

1,6,12,15,18,23,25,41,45,57-Decakis(trifluoromethyl)-1,6,12,15,18,23,25,41,45,57-decahydro(C₆₀-I_h)[5,6]fullereneIvan E. Kareev,^{a,b} Sergey F. Lebedkin,^b Alexey A. Popov,^c Susie M. Miller,^d Oren P. Anderson,^d Steven H. Strauss^{d*} and Olga V. Boltalina^d^aInstitute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Russian Federation,^bForschungszentrum Karlsruhe, Institute for Nanotechnology, Karlsruhe 76021, Germany,^cChemistry Department, Moscow State University, Moscow 119992, Russian Federation, and ^dDepartment 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 $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.047

wR factor = 0.129

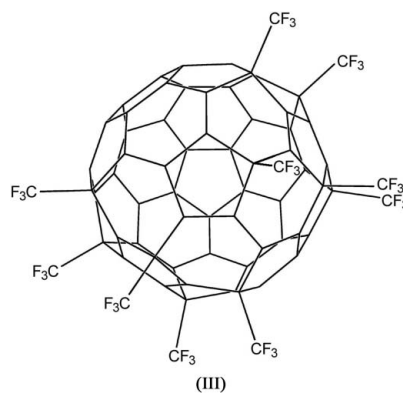
Data-to-parameter ratio = 15.1

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

The title compound, C₇₀F₃₀, which has crystallographic twofold symmetry, is one of four isomers of C₆₀(CF₃)₁₀. It has an idealized C₆₀-I_h core, with the ten CF₃ groups arranged on two symmetry-related *para-para-para-meta-meta* loops of five edge-sharing C₆(CF₃)₂ hexagons. There are no cage Csp³-Csp³ bonds. There are intramolecular F··F contacts between pairs of neighboring CF₃ groups, ranging from 2.523 (2) to 2.746 (2) Å.

Comment

The background to this work has been described in the preceding paper (Kareev *et al.*, 2006). The title compound, (III), has now been prepared and we report its crystal structure here. It also exhibits an unprecedented fullerene addition pattern.



The structure of (III) (Fig. 1) comprises an idealized C₆₀-I_h core with ten sp³ C atoms at positions 1, 1', 6, 6', 12, 12', 15, 15', 18 and 18' (IUPAC fullerene positions 1, 6, 12, 15, 18, 23, 25, 41, 45 and 57; Powell *et al.*, 2002), each of which is attached to a CF₃ group. A crystallographic twofold axis is present in (III) and it bisects the C7-C7' and C50-C50' bonds. No two fullerene core sp³ C atoms are adjacent to one another. The CF₃ groups are arranged in two symmetry-related *para-para-para-meta-meta* loops (*i.e.* two *p*³*m*² loops) of edge-sharing C₆(CF₃)₂ hexagons (see Schlegel diagram in Fig. 1). Note that the shared edges in the loop of hexagons are Csp³-Csp² bonds (*e.g.* C1-C9, C2-C12 *etc.*), not Csp²-Csp² bonds. Thus, any pair of adjacent hexagons in the loop has a common CF₃ group. In addition, the two loops are joined by a Csp²-Csp² bond (C7-C7') that is common to one of the *meta*-C₆(CF₃)₂ hexagons in each loop. As in the recently published structure of C_s-*p*⁷-C₇₀(CF₃)₈ (Goryunkov *et al.*, 2005) and the other structures listed in the preceding paper (Kareev *et al.*, 2006), there are F··F intramolecular contacts between pairs of neighboring CF₃ groups, in the range 2.523 (2)-2.746 (2) Å.

Received 22 February 2006

Accepted 6 March 2006

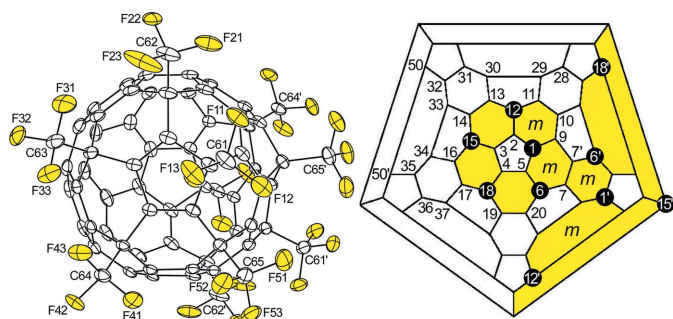


Figure 1

On the left, the molecular structure of (III), with 50% probability displacement ellipsoids. On the right, a Schlegel diagram for (III), 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 two p^3m^2 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*].

The addition patterns of (I), (II) and (III) were compared in the preceding paper (Kareev *et al.*, 2006). Here, we will describe the unusual features of the addition pattern in (III). A simple loop of Csp^3-Csp^2 edge-sharing *meta*- and *para*- $C_6(CF_3)_2$ hexagons is unprecedented in neutral fullerene(R_f) $_n$ compounds. Another unprecedented feature is the presence of adjacent *meta*- $C_6(CF_3)_2$ hexagons sharing a common Csp^3-Csp^2 bond. All other structurally characterized fullerene(R_f) $_n$ compounds (see the preceding paper; Kareev *et al.*, 2006) have either isolated *para*- $C_6(R_f)_n$ hexagons or ribbons of hexagons containing *para-meta-para* or *para-para-para* sequences. Ribbons containing *meta-meta* sequences have not been observed to date and, indeed, have been predicted to be energetically destabilizing at the density functional theory (DFT) level (Goryunkov *et al.*, 2004). Nevertheless, the p^3m^2 loops in (III) lead to a relative ΔH_f° value that is only 2.9 kJ mol $^{-1}$ higher than the value for (II) and 7.6 kJ mol $^{-1}$ higher than the value for (I), which appears to be the most stable isomer of $C_{60}(CF_3)_{10}$ at the DFT level (Popov *et al.*, 2006).

Schlegel diagrams for (III) and two related structures, the 1,6,9,12,15,18- $C_{60}Br_6$ skew-pentagonal-pyramid addition pattern, (IV) (Trojanov *et al.*, 2003), and the 6,9,12,15,18- $C_{60}Ph_5^-$ cyclopentadienide addition pattern in $Fe(\eta^5-Cp)(\eta^5-C_6Ph_5^-)$, (V) (Herber *et al.*, 2005), are shown in Fig. 2. The shortest cage C–C bonds in (III) are in the isolated *cis*-butadiene fragment C2–C3–C4–C5. The C2–C3, C3–C4 and C4–C5 distances are 1.347 (3), 1.481 (3) and 1.344 (3) Å, respectively. Note that these are pentagon–hexagon (pent–hex) junctions, all of which are *ca* 1.45 Å in C_{60} (Olmstead *et al.*, 2003). The corresponding pent–hex junction distances in the isolated *cis*-butadiene fragment in the structure of (IV), which are 1.350 (4), 1.462 (4) and 1.349 (4) Å, are the same as those in (III), to within $\pm 3\sigma$ (Trojanov *et al.*, 2003). The calculated C–C distances in planar *cis*-butadiene (*i.e.* *cis*- C_4H_8) are 1.343 and 1.470 Å (De Maré *et al.*, 1997). For comparison, the range of cage C–C distances in the $C_5Ph_5^-$ cyclopentadienide fragment in (V) is 1.428 (5)–1.441 (5) Å.

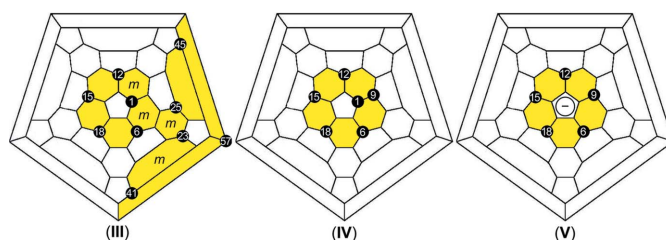


Figure 2

Schlegel diagrams for (III), (IV) ($C_{60}Br_6$) and the $C_{60}Ph_5^-$ fragment in (V), showing the locations of the exohedral substituents as black circles, the IUPAC lowest-locant numbers for the cage C atoms to which they are attached, and the loops of *meta*- and/or *para*- $C_6(CF_3)_2$ edge-sharing hexagons in (III) and (V) [*meta*- $C_6(CF_3)_2$ hexagons are indicated by the letter *m*], or in the loop of *para*- C_6Br_2 and 1,2,4- C_6Br_3 hexagons in (IV).

In principle, the addition of five radical substituents to C6, C9, C12, C15, and C18 of C_{60} would form a p^5 loop of $C_{60}X_2$ edge-sharing hexagons, with an unpaired electron formally localized on C1 (Hirsch & Brettreich, 2005). This radical can be quenched in one of two ways, by the addition of a sixth substituent to C1, producing the addition pattern exhibited by (IV) and many other $C_{60}X_6$ derivatives, or by addition of an electron, producing the cyclopentadienide pattern in (V). Alternatively, the addition of five radical substituents to C1, C6, C12, C15 and C18 of C_{60} would form a p^3m^2 loop of $C_{60}X_2$ hexagons, with an unpaired electron formally localized on C9. It is now apparent that this radical can also be quenched in two ways, by the addition of a single substituent to C9, producing (IV) in the case of $X = Br$, or by the addition of another five substituents, forming the two- p^3m^2 -loops addition pattern of (III) in the case of $X = CF_3$. The latter results in the formation of the *trans*-butadiene fragment C9'–C7–C7'–C9, with C7–C9' and C7–C7' bond distances of 1.365 (3) and 1.432 (4) Å in (III). Note that this fragment is in conjugation with the rest of the fullerene π system, unlike the isolated *cis*-butadiene fragments discussed earlier, and therefore the *trans*-butadiene fragment in (III) has a shorter single bond and marginally longer double bonds than the *cis*-butadiene fragments in (III) and (IV).

Experimental

The synthesis of (III) was accomplished by heating C_{60} in a stream of CF_3I at 733 K in a manner similar to that previously used for the synthesis of (I) and (II) (Kareev *et al.*, 2005). The compound was purified by high-performance liquid chromatography and crystals of (III) were grown by slow evaporation of a saturated benzene solution.

Crystal data

$C_{70}F_{30}$
 $M_r = 1410.70$
 Orthorhombic, $Pbcn$
 $a = 18.0971$ (11) Å
 $b = 16.2516$ (10) Å
 $c = 15.3735$ (9) Å
 $V = 4521.5$ (5) Å 3
 $Z = 4$
 $D_x = 2.072$ Mg m $^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 999 reflections
 $\theta = 2.9$ – 30.3°
 $\mu = 0.21$ mm $^{-1}$
 $T = 100$ (1) K
 Plate, orange
 $0.37 \times 0.34 \times 0.08$ mm

Data collection

Bruker Kappa APEXII
diffractometer
 φ and ω scans
Absorption correction: multi-scan
(*SADABS*; Bruker, 2000)
 $T_{\min} = 0.927$, $T_{\max} = 0.984$
61427 measured reflections

6794 independent reflections
4712 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 30.3^\circ$
 $h = -21 \rightarrow 25$
 $k = -23 \rightarrow 22$
 $l = -20 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.129$
 $S = 1.03$
6794 reflections
451 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 1.8907P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.40 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{\AA}^{-3}$

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*.

The authors thank the US National Science Foundation, the
Volkswagen Foundation (grant No. I-77/855) and the Russian
Foundation for Basic Research (project Nos. 05-03-33051a and
06-03-33147a) for supporting this study.

References

- Bruker (2000). *SADABS* (Version 2.10) and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2006). *APEX2* (Version 2.0-2). Bruker AXS Inc., Madison, Wisconsin, USA.
- De Maré, G. R., Panchenko, Y. N. & Auwera, J. V. (1997). *J. Phys. Chem.* **101**, 3998–4004.
- Goryunkov, A. A., Dorozhkin, E. I., Ignat'eva, D. F., Sidorov, L. N., Kemnitz, E., Sheldrick, G. & Troyanov, S. I. (2005). *Mendeleev Commun.* pp. 225–227.
- Goryunkov, A. A., Ioffe, I. N., Kuvychko, I. V., Yankova, T. S., Markov, V. Y., Streletskii, A. A., Dick, D. L., Sidorov, L. N., Boltalina, O. V. & Strauss, S. H. (2004). *Fullerenes Nanotube Carbon Nanostruct.* **12**, 181–185.
- Herber, R. H., Nowik, I., Matsuo, Y., Toganoh, M., Kuninobu, Y. & Nakamura, E. (2005). *Inorg. Chem.* **44**, 5629–5635.
- Hirsch, A. & Brettreich, M. (2005). *Fullerenes: Chemistry and Reactions*. Weinheim: Wiley-VCH.
- Kareev, I. E., Lebedkin, S. F., Miller, S. M., Anderson, O. P., Strauss, S. H. & Boltalina, O. V. (2006). *Acta Cryst.* **E62**, o1498–o1500.
- Kareev, I. E., Kuvychko, I. V., Lebedkin, S. F., Miller, S. M., Anderson, O. P., Seppelt, K., Strauss, S. H. & Boltalina, O. V. (2005). *J. Am. Chem. Soc.* **127**, 8362–8375.
- Olmstead, M. M., de Bettencourt-Dias, A., Lee, H. M., Pham, D. & Balch, A. L. (2003). *Dalton Trans.* pp. 3227–3232.
- Popov, A. A., Boltalina, O. V. & Strauss, S. H. (2006). Manuscript in preparation.
- Powell, W. H., Cozzi, F., Moss, G. P., Thilgen, C., Hwu, R. J.-R. & Yerin, A. (2002). *Pure Appl. Chem.* **74**, 629–695.
- Troyanov, S. I., Troshin, P. A., Boltalina, O. V. & Kemnitz, E. (2003). *Fullerenes Nanotube Carbon Nanostruct.* **11**, 61–77.