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ScienceDirect
Journal of Fluorine Chemistry 128 (2007) 545–551
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Higher trifluoromethylated derivatives of C_{60}, $C_{60}(CF_3)_{16}$ and $C_{60}(CF_3)_{18}$ Synthesis, structure, and theoretical study

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Received 4 December 2006; received in revised form 10 January 2007; accepted 19 January 2007
Available online 30 January 2007

Abstract

Three isomers of $C_{60}(CF_3)_{16}$ and one isomer of $C_{60}(CF_3)_{18}$ have been isolated by HPLC from a mixture prepared by trifluoromethylation of C_{60} with CF_3I in a glass ampoule at 380–400 °C. The molecular structures of the four new compounds have been determined by means of X-ray single crystal diffraction and discussed in terms of mechanistic pathways of their formation and relative stability according to the DFT calculations.

Keywords: Trifluoromethylated [60]fullerenes; X-ray structure; Density functional calculations

1. Introduction

Both trifluoromethylated and fluorinated fullerenes are strong electron acceptors due to the presence of electron withdrawing atoms/groups. However, CF_3 derivatives are more chemically stable than fluorofullerenes that tend to degrade, though very slowly, in solution due to hydrolysis. That is the reason why trifluoromethylated fullerene derivatives attract considerable attention as prospective building blocks for novel fullerene-based materials with useful properties. Commonly used methods for preparation of trifluoromethylated fullerenes employ agents such as CF_3I [1] or metal trifluoroacetates [2], which easily release CF_3 radicals upon heating. Usually, such methods provide complex mixtures of $C_{60/70}$ derivatives containing up to 22 CF_3 groups per fullerene cage. Subsequent separation by means of fractional sublimation and high performance liquid chromatography (HPLC) can provide individual compounds [3]. Only one trifluoromethylated fullerene, S_6-$C_{60}(CF_3)_{12}$, can be prepared selectively [4]. The list of individual compounds obtained so far includes $C_{60}(CF_3)_n$ with $n = 2$–12 and $C_{70}(CF_3)_m$ with $m = 2$–18. Direct structural determinations have been carried out for $C_{60}(CF_3)_8$ (two isomers [5,6]), $C_{60}(CF_3)_{10}$ (three isomers [7–9]), $C_{60}(CF_3)_{12}$ [4], $C_{70}(CF_3)_6$ [10], $C_{70}(CF_3)_8$ [11], $C_{70}(CF_3)_{10}$ [12], two isomers of $C_{70}(CF_3)_{12}$ [13], four isomers of $C_{70}(CF_3)_{14}$ [14], $C_{70}(CF_3)_{16}$ [15], $C_{70}(CF_3)_{18}$ [15], and oxygenated $C_{60}(CF_3)_4O$ [16]. This list clearly demonstrates that, quite uncommonly for fullerene chemistry, trifluoromethylated derivatives of C_{70} are presently even more extensively investigated than those of C_{60}. Here, we report isolation and X-ray crystallographic and theoretical study of some higher $C_{60}(CF_3)_n$ derivatives with $n = 16$ (three isomers) and $n = 18$ (one isomer).

2. Results and discussion

The reaction of C_{60} with an excess of gaseous CF_3I carried out at 380–400 °C for 18–48 h has been found to provide a mixture of trifluoromethylated [60]fullerenes, $C_{60}(CF_3)_n$ with $n = 12$–18, as analyzed by MALDI mass-spectrometry. By varying reaction temperature and/or its duration one can slightly change relative yields of products, most abundant degree of trifluoromethylation shifting from $n = 14$ to 16 in case of longer reaction times and/or lower reaction temperature.

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doi:10.1016/j.jfluchem.2007.01.008

While the time factor is quite obvious, provided the excess of CF_3I remains available, the temperature effect can be assigned to the expected increase in volatility with the increase of the number of CF_3 groups and, consequently, sublimation of deeper trifluoromethylated products from the reaction zone at lower temperatures. For comparison, the mixtures of trifluoromethylated [60]fullerene derivatives formed in a flow of CF_3I were reported to contain no more than 8–14 CF_3 groups, perhaps, due to higher reaction temperature (460 °C) and shorter contact time of reagents [7]. In our ampoule experiments, the selective formation of $C_{60}(CF_3)_{12}$ (S_6 isomer) was observed in some cases in the hot zone when clogging of the narrow middle section of the ampoule with crystalline iodine effectively blocked supply of gaseous CF_3I for further trifluoromethylation [4]. Another known method of synthesis that employs silver trifluoroacetate at elevated temperature led, as a rule, to lower trifluorometylated derivatives of [60]fullerene with $n = 2–10$ [3,17], although thermolysis of CF_3COOAg in presence of C_{60} under dynamic vacuum conditions at 300 °C can, in principle, result in formation of complex mixtures of $C_{60}(CF_3)_n$, with n up to 22 [2,18,19].

Hexane solution of the mixture was subjected to separation and purification by HPLC. A typical chromatogram of the mixture, which reveals presence of no less than 12 compounds, is shown in Fig. 1. Further HPLC analysis of the main isolated fractions provided single peaks having reasonably symmetric shapes and thus dominated by single compounds further identified by MALDI MS analysis (the numeration of the three $C_{60}(CF_3)_{16}$ isomers in this paper corresponds to the reverse order of their retention times). The isolated fractions were slowly concentrated to give, in most cases, crystalline materials. However, only the crystals obtained from the fractions eluted at 3.41, 4.02, 4.41, and 6.90 min proved suitable for X-ray crystallographic investigation. Moreover, in three cases of four such investigations required the use of synchrotron radiation because of the very small size of crystals.

In Fig. 2 we demonstrate ORTEP views of the two selected structures from the four investigated in this work. The Schlegel diagrams of all four isomers, $C_{60}(CF_3)_{16}$-I–III and $C_{60}(CF_3)_{18}$-I, can be found in Fig. 3. The diagrams for $C_{60}(CF_3)_{16}$-II and -III are given in both hexagon- and pentagon-centered projections in order to demonstrate different aspects of their addition patterns. Two more Schlegel diagrams for the known S_6-$C_{60}(CF_3)_{12}$ and the supposed C_{3v} isomer of $C_{60}(CF_3)_{18}$ are added for comparison and discussion. One can notice that among the three $C_{60}(CF_3)_{16}$ structures investigated the isomers II and III share a common feature of incorporating a triphenylene fragment (Figs. 2 top and 3a and b) and can be, therefore, supposed to originate from trifluoromethylation of such intermediates as S_6-$C_{60}(CF_3)_{12}$ or related structures (see discussion below). Noteworthy, formation of S_6-$C_{60}(CF_3)_{12}$ has been, indeed, observed in the early stages of trifluoromethylation reaction in the ampoules [4].

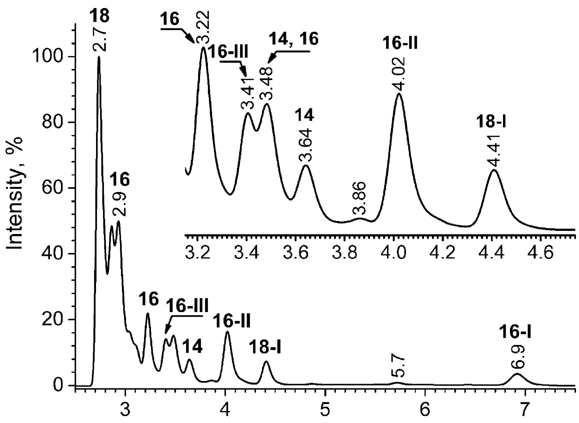

Fig. 1. Chromatogram of the mixture of the higher $C_{60}(CF_3)_n$ derivatives. The zoomed HPLC area within 3.2–4.6 min is shown on inset.

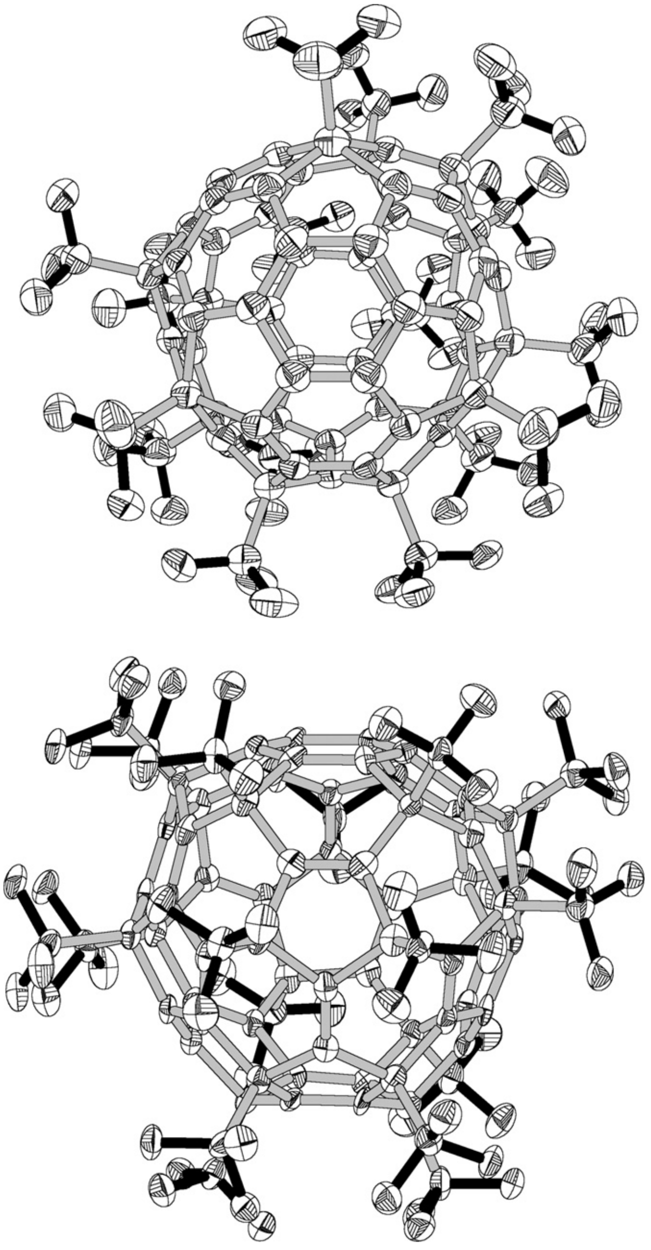

Fig. 2. Perspective views of the $C_{60}(CF_3)_{16}$-II (top) and $C_{60}(CF_3)_{18}$-I (bottom) molecules. The view directions are the same as in Fig. 3a and g, respectively. Thermal ellipsoids are given at the 40% probability level. C–F bond are shown black.

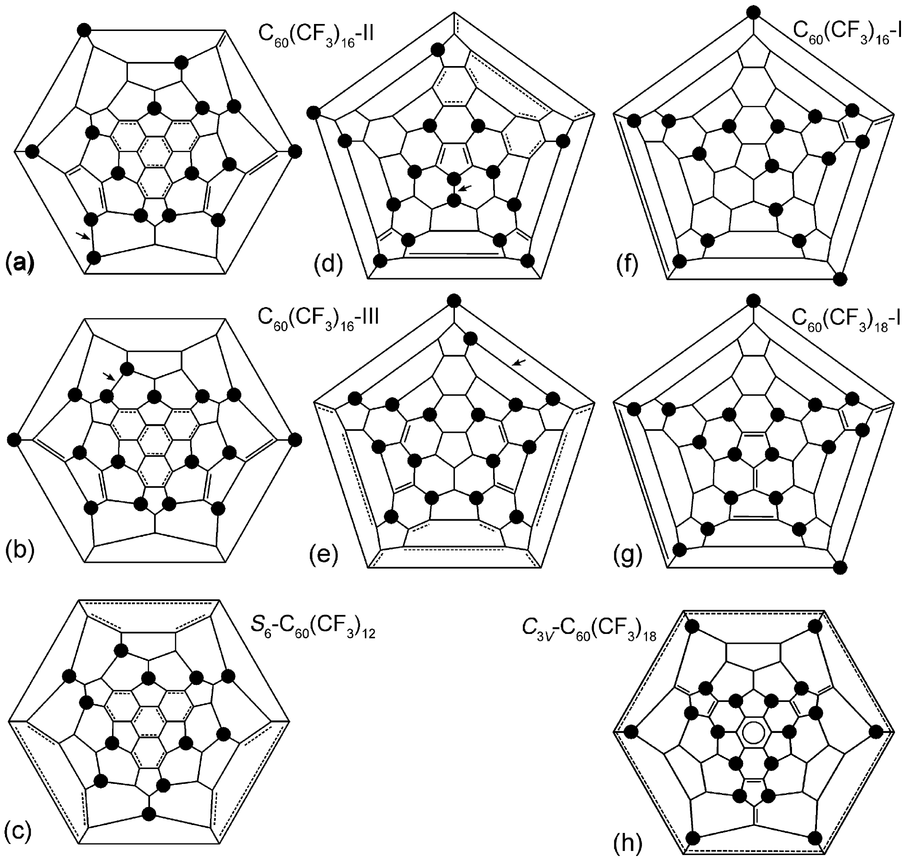

Fig. 3. Schlegel diagrams of $C_{60}(CF_3)_{16}$-II (a and d), $C_{60}(CF_3)_{16}$-III (b and e), $C_{60}(CF_3)_{16}$-I (f), and $C_{60}(CF_3)_{18}$-I (g) along with those for the known S_6-$C_{60}(CF_3)_{12}$ [4] (c) and the calculated (thermodynamically) best isomer of $C_{60}(CF_3)_{18}$ (h). Black circles denote the attached CF_3 groups.

Another common feature of $C_{60}(CF_3)_{16}$-II and -III is *ortho*-attachment of one pair of CF_3 groups, i.e. attachment to adjacent positions as marked with arrows in Fig. 3a and b. This type of attachment has not been encountered in the lower CF_3 [60]fullerene derivatives with known structures, except for one of the isomers of $C_{60}(CF_3)_6$, which was suggested to be isostructural to $C_{60}Cl_6$ and $C_{60}Br_6$ on the basis of the NMR data [16]. Probably, *ortho*-attachment should become increasingly favourable for higher trifluoromethylated derivatives with their highly crowded shell of CF_3-groups where more groups can be more freely distributed over the carbon cage at the cost of an *ortho*-pair. Notably, similar *ortho*-pairs were also observed in $C_{70}(CF_3)_m$ with $m = 16$ and 18 [15], but they were not found in the four known isomers of $C_{70}(CF_3)_{14}$ [14] as well as in all other $m < 16$ cases [10–13]. Other remarkable structural features that can be found in the molecules reported herein are a fulvene fragment in $C_{60}(CF_3)_{16}$-III (which involves the central pentagon in Fig. 3e) and the $C_{60}Br_6$-like skew pentagonal pyramid substructure in $C_{60}(CF_3)_{16}$-II (see central pentagon in Fig. 3d). Both $C_{60}(CF_3)_{16}$-II and $C_{60}(CF_3)_{16}$-III are chiral, though would become mirror symmetric upon removal of only one or two CF_3 groups, respectively, this minor asymmetry resulting in irregularities of the molecular packing of isomer III due to statistical distribution of enantiomers.

The addition pattern of the isomer $C_{60}(CF_3)_{16}$-I (Fig. 3f) differs significantly from those of isomers II and III. Neither triphenylene fragment nor 1,2-contacts of CF_3 groups can be observed in this molecule. It can be assumed that it originates from a precursor other than S_6-$C_{60}(CF_3)_{12}$. Moreover, due to close similarity in addition patterns of $C_{60}(CF_3)_{16}$-I and $C_{60}(CF_3)_{18}$-I (Figs. 2 bottom and 3g), the former may be a precursor for the latter in the course of trifluoromethylation. It is worth to note that higher trifluoromethylated derivatives of C_{60} thus reveal higher degree of structural diversity than their $C_{70}(CF_3)_m$ analogs (with $m = 12$–18 [13–15]) all containing the sub-structure of $C_{70}(CF_3)_{10}$ [12] in their addition patterns.

The aromatic fragments in $C_{60}(CF_3)_{16}$ and $C_{60}(CF_3)_{18}$ reveal certain non-planarity and bond alternation, their average lengths being 1.370 Å for “double” and 1.429 Å for “single” ones in $C_{60}(CF_3)_{16}$-II, 1.365 and 1.431 Å for two crystallographically independent molecules in $C_{60}(CF_3)_{16}$-III, and, for comparison, 1.378 and 1.432 Å in S_6-$C_{60}(CF_3)_{12}$ [4]. The isolated double bonds exhibit average lengths of 1.333 and 1.339 Å in the two crystallographically inequivalent molecules in $C_{60}(CF_3)_{16}$-III (four bonds in each, see Fig. 3e), 1.332 Å in $C_{60}(CF_3)_{16}$-II (one bond, Fig. 3d), 1.329 Å in $C_{60}(CF_3)_{16}$-I (three bonds, Fig. 3f), and 1.325 Å in $C_{60}(CF_3)_{18}$-I (six bonds, Fig. 3g). The longest C–C distance in the fullerene cage is that between two adjacent sp^3 carbon atoms involved in *ortho*-attachment in $C_{60}(CF_3)_{16}$-II: 1.569(8) Å. Analogous distances in $C_{60}(CF_3)_{16}$-III, 1.52–1.53 Å, are influenced by overlapping with sp^2–sp^3 C–C distances due to disorder and their experimental values are, therefore, not very reliable.

In order to rationalize formation of the isomers isolated, extensive calculations using semi-empirical AM1 (Austin Model 1) and density functional theory (DFT) methods have been carried out. Preliminary calculations at the AM1 level of theory involved all isomers of $C_{60}(CF_3)_{16}$ and $C_{60}(CF_3)_{18}$ with addition pattern *formally* decomposable into a combination of 1,4-$C_6(CF_3)_2$ hexagons (closer interhexagonal contacts were allowed) but without *ortho*-contacts of the CF_3 groups plus all isomers with a single *ortho*-contact involving a [6,6] bond and the remaining addition pattern decomposable in a similar way. However, due to the enormous number of structures to be considered, especially in the case of $C_{60}(CF_3)_{16}$, the isomers of the latter with an *ortho*-contact were additionally required to contain a 1,6,9,18-$C_{60}(CF_3)_4$ fragment (namely skew pentagonal pyramid without a side pair of *para*-connected CF_3 groups). These selection principles were based on the structural observations for the higher trifluoromethylated derivatives of C_{60} and C_{70} considered so far. The AM1 treatment provided a group of the most stable structures that was further refined by means of the DFT calculations The discrepancies between the relative energy values obtained with the use of these two methods did not exceed 30 kJ mol^{-1} and are illustrated in more detail in Electronic Supporting Information (ESI) provided.

The DFT survey has ultimately demonstrated that the three isolated and characterized isomers of $C_{60}(CF_3)_{16}$ are 4.1 (isomer III), 10.3 (II), and 16.0 kJ mol^{-1} (I) higher in energy than the most stable structure and rank 5th, 8th, and 11th in the isomeric stability list (see ESI for details). We see it possible that some other isomers from the top of the list are present in the chromatographically separated fractions with retention times of 2.9, 3.22, and 3.48 min (Fig. 1). In the case of $C_{60}(CF_3)_{18}$, isomer I is the sixth thermodynamically stable isomer of this composition and is 32.6 kJ mol^{-1} higher in energy than the most stable C_{3v} isomer incorporating two isolated benzenoid rings (see Fig. 3h and ESI). It is currently not exactly known, whether the C_{3v} isomer is absent from the mixture synthesized, since characterization of the first eluted chromatographic fraction at 2.7 min, which contains some isomer of $C_{60}(CF_3)_{18}$, is still far from completion. Anyway, synthesis and isolation of this isomer seems a very interesting task. Of special interest is also fourth isomer from the stability list for $C_{60}(CF_3)_{18}$. This isomer can be directly obtained via *para*-addition to $C_{60}(CF_3)_{16}$-II, so it would be quite intriguing if this isomer does not form at all. Noteworthy, the isomeric distribution over the energy scale becomes somewhat sparser when going from $C_{60}(CF_3)_{16}$ to $C_{60}(CF_3)_{18}$. This, probably, reflects the fact that both compounds are already well beyond the average level of CF_3 functionalization (the largest number of CF_3 groups observed in MALDI mass spectral experiments is 22 and the theoretical maximum is, perhaps, 24 for a $C_{60}Br_{24}$-like structure) and the number of possible arrangements of CF_3 groups thus tends to decrease upon further addition.

Unfortunately, incomplete characterization of some of the components of synthetic mixture hinders understanding of the pathways of trifluoromethylation; nevertheless, some conclusions can be still made. First of all, the thermodynamic control of trifluoromethylation is, perhaps, incomplete, if even takes place; otherwise the C_{3v} isomer of $C_{60}(CF_3)_{18}$ would clearly dominate and many other isomers of both $C_{60}(CF_3)_{16}$ and $C_{60}(CF_3)_{18}$, the ones comparable in stability to those characterized, would form in large quantities, some of these ‘‘missing’’ isomers being, moreover, closely structurally related to the reported ones. Despite HPLC and MALDI evidence of formation of at least three more not yet characterized isomers of $C_{60}(CF_3)_{16}$ and one highly abundant isomer of $C_{60}(CF_3)_{18}$ eluted at 2.7 min, the number of ‘‘missing’’ molecules is more than twice higher, so it is doubtful that the experimental chromatogram can ‘‘accommodate’’ all them, not to mention the abundance ratios. Although all the isomers characterized are among the most relatively stable, this can be, in principle, due to some purely kinetic reasons rather than partial thermodynamic control. These possible kinetic factors can be expected to be of rather complex nature. For example, our DFT results demonstrate that in radical intermediates with odd number of addends highest spin densities are observed, not surprisingly, for *ortho*-positions with respect to the addend last attached (or to more than one addend), spin densities for *para*-positions being somewhat lower. Consequently, there should be interplay of electronic factors that favor *ortho*-addition and steric factors that hinder it and thus favor *para*-addition. In a number of cases, two of them reported herein, this interplay appears to resolve in favor of a single occasion of *ortho*-attachment; therefore, there should also be some additional subtle factors that dictate such an outcome in these particular cases. On the one hand, the *ortho*-isomers may be due to some rearrangements of some preformed *para*-isomers, as discussed below, but it is hard to understand, in what cases and how far such rearrangements could proceed. On the other hand, the above additional factors may be somehow related to the co-presence of *ortho*-pairs and triphenylene fragments that was mentioned above and may be expected to provide a manifestation of a correlation between kinetic and thermodynamic trends.

A more positive conclusion can be made about precursors of the compounds characterized. Some additional experiments have been carried out to study the products of trifluoromethylation of the isolated S_6-$C_{60}(CF_3)_{12}$ [4] treated under the similar synthetic conditions. These experiments resulted in predominant formation of structurally closely related isomers II and III of $C_{60}(CF_3)_{16}$ and almost no formation of isomer I of $C_{60}(CF_3)_{16}$ and isomer I of $C_{60}(CF_3)_{18}$. Thus, the former two isomers are, indeed, due to some pathway involving S_6-$C_{60}(CF_3)_{12}$, whereas the latter two are due to some competing pathway and the branching, perhaps, occurs at some earlier stage of addition. Since isomers II and III of $C_{60}(CF_3)_{16}$ cannot, nevertheless, form from S_6-$C_{60}(CF_3)_{12}$ without migration of some CF_3 groups, one can conclude that the CF_3 shell exhibits a certain, though rather limited, ability to rearrange under the synthetic conditions. It is not known at present, whether this rearrangement proceeds via acts of synchronous replacement of one CF_3 group in one position with another CF_3 radical from the gas phase that attacks a different position, or via time-resolved acts of detachment and reattachment of single CF_3 groups or pairs thereof, or by some other mechanism. However, isomers II and III of $C_{60}(CF_3)_{16}$ being exactly the two most stable triphenylene-containing isomers, such rearrangement is likely to provide at least partial equilibration of the closely related isomers from the S_6-$C_{60}(CF_3)_{12}$-based family. In this respect, isomers 17 and 19 from the isomeric stability list of $C_{60}(CF_3)_{16}$ deserve special attention as examples of a highly relatively stable isomers (within only 21 kJ mol^{-1} from the most stable one) that can be directly formed from S_6-$C_{60}(CF_3)_{12}$ via two stages of pairwise *para*-addition of CF_3-groups with no rearrangements required. One can expect such isomers to be extremely likely kinetic products, so their absence or low abundance among the products of trifluoromethylation of S_6-$C_{60}(CF_3)_{12}$ can be hypothesized to be due to conversion into the experimental isomers II and III. In any case, we believe that many aspects of fullerene trifluroromethylation can be clarified via systematic comparison of the synthetic mixtures prepared as reported herein and those obtained under different synthetic conditions, e.g. at lower synthetic temperatures that may considerably slow down any rearrangement processes. Of major importance would be comparison of relative abundance of such molecules as isomers 17 and 19 of $C_{60}(CF_3)_{16}$ and C_{3v} isomer of $C_{60}(CF_3)_{18}$.

In summary, three $C_{60}(CF_3)_{16}$ isomers and one $C_{60}(CF_3)_{18}$ isomer were isolated from the mixture of higher thifluoromethylated [60]fullerene. Their molecular structures were determined by X-ray crystallography. Based on the analysis of molecular structures and the DFT calculation of relative energy, it can be concluded that the formation of a large number of isomers is due to different pathways in the course of high-temperature trifluoromethylation and some interplay of thermodynamic and kinetic stability of some isomers at these conditions.

3. Experimental

3.1. Synthesis

Typically, 40 mg of C_{60} (99.95%, Term-USA) were placed into a glass ampoule and ca. 0.5 mL of CF_3I (98%, Apollo) was then condensed into it under cooling with liquid nitrogen. The sealed ampoule was placed into a gradient furnace so that a section containing fullerene was heated to 380–400 °C, whereas liquid CF_3I remained at room temperature and thus developed a vapor pressure of ca. 5 bar. During the reaction time of 18–48 h more than 90% of fullerene was consumed and an orange colored layer of trifluoromethylated compounds was formed in the zone at 200–250 °C. According to the negative ion MALDI MS analysis, the collected orange sublimate (ca. 80 mg) consisted of $C_{60}(CF_3)_n$ compounds with $n = 14$–18 (see Fig. 1).

3.2. Mass spectrometric analysis

Negative ion MALDI mass spectrometry was applied to analyze the crude product and isolated HPLC fractions. The spectra were recorded with the use of a Bruker AutoFlex reflectron time-of-flight mass spectrometer equipped with N_2 laser (337 nm, 1 ns pulse). *Trans*-2-(3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene)malononitrile (DCTB, ≥99%, Fluka) was chosen as a matrix, the matrix-to-analyte ratio being 1000–4000.

3.3. Isolation

The following purification protocol was applied. 40 mg of the synthesized mixture were dissolved in 5 mL of *n*-hexane and subjected to HPLC separation (10 mm i.d. × 250 mm long Cosmosil Buckyprep column (Nakalai Tesque Inc.), hexane eluent, 4.6 mL min^{-1} flow rate, monitored at 290 nm). The fractions containing $C_{60}(CF_3)_{16}$ isomers I–III and $C_{60}(CF_3)_{18}$ isomer I were collected at the following retention times (min): $C_{60}(CF_3)_{16}$-III—3.41, $C_{60}(CF_3)_{16}$-II—4.02, $C_{60}(CF_3)_{18}$-I—4.41, and $C_{60}(CF_3)_{16}$-I—6.90. The obtained fractions (ca. 10–30 mL each) were evaporated to 2–3 mL and then transferred into vessels for further slow concentration to give crystalline material.

3.4. X-ray crystallography

Synchrotron X-ray data for the crystals of $C_{60}(CF_3)_{16}$-II, -III, and $C_{60}(CF_3)_{18}$-I were collected using a MAR345 image plate detector (Bruker) at the BL14.2 beam line at the Protein Structure Factory BESSY and Free University Berlin at BESSY (Germany). The data for $C_{60}(CF_3)_{16}$-I were collected on an IPDS diffractometer (Stoe) using graphite-monochromated Mo Kα radiation. Crystallographic data and some details of data collection and refinement are found in Table 1. Numerical absorption correction was applied for somewhat larger crystal of $C_{60}(CF_3)_{16}$-I; T(max) and T(min) were 0.9244 and 0.9866, respectively. The structures were primarily solved using the program SHELXD [20] and then extended and anisotropically refined using SHELXL97 [21]. The nearly mirror symmetrical $C_{60}(CF_3)_{16}$-III molecule was found to be disordered between two positions, obviously, due to statistical distribution of the both enantiomers at the same site. In the structure of $C_{60}(CF_3)_{16}$-I, four CF_3 groups are disordered between two positions each around the C-CF_3 axes. In the disordered CF_3 groups, the F atoms of the minor components were refined isotropically. 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 626886–626889. 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 e-mail: deposit@ccdc.cam.ac.uk).

3.5. Selection of structures for theoretical study

The following sets of $C_{60}(CF_3)_{16}$ and $C_{60}(CF_3)_{18}$ isomers for further quantum chemical calculations have been generated. We have considered (i) all possible arrangements of eight and nine 1,4-$C_6(CF_3)_2$ hexagons that result in no CF_3 adjacency (1492 and 100 isomers, respectively); (ii) $C_{60}(CF_3)_{18}$ isomers containing eight 1,4-$C_6(CF_3)_2$ hexagons plus one pair of

Table 1
Crystallographic data and some details of data collection and refinement for trifluoromethylated [60]fullerenes

Compound	$C_{60}(CF_3)_{16}$-III ($0.58C_6H_{14}$)	$C_{60}(CF_3)_{16}$-II	$C_{60}(CF_3)_{16}$-I	$C_{60}(CF_3)_{18}$-I
M	1875.01	1824.76	1824.76	1962.78
a (Å)	11.6254(4)	13.5560(2)	12.4274(9)	13.8509(8)
b (Å)	22.5836(9)	21.8448(4)	13.199(1)	21.614(2)
c (Å)	24.574(1)	19.3578(3)	19.699(2)	20.456(2)
α (°)	99.485(3)	90	90.820(7)	90
β (°)	99.270(3)	91.367(1)	93.240(6)	94.346(6)
γ (°)	103.083(2)	90	116.322(6)	90
Volume (Å^3)	6064.8(2)	5730.8(2)	2888.8(4)	6106.4(9)
D_c (g cm^{-3}); μ(Mo Kα) (mm^{-1})	2.054; 0.224	2.115; 0.234	2.098; 0.232	2.135; 0.241
Crystal size (mm)	0.10 × 0.02 × 0.01	0.1 × 0.04 × 0.04	0.25 × 0.15 × 0.05	0.04 × 0.03 × 0.02
Temperature (K)	100(2)	100(2)	140(2)	100(2)
Instrument, λ (Å)	MAR345, 0.9100	MAR345, 0.9100	IPDS, 0.71073	MAR345, 0.9100
Refls collected/independent	12869/10130	47482/8576	41494/22829	12071/6922
Data/parameters	10127/2329	8566/1169	22823/1228	6922/1189
$R_1[I \geq 2\sigma(I)]$/wR_2 (all)	0.070/0.186	0.079/0.221	0.089/0.183	0.061/0.159
$\Delta\rho$ (max/min)/(e Å^{-3})	0.898/−0.407	0.892/−0.431	0.782/−0.461	0.545/−0.341

adjacent CF_3 groups attached to a [6,6]-double bond with no more CF_3 adjacency allowed (2569 isomers); (iii) $C_{60}(CF_3)_{16}$ isomers containing six 1,4-$C_6(CF_3)_2$ hexagons plus a 1,6,9,18-$C_{60}(CF_3)_4$ motif (skew pentagonal pyramid without one side pair of *para*-connected CF_3 groups) with no more CF_3 adjacency allowed (14479 isomers). The resulting lists of isomers included 15791 symmetry inequivalent isomers for $C_{60}(CF_3)_{16}$ and 2669 isomers for $C_{60}(CF_3)_{18}$.

3.6. *Quantum chemical calculations*

Preliminary geometry optimization of all generated isomers for $C_{60}(CF_3)_{16}$ and for $C_{60}(CF_3)_{18}$ was carried out at the AM1 level of theory with the use of the PC-GAMESS software [22]. The most stable isomers of $C_{60}(CF_3)_{16}$ and $C_{60}(CF_3)_{18}$ within the gap of 30 and 50 kJ mol^{-1} (at the AM1 level of theory), respectively, were then reoptimized by means of the DFT methodology with the use of the PRIRODA software [23] that features very fast implementation of the resolution-of-identity (RI) technique for GGA functionals, an original TZ2P basis set and PBE exchange-correlation functional [24]. Even when using rather extensive triple zeta basis set to compensate for possible loss of accuracy due to the approach employed, this software enables significant economy of time and computational resources as compared to other known quantum chemistry packages, thus providing a unique possibility to perform non-semiempirical calculations for the very large isomeric sets of fullerene systems. In our experience, the results of the above computational protocol, as applied to conventional organic systems, agree well with more commonly used DFT protocols (such as B3LYP hybrid functional/Pople basis sets). The said protocol has been successfully used before for predictions of isomeric composition of various fullerene derivatives (see for example [25–27]).

4. Supplementary information

Electronic supporting information for this paper contains Schlegel diagrams, relative energies, full numbering schemes including those recommended by the IUPAC for the same isomers, and the list of possible $C_{60}(CF_3)_{16}$ and $C_{60}(CF_3)_{18}$ isomers within the gap of 30 and 50 kJ mol^{-1}, respectively, as resulted from theoretical calculations at the AM1 and DFT levels.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (05-03-04006 and 06-03-32942a), Russian Federal Purposeful Program (2006-RI-19.0/001/746), INTAS (YS-2004-83-3316), the Federal Agency of Science and Innovation (02.120.11.80.2) and the Deutsche Forschungsgemeinschaft (KE 489/26-1).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.jfluchem.2007.01.008.

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