Two Isomers of $C_{60}F_{48}$: An Indented Fullerene**

Sergei I. Troyanov,* Pavel A. Troshin, Olga V. Boltalina,* Ilya N. Ioffe, Lev N. Sidorov, and Erhard Kemnitz

$C_{60}F_{48}$ has the highest known fluorine content per fullerene molecule, and thus possesses many unique properties, such as high reduction potential[1] and high electron affinity;[2] it is able to accept up to two electrons in solution[1] and even in the gas phase.[3] Bulk preparation of $C_{60}F_{48}$ by direct fluorination as reported recently now makes it possible to explore useful properties of this remarkable compound.[4]

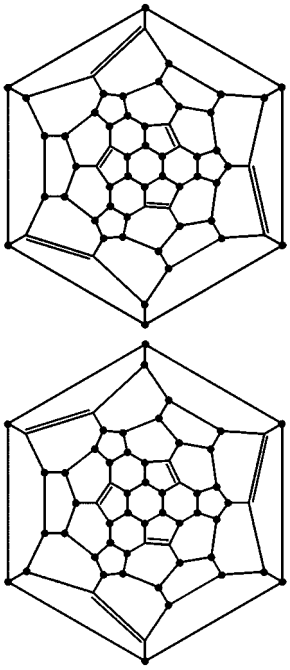

Figure 1. The Schlegel diagrams for the D_3 (top) and S_6 (bottom) isomers of $C_{60}F_{48}$.

On the basis of ^{19}F NMR spectroscopy, $C_{60}F_{48}$ was assigned a structure with D_3 symmetry.[5] The chiral D_3 isomer, which can exist in *R*,*R* and *S*,*S* forms, also has an *R*,*S* *meso* form with S_6 symmetry; both D_3 and S_6 molecules consist of two equivalent hemispheres related by C_2 rotation or inversion, respectively (Figure 1). These isomers were found to be isoenergetic and indistinguishable by simple NMR spectroscopy, and it has been suggested that infrared (IR) spectroscopy could assist with the assignment of the isomeric composition of $C_{60}F_{48}$.[6] A more definitive result could come from a single-crystal structure determination as was recently performed for $C_{60}F_{18}$ and its oxygenated and trifluoromethylated derivatives.[7] Hitherto, attempts to determine the precise structure of highly fluorinated fullerenes ($C_{60}F_x$ $x \geq 36$) by X-ray methods have been unsuccessful because of the rotational disorder of the molecules and the unavailability of specific fluorofullerenes in pure form.[8]

Herein, the first single-crystal X-ray structure of $C_{60}F_{48}$ is reported. Single crystals of molecular complexes of $C_{60}F_{48}$ with *o*-, *m*-xylenes, toluene, and mesitylene were studied, but only with the latter were we able to succeed in determining the structure by X-ray analysis. The crystal structure determination is complicated by the presence of both D_3 and S_6 isomeric $C_{60}F_{48}$ molecules, which are each statistically disordered over two positions. After careful analysis we managed to separate the contribution of the *R* and *S* configurations on both hemispheres of the $C_{60}F_{48}$ molecule.

Both structures have crystallographic three-fold symmetry and contain six isolated double bonds, three on each hemisphere (Figure 2). In the carbon cage, the C–C bonds can be divided into three groups according to the hybridization type of the C atoms:[9] $C(sp^2)-C(sp^3)$ (**A**–**D**), $C(sp^3)-C(sp^3)$ (**E**–**H**),

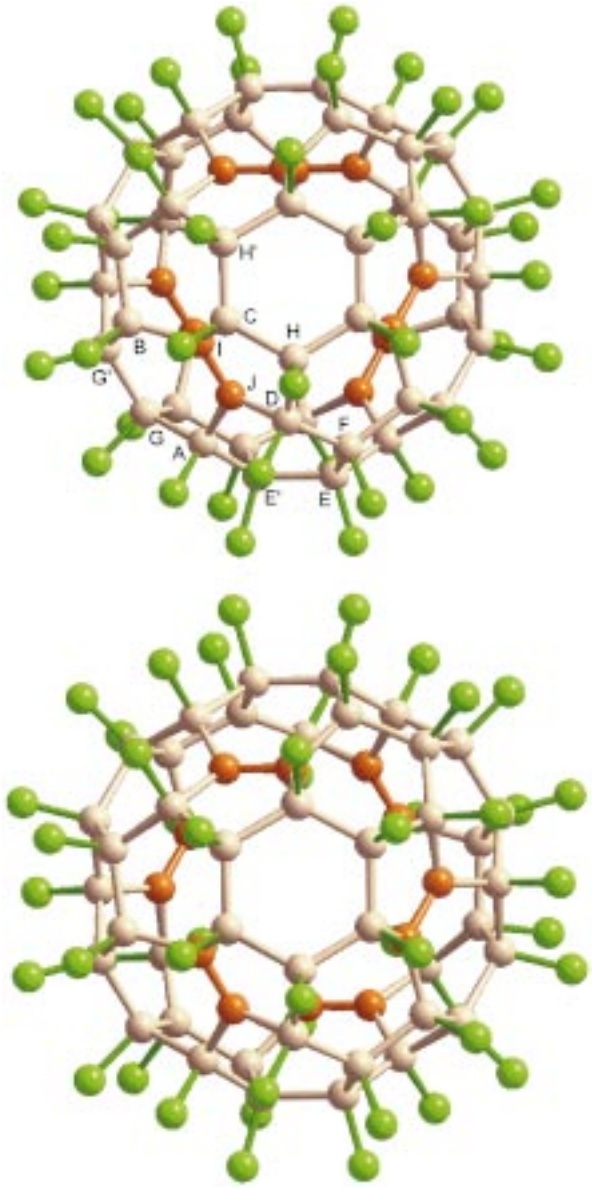

Figure 2. The structures of the D_3 (top) and S_6 (bottom) isomers of $C_{60}F_{48}$ as determined by X-ray crystallography. Double bonds and sp^2 carbons are indicated by orange color.

[*] Dr. S. I. Troyanov, Dr. O. V. Boltalina, P. A. Troshin, I. N. Ioffe, Prof. L. N. Sidorov
Chemistry Department
Moscow State University
Moscow 119899 (Russia)
Fax: (+7) 095-9391249
E-mail: troyanov@thermo.chem.msu.ru, ovb@capital.ru
Prof. Dr. E. Kemnitz
Institut für Chemie, Humboldt-Universität
Berlin, 10115 (Germany)

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C(sp^2)–C(sp^2) (**I**, **J**) with average C–C bond lengths, 1.49–1.53 Å, 1.54–1.63 Å, and 1.30 Å, respectively (Table 1). The C–F bond lengths fall in the range 1.36–1.40 Å. The C–C double bonds are much shorter than the 6,6 bonds in C_{60} (1.40 Å) and close to the value for a localized double bond (1.33–1.34 Å). The longest C–C bonds (1.60–1.63 Å) are situated near the equator of the molecule. For comparison, $C_{60}F_{18}$ has even longer C(sp^3)–C(sp^3) bonds (up to 1.67 Å).[7]

Table 1. C–C and C–F bond lengths [Å] in $C_{60}F_{48}$ (D_3 isomer) determined from the X-ray data and DFT calculations.

C–C	X-ray	Calcd	C–C	X-ray	Calcd	C–F	X-ray	Calcd
A-J	1.493(3)	1.488	**C-H**	1.566(3)	1.582	**a**	1.385(3)	1.392
B-I	1.513(4)	1.494	**C-H′**	1.544(3)	1.553	**b**	1.358(3)	1.390
C-I	1.534(4)	1.503	**D-F**	1.544(4)	1.570	**c**	1.362(3)	1.392
D-J	1.530(4)	1.510	**D-H**	1.606(4)	1.611	**d**	1.376(4)	1.387
A-E	1.562(3)	1.583	**E-F**	1.604(3)	1.633	**e**	1.370(3)	1.368
A-G	1.576(3)	1.574	**E-E′**	1.627(3)	1.636	**f**	1.395(3)	1.369
B-F	1.559(3)	1.578	**G-G′**	1.610(3)	1.610	**g**	1.366(3)	1.374
B-G	1.558(3)	1.560	**I-J**	1.301(4)	1.338	**h**	1.377(3)	1.368

Mutual repulsion of the F atoms results in a considerable shift of four F atoms bonded to carbons **A**–**D** towards the area over the double bond. Distortions of the cage in such areas are so significant that prominent concavities are formed (Figure 3). This allows us to add an "indented" fullerene molecule $C_{60}F_{48}$ to the previously reported series of distorted cages of fluorofullerenes: $C_{60}F_{18}$—a flattened cage[7] and $C_{60}F_{20}$—a squashed fullerene.[10]

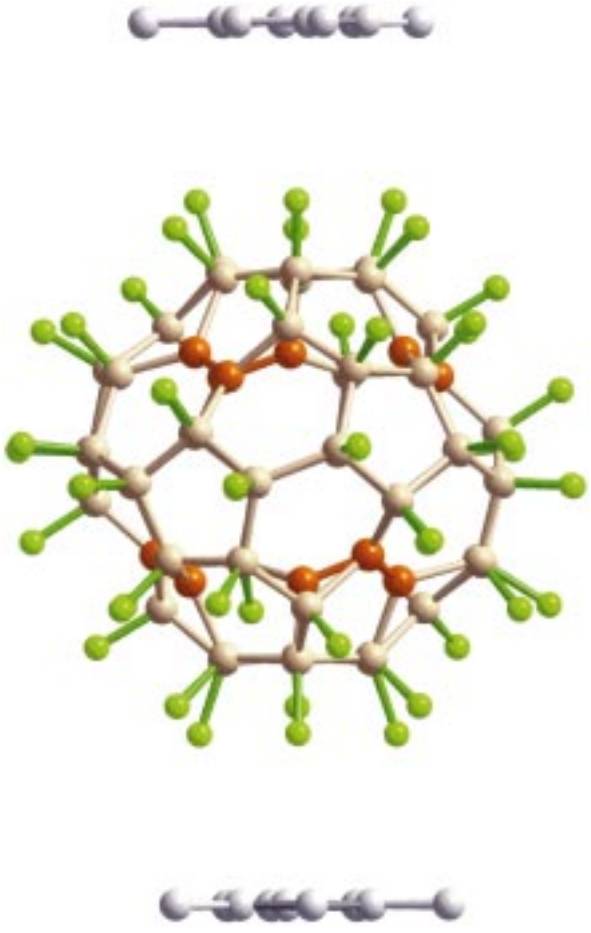

Figure 3. View of the D_3 isomer of $C_{60}F_{48}$ along the noncrystallographic twofold axis. Two mesitylene molecules are also shown.

The difference between 360° and the sum of three C-C-C angles gives the measure of convexity at a given C atom, it falls in the range 15–30° for all the "normal" sp^3 carbon atoms, whereas the C atoms in the concave regions have values of 3–5°. This results in a considerable difference in the distances of the C atoms from the center of the $C_{60}F_{48}$ carbon cage compared with that of the parent C_{60} (3.56 Å):[11] there is a dramatic shortening of the distance between the sp^2 carbons and the cage center (3.05 Å, **I**, **J**) and an increase in the distance between the cage center and the two types of sp^3 carbons (3.79 Å, **A**–**D**; 3.94 Å, **E**–**H**). For the same reason, there are two sets of cage-center to F atom distances with average values of 5.05 Å (**a**–**d**) and 5.31 Å (**e**–**h**). These values can be compared with the single-crystal data for rotating molecules in a sample with an average composition $C_{60}F_{46}$,[8] where the distance distribution was approximated by three spherical shells with radii of 3.13 Å (**I**, **J**), 3.83 Å (**A**–**H**), and 5.12 Å (fluorine shell).

One of the most important consequences of the distribution of fluorine atoms over the cage is the effective shielding of the double bonds, the F···F distances between the **a** and **c**, and the **b** and **d** atoms being only 4.2 Å (Figure 4). Thus, one might expect lower reactivity of $C_{60}F_{48}$ compared with that of $C_{60}F_x$ ($x < 48$). Indeed, $C_{60}F_{48}$ was found to be the final product of direct fluorination.[4] Furthermore, attempts to achieve perfluorination of C_{60} by applying more harsh experimental conditions resulted in cage disruption but not in the preparation of $C_{60}F_{60}$.[12]

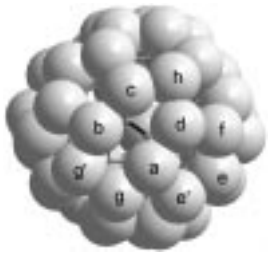

Figure 4. A drawing of the $C_{60}F_{48}$ molecule (D_3), which illustrates shielding of the C–C double bond (shown as a black line) by the adjacent fluorine atoms **a**–**d**.

The packing of $C_{60}F_{48}$ in the crystal of the mesitylene solvate can be approximated as a simple cubic arrangement with an average center–center separation of 11.6 Å. For comparison, the separation between rotating molecules in the solid $C_{60}F_{46}$ was found to be 12.2 Å.[8] Mesitylene molecules of two types are situated in parallel orientation above and below the fluorinated hexagons on the top and the bottom of $C_{60}F_{48}$ (Figure 3). The alternation of $C_{60}F_{48}$ and two types of mesitylene molecules along a threefold axis can be given as $C_{60}F_{48}$-mesitylene1–mesitylene1–$C_{60}F_{48}$–mesitylene2–mesitylene2-$C_{60}F_{48}$···. The shortest C···F separations (3.25–3.60 Å) between a mesitylene molecule and a $C_{60}F_{48}$ molecule on the same three-fold axis as well as to two other neighboring $C_{60}F_{48}$ molecules are apparently responsible for hindering rotational motion of fluorofullerenes in the crystal.

Experimental Section

$C_{60}F_{48}$ was prepared by direct fluorination of C_{60} (> 99.9 %, TERMUSA) at 350 °C as described previously[4] and used for crystal growth without further purification. The purity, estimated by chemical analysis, solid state ^{19}F NMR spectroscopy, and mass spectrometry, was around 95 %. Dark violet

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cubic crystals of $C_{60}F_{48}\cdot 2\,C_6H_3Me_3$ of X-ray quality were grown from the mesitylene solution. A crystal with dimensions $0.3\times0.3\times0.2$ mm was investigated on an image-plate diffractometer (IPDS, Stoe) at 180 K (graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $2\theta(\max)=53.5^\circ$). A primitive cubic unit-cell parameter was refined with 1267 reflections to $a=23.229(3)$ Å, $V=12534(3)$ Å^3, $Z=8$. The intensities of 99277 measured reflections were corrected for Lorentz and polarization factors and averaged, yielding 4526 unique reflections. Absorption correction was not applied ($\mu=2.16$ cm^{-1}). Space group $Pa\bar{3}$ was established on the basis of systematic absences. The structure was solved by direct methods (SHELXS-97) resulting in a raw model with a $C_{60}F_{48}$ molecule on a three-fold axis. However, a high R_1 value (20%) and splitting of some atoms were indicative of disorder. It was found that the duplicate positions of some atoms correspond to an overlap of the *R* and *S* configurations of two hemispheres. The different *R*/*S* ratios for hemisphere I (83/17) and hemisphere II (56/44) can be interpreted as overlap of $C_{60}F_{48}$ molecules with a noncrystallographic D_3 (*R*,*R*′ and *S*,*S*′) and S_6 (*R*,*S*′ and *S*,*R*′) point symmetry. In the mixture of two isomers in the single crystals, the estimated content of D_3 is in the range of 39–73%. The final refinement on F^2 with 4331 reflections and 474 parameters was carried out anisotropically for all non-hydrogen atoms (except for the 17% component on hemisphere I and H atoms of mesitylene in calculated positions), and converged to $wR_2=0.1589$ and $R_1=0.0508$(SHELXL-97).[13] As a result of a different degree of disorder, the positions of C and F atoms belonging to the main component on hemisphere I were determined with better precision (standard deviations 0.003–0.004 Å for C–C and C–F bonds), than for hemisphere II (standard deviations 0.003–0.007 Å) The more reliable values for C–C and C–F bond lengths on hemisphere I were used for comparison with the results of theoretical calculations (Table 1).

The geometry optimization was performed by using density functional theory (DFT) calculations with the PRIRODA program, which employs an economic calculating approach with insignificant loss of accuracy.[14] The PBE exchange-correlation functional[15] and a Gaussian-type basis set of TZ2P quality[14] was used. The validity of our approximations was tested on $C_{60}F_{18}$ and some other fluorocarbons, revealing good accuracy with only slight bond length overestimations (0.01 Å on average).

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$Bi_4Te_4^{4+}$—A Cube-Shaped, Polycationic Main Group Element Cluster**

Johannes Beck,* Michael Dolg, and Stefan Schlüter

Electron-rich main group elements are able to form polycationic clusters. Such ligand-free clusters are known for the halogens chlorine to iodine, for all chalcogens, for bismuth, for cadmium, and for mercury.[1] There are several methods for their synthesis, all of which involve electrophilic and acidic media such as H_2SO_4, HSO_3F, anhydrous HF, molten salts such as $Na[AlCl_4]$, or liquid SO_2. The respective elements are oxidized and converted to the polycationic clusters by suitable oxidants such as AsF_5, SbF_5, WCl_6, or $MoOCl_4$, or by an element halide in the presence of a strong halide-ion acceptor such as $AlCl_3$ or $ZrCl_4$. The number of known structure types increases with the atomic mass of the elements. Only three homonuclear cations of sulfur are known and have been structurally characterized, S_4^{2+},[2] S_8^{2+},[3] and S_{19}^{2+}.[4] In contrast, for tellurium more than a dozen ring- or chain-shaped species have been described. The situation is similar for the elements belonging to Group 15. Sb_5^{3+}[5] is poorly characterized; for bismuth, however, a family of cluster ions exists, such as Bi_5^{3+},[6] Bi_8^{2+},[7] Bi_9^{5+},[8] which were isolated as the corresponding chloroaluminates, hexachlorozirconates, and -hafnates, and Bi_5^+ and Bi_6^{2+}, which were discovered in the structure of the subbromide $Bi_{34}Ir_3Br_{37}$.[9]

Like no other element tellurium is able to form hetereonuclear polycations besides homonuclear molecules. A number of mixed clusters are known containing the lighter chalcogens sulfur and selenium, for example $Te_4Se_3^{2+}$[10] and $Te_3S_3^{2+}$.[11] So far no other mixed polycations apart from Te/Se

[*] Prof. Dr. J. Beck, Dipl.-Chem. S. Schlüter
Institut für Anorganische Chemie der Universität Bonn
Gerhard-Domagk-Strasse 1, 53121 Bonn (Germany)
Fax: (+49) 228-735660
E-mail: j.beck@uni-bonn.de
Prof. Dr. M. Dolg
Institut für Physikalische und Theoretische Chemie
der Universität Bonn
Wegelerstrasse 12, 53115 Bonn (Germany)

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