

Ivan E. Kareev,^{a,b} Sergey F. Lebedkin,^b Susie M. Miller,^c Oren P. Anderson,^c Steven H. Strauss^{c*} and Olga V. Boltalina^c

^aInstitute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Russian Federation,

^bForschungszentrum Karlsruhe, Institute for Nanotechnology, Karlsruhe 76021, Germany, and ^cDepartment of Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA

Correspondence e-mail:
steven.strauss@colostate.edu

Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.045
wR factor = 0.130
Data-to-parameter ratio = 23.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

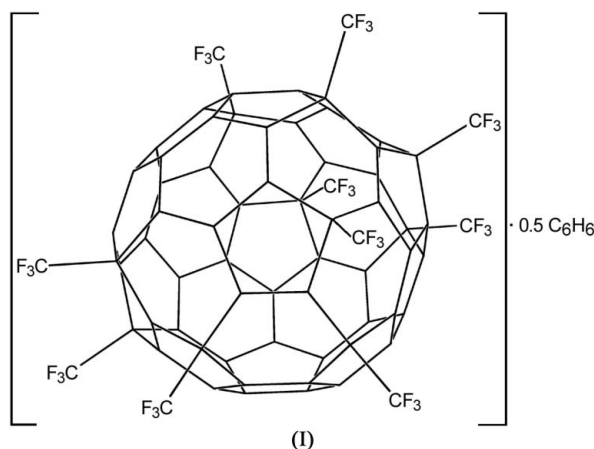
1,6,11,16,18,26,36,44,48,58-Decakis(trifluoromethyl)-1,6,11,16,18,26,36,44,48,58-decahydro($\text{C}_{60}-I_h$)[5,6]fullerene benzene hemisolvate

The title compound, $\text{C}_{70}\text{F}_{30} \cdot 0.5\text{C}_6\text{H}_6$, which crystallizes with one half-molecule of benzene in the asymmetric unit, is one of four isomers of $\text{C}_{60}(\text{CF}_3)_{10}$. The benzene molecule is disposed about a center of inversion. The fullerene molecule has an idealized $\text{C}_{60}-I_h$ core, with the ten CF_3 groups arranged in an asymmetric *para-para-para-meta-para-meta-para-meta-para* ($p^3mpmpmp$) ribbon of edge-sharing $\text{C}_6(\text{CF}_3)_2$ hexagons. There are no cage $\text{Csp}^3-\text{Csp}^3$ bonds. There are intramolecular $\text{F} \cdots \text{F}$ contacts between pairs of neighboring CF_3 groups, ranging from 2.565 (1) to 2.727 (1) Å.

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Comment

Recently reported high-temperature reactions of C_{60} , C_{70} or C_{82} fullerenes with CF_3I , $\text{C}_2\text{F}_5\text{I}$ or $\text{Ag}(\text{CF}_3\text{CO}_2)$, followed by sublimation at 673–773 K, have yielded fullerene(R_i)_n derivatives with thermodynamically stable addition patterns that are both asymmetric and unprecedented in fullerene(X)_n chemistry (Goryunkov *et al.*, 2003; Kareev, Lebedkin, Bubnov *et al.*, 2005; Kareev, Kuvychko, Lebedkin *et al.*, 2005; Dorozhkin *et al.*, 2006). Compounds characterized to date by single-crystal X-ray diffraction are 1,3,7,10,14,17,23,28,31,40- $\text{C}_{60}(\text{CF}_3)_{10}$ (Kareev, Kuvychko, Lebedkin *et al.*, 2005), 1,4,10,19,25,41,49,60,66,69- $\text{C}_{70}(\text{CF}_3)_{10}$ (Kareev, Kuvychko, Popov *et al.*, 2005), 1,4,10,19,25,32,41,49,54,60,66,69- $\text{C}_{70}(\text{CF}_3)_{12}$ (Kareev, Lebedkin, Miller *et al.*, 2006a), 1,4,10,14,19,25,35,41,49,60,66,69- $\text{C}_{70}(\text{CF}_3)_{12}$ (Kareev, Lebedkin, Miller *et al.*, 2006b), and 1,7,16,36,46,49- $\text{C}_{60}(\text{C}_2\text{F}_5)_6$ and 1,6,11,18,24,27,32,35- $\text{C}_{60}(\text{C}_2\text{F}_5)_8$ (Kareev, Kuvychko *et al.*, 2006). A related and unprecedented C_2 symmetry addition pattern has been observed in 1,6,12,15,18,23,25,41,45,57- $\text{C}_{60}(\text{CF}_3)_{10}$ (Kareev, Lebedkin, Popov *et al.*, 2006). The title compound, (I), has now been prepared and we report its crystal structure here.



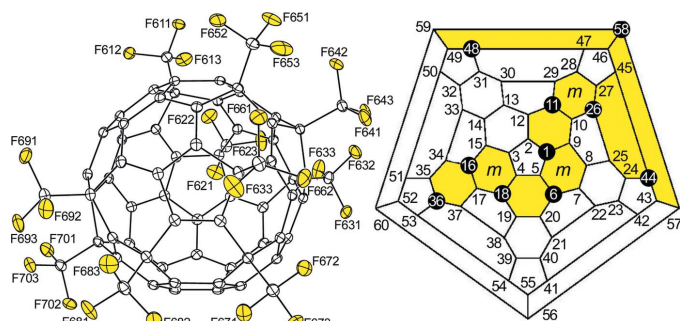


Figure 1

On the left, the molecular structure of (I), with 50% probability displacement ellipsoids. Atom F611 is attached to atom C61, atom F621 is attached to atom C62, etc. On the right, a Schlegel diagram for (I), showing the C_{60} core C-atom numbers (each core C atom bearing a CF_3 group is depicted as a black circle) and the $p^3mpmpmp$ ribbon of *meta*- and *para*- $C_6(CF_3)_2$ edge-sharing hexagons [*meta*- $C_6(CF_3)_2$ hexagons are indicated by the letter *m*].

The structure of (I) (Fig. 1) comprises an idealized $C_{60}-I_h$ core with ten sp^3 C atoms at positions 1, 6, 11, 16, 18, 26, 36, 44, 48 and 58 (Powell *et al.*, 2002), each of which is attached to a CF_3 group. The core sp^3 C atoms are not adjacent to one another. The CF_3 groups are arranged in a *para-para-para-meta-para-meta-para-meta-para* ribbon (*i.e.* a $p^3mpmpmp$ ribbon) of edge-sharing $C_6(CF_3)_2$ hexagons (see Schlegel diagram in Fig. 1). Note that the shared edges in the ribbon of hexagons are Csp^3-Csp^2 bonds (*e.g.* C16–C17, C4–C18 *etc.*), not Csp^2-Csp^2 bonds. Thus, any pair of adjacent hexagons along the ribbon has a common CF_3 group. As in the recently published structure of $C_s-p^7-C_{70}(CF_3)_8$ (Goryunkov *et al.*, 2005) and the other structures listed above, there are $F \cdots F$ intramolecular contacts between pairs of neighboring CF_3 groups, in the range 2.565 (1)–2.727 (1) Å.

To date, there are at least four isomers of $C_{60}(CF_3)_{10}$ that have been prepared at high temperature, isolated and characterized. ^{19}F NMR spectroscopy has shown that one of them has the ten CF_3 groups arranged in a ribbon of seven *meta*- and *para*- $C_6(CF_3)_2$ edge-sharing hexagons plus an isolated *para*- $C_6(CF_3)_2$ hexagon (Kareev, Kuvychko, Lebedkin *et al.*, 2005). The other three, namely compound (I), $C_1-pmp^3mpmp-C_{60}(CF_3)_{10}$, (II) (Kareev, Kuvychko, Lebedkin *et al.*, 2005), and $C_2-[p^3m^2(\text{loop})]^2-C_{60}(CF_3)_{10}$, (III) (Kareev, Lebedkin, Popov *et al.*, 2006), have been structurally characterized by single-crystal X-ray diffraction. For comparison, Schlegel diagrams for all three are shown in Fig. 2. The pmp^3mpmp ribbon in (II) forms a loop in which two of the *meta*- $C_6(CF_3)_2$ hexagons have a common Csp^2-Csp^2 bond (C2–C12). In addition, isomer (II) is the only fullerene(R_f) $_n$ derivative that has been unambiguously shown to have two R_f groups on the same pentagon. The structure of (III) is significantly different from those of the other two isomers in that every CF_3 group has two CF_3 nearest neighbors (*i.e.* there are no ‘terminal’ CF_3 groups). Instead, it has two symmetry-related p^3m^2 loops of five edge-sharing $C_6(CF_3)_2$ hexagons which are joined by a

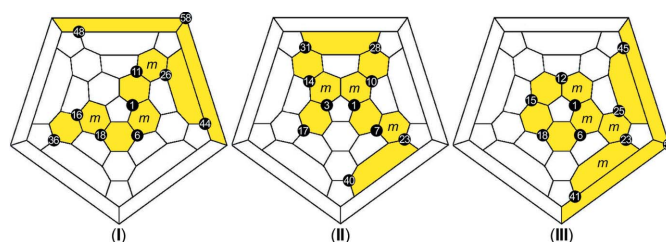


Figure 2

Schlegel diagrams for (I), (II) and (III), showing the locations of the CF_3 groups as black circles, the IUPAC lowest-locant numbers for the cage C atoms to which they are attached, and the ribbons or loops of *meta*- and *para*- $C_6(CF_3)_2$ edge-sharing hexagons [*meta*- $C_6(CF_3)_2$ hexagons are indicated by the letter *m*].

Csp^2-Csp^2 bond that is common to one of the *meta*- $C_6(CF_3)_2$ hexagons in each loop. These three structures, each of which has unique features as well as features in common with the other two, demonstrate that a given exohedral fullerene(R_f) $_n$ composition may have multiple high-temperature addition patterns that comprise ribbons and/or loops of *meta*- and *para*- $C_6(R_f)_2$ hexagons on the fullerene surface.

The four shortest cage C–C bonds in (I) are C9–C10 [1.3544 (14) Å], C28–C29 [1.3546 (15) Å], C17–C37 [1.3553 (15) Å] and C4–C5 [1.3579 (15) Å]. All four are significantly shorter than the shortest C–C bond in the most precise structure of empty C_{60} reported to date, which is 1.379 (3) Å for $C_{60}\text{-Pt}(\text{octaethylporphyrin})$ [$C_{60}\text{-Pt}(\text{OEP})$; Olmstead *et al.*, 2003]. More importantly, three of these bonds, C9–C10, C17–C37 and C4–C5, are pentagon–hexagon (pent–hex) junctions, and the shortest pent–hex junction in $C_{60}\text{-Pt}(\text{OEP})$ is 1.440 (3) Å, while the longest is 1.461 (3) Å (Olmstead *et al.*, 2003). For comparison, the ranges of the four shortest pent–hex junctions in (II) and (III) are 1.343 (3)–1.365 (3) Å (Kareev, Kuvychko, Lebedkin *et al.*, 2005) and 1.344 (3)–1.364 (3) Å (Kareev, Lebedkin, Popov *et al.*, 2006), respectively.

Experimental

The synthesis of (I) was accomplished by heating C_{60} in a stream of CF_3I at 733 K, as previously reported by Kareev, Kuvychko, Lebedkin *et al.* (2005); isomer (I) corresponds to $C_{60}(CF_3)_{10}-2$ in that paper. The compound was purified by high-performance liquid chromatography and crystals of (I) were grown by slow evaporation of a saturated benzene solution.

Crystal data

$C_{70}F_{30} \cdot 0.5C_6H_6$
 $M_r = 1449.75$
 Triclinic, $P\bar{1}$
 $a = 11.0290$ (15) Å
 $b = 13.7614$ (18) Å
 $c = 16.443$ (2) Å
 $\alpha = 87.785$ (6)°
 $\beta = 85.082$ (7)°
 $\gamma = 88.850$ (6)°
 $V = 2484.2$ (6) Å³

$Z = 2$
 $D_x = 1.938$ Mg m^{−3}
 Mo $K\alpha$ radiation
 Cell parameters from 999 reflections
 $\theta = 1.7$ – 26.4 °
 $\mu = 0.19$ mm^{−1}
 $T = 100$ (1) K
 Plate, orange
 $0.37 \times 0.22 \times 0.04$ mm

Data collection

Bruker Kappa-APEXII
diffractometer
 φ and ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2000)
 $T_{\min} = 0.933$, $T_{\max} = 0.992$
53487 measured reflections

21894 independent reflections
16852 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 35.2^\circ$
 $h = -16 \rightarrow 17$
 $k = -22 \rightarrow 22$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.130$
 $S = 1.03$
21894 reflections
928 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 1.8907P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.65 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{\AA}^{-3}$

H atoms were placed in idealized positions and refined using a riding model, with C—H = 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: APEX2 (Bruker, 2006); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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