Journal of Fluorine Chemistry 130 (2009) 241–247

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis and molecular structures of heptafluoroisopropylated fullerenes: $C_{60}(i\text{-}C_3F_7)_8$, $C_{60}(i\text{-}C_3F_7)_6$, and $C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$

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ARTICLE INFO

Article history:
Received 10 July 2008
Received in revised form 7 October 2008
Accepted 25 October 2008
Available online 5 November 2008

Keywords:
Fullerenes
Perfluoroalkylation
Heptafluoroisopropyl iodide
X-ray structure
HPLC
Mass spectrometry

ABSTRACT

One isomer of $C_{60}(i\text{-}C_3F_7)_8$, three isomers of $C_{60}(i\text{-}C_3F_7)_6$, and the first mixed perfluoroalkylated fullerene, $C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$, have been isolated by HPLC from a mixture prepared by reaction of C_{60} with heptafluoroisopropyl iodide in a glass ampoule at 260–290 °C. The molecular structures of the four new compounds have been determined by means of X-ray single crystal diffraction partially also by use of synchrotron radiation. Theoretical calculations at the DFT level of theory have been employed to rationalize the energetics of isomers and of C_{60}-R_f binding.

1. Introduction

Among the fast growing number of synthesized fullerene derivatives, perfluoroalkylated C_{60} and C_{70} show rather high chemical and thermal stability. In contrast to fullerene fluorides with F atoms directly bound to fullerene cage, perfluoroalkylated fullerenes are highly stable against hydrolysis and oxidation [1]. In the few last years, numerous trifluoromethylated fullerene derivatives $C_{60/70}(CF_3)_n$ with n ranging from 2 to 18 have been prepared by high temperature reactions with metal trifluoroacetates or trifluoromethyliodide [1–7]. For many compounds electrochemical potentials were determined [8,9] and their relative energies were theoretically calculated [4,6–9]. There were some attempts to rationalize the formation of compounds with different addition patterns by combination of thermodynamic and kinetic factors [4]. However, the trifluoromethylation process still remains not fully understood.

Pentafluoroethylated fullerenes are known for a narrower composition range: $C_{60}(C_2F_5)_n$ with $n = 6–10$ [10,11] and $C_{70}(C_2F_5)_{10}$ (seven isomers) [12], whereas isolated and characterized heptafluoropropylated fullerenes are described for four $C_{70}(n\text{-}C_3F_7)_8$ isomers [13] and only one isomer of $C_{60}(i\text{-}C_3F_7)_6$ [14]. A comparison of trifluoromethylated fullerenes with fullerene derivatives containing larger perfluoroalkylated (R_f) groups demonstrates substantial differences in their addition patterns.

Herein we report synthesis, isolation and structural characterization of four isomers containing perfluoroisopropyl groups and compare their addition patterns with those of previously known perfluoroalkylated fullerenes.

2. Results and discussion

The synthesis method used in this work – an ampoule reaction between fullerene and perfluoroisopropyl iodide at 260–290 °C for 24–72 h – closely resembles that described for preparation of perfluoroethylated [60]fullerenes [11]. The only substantial difference is the presence of metallic copper in the reaction ampoule which resulted in rather high reaction yields estimated at 85–95% based on the amount of unreacted fullerene. Our previous experiments on the synthesis of perfluoroisopropylated [60]fullerene derivatives without addition of copper always resulted in very low yields due to insufficient reactivity of fullerene. Addition of copper in similar syntheses of perfluoroalkylated fullerenes was described previously, however, without any comments concerning its function [10,15]. Addition of copper was proven to be efficient in perfluoroalkylation of organic substances which was ascribed to the formation of an intermediate copper complex like CuR_f [16,17].

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doi:10.1016/j.jfluchem.2008.10.006

Such copper derivatives are known to be thermally unstable. Therefore, it is most probably in our case that copper powder taken in a large amount reacted with iodine evolved due to decomposition of i-C_3F_7I at high temperature thus decreasing the vapor pressure of gaseous iodine and promoting the formation of i-C_3F_7 radicals. Therefore, the total amount of elemental iodine in the raw reaction product was rather low, whereas white powder of CuI was deposited on the ampoule walls. Fullerene derivatives can be simply separated from copper(I) iodide by extracting the former with toluene.

A MALDI-MS analysis of the raw product from the reaction during 24 h revealed, besides a small amount of unreacted C_{60}, the presence of $C_{60}(i\text{-}C_3F_7)_m$ compounds with $m = 2$–8 as well as of mixed CF_3/i-C_3F_7 functionalized [60]fullerenes. Rough chromatographic separation with toluene as the eluent resulted in fractions 1–3. Toluene fraction 1 was further chromatographically separated using hexane as the eluent. The main hexane sub-fractions contained $C_{60}(i\text{-}C_3F_7)_m$ isomers with $m = 8$ (one isomer) and $m = 6$ (isomers I–III) (see Fig. 1a). Negative ion MALDI mass spectra of the hexane fractions are shown in Fig. 2a–c. Slow evaporation of these fractions gave crystals suitable for X-ray crystallographic study. If the synthesis has been performed for a longer time (72 h), the toluene fraction 1 contained the same four $C_{60}(i\text{-}C_3F_7)_m$ isomers as above plus some other isomers ($m = 6$ or 8) of lower abundance. Average yields of the main components, $C_{60}(i\text{-}C_3F_7)_8$-I, $C_{60}(i\text{-}C_3F_7)_6$-I, -II, and -III, in the mixture of perfluoroalkylated derivatives can be roughly estimated as 50%, 10%, 10%, and 5%, respectively.

In typical MALDI mass spectra of $C_{60}(i\text{-}C_3F_7)_m$ ($m = 6$, 8), molecular $C_{60}(i\text{-}C_3F_7)_m^-$ ions are present along with some fragment ions with ($m - 1$) perfluoroisopropyl groups and additionally some ions due to the loss of C_2F_4. Note that such fragmentation type becomes much more pronounced at higher energy of laser pulses. This feature in the MALDI spectra was not observed for C_2F_5 and n-C_3F_7 fullerene derivatives [11,13]. Obviously, such instability is caused by branching of perfluoroisopropyl group which somehow facilitates its disintegration.

MALDI-MS analysis revealed that toluene fraction 3 contains presumably two mixed $C_{60}(CF_3)_n(i\text{-}C_3F_7)_m$ compounds which was confirmed by the analyses of the sub-fractions obtained by HPLC separation with toluene/hexane (8/2) mixture as the eluent (Fig. 1b). The compounds with $n;m = 2;2$ and 1;1 are the first well characterized examples of mixed perfluoroalkylated [60]fullerenes. Their estimated yields in the reaction mixture are 1.5% and 0.5%, respectively. MALDI mass spectrum of $C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$ recorded at middle laser pulse energy clearly demonstrates a high degree of fragmentation by the loss of either i-C_3F_7 or CF_3 group or both up to the unfunctionalized C_{60}^- (Fig. 2d).

Single crystal X-ray diffraction study resulted in structure determination of $C_{60}(i\text{-}C_3F_7)_8$, $C_{60}(i\text{-}C_3F_7)_6$-I and -II, and $C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$. Isomer $C_{60}(i\text{-}C_3F_7)_6$-III turned out to be known from the literature [14]. Molecular structures of the four new isomers are shown in Fig. 3. The molecular structure of $C_{60}(i\text{-}C_3F_7)_8$ represents an unprecedented addition pattern for $C_{60}X_8$ derivatives (Fig. 3a). Eight i-C_3F_7 groups are attached on four isolated *para*-$C_6(i\text{-}C_3F_7)_2$ hexagons on [60]fullerene cage (*p*,*p*,*p*,*p* addition pattern) as can be clearly seen on a Schlegel diagram in Fig. 4a. Thus, two experimentally determined (or proposed based on ^{19}F NMR spectra) addition patterns of $C_{60}(CF_3)_8$ isomers, as well as theoretically calculated most stable isomers of this composition all have attachment motifs with either seven or five edge-sharing $C_6(CF_3)_2$ hexagons (i.e. with no or only one isolated p-$C_6(CF_3)_2$ hexagon) [8,18,19]. Among six experimentally determined molecular structures of $C_{60}(C_2F_5)_8$, five contain an addition pattern with five edge-sharing *para*- or *meta*-$C_6(C_2F_5)_2$ hexagons and one isolated *para*-hexagon (p^3mp,p), whereas one isomer contains three edge-sharing $C_6(C_2F_5)_2$ hexagons and two isolated *para*-hexagons (*pmp*,*p*,*p*) [10,11]. The chromatogram in Fig. 1a evidences the preferred formation of only one $C_{60}(i\text{-}C_3F_7)_8$ isomer at these reaction conditions. This fact can be interpreted as an indication of a high thermodynamic stability of the experimentally found isomer. However, the influence of kinetic factors cannot be fully excluded, because some more less abundant $C_{60}(i\text{-}C_3F_7)_8$ isomers were detected in the reaction product obtained at longer reaction time (see above).

Molecular structures of the two new $C_{60}(i\text{-}C_3F_7)_6$-I and -II isomers (Fig. 3b and c) and the previously published one (isomer III) all show similar addition patterns with three isolated *para*-$C_6(i\text{-}C_3F_7)_2$ hexagons (*p*,*p*,*p* attachment) as can be seen on Schlegel diagrams in Fig. 4b–d. Theoretical calculations at the DFT level of theory reveal that the energy differences between the isomers are very moderate, isomer III being 5.6 and 12.6 kJ mol^{-1} more stable than isomers I and II, respectively. The position of four attached i-C_3F_7 groups numbered according to the IUPAC notation [20] as 1,7,16,36 on Schlegel diagrams are common for all three $C_{60}(i\text{-}C_3F_7)_6$ isomers (the same motif of four groups is also present in the molecule of $C_{60}(i\text{-}C_3F_7)_8$, see Fig. 4a). Such addition patterns were not observed for the experimentally determined $C_{60}(CF_3)_6$ structures. Among five $C_{60}(CF_3)_6$ isomers with known structures, three ones contain contiguous ribbons of edge-sharing *para*- and *meta*-$C_6(CF_3)_2$ hexagons [2,4]; one isomer is built by combination of a *pmp*-fragment of three edge-sharing $C_6(CF_3)_2$ hexagons and an isolated p-$C_6(CF_3)_2$ hexagon [4]; and one more isomer is characterized by the so-called skew pentagonal pyramidal arrangement of six CF_3 groups where two groups are attached

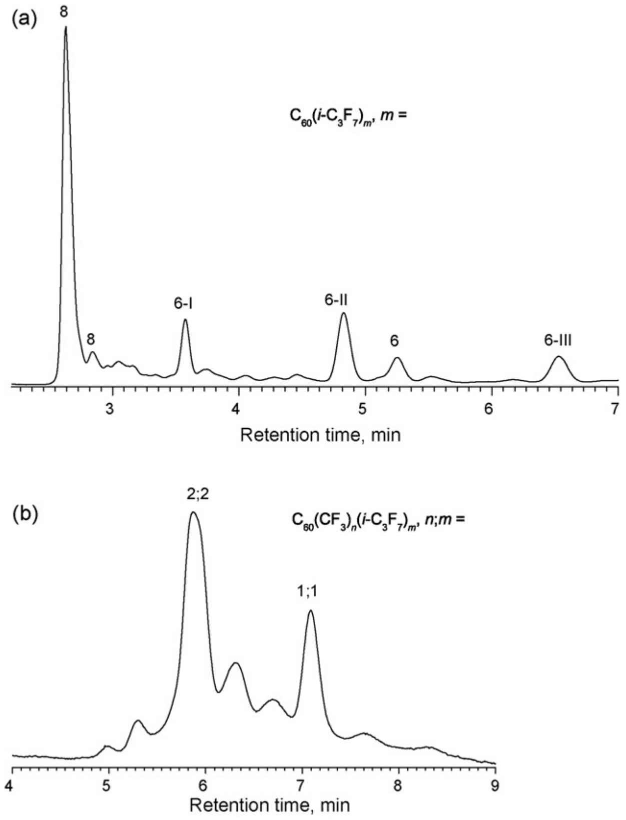

Fig. 1. (a) HPLC trace of the toluene fraction 1 recorded using hexane as the eluent. Roman numerals denote sequential isomer numbers according to the retention time. (b) HPLC trace of the toluene fraction 3 recorded using toluene/hexane mixture (v/v 8/2). Compound compositions are given as $n;m$ with n and m for the numbers of CF_3 and C_3F_7 groups, respectively.

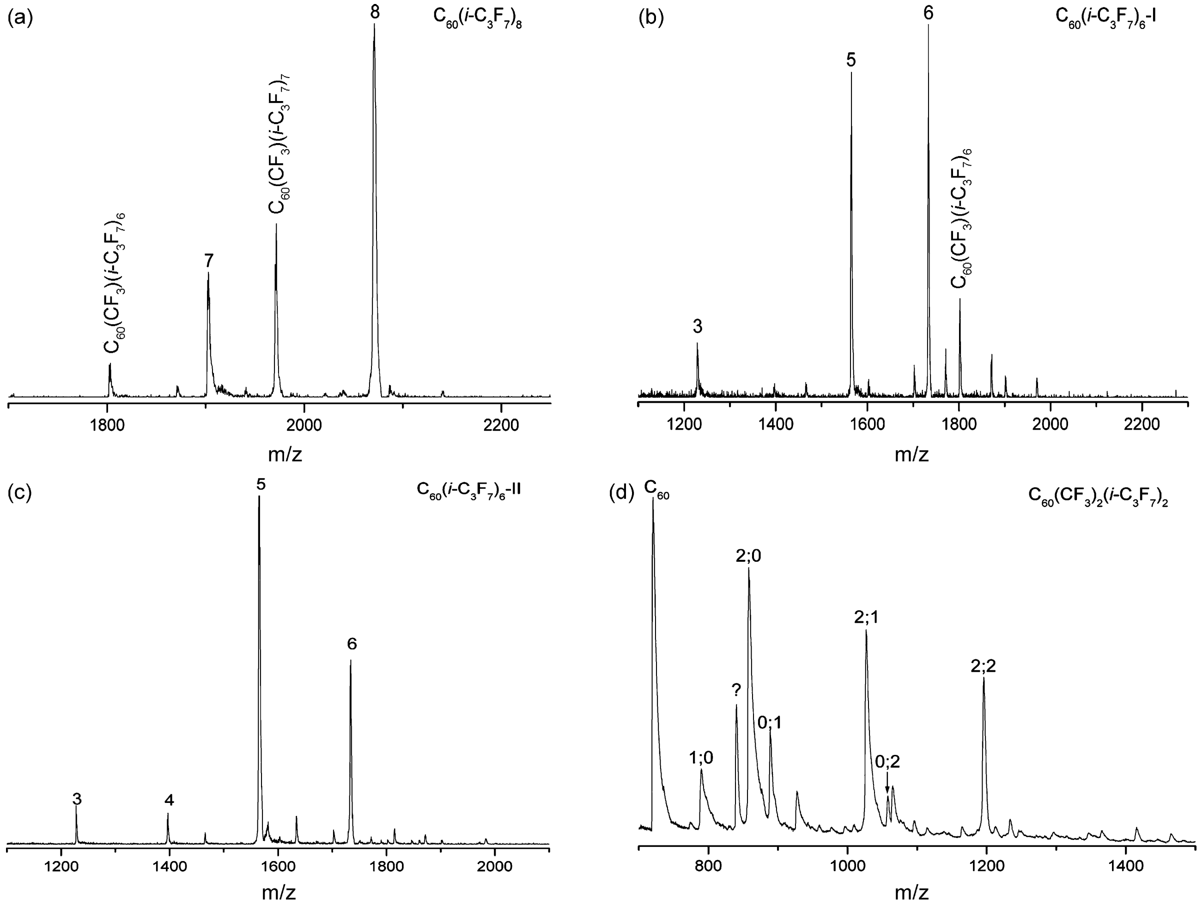

Fig. 2. Negative ion MALDI mass spectra of four sub-fractions after separation with HPLC. Arabian numbers denote the number of attached i-C_3F_7 groups (a–c). Compound compositions for (d) are given as two Arabic numbers the first one indicates the number of CF_3 groups and the second one indicates the number of i-C_3F_7 groups.

in *ortho*-position [15]. In contrast, among perfluoroethylated [60]fullerenes, the two known $C_{60}(C_2F_5)_6$ isomers both have a *p,p,p* arrangement of three isolated $C_6(C_2F_5)_2$ hexagons [10,11]. Moreover, one of the two $C_{60}(C_2F_5)_6$ isomers has an addition pattern which is identical with that of $C_{60}(i\text{-}C_3F_7)_6$-II [10].

The presence of only isolated *para*-$C_6(i\text{-}C_3F_7)_2$ hexagons in molecular structures of $C_{60}(i\text{-}C_3F_7)_n$ isomers may be explained by the bulkiness of the i-C_3F_7 group due to its branching. Interestingly, the known structures of $C_{70}(n\text{-}C_3F_7)_8$ isomers [13] all contain *pmp* fragments, apparently due to an unbranched structure of the *n*-perfluoropropyl group resulting in a smaller steric demand. In structures of all $C_{60}(i\text{-}C_3F_7)_n$ isomers, mutual orientation of two i-C_3F_7 groups in each *para*-$C_6(i\text{-}C_3F_7)_2$ hexagon provide a minimum repulsion, because $(CF_3)_2C$–F bonds are directed to each other (with a small skewing; F···F contacts range from 2.45 to 2.69 Å), whereas CF_3 branches of two i-C_3F_7 groups are at maximum distances from each other. On the contrary, in the known structures of trifluoromethylated fullerenes (for example, in $C_{60}(CF_3)_2$ or 1,7,16,36-$C_{60}(CF_3)_4$ [4]), two CF_3 groups of isolated *para*-$C_6(CF_3)_2$ hexagons are always in a near perfect staggered orientation indicating the absence of mutual repulsion.

A possible source of CF_3 groups for the formation of mixed perfluoroalkylated fullerenes could be a partial thermal decomposition of attached heptafluoroisopropyl groups due to an increased sensibility of perfluoroisopropyl fullerene derivatives to energy impact that was observed in the MALDI mass spectrometric experiments. Molecular structure of the isolated $C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$ isomer contains four attached perfluoroalkyl groups that form a p^3 ribbon of three edge-sharing $C_6(R_f)_2$ hexagons (Figs. 3d and 4e). Such arrangement of the two pairs of CF_3 and i-C_3F_7 groups results in a C_s symmetry of the addition pattern, which coincides with the crystallographically imposed mirror symmetry of the whole molecule. It is noteworthy that the i-C_3F_7 groups are oriented in such a way that their fluoromethine F atoms are directed towards the F atom of the CF_3 groups of the same $C_6(CF_3)(i\text{-}C_3F_7)$ hexagon (the shortest F···F distance between two groups is 2.66 Å). Significantly, the p^3 addition pattern corresponds to the energetically most favorable arrangement of four CF_3 groups on the C_{60} fullerene cage (1,7,11,24-$C_{60}(CF_3)_4$ [4]). However, so far this $C_{60}(CF_3)_4$ isomer has not been isolated as individual compound. It was only mentioned in [2] as a ca. 15% impurity to 1,7-$C_{60}(CF_3)_2$ due to similar retention times of the both compounds. In contrast, its oxide (epoxide) C_s-$C_{60}(CF_3)_4O$ with oxygen atom spanning C26 and C27 atoms (thus producing a skew-pentagonal-pyramid pattern) has been obtained, isolated, and structurally characterized [4,15] as well as its pentafluoroehylated analog, C_s-$C_{60}(C_2F_5)_4O$ [15]. Apparently, the pronounced tendency to the formation of an epoxide is due to enhanced reactivity of the C26–C27 double bond towards further addition that occurs either during the synthesis or in the course of a workup in air. It is most probable that the isolation of a not oxidized $C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$ with 1,7,11,24 addition pattern became possible due to the orientation of the two i-C_3F_7 groups protecting the C26–C27 double bond from further addition (see Fig. 3d).

MALDI-MS analysis of the second toluene/hexane fraction eluted at 7.08 min showed the presence of a mixed perfluoroalkylated fullerene containing one CF_3 and one i-C_3F_7 group, $C_{60}(CF_3)(i\text{-}C_3F_7)$ (Fig. 1b). Addition pattern of this isomer can be

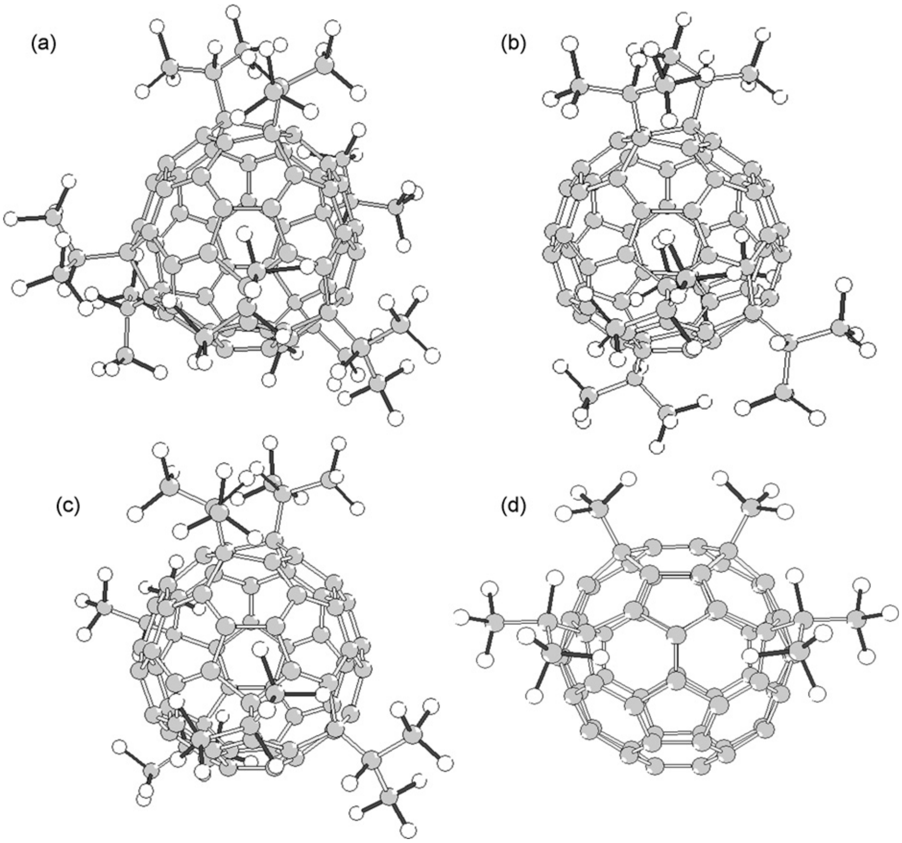

Fig. 3. Molecular structures of the four isomers $C_{60}(i\text{-}C_3F_7)_8$ (a), $C_{60}(i\text{-}C_3F_7)_6$-I (b), $C_{60}(i\text{-}C_3F_7)_6$-II (c) and $C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$ (d).

suggested on the basis of the previously known or predicted molecular structures containing two attached groups or atoms. Difluoride, $C_{60}F_2$, was shown to be a 1,9 isomer with two F atoms in *ortho* position on a 6:6 junction [21,22]. For a mixed fluoro-trifluoromethyl compound, $C_{60}F(CF_3)$, DFT calculations predict even higher stability of the 1,9 isomer over the 1,7 one (with addends in a *para* position), but the energy difference is as low as 9.8 kJ mol^{-1} [23]. In the case of $C_{60}(CF_3)_2$, 1,7 isomer becomes 34.7 kJ mol^{-1} more stable than the 1,9 isomer due to steric reasons. Therefore, most probably the CF_3 and the still bulkier i-C_3F_7 groups are attached in *para* position to one another in the mixed compound $C_{60}(CF_3)(i\text{-}C_3F_7)$ with the addition pattern of 1,7 isomer shown in Fig. 4f. This assumption is also supported by the molecular structure of $C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$ (determined in this work) containing only *para*-$C_6(CF_3)(i\text{-}C_3F_7)$ hexagons.

Some characteristic (averaged) bond lengths in molecules of perfluoroisopropylated [60]fullerenes are given in Table 1. In general, most structural features found in these compounds are also common with other perfluoroalkylated fullerenes. Thus, the C–C bonds on fullerene cage outgoing from the sp^3 carbons bearing perfluoroisopropyl groups are significantly elongated compared with other C–C cage bonds. This type of C–C bonds can be subdivided into bonds at 6:6 junctions and those at 5:6 junctions, the former (1.549–1.552 Å) being somewhat longer than the latter (1.520–1.523 Å). The shortest are nearly double sp^2–sp^2 C–C bonds within $C_6(i\text{-}C_3F_7)_2$ hexagons (indicated in Fig. 4) with average lengths in the range of 1.364–1.369 Å. All C–C bonds connecting the fullerene cage with perfluoproisopropyl groups are unusually elongated (1.574–1.583 Å) when compared with similar C–C bonds in trifluoromethylated [4,5,18], pentafluoroethylated [10,11], and n-heptafluoropropylated [13] fullerenes (1.53–1.56 Å). Apparently, branching of the perfluoproisopropyl group results in an increased repulsion from the fullerene cage, because some F atoms of two CF_3 groups also have rather close contacts (at 2.7–2.9 Å) with the cage carbon atoms.

In view of the fact that the C_{60}–$CF(CF_3)_2$ bonds appear to be markedly elongated (1.578 Å (XRD); 1.59 Å (DFT)), we decided to estimate computationally the binding energy of CF_3 and i-C_3F_7 addends. It has been found in agreement with the above elongation that the difference reaches ca. 100 kJ mol^{-1} in favor of CF_3. One can attribute this to stronger unfavorable steric interactions of C_{60} with bulkier i-C_3F_7. The calculations also revealed that the removal of CF_3 from an isolated fluoroisopropyl radical demands 80 kJ mol^{-1} more energy than the removal of a CF_3 radical from a fluoroisopropyl group attached to the fullerene cage, obviously due to partial electron delocalization on a fullerene cage in the latter case. More generally, one can expect that larger perfluorinated addends are more prone to thermal detachment from C_{60}, which may result in easier attainment of the equilibrium isomeric mixtures and also in disproportionate enrichment of the synthetic products with CF_3 moieties.

3. Experimental

3.1. Synthesis

C_{60} (40 mg, 99.98%), 250 mg copper powder and the excess amount of i-C_3F_7I (0.3 ml, 98%, TCI) were heated at 260–290 °C in a sealed glass ampoule for 24–72 h. After that the ampoule was opened, and the excess of i-C_3F_7I and a small amount of iodine were removed from a brown coloured reaction product by heating at ca. 100 °C in open air for 1 h. Perfluoroalkylated derivatives of C_{60} were separated from copper monoiodide by extraction with toluene. Subsequent chromatographic analysis showed the

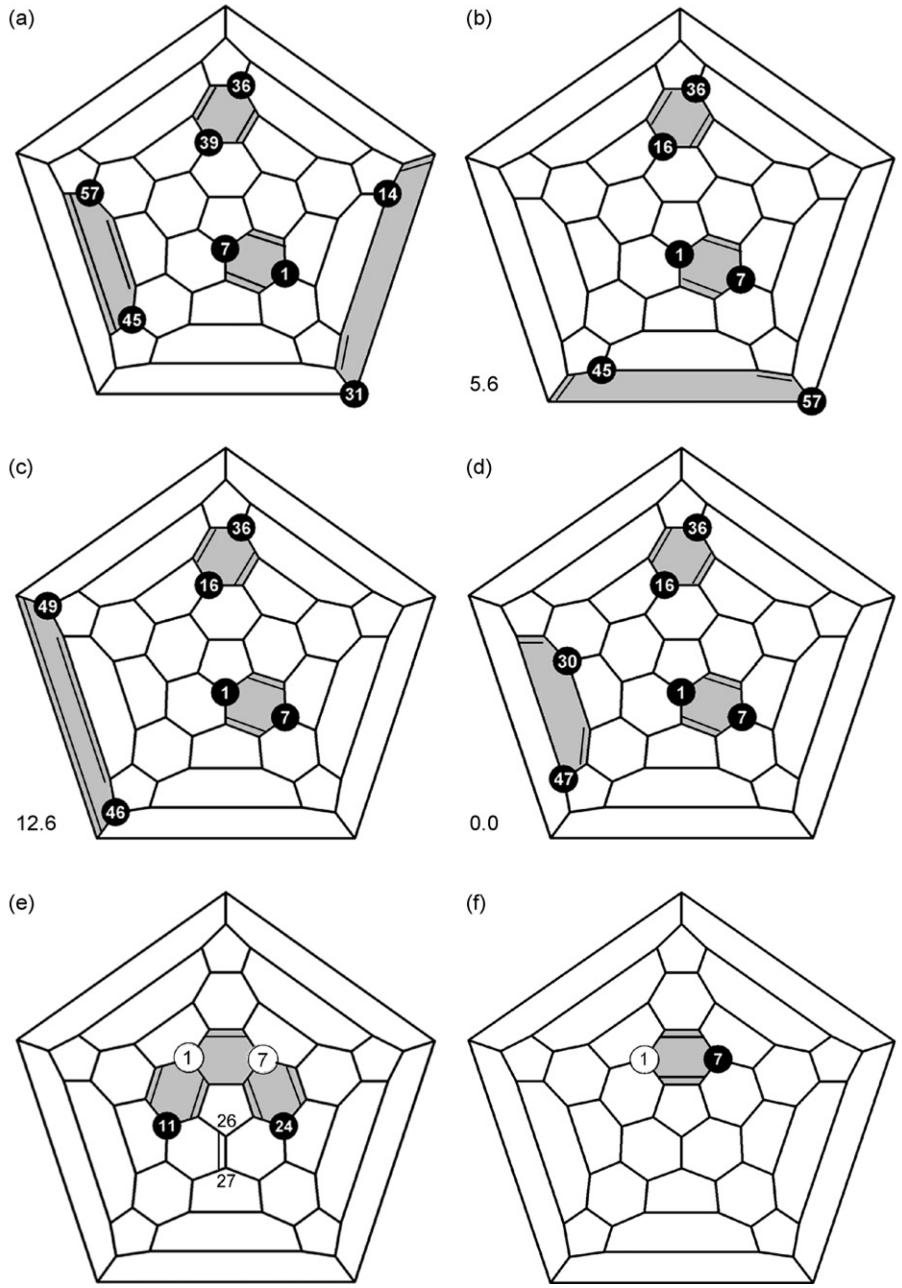

Fig. 4. Schlegel diagrams for the structures of $C_{60}(i\text{-}C_3F_7)_8$ (a), $C_{60}(i\text{-}C_3F_7)_6$-I (b), $C_{60}(i\text{-}C_3F_7)_6$-II (c), $C_{60}(i\text{-}C_3F_7)_6$-III (d), $C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$ (e), and of the proposed structure of $C_{60}(CF_3)(i\text{-}C_3F_7)$ (f). DFT-predicted relative energies (kJ mol^{-1}) are given for the three $C_{60}(i\text{-}C_3F_7)_6$ isomers. Black and white circles represent $i\text{-}C_3F_7$ and CF_3 groups, respectively.

presence of only several percents of C_{60} so that overall yield of perfluoroalkylated fullerenes can be estimated as 85–95% in different synthesis runs.

3.2. Chromatographic isolation and mass-spectrometric analyses

Negative ion matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) was applied to analyze the crude product and isolated HPLC fractions. The spectra were recorded with a Voyager-DE time-of-flight mass spectrometer equipped with an UV laser (337 nm, 3 ns pulse) and using *trans*-2-(3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene)malonitrile (DCTB) as matrix. The reaction mixture was roughly divided in three fractions by HPLC with a KNAUER chromatographic system and a Cosmosil Buckyprep column (Nacalai tesque Inc., 10 mm ID × 25 cm long) using toluene as the eluent, flow rate 4.6 mL min^{-1}, monitored at 290 nm. The collection time intervals for the toluene fractions 1, 2, and 3 were 2.5–3.1, 3.1–3.7, and 3.7–5.2 min, respectively. An admixture of C_{60} eluted at 7.6 min was removed at this stage.

Toluene fractions 1 and 3 were further separated using the same column and flow rate. HPLC separation of toluene fraction 1 carried out using hexane as the eluent resulted in six sub-fractions (Fig. 1a) all containing $C_{60}(i\text{-}C_3F_7)_m$ ($m = 6,\ 8$) compounds according to MALDI-MS analyses (Fig. 2a–c). Toluene fraction 3 was HPLC separated using toluene/hexane mixture (v/v 8/2) as eluent into two sub-fractions eluted at 5.87 and 7.08 min (Fig. 1b), MALDI-MS analyses of which revealed the presence of mixed $CF_3/i\text{-}C_3F_7$ functionalized [60]fullerenes (Fig. 2d). Toluene fraction 2 was not subjected to HPLC separation due to a very complex isomeric composition and a poor peak separation. Slow concentration of

Table 1
Selected (averaged) C–C bond lengths (Å) in perfluoroisopropylated [60]fullerenes.

Bond type	$C_{60}(i\text{-}C_3F_7)_8$	$C_{60}(i\text{-}C_3F_7)_6$-I	$C_{60}(i\text{-}C_3F_7)_6$-II	$C_{60}(i\text{-}C_3F_7)_6$-III [14]	$C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$
C–C (sp^2–sp^3)[a]	1.550	1.551	1.549	1.550	1.540 (CF_3) 1.552 ($i\text{-}C_3F_7$)
C–C (sp^2–sp^3)[b]	1.520	1.523	1.522	1.521	1.516
C–C (sp^2–sp^2)[c]	1.369	1.369	1.367	1.368	1.364
C(cage)–R_f	1.580	1.577	1.574	1.583	1.538 (CF_3) 1.583 ($i\text{-}C_3F_7$)
Esd of individual C–C bonds	0.004	0.002-0.003	0.004	0.005	0.003

[a] C–C bond at a 5:6 junction.
[b] C–C bond at a 6:6 junction.
[c] A nearly double C–C bond (see Schlegel diagrams in Fig. 4).

Table 2
Crystallographic data and some details of data collection and structure refinement for heptafluoroisopropylated [60]fullerenes.

Compound	$C_{60}(i\text{-}C_3F_7)_8 0.8C_6H_{14}$	$C_{60}(i\text{-}C_3F_7)_6$-I	$C_{60}(i\text{-}C_3F_7)_6$-II	$C_{60}(CF_3)_2(i\text{-}C_3F_7)_2$
M	2141.06	1734.78	1734.78	1196.68
Symmetry	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group; Z	$C2/c$; 8	P-1; 2	$P2_1/n$; 4	$P2_1/m$; 2
a (Å)	14.9244(1)	10.5013(1)	16.4566(5)	9.9093(1)
b (Å)	37.9751(2)	12.7563(1)	14.3939(3)	19.8900(3)
c (Å)	25.1502(1)	21.1610(2)	23.2182(6)	10.3660(1)
α (°)	90	88.3558(3)	90	90
β (°)	90.6720(3)	82.9207(3)	94.2260(2)	109.1898(6)
γ (°)	90	77.3202(3)	90	90
V (Å^3)	14253.0(1)	2744.47(4)	5484.9(2)	1929.57(4)
D_c (g cm^{-3})	1.996	2.099	2.101	2.060
Crystal size (mm)	0.04 × 0.04 × 0.01	0.04 × 0.03 × 0.01	0.4 × 0.4 × 0.3	0.05 × 0.05 × 0.01
Instrument, λ (Å)	MAR225, 0.9050	MAR225, 0.9050	IPDS, 0.71073	MAR225, 0.9050
Temperature (K)	100	100	100	100
Reflection collected/independent	99,041/15,347	32,718/9020	55,280/14,623	25,476/4060
Data/parameters	15,333/1459	9017/1081	14,619/1127	4050/403
R_1 $[I \geq 2\sigma(I)]/wR_2$ (all)	0.075/0.203	0.040/0.100	0.069/0.139	0.054/0.143
$\Delta\rho$ (max./min.) (e Å^{-3})	0.732/−0.515	0.446/−0.231	0.716/−0.783	0.479/−0.266

hexane sub-fractions (obtained from toluene fraction 1) eluted at 2.62, 3.57, 4.82, and 6.53 min gave crystalline solids. From sub-fractions obtained from toluene fraction 3, only the fraction eluted at 5.87 min gave small crystals after recrystallization from hexane. UV–vis spectra of four $C_{60}(i\text{-}C_3F_7)_m$ compounds and one mixed CF_3/$i\text{-}C_3F_7$ dervative are given in the Supporting Information.

3.3. X-ray crystallography

Data collection for the crystal of $C_{60}(i\text{-}C_3F_7)_6$-II was carried out on an image plate diffractometer (IPDS2, Stoe), whereas crystals of all other compounds were too small for the use of the laboratory equipment. Data collection for these crystals was performed on a MAR225 image plate with a CCD detector using synchrotron radiation at the BESSY storage ring (PSF of the Free University Berlin). Determination of unit cell parameters for crystals obtained from the hexane sub-fraction eluted at 6.53 min revealed the presence of the $C_{60}(i\text{-}C_3F_7)_6$ isomer known from the literature [14] (isomer III in our notation).

Structures were solved with SHELXS97 and anisotropically refined with SHELXL97 [24]. No absorption correction was applied due to small linear absorption coefficients and small crystal sizes. Structure refinements were complicated due to disorder phenomena. In the structure of $C_{60}(i\text{-}C_3F_7)_8$ $0.8C_6H_{14}$, several perfluoroisopropyl groups were disordered by small rotation around the C–C bond connecting them with the fullerene cage. Hexane molecules are in partially occupied positions and are also strongly disordered. In the structure of $C_{60}(i\text{-}C_3F_7)_6$-II, rotational disorder of the same type was observed for one $i\text{-}C_3F_7$ group. Crystallographic data for the four new compounds along with some details of data collection and structure refinements are given in Table 2. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 692431–692434. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or email: deposit@ccdc.cam.ac.uk

3.4. Quantum chemical calculations

The geometry optimization and energy values were evaluated at the DFT level of theory with the use of the PRIRODA code [25], which employs an efficient implementation of the resolution-of-the-identity (RI) approach. A PBE exchange-correlation GGA-type functional [26] and a built-in TZ2P basis set were used.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (KE 489/26-2) and the Russian Foundation for Basic Research (05-03-04006). We are thankful to N.B. Tamm for recording UV–vis spectra. We are also grateful to the PSF (Free University Berlin) at BESSY for the provision of synchrotron beamtime.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2008.10.006.

References

[1] P.J. Fagan, P.J. Krusic, C.N. McEwen, J. Lazar, D.H. Parker, N. Herron, E. Wasserman, Science 262 (1993) 404–407.
[2] A.A. Goryunkov, I.V. Kuvychko, I.N. Ioffe, D.L. Dick, L.N. Sidorov, S.H. Strauss, O.V. Boltalina, J. Fluorine Chem. 124 (2003) 61–64.
[3] 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.Yu. Markov, J. Spandal, S.H. Strauss, O.V. Boltalina, Chem. Eur. J. 12 (2006) 3876–3889.
[4] E.I. Dorozhkin, A.A. Goryunkov, I.N. Ioffe, S.M. Avdoshenko, V.Yu. Markov, N.B. Tamm, D.V. Ignat'eva, L.N. Sidorov, S.I. Troyanov, Eur. J. Org. Chem. (2007) 5082–5094.
[5] N.A. Omelyanyuk, A.A. Goryunkov, N.B. Tamm, S.M. Avdoshenko, I.N. Ioffe, L.N. Sidorov, E. Kemnitz, S.I. Troyanov, Chem. Commun. (2007) 4794–4796.
[6] S.M. Avdoshenko, A.A. Goryunkov, I.N. Ioffe, D.V. Ignat'eva, L.N. Sidorov, Ph. Pattison, E. Kemnitz, S.I. Troyanov, Chem. Commun. (2006) 2463–2465.
[7] S.I. Troyanov, A.A. Goryunkov, E.I. Dorozhkin, D.V. Ignat'eva, N.B. Tamm, S.M. Avdoshenko, I.N. Ioffe, V.Yu. Markov, L.N. Sidorov, K. Scheurel, E. Kemnitz, J. Fluorine Chem. 128 (2007) 545–551.
[8] A.A. Popov, I.E. Kareev, N.B. Shustova, E.B. Stukalin, S.F. Lebedkin, K. Seppelt, S.H. Strauss, O.V. Boltalina, L. Dunsch, J. Am. Chem. Soc. 129 (2007) 11551–11568.
[9] A.A. Popov, I.E. Kareev, N.B. Shustova, S.F. Lebedkin, S.H. Strauss, O.V. Boltalina, L. Dunsch, Chem. Eur. J. 14 (2008) 107–121.
[10] 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.
[11] N.B. Tamm, S.M. Avdoshenko, E. Kemnitz, S.I. Troyanov, Russ. Chem. Bull. 56 (2007) 915–921.
[12] N.B. Tamm, S.I. Troyanov, Mendeleev Commun. 17 (2007) 172–174.
[13] T. Mutig, E. Kemnitz, S.I. Troyanov, Eur. J. Org. Chem. (2008) 3256–3259.
[14] N.B. Shustova, I.V. Kuvychko, O.V. Boltalina, S.H. Strauss, Acta Cryst. E63 (2007) o4575.
[15] 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. 128 (2006) 12268–12280.
[16] D.J. Burton, Z.-Y. Yang, Tetrahedron 48 (1992) 189–275.
[17] G.J. Chen, C. Tamborski, J. Fluorine Chem. 46 (1990) 137–159.
[18] I.E. Kareev, N.B. Shustova, B.S. Newell, S.M. Miller, O.P. Anderson, S.H. Strauss, O.V. Boltalina, Acta Cryst. E62 (2006) o3154.
[19] A.A. Goryunkov, E.I. Dorozhkin, N.B. Tamm, D.V. Ignat'eva, S.M. Avdoshenko, L.N. Sidorov, S.I. Troyanov, Mendeleev Commun. 17 (2007) 110–112.
[20] F. Cozzi, W.H. Powell, C. Thilgen, Pure Appl. Chem. 77 (2005) 843–923.
[21] O.V. Boltalina, A.Yu. Lukonin, J.M. Street, R. Taylor, Chem. Commun. (2000) 1601–1602.
[22] B.W. Clare, D.L. Kepert, Theochem 621 (2003) 211–231.
[23] I.E. Kareev, G.S. Quiñones, I.V. Kuvychko, P.A. Khavrel, I.N. Ioffe, I.V. Goldt, S.F. Lebedkin, K. Seppelt, S.H. Strauss, O.V. Boltalina, J. Am. Chem. Soc. 127 (2005) 11497–11504.
[24] G.M. Sheldrick, Acta Cryst. A64 (2008) 112–122.
[25] D.N. Laikov, Chem. Phys. Lett. 281 (1997) 151–156.
[26] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.