SUPPORTING INFORMATION

X-ray structure and DFT study of C_1-$C_{60}(CF_3)_{12}$. A high-energy kinetically-stable isomer prepared at 500 °C

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Contents

Complete list of references to published structures of fullerene$(R_f)_n$ derivatives

C_1- and C_s-$C_{60}F_{17}(CF_3)$ (disordered solid soln. of both compounds)
O. V. Boltalina, P. B. Hitchcock, P. A. Troshin, J. M. Street, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **2000**, 2410-2414.

1,9-O-6,12,15,18-$C_{60}(CF_3)_4$ and 1,9-O-6,12,15,18-$C_{60}(C_2F_5)_4$ (both C_s symmetry)
I. E. Kareev, N. B. Shustova, I. V. Kuvychko, S. F. Lebedkin, S. M. Miller, O. P. Anderson, A. A. Popov, S. H. Strauss, O. V. Boltalina, *J. Am. Chem. Soc.* **2006**, *128*, 12268-12280.

1,7,16,36,46,49-$C_{60}(C_2F_5)_6$ and 1,6,11,18,24,27,32,35-$C_{60}(C_2F_5)_8$ (both C_1 symmetry)
I. E. Kareev, I. V. Kuvychko, S. F. Lebedkin, S. M. Miller, O. P. Anderson, S. H. Strauss, O. V. Boltalina, *Chem. Commun.* **2006**, 308-310.

1,6,11,18,24,27,52,55-$C_{60}(CF_3)_8$ (C_1 symmetry)
I. E. Kareev, N. B. Shustova, B. S. Newell, S. M. Miller, O. P. Anderson, S. H. Strauss, O. V. Boltalina, *Acta Crystallogr.* **2006**, *E62*, o3154-o3156.

1,6,11,16,18,26,36,44,48,58-$C_{60}(CF_3)_{10}$ ($C_{60}(CF_3)_{10}$-2; C_1 symmetry)
I. E. Kareev, S. F. Lebedkin, S. M. Miller, O. P. Anderson, S. H. Strauss, O. V. Boltalina, *Acta Crystallogr.* **2006**, *E62*, o1498-o1500.

1,3,7,10,14,17,23,28,31,40-$C_{60}(CF_3)_{10}$ ($C_{60}(CF_3)_{10}$-3; C_1 symmetry)
I. E. Kareev, I. V. Kuvychko, S. F. Lebedkin, S. M. Miller, O. P. Anderson, K. Seppelt, S. H. Strauss, O. V. Boltalina, *J. Am. Chem. Soc.* **2005**, *127*, 8362-8375.

1,6,12,15,18,23,25,41,45,57-$C_{60}(CF_3)_{10}$ ($C_{60}(CF_3)_{10}$-4; C_2 symmetry)
I. E. Kareev, S. F. Lebedkin, A. A. Popov, S. M. Miller, O. P. Anderson, S. H. Strauss, O. V. Boltalina, *Acta Crystallogr.* **2006**, *E62*, o1501-o1503.

1,6,11,16,18,26,36,44,46,49,54,60-$C_{60}(CF_3)_{12}$ ($C_{60}(CF_3)_{12}$-1; S_6 symmetry)
S. I. Troyanov, A. Dimitrov, E. Kemnitz, *Angew. Chem. Int. Ed.* **2006**, *45*, 1971-1974.

1,3,6,11,13,18,26,32,35,41,44,57-$C_{60}(CF_3)_{12}$ ($C_{60}(CF_3)_{12}$-2; C_1 symmetry; ***this work***)
I. E. Kareev, Natalia B. Shustova, Dmitry V. Peryshkov, S. F. Lebedkin, S. M. Miller, O. P. Anderson, A. A. Popov, O. V. Boltalina, S. H. Strauss, *Chem. Commun.* **2006**, submitted for publication.

[continued on next page]

1,4,10,19,25,41-$C_{70}(CF_3)_6$ (C_1 symmetry)
E. I. Dorozhkin, D. V. Ignat'eva, N. B. Tamm, N. V. Vasilyuk, A. A. Goryunkov, S. M. Avdoshenko, I. N. Ioffe, L. N. Sidorov, P. Pattison, E. Kemnitz, S. Troyanov, I., *J. Fluorine Chem.* **2006**, *127*, 1344-1348.

1,4,19,41,49,60,66,69-$C_{70}(CF_3)_8$ (C_s-$C_{70}(CF_3)_8$)
A. A. Goryunkov, E. I. Dorozhkin, D. V. Ignat'eva, L. N. Sidorov, E. Kemnitz, G. M. Sheldrick, S. I. Troyanov, *Mendeleev Commun.* **2005**, 225-227.

1,4,10,19,25,41,49,60,66,69-$C_{70}(CF_3)_{10}$ (C_1-$C_{70}(CF_3)_{10}$)
I. E. Kareev, I. V. Kuvychko, A. A. Popov, S. F. Lebedkin, S. M. Miller, O. P. Anderson, S. H. Strauss, O. V. Boltalina, *Angew. Chem. Int. Ed.* **2005**, *44*, 7984-7987.

1,4,10,19,25,32,41,49,54,60,66,69-$C_{70}(CF_3)_{12}$ (C_1 symmetry)
I. E. Kareev, S. M. Miller, O. P. Anderson, S. H. Strauss, O. V. Boltalina, *Acta Crystallogr.* **2006**, *E62*, o617-o619.

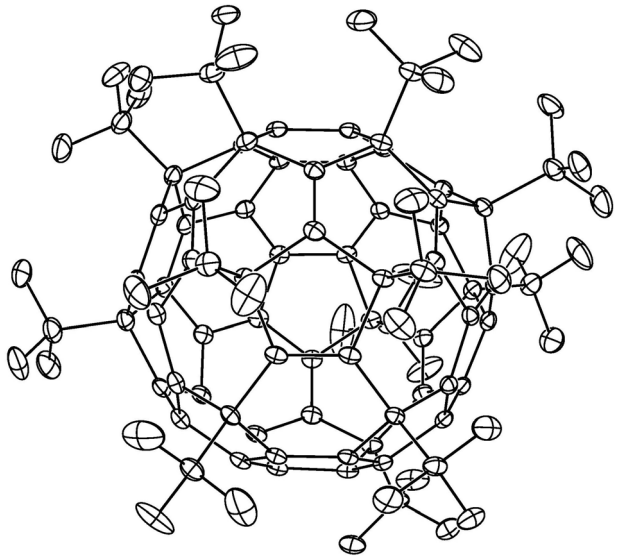
1,4,10,14,19,25,35,41,49,60,66,69-$C_{70}(CF_3)_{12}$ (C_1 symmetry)
I. E. Kareev, S. M. Miller, O. P. Anderson, S. H. Strauss, O. V. Boltalina, *Acta Crystallogr.* **2006**, *E62*, o620-o622.

1,4,10,19,23,25,32,41,44,49,54,60,66,69-$C_{70}(CF_3)_{14}$,
1,4,10,19,25,32,37,41,49,54,56,60,66,69-$C_{70}(CF_3)_{14}$,
1,4,10,14,19,23,25,35,41,44,49,60,66,69-$C_{70}(CF_3)_{14}$,
and 1,4,10,13,15,19,25,29,34,41,49,60,66,69-$C_{70}(CF_3)_{14}$ (all C_1 symmetry)
A. A. Goryunkov, D. V. Ignat'eva, N. B. Tamm, N. N. Moiseeva, I. N. Ioffe, S. M. Avdoshenko, V. Y. Markov, L. N. Sidorov, E. Kemnitz, S. Troyanov, I., *Eur. J. Org. Chem.* **2006**, 2508-2512.

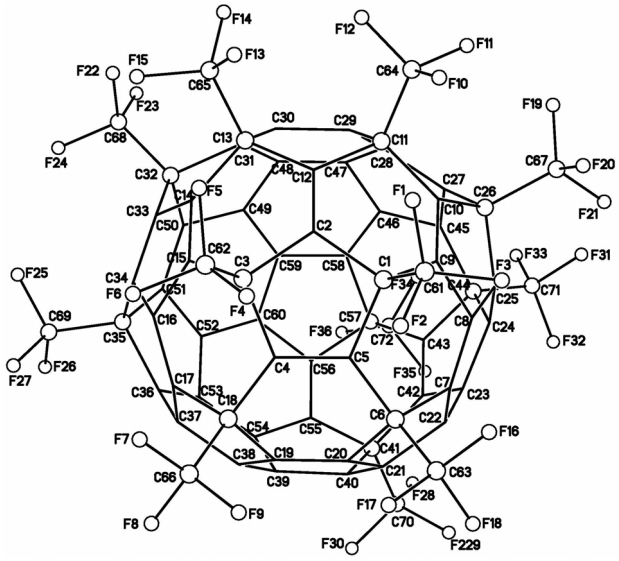
1,4,10,16,19,25,33,34,37,41,49,53,56,60,66,69-$C_{70}(CF_3)_{16}$ and
1,4,10,16,19,23,25,33,34,37,41,44,49,53,56,60,66,69-$C_{70}(CF_3)_{18}$ (both C_1 symmetry)
S. M. Avdoshenko, A. A. Goryunkov, I. N. Ioffe, D. V. Ignat'eva, L. N. Sidorov, P. Pattison, E. Kemnitz, S. Troyanov, I., *Chem. Commun.* **2006**, 2463-2465.

2,5,11,19,27,37,43,47,52,56,62,68-$C_{74}(CF_3)_{12}$
and 7,14,19,23,32,39,46,51,58,66,69,74-$C_{78}(CF_3)_{12}$ (both C_2 symmetry)
N. B. Shustova, A. A. Popov, B. S. Newell, S. M. Miller, O. P. Anderson, K. Seppelt, R. D. Bolskar, O. V. Boltalinaa, S. H. Strauss, submitted for publication.

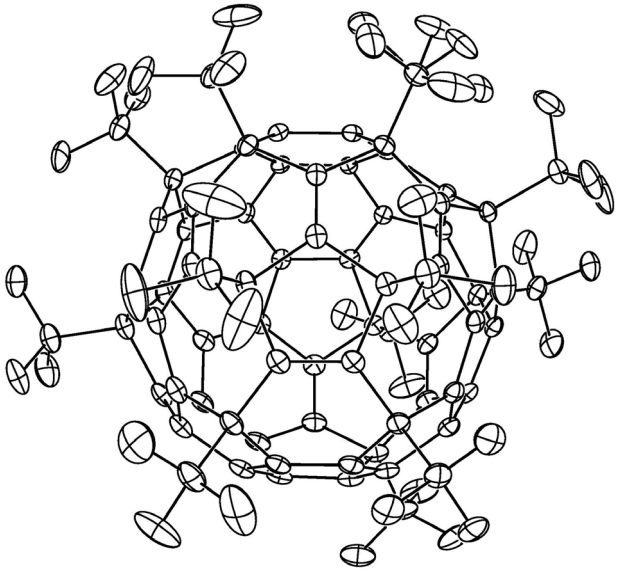
IUPAC-numbered thermal ellipsoid plots of the two independent C_1-$C_{60}(CF_3)_{12}$ molecules



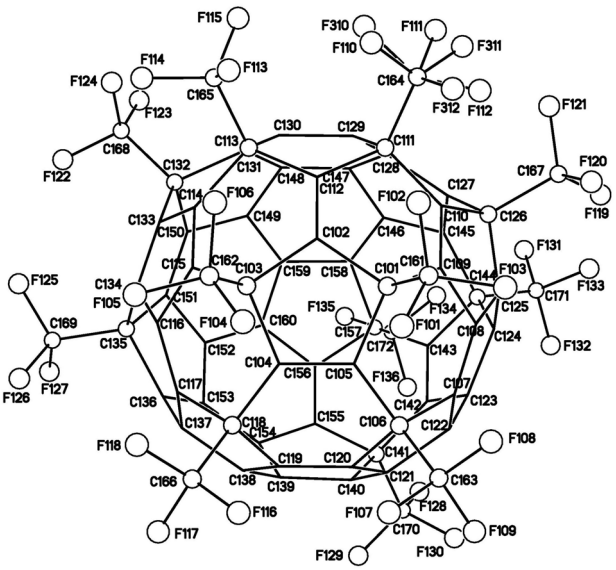
$C_{60}(CF_3)_{12}$ molecule 1 (50% ellipsoids)



numbering for $C_{60}(CF_3)_{12}$ molecule 1



$C_{60}(CF_3)_{12}$ molecule 2 (50% ellipsoids)



numbering for $C_{60}(CF_3)_{12}$ molecule 2

Table of DFT relative energies for $C_{60}(CF_3)_{12}$ isomers (kJ mol^{-1})

The AM1 calculations were carried out with the PC version of GAMESS.[S-1] More than 10,000 possible addition patterns based on the four strategies below were tested at the AM1 level. Except for the skew-pentagonal pyramid (*SPP*) addition-pattern fragment or fragments (i.e., each fragment would have a local 1,6,9,12,15,18-$C_{60}(CF_3)_6$ geometry), no other addition pattern with adjacent sp^3 cage C atoms were considered. This is because all other calculations of compositions with 12 or fewer CF_3 groups have shown adjacent sp^3 cage C atoms to be significantly destabilizing.[S-2-S-4] Only the most stable ones were then re-optimized at the DFT level (PRIRODA package,[S-5] GGA functional of Perdew, Burke and Ernzerhof (PBE);[S-6] {6,1,1,1,1,1/4,1,1/1,1} Gaussian basis set for C and F atoms. The quantum-chemical code employed expansion of the electron density in an auxiliary basis set to accelerate the evaluation of the Coulomb and exchange-correlation terms. Two structures, $C_{60}(CF_3)_{12}$-1 and $C_{60}(CF_3)_{12}$-2, were also optimized using the B3LYP functional and a 6-31G* basis set).

Structures based only on 1,4 additions (resulting in the formation of some *m*-$C_6(CF_3)_2$ hexagons)	AM1	DFT (PBE)
1,6,11,16,18,26,36,44,46,49,54,60-$C_{60}(CF_3)_{12}$ ($C_{60}(CF_3)_{12}$-1)	0.0	0.0 (B3LYP 0.0)
1,7,10,17,28,30,33,35,43,48,55,58-$C_{60}(CF_3)_{12}$	22.5	18.8
1,7,10,17,23,28,30,33,35,40,50,60-$C_{60}(CF_3)_{12}$	22.8	21.1
1,7,10,17,23,28,30,33,35,40,48,58-$C_{60}(CF_3)_{12}$	23.0	20.0
1,3,7,13,17,25,35,43,45,50,55,60-$C_{60}(CF_3)_{12}$	33.2	35.5
1,3,7,10,13,17,23,28,35,40,50,60-$C_{60}(CF_3)_{12}$	45.7	32.1
1,3,6,11,13,18,26,32,35,41,44,57-$C_{60}(CF_3)_{12}$ ($C_{60}(CF_3)_{12}$-2)	53.3	39.8 (B3LYP 36.6)

Structures based on 1,6,12,15,18,23,25,41,45,57-$C_{60}(CF_3)_{10}$[S-7] plus one more 1,4 addition	AM1	DFT
1,6,12,15,18,23,25,41,45,57,32,35-$C_{60}(CF_3)_{12}$	39.8	42.0
1,6,12,15,18,23,25,41,45,57,33,51-$C_{60}(CF_3)_{12}$	50.7	51.4
1,6,12,15,18,23,25,41,45,57,34,50-$C_{60}(CF_3)_{12}$	52.1	45.9
1,6,12,15,18,23,25,41,45,57,29,48-$C_{60}(CF_3)_{12}$	60.6	53.9
1,6,12,15,18,23,25,41,45,57,30,33-$C_{60}(CF_3)_{12}$	71.3	62.1
1,6,12,15,18,23,25,41,45,57,34,37-$C_{60}(CF_3)_{12}$	74.3	73.6
1,6,12,15,18,23,25,41,45,57,30,47-$C_{60}(CF_3)_{12}$	83.4	86.3

Structures based on two SPP fragments	AM1	DFT
1,6,9,12,15,18,43,46,49,52,55,60-$C_{60}(CF_3)_{12}$	43.8	32.6
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	44.2	32.7
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	45.2	34.2
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	84.1	61.4
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	86.8	65.5
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	88.2	61.4
1,6,9,12,15,18,34,37,50,53,54,60-$C_{60}(CF_3)_{12}$	88.2	61.4
1,6,9,12,15,18,34,37,50,52,54,60-$C_{60}(CF_3)_{12}$	90.7	61.1
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	98.8	
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	98.9	
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	103.1	
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	103.1	
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	103.1	
1,6,9,12,15,18,34,36,37,50,54,60-$C_{60}(CF_3)_{12}$	111.3	
1,6,9,12,15,18,21,38,42,53,54,56-$C_{60}(CF_3)_{12}$	122.5	

Structures based on an *SPP* fragment and three 1,4 additions	AM1
1,6,9,12,15,18,38,43,46,49,53,55-$C_{60}(CF_3)_{12}$	47.1
1,6,9,12,15,18,22,41,43,46,49,52-$C_{60}(CF_3)_{12}$	48.1
1,6,9,12,15,18,34,43,46,50,52,55-$C_{60}(CF_3)_{12}$	49.3
1,6,9,12,15,18,21,42,46,49,52,55-$C_{60}(CF_3)_{12}$	49.8
1,6,9,12,15,18,22,41,43,46,51,59-$C_{60}(CF_3)_{12}$	55.0
1,6,9,12,15,18,38,43,48,53,55,58-$C_{60}(CF_3)_{12}$	55.5
1,6,9,12,15,18,34,45,50,52,55,57-$C_{60}(CF_3)_{12}$	57.6
1,6,9,12,15,18,24,27,29,48,51,59-$C_{60}(CF_3)_{12}$	57.6
1,6,9,12,15,18,30,42,47,49,52,56-$C_{60}(CF_3)_{12}$	57.7
1,6,9,12,15,18,23,38,40,50,53,60-$C_{60}(CF_3)_{12}$	58.5

S-1. A. A. Granovsky, *PC GAMESS URL: http://classic.chem.msu.su/gran/gamess/index.html*.

S-2. E. I. Dorozhkin, D. V. Ignat'eva, N. B. Tamm, A. A. Goryunkov, P. A. Khavrel, I. N. Ioffe, A. A. Popov, I. V. Kuvychko, A. V. Streletskiy, V. Y. Markov, J. Spandl, S. H. Strauss and O. V. Boltalina, *Chem. Eur. J.*, 2006, **12**, 3876-3889.

S-3. E. I. Dorozhkin, D. V. Ignat'eva, N. B. Tamm, N. V. Vasilyuk, A. A. Goryunkov, S. M. Avdoshenko, I. N. Ioffe, L. N. Sidorov, P. Pattison, E. Kemnitz and S. Troyanov, I., *J. Fluorine Chem.*, 2006, **127**, 1344-1348.

S-4. N. B. Shustova, I. V. Kuvychko, R. D. Bolskar, K. Seppelt, S. H. Strauss, A. A. Popov and O. V. Boltalina, *J. Am. Chem. Soc.*, 2006, **128**, 0000 (doi 10.1021/ja065178l).

S-5. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151-156.

S-6. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

S-7. I. E. Kareev, S. F. Lebedkin, A. A. Popov, S. M. Miller, O. P. Anderson, S. H. Strauss and O. V. Boltalina, *Acta Crystallogr.*, 2006, **E62**, o1501-o1503.