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Synthesis and X-ray structure of C_2-C_{96}(176)(CF_3)$_{18}$

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C_2-C_{96}(176)(CF_3)$_{18}$ was isolated by HPLC from the trifluoromethylation products of a mixture of C_{94} and C_{96} fullerenes and its structure was determined by single crystal X-ray diffraction. The trifluoromethylation pattern is characterized by the additions in edge-sharing *para* $C_6(CF_3)_2$ hexagons and the presence of stabilizing benzenoid rings and isolated C=C bonds on the fullerene cage.

Among the higher fullerenes of fullerene soot, C_{96} belong to those of the lowest abundance, which can still be investigated by ^{13}C NMR spectroscopy. Higher fullerenes can exist in several topologically possible isomers the number of which rapidly increases with the number of carbon atoms in the fullerene cage.[1] The number of topologically possible isolated pentagon rule (IPR) isomers of C_{96} is 187. Earlier,[2] the C_{96} fraction investigated by ^{13}C NMR spectroscopy was shown to consist of at least ten different C_{96} isomers, though without reliable structural identification.

Four C_{96} isomers in the pristine form were isolated by HPLC and characterized by UV-VIS spectroscopy, and two of them [nos. 3 (D_{3d}) and 181 (C_1); numeration according to the spiral algorithm[1]] were identified by X-ray crystallography as co-crystals with Ni^{II}(OEP) (OEP = octaethylporphyrin).[3] Several other isomers of C_{96} were structurally characterized as pentafluoroethyl and chloro derivatives. Previously, we reported the structure determination of $C_{96}(C_2F_5)_{12}$ that contained the carbon cage of isomer C_1-C_{96}(145).[4] Other C_{96} isomers were identified by chlorination followed by single crystal X-ray diffraction of chlorides. In this way, IPR isomers of C_{96} nos. 144 (C_1), 145 (C_1), 175 (C_1), 176 (C_2), and 183 (D_2) have been unambiguously identified in chlorides $C_{96}Cl_{20–24}$ by the analysis of carbon cage connectivities.[5,6] The presence of two other isomers, C_2-C_{96}(80) and C_1-C_{96}(114), was deduced by the structural reconstruction of cage transformations (C_2 losses) occurring upon the chlorination of C_{96} with the formation of non-classical (*NC*) fullerene chlorides, C_{92}(*NC*2)Cl_{32} and C_{94}(*NC*1)Cl_{28}, respectively (the numeral after *NC* denotes the number of heptagons in a non-classical cage).[6]

Here, we report the synthesis, isolation and structural characterization of the first CF_3 derivative of C_{96} fullerene, $C_{96}(CF_3)_{18}$, with a carbon cage connectivity of isomer C_2-C_{96}(176). The addition pattern of 18CF_3 groups is discussed and compared with the chlorination pattern of the known $C_{96}(176)Cl_{22}$.

The arc-discharge fullerene soot was separated by HPLC using a preparative Buckyprep column (20 mm i.d. × 250 mm, Nacalai Tesque Inc.) and toluene as an eluent. The isolated fraction with C_{94} fullerene was slightly contaminated by C_{96} according to MALDI MS TOF analysis. This fraction was trifluoromethylated with gaseous CF_3I in quartz ampoules at 450 °C for 1.5 h following a procedure described previously.[7,8] The product containing mainly $C_{94}(CF_3)_n$ (n = 14–20) and a small admixture of $C_{96}(CF_3)_{16–20}$ was dissolved in n-hexane and separated by HPLC using a semi-preparative Buckyprep column (4.6 mm i.d. × 250 mm, Nacalai Tesque Inc.) and n-hexane as an eluent at 1.0 ml min^{-1} flow rate. Among 33 HPLC fractions containing nearly pure $C_{94}(CF_3)_{14–20}$ compounds (trace amounts of other species were always present), a fraction eluted between 15.7 and 16.3 showed the predominant content of $C_{96}(CF_3)_{18}$, the small admixtures being $C_{94}(CF_3)_{16/18}$ according to MALDI MS analysis. Slow evaporation of hexane afforded small crystals. The X-ray diffraction study with the use of synchrotron radiation revealed the structure of C_{96}(176)$(CF_3)_{18}$ solvated with disordered hexane molecules.†

The presence of an admixture of C_{96} in the starting C_{94} fraction before trifluoromethylation is due to some overlap of the tail of C_{94} and the front of C_{96} HPLC fractions during chromatographic separation of the pristine fullerene mixture. Note that the isomer C_{96}(176) possesses a shorter retention time than those of other C_{96} isomers;[6] therefore, it elutes just after the last isomer of C_{94} in the course of HPLC separation. The isomer C_2-C_{96}(176) belongs to the isomers of C_{96} with a moderate formation energy of 31.1 kJ mol^{-1} relative to the most stable isomer D_2-C_{96}(181).[6] Therefore, its occurrence in the fullerene soot is less expected than the presence of a more stable isomer C_1-C_{96}(145) (11.9 kJ mol^{-1}), which has been confirmed earlier.[4] Note that C_2-C_{96}(176)$(CF_3)_{18}$ is the first structurally characterized CF_3 derivative of C_{96} fullerene in addition to a pentafluoroethyl derivative, C_1-C_{96}(145)$(C_2F_5)_{12}$, which was described previously.[4] Both compounds represent the largest fullerene so far structurally investigated as perfluoroalkylated derivatives. Two projections of the C_2-C_{96}(176)$(CF_3)_{18}$ molecule are presented in Figure 1.

The addition pattern of 18 CF_3 groups follows the C_2 symmetry of the pristine C_2-C_{96}(176) cage with a two-fold axis passing through the midpoints of two opposite C–C bonds (Figures 1 and 2). The trifluoromethylation pattern is characterized by the attachment of CF_3 groups in the *para* positions of edge-sharing $C_6(CF_3)_2$ hexagons, which results in the formation of three- and four-membered *para* chains. Six of 12 cage pentagons bear one

† *Crystal data.* Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2, Berlin, PSF, Germany) using a MAR225 CCD detector, λ = 0.8856 Å. The crystal structure was solved by SHELXD and refined with SHELXL. C_2-$C_{96}(CF_3)_{18}$·0.75n-C_6H_{14}, monoclinic, $C2/c$, a = 48.557(4), b = 13.288(1) and c = 28.015(2) Å, β = 111.991(9)°, V = 16761(2) Å^3, Z = 8. Anisotropic refinement with 16812 reflections and 1539 parameters converged to wR_2 = 0.374 and R_1 = 0.154 for 7921 reflections with $I > 2\sigma(I)$. Rather high residue values are due to the very weak diffraction from a tiny crystal. Nevertheless, the positions of 18 attached CF_3 groups on the C_{96} cage are determined unambiguously. Partially occupied and disordered n-hexane molecules are located near a C_2 axis and an inversion centre.

CCDC 1049912 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

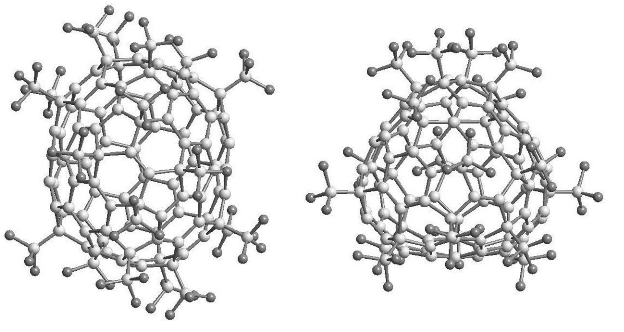
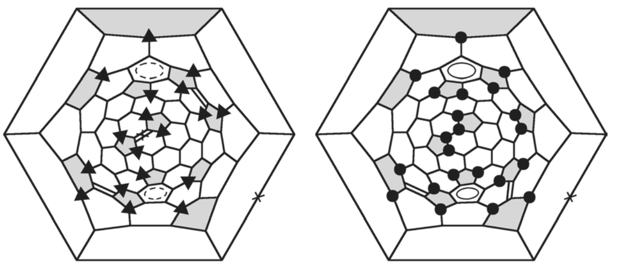


Figure 1 Two views of the C_2-$C_{96}(176)(CF_3)_{18}$ molecule. The projections are presented along (left) and perpendicular (right) to the two-fold symmetry axis, respectively.

CF_3 group, whereas other six are occupied by two CF_3 groups thus contributing to the formation of three isolated double C=C bonds on the carbon cage that stabilize the structure. Another stabilizing factor is the formation of two nearly isolated benzenoid rings.

It is interesting to compare the addition patterns of C_2-$C_{96}(176)(CF_3)_{18}$ and previously[5] studied C_1-$C_{96}(176)Cl_{22}$ (Figure 2). In the chloride, 18 of 22 chlorine atoms are attached symmetrically, whereas four others destroy C_2 symmetry. Most features of the addition patterns such as the formation of isolated or nearly isolated benzenoid fragments and the formation of isolated C=C double bonds are common in both molecules. The differences are due to different effective volumes of CF_3 groups and Cl atoms. Therefore, the addition of CF_3 groups strictly follows the attachment in the *para* positions in hexagons. Smaller Cl atoms can be arranged in a tighter manner, *i.e.*, in the *ortho* positions. In the structure of $C_{96}(176)Cl_{22}$, there are a pair of 1,2 attachment and a short four-membered chain of adjacent attachments.



$C_{96}(176)(CF_3)_{18}$ $C_{96}(176)Cl_{22}$

Figure 2 Schlegel diagrams of C_2-$C_{96}(176)(CF_3)_{18}$ and C_1-$C_{96}(176)Cl_{22}$.[5] Cage pentagons are highlighted in grey. Black triangles and circles indicate the positions of attached CF_3 groups and Cl atoms, respectively. Isolated (and nearly isolated) benzenoid rings and isolated C=C bonds are indicated. Small crosses denote the position of a C_2 axis.

In summary, the first CF_3 derivative of C_{96} fullerene, C_2-$C_{96}(176)(CF_3)_{18}$, was isolated by HPLC and structurally investigated by X-ray crystallography. Its trifluoromethylation pattern is characterized by the additions in edge-sharing *para* $C_6(CF_3)_2$ hexagons and the presence of stabilizing benzenoid rings and isolated C=C bonds on the fullerene cage.

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