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Synthesis and X-ray structure of $C_{88}(7)(CF_3)_{12/16}$

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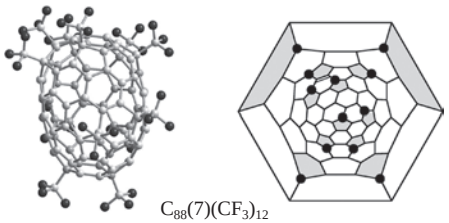
Compounds $C_{88}(7)(CF_3)_{12}$ and $C_{88}(7)(CF_3)_{16}$ were isolated by HPLC from the trifluoromethylation products of a mixture of C_{88} isomers. An X-ray diffraction study revealed that the trifluoromethylation patterns are characterized by the additions in edge-sharing *para* and *meta* $C_6(CF_3)_2$ hexagons and the presence of stabilizing isolated and partially isolated C=C bonds on the fullerene cage.



Fullerene C_{88} can exist in the form of 35 topologically possible isomers obeying the Isolated Pentagon Rule (IPR).[1] Earlier, the chromatographic (HPLC) isolation of a C_{88} fraction and its ^{13}C NMR study were interpreted as the existence of a single isomer of C_2 symmetry.[2] In the further work, the C_{88} fraction was separated into three subfractions by multi-step HPLC, and a ^{13}C NMR spectroscopic study allowed one to make their assignment as one isomer with C_s and two isomers with C_2 symmetry.[3] These assumptions were supported by the theoretical prediction of ^{13}C NMR shifts for three most probable isomers with nos. 7 (C_2), 17 (C_s), and 33 (C_2),[4] which were shown to be most stable ones according to the theoretical calculations of formation energies.[4–6]

The unambiguous confirmation of cage connectivity by direct experimental methods has been accomplished for isomer C_2-$C_{88}(33)$ based on the X-ray crystallographic study of its trifluoromethylated derivatives $C_{88}(33)(CF_3)_{16/18/20}$.[7,8] The presence of isomer $C_{88}(17)$ in the fullerene soot was confirmed by the synthesis and X-ray crystallographic investigation of chloro derivatives, $C_{88}(17)Cl_{16}$ and $C_{88}(17)Cl_{22}$.[9] Herein, we report the trifluoromethylation of a C_{88} fraction followed by the HPLC isolation and X-ray crystallographic study of two CF_3 derivatives, $C_{88}(7)(CF_3)_{12}$ and $C_{88}(7)(CF_3)_{16}$, thus unambiguously confirming the occurrence of isomer C_2-$C_{88}(7)$ in the fullerene soot.

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 the eluent. The isolated fraction with C_{88} fullerene was slightly contaminated by C_{90} according to MALDI-TOF mass spectrometric analysis data. The trifluoromethylation of this fraction with gaseous CF_3I was carried out in quartz ampoules at 450 °C for 1.5 h following a procedure described previously.[10] The reaction product containing mainly $C_{88}(CF_3)_n$ (n = 2–20) with a maximum content of $C_{88}(CF_3)_{16/18}$ and a small admixture of $C_{90}(CF_3)_{16–18}$ was dissolved in toluene and subjected to HPLC separation using a semi-preparative Buckyprep column (10 mm i.d. × 250 mm, Nacalai Tesque Inc.) and toluene as the eluent at a flow rate of 4.6 ml min^{-1} affording 11 fractions with retention times of 2.6–21.0 min.

Toluene fractions were additionally purified by HPLC in *n*-hexane or *n*-hexane–toluene mixtures. The first toluene fraction (retention time, 2.6–3.7 min) was HPLC separated in *n*-hexane at flow rate of 2.3 ml min^{-1}. The hexane subfraction eluted at 11.8 min gave nearly pure $C_{88}(CF_3)_{16}$, which was recrystallized from toluene. The hexane subfraction eluted at 8.4 min showed the composition of $C_{90}(CF_3)_{18}$; it was recrystallized from *p*-xylene affording the crystals of $C_{90}(35)(CF_3)_{18}\cdot 1.17\,p\text{-}C_6H_4Me_2$.[11] The third toluene fraction (retention time, 4.8 min) was HPLC separated in a *n*-hexane–toluene mixture (6:4 v/v) at a flow rate of 4.6 ml min^{-1}. A subfraction eluted at 20.5 min gave pure $C_{88}(CF_3)_{12}$, which was recrystallized from toluene. The obtained crystals containing $C_{88}(CF_3)_n$ were investigated by X-ray diffraction with the use of synchrotron radiation revealing the structures of $C_{88}(7)(CF_3)_{16}$ and $C_{88}(7)(CF_3)_{12}$, respectively, both solvated by toluene.†

The presence of an impurity of C_{90} in the starting C_{88} fraction before trifluoromethylation is due to some overlap of the tail of C_{88} and the front of C_{90} HPLC fractions during chromatographic separation of the pristine fullerene mixture. The isolation of $C_{90}(35)(CF_3)_{18}$ from the trifluoromethylation products corresponds to the fact that the first of three C_{90} fractions contains isomer $C_{90}(35)$, as has been shown by the isolation and crystal structure elucidation of its chlorination products, $C_{90}(35)Cl_{24}$ and $C_{90}(35)Cl_{28}$.[12]

Two molecular structures of $C_{88}(7)(CF_3)_{12/16}$ unambiguously confirm the presence of isomer $C_{88}(7)$ in the fullerene soot. In fact, isomer $C_{88}(7)$ was expected to be found in fullerene mixtures on

† *Crystal data.* Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2, PSF, Berlin, Germany) using a MAR225 CCD detector, λ = 0.8950 and 0.8434 Å. The crystal structures were solved by SHELXD and refined with SHELXL.

$C_{88}(CF_3)_{12}\cdot 1.59$ PhMe, triclinic, space group $P\bar{1}$, a = 12.9251(7), b = = 14.4469(8) and c = 21.5902(9) Å, α = 88.060(2)°, β = 81.159(3)°, γ = 88.291(4)°, V = 3980.1(4) Å^3, Z = 2. Anisotropic refinement with 15302 reflections and 1313 parameters converged to wR_2 = 0.194 and R_1 = 0.078 for 12129 reflections with $I > 2\sigma(I)$.

$C_{88}(CF_3)_{16}\cdot 1.5$ PhMe, triclinic, space group $P\bar{1}$, a = 13.421(1), b = = 13.913(1) and c = 23.105(2) Å, α = 97.756(9)°, β = 101.739(10)°, γ = 106.155(8)°, V = 3972.5(6) Å^3, Z = 2. Anisotropic refinement with 17407 reflections and 1502 parameters converged to wR_2 = 0.164 and R_1 = 0.064 for 11731 reflections with $I > 2\sigma(I)$.

CCDC 1448825 and 1448826 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.

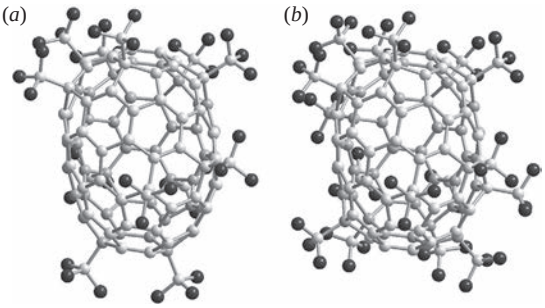


Figure 1 Projections of the (*a*) $C_{88}(7)(CF_3)_{12}$ and (*b*) $C_{88}(7)(CF_3)_{16}$ molecules shown along the two-fold axis of the pristine C_2-$C_{88}(7)$ carbon cage passing through the midpoints of two opposite C–C bonds. Most substantial distinctions in the addition of CF_3 groups are seen in the bottom region of the molecules.

the basis of theoretical calculations of relative formation energies and ^{13}C NMR spectroscopic study.[4,5] Three isomers of C_{88} fullerene nos. 7, 17, and 33 possess low (and very close) formation energies and all three have been confirmed now by the structure determination of CF_3 or chloro derivatives.[7–9] Apparently, three C_{88} fractions I–III isolated previously[9] contain C_{88} isomers with nos. 17, 7, and 33, respectively.

Figure 1 shows the projections of the $C_{88}(7)(CF_3)_{12}$ and $C_{88}(7)(CF_3)_{16}$ molecules. While the C_2-$C_{88}(7)$ cage possesses two-fold axial symmetry, both trifluoromethylated molecules are asymmetric due to the arrangement of CF_3 groups. A comparison of two projections demonstrates certain similarity in the attachment positions of CF_3 groups, especially, in the upper region of the molecules.

The arrangement of CF_3 groups in both molecules is shown schematically in Figure 2 as Schlegel diagrams. The addition pattern of $C_{88}(7)(CF_3)_{12}$ is characterized by an asymmetrical distribution of 12 CF_3 groups in all 12 cage pentagons. Six CF_3 groups are attached in *para* positions of three separate $C_6(CF_3)_2$ hexagons, whereas other six CF_3 groups occupy edge-sharing *para* and *meta* $C_6(CF_3)_2$ hexagons to form a *pmp*^{3} ribbon. One nearly isolated C=C bond is formed flanked by three *sp*^{3} carbons instead of four such sites in the case of a completely isolated C=C bond. This C–C bond 1.338(6) Å in length is the shortest

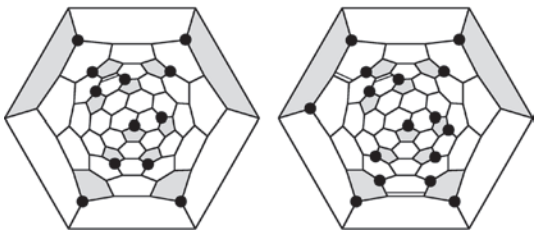


Figure 2 Schlegel diagrams of $C_{88}(7)(CF_3)_{12}$ and $C_{88}(7)(CF_3)_{16}$. Cage pentagons are highlighted in gray. Black circles indicate the positions of attached CF_3 groups. Isolated and nearly isolated C=C bonds are indicated by double lines.

one on the carbon cage, whereas other C–C bonds with partially double characters are 1.356(6)–1.383(6) Å long.

The addition pattern of 16 CF_3 groups in the $C_{88}(7)(CF_3)_{16}$ molecule has 10 common attachment positions with $C_{88}(7)(CF_3)_{12}$. The same *pmp*^{3} ribbon of edge-sharing $C_6(CF_3)_2$ hexagons is present (see the upper regions of Schlegel diagrams), whereas other CF_3 groups are attached in a separate *para* hexagon and two-, and four-membered *para* ribbons. Two partially isolated and one isolated C=C bonds are formed with an average C=C distance of 1.333(5) Å. For comparison, the structure of the same chemical composition, $C_{88}(33)(CF_3)_{16}$, retains two-fold symmetry of isomer C_2-$C_{88}(33)$. The addition pattern of 16 CF_3 groups is stabilized by the formation of two isolated C=C bonds and two benzenoid rings on the carbon cage.[8]

In summary, the trifluoromethylation of a C_{88} isomer mixture with CF_3I followed by the HPLC separation of CF_3 derivatives resulted in the isolation and structure determination of $C_{88}(7)(CF_3)_{12}$ and $C_{88}(7)(CF_3)_{16}$ by X-ray crystallography thus confirming the presence of isomer $C_{88}(7)$ in the fullerene soot. The trifluoromethylation patterns of both molecules have 10 attachment positions in common. The shortest on the carbon cages are double C=C bonds, which are completely or partially isolated by adjacent *sp*^{3} sites.

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