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Isolation and crystal structure of the trifluoromethyl derivative $C_{84}(24)(CF_3)_{18}$ of a minor C_{84} fullerene isomer

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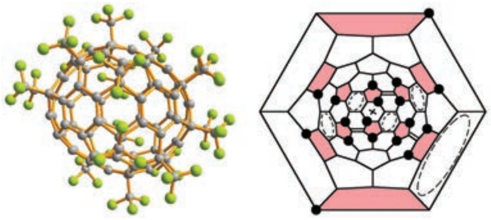
C_1-$C_{84}(24)(CF_3)_{18}$ was isolated by HPLC from the trifluoromethylation products of a C_{84} fullerene mixture. Its molecular structure was determined by single crystal X-ray diffraction using synchrotron radiation. In the addition pattern, 18 CF_3 groups are arranged near the cage equator, thus isolating five benzenoid rings and three C=C bonds on the carbon cage.



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In addition to C_{60} and C_{70}, C_{84} fullerene possesses the highest abundance in fullerene soot thus prevailing among higher fullerenes. Fullerene C_{84} has 24 topologically possible isomers obeying the isolated pentagon rule (IPR).[1] In the arc-discharge fullerene soot obtained with the use of undoped graphite rods, the most abundant C_{84} isomers are D_2-$C_{84}(22)$ and D_{2d}-$C_{84}(23)$ (isomer numbering according to the spiral algorithm[1] is given in parentheses).[2,3] Minor isomers such as D_{2d}-$C_{84}(4)$, D_2-$C_{84}(5)$, C_2-$C_{84}(11)$, C_s-$C_{84}(14)$, and C_s-$C_{84}(16)$ were isolated and confirmed by ^{13}C NMR spectroscopy.[2–4] Two isomers with high cage symmetry, D_{3d}-$C_{84}(19)$ and D_{6h}-$C_{84}(24)$, were detected in fullerene soot produced using Gd-doped graphite rods.[5]

The pristine isomers of C_{84} identified by ^{13}C NMR spectroscopy were confirmed crystallographically in co-crystals with metal porphyrins[6] or as exohedral derivatives.[7–12] Isomer $C_{84}(14)$ was identified in co-crystals with silver tetraphenylporphyrin.[6] High-temperature chlorination and X-ray crystallographic investigation of chlorides resulted in the confirmation of C_{84} isomer nos. 5,[7] 11, 14, and 16.[8] The synthesis, isolation, and X-ray crystallography of perfluoroalkylated $C_{84}(CF_3)_n$ and $C_{84}(C_2F_5)_n$ allowed one to confirm C_{84} isomer nos. 4,[9] 5,[7] 11,[9,10] 16,[8,9,11] 22,[12,13] and 23.[14] In addition, a new isomer, C_{2v}-$C_{84}(18)$, was identified in $C_{84}(CF_3)_n$ compounds.[9,11] The presence of isomer D_{6h}-$C_{84}(24)$ in usual fullerene soot as $C_{84}(24)(CF_3)_{12}$ was reported previously,[15] but it needs further confirmation due to uncertainties in X-ray crystallographic data.

Here, we report the synthesis, isolation, and crystal structure of $C_{84}(24)(CF_3)_{18}$ and the behavior of this isomer in a trifluoromethylation reaction.

An extract from arc-discharge fullerene soot was separated by HPLC in toluene using a preparative Buckyprep column (20 mm i.d. × 250 mm, Nacalai Tesque). The C_{84} fraction was trifluoromethylated in quartz ampoules by a reaction with gaseous CF_3I at 450 °C for 6 h in accordance with a procedure described previously.[11,12,14] The product containing mainly $C_{84}(CF_3)_n$ (n = 14–18) was dissolved in n-hexane and separated by HPLC using a semi-preparative Buckyprep column (10 mm i.d. × 250 mm, Nacalai Tesque) and n-hexane as the eluent at a flow rate of 4.6 ml min^{-1}. The chromatographic fractions collected between 3 and 75 min gave small crystals by slow concentration or recrystallization from p-xylene. In this way, known structures of $C_{84}(CF_3)_n$ with isomers $C_{84}(22)$ and $C_{84}(23)$ were isolated and identified by unit call parameters. New crystalline phases were isolated from fractions eluted after 4.2 and 19.4 min. The crystals were studied by X-ray diffraction using synchrotron radiation. The former crystals of the known isomer C_2-$C_{84}(22)(CF_3)_{16}$-I crystallized as a solvate with three p-xylene molecules,[†] whereas previous data referred to a solvate with toluene.[12] The addition pattern of C_2-$C_{84}(22)(CF_3)_{16}$-I and its comparison with isomers II–IV were discussed in detail elsewhere.[12]

According to MALDI TOF mass-spectrometric analysis, the fraction eluted at 19.4 min contained $C_{84}(CF_3)_{18}$, and the crystals obtained had the structure of $C_{84}(24)(CF_3)_{18} \cdot p\text{-}C_6H_4(CF_3)_2$.[†] Figure 1 shows the molecular structure of $C_{84}(24)(CF_3)_{18}$ in two projections.

The presence of two coronene subunits on the opposite poles of the carbon cage results in a flattening of the molecule in these regions. The C_1-$C_{84}(24)(CF_3)_{18}$ molecules in crystals are disordered because two orientations overlap statistically in the same crystallographic site, thus imitating a twofold symmetry.

[†] *Crystal data.* Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2, PSF, Germany) using a MAR225 CCD or a Pilatus3S 2M pixel detector (λ = 0.8856 or 0.8266 Å). The crystal structures were solved by SHELXD and refined with SHELXL. $C_{84}(CF_3)_{16} \cdot 3C_6H_4(CH_3)_2$, monoclinic, $P2_1/c$, a = 14.348(1), b = 26.179(2) and c = 24.316(2) Å, β = 102.62(1)°, V = 8912.8(12) Å^3, Z = 4. Anisotropic refinement with 18698 reflections and 1583 parameters converged to wR_2 = 0.208 and R_1 = 0.080 for 14026 reflections with $I > 2\sigma(I)$. $C_{84}(CF_3)_{18} \cdot C_6H_4(CH_3)_2$, monoclinic, $C2/c$, a = 13.636(1), b = 23.826(2) and c = 24.806(2) Å, β = 101.04(1)°, V = 7910.1(11) Å^3, Z = 4. Anisotropic refinement with 10748 reflections and 887 parameters converged to wR_2 = 0.251 and R_1 = 0.110 for 2492 reflections with $I > 2\sigma(I)$. One CF_3 group is disordered around the C–CF_3 axis with occupation ratios of 0.56/0.44(2).

CCDC 1980125 and 1980126 contain 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.

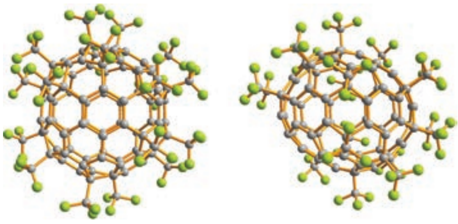

Figure 1 Two views of the C_1-$C_{84}(24)(CF_3)_{18}$ molecule. The projections on the left and on the right are presented along the sixfold axis of the D_{6h}-$C_{84}(24)$ cage and the pseudo C_2 axis of the $C_{84}(24)(CF_3)_{18}$ molecule, respectively.

Deviations from twofold symmetry due to asymmetric positions of 2 from 18 CF_3 groups can be seen in Figure 1. In the crystal structure, these two CF_3 groups are present, though with half-occupancies, on both sides of the disordered molecule. Therefore, the molecular symmetry of $C_{84}(24)(CF_3)_{18}$, *i.e.*, the addition pattern symmetry, is C_1, whereas the crystallographic symmetry of the disordered molecule is higher, C_2.

The addition pattern of the C_1-$C_{84}(24)(CF_3)_{18}$ molecule can be discussed using Schlegel diagrams (Figure 2), which are presented through the central hexagon of the coronene subunit (left) and through the side hexagon parallel to the crystallographic twofold axis. Note that the addition pattern contains the contiguous arrangement of 12 CF_3 groups [as a loop of *para* additions in $C_6(CF_3)_2$ hexagons] in the equatorial cage region, as reported previously for D_{3d}-$C_{84}(24)(CF_3)_{12}$.[15] The additional six CF_3 groups are attached asymmetrically, four and two, in *para* $C_6(CF_3)_2$ hexagons belonging to both coronene subunits of the carbon cage. This choice of the arrangement, as an interpretation of disorder in the crystal structure, corresponds to the closed electronic configuration in contrast to any arrangement of three CF_3 groups in both coronene subunits, which correspond to radicals. Theoretical calculations of the formation energies revealed that the (4 + 2) arrangement chosen is at least 117 kJ mol^{-1} more favorable than any of (3 + 3) arrangements in radicals.

The deviations from twofold symmetry can be clearly seen on the right diagram (Figure 2) oriented parallel to the pseudo twofold axis. Note that the addition pattern of C_1-$C_{84}(24)(CF_3)_{18}$ is characterized by the presence of five benzenoid rings and three isolated C=C bonds on the carbon cage, which contribute to the stabilization of the whole molecule. In contrast, stabilizing substructures of these types are not formed in the D_{3d}-$C_{84}(24)(CF_3)_{12}$ molecule where a loop of 12 attached CF_3 groups divides the electronic system into two separate 36-electronic subsystems within isolated coronene subunits. Nevertheless, the calculated enthalphy of trifluoromethylation (per CF_3 group) in $C_{84}(24)(CF_3)_{12}$ is 9.0 kJ mol^{-1} higher than that in $C_{84}(24)(CF_3)_{18}$, which corresponds to the general tendency of decreasing the addition enthalpy (per group) with the number of attached groups.[16]

Thus, we confirmed the previous conclusion on the presence of isomer D_{6h}-$C_{84}(24)$, though in very small quantities, in the arc-discharge fullerene soot produced with the use of undoped graphite rods. According to our DFT calculations of formation energies and published data,[17] isomer $C_{84}(24)$ is ranked third in the stability row, only 29 kJ mol^{-1} above the most stable $C_{84}(22)$ and $C_{84}(23)$. While the latter have high abundances in the fullerene soot, $C_{84}(24)$ is much less abundant. It was isolated only recently as two compounds $C_{84}(24)(CF_3)_{12}$[15] and $C_{84}(24)(CF_3)_{18}$ (this work), whereas several much less stable C_{84} fullerene isomers in the forms of chloro and perfluoroalkyl derivatives have been reported.[7–10]

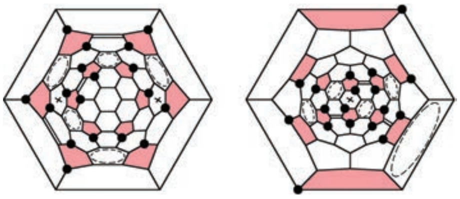

Figure 2 Schlegel diagrams of C_1-$C_{84}(24)(CF_3)_{18}$. Cage pentagons are highlighted in red. Black circles indicate the positions of attached CF_3 groups. Isolated double C=C bonds and benzenoid rings are indicated by double lines and dashed ovals, respectively. Small crosses denote the positions of a pseudo C_2 axis.

In summary, the high-temperature trifluoromethylation of a mixture of C_{84} isomers followed by HPLC separation, recrystallization, and X-ray diffraction analysis revealed the crystal and molecular structures of C_1-$C_{84}(24)(CF_3)_{18}$. The addition pattern of 18 CF_3 groups to a C_{84} carbon cage is characterized by a near-equatorial loop of edge-sharing p-$C_6(CF_3)_2$ hexagons and six additional groups on both coronene subunits. The presence of the isomer D_{6h}-$C_{84}(24)$ in the fullerene soot produced using undoped graphite rods was confirmed unambiguously.

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