Higher Fullerenes

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C_1-(C_{84}-C_2(11))(CF_3)$_{12}$: Trifluoromethylation Yields Structural Proof of a Minor C_{84} Cage and Reveals a Principle of Higher Fullerene Reactivity**

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The number of isolable molecular allotropes of carbon known as fullerenes[1] continues to grow each year. There are eight that have been unambiguously proven to exist by single-crystal X-ray diffraction studies of the bare cages or their derivatives (endohedral fullerenes are not considered here because their existence alone does not prove the independent existence of the corresponding hollow cage). These are C_{60} and C_{70},[2] C_{74}-D_{3h}(1),[3] C_{76}-D_2(1),[4] C_{78}-C_{2v}(2) and C_{78}-C_{2v}(3),[5] C_{78}-D_{3h}(5),[3] and C_{84}-D_{2d}(23)[6] (the parenthetical numbers are the isomer numbers listed in reference [1]). More than a dozen additional allotropes have been identified using NMR spectra of the bare cages[7,8] or derivatives,[9] including eight additional isolated-pentagon-rule (IPR)[1] isomers of C_{84}.[10–12]

Nevertheless, exohedral additions to fullerenes other than C_{60} and C_{70} (i.e., hollow higher fullerenes, HHFs) remain relatively unexplored because of the scarcity and high cost of pure HHFs, which are due to their low abundance in arc-generated soot and the laborious, multiple-cycle HPLC processing required. Even when supramolecular methodologies result in the isolation of fullerene mixtures enriched in particular compositions (e.g., C_{84}[13] or C_{94}/C_{96}[14]), extensive HPLC processing is still necessary if individual cage isomers are desired. In a few cases, relatively pure exohedral derivatives of HHF isomers have been isolated because the derivatives are easier to purify than the bare cages by fractional crystallization[6] or by HPLC.[9,15] In one case, subsequent removal of the substituents resulted in "pure" samples of three C_{84} cages.[15]

Progress in HHF derivatization is also hampered by the lower symmetry of most HHFs relative to C_{60} and C_{70}, which leads to a greater number of possible addition patterns for a given HHF(X)$_n$ composition and makes the interpretation of spectroscopic data much more challenging. Consider the addition of two groups to form a p-C_6X_2 hexagon on the fullerene without using triple-hexagon junctions (THJs; there are no examples of hollow fullerene(X)$_n$ compounds with substituents on THJs if $n < 38$, including $C_{76}Cl_{18}$[4] and two isomers of $C_{78}Br_{18}$;[5] two exceptions with $n = 38$ are $C_{70}F_{38}$[16] and $C_{74}F_{38}$[17]). One isomer can be made from C_{60}, four from C_{70}, five from C_{74}-D_{3h}(1), eight from C_{76}-D_2(1), and thirteen from C_{78}-C_{2v}(2) (a pair of enantiomers is counted as one addition pattern).

We recently reported that a complex mixture of insoluble HHFs can be trifluoromethylated with CF_3I and that the products contained seven HHF(CF_3)$_{12}$ derivatives that were 1) soluble in organic solvents, 2) stable in the presence of air and light and at elevated temperatures, and 3) easy to purify by HPLC.[9] The presence of multiple CF_3 groups, which generally form ribbons or loops of edge-sharing m- and/or p-$C_6(CF_3)_2$ hexagons on the fullerene surface when $n \leq 12$, makes ^{19}F NMR spectroscopy coupled with DFT-predicted relative energies and HOMO–LUMO gaps almost as powerful as X-ray crystallography for addition-pattern elucidation.[18,19] Chemical shifts, multiplet patterns, 2D COSY correlations, and "through-space" $^{5,6,7}J_{FF}$ values contain addition-pattern information that is not available when X = H, CH_3, Ph, Cl, Br, OR, NR_2, etc., especially when at least one element of symmetry is present.[20,21] In addition, there are now more than 40 fullerene(CF_3)$_n$ X-ray structures, and the vast majority of them with $n \leq 12$ do not have addition patterns with $C_5(CF_3)_2$ or $C_6(CF_3)_3$ moieties or with CF_3 groups on adjacent cage C atoms, and those that do exhibit telltale ^{19}F NMR signatures.[20,22] Finally, except for $C_{60}(CF_3)_n$ compounds, ribbons containing m-$C_6(CF_3)_2$ hexagons are uncommon for $n \leq 12$.[18,19]

We are now investigating the trifluoromethylation of soluble HHFs. A mixture of extractable fullerenes from which C_{60} and C_{70} had been removed by HPLC was treated with

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CF_3I at 520–550 °C in a hot tube (the general procedure was described previously[18–20]). HPLC purification of the products resulted in a number of $HHF(CF_3)_{8,10,12,14}$ compounds. Three of the isolated compounds were shown by APCI mass spectrometry to have the composition $C_{84}(CF_3)_{12}$. The isomer that is the subject of this paper is abbreviated **84-12-2**. The others will be reported in a full paper along with more than a dozen other $HHF(CF_3)_n$ derivatives.

The 1D and 2D COSY ^{19}F NMR spectra of the asymmetric compound **84-12-2** are shown in Figure 1. The six quartets, two of which have the same J_{FF} value, require some combination of three ribbons of $C_6(CF_3)_2$ hexagons or an isolated p-$C_6(CF_3)_2$ hexagon and two ribbons. The 2D spectrum revealed that the addition pattern has an isolated p-$C_6(CF_3)_2$ hexagon and separate ribbons of three and seven CF_3 groups (i.e., a 7+3+2 addition pattern). Given that an asymmetric $C_{84}(CF_3)_{12}$ compound could have any of the 24 IPR C_{84} cages, there are too many possible 7+3+2 isomers to consider them all in a reasonable computational study, even at a low level of theory (this would also be true even if the possible cages were limited to the nine known C_{84} isomers). Fortunately, **84-12-2** afforded well-ordered single crystals suitable for X-ray diffraction. The 7+3+2 structure, shown in Figure 2, contains the C_{84}-$C_2(11)$ cage, the first unambiguous proof of the existence of this fullerene, although it is believed to be the third most abundant C_{84} cage after C_{84}-$D_2(22)$ and C_{84}-$D_{2d}(23)$ and DFT calculations predict it to be the third most stable C_{84} cage.[23,24] The DFT-predicted HOMO–LUMO gap of **84-12-2** is 1.558 eV (see Supporting Information for more information about the DFT-optimized structure). Note that **84-12-2** has one CF_3 per pentagon, as is also the case for C_2-p^{11}-(C_{74}-$D_{3h}(1)$)-$(CF_3)_{12}$[3–5] (**74-12-1**) and C_2-p^{11}-(C_{78}-$D_{3h}(5)$)$(CF_3)_{12}$ (**78-12-1**).[3]

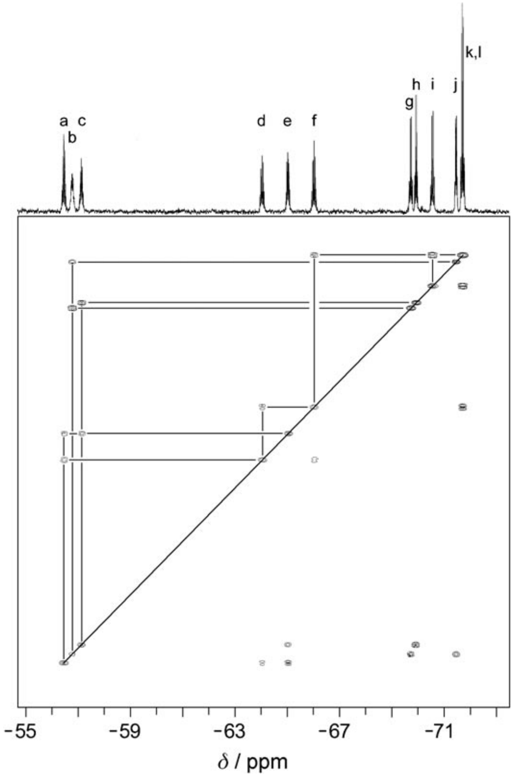

Figure 1. The 1D and 2D COSY ^{19}F NMR spectra of **84-12-2** (376.5 MHz; $CDCl_3$). The 2D spectrum demonstrates that the asymmetric compound has an isolated $C_6(CF_3)_2$ hexagon (CF_3 groups i and l), a ribbon of two edge-sharing $C_6(CF_3)_2$ hexagons (CF_3 groups j, b, g), and a ribbon of six $C_6(CF_3)_2$ hexagons (CF_3 groups k, f, d, a, e, c, h).

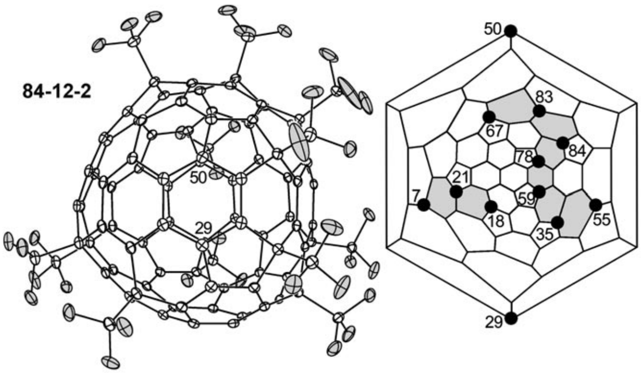

Figure 2. The X-ray structure (50 % probability ellipsoids) and a Schlegel diagram of C_1-p^6,p^2,p-(C_{84}-$C_2(11)$)$(CF_3)_{12}$ (**84-12-2**). The intramolecular F···F contacts between hexagon-sharing CF_3 groups, which are omitted for clarity, range from 2.535(2) to 2.923(2) Å.

The structures of **84-12-2**, **74-12-1**, **78-12-1**, and other $HHF(X)_n$ compounds with bulky substituents on ribbons of p-C_6X_2 hexagons[9] have revealed a fundamental and previously unappreciated aspect of HHF reactivity. One HHF reactivity principle that has been widely discussed is that cage C–C bonds between the most pyramidal C atoms (those C atoms with the largest θ_p angles ($\theta_p + 90°$ has been defined as the π-orbital axis vector (POAV) angle, a pyramidal figure of merit for fullerene C atoms)[1,25] are the most reactive bonds as far as HHF addition reactions are concerned.[8,26,27] (This is consistent with the observation that substituents do not add to THJs (the two exceptions cited above notwithstanding), and THJs are the least pyramidal C atoms in HHFs.) The tendency of substituents to add to large-θ_p C atoms appears to be valid for cycloadditions and other 1,2 additions, but it is not valid for ribbons of 1,4 additions, which are common for CF_3 groups[3,18,19] or large "non-cycloadduct" groups.[28,29] Another HHF principle is needed.

In more than 36 DFT-optimized HHFs we have examined, either previously[9] or for this paper, the shortest cage C–C bonds (i.e., bonds with the most double-bond character) are between C atoms that 1) include those with the largest θ_p values and 2) connect two pentagons (i.e., interpentagonal C–C bonds, or ICCBs; these are generally 1.35–1.40 Å). There are 12 ICCBs in the DFT-optimized C_{84}-$C_2(11)$ cage. The θ_p values for those 24 C atoms are the gray ovals in Figure 3a (the largest θ_p values are 11.7–11.5°). The 12 ICCBs remain 12 of the 18 shortest C–C bonds in **84-12-2** (their distances range from 1.350(2) to 1.384(2) Å), and therefore the CF_3 groups are attached to other C atoms which had smaller θ_p values in the bare cage (all but three had $\theta_p \leq 10.7°$ in the bare cage, and none had $\theta_p > 11.2°$). There are 15 ICCBs in **74-12-1** (see Schlegel diagram in Figure 3b).[3] These 30 C atoms have the highest θ_p values in DFT-optimized C_{74}-$D_{3h}(1)$ (they range

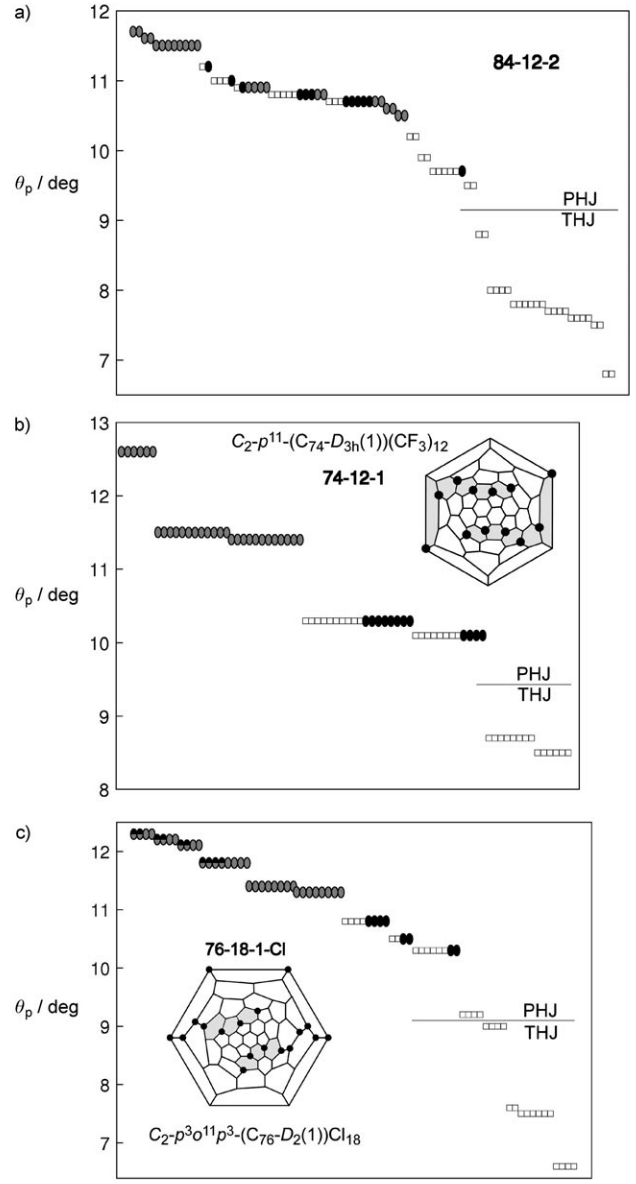

Figure 3. Plots showing the θ_p angles for each bare-cage C atom in a) C_{84}-C_2(11), b) C_{74}-D_{3h}(1), and c) C_{76}-D_2(1) (each oval or square represents one cage C atom in the bare HHF cages). Gray ovals represent the C atoms that make up the interpentagonal C–C bonds (ICCBs) in the bare cages and black ovals also represent the C atoms to which substituents are attached in the indicated fullerene(X)$_n$ derivative of that cage. There are ten Cl atoms on ICCB C atoms in **76-18-1-Cl**, and these are depicted as ovals that are half gray and half black. PHJ = pent-hex-hex junction C atoms, THJ = triple hexagon junction C atoms.

from 12.6° to 11.4°), as shown in Figure 3b. Significantly, the CF_3 groups in **74-12-1** are attached to cage C atoms which had the smallest θ_p values in the bare cage (not counting THJs), 10.3° and 10.1°.[3] The substituents are also on small-θ_p C atoms in **78-12-1**,[3] both isomers of $C_{78}Br_{18}$ characterized by X-ray diffraction[5] (all three of which also do not have contiguous C(sp^3) atoms; see Supporting Information for θ_p plots), an isomer of $C_{70}(CF_3)_6$,[19] both isomers of $C_{70}(CF_3)_8$,[19,30] an isomer of $C_{70}(CF_3)_{10}$,[19] and $C_{70}Br_{10}$.[31] However, the generality of this behavior (i.e., the "second" principle) and its possible underlying reason(s) have not been addressed in the literature until now.

The reasons are undoubtedly a combination of steric and electronic factors. Some possibilities are as follows. First, it is known that double bonds in pentagons (DBIPs) are destabilizing,[32,33] and we will assume that placing substituents on THJs is also destabilizing. If an HHF hexagon has three adjoining pentagons (like all hexagons in C_{60}) then it has three ICCBs, and any 1,4-addition produces a double bond in one of its adjoining pentagons. Second, if an HHF hexagon has two adjoining pentagons then it either has no ICCBs (if the pentagons are on opposite sides of the hexagon) or it has one ICCB, and in the latter case the ICCB C atoms are both *para* to THJs, and 1) the ribbon must end at the ICCB C atom or 2) a *m*-C_6X_2 hexagon would have to be formed. Clare and Kepert have shown that a longer ribbon of *m*- and/or *p*-C_6X_2 hexagons is more stable than several shorter ribbons or isolated *p*-C_6X_2 hexagons,[29] and we have shown that *m*-C_6X_2 hexagons produce very short, terminal DBIPs (see reference [18] for more details about terminal DBIPs). For example, the three shortest cage C–C bonds in an isomer of $C_{60}(CF_3)_{10}$ are DBIPs associated with *m*-C_6X_2 hexagons,[20] with distances that range from 1.339(3) to 1.343(3) Å. For comparison, none of the bonds common to a pentagon and a hexagon in **84-12-2** or **74-12-1** are shorter than 1.370(3) or 1.400(2) Å, respectively. Therefore, in general, the energetic advantage of converting the most pyramidal cage C(sp^2) atoms into C(sp^3) atoms bearing bulky substituents must be more than offset by the destabilization of creating shorter ribbons or DBIPs or sp^3 THJs. There are also other factors related to the conjugation of the remaining π system.[7,8]

It is not yet clear whether high-temperature additions of CF_3 groups to fullerenes are under kinetic or thermodynamic control (or both, depending on reaction conditions).[9,18,19] Therefore, even though we shall follow the terminology used in the literature[27] and refer to the new principle as a "reactivity principle" (which implies kinetic control), we hope that this term will be interpreted as being neutral about this issue until proven otherwise.

The recently published structure of $C_{76}Cl_{18}$ provides an interesting test of the new HHF addition-pattern principle described above because it has ten Cl atoms attached to a string of contiguous cage C(sp^3) atoms as well as a p^3 ribbon at each end of the string (see Schlegel diagram in Figure 3c).[4] The ten contiguous C(sp^3) atoms are those in ICCBs in DFT-optimized bare cage C_{76}-D_2(1) (and they have four of the largest θ_p values in bare cage C_{76}-D_2(1), 12.3–11.8°), but the eight p^3-ribbon C atoms are those that have three of the four smallest θ_p values in C_{76}-D_2(1) (not counting THJs), 10.8–10.3°, as shown in Figure 3c.

In summary, for reasons that are qualitatively sensible but remain to be investigated by future computational studies, when six or more bulky groups are added to hollow higher fullerenes, ribbons of *p*-C_6X_2 hexagons tend to form and the otherwise "most reactive" double bonds in the parent fullerene remain intact.

Experimental Section

The compound **84-12-2** was prepared using an apparatus previously described[18,19,34] from a 80 mg mixture of extractable (soluble) higher fullerenes and CF_3I at 520–550 °C. HPLC purification was carried out with a 250 mm × 10 mm ID Cosmosil Buckyprep column with 60:40 (v/v) toluene/heptane. Negative ion APCI MS and 1D ^{19}F NMR showed that the compositional purity and the isomeric purity, respectively, of **84-12-2** was greater than 98 % (ca. 3 mg of the purified compound were isolated form the mixture of products). X-ray diffraction data for **84-12-2** were obtained using a Bruker Kappa APEX II CCD diffractometer ($Mo_{K\alpha}$ $\lambda = 0.71073$ Å; graphite monochromator).[35] A semi-empirical absorption correction was applied using SADABS.[36] The structure was refined using SHELTXL.[37] DFT calculations were performed as previously described.[9,18,19]

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[35] Crystals of C_1-p^6,p^2,p-(C_{84}-$C_2(11)$)$(CF_3)_{12}$·2(toluene) were grown by slow evaporation of a saturated toluene solution: $0.17 \times 0.24 \times 0.60$ mm; triclinic; $P\bar{1}$; $a = 13.9099(5)$, $b = 14.6260(4)$, $c = 17.9550(6)$ Å, $\alpha = 89.851(2)$; $\beta = 82.939(2)$; $\gamma = 86.584(2)°$; $V = 3618.7(2)$ Å^3 ($Z = 2$); $\rho_{calcd} = 1.855$ Mg m^{-3}; $2\theta_{max} = 28.28°$; $-18 < h < 18$, $-19 < k < 19$, $-23 < l < 23$; $\lambda = 0.71073$ Å; $T = 100(1)$ K; no. reflections = 133 206; no. independent reflections = 17 774 (R(int) = 0.0324); restraints/parameters = 18/1346; full-matrix least-squares refinement on F^2; semi-empirical absorption correction from equivalents; μ = 0.173 mm^{-1}; final R indices ($I > 2\sigma(I)$) are $R_1 = 0.0439$ and $wR_2 = 0.1196$; largest diff. peak and hole = 0.799 and −0.637 Å^{-3}. CCDC 684847 (C_1-p^6,p^2,p-(C_{84}-$C_2(11)$)$(CF_3)_{12}$·2(toluene)) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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