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1,4,10,19,25,32,41,49,54,60,66,69-Dodecakis(trifluoromethyl)-1,4,10,19,25,32,41,-49,54,60,66,69-dodecahydro(C_{70}-$D_{5h(6)}$)-[5,6]fullerene benzene 2.5-solvate

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The title compound, which crystallized with 2.5 molecules of benzene in the asymmetric unit $C_{82}F_{36}\cdot 2.5C_6H_6$, 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 intramolecular F···F contacts between pairs of neighboring CF_3 groups ranging from 2.486 (3) to 2.864 (3) Å.

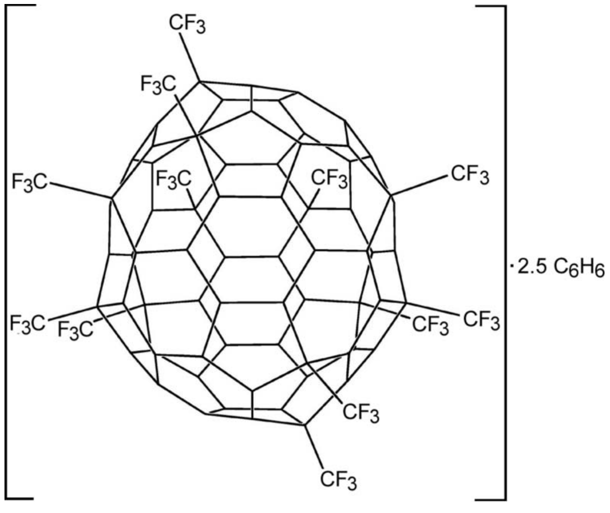
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.047
wR factor = 0.130
Data-to-parameter ratio = 11.1

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

Comment

Recently reported 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 asymmetric addition patterns that are unprecedented in fullerene$(X)_n$ chemistry. Those characterized by single-crystal X-ray diffraction include 1,3,7,10,14,17,23,28,31,40-$C_{60}(CF_3)_{10}$ (Kareev, Kuvychko, Lebedkin, Miller, Anderson, Seppelt *et al.*, 2005), 1,4,10,19,25,41,49,60,66,69-$C_{70}(CF_3)_{10}$ (Kareev, Kuvychko, Popov *et al.*, 2005), 1,7,16,36,46,49-$C_{60}(C_2F_5)_6$, and 1,6,11,18,24,27,32,35-$C_{60}(C_2F_5)_8$ (Kareev, Kuvychko, Lebedkin, Miller, Anderson, Strauss & Boltalina, 2006). The title compound, (I), has now been prepared and we report its crystal structure here.



(I)

The structure of (I), shown in Fig. 1, consists of an idealized D_{5h}-C_{70} core with 12 Csp^3 atoms at positions 1, 4, 10, 19, 25, 32,

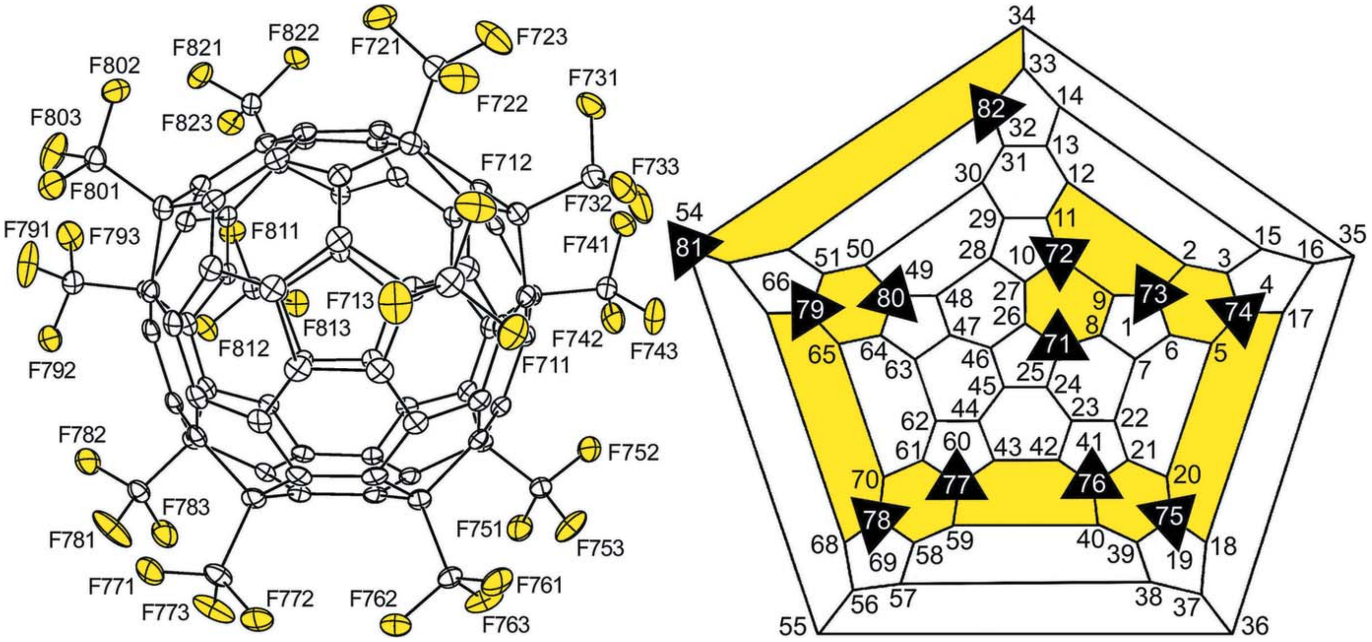


Figure 1
The molecular structure of (I) (50% probability ellipsoids) (left) and a Schlegel diagram of (I) (right), showing C-atom numbers (each CF_3 group is depicted as a triangle), the p^7mp ribbon of edge-sharing $C_6(CF_3)_2$ hexagons, and the isolated $C_6(CF_3)_2$ hexagon.

41, 49, 54, 60, 66, and 69 (Powell *et al.*, 2002), each of which is 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···F intramolecular contacts between pairs of neighboring CF_3 groups that range from 2.486 (3) to 2.864 (3) Å.

The p^7mp ribbon in (I) 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 C67—C68 [1.354 (3) Å], C8—C9 [1.358 (3) Å], C17—C18 [1.368 (3) Å], C50—C51 [1.370 (3) Å], and C52—C53 [1.373 (3) Å]. Note that both C8—C9 and C52—C53 are pent-hex junctions.

Experimental

The synthesis of (I) was accomplished by heating C_{70} in a stream of CF_3I at 693–723 K as described in Kareev, Kuvychko, Lebedkin, Miller, Anderson, Seppelt *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

$C_{82}F_{36}\cdot 2.5C_6H_6$
$M_r = 1864.09$
Triclinic, $P\overline{1}$
$a = 12.3839$ (17) Å
$b = 12.7864$ (18) Å
$c = 22.274$ (3) Å
$\alpha = 89.374$ (2)°
$\beta = 82.468$ (2)°
$\gamma = 70.221$ (2)°
$V = 3288.1$ (8) Å^3
$Z = 2$
$D_x = 1.883$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 999 reflections
$\theta = 1.7$–26.4°
$\mu = 0.18$ mm^{-1}
$T = 100$ (2) K
Block, orange
0.23 × 0.20 × 0.15 mm

Data collection

Bruker SMART 1K CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.960$, $T_{\max} = 0.973$
27678 measured reflections
13271 independent reflections
9305 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$
$\theta_{\max} = 26.4°$
$h = -15 \rightarrow 15$
$k = -15 \rightarrow 15$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.130$
$S = 1.02$
13271 reflections
1198 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 1.8907P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used

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to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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