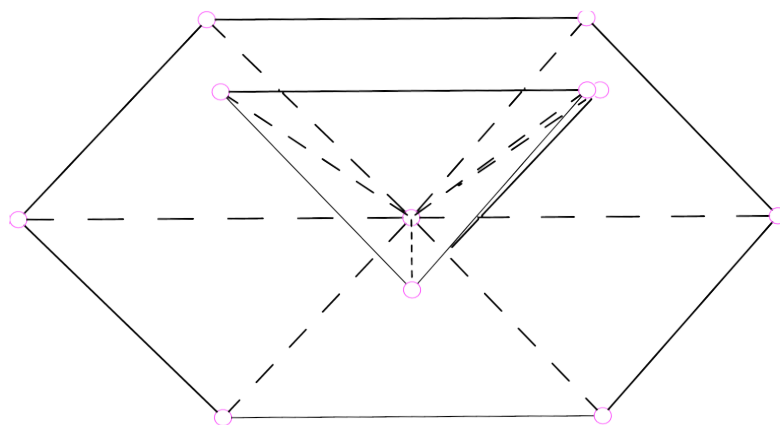


Figure 6.19. Distorted hexagonal close packing of $\text{C}_{60}(\text{CH}_3)_5\text{H}$ molecules in $\text{C}_{60}(\text{CH}_3)_5\text{H} \cdot \text{C}_5\text{H}_{12}$ structure.¹⁶⁸ The pink circles are C_{60} centroids.

CHAPTER 7. X-RAY CRYSTALLOGRAPHY OF PERFLUOROALKYLATED FULLERENES (PFAFS): GENERAL ASPECTS

7.1 X-ray Crystal Structures of PFAFs

Studies of fullerene perfluoroalkylation resulted in determination of over a hundred X-ray crystal structures of fullerene(R_F)_n (even $n = 2-20$) compounds.^{31,36,39,41,43,53,54,56-58,64,66,82,127,133-137,173-180} It constitutes over ten per cent of all reported X-ray structures of fullerenes and their derivatives. Structural information provided by crystallographic studies is usually used for i) determination of fullerene(R_F)_n addition patterns (especially for the compounds with C_mF_{2m+1} ($m > 1$) groups); ii) distinction between the primarily single bonds and double bonds with following prediction of the most likely addition sites for the functional groups; and iii) validation of theoretical calculations.

7.1.1. Determination of PFAF Addition Patterns. Electrochemical studies of the trifluoromethylated fullerenes demonstrate that the redox properties of fullerene(CF₃)_n derivatives are linked to their addition patterns.³² For a given substituent, the addition pattern in many cases is more important than the number of substituents in determining reduction potential values. For instance, $E_{1/2}$ can vary by more than 500 mV for C₆₀(CF₃)₁₀ isomers.³² It was found that high reduction potentials (> 0.3 V) are associated with addition patterns containing conjugated non-terminal double bonds in pentagons (*nt*-DBIPs). In addition, *nt*-DBIPs are also in conjugation with a common

hexagon-hexagon junction double bond junction double bond, forming a fulvene-like fragment.³² This fulvene fragment leads to highly delocalized LUMOs with lower energies, and, therefore, more positive reduction potentials for **60-10-2-CF₃**, **60-10-6-CF₃**, and **60-10-1-CF₃** compounds (Table 7.1).³² For the **60-10-3-CF₃** derivative the fulvene fragment is isolated from the rest of the fullerene π system by six of the ten cage sp^3 carbon atoms and the potential is only 0.17 V. In this case, the LUMO is essentially a localized fulvene-like π^* molecular orbital, and this highly localized orbital leads to a relatively high LUMO energy and a relatively negative reduction potential.³² Thus, combination of X-ray crystallography, which provides the information about the location of the perfluoroalkyl groups on a fullerene cage, with theoretical studies plays an important role for understanding and prediction of the PFAF electrochemical behavior.

X-ray crystallographic studies of the fullerene(CF₃)_n compounds led to the determination of the common structural principles which are successfully used for the prediction of the most probable addition patterns of the unknown trifluoromethylated derivatives using only spectroscopic data and theoretical calculations.^{31-33,39} It was found that the addition patterns of fullerene(CF₃)_n are ribbons or loops of edge-sharing *m*- and *p*-C₆(CF₃)₂ hexagons (Tables 7.1 and 7.2, Figures 4.14–4.19, (Chapter 4), and Figure 5.7 (Chapter 5)), occasionally with an isolated *p*-C₆(CF₃)₂ hexagon added (e.g., **60-8-2-CF₃**, **60-8-3-CF₃**, and C₈₀(CF₃)₁₂ (Figure 5.7, Chapter 5)). The ribbons usually end with a *p*-C₆(CF₃)₂ hexagon (e.g., **60-4-1-CF₃**, **60-6-1-CF₃** (Table 7.1), C₈₀(CF₃)₁₂, and C₇₄(CF₃)₁₂ (Figure 5.7, Chapter 5)), and end with a *para-para-para* (*p*³) (e.g., **60-8-1-CF₃** (Table 7.1), C₇₈(CF₃)₁₂, C₇₄(CF₃)₁₂ (Figure 5.7)) or *para-meta-para* (*pmp*) sequence (e.g., **60-4-1-CF₃** and **60-6-6-CF₃**). Notably, the situation can be different for trifluoromethyl

derivatives of endohedral metallofullerenes. For example, CF_3 groups in the hollow fullerenes do not attach to the triple-hexagon junctions (THJs), because these are the least pyramidalized of fullerene sp^2 carbon atoms, and they resist further pyramidalization that occurs when an exohedral substituent is added. The only exception for hollow fullerene(CF_3)_n is $\text{C}_{94}(\text{CF}_3)_{20}$ compound in which two CF_3 groups attach to THJs.¹³⁷ Troyanov and co-workers proposed that such addition takes place due to a high number of the relatively bulky CF_3 groups.¹³⁷ In case of endometallofullerenes, up to 8 trifluoromethyl groups can be attached to the THJs which can be explained by the influence of the metal cluster inside the fullerene cage (Figure 7.1, see Chapter 4 for more details).

The combination of 1D and 2D-COSY ^{19}F NMR spectral data along with X-ray crystal structures of fullerene(CF_3)_n compounds were used to establish a correlation between the chemical shift and the conformation of a particular CF_3 group.^{33,34} It was found that CF_3 groups that have eclipsed or nearly eclipsed conformations with respect to the cage have $-\delta$ values less than 60 ppm. For instance, in the $\text{C}_2\text{-C}_{74}(\text{CF}_3)_{12}$ crystal structure two trifluoromethyl groups have eclipsed conformations (the $\text{F782-C78}\cdots\text{C27-C28}$ and $\text{F782-C78}\cdots\text{C27-C28}$ torsion angles are $0.8(1)^\circ$ and $0.9(1)^\circ$, respectively) which correspond to a CF_3 multiplet with $-\delta = 55.2$ ppm (Table 5.1, Chapter 5).

In addition, it was found that through-space Fermi-contact J_{FF} values depend on $\text{F}\cdots\text{F}$ distances between CF_3 groups and $\text{F-C}\cdots\text{C-F}$ torsion angles, i.e. shorter distances and larger torsion angles lead to larger J_{FF} coupling constant values. For instance, $\text{F751}\cdots\text{F762}$ (the $\text{F762-C76}\cdots\text{C75-F751}$ torsion angle is $75.15(1)^\circ$) and $\text{F782}\cdots\text{F792}$ (the $\text{F792-C79}\cdots\text{C78-F782}$ torsion angle is $56.06(1)^\circ$) distances in $\text{C}_2\text{-C}_{74}(\text{CF}_3)_{12}$ structure are

2.6325(2) and 2.8079(14) Å, respectively (Figure 7.3). These F...F distances are fully consistent with different $^7J_{\text{FF}}$ values of 15.0 (F751...F762) and 12.0 Hz (F782...F792). Thus, due to careful examination of the structural information obtained from the crystallographic studies, a combination of NMR spectroscopy with DFT calculations can be used to reveal new addition patterns of fullerene(CF₃)_n compounds with almost the same success as X-ray crystallography. However, for perfluoroalkylated fullerenes with *n*-C_mF_{2m+1} (*m* > 1, e.g., C₂F₅ or *n*-C₃F₇) substituents, growth of single crystals suitable for X-ray diffraction is still the only possible way to determine their addition patterns. For instance, the addition patterns of C₆₀(C₂F₅)₁₀, C₇₀(C₂F₅)₁₀, and C₇₀(C₂F₅)₁₂ compounds, which were discussed in detail in Chapter 2, were determined by X-ray crystallography. The high complexity of the ¹⁹F NMR spectra of these derivatives obstructs the interpretation of the spectra and the assignment of structure from the spectra. Thus, X-ray crystallography is still the only method for an unambiguous determination of addition patterns of PFAFs with long perfluoroalkyl chains.

7.1.2. Single and Double Bonds in Fullerene(CF₃)_n Compounds and Validation of DFT Calculations. The relative stabilities of various fullerene(CF₃)_n isomers are determined by at least four factors: (i) the degree of delocalization/aromatization of the remaining π bonds, (ii) the presence or absence of the double bonds in the pentagons, (iii) steric repulsion between substituents, and (iv) rotational conformation of each substituent (CF₃ group) with respect to its underlying cage C–C bond. Thus, any attempt to understand the stability of the addition pattern of a given fullerene(CF₃)_n will have to include an analysis of the cage C–C σ and π bonds. The most straightforward experimental parameter that can be obtained from

crystallographic data and used to estimate relative bond strength (and hence relative bond order) is the C–C distance. In favorable cases, the precision of fullerene X-ray structures (i.e., the estimated standard deviation for individual cage C–C bonds) allows one to determine statistically significant variations in C–C distances. Furthermore, X-ray crystallography provides important information about whether a particular computational method can be trusted with a sufficient degree of confidence to give accurate bond distances and angles in the absence of a crystal structure or when the estimated standard error is too large. For visualization of such validations, it is convenient to plot the DFT-calculated bond distances versus X-ray determined bond distances.³⁶ For instance, Figure 7.4 shows the correlation between the cage C–C distances in the crystal structure of the isomer of 1,6,11,16,18,26,36,44,48,58- $C_{60}(CF_3)_{10}$ (**60-10-2- CF_3**) and the DFT-predicted cage C–C distances for this molecule.⁴⁸ This particular **60-10-2- CF_3** isomer is a good example for comparison because it is asymmetric, providing a comparison of 90 unique cage C–C distances, and it is one of the most precisely determined fullerene X-ray structures (σ values for individual cage C–C bonds range from 0.0014 to 0.0016 Å).⁴⁸ The experimental and calculated C–C distances are in good agreement with each other; the largest difference is less than 6σ , and most of the differences are within 3σ .

Thus, X-ray crystallographic data confirm that DFT calculations can provide meaningful bond distances for PFAFs.

In the $C_{60}\cdot Pt^{II}(OEP)\cdot 2C_6H_6$ structure, there are two types of cage C–C bonds which exhibit very narrow ranges 1.379(3)–1.391(3) (single bonds) and 1.440(3)–1.461(3) Å (double bonds).¹⁸¹ The addition of substituents should decrease the number of the C–C double bonds. For instance, the addition of 10 CF_3 groups should lead to 25

double bonds instead of the 30 observed for C_{60} structure. Figure 7.5 shows that the 25 short cage C–C bond distances in **60-10-2- CF_3** vary from 1.354(2) to 1.402(2) Å. The other C–C bond lengths are in range from 1.422(2) to 1.552(2) Å. Thus, the bond lengths in PFAFs are in a broader range compared to pristine C_{60} and can be assigned as primarily “single bonds” or “double bonds” only as a first approximation. However, despite a wide range of the bond lengths for the observable “double bonds”, the shortest ones have the most double bond character and therefore, they can be considered as the most probable reactive sites for further derivatization. For example, the analysis of the **70-10-1- CF_3** structure shows that the C–C cage distances vary from 1.347(3) to 1.562(3) Å. The C33–C34 bond is the shortest bond (1.386(3) Å) in that compound which does not have connection with $C(sp^3)$ vertexes (Table 7.2, Figure 7.6). This bond connects two unoccupied pentagons (the other 10 pentagons have one CF_3 group on each), and it should be the most reactive site, e.g., for further cycloaddition reactions. Recent structural characterizations of the $C_{70}(CF_3)_{10}[C(CO_2Et)_2]^{176}$ and $C_{70}(CF_3)_{10}C_2H_4[C_6H_2(MeO)_2]^{182}$ cycloadducts proved the correctness of the assumption about the high reactivity of C33–C34 bond.¹⁸² Figure 7.6 shows that cycloaddition in case of Bingel and Diels-Alder reactions occurred at C33–C34, which led to a high yield of regioisomers.^{176,182}

Thus, based on information about $C(sp^2)$ – $C(sp^2)$ bond lengths obtained from X-ray crystallographic studies, it is possible to predict the most reactive sites for the further derivatization of PFAFs.

7.2 Problems in Crystallography of PFAFs

In this work, slow solvent evaporation and solvent diffusion were the most common techniques used for the growth of single crystals of PFAFs suitable for X-ray diffraction. These methods work very well for the majority of the perfluoroalkylated compounds, even for sub-mg samples, which are often available for crystallization.^{36,53,135,174} Because PFAFs are composed of atoms with low X-ray scattering factors (C, O, F) and the size of the crystals is usually small (10–80 μm), synchrotron radiation sources are often employed for the data collection. For validations of DFT calculations (see above), it is imperative that crystallographic data (bond distances and angles) are known with high precision. In most cases, in order to improve the quality of the structural model some crystallographic problems have to be overcome. First, the positional disorder of R_F group(s) or a fullerene cage frequently occurs in the fullerene(R_F) $_n$ structures.^{36,41} Two or three orientations of R_F groups that can be generated by rotation around the C–C bonds of perfluoroalkyl chain are observed in many cases. The positional R_F disorder is most likely static: different orientations of the R_F group are distributed in different unit cells. The simplest example of the disorder of CF_3 group between two orientations is shown in Figure 7.7. Increase of the length of the perfluoroalkyl chain in PFAF leads to complication of the structural models.^{53,54,56,63}

Second, positional disorder of the fullerene cage is often observed for derivatives with a low number of addends. In such cases, different fullerene cage orientations may be observed even if the perfluoroalkyl groups are not disordered, as shown in Figure 7.8 using the crystal structure of $\text{C}_{60}(i\text{-C}_3\text{F}_7)_2$ as an example. Rigid group constraints (*e.g.*,

the FRAG instruction in SHELXL²¹) are normally used to locate the positions of the disordered cage carbon atoms, especially at the early stage of the structure refinement.

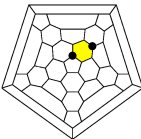
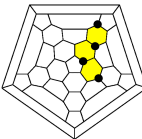
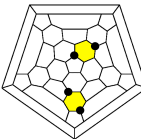
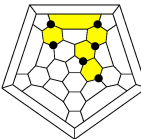
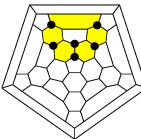
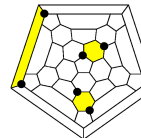
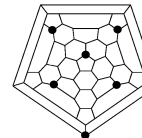
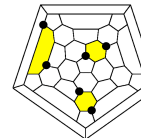
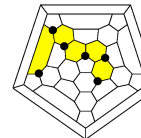
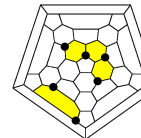
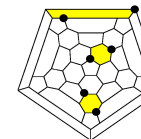
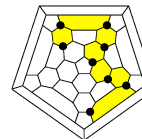
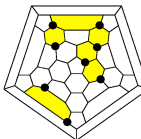
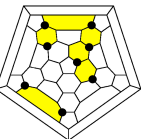
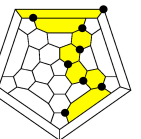
The design of molecular assemblies in which fullerene molecules are surrounded by solvent molecules in an orderly fashion can lead to a decrease in the positional disorder and improvement of the crystal quality. Many examples exist in the literature in which bowl-shaped molecules, including metal complexes of octaethylporphyrin,¹¹⁶ calixarenes,¹⁸³ cyclodextrins¹⁸⁴ or cyclotrimeratrylene,¹⁸⁵ were used for co-crystallization with the underivatized hollow fullerenes and with endohedral metallofullerenes.

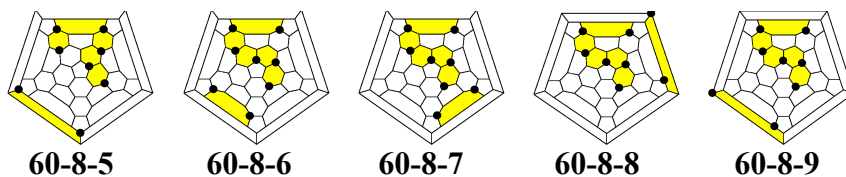
This approach may not be successful when used for highly substituted fullerene(R_F)_n compounds due to the shielding of the fullerene π system by multiple R_F groups. However, the use of flat surfaces of the aromatic hydrocarbons may allow benzene rings to surround the perfluoroalkylated compounds. As shown in Figures 4.54, 4.55 (Chapter 4), and 5.7 (Chapter 5), the *p*-xylene molecule appears to be a suitable candidate for creating such interactions. In case of the C₇₄(CF₃)₁₂,³⁴ Sc₃N@C₈₀(CF₃)₁₀, and Sc₃N@C₈₀(CF₃)₁₄ crystal structures,³⁶ *p*-xylene molecules form channels or layers which may restrict the positional disorder in these fullerene(R_F)_n structures.

However, solvent molecules themselves (*e.g.*, heptane, hexane or dichloromethane) may exhibit positional disorder, which leads to a decrease of the structure quality. In some cases, solvent molecules are severely disordered, and it is not possible to resolve their distinct orientations. The contribution of the disordered solvent to the structure can be estimated and accounted for by using the SQUEEZE technique.^{34,186,187}

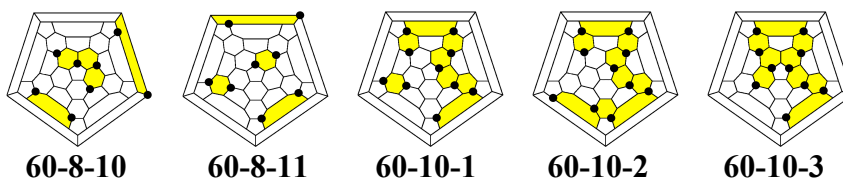
Third, a disorder in the positions of the metal or metal cluster can be observed in the X-ray crystal structures of endohedral metallofullerenes and their derivatives. For example, up to five different orientations of the Sc_3N cluster were reported.¹⁰³ Attachment of a large number of CF_3 groups results in electron-rich and electron-poor regions on the carbon cage in comparison with the naked endometallofullerenes. This effect makes a certain cluster orientation more stable than alternatives, which was demonstrated by the absence of Sc_3N disorder in $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_{10}$, $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_{12}$, and $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_{14}$ crystal structures (Chapter 4, Figures 4.16, 4.17, and 4.30).

Table 7.1. The addition patterns of $C_{60}(R_F)_n$ derivatives determined based on ^{19}F NMR spectroscopy, DFT calculations, and X-ray crystallography.

				
60-2-1	60-4-1	60-4-2	60-6-1	60-6-2
60-2-1	1,7- $C_{60}(R_F)_2$	$R_F = CF_3$ (ref ^{66,80})		
60-4-1	1,6,11,18- $C_{60}(R_F)_4$	$R_F = CF_3$ (ref ^{66,80})		
60-4-2	1,7,16,36- $C_{60}(R_F)_4$	$R_F = CF_3$ (ref ⁶⁶)		
60-6-1	1,6,11,18,24,27- $C_{60}(R_F)_6$	$R_F = CF_3$ (ref ^{66,80})		
60-6-2	1,6,9,12,15,18- $C_{60}(R_F)_6$	$R_F = CF_3$ (ref ⁶⁵)		
				
60-6-3	60-6-4	60-6-5	60-6-6	60-6-7
60-6-3	1,7,16,36,46,49- $C_{60}(R_F)_6$	$R_F = C_2F_5$ (ref ⁵¹)		
60-6-4	1,23,28,33,38,60- $C_{60}(R_F)_6$	$R_F = CF_3$ (ref ³²)		
60-6-5	1,7,16,30,36,47- $C_{60}(R_F)_6$	$R_F = i-C_3F_7$ (ref ⁵²)		
60-6-6	1,6,11,18,28,31- $C_{60}(R_F)_6$	$R_F = CF_3$ (ref ⁶⁶)		
60-6-7	1,6,11,18,33,51- $C_{60}(R_F)_6$	$R_F = CF_3$ (ref ^{55,66})		
				
60-6-8	60-8-1	60-8-2	60-8-3	60-8-4
60-6-8	1,7,16,36,45,57- $C_{60}(R_F)_6$	$R_F = C_2F_5$ (ref ⁵⁵), $i-C_3F_7$ (ref ⁸²)		
60-8-1	1,6,11,16,18,24,27,36- $C_{60}(R_F)_8$	$R_F = CF_3$ (ref ¹⁸⁸),		
60-8-2	1,6,11,18,24,27,52,55- $C_{60}(R_F)_8$	$R_F = CF_3$ (ref ⁴⁹)		
60-8-3	1,6,11,18,24,27,53,56- $C_{60}(R_F)_8$	$R_F = CF_3$ (ref ³²)		
60-8-4	1,6,11,16,18,28,31,36- $C_{60}(R_F)_8$	$R_F = CF_3$ (ref ³²)		



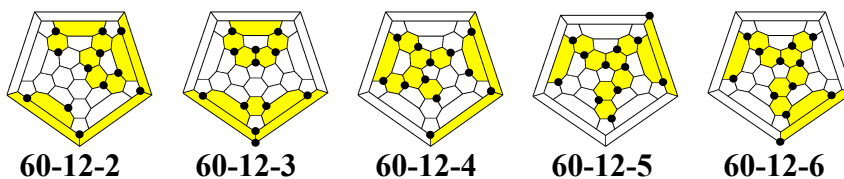
60-8-5	1,6,11,18,24,27,33,51- $C_{60}(R_F)_8$	$R_F = CF_3$ (ref ³²)
60-8-6	1,6,11,18,24,27,32,35- $C_{60}(R_F)_8$	$R_F = C_2F_5$ (ref ⁵¹)
60-8-7	1,6,11,18,24,27,36,39- $C_{60}(R_F)_8$	$R_F = C_2F_5$ (Chapter 2)
60-8-8	1,6,11,18,24,27,41,57- $C_{60}(R_F)_8$	$R_F = C_2F_5$ (ref ⁵⁵)
60-8-9	1,6,11,18,24,27,51,59- $C_{60}(R_F)_8$	$R_F = C_2F_5$ (ref ⁵⁵)



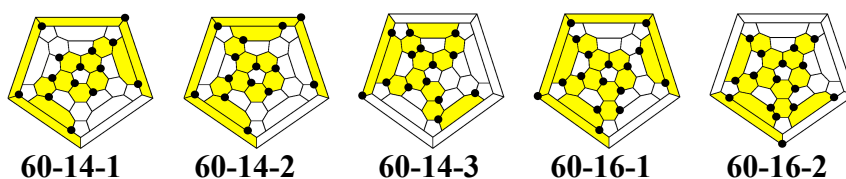
60-8-10	1,6,11,18,32,35,42,56- $C_{60}(R_F)_8$	$R_F = C_2F_5$ (ref ⁵⁵)
60-8-11	1,7,14,31,36,39,45,57- $C_{60}(R_F)_8$	$R_F = i-C_3F_7$ (ref ⁸²)
60-10-1	1,6,11,16,18,24,27,36,41,57- $C_{60}(R_F)_{10}$	$R_F = CF_3$ (ref ³²)
60-10-2	1,6,11,16,18,24,27,36,54,60- $C_{60}(R_F)_{10}$	$R_F = CF_3$ (ref ⁴⁸)
60-10-3	1,3,7,10,14,17,23,28,31,40- $C_{60}(R_F)_{10}$	$R_F = CF_3$ (ref ³⁸)



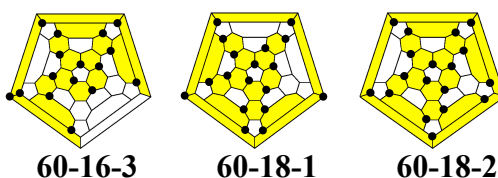
60-10-4	1,6,12,15,18,23,25,41,45,57- $C_{60}(R_F)_{10}$	$R_F = CF_3$ (ref ⁵⁰)
60-10-5	1,6,11,16,18,26,36,41,44,57- $C_{60}(R_F)_{10}$	$R_F = CF_3$ (ref ³²)
60-10-6	1,6,11,18,24,27,33,51,54,60- $C_{60}(R_F)_{10}$	$R_F = CF_3$ (ref ⁶⁷), C_2F_5 (ref ⁵⁵ , Chapter 2)
60-10-7	1,6,11,16,18,28,31,36,42,56- $C_{60}(R_F)_{10}$	$R_F = C_2F_5$ (ref ⁵⁵)
60-12-1	1,6,11,16,18,26,36,44,46,49,54,60- $C_{60}(R_F)_{12}$	$R_F = CF_3$ (ref ⁴⁰)



- 60-12-2** 1,3,6,11,13,18,26,32,35,41,44,57- $C_{60}(R_F)_{12}$ $R_F = CF_3$ (ref⁴¹)
- 60-12-3** 1,6,9,12,15,18,43,46,49,52,55,60- $C_{60}(R_F)_{12}$ $R_F = CF_3$ (ref^{32,43})
- 60-12-4** 1,3,7,10,14,17,21,28,31,42,52,55- $C_{60}(R_F)_{12}$ $R_F = CF_3$ (ref¹²⁷)
- 60-12-5** 1,6,8,11,16,18,23,28,31,36,41,57- $C_{60}(R_F)_{12}$ $R_F = CF_3$ (ref¹⁷⁷)
- 60-12-6** 1,6,8,11,16,18,23,28,31,36,54,60- $C_{60}(R_F)_{12}$ $R_F = CF_3$ (ref¹⁷⁷)

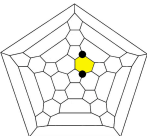
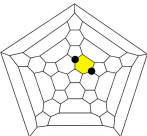
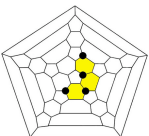
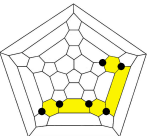
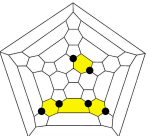
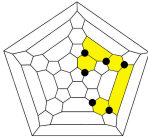
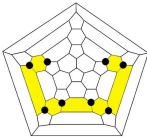
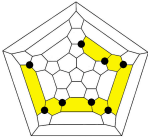
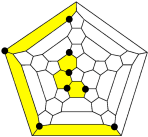
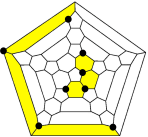
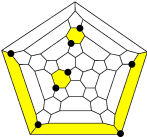
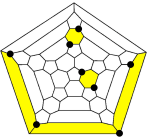
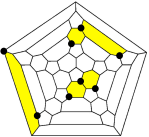
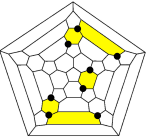
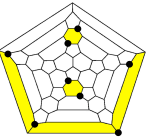


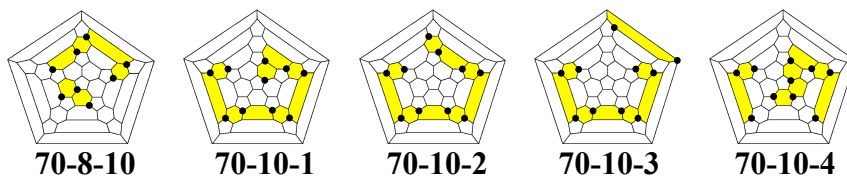
- 60-14-1** 1,3,6,8,11,13,18,23,33,41,46,49,51,57- $C_{60}(R_F)_{14}$ $R_F = CF_3$ (ref⁴³)
- 60-14-2** 1,3,6,11,13,18,26,33,41,44,46,49,51,57- $C_{60}(R_F)_{14}$ $R_F = CF_3$ (ref⁴³)
- 60-14-3** 1,3,7,10,11,14,17,24,27,31,36,39,47,59- $C_{60}(R_F)_{14}$ $R_F = CF_3$ (ref¹⁷⁷)
- 60-16-1** 1,3,6,11,13,18,22,28,31,34,37,41,43,46,51,59- $C_{60}(R_F)_{16}$ $R_F = CF_3$ (ref¹⁶¹)
- 60-16-2** 1,3,6,8,11,13,18,23,28,31,34,35,37,50,54,60- $C_{60}(R_F)_{16}$ $R_F = CF_3$ (ref¹⁶¹)



- 60-16-3** 1,3,6,11,13,18,22,24,27,33,41,43,46,49,51,59- $C_{60}(R_F)_{16}$
 $R_F = CF_3$ (ref¹⁶¹)
- 60-18-1** 1,3,6,8,11,13,18,23,28,31,34,37,43,46,51,53,56,59- $C_{60}(R_F)_{18}$
 $R_F = CF_3$ (ref¹⁶¹)
- 60-18-2** 1,3,6,11,13,18,22,24,27,32,35,37,41,43,46,49,52,54- $C_{60}(R_F)_{18}$
 $R_F = CF_3$ (ref¹⁷⁴)

Table 7.2. The addition patterns of $C_{70}(R_F)_n$ derivatives determined based on ^{19}F NMR spectroscopy, DFT calculations, and X-ray crystallography.

				
70-2-1	70-2-2	70-4-1	70-6-1	70-6-2
70-2-1	7,24- $C_{70}(R_F)_2$	$R_F = \text{CF}_3$ (ref ^{58,60,173}), C_2F_5 (ref ⁵⁸)		
70-2-2	8,23- $C_{70}(R_F)_2$	$R_F = \text{CF}_3$ (ref ³¹)		
70-4-1	7,24,44,47- $C_{70}(R_F)_4$	$R_F = \text{CF}_3$ (ref ⁶⁰)		
70-6-1	1,4,11,19,31,41- $C_{70}(R_F)_6$	$R_F = \text{CF}_3$ (ref ⁶⁰)		
70-6-2	1,4,11,23,31,44- $C_{70}(R_F)_6$	$R_F = \text{CF}_3$ (ref ³¹)		
				
70-6-3	70-8-1	70-8-2	70-8-3	70-8-4
70-6-3	1,4,10,19,25,41- $C_{70}(R_F)_6$	$R_F = \text{CF}_3$ (ref ⁶⁰)		
70-8-1	1,4,11,19,31,41,51,64- $C_{70}(R_F)_8$	$R_F = \text{CF}_3$ (ref ⁶⁰), C_2F_5 (ref ⁵⁴)		
70-8-2	1,4,11,19,31,41,51,60- $C_{70}(R_F)_8$	$R_F = \text{CF}_3$ (ref ^{31,60,175})		
70-8-3	7,17,24,36,44,47,53,56- $C_{70}(R_F)_8$	$R_F = \text{C}_2\text{F}_5$ (ref ⁵⁴), $n\text{-C}_3\text{F}_7$ (ref ⁵⁶)		
70-8-4	7,15,24,34,44,47,53,56- $C_{70}(R_F)_8$	$R_F = \text{C}_n\text{F}_{2n+1}$, $n = 1-3$ (ref ^{54,56})		
				
70-8-5	70-8-6	70-8-7	70-8-8	70-8-9
70-8-5	1,4,23,28,36,44,46,57- $C_{70}(R_F)_8$	$R_F = \text{C}_2\text{F}_5$ (ref ⁵⁴), $n\text{-C}_3\text{F}_7$ (ref ⁵⁶)		
70-8-6	1,4,23,28,34,44,46,52- $C_{70}(R_F)_8$	$R_F = \text{C}_2\text{F}_5$ (ref ⁵⁴), $n\text{-C}_3\text{F}_7$ (ref ¹⁸⁹)		
70-8-7	1,4,11,24,43,52,54,68- $C_{70}(R_F)_8$	$R_F = \text{C}_2\text{F}_5$ (ref ⁵⁴)		
70-8-8	1,4,11,33,53,58,61,64- $C_{70}(R_F)_8$	$R_F = \text{C}_2\text{F}_5$ (ref ⁵⁴)		
70-8-9	1,4,23,28,44,46,55,67- $C_{70}(R_F)_8$	$R_F = \text{C}_2\text{F}_5$ (ref ⁵⁴)		



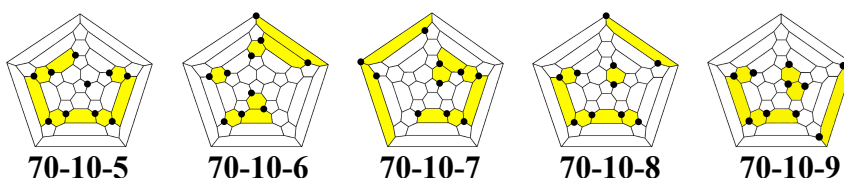
70-8-10 1,4,11,19,31,55,57,67- $C_{70}(R_F)_8$ $R_F = C_2F_5$ (ref⁵⁴)

70-10-1 1,4,10,19,25,41,49,60,66,69- $C_{70}(R_F)_{10}$ $R_F = CF_3$ (ref⁴⁷), C_2F_5 (ref⁵⁴)

70-10-2 1,4,11,19,31,41,49,60,66,69- $C_{70}(R_F)_{10}$ $R_F = CF_3$ (ref³¹)

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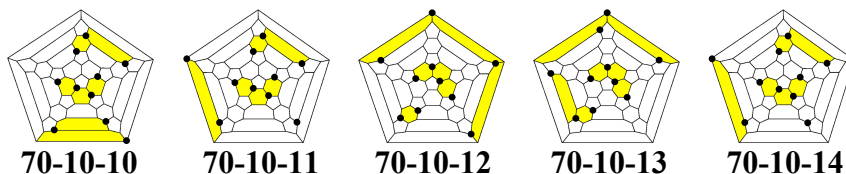
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70-10-6 1,4,10,19,25,41,55,60,67,69- $C_{70}(R_F)_{10}$ $R_F = CF_3$ (ref¹³¹)

70-10-7 7,13,15,24,29,34,42,49,66,69- $C_{70}(R_F)_{10}$ $R_F = CF_3$

70-10-8 1,4,11,19,31,41,46,55,62,67- $C_{70}(R_F)_{10}$ $R_F = C_2F_5$ (ref⁵³)

70-10-9 1,4,11,19,23,31,44,55,57,67- $C_{70}(R_F)_{10}$ $R_F = C_2F_5$ (ref⁵³)



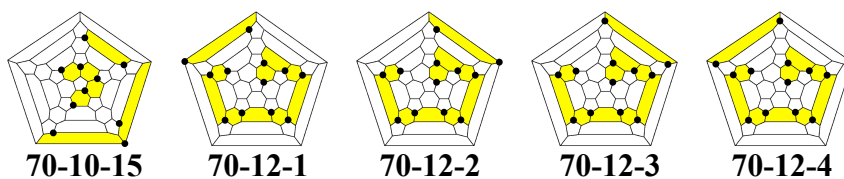
70-10-10 1,4,11,33,38,46,53,55,62,64- $C_{70}(R_F)_{10}$ $R_F = C_2F_5$ (ref⁵³)

70-10-11 1,4,11,24,33,38,43,48,53,55- $C_{70}(R_F)_{10}$ $R_F = C_2F_5$ (ref⁵³)

70-10-12 1,4,23,28,33,38,44,46,53,55- $C_{70}(R_F)_{10}$ $R_F = C_2F_5$ (ref⁵³)

70-10-13 1,4,11,33,38,46,48,53,55,62- $C_{70}(R_F)_{10}$ $R_F = C_2F_5$ (ref⁵³)

70-10-14 1,4,11,24,33,38,43,53,55,64- $C_{70}(R_F)_{10}$ $R_F = C_2F_5$ (ref⁵⁴)



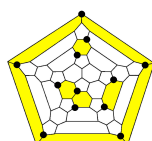
70-10-15 1,11,16,18,33,46,48,54,62,68- $C_{70}(R_F)_{10}$ $R_F = C_2F_5$ (ref⁵⁴)

70-12-1 1,4,10,19,25,32,41,49,54,60,66,69- $C_{70}(R_F)_{12}$ $R_F = CF_3$ (ref¹⁹⁰)

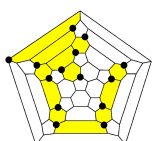
70-12-2 1,4,10,14,19,25,35,41,49,60,66,69- $C_{70}(R_F)_{12}$ $R_F = CF_3$ (ref¹⁹⁰)

70-12-3 1,4,8,11,18,23,31,35,51,58,61,64- $C_{70}(R_F)_{12}$ $R_F = CF_3$ (ref³¹)

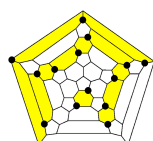
70-12-4 1,4,8,11,23,31,38,51,55,58,61,64- $C_{70}(R_F)_{12}$ $R_F = CF_3$ (ref³¹)



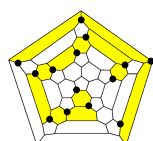
70-12-5



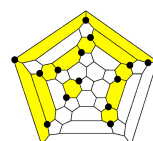
70-14-1



70-14-2



70-14-3



70-14-4

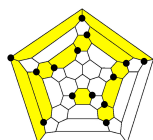
70-12-5 1,4,23,25,27,31,38,44,47,51,55,68- $C_{70}(R_F)_{12}$ $R_F = C_2F_5$ (Chapter 2)

70-14-1 1,4,7,11,18,21,24,31,35,39,51,58,61,64- $C_{70}(R_F)_{14}$ $R_F = CF_3$ (ref¹³²)

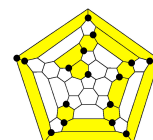
70-14-2 1,4,8,11,19,24,27,31,41,43,51,54,64,68- $C_{70}(R_F)_{14}$ $R_F = CF_3$ (ref¹⁹¹)

70-14-3 1,4,8,11,19,23,26,31,41,48,55,60,67,69- $C_{70}(R_F)_{14}$ $R_F = CF_3$ (ref¹⁹¹)

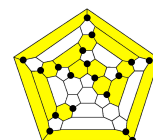
70-14-4 1,4,8,11,19,24,27,31,36,41,43,51,57,64- $C_{60}(R_F)_{14}$ $R_F = CF_3$ (ref¹⁹¹)



70-14-5



70-16-1



70-18-1

70-14-5 1,4,8,11,19,24,27,31,41,43,51,53,56,64- $C_{70}(R_F)_{14}$ $R_F = CF_3$ (ref¹⁷³)

70-16-1 1,4,8,11,18,23,24,27,31,35,44,47,51,58,61,64- $C_{70}(R_F)_{16}$
 $R_F = CF_3$ (ref¹⁹²)

70-18-1 1,4,8,11,16,19,23,27,31,34,37,41,44,46,47,52,60,69- $C_{70}(R_F)_{18}$
 $R_F = CF_3$ (ref¹⁹²)

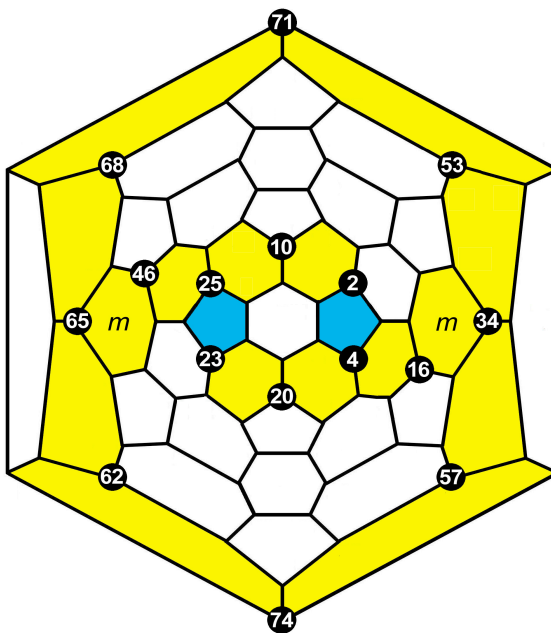


Figure 7.1. The Schlegel diagram of $\text{Sc}_3\text{N}@\text{C}_{80}(\text{CF}_3)_{16}$ compound.³⁶ The CF_3 groups attached to C34, C53, C57, C62, C65, C68, C71, and C74 carbon atoms are located on the triple-hexagon junctions.

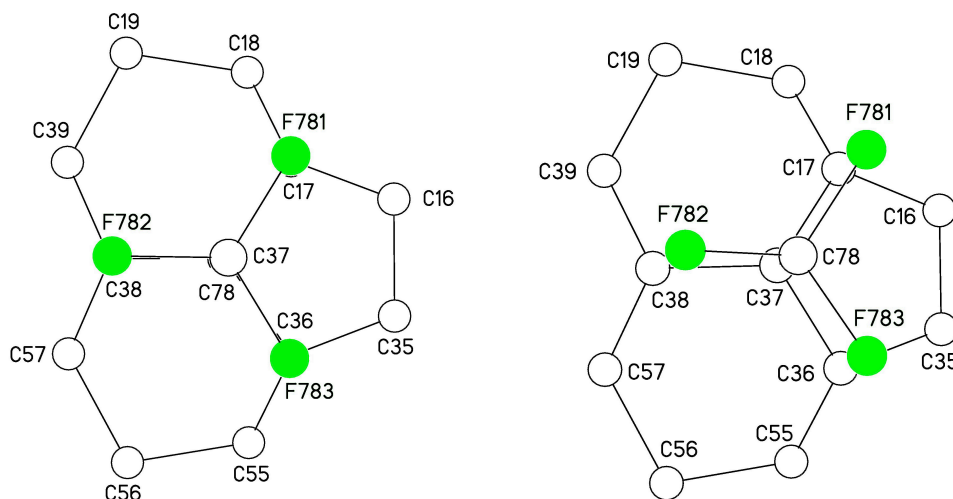


Figure 7.2. Two views of the eclipsed conformation of one CF_3 group in $\text{C}_2\text{-C}_{74}(\text{CF}_3)_{12}$ crystal structure.³³

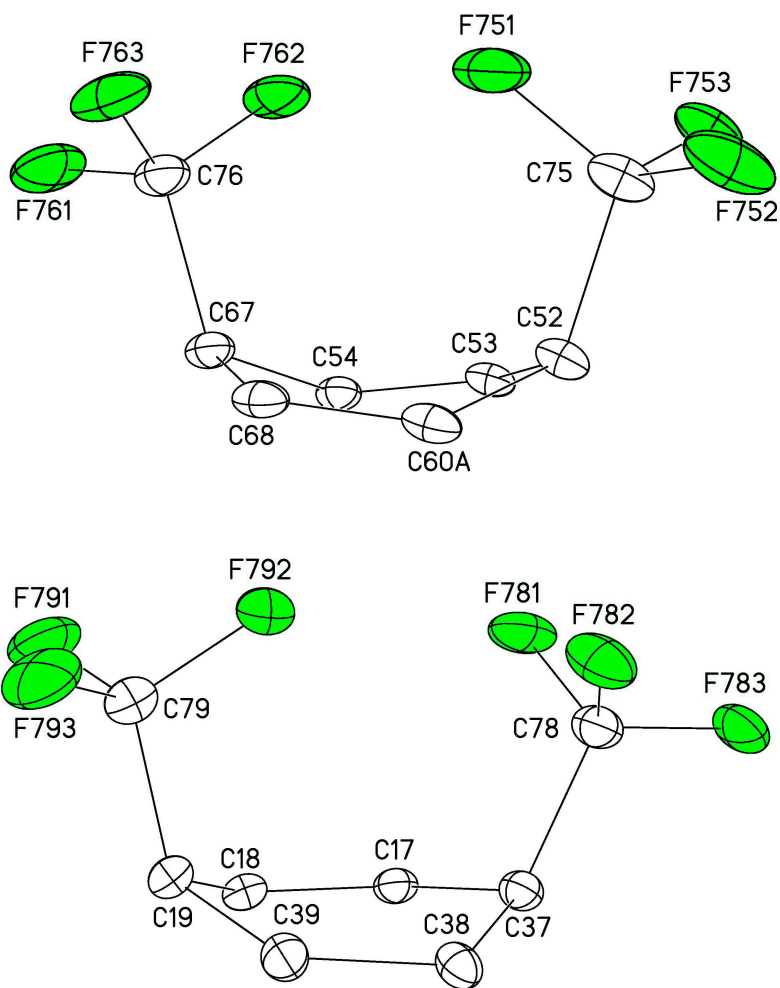


Figure 7.3. Two pairs of CF₃ groups in C₂-C₇₄(CF₃)₁₂ crystal structure.³³ The F751...F762 and F782...F792 distances are 2.6325(2) and 2.8079(14) Å, respectively. The F792-C79...C78-F782) and F762-C76...C75-F751 torsion angles are 56.06(1)° and 75.15(1)°, respectively.

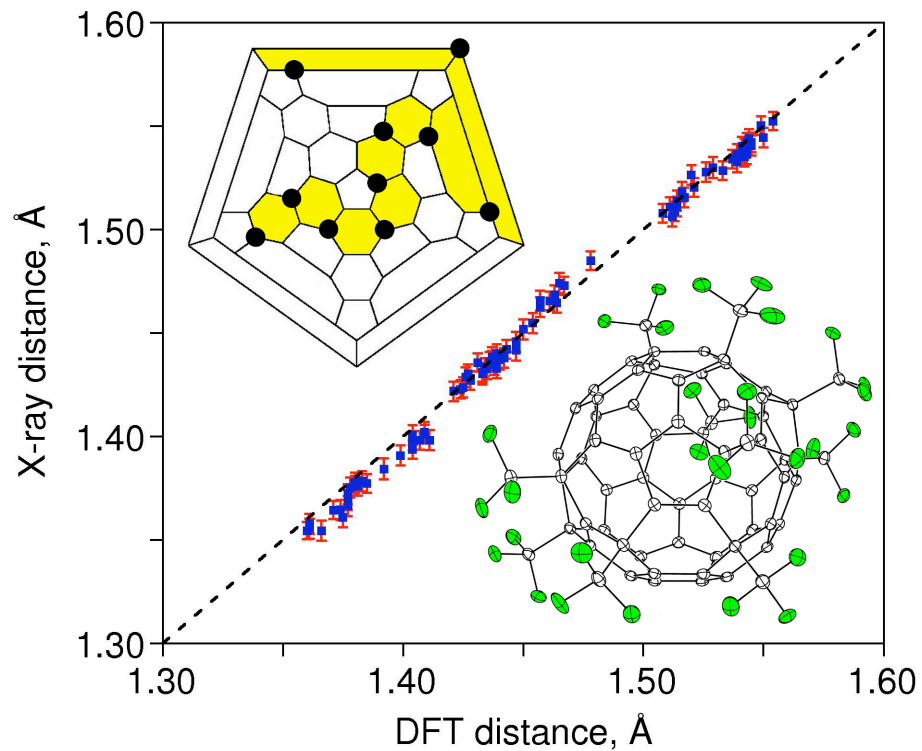


Figure 7.4. The plot shows the correlation between the X-ray determined cage C–C distances ($\pm 3\sigma$ error bars) and the DFT-calculated cage C–C distances in the structure of **60-10-2** isomer.⁴⁸ The X-ray structure (50 % probability ellipsoids) and Schlegel diagram of **60-10-2** isomer are shown in the insets.

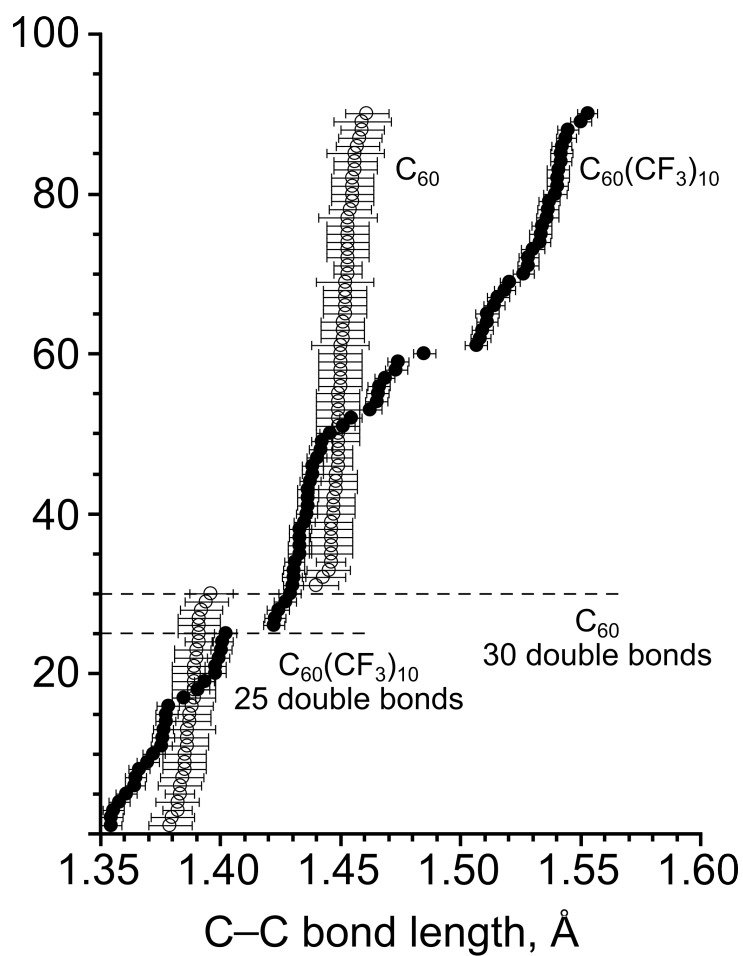


Figure 7.5. C–C cage bond length ($\pm 3\sigma$ error bars) for C_{60}^{181} and $C_{60}(CF_3)_{10}$ (**60-10-2**) crystal structures.⁴⁸ Black circles and unfilled circles correspond to C–C bond lengths in **60-10-2** to C_{60} structures, respectively.

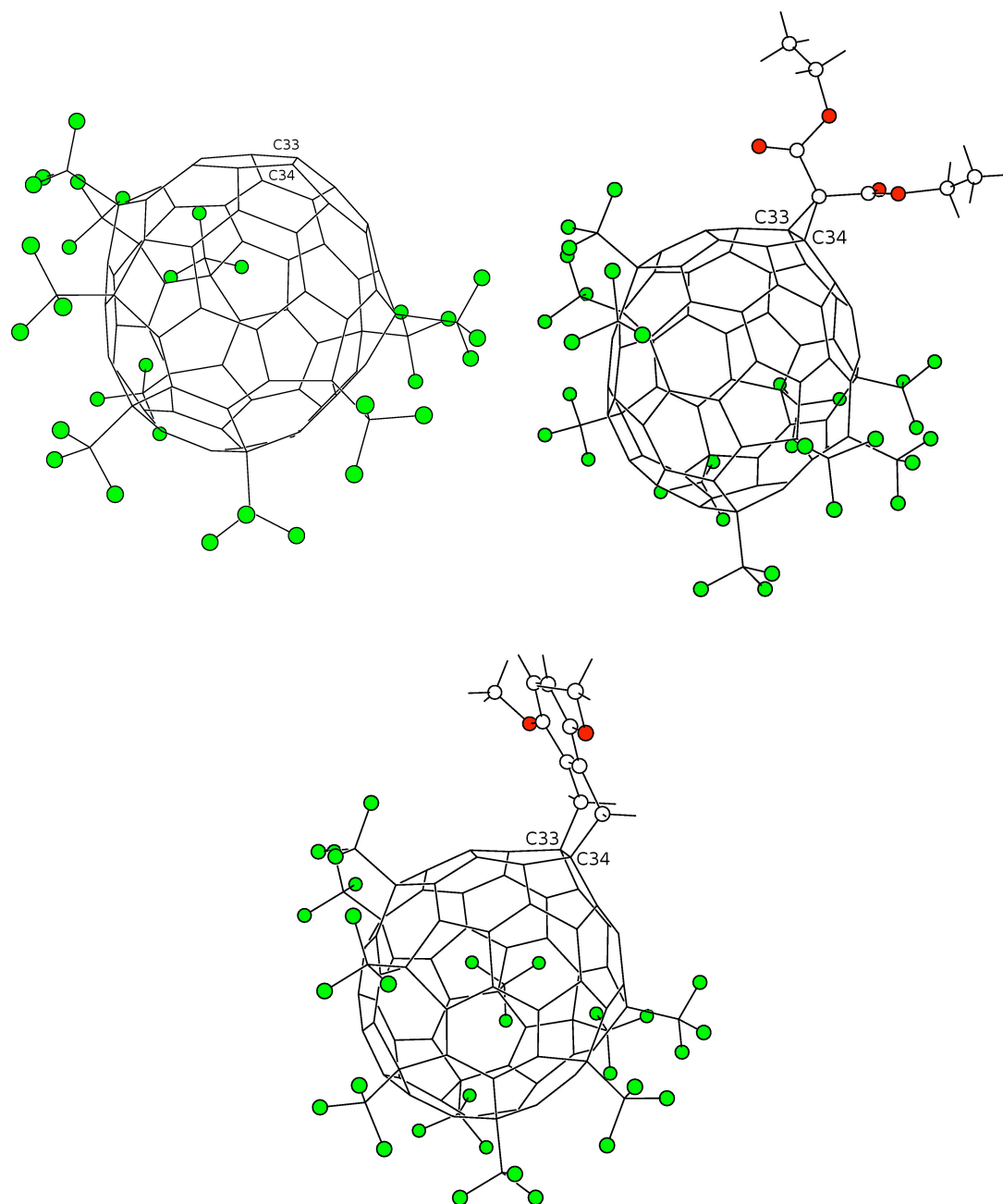


Figure 7.6. Top: X-ray crystal structures of $C_{70}(CF_3)_{10-1}$ (**70-10-1**, left)⁴⁷ and $C_{70}(CF_3)_{10}[C(CO_2Et)_2]$.¹⁷⁶ Bottom: X-ray crystal structure of $C_1-C_{70}(CF_3)_{10}C_2H_4[C_6H_2(MeO)_2]$.¹⁸²

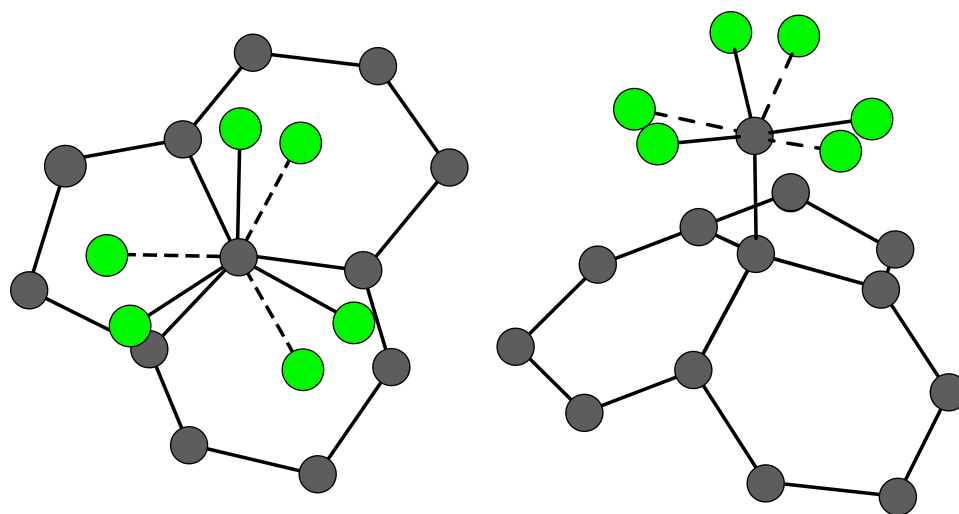


Figure 7.7. Positional disorder of the CF_3 group between two orientations. Corresponding C–F distances in disordered components are restrained to be similar during structure refinement.

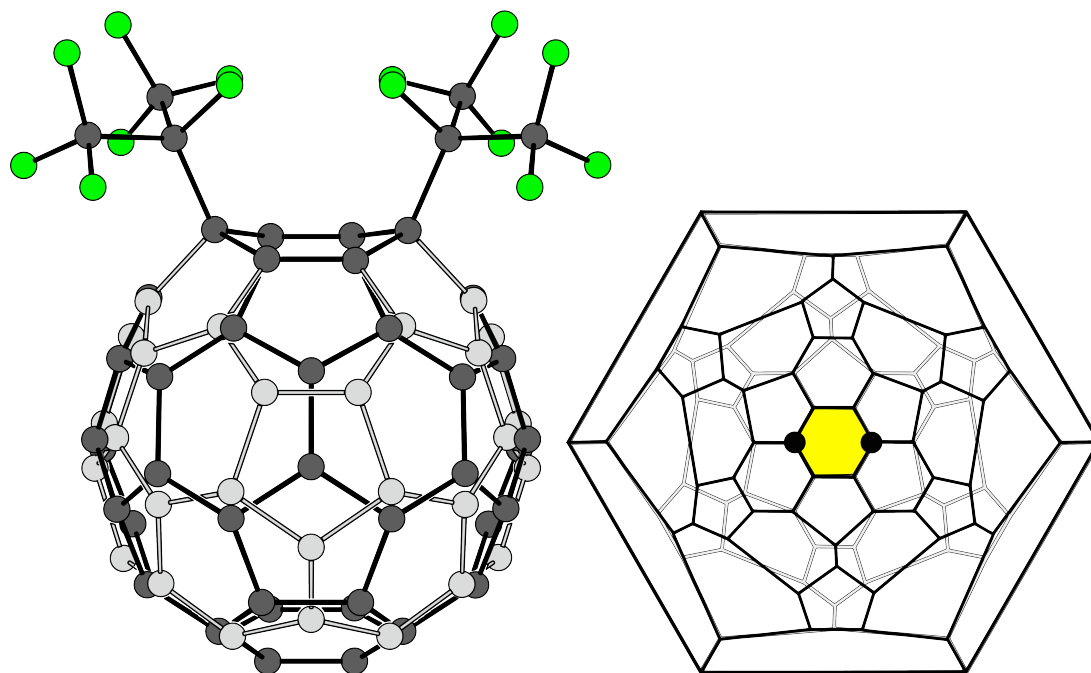


Figure 7.8. Example of the positional cage disorder in $C_s-C_{60}(i-C_3F_7)_2$ crystal structure. There are two observed orientations of C_{60} cage rotated 180° relative to each other. The superposition of two orientations is shown on the Schlegel diagram (right) and X-ray structure (left). The presence of the mirror plane and the absence of the two-fold axis in the molecular structure lead to two possible orientations of C_{60} cage with exactly the same positions of the $i-C_3F_7$ groups.

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APPENDIX

Table A.1. List of abbreviations.

abbreviation	full name
60-10-2-CF ₃	C ₆₀ (CF ₃) ₁₀ -2
70-10-2-C ₂ F ₅	C ₇₀ (C ₂ F ₅) ₁₀ -2
60-6-3-C ₃ F ₇	C ₆₀ (<i>i</i> -C ₃ F ₇) ₆ -3
MS	mass spectrometry
UV-Vis	ultraviolet-visible spectroscopy
NMR	nuclear magnetic resonance
AgTFA	silver (I) trifluoroacetate
HPLC	high-performance liquid chromatography
TGA	thermogravimetric analysis
APCI	atmospheric pressure chemical ionization
APPI	atmospheric pressure photoionization
THJ	triple-hexagon junction
EMF	endohedral metallofullerene
MNF	metallic nitride fullerene
PFAF	perfluoroalkylated fullerene
FF	fluorinated fullerenes

FA	fluorinating agent
TMF	trifluoromethylfullerene
EI	electron ionization
NI	negative ion
SPP	skew pentagonal pyramid
MALDI	matrix-assisted laser desorption/ionization
HHF	hollow higher fullerene
IPR	isolated pentagon rule

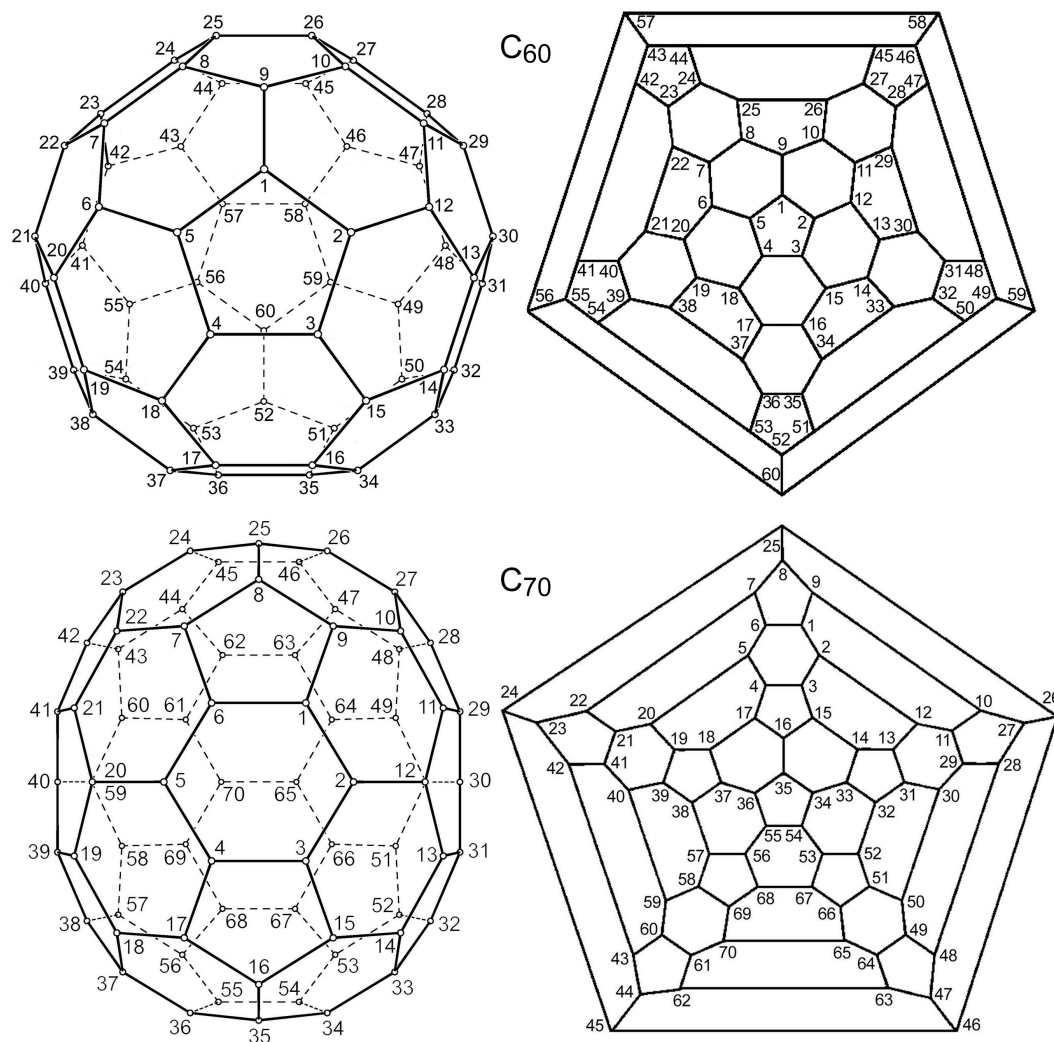


Figure A.2. The structures and Schlegel diagrams of C_{60} and C_{70} fullerenes.