Journal of Fluorine Chemistry 131 (2010) 861–866

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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

Synthesis and molecular structures of heptafluoropropylated fullerenes: $C_{70}(n\text{-}C_3F_7)_8$, $C_{70}(n\text{-}C_3F_7)_6O$, and $C_{70}(C_3F_7)_4$

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ARTICLE INFO

Article history:
Received 18 March 2010
Received in revised form 5 May 2010
Accepted 7 May 2010
Available online 13 May 2010

Keywords:
Fullerenes
Perfluoroalkylation
Heptafluoropropyl iodide
X-ray structure
HPLC

ABSTRACT

Ampoule reactions of C_{70} with *n*- and *i*-C_3F_7I were carried out at 250–310 °C. Two step HPLC separations allowed the isolation of several $C_{70}(n\text{-}C_3F_7)_{4-8}$ and $C_{70}(i\text{-}C_3F_7)_4$ compounds. Crystal and molecular structures of $C_{70}(n\text{-}C_3F_7)_8$-V, $C_{70}(n\text{-}C_3F_7)_6O$, $C_{70}(n\text{-}C_3F_7)_4$, and three isomers of $C_{70}(i\text{-}C_3F_7)_4$ have been determined by X-ray crystallography using synchrotron radiation. Molecular structures of the new compounds were compared with the known examples and discussed in terms of addition patterns and relative energies of their formation.

1. Introduction

In the last few years, synthesis and investigation of perfluoroalkylated fullerenes attract much attention due to high diversity of their structures combined with high chemical and thermal stability. Most investigation were performed for trifluoromethylated [60]- and [70]fullerenes, while derivatives with pentafluoroethyl and heptafluoropropyl groups are investigated in lesser extent. $C_{60/70}(CF_3)_m$ compounds were isolated and structurally investigated for $m = 2–18$ [1–4], whereas much narrower compositional ranges were reported for $C_{60}(C_2F_5)_m$ ($m = 6–10$) [5,6] and $C_{70}(C_2F_5)_m$ ($m = 8, 10$) [7,8]. Perfluoropropylated fullerenes can exist as *n*-C_3F_7 or *i*-C_3F_7 derivatives. Structurally characterized were four isomers of $C_{70}(n\text{-}C_3F_7)_8$ [9] and several $C_{60}(i\text{-}C_3F_7)_m$ compounds ($m = 6, 8$) [10,11] that provided only restricted possibilities of their comparison. Thus more systematic investigations are required in this field for understanding the dependence of compound formation on the nature of perfluoroalkyl radicals. Herein we report the synthesis, separation and structural investigation of new perfluoropropyl derivatives of [70]fullerene which should extend the possibilities for more comprehensive comparison between compounds with different perfluoroalkyl groups.

2. Results and discussion

2.1. Synthesis and separation

Synthesis methods used previously for preparation of $C_{70}(n\text{-}C_3F_7)_8$ [9] or $C_{60}(i\text{-}C_3F_7)_m$ ($m = 6, 8$) [11] have been further developed in this work for obtaining new perfluoropropyl derivatives of C_{70}. For example, the ampoules were temporarily cooled and shaken or kept in ultrasonic bath in order to homogenize the content. Both C_{70}–*n*-C_3F_7I and C_{70}–*i*-C_3F_7I systems are very complex so that ampoule reactions at elevated temperatures, 300–310 and 250 °C, respectively, result in mixtures containing a large diversity of constitutional and geometrical isomers.

According to MALDI-MS analysis, the reaction product in the system C_{70}–*n*-C_3F_7I contained $C_{70}(n\text{-}C_3F_7)_{2-10}$ compounds, similarly to those described in the previous paper [9]. Rough chromatographic separation of product mixture with toluene as the eluent resulted in two fractions (Fig. 1a). Toluene fraction 1 collected between 2.5 and 3.1 min was subjected to further chromatographic separation using hexane as the eluent. The main hexane sub-fractions contained $C_{70}(n\text{-}C_3F_7)_m$ isomers with $m = 6–10$, those with $m = 8$ being prevailed. The chromatogram in Fig. 1b shows the presence of all four $C_{70}(n\text{-}C_3F_7)_8$ isomers I–IV isolated previously, which was confirmed by X-ray data for the crystals obtained from these fraction. These results demonstrate a good reproducibility of the ampoule method, though relative contents of $C_{70}(n\text{-}C_3F_7)_8$ isomers deviated in different experiments. Isomer III

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doi:10.1016/j.jfluchem.2010.05.002

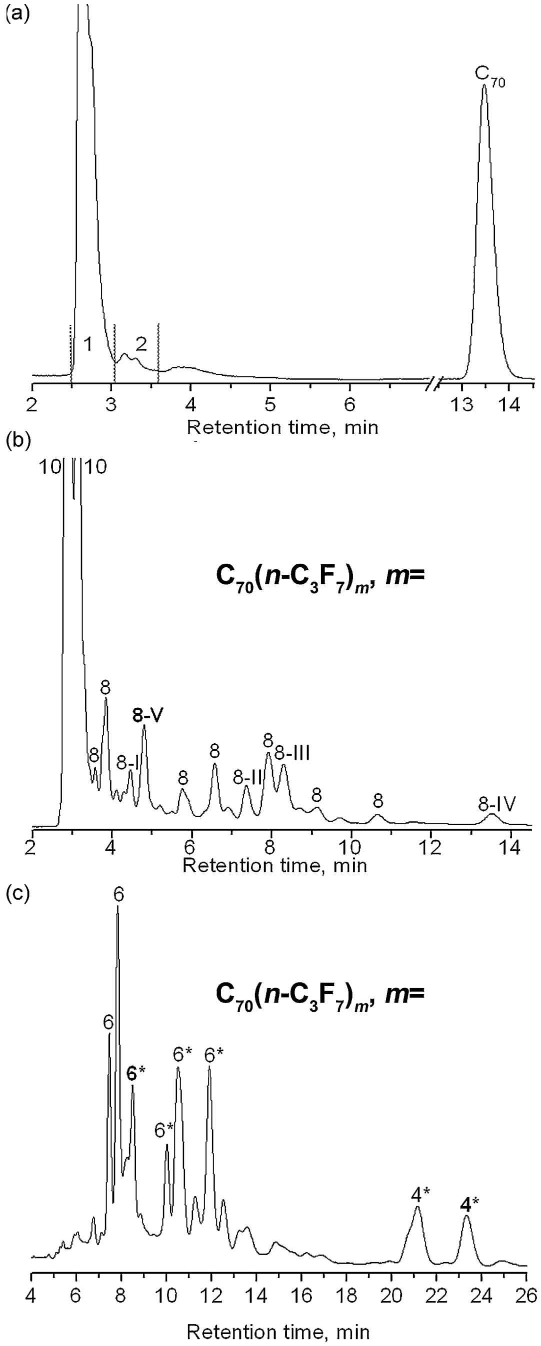

Fig. 1. HPLC separation of $C_{70}(n\text{-}C_3F_7)_m$ compounds. (a) Separation of the row reaction product in toluene. (b) Separation of toluene fraction 1 performed in hexane. Roman numbers denote the isomers with known structure. (c) Separation of toluene fraction 2 performed in toluene/hexane mixture (v/v 8/2). Numbers with asterisk denote the fractions with considerable content of the corresponding oxide according to MALDI mass spectra.

gave a new crystalline form free of any solvating molecule (see below). In addition a new $C_{70}(n\text{-}C_3F_7)_8$ isomer V has been successfully separated and its molecular structure has been determined.

Toluene fraction 2, which contained several $C_{70}(n\text{-}C_3F_7)_6$ and $C_{70}(n\text{-}C_3F_7)_4$ isomers, was chromatographically separated in toluene/hexane mixture (Fig. 1c). Isolation of individual isomers was successful for one isomer of $C_{70}(n\text{-}C_3F_7)_4$ and one [70]fullerene epoxide containing six attached perfluoropropyl groups, $C_{70}(n\text{-}C_3F_7)_6O$, followed by determination of their molecular structures by X-ray crystallography. Addition of oxygen to fullerenes easily occurs at heating and the conceivable source of oxygen might be due to a small contamination of starting materials or, most probably, in the course of iodine removal from crude product by heating in open air.

Ampoule synthesis of perfluoro-*iso*-propyl derivatives of [70]fullerenes was performed as described previously for $C_{60}(i\text{-}C_3F_7)_m$ compounds [10]. In contrast to the synthesis protocol used in the case of $n\text{-}C_3F_7$ derivatives, addition of copper powder to the reaction mixture turned out to be essential for achieving yields of 14–16%. Otherwise, the amount of perfluoroalkylated fullerenes in the reaction mixture was negligible even after 100 h heating at 310 °C. The same situation was observed previously for the system with [60]fullerene [11]. Possible differences in the behavior of systems with *n*- or $i\text{-}C_3F_7I$ reagents in respect to addition of copper may be connected with different stabilities of *n*- or $i\text{-}C_3F_7^{\bullet}$ radicals. The more branched radicals should be more stable what has been exemplified by a high stability of many perfluorinated highly branched radicals [12,13]. Therefore, removal of iodine by the reaction with copper may produce a larger concentration of perfluoro-*iso*-propyl radicals than will be the case in the systems with $n\text{-}C_3F_7I$ reagent.

MALDI-MS analysis of the reaction product revealed the presence of both $C_{70}(i\text{-}C_3F_7)_{2-8}$ and mixed $C_{70}(CF_3)_k(i\text{-}C_3F_7)_m$ derivatives with $k = 1–3$ and $m = 0–8$. A possible source of CF_3 groups for the formation of the latter might be easier detachment of CF_3 radicals from coordinated $i\text{-}C_3F_7$ groups. The same phenomenon was observed for the system with [60]fullerene [11]. The reaction product was roughly divided by HPLC in toluene in five fractions. Toluene fraction 3 was subjected to further chromatographic separation using hexane/toluene mixture as the eluent (Fig. 2b). The main sub-fractions contained $C_{70}(i\text{-}C_3F_7)_4$ isomers. Recrystallization from hexane produced crystals suitable for X-ray crystallographic study (isomers I–III).

2.2. Molecular structures

Single crystal X-ray diffraction study resulted in structure determination of a new isomer of $C_{70}(n\text{-}C_3F_7)_8$ and the first isomer with six attached $n\text{-}C_3F_7$ groups, $C_{70}(n\text{-}C_3F_7)_6O$ (Fig. 3). Schlegel diagrams for these new molecules and four other known $C_{70}(n\text{-}C_3F_7)_8$ isomers [11] are shown in Fig. 4. It can be concluded that the addition pattern of isomer $C_{70}(n\text{-}C_3F_7)_8$-V is very close to those of isomers III and IV, which are characterized by the presence of four and two $n\text{-}C_3F_7$ groups on the poles, whereas two groups occupy the positions near to the cage equator of the molecule. The pairs of groups are always attached in *para* positions on cage hexagons; four attached groups form a *para–meta–para* sequence of edge-sharing $C_6(n\text{-}C_3F_7)_2$ hexagons. The differences between addition patterns of isomers III–V concern attachment positions of two $n\text{-}C_3F_7$ groups on one of the poles. Isomers I and II have four $n\text{-}C_3F_7$ groups on the both poles in *pmp* positions. According to [70]fullerene numbering scheme [14] and lowest-location IUPAC abbreviation, isomer V adopts the notation 1,4,23,28,44,46,55,67-$C_{70}(n\text{-}C_3F_7)_8$.

Theoretical calculations of relative formation energies revealed that isomer I is more stable (0.0 kJ mol^{-1}) and isomer IV is less stable (12.9 kJ mol^{-1}) than the other isomers, whereas isomer V has an intermediate energy of 5.2 kJ mol^{-1} (see Fig. 4). It should be noted that relative content of isomers I–V does not correlate with their relative energies. In addition, the reaction product contains many other $C_{70}(n\text{-}C_3F_7)_8$ isomers detected by MALDI-MS analysis of chromatographic fractions. The presence of this large number of isomers does not allow us to make suggestion about possible thermodynamic control of perfluoropropylation of C_{70}.

In the molecular structure of $C_{70}(n\text{-}C_3F_7)_8$-V, there are several nearly isolated C–C bond with a double character which have typical bond length of 1.34 Å. C–C_3F_7 bonds have average bond

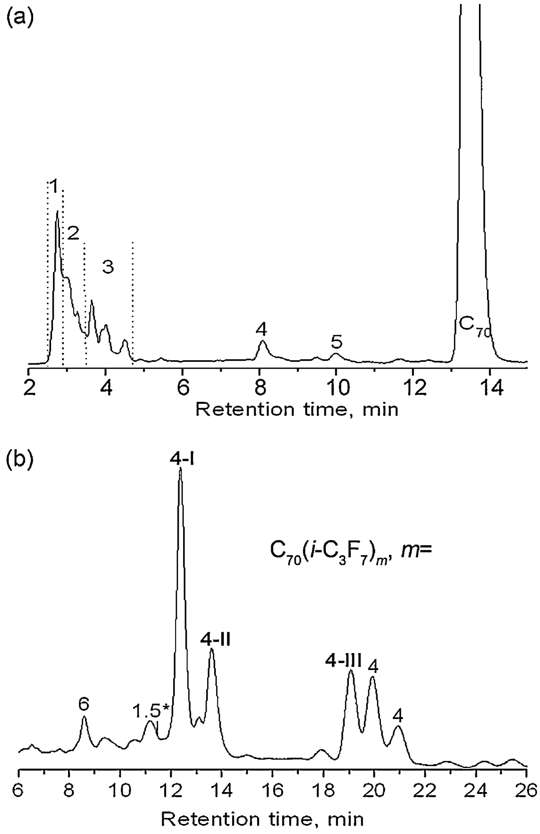

Fig. 2. HPLC separation of $C_{70}(i\text{-}C_3F_7)_m$ compounds. (a) Separation of the row reaction product into five fractions performed in toluene. (b) Separation of toluene fraction 3 performed in hexane/toluene mixture (v/v 8/2). Roman numbers denote the isomers with known structures. The fraction containing $C_{70}(CF_3)(i\text{-}C_3F_7)_5$ is denoted with asterisk.

length of 1.565 Å (1.56–1.57 Å in isomers I–IV [9]). Structural determination of isomer $C_{70}(n\text{-}C_3F_7)_8$-III was performed for a different crystalline form as compared to the result of previous work [9]. Although the molecular fullerene structures are the same, no solvate molecules were found in the present work, whereas at least three solvated small molecules (supposed to be water) have been present in wavy channels of the previous structure. Therefore, the present $C_{70}(n\text{-}C_3F_7)_8$-III structure is more densely packed in the crystal providing no space for molecules of solvation. Thus, the calculated volumes per $C_{70}(n\text{-}C_3F_7)_8$-III molecule are 1905 and 1768 Å^3 in the solvated and solvent free structures, respectively.

It is interesting that the addition patterns of isomers $C_{70}(n\text{-}C_3F_7)_8$-I–V encounter among known isomers of $C_{70}(C_2F_5)_8$, but formation energy differences between the latter are much less pronounced being in the range of 10.0–13.7 kJ mol^{-1} relative to the most stable C_s isomer with equatorial p^7 ribbon of attached C_2F_5 groups [8]. The same C_s addition pattern is known to be the most stable also among $C_{70}(CF_3)_8$ isomers [15], but relative formation energies of isomers with addition patterns of $C_{70}(n\text{-}C_3F_7)_8$-I–IV are much higher, 24.5–33.2 kJ mol^{-1} [9]. According to theoretical calculations, relative energy of the hypothetical C_s–$C_{70}(n\text{-}C_3F_7)_8$ is 5.6 kJ mol^{-1}, i.e. it is no more the most stable isomer. Thus, the size (bulkiness) of attached groups affects the stability of isomers with polar and equatorial addition patterns. Mutual repulsion of addends is less pronounced in the polar regions having higher curvature than the equatorial region.

The molecular structure of $C_{70}(n\text{-}C_3F_7)_6O$ provides the first example of the compound with six $n\text{-}C_3F_7$ groups. Its addition pattern can be derived from that of $C_{70}(n\text{-}C_3F_7)_8$-I by removal of two groups from one of the poles (Fig. 4). The attachment of epoxidic oxygen along a 6:6 C–C bond on the cage (in positions 7 and 22; C7–C22 1.496(6) Å) results in the formation of a nearly isolated C8–C9 double bond (between positions 7, 10, and 25) with bond length of 1.330(6) Å.

Four $C_{70}(C_3F_7)_4$ molecules have been structurally characterized in this work, one with $n\text{-}C_3F_7$ groups and three with $i\text{-}C_3F_7$ attached groups. All four $C_{70}(C_3F_7)_4$ molecules have similar distribution of attached C_3F_7 groups in two pairs of *para*-$C_6(C_3F_7)_2$ hexagons on the opposite poles (Fig. 5). Isomers $C_{70}(i\text{-}C_3F_7)_4$-I, -II, and -III differ in the relative position of p-$C_6(C_3F_7)_6$ hexagons resulting in C_1, C_2, and C_2 (crystallographic) symmetries of the addition patterns (Fig. 6). The whole C_2-$C_{70}(i\text{-}C_3F_7)_4$-II and -III molecules possess, respectively, non-crystallographic and crystallographically imposed symmetries which can be seen in conformation of attached perfluoro-*iso*-propyl groups (Fig. 5b and c). Isomer C_2-$C_{70}(n\text{-}C_3F_7)_4$-I has the same C_2 addition pattern as C_2-$C_{70}(i\text{-}C_3F_7)_4$-III, but the whole molecule has deviations from strict axial symmetry due to the conformation of $n\text{-}C_3F_7$ groups (Fig. 5c and d).

According to theoretical DFT calculations, relative energies of isomers $C_{70}(i\text{-}C_3F_7)_4$-I, -II, and -III differ insignificantly being, respectively, 3.3, 1.7, and 0.0 kJ mol^{-1}. Obviously, these small differences are not due to intramolecular repulsion of perfluoro-

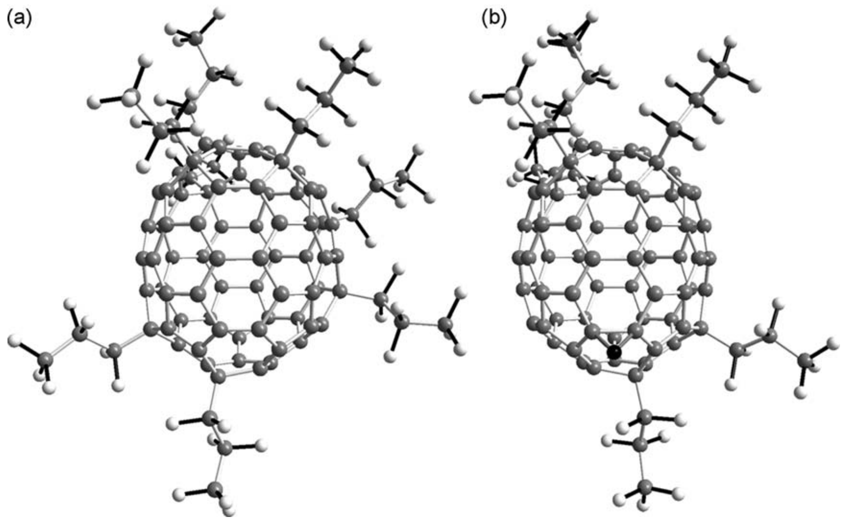

Fig. 3. Molecular structures of $C_{70}(n\text{-}C_3F_7)_8$-V (left) and $C_{70}(n\text{-}C_3F_7)_6O$.

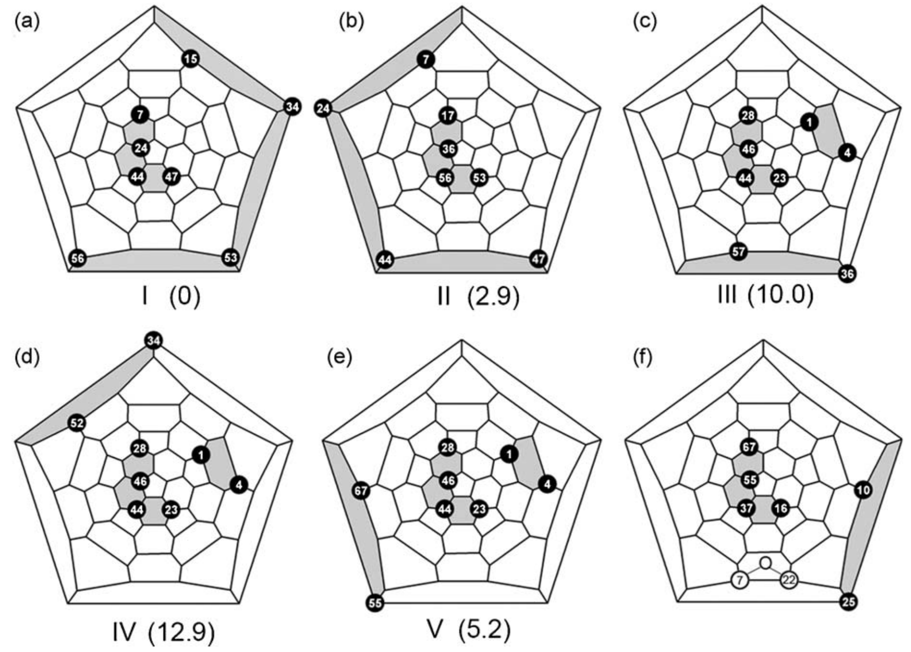

Fig. 4. Schlegel diagrams of $C_{70}(n\text{-}C_3F_7)_8$ (isomers I–V) and $C_{70}(n\text{-}C_3F_7)_6O$. Black and white circles are the attachment positions of $n\text{-}C_3F_7$ groups and oxygen, respectively. The numbers in circles correspond to lowest-locant IUPAC numeration according to [14]. DFT calculated relative energies of $C_{70}(n\text{-}C_3F_7)_8$ isomers (in kJ mol^{-1}) are given in the parentheses.

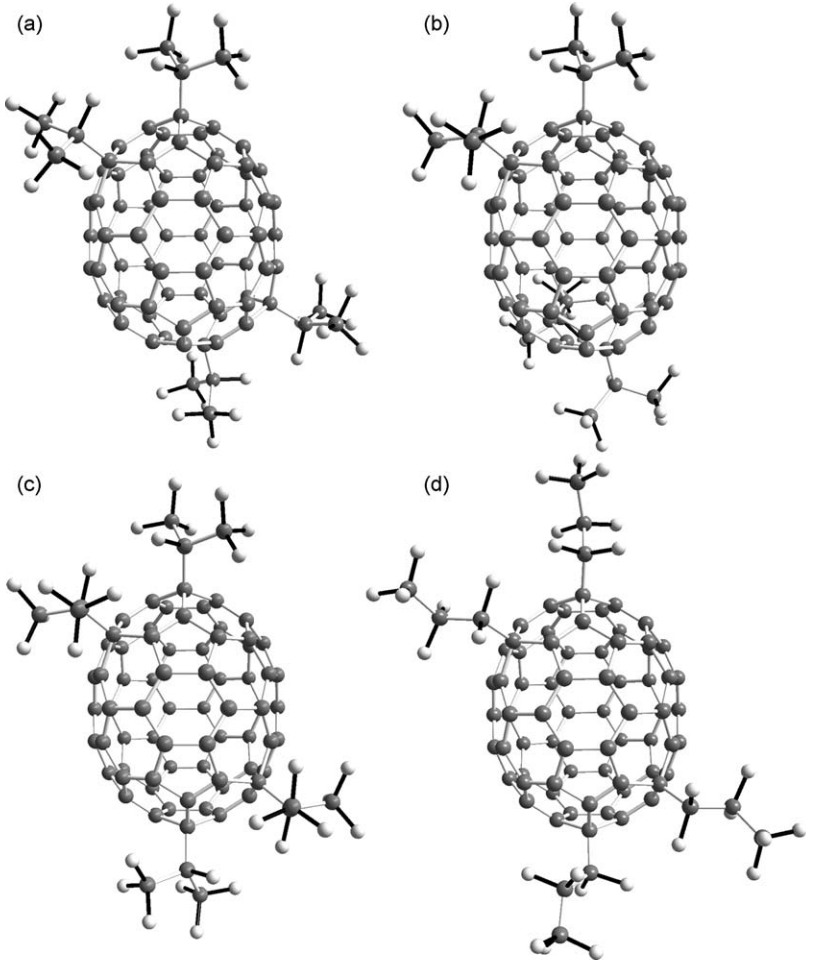

Fig. 5. Molecular structures of $C_{70}(i\text{-}C_3F_7)_4$-I (a), -II (b), and -III (c) and $C_{70}(i\text{-}C_3F_7)_4$ (d).

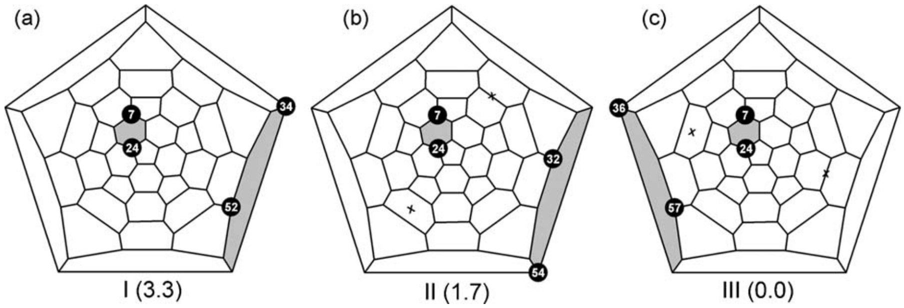

Fig. 6. Schlegel diagrams of $C_{70}(i\text{-}C_3F_7)_4$ (isomers I–III). Crosses denote the position of C_2 axes. Addition pattern of $C_{70}(n\text{-}C_3F_7)_4$ is the same as that of $C_{70}(i\text{-}C_3F_7)_4$-III. The numbers in circles correspond to lowest-locant IUPAC numeration according to [14]. Calculated relative energies (in kJ mol^{-1}) are given in the parentheses.

iso-propyl groups (that can take place in isomers with larger number of attached groups) but rather due to subtle differences in the electronic structure of the conjugated π-systems of the remaining non-functionalized fullerene cage. In the same scale, isomer $C_{70}(n\text{-}C_3F_7)_4$-I has a relative energy of −4.7 kJ mol^{-1}, i.e. it is slightly more stable than isomer $C_{70}(i\text{-}C_3F_7)_4$-III with the same addition pattern. For comparison, most stable isomers of $C_{70}(CF_3)_4$ have all four CF_3 groups in one p^3 or *pmp* ribbon of three $C_6(CF_3)_2$ edge-sharing hexagons that indicates much weaker mutual repulsion between attached trifluoromethyl groups [16].

Similar to the known $C_{60}(i\text{-}C_3F_7)_n$ isomers, mutual orientation of two $i\text{-}C_3F_7$ groups in each *para*-$C_6(i\text{-}C_3F_7)_2$ hexagon provides a minimum repulsion, because $(CF_3)_2C$–F bonds are directed to each other (with a small skewing; shortest F···F contacts range from 2.52 to 2.66 Å), whereas CF_3 branches of two $i\text{-}C_3F_7$ groups are at maximum distances from each other. Structural data reveal that fullerene–C_3F_7 bonds are noticeably longer in isomers with $i\text{-}C_3F_7$ groups than with $n\text{-}C_3F_7$ (or C_2F_5 and CF_3). While the former are in the range of 1.57–158 Å in $C_{70}(i\text{-}C_3F_7)_4$-I–III molecules, the latter are only 1.54–1.56 Å in $C_{70}(n\text{-}C_3F_7)_4$-I. The same differences were found for perfluoropropyl derivatives of C_{60} [11]. Apparently, branching of the perfluoro-*iso*-propyl 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. This could be the reason why, according to DFT calculation, $C_{70}(i\text{-}C_3F_7)_4$-III is slightly less stable than $C_{70}(n\text{-}C_3F_7)_4$-I with the same addition pattern.

In conclusion, comparison of the addition patterns in heptafluoropropylated C_{70} with those in pentafluoroethylated and trifluoromethylated derivatives of C_{70} reveals the influence of the group size on the distribution of attached groups on the fullerene cage. The larger are the groups, the more pronounced is their mutual repulsion and, consequently, they are located more distant from each other in most stable isomers. By the same reason, equatorial isomers became less stable for derivatives with bulkier perfluoroalkyl groups.

$C_{70}(C_3F_7)_4$ isomers hardly differ in energy because two pairs of attached groups are very distant from one another on the fullerene cage. In this case, derivatives with *i*- and $n\text{-}C_3F_7$ groups can possess the same addition patterns. However, the repulsion of the attached $i\text{-}C_3F_7$ groups (F atoms) from the cage results in somewhat longer C–C bonds between the cage and perfluoropropyl groups.

3. Experimental

3.1. Synthesis of $C_{70}(n\text{-}C_3F_7)_{4-8}$

C_{70} (58 mg, 98.5%) and an excess $n\text{-}C_3F_7I$ (0.4 mL, 95%, TCI) were heated at 300–310 °C in a sealed glass ampoule for 40–90 h under constant stirring. After opening the ampoule, the excess $n\text{-}C_3F_7I$ and iodine were removed from a brown-coloured reaction product by heating at ca. 100 °C in open air for 5–6 h. MALDI-MS analysis revealed the presence of $C_{70}(n\text{-}C_3F_7)_m$ compounds with $m = 2–10$ along with the unreacted C_{70} (estimated yield about 50%). The mixture was roughly divided into two fractions by HPLC with toluene as the eluent. An admixture of C_{70} was removed at this stage. Toluene fraction 1 collected between 2.5 and 3.1 min contained $C_{70}(n\text{-}C_3F_7)_m$ compounds with $m = 8–10$ (Fig. 1a). This mixture was further separated by HPLC using hexane as the eluent at a flow rate of 4.6 mL min^{-1} (Fig. 1b). Small crystals were isolated from several fractions. In addition to the known $C_{70}(n\text{-}C_3F_7)_8$ isomers I–IV [11], the crystals obtained from the fraction eluted at 4.8 min by recrystallization from toluene revealed the presence of a new isomer, $C_{70}(n\text{-}C_3F_7)_8$-V. After recrystallization from toluene, the fraction of isomer III (retention time 8.25 min) gave a new crystalline form of this isomer, which did not contain solvated molecules.

Toluene fraction 2 (3.10–3.54 min) contained $C_{70}(n\text{-}C_3F_7)_6$ and $C_{70}(n\text{-}C_3F_7)_4$ isomers, which were contaminated by their oxides (Fig. 1c). It was separated by HPLC in hexane/toluene (v/v 8/2) mixture. Crystals of $C_{70}(n\text{-}C_3F_7)_4$ were grown by slow evaporation of saturated hexane/toluene solution from the subfraction eluted at 23.4 min. Crystals of $C_{70}(n\text{-}C_3F_7)_6O$ were obtained from the subfraction eluted at 8.5 min by its recrystallization from *o*-xylene.

3.2. Synthesis of $C_{70}(i\text{-}C_3F_7)_4$

C_{70} (33 mg, 98.5%), 172 mg copper powder and the excess $i\text{-}C_3F_7I$ (0.3 mL, 98%, TCI) were heated at 250 °C in a sealed glass ampoule for 38 h. After cooling down, the ampoule was opened, and the excess $i\text{-}C_3F_7I$ and a small amount of iodine were removed from a brown-coloured reaction product by heating at ca. 100 °C in open air for several hours. Perfluoroalkylated derivatives of C_{70} were separated from copper monoiodide by extraction with toluene. Estimated yields based on remaining C_{70} were in the range of 14–16%.

The product mixture was roughly divided by HPLC in five fractions using toluene as the eluent (Fig. 2a). MALDI-MS analysis showed that, in addition to $C_{70}(i\text{-}C_3F_7)_m$, some fractions contained $C_{70}(CF_3)_k(i\text{-}C_3F_7)_m$ molecules. The composition ranges for the toluene fractions were: $m = 6–8$ (fraction 1), $k = 0–1$, $m = 2–6$ (fraction 2), $k = 0–1$, $m = 4–6$ (fraction 3), $m = 2$ (fraction 4), and $k = 0–3$ and $m = 0–1$ (fraction 5). The toluene fraction 3 collected at 3.27–4.38 min was further chromatographically separated using a hexane/toluene (v/v 8/2) mixture as the eluent. Fractions eluted at 12.4, 13.6 and 19.1 min containing $C_{70}(i\text{-}C_3F_7)_4$ (isomers I, II, and III, respectively) were recrystallized from hexane yielding small crystals suitable for X-ray study with synchrotron radiation.

3.3. Chromatographic isolation and MS analysis

Separation of fullerene derivatives was performed by HPLC with a KNAUER chromatographic system and a Cosmosil Buckyprep column (Nacalai Tesque Inc., 10 mm ID; 25 cm length), flow rate

Table 1
Crystallographic data and some details of data collection and structure refinement for heptafluoropropylated [70]fullerenes.

Compound	$C_{70}(n\text{-}C_3F_7)_8$-III	$C_{70}(n\text{-}C_3F_7)_8$-V	$C_{70}(n\text{-}C_3F_7)_6O$	$C_{70}(n\text{-}C_3F_7)_4$-I	$C_{70}(i\text{-}C_3F_7)_4$-I	$C_{70}(i\text{-}C_3F_7)_4$-II	$C_{70}(i\text{-}C_3F_7)_4$-III
Sovate molecule	–	–	$1.59C_6H_5(CH_3)$	$1.2C_6H_5(CH_3)$	$0.5C_6H_{14}$	$C_6H_5(CH_3)$	–
M	2192.94	2192.94	2017.24	1626.99	1559.15	1608.95	1516.82
Symmetry	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group; *Z*	$P\bar{1}$; 2	$C2/c$; 8	$P\bar{1}$; 2	$P\bar{1}$; 2	$P2_1/c$; 4	$P2_1/c$; 4	$C2/c$; 4
a (Å)	14.968(1)	33.918(2)	14.641(1)	10.2506(4)	17.1411(2)	15.5038(3)	18.1127(3)
b (Å)	15.743(1)	16.264(1)	14.977(1)	16.0216(6)	16.9417(2)	18.1380(3)	10.1948(2)
c (Å)	16.905(1)	28.027(2)	18.815(2)	19.0358(8)	20.5256(3)	19.9898(4)	28.1018(5)
α (°)	70.708(2)	90	110.224(2)	99.330(2)	90	90	90
β (°)	86.055(2)	98.023(2)	99.142(4)	105.311(2)	113.4081(6)	92.4977(7)	107.1116(6)
γ (°)	70.317(4)	90	106.945(3)	90.061(2)	90	90	90
V (Å^3)	3536.1(4)	15,309.5(17)	3549.6(5)	2972.3(2)	5470.1(1)	5615.95(18)	4959.4(2)
D_c (g cm^{-3})	2.060	1.903	1.887	1.818	1.894	1.903	2.031
Crystal size (mm)	0.05 × 0.03 × 0.01	0.04 × 0.04 × 0.01	0.04 × 0.04 × 0.02	0.10 × 0.02 × 0.01	0.04 × 0.04 × 0.005	0.04 × 0.04 × 0.02	0.05 × 0.03 × 0.01
Temperature (K)	100	100	100	100	100	100	100
Refls collected; R_{int}	40,865; 0.153	102,515; 0.158	47,186; 0.053	27,203; 0.054	69,599; 0.036	46,624; 0.043	55,726; 0.070
Data/parameters	11,050/1370	14,527/1398	12,709/1346	9200/1050	11,429/1092	11,976/1193	5154/496
R_1 [$I \geq 2\sigma(I)$]/wR_2 (all)	0.092/0.241	0.108/0.262	0.080/0.197	0.119/0.276	0.055/0.137	0.073/0.195	0.044/0.113
$\Delta\rho$ (max/min) (e Å^{-3})	0.71/−0.59	0.72/−0.40	0.62/−0.51	0.72/−0.59	0.72/−0.61	0.81/−0.69	0.47/−0.25

4.6 mL min^{-1}, monitored at 290 nm. 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-tertbutylphenyl)-2-methyl-2-propenylidene)-malonitrile (DCTB) as a matrix.

3.4. X-ray crystallography

Data collection for single crystal X-ray study of compounds $C_{70}(n\text{-}C_3F_7)_n$ and $C_{70}(i\text{-}C_3F_7)_m$ was performed with a MAR225 CCD detector at 100 K using synchrotron radiation at the BESSY storage ring (λ = 0.9050 Å, BL14.2, PSF of the Free University of Berlin, Germany). Absorption correction was not applied in all cases. Structure solution and refinement were carried out with SHELXS97 (or SHELXD) and SHELXL97, respectively [17].

Some structure refinements were complicated due to disorder phenomena. In the structures of $C_{70}(n\text{-}C_3F_7)_8$-III, -V, and $C_{70}(n\text{-}C_3F_7)_6O$ terminal parts of one $n\text{-}C_3F_7$ group are disordered. In the structures of $C_{70}(i\text{-}C_3F_7)_4$-I and -II, respectively, one and three $i\text{-}C_3F_7$ groups are disordered by small rotation around the C–C bond connecting them with the fullerene cage. Both toluene solvate molecules in $C_{70}(n\text{-}C_3F_7)_4\text{-I}\cdot 1.2C_7H_8$ have partial occupancies. Toluene molecules are strongly disordered in the $C_{70}(n\text{-}C_3F_7)_6O\cdot 1.59C_7H_8$ solvate. Crystallographic data and some details of data collection and structure refinement for seven perfluoropropylated [70]fullerenes are presented in Table 1. 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 769677–769683. 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).

3.5. Quantum chemical calculations

The geometry optimization and energy values were evaluated at the DFT level of theory with the use of the PRIRODA code [18], which employs an efficient implementation of the resolution-of-the-identity (RI) approach. A PBE exchange-correlation GGA-type functional [19] 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 (09-03-91337). The authors are thankful to S.M. Avdoshenko and I.N. Ioffe for theoretical calculations. We are also grateful to the PSF (Free University of Berlin) at the BESSY for the provision of synchrotron beam time.

References

[1] 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.
[2] 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.
[3] T. Mutig, E. Kemnitz, S.I. Troyanov, Mendeleev Commun. 19 (2009) 30–31.
[4] 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.
[5] 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.
[6] N.B. Tamm, S.M. Avdoshenko, E. Kemnitz, S.I. Troyanov, Russ. Chem. Bull. 56 (2007) 915–921.
[7] N.B. Tamm, S.I. Troyanov, Mendeleev Commun. 17 (2007) 172–174.
[8] N.B. Tamm, I.N. Ioffe, E. Kemnitz, S.I. Troyanov, Dalton Trans. (2009) 2740–2745.
[9] T. Mutig, E. Kemnitz, S.I. Troyanov, Eur. J. Org. Chem. (2008) 3256–3259.
[10] N.B. Shustova, I.V. Kuvychko, O.V. Boltalina, S.H. Strauss, Acta Crystallogr. E63 (2007) o4575.
[11] T. Mutig, S.M. Avdoshenko, E. Kemnitz, S.I. Troyanov, J. Fluorine Chem. 130 (2009) 241–247.
[12] K.V. Scherer, T. Ono, K. Yamanouchi, R. Fernandez, P. Henderson, J. Am. Chem. Soc. 107 (1985) 718–719.
[13] U. Gross, St. Rüdiger, A. Dimitrov, J. Fluorine Chem. 76 (1996) 139–144.
[14] F. Cozzi, W.H. Powell, C. Thilgen, Pure Appl. Chem. 77 (2005) 843–923.
[15] 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.
[16] 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.
[17] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112–122.
[18] D.N. Laikov, Chem. Phys. Lett. 281 (1997) 151–156.
[19] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.