Available online at www.sciencedirect.com

SCIENCE DIRECT®

Mendeleev Commun., 2007, **17**, 110–112

Mendeleev Communications

Synthesis and molecular structure of 1,6,11,16,18,24,27,36-$C_{60}(CF_3)_8$

Alexey A. Goryunkov, Evgenii I. Dorozhkin, Nadezhda B. Tamm, Daria V. Ignat'eva, Stanislav M. Avdoshenko, Lev N. Sidorov[†] and Sergey I. Troyanov*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation. Fax: +7 495 939 1240; e-mail: stroyano@thermo.chem.msu.ru

DOI: 10.1016/j.mencom.2007.03.020

1,6,11,16,18,24,27,36-$C_{60}(CF_3)_8$ was synthesised by a reaction of C_{60} with CF_3I at 420 °C followed by HPLC separation; its molecular structure contains eight CF_3 groups attached in a continuous *para-para-para-meta-para-meta-para* ribbon of seven edge-sharing $C_6(CF_3)_2$ hexagons on a C_{60} cage.

A significant progress in the preparation of poly(trifluoromethyl) derivatives of fullerenes and the determination of their structures was achieved. These derivatives possess high thermal stability and good solubility in organic solvents that allows their study by mass-spectrometric methods in a gas phase and by NMR spectroscopy in solution. Known synthetic methods are based on reactions of fullerenes with compounds that easily release CF_3 radicals, such as CF_3I[1] or metal trifluoroacetates.[2] These methods usually result in complex mixtures of CF_3 derivatives, which should be separated by high performance liquid chromatography (HPLC).[3]

In the case of C_{70}, the molecular structures of $C_{70}(CF_3)_n$ unambiguously elucidated by X-ray crystallography contain from 6 to 18 CF_3 groups attached to the [70]fullerene cage.[4] The known structurally characterised $C_{60}(CF_3)_n$ molecules include those with $n = 8–12$.[5] Some $C_{60}(CF_3)_8$ isomers were isolated and characterised by ^{19}F NMR only.[2(b)] However, the structures proposed[2(b)] containing mostly contiguous addition patterns are doubtful because the NMR spectra do not contain signals characteristic of the *ortho* contacts of CF_3 groups.[6]

Here we report the synthesis, isolation and X-ray crystallographic study of a new $C_{60}(CF_3)_8$ isomer and discuss its molecular structure and calculated relative energy in comparison with those for related compounds.

A reaction of C_{60} (99.95%, Term-USA) with CF_3I (98%, Apollo) was carried out in a glass ampoule at 420 °C for 6 h (see ref. 4 for experimental details). The sublimate in the colder zone (150–200 °C) was a mixture of higher CF_3 derivatives, as shown by MALDI mass spectrometry, whereas the hot zone (400–420 °C) contained unreacted C_{60}, as well as lower CF_3 derivatives (n = 6 and 8) and known S_6-$C_{60}(CF_3)_{12}$.[5(e)] The extraction of the hot zone product with toluene allowed the separation of lower CF_3 derivatives (in solution) from crystalline (insoluble) S_6-$C_{60}(CF_3)_{12}$. The composition of the soluble product was close to that of the product obtained by the reaction of C_{60} with CF_3COOAg at 400 °C followed by sublimation. The solution was separated by HPLC in toluene as an eluent (4.6 mm i.d. × 25 cm Cosmosil Buckyprep column; flow rate, 2 ml min^{-1}; 290 nm). The fraction eluted at a retention time of 1.76 min was collected and purified by HPLC in toluene–hexane (1:4) as an eluent. The purified fraction eluted at a retention time of 9.75 min contained mainly $C_{60}(CF_3)_8$ according to MALDI analysis with $C_{60}(CF_3)_8O$ as the most abundant admixture (Figure 1). The slow concentration of this fraction gave small crystals suitable for an X-ray crystallographic study by using synchrotron radiation.

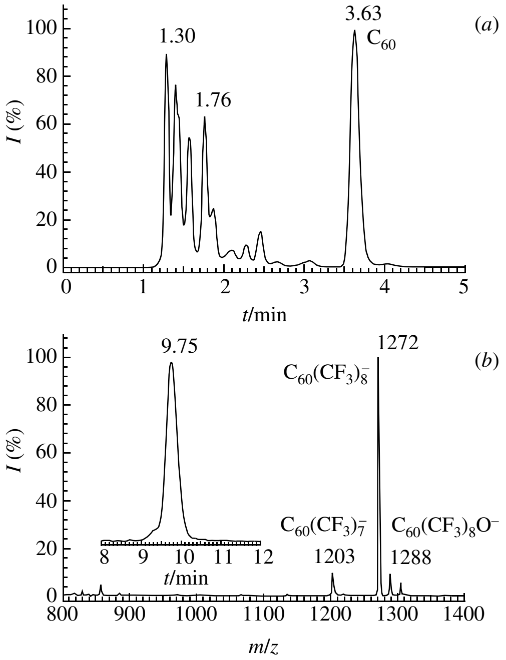


Figure 1 (*a*) HPLC chromatogram of the crude $C_{60}(CF_3)_n$ mixture (toluene as an eluent, 2 ml min^{-1}); (*b*) HPLC chromatogram of the purified fraction containing mostly the 1,6,11,16,18,24,27,36-isomer of $C_{60}(CF_3)_8$ [toluene–hexane (1:4) as an eluent; 2 ml min^{-1}] (inset) and the corresponding MALDI mass spectrum.

The crystal structure was solved using conventional direct methods (SHELXS97) and refined using SHELXL97.[‡] Top and side views of the $C_{60}(CF_3)_8$ molecule are shown in Figure 2 and its Schlegel diagram is presented in Figure 3(*a*). In addition to the IUPAC notation,[7] 1,6,11,16,18,24,27,36-$C_{60}(CF_3)_8$, the arrangement of the eight trifluoromethyl groups on a [60]fullerene carbon cage can be represented as a *para-para-para-meta-para-meta-para* ribbon [a $p^3(mp)^2$ ribbon] formed by seven edge-sharing $C_6(CF_3)_2$ hexagons. Figure 3 also shows the Schlegel diagrams for some related addition patterns. In contrast to the isomer investigated in this work, the known 1,6,11,18,24,27,52,55-$C_{60}(CF_3)_8$ isomer contains a p^3mp ribbon of five edge-sharing $C_6(CF_3)_2$ hexagons and an isolated *para*-$C_6(CF_3)_2$ hexagon [p^3mp,p-2, Figure 3(*e*)].[5(a)] In order to further compare these two and other possible addition patterns for the composition $C_{60}(CF_3)_8$, we performed a theoretical study at

---

[†] A lecturer at the Higher Chemical College of the RAS in 1995.

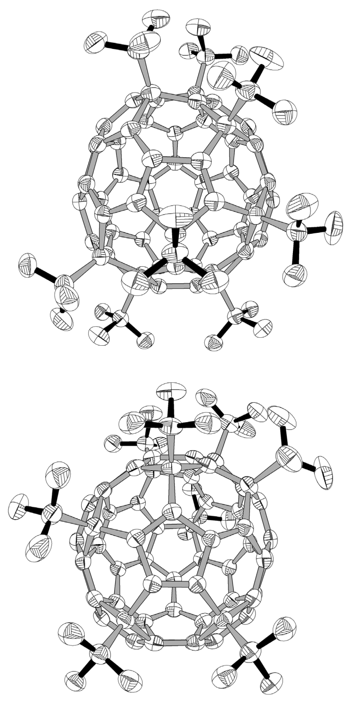
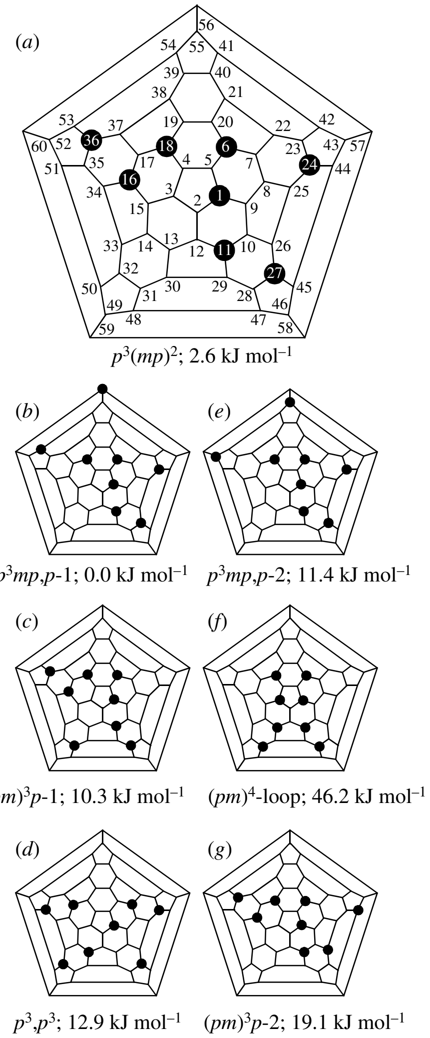


Figure 2 Side (above) and top (below) views of the $C_{60}(CF_3)_8$ molecule. Thermal ellipsoids are given at a 40% probability level.



(a) $p^3(mp)^2$; 2.6 kJ mol^{-1}

(b) p^3mp,p-1; 0.0 kJ mol^{-1} (e) p^3mp,p-2; 11.4 kJ mol^{-1}

(c) $(pm)^3p$-1; 10.3 kJ mol^{-1} (f) $(pm)^4$-loop; 46.2 kJ mol^{-1}

(d) p^3,p^3; 12.9 kJ mol^{-1} (g) $(pm)^3p$-2; 19.1 kJ mol^{-1}

Figure 3 Schlegel diagrams and DFT relative energies of the experimental (*a*) 1,6,11,16,18,24,27,36-$C_{60}(CF_3)_8$, (*e*) 1,6,11,18,24,27,52,55-$C_{60}(CF_3)_8$ and (*b*)–(*d*), (*f*), (*g*) some related theoretically considered $C_{60}(CF_3)_8$ isomers. Black circles denote attached CF_3 groups.

the AM1 level of theory for 1154 isomers constituting different combinations of *para*-$C_6(CF_3)_2$ hexagons, but excluding isomers with an *ortho* contact between CF_3 groups. The most stable isomers within the gap of 30 kJ mol^{-1} were then reoptimised at the DFT level of theory (see Online Supplementary Materials).[§] According to our calculations, the experimental $p^3(mp)^2$-$C_{60}(CF_3)_8$ isomer is second in stability among the full set of considered isomers and 8.8 kJ mol^{-1} more stable than structurally characterised p^3mp,p-2-$C_{60}(CF_3)_8$.[5(a)] The most thermodynamically stable p^3mp,p-1-$C_{60}(CF_3)_8$ isomer [Figure 3(*b*)] has only 2.6 kJ mol^{-1} lower energy, whereas the isomer with an addition pattern of $C_{60}Br_8$ [fused $(pm)^4$-loop; Figure 3(*f*)] shows a much higher energy of 46.2 kJ mol^{-1}, *i.e.*, a lower thermodynamic stability. The latter addition pattern contains some isolated double bonds in the carbon cage that should stabilise this arrangement. This is the case of $(pm)^4$-loop-$C_{60}X_8$ with X = Br (and, possibly, Cl) in spite of the presence of two destabilising fragments with two addends situated in the same pentagon.[8,9] However, the CF_3 groups represent more bulky addends than Cl or Br atoms, thus destabilising the molecule with this addition pattern. Due to mutual repulsion between the CF_3 groups in the same pentagons, the C–CF_3 distances (in the calculated structure) are elongated and the conformation of CF_3 groups relative to C–C bonds of the cage is skewed, being intermediate between the staggered and eclipsed ones. The rearrangement, which includes the removal of two CF_3 groups from these pentagons, released the conformation strain and resulted in the relatively stable (10.3 kJ mol^{-1}) $(pm)^3p$-1-$C_{60}(CF_3)_8$ isomer [Figure 3(*c*)].

It is interesting to follow up some relationships between experimental and theoretically considered $C_{60}(CF_3)_8$ isomers and experimentally found isomers with a higher degree of trifluoromethylation. The addition pattern of $p^3(mp)^2$-$C_{60}(CF_3)_8$ is included in the patterns of known 1,6,11,16,18,24,27,36,54,60-$C_{60}(CF_3)_{10}$ [$p^3(mp)^3$ ribbon][5(c),¶] and 1,3,7,10,14,17,23,28,31,40-$C_{60}(CF_3)_{10}$

[‡] *Crystal data*: $C_{60}(CF_3)_8$, crystal dimensions 0.05×0.03×0.02 mm, $M = 1484.91$, orthorhombic, space group *Pbca*, $a = 12.0266(1)$, $b = 18.0732(1)$, $c = 39.1245(4)$ Å, $V = 8504.1(1)$ Å^3, $\mu = 0.190$ mm^{-1}, $Z = 8$. Data collection was performed with a MAR225 CCD detector at 100 K using synchrotron radiation at the BESSY storage ring ($\lambda = 0.9050$ Å), PSF BL 14.1 of the Free University of Berlin, Germany. Reflections collected, 49588; independent, 6801, $R_{\text{int}} = 0.110$. Anisotropic refinement with 825 parameters yielded a conventional $R_1(F) = 0.077$ for 5593 reflections with $I > 2\sigma(I)$ and $wR_2(F^2) = 0.165$ for all reflections.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 637713. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2007.

[§] The set of $C_{60}(CF_3)_8$ isomers under theoretical study was restricted by all possible isomers which (i) contained four pairs of *para*-$C_6(CF_3)_2$ hexagons and (ii) had no *ortho*-$C_6(CF_3)_2$ hexagons. The large number of the possible isomeric $C_{60}(CF_3)_8$ structures forces us to find the ways to increase the efficiency of molecular models building, calculations and data processing. In result, the software package (implemented on the basis of the PERL and Object Pascal language) for automation of these tasks was developed, which significantly improved calculation and data processing performances and allowed us to avoid possible operator’s inaccuracies. Preliminary geometry optimization of 1154 $C_{60}(CF_3)_8$ isomers was carried out at the AM1 level of theory with the use of the PC GAMESS software.[10] The most stable isomers within the gap of 30 kJ mol^{-1} (AM1) were then reoptimised at the DFT level of theory using the PRIRODA program,[11] the TZ2P basis set and the PBE exchange-correlation functional.[12]

Table 1 Selected C–C bonds (Å) in the isomers of $C_{60}(CF_3)_8$ and $C_{60}(CF_3)_{10}$.[a]

Bond	$C_{60}(CF_3)_8$ $p^3(mp)^2$	$C_{60}(CF_3)_8$ p^3mp,p-2 [ref. 5(*a*)]	$C_{60}(CF_3)_{10}$ $p^3(mp)^3$ [ref. 5(*c*)]	$C_{60}(CF_3)_{10}$ $pmp^3(mp)^2$ [ref. 5(*b*)]
C(4)–C(5)	1.346(4)	1.345(3)	1.339(3)	1.354(1)
C(17)–C(37)	1.349(4)	1.431(4)	1.341(3)	1.358(2)
C(7)–C(8)	1.347(4)	1.351(4)	1.344(3)	1.377(1)
C(9)–C(10)	1.363(4)	1.358(4)	1.365(3)	1.366(2)
C(25)–C(26)	1.355(4)	1.362(4)	1.360(3)	1.361(2)
C(2)–C(12)	1.360(4)	1.372(4)	1.368(3)	1.372(2)
$C–CF_3$ (av.)	1.531	1.532	1.541	1.540

[a] For $C_{60}(CF_3)_{10}$ isomers, the distances corresponding to the same $p^3(mp)^2$ fragments are given.

[$pmp^3(mp)^2$ ribbon][5(*b*)] isomers. Therefore, $p^3(mp)^2$-$C_{60}(CF_3)_8$ may be regarded as a possible precursor of these $C_{60}(CF_3)_{10}$ isomers. The most thermodynamically stable p^3mp,p-1-$C_{60}(CF_3)_8$ isomer is contained in the pattern of $pmp^3(mp)^2$-$C_{60}(CF_3)_{10}$. The p^3,p^3-$C_{60}(CF_3)_8$ isomer [12.9 kJ mol^{-1}, Figure 3(*d*)] is the substructure and a possible precursor of the third experimentally observed isomer of $C_{60}(CF_3)_{10}$, 1,6,12,15,18,23,25,41,45,57-$C_{60}(CF_3)_{10}$.[5(*d*)] Less stable $(pm)^3p$-2-$C_{60}(CF_3)_8$ [19.1 kJ mol^{-1}, Figure 3(*g*)] is in a similar relation to S_6-$C_{60}(CF_3)_{12}$[5(e)] (see Supplement *S*10 for more detail).

Table 1 compares characteristic bond lengths in the molecular structures of the known $C_{60}(CF_3)_8$ and $C_{60}(CF_3)_{10}$ isomers having in common the $p^3(mp)^2$ arrangement of six CF_3 groups. The nearly isolated double bonds, C(4)–C(5), have virtually the same length of 1.34–1.35 Å, as expected. The bonds of the same type, C(17)–C(37), with distances of 1.34–1.36 Å are present in only three structures containing the continuous $C_6(CF_3)_2$ ribbon [Figure 3(*a*)]. The second group of the bonds with a presumably double character, C(7)–C(8), C(9)–C(10) and C(25)–C(26), is similar in all four structures (1.36–1.37 Å). The ranges of the $C–CF_3$ bond lengths and the average values between 1.53 and 1.54 Å are practically the same in the four molecules.

In summary, the isolation of a new isomer of $C_{60}(CF_3)_8$ with a $p^3(mp)^2$ ribbon of edge-sharing $C_6(CF_3)_2$ hexagons allowed its comparison with the known isomer containing a p^3mp ribbon and an isolated p-$C_6(CF_3)_2$ hexagon. The both structurally characterised isomers and some relative ones were compared on the basis of the DFT calculations.

This work was partially supported by the Russian Foundation for Basic Research (grant nos. 05-03-04006 and 06-03-32942a) and the Federal Agency of Science and Innovation (project no. 02.120.11.80.2).

Online Supplementary Materials

The results of DFT calculations for $C_{60}(CF_3)_8$ isomers within the gap of 21 kJ mol^{-1}; Schlegel diagrams showing the relations between different isomers are presented in Online Supplementary Materials which can be found in the online version at doi:10.1016/j.mencom.2007.03.020.

References

1 P. J. Fagan, P. J. Krusic, C. N. McEwen, J. Lazar, D. H. Parker, N. Herron and E. Wasserman, *Science*, 1993, **262**, 404.

2 (*a*) I. S. Uzkikh, E. I. Dorozhkin, O. V. Boltalina and A. I. Boltalin, *Dokl. Akad. Nauk*, 2001, **379**, 344 [*Dokl. Chem.* (*Engl. Transl.*), 2001, **379**, 204]; (*b*) A. D. Darwish, A. K. Abdul-Sada, A. G. Avent, Y. Lyakhovetsky, E. A. Shilova and R. Taylor, *Org. Biomol. Chem.*, 2003, **1**, 3102.

3 (*a*) A. A. Goryunkov, I. V. Kuvychko, I. N. Ioffe, D. L. Dick, L. N. Sidorov, S. H. Strauss and O. V. Boltalina, *J. Fluorine Chem.*, 2003, **124**, 61; (*b*) E. I. Dorozhkin, D. V. Ignat'eva, A. A. Goryunkov, N. B. Tamm, I. N. Ioffe, P. A. Khavrel, A. A. Streletskiy, V. Yu. Markov, A. A. Popov, J. Spandl, I. V. Kuvychko, S. H. Strauss and O. V. Boltalina, *Chem. Eur. J.*, 2006, **12**, 3876.

4 (*a*) 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, Ph. Pattison, E. Kemnitz and S. I. Troyanov, *J. Fluorine Chem.*, 2006, **127**, 1344; (*b*) S. M. Avdoshenko, A. A. Goryunkov, I. N. Ioffe, D. V. Ignat'eva, L. N. Sidorov, Ph. Pattison, E. Kemnitz and S. I. Troyanov, *Chem. Commun.*, 2006, 2463 and references therein.

5 (*a*) I. E. Kareev, N. B. Shustova, B. S. Newell, S. M. Miller, O. P. Anderson, S. H. Strauss and O. V. Boltalina, *Acta Crystallogr.*, 2006, **E62**, o3154; (*b*) I. E. Kareev, I. V. Kuvychko, S. F. Lebedkin, S. M. Miller, O. P. Anderson, K. Seppelt, S. H. Strauss and O. V. Boltalina, *J. Am. Chem. Soc.*, 2005, **127**, 8362; (*c*) I. E. Kareev, S. F. Lebedkin, S. M. Miller, O. P. Anderson, S. H. Strauss and O. V. Boltalina, *Acta Crystallogr.*, 2006, **E62**, o1498; (*d*) 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; (*e*) S. I. Troyanov, A. Dimitrov and E. Kemnitz, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 1971.

6 I. E. Kareev, N. B. Shustova, I. V. Kuvychko, S. F. Lebedkin, S. M. Miller, O. P. Anderson, A. A. Popov, S. H. Strauss and O. V. Boltalina, *J. Am. Chem. Soc.*, 2006, **128**, 12268.

7 F. Cozzi, W. H. Powell and C. Thilgen, *Pure Appl. Chem.*, 2005, **77**, 843.

8 (*a*) P. R. Birkett, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *Nature*, 1992, **357**, 479; (*b*) S. I. Troyanov, P. A. Troshin, O. V. Boltalina and E. Kemnitz, *Fullerenes Nanotubes Carbon Nanostruct.*, 2002, **11**, 61.

9 B. W. Clare and D. L. Kepert, *J. Mol. Struct. Theochem*, 2003, **621**, 211.

10 (*a*) A. Granovsky, *http://classic.chem.msu.su/gran/gamess/index.html*; M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.

11 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **28**, 151.

12 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

Received: 9th October 2006; Com. 06/2791

¶ In ref. 5(*c*), this isomer was erroneously referred to as 1,6,11,16,18,26,36,44,48,58-$C_{60}(CF_3)_{10}$.