

Five Isolated Pentagon Rule Isomers of Higher Fullerene C_{94} Captured as Chlorides and CF_3 Derivatives: $C_{94}(34)Cl_{14}$, $C_{94}(61)Cl_{20}$, $C_{94}(133)Cl_{22}$, $C_{94}(42)(CF_3)_{16}$, and $C_{94}(43)(CF_3)_{18}$

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Supporting Information

ABSTRACT: High-temperature chlorination and trifluoromethylation of C_{94} isomeric mixtures followed by single-crystal X-ray diffraction with the use of synchrotron radiation resulted in the structure determination of $C_{94}(34)Cl_{14}$, $C_{94}(61)Cl_{20}$, $C_{94}(133)Cl_{22}$, $C_{94}(42)(CF_3)_{16}$, and $C_{94}(43)(CF_3)_{18}$. Their addition patterns are stabilized by the formation of isolated C=C bonds and aromatic substructures. Four cage isomers of C_{94} (nos. 34, 42, 43, and 133) have been experimentally confirmed for the first time.

The investigation and even identification of higher fullerenes are hampered by their low abundance in the fullerene soot and the existence of many cage isomers.¹ Whereas ^{13}C NMR spectroscopy was successfully exploited for the unambiguous identification of several isomers of C_{84} , C_{86} , and C_{88} ,² this method failed for even higher fullerenes because of the existence of a larger number of isomers with the same symmetry. The use of direct diffraction methods is restricted because of the rotational/librational mobility of fullerenes in crystals. Therefore, cocrystallization with metal porphyrins is used to fix a fullerene cage in the crystal lattice that allowed structural studies of some empty higher fullerenes such as C_{86} , C_{90} , and C_{96} .³

An alternative identification method includes the derivatization of a fullerene or fullerene mixtures followed by the separation and structural characterization of individual derivatives. In this way, trifluoromethylation and chlorination not only resulted in the identification of several isomers of higher fullerenes (C_{90} and C_{96})⁴ and even giant fullerenes (C_{102} and C_{104})⁵ but also provided information concerning their reactivity.

For empty fullerene C_{94} with 134 topologically possible isolated pentagon rule (IPR) isomers,¹ experimental data on the isomeric composition is very scarce. Earlier, the ^{13}C NMR spectroscopic data on a C_{94} isomeric mixture was interpreted as the coexistence of four isomers with C_2 , C_s , C_2 , and C_2 symmetry.⁶ Two theoretical studies on C_{94} isomers pointed out isomer $C_{94}(133)$ as the system ground state but gave different stability orders of other isomers.⁷ The only experimental confirmation exists for isomer $C_{94}(61)$, structurally investigated as $C_{94}(61)(CF_3)_{20}$.⁸

Herein we report the isolation and structural characterization of CF_3 and chloro derivatives of five C_{94} isomers (nos. 34, 42, 43,

61, and 133), four of which were experimentally confirmed for the first time. The addition patterns are discussed in terms of the formation of stabilizing substructures on the carbon cages.

Trifluoromethylation of a C_{94} high-performance liquid chromatography (HPLC) fraction (ca. 6 mg) with gaseous CF_3I was carried out in a quartz ampule at 450 °C for 1.5 h following a procedure described previously.⁹ The product containing $C_{94}(CF_3)_{14-20}$ was dissolved in *n*-hexane and subjected to HPLC separation using a Buckyprep column (4.6 × 250 mm, Nacalai Tesque Inc.) and *n*-hexane as the eluent at 1.0 mL min⁻¹ flow rate. A total of 3 of the 33 fractions, with retention times of 4.7, 37.3, and 68.2 min, gave small crystals upon the slow removal of hexane or recrystallization from *p*-xylene. An X-ray diffraction study with the use of synchrotron radiation revealed respectively the structures of $C_{94}(61)(CF_3)_{20}$, $C_{94}(42)(CF_3)_{16}$, and $C_{94}(43)(CF_3)_{18}$,¹⁰ with the former being identified on the basis of the known unit cell parameters.⁸

In another series of studies, three C_{94} HPLC fractions (I–III; see the Supporting Information for details) were chlorinated with excess VCl_4 in thick-walled glass ampules at 350–360 °C for 6–12 weeks. Only the fraction $C_{94}(II)$ gave small crystals suitable for X-ray diffraction with the use of synchrotron radiation that revealed (in different chlorination experiments) the molecular structures of $C_{94}(34)Cl_{14}$, $C_{94}(61)Cl_{20}$, and $C_{94}(133)Cl_{22}$.¹⁰

The molecules of CF_3 and chloro derivatives of C_{94} are shown in Figure 1. A common feature of the cage isomers of $C_{1-}C_{94}(34)$, $C_s-C_{94}(42)$, and $C_2-C_{94}(43)$ is a group of four closely spaced pentagons that are connected by interpentagonal C–C bonds (ICCBs; see Figure 1d). The presence of this group is responsible for the pearlike shape of the carbon cages. Projection of the $C_{94}(42)(CF_3)_{16}$ molecule is given perpendicular to the mirror plane of the carbon cage so that small deviations from strict molecular C_s symmetry due to the asymmetric arrangement of five CF_3 groups can be seen. The $C_{94}(43)(CF_3)_{18}$ molecule possesses a small deviation from C_2 symmetry because of the asymmetric arrangement of two CF_3 groups and their turns around the C– CF_3 bonds.

The $C_2-C_{94}(61)Cl_{20}$ molecule has a symmetric addition pattern with an egglike C_2-C_{94} carbon cage, whereas the $C_{1-}C_{94}(133)Cl_{22}$ molecule deviates from C_2 symmetry because of a somewhat asymmetric chlorination pattern. In fact, two very

Received: December 30, 2014

Published: February 20, 2015

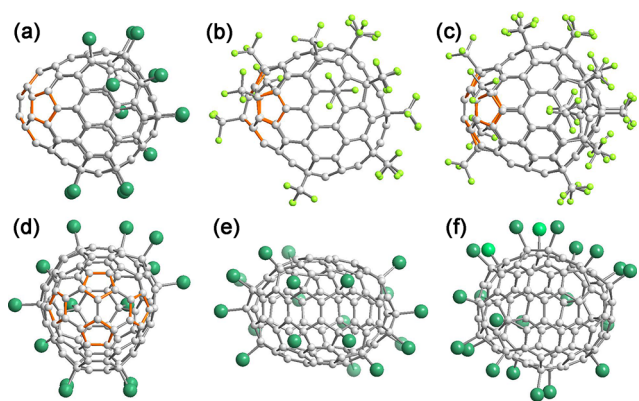


Figure 1. Projections of $C_{94}(34)Cl_{14}$ (a and d), $C_{94}(42)(CF_3)_{16}$ (b), $C_{94}(43)(CF_3)_{18}$ (c), $C_{94}(61)Cl_{20}$ (e), and $C_{94}(133)Cl_{22}$ (f) molecules. In parts a–d, four closely arranged pentagons are highlighted in orange. Two Cl atoms with partial occupancies in $C_{94}(133)Cl_{22}$ are shown in light green.

similar molecules, $C_{94}(133)Cl_{20}$ and $C_{94}(133)Cl_{22}$, overlap in the same crystallographic site, thus resulting in an averaged composition of $C_{94}Cl_{21.67}$. Such a kind of cocrystallization typical for polychloro derivatives of higher fullerenes has also been observed in the crystal structures of $C_{76}Cl_{24-34}$ and $C_{86}Cl_{18-22}$.¹¹

The addition patterns of five chloro and CF_3 derivatives of different C_{94} isomers can be discussed in more detail using Schlegel diagrams (Figure 2). The $C_1-C_{94}(34)Cl_{14}$ molecule

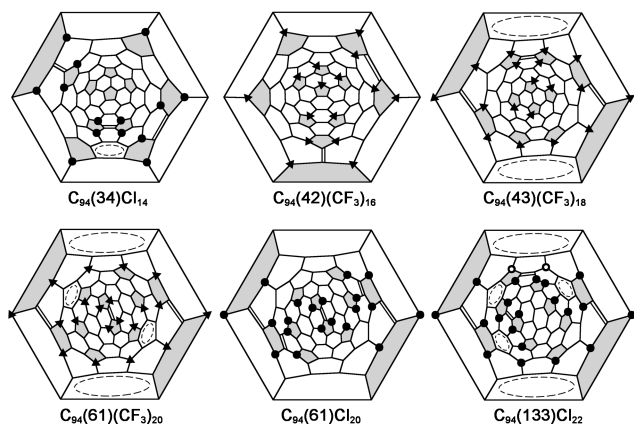


Figure 2. Schlegel diagrams of five new CF_3/Cl derivatives and the known $C_{94}(61)(CF_3)_{20}$.⁸ Cage pentagons are highlighted with gray. Black circles and triangles denote respectively the positions of the attached Cl atoms and CF_3 groups. The Schlegel diagram of $C_{94}(42)(CF_3)_{16}$ is presented parallel to the cage mirror plane; other diagrams [except for $C_{94}(34)Cl_{14}$] are oriented parallel to the cage C_2 axes. Isolated $C=C$ bonds and benzenoid rings are also indicated. The attachment positions of two Cl atoms with partial occupancies in $C_{94}(133)Cl_{22}$ are shown by empty circles.

possesses a remarkable chlorination pattern because 14 Cl atoms are distributed nonuniformly on the carbon cage, leaving 4 of 12 pentagons (those of a group of four) free from attachment. Instead, there are six pentagons bearing two Cl atoms each, thus contributing to the formation of three isolated double $C-C$ bonds and two (nearly) isolated benzenoid rings. Such relatively rare cases of fullerene chlorides with more than 12 Cl atoms and nonoccupied pentagons are also known for structures of $C_{88}(17)Cl_{16}$,¹² $C_{102}(258)Cl_{16}$,^{5b} and nonclassical $C_{96}Cl_{20}$.¹³

In $C_{94}(42)(CF_3)_{16}$, the arrangement of only 11 of 16 CF_3 groups obeys the mirror symmetry of the pristine C_s-C_{94} cage. All 12 pentagons are occupied, resulting in the formation of two isolated $C=C$ bonds and one benzenoid ring. Two C atoms of ICCBs in a group of four bear CF_3 groups. Similar examples are known in the structures of $C_{76}(1)(CF_3)_{14-18}$ and $C_{84}(5)-(CF_3)_{16}$,¹⁴ whereas ICCBs remain free from attachments in numerous $C_{84}(CF_3)_{12-20}$ structures of other isomers of C_{84} .⁹

In $C_{94}(43)(CF_3)_{18}$, the attachment of 16 CF_3 groups follows C_2 symmetry of the pristine $C_2-C_{94}(43)$ cage. There are three isolated $C=C$ bonds and two benzenoid rings. Contrary to the case of $C_{94}(42)(CF_3)_{16}$, no ICCB bears CF_3 groups.

The structure of $C_2-C_{94}(61)Cl_{20}$ is particularly interesting because the structure of $C_2-C_{94}(61)(CF_3)_{20}$ is also known. Two structures have 16 attachment positions in common. While $C_2-C_{94}(61)Cl_{20}$ contains five isolated $C=C$ bonds on the carbon cage, the $C_2-C_{94}(61)(CF_3)_{20}$ molecule has only three such bonds supplemented with four benzenoid rings as stabilizing structural fragments of the enhanced local aromaticity. An unusual feature of $C_2-C_{94}(61)(CF_3)_{20}$ is the attachment of two CF_3 groups in the positions of triple hexagon junctions (THJs) probably because of the simultaneous formation of two isolated benzenoid rings. Whereas no THJ is occupied in $C_2-C_{94}(61)Cl_{20}$, two pairs of Cl atoms are attached in adjacent positions, a feature that is typically avoided for the addition of larger CF_3 groups.

In $C_{94}(133)Cl_{22}$, 18 of 22 CF_3 groups are attached symmetrically on the $C_2-C_{94}(133)$ carbon cage, whereas four others destroy the C_2 symmetry. There are four isolated $C=C$ bonds and five benzenoid rings as stabilizing fragments. Only one pair of Cl atoms is attached in the ortho position in both the $C_{94}(133)Cl_{20}$ and $C_{94}(133)Cl_{22}$ molecules.

In all investigated structures, the $C-C$ distances on the carbon cages lie in a wide range of values dependent on the addition patterns. Isolated $C=C$ bonds are the shortest, with typical lengths of 1.31–1.33 Å. The average $C-C$ bond lengths of benzenoid rings are in the narrow range of 1.39–1.40 Å, whereas the longest $C-C$ bonds of the sp^3-sp^3 type, 1.58–1.59 Å, are present only in the $C_{94}(61)Cl_{20}$ and $C_{94}(133)Cl_{22}$ molecules. The $C-Cl$ bonds in the structures of chlorides have a typical average length of 1.82 Å, whereas the $C-CF_3$ bonds in CF_3 derivatives are, on average, 1.55 Å in length.

Density functional theory calculation of the average energy of $C-Cl$ bonds in the C_{94} chlorides with 14, 20, and 22 attached Cl atoms gave respectively the values of +7.2, +4.1, and +4.2 kJ mol⁻¹ relative to the standard value for $D_{3d}C_{60}Cl_{30}$.¹⁵ These results confirm the general trend: a decrease of the average $C-Cl$ energy with increasing number of attached Cl atoms irrespective of the carbon cage size.^{11a,12}

It is instructive to compare a set of C_{94} isomers confirmed in the present study with theoretical predictions based on calculations of the relative formation energies.⁷ Two quantum-chemical studies were performed initially with four different semiempirical methods for the full set of 134 isomers of C_{94} followed by ab initio calculations for selected cages at the HF/4-31G and B3LYP/6-31G* levels. Although isomer $C_{94}(133)$ showed the highest stability in both treatments, further stability orders were significantly different: 133 > 3 > 15 > 92 > 42 > 43 (HF/4-31G)^{7b} and 133 > 42 > 43 > 61 > 34 (B3LYP/6-31G*).^{7a} It is evident that only the latter theoretical prediction is adequately confirmed by our experimental findings. Moreover, our data correlate well with the former conclusions concerning the molecular symmetry of the cages (C_2 , C_s , C_2 , and C_2) that are present in the C_{94} fraction.⁶

It is worth noting that three experimental isomers of C_{94} , nos. 34, 42, and 43, all containing a closely arranged group of four pentagons in the carbon cage, are interrelated with each other by only two Stone–Wales rearrangements (SWRs), i.e., a rotation of a C–C bond in a pyraclyene patch by 90° (Figure 3a). The

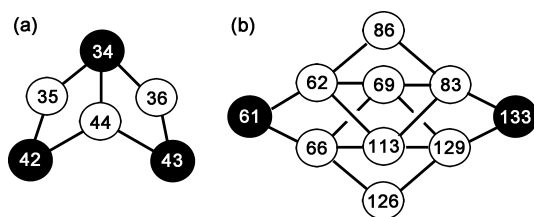


Figure 3. Interconnection between the experimental isomers of C_{94} (black circles). Each line represents a single SWR of the pyraclyene type.

intermediate isomers, $C_{1-C_{94}}$ (35), $C_{1-C_{94}}$ (36), and $C_{5-C_{94}}$ (44), possess a relatively low formation energy^{7a} and, therefore, can participate in the establishment of equilibrium in the C_{94} isomeric mixture at high temperatures of fullerene synthesis so that their presence in the fullerene soot cannot be excluded. Therefore, these isomers, together with isomers 42 and 43, are possible candidates for fractions C_{94} (I) and C_{94} (III).

In contrast, the experimental fullerenes C_{94} (61) and C_{94} (133) are interconnected by four SWRs (Figure 3b), and all intermediates have high relative formation energy so that their presence in the fullerene soot is less probable. Notably, two groups of C_{94} isomers shown in Figure 3 cannot be transformed into each other by any number of SWRs.

In summary, the chlorination and trifluoromethylation of pristine C_{94} fullerene followed by structure determination of the derivatives revealed the existence of five C_{94} isomers (nos. 34, 42, 43, 61, and 133) in the fullerene soot. These findings are in good agreement with the theoretical prediction of the most stable isomers of C_{94} .^{7a} Thus, the derivatization of higher fullerenes supplemented by separation and structure determination is proven again as a reliable method for the establishment of the identity of fullerene isomers even in cases of their minute amounts.

■ ASSOCIATED CONTENT

■ Supporting Information

Data on the isolation of C_{94} fractions and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants 21132007, 21371164, and 21311120060), National Basic Research Program of China (Grant 2011CB921401), and Russian Foundation for Basic Research (Grants 15-03-04464 and 13-03-91162).

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- (10) Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2, PFS, Berlin, Germany) using a MAR225 CCD detector; $\lambda = 0.8731\text{--}0.9050$ Å. $C_{94}(34)Cl_{14}$: monoclinic, $P2_1/n$, $a = 12.404(1)$ Å, $b = 22.166(1)$ Å, $c = 20.763(1)$ Å, $\beta = 93.37(1)^\circ$, $V = 5698.9(6)$ Å³, $Z = 4$, $R1(F)/wR2(F^2) = 0.075/0.164$ for 5302/11885 reflections and 973 parameters. $C_{94}(42)(CF_3)_{16}n-C_6H_{14}$: monoclinic, $P2_1/c$, $a = 14.427(1)$ Å, $b = 22.370(1)$ Å, $c = 26.087(2)$ Å, $\beta = 103.584(10)^\circ$, $V = 8183.6(9)$ Å³, $Z = 4$, $R1(F)/wR2(F^2) = 0.075/0.194$ for 11264/17822 reflections and 1479 parameters. $C_{94}(43)(CF_3)_{18}1.16p-C_8H_{10}$: monoclinic, $P2_1/n$, $a = 14.483(1)$ Å, $b = 27.830(2)$ Å, $c = 21.466(1)$ Å, $\beta = 91.513(10)^\circ$, $V = 8649.1(10)$ Å³, $Z = 4$, $R1(F)/wR2(F^2) = 0.057/0.146$ for 11124/17123 reflections and 1644 parameters. $C_{94}(61)Cl_{20}$: orthorhombic, $Pbca$, $a = 19.196(1)$ Å, $b = 16.520(1)$ Å, $c = 40.749(3)$ Å, $V = 12922.2(14)$ Å³, $Z = 8$, $R1(F)/wR2(F^2) = 0.057/0.146$ for 11615/14650 reflections and 1027 parameters. $C_{94}(133)Cl_{21.67}$: monoclinic, $C2/c$, $a = 35.685(3)$ Å, $b = 20.281(1)$ Å, $c = 21.358(2)$ Å, $\beta = 122.417(9)^\circ$, $V = 13048.6(18)$ Å³, $Z = 8$, $R1(F)/wR2(F^2) = 0.048/0.126$ for 10347/13322 reflections and 1046 parameters.
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