Higher Fullerenes

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Crystal Structures of $C_{94}(CF_3)_{20}$ and $C_{96}(C_2F_5)_{12}$ Reveal the Cage Connectivities in C_{94} (61) and C_{96} (145) Fullerenes**

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Investigation of higher fullerenes and their derivatives is hampered not only by the small quantities of materials available but also because for each fullerene two or more cage isomers can exist that obey the Isolated Pentagon Rule (IPR).[1] Typically higher fullerenes and their mixtures are characterized by ^{13}C NMR spectroscopy of HPLC fractions which yields information on molecular symmetry but not always on definitive isomer cages.[2,3] Theoretical calculations provide information concerning the relative stability or the expected line distribution in the NMR spectra, thus assisting the cage assignment.[4–6]

Derivatization can help in characterizing higher fullerenes because their derivatives are easier to separate. In this way, metalation and chlorination of higher fullerenes contributed to the determination of cage connectivities in C_{76}–C_{80}, C_{84}, and C_{90}. Perfluoroalkylation followed by HPLC separation and X-ray structure determination of perfluoroalkyl (R^F) derivatives confirmed the cage connectivities in isomers of C_{76}–C_{78},[7] C_{84}–C_{88},[8,9] and C_{92}.[9] Experimental observations of even higher fullerenes, C_{94} and C_{96}, have been limited to ^{13}C NMR and UV/Vis spectra of the HPLC fractions containing isomer mixtures.[2,3,10] Here we report the synthesis, separation, and X-ray structure determination of R^F derivatives $C_{94}(CF_3)_{20}$ and $C_{96}(C_2F_5)_{12}$. The results provide direct proof of the cage connectivities of the highest fullerenes investigated so far, C_{94} and C_{96}, for which respectively 134 and 187 IPR isomers are possible.[1]

A mixture of higher fullerenes C_{76}–C_{96} (30 mg) also containing small amounts of C_{60} and C_{70} was allowed to react with excess CF_3I (98 %) in a glass ampoule at 400–420 °C and a pressure of roughly 6 bar for 3 days. The orange-colored sublimate that deposited in the colder part of the ampoule contained a complex mixture of CF_3 derivatives of C_{60}, C_{70}, and C_{76}–C_{96} according to MALDI MS analysis. The number of attached CF_3 groups ranged from 12 to 20. The mixture was partially dissolved in hexane and subjected to HPLC separation using a Cosmosil Buckyprep column (10 mm i.d., 25 cm length), hexane as the eluent (4.6 mL min^{-1}), monitored at the wavelength of 290 nm. Several fractions containing $C_{94}(CF_3)_n$ compounds were eluted between 4 and 38 min. The fraction eluting at 4.64 min contained $C_{94}(CF_3)_{20}$ as the main component. After an additional HPLC separation and recrystallization from a toluene/hexane mixture, small orange crystals were obtained which were investigated by X-ray diffraction with the use of synchrotron radiation.[11] The same reaction batch provided some other CF_3 compounds which were isolated and characterized by X-ray diffraction: $C_{84}(CF_3)_{12,16}$,[8b] $C_{86}(CF_3)_{16,18}$,[8c] $C_{88}(CF_3)_{18}$,[9] and $C_{92}(CF_3)_{16}$.[9]

The same mixture of higher fullerenes (15 mg) was allowed to react with excess C_2F_5I (98 %, Apollo) in a glass ampoule at 250 °C under a pressure of about 20 bar for 5 days. After the ampoule had been opened, the excess C_2F_5I and I_2 were removed by heating at 100 °C in air for 6 h. According to MALDI MS analysis, the deep-brown-colored product contained numerous C_2F_5 derivatives of C_{60}, C_{70} and higher fullerenes with the number of attached groups ranging from 8 to 12. The mixture was partially dissolved in hexane, and the solution was subjected to HPLC separation using the same column and hexane as the eluent (flow rate 4.6 mL min^{-1}). MALDI MS analyses of most fractions eluting between 8 and 27 min revealed the presence of $C_{96}(C_2F_5)_{12}$ as minor or trace components. Additional separation of the fraction eluting at 10.8 min followed by recrystallization from toluene yielded small crystals suitable for X-ray investigation.[11] X-ray diffraction study of crystals obtained from other chromatographic fractions allowed the structural determination of $C_{78}(C_2F_5)_{10}$[7c] and $C_{84}(C_2F_5)_{12}$ with different C_{84} cages.[8b]

The molecular structure of C_2-$C_{94}(CF_3)_{20}$ is shown in Figure 1 in two projections. A close look at the cage connectivity reveals the presence of the cage isomer C_2-C_{94}

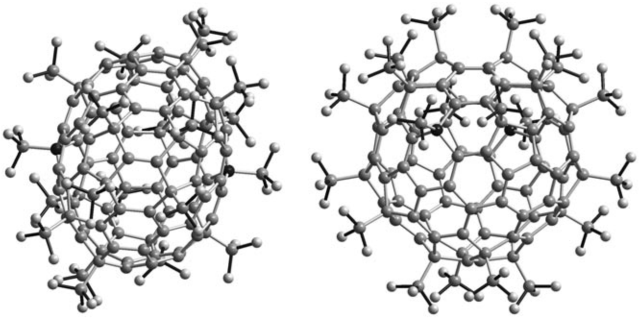

Figure 1. Molecular structure of C_2-$C_{94}(CF_3)_{20}$ shown along the twofold axis (left) and perpendicular to it (right). Two C atoms in black represent the attachment sites in THJ positions.

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(61) according to the previously proposed numbering system.[1] In preliminary notes, the C_{94} HPLC fraction was reported to contain two C_2 isomers on the basis of ^{13}C NMR spectra.[2a,b] Later on, a mixture containing four isomers of C_{94} was reported: C_2, C_s, C_2, and C_2.[3] Theoretical calculations of the relative energies of all 134 possible IPR isomers predict isomer 133 (C_2) to be the lowest in energy followed by isomers 42 (C_s), 37 (C_1), 44 (C_s), and 34 (C_1). Another theoretical approach resulted in the sequence: 133, 3 (C_2), 15 (C_1), 92 (C_1), and 42.[4] According to these data, isomer C_{94} (61) ranks between 18th and 20th in terms of stability, and the calculations of its relative amount in isomeric mixture over a wide temperature range did not change its position substantially. However, it ranked fourth when a combined B3LYP/6-31G*//SAM1 approach was used.[4b] Therefore, our finding does not contradict the former experimental data on isomer symmetry (C_2),[2] but it demonstrates rather poor agreement with most theoretical predictions. Nevertheless, the presence of CF_3 derivatives with other C_{94} cages is quite possible in other HPLC fractions.

In the $C_{94}(CF_3)_{20}$ molecule, the 20 CF_3 groups add in a C_2-symmetric fashion (Figure 2). All CF_3 groups are attached in edge-sharing *para* $C_6(R^F)_2$ hexagons with formation of three loops. There are three isolated "interpentagonal" C=C double bonds with an average bond length of 1.31 Å and two nearly flat benzenoid rings with an average C=C bond length of 1.40 Å. While 18 CF_3 groups are attached in positions of pentagon-hexagon-hexagon (PHH) junctions, two groups are attached in triple hexagon junctions (HHH or THJ) on the fullerene cage. The latter are believed to be poorly accessible for addition because of resulting local strain. However, additions at THJs become more probable in overcrowded molecules with a large number of addends. In fact, such additions were first found in two isomers of $C_{70}F_{38}$.[12] Because of the higher steric demand of bulkier CF_3 groups, the $C_{94}(CF_3)_{20}$ molecule can be regarded as overcrowded. For comparison, all other structurally characterized CF_3 derivatives of fullerenes (C_{60},[13] C_{70},[14] C_{86}[7c]), or C_{88}[9]) contain at most 18 attached groups. It should be noted that the average C-C-CF_3 angle at THJ positions (109.8°) is significantly smaller than at PHH junctions (112.5°) owing to the difference in cage curvature.

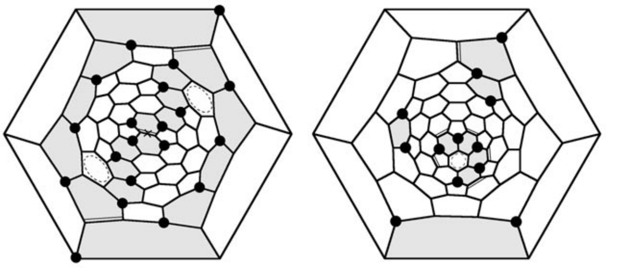
$C_{94}(CF_3)_{20}$ (61) $C_{96}(C_2F_5)_{12}$ (145)

Figure 2. Schlegel diagrams of C_2-$C_{94}(CF_3)_{20}$ and C_1-$C_{96}(C_2F_5)_{12}$ with black circles denoting the attached R^F groups. *para* $C_6(R^F)_2$ hexagons are highlighted in gray. Cage C=C double bonds and benzenoid fragments are indicated by double lines and dashed circles, respectively.

The C_1-$C_{96}(C_2F_5)_{12}$ molecule contains the carbon cage of isomer C_1-C_{96} no. 145 (Figure 3) according to the established numbering scheme.[1] The earlier experimental ^{13}C NMR data on the complex mixture of C_{96} isomers obtained by HPLC suggest the presence of four C_1 and three C_2 isomers as well as one of each C_s, D_2, and D_{3d} isomers, in order of decreasing abundance.[3]

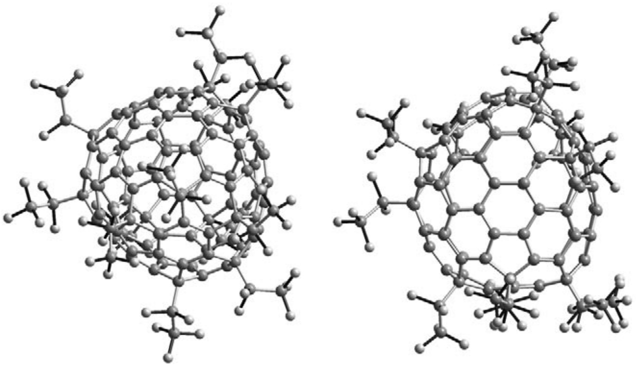

Figure 3. Two views of the C_1-$C_{96}(C_2F_5)_{12}$ molecule. The left view is given in the same orientation as in the Schlegel diagram in Figure 2, right.

Theoretical calculations for all 187 possible IPR isomers of C_{96} predict isomer 183 (D_2) to be most stable at low temperatures followed by isomers 181 (C_2), 144 (C_1), and 145.[5a] Significantly, calculations also showed that enthalpy–entropy interplay results in interchange of relative populations at higher temperatures so that above 2200 K the abundance sequence becomes $181 > 144 > 145 > 183$. Therefore, the correspondence between our result for isomer 145 and the previous experimental data as well as theoretical calculations can be considered satisfactory, especially if one takes into account the detection of $C_{96}(C_2F_5)_{12}$ compounds in other chromatographic fractions that might contain isomers with different C_{96} cages.

In contrast to CF_3 derivatives of fullerenes, derivatives with more than 12 C_2F_5 groups are unknown among pentafluoroethylated fullerenes produced by reactions at higher temperatures, apparently because of the greater steric demand of a C_2F_5 group. The addition of twelve C_2F_5 groups in the C_1-$C_{96}(C_2F_5)_{12}$ molecule is shown as a Schlegel diagram in Figure 2, right. All C_2F_5 groups in $C_{96}(C_2F_5)_{12}$ (with one group per cage pentagon) are attached in p-$C_6(C_2F_5)_2$ hexagons forming four domains isolated from each other (p^4,p^2,p,p notation). While addition of 12 CF_3 groups to fullerene cages proceeds mostly with formation of longer chains of edge-sharing $C_6(R^F)_2$ hexagons (as in $C_{60}(CF_3)_{12}$-II,[15a] $C_{70}(CF_3)_{12}$-I and -II,[16] and $C_{84}(11)(CF_3)_{12}$[8a]) or loops (as in $C_{60}(CF_3)_{12}$-I[15b]), bulkier C_2F_5 groups typically form shorter chains (as in $C_{84}(C_2F_5)_{12}$ with cage isomers 11, 18, 22, and 23[8b]). The carbon cage in C_1-$C_{96}(C_2F_5)_{12}$ is characterized by the presence of several C=C bonds with nearly double-bond character (average length 1.35 Å) and a benzenoid ring with an average C–C bond length of 1.41 Å.

In conclusion, perfluoroalkylation of mixtures of higher fullerenes followed by HPLC separation of R^F derivatives and X-ray structure determination has revealed, for the first time, the cage connectivities in the highest fullerene cages, C_{94} (isomer 61) and C_{96} (isomer 145), investigated so far. Further studies on the structures of higher fullerene derivatives are in progress.

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Keywords: cage connectivity · fullerenes · perfluoroalkylation · structure elucidation

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[1] P. W. Fowler, D. E. Manolopoulous, *An Atlas of Fullerenes*, Clarendon, Oxford, **1995**.

[2] a) Y. Achiba, K. Kikuchi, Y. Aihara, T. Wakabayashi, Y. Miyake, M. Kainosho in *Science and Technology of Fullerene Materials* (Eds.: P. Bernier, et al.), MRS Symposia Proceedings, Pittsburgh, **1995**, *359*, 3–9; b) Y. Achiba, K. Kikuchi, Y. Aihara, T. Wakabayashi, Y. Miyake, M. Kainosho in *The Chemical Physics of Fullerenes 10 (and 5) Years Later* (Ed.: W. Andreoni), Kluwer, Dordrecht, **1996**, pp. 139–147.

[3] T. Minami, Y. Miyake, K. Kikuchi, Y. Achiba, In: *The 18th Fullerene General Symposium*, The Fullerene Research Association of Japan, Okazaki, **2001**, p. 42.

[4] a) X. Zhao, Z. Slanina, H. Goto, E. Osawa, *J. Chem. Phys.* **2003**, *118*, 10534–10540; b) Z. Slanina, X. Zhao, F. Uhlik, S.-L. Lee, *J. Mol. Struct. (Theochem)* **2003**, *630*, 205–213.

[5] a) X. Zhao, Z. Slanina, H. Goto, *J. Phys. Chem. A* **2004**, *108*, 4479–4484; b) Z. Slanina, X. Zhao, F. Uhlik, S.-L. Lee, L. Adamowicz, *Int. J. Quantum Chem.* **2004**, *99*, 640–653.

[6] G. Sun, *Chem. Phys.* **2003**, *289*, 371–380.

[7] a) N. B. Shustova, I. V. Kuvychko, R. D. Bolskar, K. Seppelt, S. H. Strauss, A. A. Popov, O. V. Boltalina, *J. Am. Chem. Soc.* **2006**, *128*, 15793–15798; b) I. E. Kareev, A. A. Popov, I. V. Kuvychko, N. B. Shustova, S. F. Lebedkin, V. P. Bubnov, O. P. Anderson, K. Seppelt, S. H. Strauss, O. V. Boltalina, *J. Am. Chem. Soc.* **2008**, *130*, 13471–13489; c) N. B. Tamm, S. I. Troyanov, *Mendeleev Commun.* **2009**, *19*, 198–199.

[8] a) I. E. Kareev, I. V. Kuvychko, N. B. Shustova, S. F. Lebedkin, V. P. Bubnov, O. P. Anderson, A. A. Popov, O. V. Boltalina, S. H. Strauss, *Angew. Chem.* **2008**, *120*, 6300–6303; *Angew. Chem. Int. Ed.* **2008**, *47*, 6204–6207; b) N. B. Tamm, L. N. Sidorov, E. Kemnitz, S. I. Troyanov, *Chem. Eur. J.* **2009**, *15*, 10486–10492; c) S. I. Troyanov, N. B. Tamm, *Crystallogr. Rep.* **2009**, *54*, 598–602.

[9] N. B. Tamm, S. I. Troyanov, *Chem. Commun.* **2009**, 6035–6037.

[10] H. Richter, A. J. Labrocca, W. J. Grieco, K. Taghizadeh, A. L. Lafleur, J. B. Howard, *J. Phys. Chem. B* **1997**, *101*, 1556–1560.

[11] Data collection was performed on a MAR225 CCD detector at 100 K using synchrotron radiation at the BESSY storage ring ($\lambda = 0.9050$ Å, BL14.2, PSF of the Free University of Berlin, Germany). Structure solution and refinement with SHELXS97 and SHELXL97, respectively. $C_{94}(CF_3)_{20}\cdot C_6H_5(CH_3)\cdot C_6H_{14}$: $M = 2687.45$, monoclinic, $C2/c$, $a = 13.2480(6)$, $b = 43.6743(12)$, $c = 16.8236(6)$ Å, $\beta = 103.4909(15)°$, $V = 9465.5(6)$ Å^3, $Z = 4$, $wR_2 = 0.193$ (for 9931 reflections and 914 parameters), $R_1 = 0.068$ (for 6230 reflections with $I > 2\sigma(I)$). $C_{96}(C_2F_5)_{12}\cdot 1.5\,C_6H_5(CH_3)$: triclinic, $P\bar{1}$, $a = 15.415(1)$, $b = 16.002(1)$, $c = 20.698(1)$ Å, $\alpha = 108.687(3)$, $\beta = 90.439(3)$, $\gamma = 98.456(3)°$, $V = 4775.7(5)$ Å^3, $Z = 2$, $wR_2 = 0.197$ (for 17745 reflections and 1770 parameters), $R_1 = 0.074$ (for 10076 reflections with $I > 2\sigma(I)$). CCDC 742195, 742196 contain 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.

[12] a) P. B. Hitchcock, A. G. Avent, N. Martsinovich, P. A. Troshin, R. Taylor, *Chem. Commun.* **2005**, 75–77; b) P. B. Hitchcock, A. G. Avent, N. Martsinovich, P. A. Troshin, R. Taylor, *Org. Lett.* **2005**, *7*, 1975–1978.

[13] N. A. Samokhvalova, P. A. Khavrel, V. Yu. Markov, P. S. Samokhvalov, A. A. Goruynkov, E. Kemnitz, L. N. Sidorov, S. I. Troyanov, *Eur. J. Org. Chem.* **2009**, 2935–2938.

[14] S. M. Avdoshenko, A. A. Goryunkov, I. N. Ioffe, D. V. Ignat'eva, L. N. Sidorov, P. Pattison, E. Kemnitz, S. I. Troyanov, *Chem. Commun.* **2006**, 2463–2465.

[15] a) I. E. Kareev, N. B. Shustova, D. V. Peryshkov, S. F. Lebedkin, S. M. Miller, O. P. Anderson, A. A. Popov, O. V. Boltalina, S. H. Strauss, *Chem. Commun.* **2007**, 1650; b) S. I. Troyanov, A. Dimitrov, E. Kemnitz, *Angew. Chem.* **2006**, *118*, 2005–2008; *Angew. Chem. Int. Ed.* **2006**, *45*, 1971–1974.

[16] D. V. Ignat'eva, A. A. Goryunkov, N. B. Tamm, I. N. Ioffe, S. M. Avdoshenko, L. N. Sidorov, A. Dimitrov, E. Kemnitz, S. I. Troyanov, *Chem. Commun.* **2006**, 1778–1780.

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