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**Trifluoromethyl Derivatives of Insoluble
Small-HOMO–LUMO-Gap Hollow Higher Fullerenes.
NMR and DFT Structure Elucidation of $C_2-(C_{74}-D_{3h})(CF_3)_{12}$,
 $C_5-(C_{76}-T_d(2))(CF_3)_{12}$, $C_2-(C_{78}-D_{3h}(5))(CF_3)_{12}$,
 $C_5-(C_{80}-C_{2v}(5))(CF_3)_{12}$, and $C_2-(C_{82}-C_2(5))(CF_3)_{12}$**

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Abstract: Reaction of a mixture of insoluble higher fullerenes with CF_3I at 500 °C produced a single abundant isomer of $C_{74}(CF_3)_{12}$, $C_{76}(CF_3)_{12}$, and $C_{80}(CF_3)_{12}$, two abundant isomers of $C_{78}(CF_3)_{12}$ and $C_{82}(CF_3)_{12}$, and an indeterminate number of isomers of $C_{84}(CF_3)_{12}$. Using a combination of ^{19}F NMR spectroscopy, DFT calculations, and the structures and spectra of previously reported fullerene(CF_3)_n compounds, the most-probable structures of six of the seven isolated compounds were determined to be specific isomers of $C_2-(C_{74}-D_{3h})(CF_3)_{12}$, $C_5-(C_{76}-T_d(2))(CF_3)_{12}$, $C_2-(C_{78}-D_{3h}(5))(CF_3)_{12}$, $C_5-(C_{80}-C_{2v}(5))(CF_3)_{12}$, $C_2-(C_{82}-C_2(5))(CF_3)_{12}$, and $C_2-(C_{82}-C_2(3))(CF_3)_{12}$ containing ribbons and/or loops of edge-sharing *para*- $C_6(CF_3)_2$ hexagons. The seventh isolated compound is a C_1 isomer of $C_{78}(CF_3)_{12}$ containing two such ribbons. This set of compounds represents only the second reported isolable compound with the hollow $C_{74}-D_{3h}$ cage and the first experimental evidence for the existence of the hollow fullerenes $C_{76}-T_d(2)$, $C_{78}-D_{3h}(5)$, $C_{80}-C_{2v}(5)$, and $C_{82}-C_2(5)$ in arc-discharge soots.

Introduction

The hollow carbon polyhedra known as fullerenes^{1–3} range in size from C_{20} to cages with over 400 carbon atoms.^{4,5} Only a tiny fraction of the geometrically possible isolated-pentagon-rule (IPR) hollow fullerene cages have been isolated and characterized.^{6–12} The first two decades of hollow (i.e., non-

endohedral) fullerene research were focused almost exclusively on soluble hollow fullerenes, especially with respect to exohedral derivatization^{2,13,14} (see Supporting Information (SI) for additional references). However, it is generally believed that a considerable number of insoluble hollow higher fullerenes (HHFs) are also present in the soots, waiting to be discovered. Their insolubility has been attributed to their covalently linked polymeric nature, which is believed to be due to their small (or zero) HOMO–LUMO gaps.^{15,16}

In 1993, Yeretjian and co-workers reported (i) that the yield of insoluble C_{74} in soots was similar to the yields of soluble HHFs C_{2n} with $2n > 74$ and (ii) that C_{74} was sufficiently stable to be sublimed.¹⁷ In 1998, Diener and Alford demonstrated that insoluble HHFs included C_{2n} isomers with all values of $2n$ from 74 to 104.¹⁶ They reported that insoluble small-gap and open-shell HHFs could be solubilized (and subsequently chromatographed) by electrochemical reduction to their respective closed-shell anions.¹⁶ A sample of C_{74} -enriched insoluble HHFs was subsequently fluorinated to yield $D_3-C_{74}F_{38}$, the first derivative

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of the elusive $C_{74}\text{-}D_{3h}$ cage (its structure was inferred from ^{19}F NMR spectra and quantum-chemical calculations at the DFT level of theory).¹⁸ We now report that high-temperature trifluoromethylation of a mixture of many insoluble HFFs resulted in the isolation of one or two relatively abundant isomers of the six compositions $C_{2n}(\text{CF}_3)_{12}$ ($2n = 74, 76, 78, 80, 82, 84$). Four of the compounds are derivatives of four hollow fullerene cages that have not been previously observed.

Results and Discussion

Fullerene(CF_3) $_n$ derivatives are more stable at higher temperatures than any other class of exohedral fullerene derivatives reported to date.¹⁹ For this reason, and because fullerene(CF_3) $_n$ derivatives are stable in organic solvents and can exhibit nearly fragmentation-free mass spectra,²⁰ trifluoromethylation seemed like the most appropriate way to produce a series of derivatized HFFs for detailed study. In addition, ^{19}F NMR spectroscopy in combination with DFT calculations has proven to be almost as useful as X-ray diffraction for structure elucidation of fullerene(CF_3) $_n$ compounds. This is because proximate CF_3 groups experience detectable through-space J_{FF} coupling and therefore indicate which CF_3 groups share the same hexagon.^{20,21}

Trifluoromethyl groups are sterically more demanding than CH_3 , Br, or even Ph substituents.^{22,23} For this reason, we tried to find reaction conditions that would lead to $\text{HHF}(\text{CF}_3)_{12}$ derivatives, anticipating that they would have one CF_3 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 $\text{HHF}(\text{CF}_3)_{12}$ 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 ^{19}F NMR spectroscopy.

The APCI mass spectra of HPLC-purified samples of a single isomer of $C_2\text{-}C_{74}(\text{CF}_3)_{12}$, $C_5\text{-}C_{76}(\text{CF}_3)_{12}$, $C_1\text{-}C_{78}(\text{CF}_3)_{12}$, and $C_5\text{-}C_{80}(\text{CF}_3)_{12}$, of $C_2\text{-}C_{82}(\text{CF}_3)_{12}\text{-}2$, and of a mixture of at least two isomers of $C_{84}(\text{CF}_3)_{12}$ are shown in Figure 1. The mass spectra of $C_2\text{-}C_{78}(\text{CF}_3)_{12}$ and $C_2\text{-}C_{82}(\text{CF}_3)_{12}\text{-}1$ (not shown) were similar to those of $C_1\text{-}C_{78}(\text{CF}_3)_{12}$ and $C_2\text{-}C_{82}(\text{CF}_3)_{12}\text{-}2$.

Fluorine-19 NMR spectra of seven of the new compounds are shown in Figure 2 (the amounts of individual isomers of $C_{84}(\text{CF}_3)_{12}$ present in the mixture are insufficient for detailed NMR study at this time). In addition, spectra of $S_6\text{-}C_{60}(\text{CF}_3)_{12}$ and an isomer of $C_1\text{-}C_{70}(\text{CF}_3)_{12}$ are included for comparison. (Contrary to the literature report,²⁴ we find that $S_6\text{-}C_{60}(\text{CF}_3)_{12}$ is soluble in benzene- d_6 .) The δ and J_{FF} values are similar to those for $C_{60}(\text{CF}_3)_n$ ($n = 2\text{--}10$),^{19,25} $S_6\text{-}C_{60}(\text{CF}_3)_{12}$ (NMR data

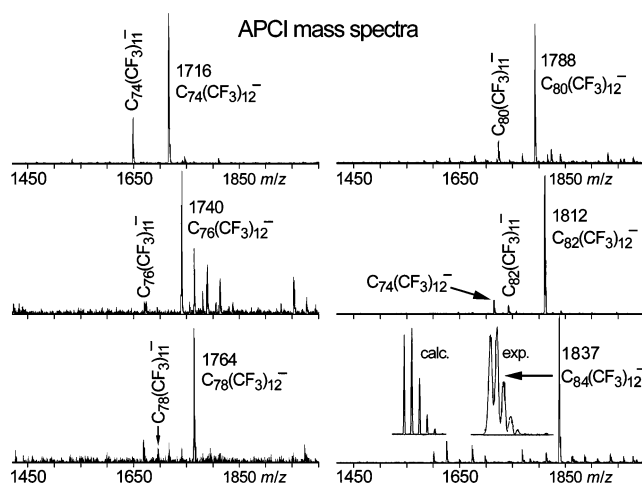


Figure 1. Atmospheric-pressure chemical-ionization mass spectra of $C_2\text{-}C_{74}(\text{CF}_3)_{12}$, $C_5\text{-}C_{76}(\text{CF}_3)_{12}$, $C_1\text{-}C_{78}(\text{CF}_3)_{12}$, $C_5\text{-}C_{80}(\text{CF}_3)_{12}$, $C_2\text{-}C_{82}(\text{CF}_3)_{12}\text{-}2$, and a mixture of isomers of $C_{84}(\text{CF}_3)_{12}$.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

reported here for the first time), $C_{70}(\text{CF}_3)_n$ ($n = 2\text{--}10$),^{20,21} $C_1\text{-}C_{70}(\text{CF}_3)_{12}$ (NMR data reported here for the first time),^{26,27} and two isomers of $Y@C_{82}(\text{CF}_3)_5$,²⁸ all of which have been structurally characterized by ^{19}F NMR/DFT or by X-ray crystallography. We have applied the structural principles consistently observed for virtually all previously reported fullerene(CF_3) $_n$ addition patterns and their associated ^{19}F NMR spectra, plus new DFT-predicted relative ΔH_f° values and HOMO–LUMO gaps and other geometric principles, to determine the most likely structures for six of the seven new compounds.

The structural principles are (i) addition patterns are ribbons or loops of edge-sharing m - and p - $C_6(\text{CF}_3)_2$ hexagons, occasionally with an isolated p - $C_6(\text{CF}_3)_2$ hexagon added, (ii) ribbons always end with a p - $C_6(\text{CF}_3)_2$ hexagon, never with a m - $C_6(\text{CF}_3)_2$ hexagon, and always end with a p^3 or pmp sequence, never with an mpp sequence, (iii) CF_3 groups that have eclipsed or nearly eclipsed conformations with respect to the cage have $-\delta(^{19}\text{F})$ values less than 60 (examples are $C_1\text{-}p^7mp\text{-}C_{70}(\text{CF}_3)_{10}$ ($-\delta = 59.2$ for a nearly eclipsed CF_3 group)^{19,21} and two isomers of $C_1\text{-}p^4\text{-}Y@C_{82}(\text{CF}_3)_5$ ($-\delta = 52.8\text{--}53.1$ for four CF_3 groups predicted to be eclipsed in DFT-optimized structures),²⁸ note that the spectrum of $C_1\text{-}C_{70}(\text{CF}_3)_{12}$ has no $-\delta$ values less than 60 (the lowest value is 61.3), and its structure has no CF_3 group with a CCCF torsion angle less than 14°),²⁶ (iv) 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,^{19,29} (v) for $n \leq 12$, two CF_3 groups are very rarely on adjacent cage carbon atoms (only one example is known³⁰) or on the same pentagon (only one example is known¹⁹), and (vi) CF_3 groups are not attached to

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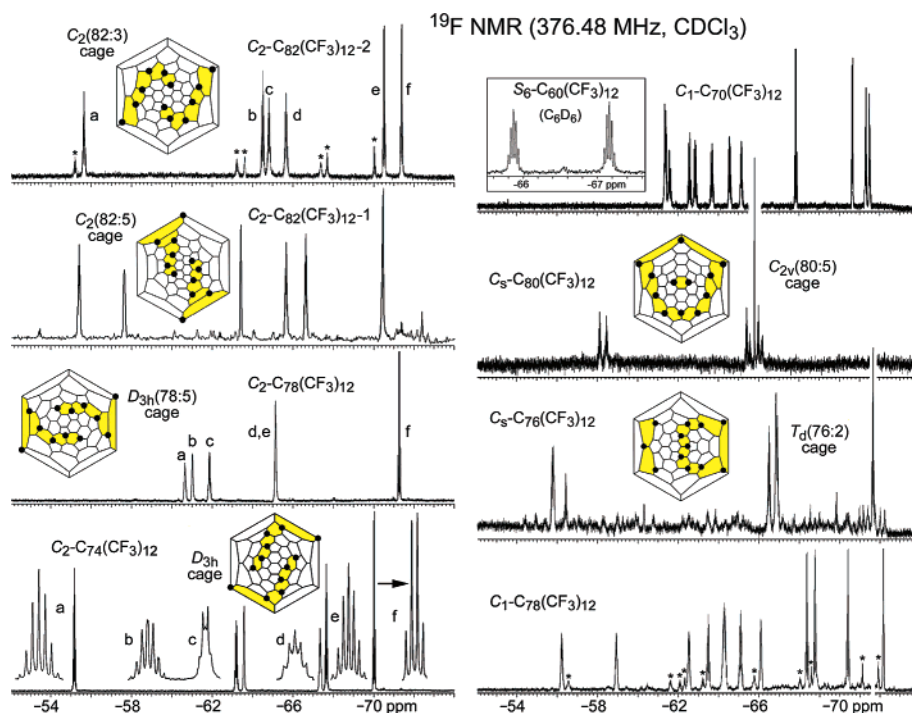


Figure 2. 376.5 MHz ^{19}F NMR spectra (chloroform-*d* except as noted), 25 °C, C_6F_6 int. std. ($\delta -164.9$) of (left bottom to top) $\text{C}_2\text{-C}_{74}(\text{CF}_3)_{12}$ (I), $\text{C}_2\text{-C}_{78}(\text{CF}_3)_{12}$ (II), $\text{C}_2\text{-C}_{82}(\text{CF}_3)_{12-1}$ (III), $\text{C}_2\text{-C}_{82}(\text{CF}_3)_{12-2}$ (IV), and (right bottom to top) $\text{C}_1\text{-C}_{78}(\text{CF}_3)_{12}$ (V), $\text{C}_5\text{-C}_{76}(\text{CF}_3)_{12}$ (VI), $\text{C}_5\text{-C}_{80}(\text{CF}_3)_{12}$ (VII), $\text{C}_1\text{-C}_{70}(\text{CF}_3)_{12}$, and $\text{S}_6\text{-C}_{60}(\text{CF}_3)_{12}$ (benzene-*d*₆). The structure of I was confirmed by X-ray crystallography (to be published elsewhere) and is shown as a Schlegel diagram. The most likely structures of II–IV, VI, and VII are also shown as Schlegel diagrams. The multiplets marked with asterisks in the spectrum of IV are due to a small amount of I in the sample. The multiplets marked with asterisks in the spectrum of V may be due to another isomer of $\text{C}_1\text{-C}_{78}(\text{CF}_3)_{12}$.

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.³¹ In fact, no exohedral derivative of any hollow fullerene with 18 or fewer substituents has an sp^3 THJ, including $\text{C}_{70}(\text{CF}_3)_{14}$ (four isomers),³² $\text{C}_{70}(\text{CF}_3)_{16,18}$ (one isomer each),³³ $\text{C}_{70}\text{Cl}_{16}$ (two isomers),³⁴ and $\text{C}_{78}\text{Br}_{18}$ (two isomers).³⁵ The situation is more complicated for exohedral derivatization of endohedral metallofullerenes, but even here the few known cycloadducts with an sp^3 THJ rearrange at 130–160 °C to (presumably more stable) isomers with no sp^3 THJs.^{36,37}

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 the one on the left in the top of Figure 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

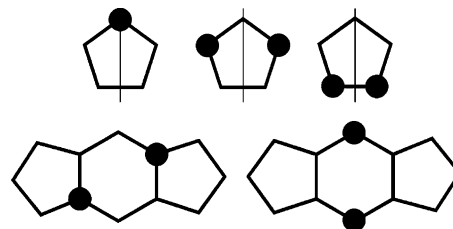


Figure 3. (Top) Three possible situations for attachment of substituents to fullerene pentagons that sit on a plane of symmetry. The symmetry plane is depicted as a thin vertical line. Only the situation on the left is possible for fullerene(CF_3)₁₂ derivatives if two CF_3 groups are not on adjacent carbon atoms and if two CF_3 groups do not share the same pentagon. (Bottom) Two possible situations for a pair of substituents to share a fullerene hexagon through which passes a perpendicular C_2 symmetry axis. Only the situation on the left is possible for fullerene(X)_n derivatives if the substituents are not attached to triple-hexagon junctions.

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 $p\text{-C}_6(\text{CF}_3)_2$ hexagon in the middle of the ribbon that lies on the C_2 axis, as shown at the bottom of Figure 3 (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. Finally, very few of the IPR cages for $\text{C}_{74}\text{--C}_{82}$ 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 $\text{C}_{82}(\text{CF}_3)_{12}$ 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

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symmetry. Therefore, C_1 symmetry will not be considered further for the compounds isolated in this work.

C_2 - $C_{74}(\text{CF}_3)_{12}$ (I). The only IPR isomer of C_{74} has D_{3h} symmetry and is not soluble in organic solvents.^{1,16} The ^{19}F NMR spectrum of **I** consists of five multiplets based on quartets of quartets (some are apparent septets)^{19,20} plus one simple quartet, all of equal intensity. This requires a single ribbon of 11 edge-sharing $C_6(\text{CF}_3)_2$ 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 2 (and proven by X-ray diffraction) 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 **I**, underscoring the instability of isomers with substituents on THJs. Compound **I** is only the second stable exohedral derivative of C_{74} to be reported (D_3 - $C_{74}\text{F}_{38}$ was the first¹⁸). Significantly, it can be prepared in ca. 25 mg batches with 97+% purity. The preliminary X-ray structure cannot be published at this time because the data are of insufficient quality. However, the data clearly show the idealized D_{3h} cage and the proposed C_2 - p^{11} single-ribbon addition pattern.

The ^{19}F multiplets are labeled **a–f**. Quartet **f** arises from the terminal CF_3 groups. The 2D-COSY ^{19}F NMR spectrum of **I** indicated that the ribbon sequence is **f**→**b**→**e**→**a**→**d**→**c**→**c'**→ etc. The X-ray and DFT-optimized structures of **I** both show that the pair of CF_3 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 (see SI for details). Fully eclipsed CF_3 groups are uncommon in $C_{60,70}(\text{CF}_3)_n$ structures (see SI for a complete list of X-ray structure references). In harmony with the guidelines, multiplet **a** has a $-\delta$ value of 55.2, well below the threshold value of 60.

Finally, the electronic spectrum of a dichloromethane solution of **I**, which is yellow in color, has weak bands at 430 nm (2.88 eV) and 400 nm and an intense band at 280 nm. The DFT-predicted HOMO–LUMO gap for **I** is 2.17 eV. Because all of the new compounds are yellow to red-orange in color, we tentatively assume that any isomer of the new compositions that does not have a DFT-predicted gap of at least 1.0 eV is not a viable isomer (see SI for more details).

C_2 - $C_{78}(\text{CF}_3)_{12}$ (II). There are five IPR isomers of C_{78} ,¹ three of which are known to be soluble: C_{78} - $D_3(1)$; C_{78} - $C_{2v}(2)$; and C_{78} - $C_{2v}(3)$.^{7,9} The ^{19}F NMR spectra of **II** and **I** are topologically congruent, so **II** also has a single ribbon with either C_2 or C_s symmetry (none of the IPR C_{78} cages has an inversion center). Applying the guidelines narrows the list of potential isomers to three, one each derived from C_{78} - $D_3(1)$, C_{78} - $D_{3h}(4)$, and C_{78} - $D_{3h}(5)$. The isomer derived from soluble C_{78} - $D_3(1)$, viz., C_2 - $pmpmp^3mpmp$ - $(C_{78}$ - $D_3(1))(\text{CF}_3)_{12}$, can be ruled out on the basis of its DFT-predicted HOMO–LUMO gap of only 0.91 eV. The isomer C_s - $pmpmp^3mpmp$ - $(C_{78}$ - $D_{3h}(4))(\text{CF}_3)_{12}$ can be ruled out in part because the C_{78} - $D_{3h}(4)$ cage is predicted to be 109 kJ mol⁻¹ less stable than the lowest energy cage, C_{78} - $C_{2v}(3)$, and 83 kJ mol⁻¹ less stable than C_{78} - $D_{3h}(5)$.³⁸ Furthermore, its DFT-optimized structure is not consistent with the ^{19}F NMR δ values. Therefore, the most probable structure of **II** is C_2 - p^{11} - $(C_{78}$ - $D_{3h}(5))(\text{CF}_3)_{12}$ (see SI for details), the first exohedral derivative of hollow C_{78} - $D_{3h}(5)$ to be isolated and characterized. This is the

first experimental evidence that the hollow fullerene C_{78} - $D_{3h}(5)$ does exist in arc-discharge soots.

C_2 - $C_{82}(\text{CF}_3)_{12}$ -1 (III). There are nine IPR isomers of C_{82} .¹ The predominant soluble isomer, which has been characterized by ^{13}C NMR spectroscopy, is C_{82} - $C_2(3)$.^{7,8} The ^{19}F NMR spectrum of **III** consists of six equal-intensity apparent septets or unresolved multiplets (two are accidentally isochronous) including one quartet. It is congruent with the spectra of **I** and **II** 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 four potential isomers of **III** are considered in the SI and narrowed down to one on the basis of the fact that three of them have DFT HOMO–LUMO gaps ≤ 0.55 eV. The remaining isomer, with a DFT-predicted HOMO–LUMO gap of 1.80 eV, is C_2 - p^{11} - $(C_{82}$ - $C_2(5))(\text{CF}_3)_{12}$, and is therefore the most likely structure of **III**. Two of the ^{19}F NMR multiplets have $-\delta$ values below 60. The DFT-optimized structure of C_2 - p^{11} - $(C_{82}$ - $C_2(5))(\text{CF}_3)_{12}$ correctly shows that two pairs of CF_3 groups are nearly eclipsed (CF_3 torsion angles ($\text{tors}(\text{CCCCF})$) of 6° for one pair and 14° for the other; see SI for details).

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.⁸ As far as we are aware, C_{82} - $C_2(5)$ is not one of the known, soluble isomers of C_{82} . Furthermore, no exohedral derivatives of hollow C_{82} - $C_2(5)$ have been reported, and the only endohedral compound that is claimed to have the C_{82} - $C_2(5)$ cage is one of three isomers of $\text{Tm}@C_{82}$.³⁹ Therefore, the compound C_2 - p^{11} - $(C_{82}$ - $C_2(5))(\text{CF}_3)_{12}$ is the first experimental evidence for the presence of the hollow fullerene C_{82} - $C_2(5)$ in arc-discharge soots.

C_2 - $C_{82}(\text{CF}_3)_{12}$ -2 (IV). Like the ^{19}F NMR spectra of **I**, **II**, and **III**, the spectrum of **IV** consists of six equal-intensity apparent septets or unresolved multiplets. However, two of them 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. Of all possible isomers of all nine C_{82} cages, only the isomer C_2 - p^5 , p^5 - $(C_{82}$ - $C_2(3))(\text{CF}_3)_{12}$ is consistent with the structural/geometric principles and the NMR data and has a HOMO–LUMO gap > 1 eV (its predicted gap is 2.08 eV; see SI for details). The 2D-COSY spectrum showed that the ribbon sequence is **f**→**c**→**a**→**b**→**d**→**e**, demonstrating that the third CF_3 group from one end of each ribbon should be eclipsed or nearly eclipsed (i.e., the $-\delta$ value for multiplet **a** is 55.7). The DFT-optimized structure of C_2 - p^5 , p^5 - $(C_{82}$ - $C_2(3))(\text{CF}_3)_{12}$ correctly shows that $\text{tors}(\text{CCCCF}) = 13^\circ$ for the third CF_3 group from the end of each ribbon. Therefore, C_2 - p^5 , p^5 - $(C_{82}$ - $C_2(3))(\text{CF}_3)_{12}$ is clearly the most probable structure of **IV**.

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 (see Experimental Section). 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-

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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 **I–VII** is not clear at this time.

$C_1-C_{78}(CF_3)_{12}$ (V). The ^{19}F NMR spectrum of **V** consists of 12 equal-intensity multiplets (the two at $\delta -63.3$ and -63.4 are nearly isochronous) including four quartets, requiring 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 **V**, is known to have an isolated hexagon.²⁷ The spectrum of **V** 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. The structure of $C_1-C_{78}(CF_3)_{12}$, including which of the five C_{78} cages is present, 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.

$C_s-C_{76}(CF_3)_{12}$ (VI). The two IPR isomers of [76]fullerene are $C_{76}-D_2(1)$ and $C_{76}-T_d(2)$,¹ and only the soluble D_2 empty cage was known to exist before this work.¹² The ^{19}F NMR spectrum of **VI** (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. 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 groups²⁴). 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 each⁴⁰). The DFT-optimized structure of $C_s-(C_{76}-T_d(2))(CF_3)_{12}$ is entirely consistent with the ^{19}F NMR δ values (see SI). This is the first experimental evidence for the existence of the $C_{76}-T_d(2)$ cage in arc-discharge soots, with or without the inclusion of endohedral atoms.

$C_s-C_{80}(CF_3)_{12}$ (VII). There are seven IPR isomers of C_{80} ,¹ but only $C_{80}-D_{5d}(1)$ and $C_{80}-D_2(2)$ are soluble and have been isolated and characterized.^{10,11} The ^{19}F NMR spectrum of **VII** is unusual for fullerene(CF_3)_n derivatives. 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 2. Its DFT-optimized structure is entirely consistent with the ^{19}F NMR δ values (see SI), and its HOMO–LUMO gap is 1.93 eV. This compound is the first exohedral derivative of hollow $C_{80}-C_{2v}(5)$ to be isolated and characterized as well as the first evidence for the existence of hollow $C_{80}-C_{2v}(5)$ in arc-discharge soots.

Summary and Conclusions

Seven new HHF derivatives $C_{2n}(CF_3)_{12}$ have been characterized by ^{19}F NMR spectroscopy and studied by DFT. Except for published mass spectra of complex, intractable mixtures of CF_3 derivatives of soluble HHFs,⁴¹ **I–VII** are the first HHF- $(CF_3)_n$ derivatives to be 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 $C_{82}-C_2(82:5)$. In ongoing work, we will obtain X-ray structures of as many of these compounds as possible and will prepare fullerene(CF_3)₁₂ derivatives of soluble HHFs as well as endohedral metallofullerenes.

Experimental Section

Fullerene-containing soot was generated by the standard direct-current arc-discharge of graphite rods (Poco Graphite, 6 in. length, 0.25 in. diameter, ca. 7 g) using a custom-built arc apparatus operating at 150 Torr of helium, 175 A, and 30 V. The fullerenes were sublimed from the raw arc-discharge soot at 750 °C and 10^{-3} Torr onto a cold finger inside the arc chamber. Using a Soxhlet extractor inside an argon-filled glovebox, the sublimate (a mixture of soluble and insoluble fullerenes, typically 400 mg per graphite rod), which had not been exposed to air, was washed with *o*-dichlorobenzene at 40 Torr and 100 °C until the washings were colorless. The remaining higher-fullerene-enriched residue was washed with hexane to remove any remaining *o*-dichlorobenzene and dried under vacuum. The Soxhlet extraction was repeated a second time. Yields of insoluble higher fullerenes prepared in this manner were typically 40 mg.

In a typical trifluoromethylation reaction, a sample of insoluble HHFs was mixed with copper powder and heated at 500 °C for 5 h in the presence of gaseous CF_3I in an apparatus previously described.¹⁹ The amounts of HHFs and copper powder used in 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 I_2 was removed under vacuum, processed by HPLC (10 mm i.d. \times 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(CF_3)₁₂ compounds that condensed in the cold zone of the reaction tube (the combined products from one of the 45 mg preparations and the 74 mg preparation) contained ca. 25% of **I** (ca. 30 mg), 3–5% of **II–VII**, and smaller amounts of $C_{2n}(CF_3)_{12}$ ($2n = 60, 70, 86, 88, 90, 92, 94, \text{ and } 96$).

Atmospheric-pressure chemical-ionization (APCI) mass spectra were recorded using a ThermQuest Finnigan LCQ-DUO spectrometer. Fluorine-19 NMR spectra were recorded using a Bruker INOVA-400 spectrometer (376.48 MHz, chloroform-*d* solutions, 25 °C, C_6F_6 internal standard ($\delta -164.9$)).

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DFT calculations were performed with the PBE functional⁴² and TZ2P-quality basis set implemented by the PRIRODA package.⁴³

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Note Added in Proof. A high-precision structure of **I**, verifying the structure proposed in this paper, has now been determined and has been submitted for publication elsewhere.

Supporting Information Available: Additional references and detailed analysis of the correlation of NMR chemical shifts with DFT-optimized CF₃ torsion angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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