Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

1,4,10,14,19,25,35,41,49,60,66,69-Dodecakis(trifluoromethyl)- 1,4,10,14,19,25,35,41,-49,60,66,69-dodecahydro(C_{70}-$D_{5h(6)}$)[5,6]-fullerene benzene disolvate

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

[a]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Russia, [b]Forschungszentrum Karlsruhe, Institute for Nanotechnology, Karlsruhe 76021, Germany, and [c]Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA

‡ Also at: Forschungszentrum Karlsruhe Institute for Nanotechnology Karlsruhe 76021 Germany

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

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.006 Å
R factor = 0.054
wR factor = 0.148
Data-to-parameter ratio = 9.9

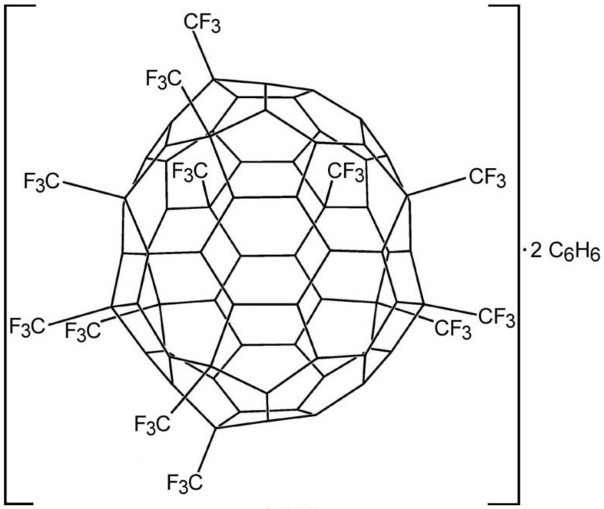
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 12 December 2005
Accepted 6 January 2006

The title compound, which crystallized with two molecules of benzene in the asymmetric unit, $C_{82}F_{36}\cdot 2C_6H_6$, is one of two isomers of $C_{70}(CF_3)_{12}$ that represent the first structurally characterized fullerene derivatives with exactly 12 substituents. This isomer consists of an idealized D_{5h}-C_{70} core with the 12 CF_3 groups arranged on a *para*^{7}–*meta*–*para* ribbon of edge-sharing $C_6(CF_3)_2$ hexagons plus an isolated $C_6(CF_3)_2$ hexagon. There are no cage Csp^3—Csp^3 bonds. As in the recently published structures of C_s-$C_{70}(CF_3)_8$ and C_1-$C_{70}(CF_3)_{10}$, there are numerous F···F intramolecular contacts between pairs of neighboring CF_3 groups that range from 2.526 (5) to 2.930 (5) Å.

Comment

High-temperature reactions of C_{60}, C_{70}, or Y@C_{82} with CF_3I, C_2F_5I, or Ag(CF_3CO_2) followed by sublimation at 673–773 K have yielded fullerene$(R_f)_n$ derivatives with thermodynamically stable addition patterns that are both asymmetric and unprecedented in fullerene$(X)_n$ chemistry. The asymmetric isomer 1,4,10,19,25,32,41,49,54,60,66,69-$C_{70}(CF_3)_{12}$, (I), is reported in the preceding paper in this issue (Kareev *et al.*, 2006). The title compound, (II), a different asymmetric isomer of the same composition, has also been prepared and we report its crystal structure here.



(II)

The structure of (II), shown in Fig. 1, consists of an idealized D_{5h}-C_{70} core with 12 Csp^3 atoms at positions 1, 4, 10, 14, 19, 25, 35, 41, 49, 60, 66, and 69 (Powell *et al.*, 2002), each of which is

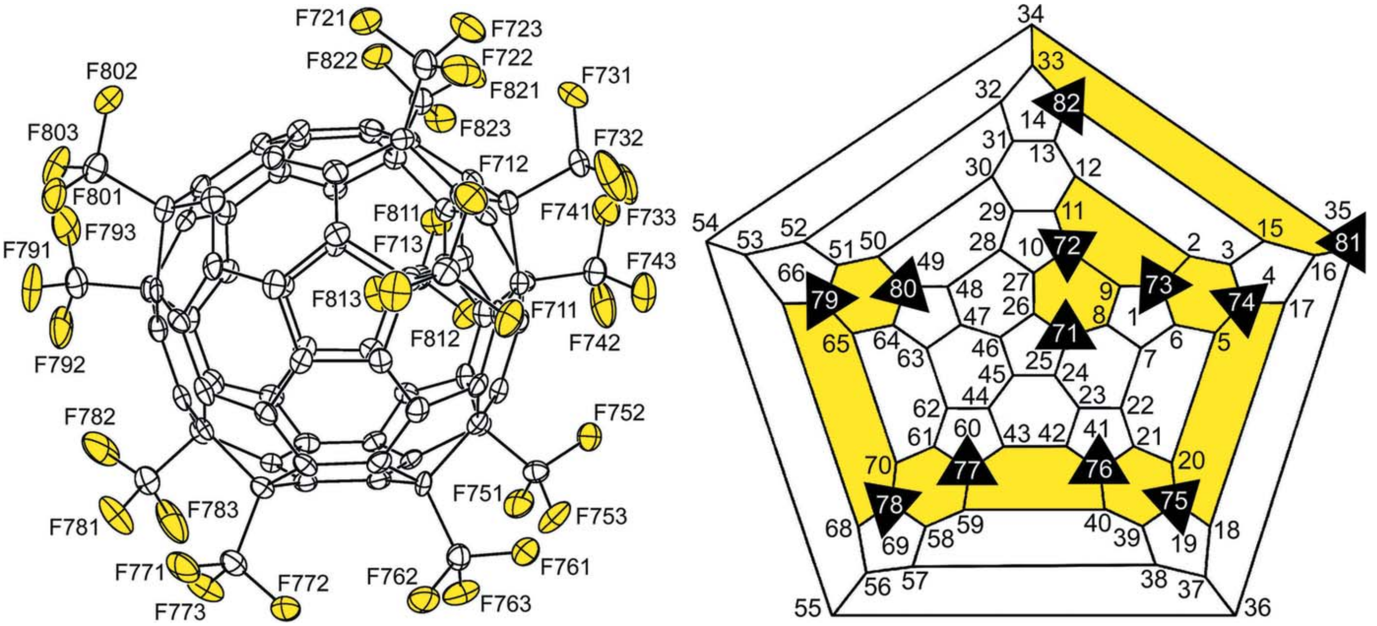


Figure 1

The molecular structure of (II) (50% probability ellipsoids) (left) and a Schlegel diagram of (II) (right), showing C-atom numbers (each CF_3 group is depicted as a triangle), the p^7mp ribbon of edge-sharing $C_6(CF_3)_2$ hexagons and the isolated $C_6(CF_3)_2$ hexagon.

attached to a CF_3 group. None of the core Csp^3 atoms is adjacent to one another. Thus, the CF_3 groups are arranged on a *para*^{7}–*meta*–*para* ribbon (p^7mp ribbon) of edge-sharing $C_6(CF_3)_2$ hexagons plus an isolated $C_6(CF_3)_2$ hexagon (see Schlegel diagram in Fig. 1). As in the recently published structures of C_s-$C_{70}(CF_3)_8$ (Goryunkov *et al.*, 2005) and C_1-$C_{70}(CF_3)_{10}$ (Kareev, Kuvychko, Popov *et al.* 2005), there are the usual F$\cdots$F intramolecular contacts between pairs of neighboring CF_3 groups that range from 2.526 (5) to 2.930 (5) Å. Isomer (I) differs from (II) in that the CF_3 groups attached to C14 and C35 in (II) are instead attached to C32 and C54 in (I).

The p^7mp ribbon in (II) is virtually identical to the p^7mp ribbon in (I) and may be a particularly stable feature in $C_{70}(CF_3)_n$ derivatives for $n > 8$. The same p^7mp ribbon is seen in the structure of C_1-$C_{70}(CF_3)_{10}$ (Kareev, Kuvychko, Popov *et al.* 2005) and in another isomer of $C_{70}(CF_3)_{12}$ (Kareev *et al.*, 2006). Additionally, the structure of C_s-$C_{70}(CF_3)_8$ is derived from C_1-$C_{70}(CF_3)_{10}$ by removing the C71 and C72 CF_3 groups, leaving a p^7 ribbon (Goryunkov *et al.*, 2005).

The five shortest cage C—C bonds are C8—C9 [1.338 (6) Å], C15—C16 [1.351 (6) Å], C2—C3 [1.354 (6) Å], C33—C34 [1.365 (6) Å] and C50—C51 [1.366 (6) Å]. Note that both C8—C9 and C15—C16 are pent-hex junctions.

Experimental

The synthesis of (II) was accomplished by heating C_{70} in a stream of CF_3I at 693–723 K, as described in Kareev, Kuvychko, Lebedkin *et al.* (2005) for C_1-$C_{60}(CF_3)_{10}$ and C_1-$C_{70}(CF_3)_{10}$. Crystals were grown by slow evaporation of a saturated benzene solution.

Crystal data

$C_{82}F_{36}\cdot 2C_6H_6$
$M_r = 1825.04$
Monoclinic, $P2_1/c$
$a = 19.092$ (4) Å
$b = 12.556$ (3) Å
$c = 27.390$ (6) Å
$\beta = 101.249$ (4)°
$V = 6440$ (2) Å^3
$Z = 4$
$D_x = 1.882$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 999 reflections
$\theta = 1.7$–25.2°
$\mu = 0.18$ mm^{-1}
$T = 100$ (2) K
Plate, orange
0.22 × 0.09 × 0.03 mm

Data collection

Bruker SMART 1K CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.961$, $T_{max} = 0.995$
48971 measured reflections
11608 independent reflections
5830 reflections with $I > 2\sigma(I)$
$R_{int} = 0.132$
$\theta_{max} = 25.2°$
$h = -22 \rightarrow 22$
$k = -15 \rightarrow 15$
$l = -32 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.149$
$S = 0.99$
11608 reflections
1172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 0.436P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.00242 (19)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; 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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The authors thank the U.S. National Science Foundation, the Volkswagen Foundation (I-77/855), and the Russian Foundation for Basic Research (Project Nos. 05–03-33051a and 06-03-33147a) for supporting this study.

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