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Isomer $C_{78}(2)$ captured as the perfluoroethyl derivative $C_{78}(C_2F_5)_{10}$

Nadezhda B. Tamm and Sergey I. Troyanov*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 1240; e-mail: stroyano@thermo.chem.msu.ru

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The pentafluoroethylation of higher fullerenes followed by the HPLC separation of C_2F_5 derivatives resulted in the isolation of $C_{78}(C_2F_5)_{10}$, the molecular structure of which was determined by single crystal X-ray crystallography and revealed the presence of a $C_{78}(2)$ isomeric cage.

Since the discovery of fullerenes, the chemistry of C_{60} and C_{70} has been developed very rapidly, whereas the isolation and study of higher fullerenes (beyond C_{70}) remained a continuous task. Higher fullerenes are much less abundant in fullerene soot. Furthermore, the existence of different cage isomers with similar properties drastically complicates the isolation of individual isomers.[1] Functionalization of higher fullerenes significantly contributes to the characterization of corresponding cage isomers because fullerene derivatives are easier to separate.[2,3] In the case of C_{78} possessing five possible IPR isomers,[4] several derivatives have been isolated and structurally characterized by X-ray crystallography or/and NMR spectroscopy. Bromide ($C_{78}Br_{18}$) and chlorides ($C_{78}Cl_{18}$) show the same addition pattern of 18 halogen atoms on C_{78} fullerene cage independent on the cage isomer of parent C_{78}, C_{2v} (isomers 2 and 3)[5] or D_3 (isomer 1).[6] In contrast, the trifluoromethylation of C_{78} resulted in substantially different addition patterns for $C_{78}(CF_3)_{10}$ and $C_{78}(CF_3)_{12}$ compounds.[3,7] Herein, we report the synthesis, isolation and crystallographic characterization of the first pentafluoroethyl derivative of C_{78}, $C_{78}(C_2F_5)_{10}$, and discuss its addition pattern in comparison with other known examples of $C_{78}X_n$ compounds.

A mixture of higher fullerenes C_{76}–C_{96} and small amounts of C_{60} and C_{70} (15 mg, MER Corp.[8]) reacted with excess C_2F_5I in a glass ampoule at 250 °C for 4–5 days. After ampoule opening, the excess C_2F_5I and I_2 were removed by heating at 100 °C in open air for several hours. According to MALDI mass-spectrometric analysis, the deep brown reaction product contained numerous C_2F_5 derivatives of C_{60}, C_{70} and higher fullerenes with the number of attached groups from 8 to 12. The mixture was partially dissolved in hexane and the solution was subjected to HPLC separation using a Cosmosil Buckyprep column (10 mm i.d. × 25 cm) and hexane as the eluent (4.6 ml min^{-1}), monitored at 290 nm. MALDI MS analyses of chromatographic fractions eluted between 3.5 and 35 min revealed the presence of $C_{78}(C_2F_5)_n$ compounds with n = 8–12. The fraction eluted at 20.5 min, which contained $C_{78}(C_2F_5)_{10}$ as the main component [with a small admixture of $C_{70}(C_2F_5)_{10}$ according to MALDI MS], was evaporated to dryness. Recrystallization from *p*-xylene and toluene afforded small red crystals, which were investigated by singe crystal X-ray diffraction with the use of synchrotron radiation.†

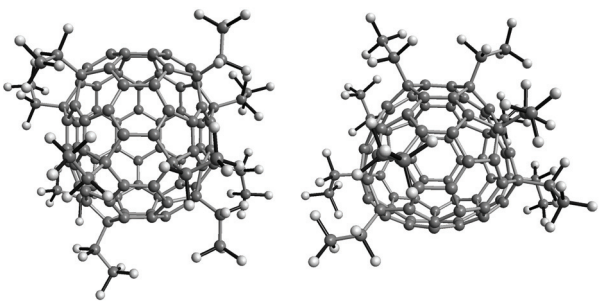

Figure 1 Top and side views of the $C_{78}(C_2F_5)_{10}$ molecule.

The first perfluoroethylated C_{78}, C_1-$C_{78}(C_2F_5)_{10}$, turned out to be a derivative of the cage isomer 2 possessing C_{2v} point group symmetry (Figure 1).[4] Ten C_2F_5 groups are attached in three different regions on the cage forming a p^5 ribbon of five edge-sharing *para*-$C_6(C_2F_5)_2$ hexagons and two separate *para*-$C_6(C_2F_5)_2$ hexagons. Therefore, the addition pattern of ten groups can be described as p^5,p,p (Figure 2).‡ It can be compared with a p^9 ribbon of $C_6(CF_3)_2$ hexagons in the molecule of C_s-$C_{78}(CF_3)_{10}$ also formed by the C_{78} (2) isomer.[7] Schlegel diagrams in Figure 2 demonstrate that the addition patterns of the both molecules differ by the positions of only two fluoroalkyl groups. While all CF_3 groups in C_s-$C_{78}(CF_3)_{10}$ are attached to C atoms not belonging to interpentagonal C–C bonds (ICCB's), two C_2F_5 groups in $C_{78}(C_2F_5)_{10}$ occupy such positions. Therefore, the addition pattern in $C_{78}(C_2F_5)_{10}$ violates the rule concerning a non-involvement of ICCB C atoms formulated for addition of bulky groups to higher hollow fullerenes.[3] Other exceptions were provided recently.[7]

† *Crystal data.* Synchrotron X-ray data were collected at 100 K at the BL 14.2 at the BESSY storage ring (PSF at the Free University of Berlin, Germany) using a MAR225 CCD detector, λ = 0.9050 Å.

$C_{78}(C_2F_5)_{10}$·*p*-$C_6H_4(CH_3)_2$: M = 2233.14, monoclinic, space group $P2_1/n$, a = 14.2735(1), b = 14.4448(1) and c = 37.7172(3) Å, β = 99.5307(4)°, V = 7669.1(1) Å^3, μ = 0.198 mm^{-1}, Z = 4. Reflections collected 76595, independent 15282, R_{int} = 0.092. Anisotropic refinement with 1499 parameters yielded a conventional $R_1(F)$ = 0.087 for 11746 reflections with $I > 2\sigma(I)$ and $wR_2(F^2)$ = 0.224 for all reflections. Two C_2F_5 groups are disordered between two orientations each.

$C_{78}(C_2F_5)_{10}$·$C_6H_5(CH_3)$: M = 2219.11, triclinic, space group $P\bar{1}$, a = = 14.6617(6), b = 18.746(1) and c = 28.558(2) Å, α = 75.231(2)°, β = = 85.983(2)° and γ = 84.810(3)°, V = 7549.7(7) Å^3, μ = 0.201 mm^{-1}, Z = 4. Reflections collected 89105, independent 27597, R_{int} = 0.295. Anisotropic refinement with 2821 parameters yielded a conventional $R_1(F)$ = 0.074 for 11093 reflections with $I > 2\sigma(I)$ and $wR_2(F^2)$ = 0.182 for all reflections. One C_2F_5 group is disordered between two orientations.

Esd's of C–C bonds within the fullerene cage are 0.006–0.008 Å for the both structures.

CCDC 735641 and 735642 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, 2009.

‡ IUPAC lowest-locant abbreviation reads: 8,28,34,37,46,55,60,65,69,72-$C_{78}(C_2F_5)_{10}$.

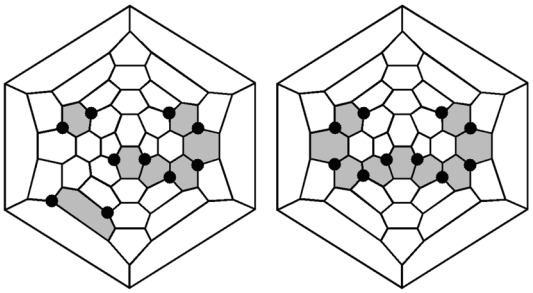

Figure 2 Schlegel diagrams of the $C_{78}(C_2F_5)_{10}$ (left) and $C_{78}(CF_3)_{10}$ (right) molecules both containing the $C_{78}(2)$ isomeric cage. $C_6(C_2F_5)_2$ hexagons are high-lighted with grey colour.

Each C_{78} isomer possesses its own stereochemical behaviour in respect of the addition of bulky groups such as perfluoroalkyls. Therefore, the addition pattern of $C_{78}(C_2F_5)_{10}$ cannot be directly compared with the known CF_3 derivatives of C_{78} isomers 1, 3 and 5.[3,7] It is remarkable that the higher chlorides, $C_{78}Cl_{18}$, of the three different C_{78} isomers 2, 3 and 5 (chlorides of isomers 1 and 4 are unknown) have the same addition pattern in respect of mutual positions of 18 Cl atoms.[5,6] In these cases, the same distribution of 18 Cl atoms produces very similar combinations of two triphenylene fragments, three benzenoid rings and three isolated double bonds on C_{78} fullerene cages. As a result, solvent-free crystals of $C_{78}Cl_{18}$ exhibit the same hexagonal packing motifs (and similar unit cell parameters) though the $C_{78}Cl_{18}$ molecule as a packing unit can be represented either by a molecule with distinct C_{78} cage isomer[5(*c*),6] or by a combination (overlap) of molecules containing different C_{78} cages.[5(*b*)]

In summary, the pentafluoroethylation of a mixture of higher fullerenes followed by the HPLC separation of pentafluoroethyl derivatives afford $C_{78}(C_2F_5)_{10}$. Single crystal X-ray crystallography revealed the presence of $C_{78}(2)$ cage and ten C_2F_5 groups forming the p^5,*p*,*p* addition pattern with two groups attached to carbon atoms of interpentagonal C–C bonds.

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