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# Trifluoromethyl derivatives of $C_{88}$ (33) fullerene

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**The synthesis, separation and X-ray crystallographic analysis of the trifluoromethyl derivatives of fullerene $C_{88}$ (isomer 33), $C_{88}(CF_3)_n$ ($n$ = 16, 18 and 20), revealed close relations between their addition patterns, which indicate the formation of higher derivatives from lower ones by the addition of $CF_3$ groups.**

With respect to $C_{60}$ and $C_{70}$, higher fullerenes are difficult to investigate due to their low abundance in fullerene soot and a growing number of possible IPR (Isolated Pentagon Rule) isomers.[1] $^{13}$C NMR spectroscopy does not always provide the unambiguous identification of higher fullerenes, whereas the use of single crystal X-ray diffraction for purified crystalline samples is hampered due to an orientational disorder of fullerene molecules in crystals. The derivatization of higher fullerenes is an effective method for studying higher fullerenes because of more simple separation and a rigid fixation of derivatized molecules in the crystal packing.

Topological analysis shows that $C_{88}$ has 35 isomers obeying the IPR.[1] Only a single isomer of $C_2$ symmetry was found in the HPLC isolated $C_{88}$ on the basis of $^{13}$C NMR spectra.[2] The $C_{88}$ fraction was separated into three subfractions by multistep HPLC. A $^{13}$C NMR-spectroscopic study allowed one to assign them as one isomer with $C_s$ symmetry and two isomers with $C_2$ symmetry.[3] Interpretation of these results has been supported by the theoretical prediction of $^{13}$C NMR shifts. Three most probable isomer nos. 7 ($C_2$), 17 ($C_s$) and 33 ($C_2$), were suggested, which were found most stable according to theoretical calculations.[4–6] So far the unambiguous confirmation of cage connectivity by the X-ray crystallographic study of derivatives has been accomplished for isomer 33 as the trifluoromethylated derivative $C_{88}(33)(CF_3)_{18}$[7] and, very recently, for isomer 17 as the chlorinated derivatives $C_{88}(17)Cl_{16}$ and $C_{88}(17)Cl_{22}$.[8] Here, we report the further development of the chemistry of $C_{88}$ (33) by the synthesis, isolation and structural characterization of three $C_{88}(33)(CF_3)_n$ compounds with $n$ = 16, 18 and 20.

Trifluoromethylated derivatives were synthesized by the reaction of a mixture of higher fullerenes $C_{76}$–$C_{90}$ (MER Corp.) with $CF_3I$ (98%, Apollo) in sealed glass ampoules at 400 °C for 40–60 h or in sealed quartz ampoules at 550 °C for 1 h. The ampoules were opened and an excess of $CF_3I$ and $I_2$ was removed by heating in open air. The orange sublimates deposited in the colder part of the ampoules contained a complex mixture of $CF_3$ derivatives of $C_{60}$, $C_{70}$ and $C_{76}$–$C_{96}$ according to MALDI MS analysis performed in the negative ion mode using a Bruker AutoFlex II time-of-flight reflectron device (DCTB matrix). The number of $CF_3$ groups attached to different fullerenes ranged from 10 to 20, whereas the derivatives of $C_{88}$ contained from 16 to 20 $CF_3$ groups.

The sublimate of the synthesis at 400 °C was dissolved in hexane and separated by HPLC (10×250 mm Cosmosil Buckyprep column; eluent, hexane; flow rate, 4.6 ml min$^{-1}$). The fractions eluted at 8.9 and 47.0 min contained $C_{88}(CF_3)_{20}$ and $C_{88}(CF_3)_{18}$ compounds, respectively, as main components according to MALDI mass spectrometry (Figure 1). The yellow crystals of $C_{88}(CF_3)_{20}$ were grown by the slow concentration of a hexane solution, whereas the yellow crystals of $C_{88}(CF_3)_{18}$ were obtained after recrystallization from toluene or *o*-dichlorobenzene as corresponding solvates. X-ray analysis with the use of synchrotron radiation proved the formation of $C_{88}(CF_3)_{20}$, $C_{88}(CF_3)_{18}\cdot1.5C_6H_5Me$ and $C_{88}(CF_3)_{18}\cdot0.82\,o$-DCB, respectively.†

The sublimed product of the synthesis at 550 °C was dissolved in toluene and first subjected to HPLC separation in toluene at a flow rate of 4.6 ml min$^{-1}$. The toluene fraction eltuted between 4.6 and 7.8 min was subjected to further separation using a toluene–hexane mixture (3 : 7) as an eluent at a flow rate of 4.6 ml min$^{-1}$. According to MALDI mass spectrometry analyses, the fraction with a retention time of 8.5 min contained $C_{88}(CF_3)_{16}$ with small amounts of $C_{84}(CF_3)_{16}$ and $C_{90}(CF_3)_{14}$. After recrystallization from toluene, yellow crystals of $C_{88}(CF_3)_{16}$ were obtained, which were investigated by X-ray crystallography using synchrotron radiation.†

† *Crystal data*. Synchrotron X-ray data were collected at 100 K at the BL14.2 at the BESSY storage ring (PSF at the Free University of Berlin, Germany) using a MAR225 CCD detector, $\lambda$ = 0.9050 or 0.8856 Å. Structures were solved by SHELXD and refined with SHELXL.

Crystals of $C_{88}(CF_3)_{16}$ are monoclinic, space group $C2/c$, $a$ = 30.849(2), $b$ = 12.5551(5) and $c$ = 21.623(1) Å, $\beta$ = 123.465(9)°, $V$ = 6986.5(6) Å$^3$, $Z$ = 4. The $C_{88}(CF_3)_{16}$ molecule is situated on a two-fold axis. Anisotropic refinement with 7368 reflections and 685 parameters to $wR_2$ = 0.190 and $R_1$ = 0.074 for 5167 reflections with $I > 2\sigma(I)$.

Crystals of $C_{88}(CF_3)_{18}\cdot0.82o$-$C_6H_4Cl_2$ are triclinic, space group $P\bar{1}$, $a$ = 13.388(1), $b$ = 14.686(1) and $c$ = 21.351(2) Å, $\alpha$ = 85.919(3)°, $\beta$ = = 82.763(3)°, $\gamma$ = 70.874(3)°, $V$ = 3932.6(5) Å$^3$, $Z$ = 2. Refinement with 13623 reflections and 1514 parameters to $wR_2$ = 0.217 and $R_1$ = 0.078 for 6473 reflections with $I > 2\sigma(I)$.

Crystals of $C_{88}(CF_3)_{18}\cdot1.5C_6H_5Me$ are triclinic, space group $P\bar{1}$, $a$ = = 13.6318(6), $b$ = 13.8220(6) and $c$ = 22.888(1) Å, $\alpha$ = 86.149(2)°, $\beta$ = = 85.841(2)°, $\gamma$ = 74.468(2)°, $V$ = 4139.0(3) Å$^3$, $Z$ = 2. Anisotropic refinement with 15249 reflections and 1624 parameters yielded a conventional $R_1$ = 0.061 for 12047 reflections with $I > 2\sigma(I)$ and $wR_2$ = 0.165 for all reflections. One of toluene molecules is disordered over two positions around an inversion centre.

Crystals of $C_{88}(CF_3)_{20}$ are triclinic, space group $P\bar{1}$, $a$ = 16.3307(6), $b$ = 22.273(1) and $c$ = 22.853(1) Å, $\alpha$ = 104.809(3)°, $\beta$ = 90.038(2)°, $\gamma$ = 102.597(2)°, $V$ = 7828.8(6) Å$^3$, $Z$ = 4. The asymmetric unit contains two $C_{88}(CF_3)_{20}$ molecules. Anisotropic refinement with 28568 reflections and 3109 parameters yielded a conventional $R_1$ = 0.083 for 19035 reflections with $I > 2\sigma(I)$ and $wR_2$ = 0.219 for all reflections.

CCDC 857643–857646 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

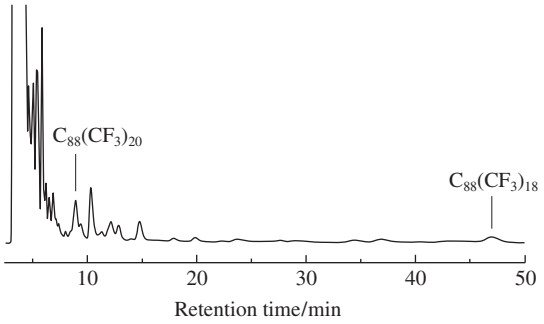


**Figure 1** HPLC trace of the mixture of trifluoromethylated fullerenes recorded in hexane (Cosmosil Buckyprep column, flow rate of 4.6 ml $min^{-1}$). The positions of the $C_{88}(33)(CF_3)_{18}$ and $C_{88}(33)(CF_3)_{20}$ fractions are shown.

Note that the ampoule syntheses performed at 400 and 550 °C resulted in similar compositions of the sublimates in the colder part of the ampoules. All three compounds of interest were present in both of the syntheses. However, the following separation and crystallization procedures were different, and they did not allow us to isolate crystalline materials from all chromatographic fractions.

The analysis of the connectivity in four crystallographically characterized $C_{88}(CF_3)_{16–20}$ compounds proved them to contain the same carbon cage of fullerene $C_{88}$ isomer 33 possessing $C_2$ symmetry. $C_{88}(33)(CF_3)_{18}$ was reported previously as a solvate with *p*-xylene and a solvent-free compound,[7] whereas two new crystal structures represent the solvates with toluene and *o*-dichlorobenzene, respectively. Note that the $C_1$-$C_{88}(33)(CF_3)_{18}$ molecule remains essentially the same in all four crystal structures. Two other derivatives of $C_{88}$ (33) with 16 and 20 $CF_3$ groups have been isolated and structurally characterized for the first time.

Three $C_{88}(33)(CF_3)_n$ ($n$ = 16, 18 and 20) molecules are shown in Figure 2 as projections along the two-fold axes of $C_{88}$ (33) carbon cages. It can be seen that the simple addition of two $CF_3$ groups to the $C_2$-$C_{88}(33)(CF_3)_{16}$ molecule (with crystallographically imposed two-fold symmetry) produces the $C_1$-$C_{88}(33)(CF_3)_{18}$ molecule, whereas the further addition of two $CF_3$ groups to the latter results in the formation of $C_2$-$C_{88}(33)(CF_3)_{20}$ (with non-crystallographic two-fold symmetry). The $C_2$ symmetry of a hypothetical molecule of $C_{88}(33)(CF_3)_{20}$ as a product of the further trifluoromethylation of $C_1$-$C_{88}(33)(CF_3)_{18}$ has been suggested previously.[7]

A more detailed comparison and discussion of the addition patterns of the three $C_{88}(33)(CF_3)_n$ molecules is possible by the examination of their Schlegel diagrams presented in Figure 3. Common features of all three addition patterns are the attachments exclusively to the positions of pentagon-hexagon-hexagon junctions, thus avoiding attachments in position of less favourable triple hexagon junctions (THJs). Most $CF_3$ groups are attached in *para* positions in hexagons under formation of nearly isolated benzenoid rings (with typical C–C distances of 1.39–1.40 Å) and isolated or nearly isolated C=C double bonds on the fullerene cage (with C–C distances in the range of 1.32–1.34 Å).

The addition pattern of $C_2$-$C_{88}(33)(CF_3)_{16}$ is characterized by the presence of two nearly isolated benzenoid cycles and two

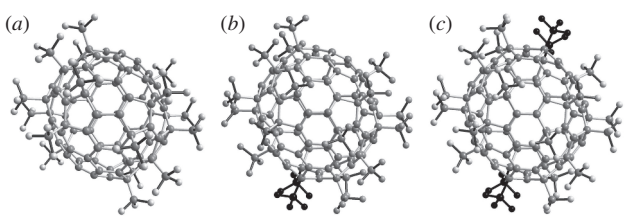


**Figure 2** Molecular structures of $C_{88}(33)(CF_3)_{16,18,20}$ shown along two-fold axes of the $C_{88}$ fullerene cages. Additional pairs of $CF_3$ groups on going from $n$ = 16 (*a*) to $n$ = 20 (*c*) are marked black.

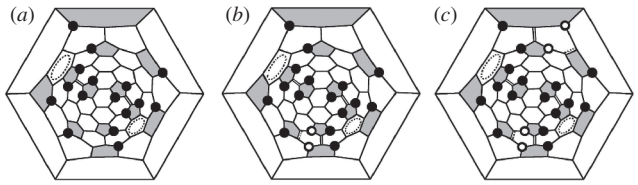


**Figure 3** Schlegel diagrams of $C_{88}(33)(CF_3)_{16,18,20}$ (*a*)–(*c*). Black circles denote the positions of attached $CF_3$ groups, whereas empty circles indicate the groups attached additionally to the structure of $C_{88}(33)(CF_3)_{16}$ (*a*). Cage pentagons are shown in grey. Nearly aromatic (benzenoid) cycles, as well as isolated (and nearly isolated) double C=C bonds, are also indicated.

isolated C–C double bonds on the $C_{88}$ fullerene cage. 16 $CF_3$ groups form two domains of 8 groups situated symmetrically. In the $C_1$-$C_{88}(33)(CF_3)_{18}$ molecule, two additional $CF_3$ groups occupy *para* positions in a hexagon, which leads to the formation of one isolated and one nearly isolated C–C double bonds. Two additional $CF_3$ groups in $C_2$-$C_{88}(33)(CF_3)_{20}$ restore the two-fold symmetry of the whole molecule. There are two nearly isolated benzenoid rings, four isolated and two nearly isolated C–C double bonds on the fullerene cage. It can be suggested that the simple structural relations between the $C_{88}(33)(CF_3)_n$ molecules with 16, 18 and 20 $CF_3$ groups correspond to the addition pathway in the trifluoromethylation of $C_{88}$ (33). Similarly, the successive additions of $CF_3$ groups have also been found among the $CF_3$ derivatives of $C_{60}$[9] and $C_{70}$.[10]

In summary, the trifluoromethylation of a mixture of higher fullerenes followed by the HPLC separation of $C_{88}(CF_3)_n$ and the X-ray analysis of crystalline samples resulted in the structure determination of derivatives of $C_{88}$ (33) with $n$ = 16, 18 and 20. The fact that the addition pattern of $C_{88}(33)(CF_3)_{16}$ is a substructure of $C_{88}(33)(CF_3)_{18}$, whereas the latter in its turn is a substructure of $C_{88}(33)(CF_3)_{20}$, allowed us to suggest that the lower derivative represents a precursor of the higher derivative in the course of trifluoromethylation.

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