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Synthesis and X-ray structure of C_2-C$_{84}$(22)(CF$_3$)$_6$

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C_2-C$_{84}$(22)(CF$_3$)$_6$ was isolated by HPLC from the products of trifluoromethylation of fullerene C$_{84}$. Its molecular structure elucidated by single crystal X-ray diffraction has an addition pattern with a six-membered chain of *para* additions of CF$_3$ groups. C_2-C$_{84}$(22)(CF$_3$)$_6$ is the most stable isomer on a pathway to the known C_2 and D_2 isomers of C$_{84}$(22)(CF$_3$)$_{12}$; the molecular structure of the latter was refined with a better accuracy.

After C$_{60}$ and C$_{70}$, fullerene C$_{84}$ belongs to the most abundant species in fullerene soot. According to the Isolated Pentagon Rule (IPR), there is only one stable isomer of both C$_{60}$ and C$_{70}$, whereas C$_{84}$ can exist in the form of 24 different isomers.[1] Among ten experimentally confirmed C$_{84}$ isomers,[2–5] two isomers with nos. 22 and 23 (numbering according to the spiral algorithm[1]) possess much higher stability than others; therefore, they are much more abundant.[2] Investigation of the reactivity of C$_{84}$, as most other higher fullerenes, is strongly complicated due to relatively low content in mixtures and the presence of several isomers, which are difficult to separate. The derivatization of fullerene (and isomer) mixtures allows one to perform a separation process more effectively. Recent advances in the chemistry of C$_{84}$ fullerenes were achieved with perfluoroalkyl and chloro derivatives.[5–8]

The CF$_3$ derivatives of two major isomers, C$_{84}$(22) and C$_{84}$(23), have been studied in more detail. The synthesis, HPLC isolation and X-ray structural characterization of several isomers of C$_{84}$(22)(CF$_3$)$_{2n}$ ($2n$ = 12–16, 20)[9] and C$_{84}$(23)(CF$_3$)$_{2m}$ ($2m$ = 4, 8–18),[10] supported by theoretical DFT calculations, allowed us to hypothesize the most probable pathways of successive trifluoromethylation from lower ($2n$, $2m$ = 2) to higher derivatives. Note that the compositional range ($2n$ or $2m$) of structurally studied compounds is significantly larger for C$_{84}$(23) than for C$_{84}$(22). Here, we report on the synthesis, isolation and structural elucidation of an important intermediate, C$_{84}$(CF$_3$)$_6$, on the pathway from C$_{84}$(22) to C$_{84}$(22)(CF$_3$)$_{12}$. In addition, the molecular structure of D_2-C$_{84}$(CF$_3$)$_{12}$ was determined.† The discussion concerns the relations between addition patterns and relative formation energies of different isomers.

A fraction of C$_{84}$ fullerene containing a small amount of C$_{82}$ was isolated from the fullerene soot by HPLC using a preparative Buckyprep column (20 mm i.d., 25 cm in length, Nacalai Tesque Inc.). Trufluoromethylation of a C$_{84}$/C$_{82}$ mixture was carried out in a sealed quartz ampoule at 550 °C for ~1 h as described elsewhere.[9,10] A mixture of trifluoromethylated fullerenes collected in a hot zone of the ampoule contained C$_{84}$(CF$_3$)$_{2n}$ ($2n$ = 2–10) and C$_{82}$(CF$_3$)$_{2n}$ ($2n$ = 2–8) compounds. The first HPLC separation was performed in toluene using a semi-preparative Buckyprep column (10 mm i.d., 25 cm in length, Nacalai Tesque Inc.) at a flow rate of 3.5 ml min^{-1}. A fraction eluted at 19.5–21.0 min was then separated on the same column using a toluene–hexane mixture (6:4, v/v). The fraction collected between 39.6 and 40.3 min contained mostly C$_{84}$(CF$_3$)$_6$ and a small admixture of C$_{84}$(CF$_3$)$_4$ according to MALDI MS TOF analysis (Figure 1). Recrystallization from *p*-xylene afforded small black crystals. X-ray crystallography with the use of synchrotron radiation revealed the structure of C_2-C$_{84}$(22)(CF$_3$)$_6$ · *p*-xylene.†

The separation of the product sublimed into the cold part of a reaction ampoule was carried out by two-step HPLC using a semi-preparative Buckyprep column (see above). In the first step, the separation was performed in toluene with a flow rate of 4.6 ml min^{-1}. The fraction eluted at 3.5 min was further separated in a toluene–hexane mixture (15 : 85, v/v). The fraction eluted between 27.5 and 28.9 min was slowly evaporated affording two

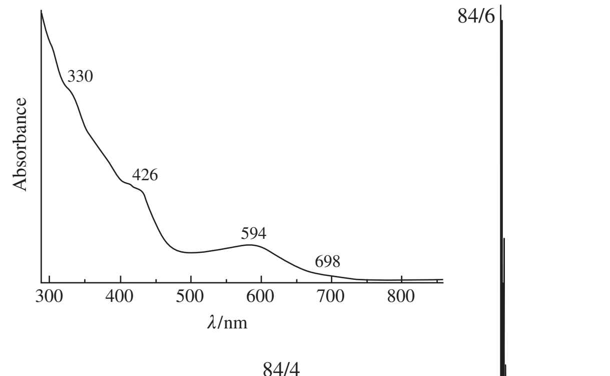

Figure 1 MALDI mass spectrum of a sample of C_2-C$_{84}$(22)(CF$_3$)$_6$ with peak compositions denoted as 84/6 and 84/4. Inset shows the UV-VIS spectrum of C_2-C$_{84}$(22)(CF$_3$)$_6$ recorded in toluene.

† *Crystal data*. Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2, PSF at the Free University of Berlin, Germany) using a MAR225 CCD detector, λ = 0.8856 Å. Structures were solved by SHELXD and refined with SHELXL.

C_2-C$_{60}$(CF$_3$)$_6$ · *p*-C$_6$H$_4$Me$_2$, triclinic, $P\bar{1}$, a = 11.753(1), b = 21.152(1) and c = 24.533(2) Å, α = 94.159(5)°, β = 103.445(10)°, γ = 99.886(8)°, V = 5803.3(7) Å^3, Z = 4. The asymmetric unit contains two fullerene and three (one and two halves) *p*-xylene molecules. Anisotropic refinement with 22 389 reflections and 2375 parameters converged to wR_2 = 0.314 and R_1 = 0.133 for 19 029 reflections with $I > 2\sigma(I)$.

D_2-C$_{84}$(CF$_3$)$_{12}$, tetragonal, $I4_1/acd$, a = 16.311(1) and c = 44.417(2) Å, V = 11817.1(12) Å^3, Z = 8. The main D_2-C$_{84}$(CF$_3$)$_{12}$ molecule overlaps with C_2-C$_{82}$(CF$_3$)$_{12}$ at the same crystallographic site that results in disorder in two carbon cage regions. Anisotropic refinement with 3611 reflections and 419 parameters converged to wR_2 = 0.208 and R_1 = 0.088 for 2998 reflections with $I > 2\sigma(I)$.

CCDC 984743 and 984744 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. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2014.

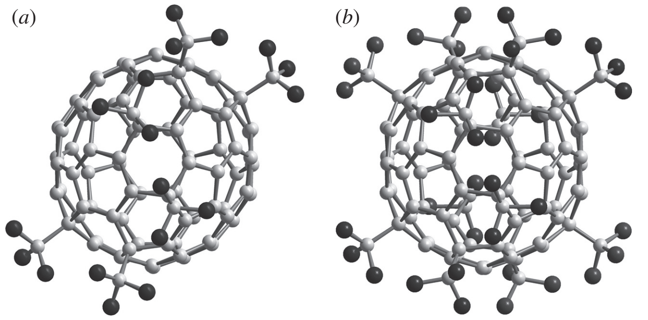

Figure 2 The molecules of (*a*) C_2-$C_{84}(22)(CF_3)_6$ and (*b*) D_2-$C_{84}(22)(CF_3)_{12}$.

types of crystals. X-ray crystallography with the use of synchrotron radiation revealed that yellow needle-like crystals represent $C_{84}(11)(CF_3)_{16}$ (will be reported elsewhere), whereas orange plates contain D_2-$C_{84}(22)(CF_3)_{12}$.[†]

The compound $C_{84}(22)(CF_3)_6$ represents the lowest CF_3 derivative of $C_{84}(22)$ isolated and structurally characterized so far. Previously, two isomers of $C_{84}(22)(CF_3)_{12}$ were the lowest ones for the $C_{84}(22)$ cage, whereas the structure of $C_{84}(23)(CF_3)_4$ had the smallest number of CF_3 groups among structurally elucidated compounds. The molecule of C_2-$C_{84}(22)(CF_3)_6$ contains all six attached CF_3 groups on one hemisphere of a $C_{84}(22)$ cage [Figure 2(*a*)]. All CF_3 groups are arranged in *para* positions in edge-sharing $C_6(CF_3)_2$ hexagons forming an S-like addition motif on a Schlegel diagram [Figure 3(*a*)]. According to the DFT calculation of relative formation energy,[9] this isomer is the most stable one among all $C_{84}(22)(CF_3)_6$ compounds; the next isomer containing an asymmetric S-like addition motif is less stable by 12.7 kJ mol^{-1}. The isolation of this isomer confirms the previous conclusion that the products of high temperature trifluoromethylation contain predominantly the most stable isomers.[9,10]

It is noteworthy that C_2-$C_{84}(22)(CF_3)_6$ represents a precursor on the trifluoromethylaion pathway to both stable isomers with 12 attached CF_3 groups, which possess D_2 and C_2 molecular symmetry.[9] The addition pattern of D_2-$C_{84}(22)(CF_3)_{12}$ has been confirmed previously.[9,11] The present X-ray structure elucidation is more accurate and, in addition, the D_2 molecular symmetry of the molecule coincides with the crystallographic symmetry (222) within the crystal structure. Significantly, D_2-$C_{84}(22)(CF_3)_{12}$ comprises two symmetrically arranged substructures of C_2-$C_{84}(22)(CF_3)_6$ [Figures 2(*b*) and 3(*b*)]. Further trifluoromethylation of D_2-$C_{84}(22)(CF_3)_{12}$ by the addition of CF_3 groups in *para* positions in $C_6(CF_3)_2$ hexagons, *i.e.*, the continuation of S-like addition motifs, is energetically unfavorable because all such positions are triple hexagon junctions (THJs). Therefore, D_2-$C_{84}(22)(CF_3)_{12}$ is a dead-end product of trifluoromethylation. The formation of $C_{84}(22)(CF_3)_{14}$ and $C_{84}(22)(CF_3)_{16}$ isomers, which were also confirmed experimentally, occurs by the addition of CF_3 groups to C_2-$C_{84}(22)(CF_3)_{12}$.

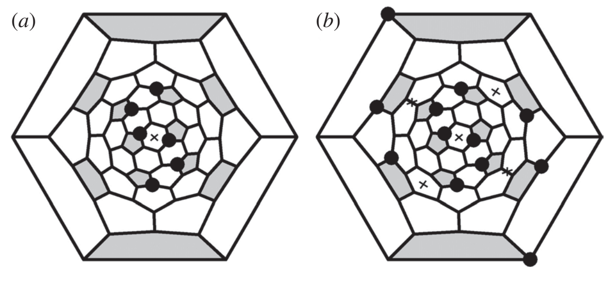

Figure 3 Schlegel diagrams of (*a*) C_2-$C_{84}(22)(CF_3)_6$ and (*b*) D_2-$C_{84}(22)(CF_3)_{12}$.

In summary, C_2-$C_{84}(22)(CF_3)_6$ was isolated by HPLC from the products of trifluoromethylation of C_{84}. Its molecular structure was elucidated by single crystal X-ray diffraction. C_2-$C_{84}(22)(CF_3)_6$ is formed as the most stable isomer on the pathway to the known C_2 and D_2 isomers of $C_{84}(22)(CF_3)_{12}$. The molecular structure of D_2-$C_{84}(22)(CF_3)_{12}$ was determined with a better accuracy than that in the previous work.

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