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Synthesis, Structure, and Theoretical Study of Lower Trifluoromethyl Derivatives of [60]Fullerene

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A number of $C_{60}(CF_3)_n$ compounds with $n = 2–10$ have been synthesized by the reaction of C_{60} with silver trifluoroacetate and successfully isolated by means of HPLC. This resulted in the first crystal structure determination of six lower trifluoromethyl derivatives with $n = 2$ (single isomer), 4 (two isomers), and 6 (three isomers). A kinetic model of sequential trifluoromethylation based on the Bell–Evans–Polanyi principle has been used to explain the experimentally observed isomeric distribution in the mixtures of $C_{60}(CF_3)_n$ compounds up to $n = 6$.

Introduction

Perfluoroalkyl derivatives of fullerenes were first obtained in 1993 by the DuPont group by the reaction of fullerenes with perfluoropropionyl peroxide or perfluoroalkyl iodides,[1] the maximum number of addends being 14. The first individual trifluoromethylated fullerene $C_{60}(CF_3)_2$ was isolated from byproducts of the fluorination of C_{60} with K_2PtF_6 and AgF.[2] It was found that pyrolytic decarboxylation of silver trifluoroacetate in the presence of [60]fullerene leads to the addition up to 22 CF_3 groups.[3] The development of this method resulted in the synthesis, separation, and characterization of trifluoromethylated fullerenes $C_{60}(CF_3)_n$ (n = 2–14),[4–6] $C_{70}(CF_3)_n$ (n = 2–10),[7–10] and the products of the trifluoromethylation of higher fullerenes C_m (m = 76, 78, 84) and aza[60]fullerene $C_{59}N$.[11] Further improvements in the overall yields and selectivities of trifluoromethylated fullerenes were achieved by passing a flow of gaseous CF_3I through a hot tube containing either C_{60} or C_{70}.[12] These reactions in a flow reactor led to the formation of mixtures of $C_{60}(CF_3)_n$ or $C_{70}(CF_3)_m$ compounds having narrow composition ranges of n (n = 6–12) and m (m = 8–14). The interaction of CF_3I vapors (ca. 5 atm) with fullerenes in a sealed glass ampoule with a temperature gradient of 25–440 °C resulted in the selective synthesis of a single S_6 isomer of $C_{60}(CF_3)_{12}$ in the case of C_{60}[13] or a mixture of derivatives with a high degree of trifluoromethylation in the case of C_{70}.[14,15] Although a large number (more than 60) of $C_{60}(CF_3)_n$ isomers are known, their structures are far from having been unambiguously characterized. Furthermore, the generally low symmetry of trifluoromethylated fullerene (unlike polyhydro- and polyfluorofullerenes) have made it difficult to apply NMR spectroscopy to their structural characterization. In particular, ^{19}F NMR spectra of the same $C_{60}(CF_3)_n$ compounds, tentatively interpreted by various methods, resulted in differently assigned structures.[4,6] Energetic considerations have allowed us to validate the proposed structures.[4,16] However, the energetic control of the pyrolytic trifluoromethylation process is, perhaps, incomplete and the experimental isomeric composition may differ notably from theoretical predictions.[15] For most trifluoromethylated fullerenes, only single-crystal X-ray crystallography makes possible unambiguous structural characterization. To date, the structures of the following $C_{60}(CF_3)_n$ compounds have been uniquely established: $C_{60}(CF_3)_8$ (two isomers),[17,18] $C_{60}(CF_3)_{10}$ (three isomers),[12,19,20] $C_{60}(CF_3)_{12}$ (two isomers),[13,21] $C_{60}(CF_3)_{16}$ (three isomers),[22] and $C_{60}(CF_3)_{18}$ (one isomer).[22]

In this paper, X-ray crystallographic data for $C_{60}(CF_3)_2$ (one isomer), $C_{60}(CF_3)_4$ (two isomers), and $C_{60}(CF_3)_6$ (three isomers) are reported and the data for two isomers of $C_{60}(CF_3)_8$,[17,18] $(p^3m^2)^2$-loop-$C_{60}(CF_3)_{10}$ (isomer I),[20] and $C_{60}(CF_3)_4O$[23] are included for comparison and discussion. Such a representative set of X-ray data, accompanied by extensive DFT calculations of the relative stability of $C_{60}(CF_3)_n$ isomers (n = 2–6), have allowed a mechanistic model to be proposed for the consecutive addition of CF_3 groups to [60]fullerene, a systematic analysis of the addition patterns governing the trifluoromethylation of C_{60} to form $C_{60}(CF_3)_n$ up to n = 6, and a comparison of our approach with those developed for fluorofullerenes.[24,25]

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Results and Discussion

Synthesis

Initially, the trifluoromethylated fullerenes were obtained by the reaction of CF_3I with C_{60} in solution at 200 °C in a glass ampoule.[1] The presence of hydrogen-containing solvents led to the formation of mixed $C_{60}(CF_3)_nH_m$ compounds, whereas a perfluorinated solvent, hexafluorobenzene, enabled the formation of $C_{60}(CF_3)_n$ compounds (n = 2–14). The solvent-free preparation methods suggested later involve the reaction of fullerenes with CF_3 radicals generated by pyrolysis of transition-metal trifluoroacetates[3] or gaseous CF_3I.[12,13] Although the common stage of these approaches is the reaction of fullerene with the CF_3 radical (also generated sometimes by light irradiation),[1,26] variation of the conditions results in variegated products. Synthesis in a flow apparatus, that is, with gaseous CF_3I passing at atmospheric pressure over C_{60} or C_{70} at 460 °C followed by the collection of volatile compounds in a cold zone, resulted in the formation of $C_{60}(CF_3)_n$ (n = 8, 10, 12)[12,17,19–21] and $C_{70}(CF_3)_n$ (n = 10, 12).[27–29] Synthesis at a higher temperature (550 °C) led to the lower trifluoromethylated fullerenes $C_{60}(CF_3)_n$ (n = 2–100).[23] The interaction of C_{60} or C_{70} fullerenes with CF_3I vapor at around 5 atm in a sealed glass ampoule at 440 °C is used for the high-yielding preparation of higher polytrifluoromethyl derivatives, $C_{60/70}(CF_3)_n$ (n = 12, 14, 16, 18).[13,14,22,30,31]

The trifluoromethylation of fullerenes with CF_3COOAg was carried out by the Sussex University and Moscow State University research groups, although their approaches were slightly different. In the work published in refs.[5,6,9] C_{60} (or C_{70}) and CF_3COOAg were placed in a tube connected to a vacuum pump. The tube was heated up to 240 °C to remove any moisture. Then the temperature was raised to 285 °C for 1 h and then raised further to 300 °C for an additional 1 h. The products of interest were then extracted by toluene, filtered to remove traces of silver, and separated by HPLC. As a result, the authors isolated 60 isomers of $C_{60}(CF_3)_n$ (n = 2–14)[6] and 46 isomers of $C_{70}(CF_3)_n$ (n = 2–14)[9] which were partially characterized by ^{19}F NMR spectroscopy. In our previous studies,[4,10] the reaction mixture was heated in a closed tube at 280–340 °C for 1–6 h. The crude product obtained was then fractionally sublimed at 380–520 °C and the resulting sublimation fractions were separated by HPLC. It was found that sublimation of the crude product is accompanied by a decrease in the total number of isomers and by significant simplification of the HPLC separation procedure. Thus, in the case of reaction with C_{70}, (C_s)-

Table 1. Reaction conditions and reaction/sublimation yields.

No.	C_{60} [mg mmol^{-1}]	CF_3COOAg [mg mmol^{-1}]	Molar ratio n/n	T_{rxn} [°C] ($t_{rxn.}$ [h])	Sublimation fraction [mg] (sublimation time 1 h) 420 °C	480 °C	520 °C	Total[a]
1	100.1/0.139	104.5/0.473	3.4	300 (3)	–[b]	–	–	–
2	177.0/0.246	744.2/3.369	13.7	320 (1)	62.2	61.2	16.3	139.7
3	146.4/0.203	648.2/2.935	14.5	320 (1)	23.0	34.3	5.6[c]	62.9
4	247.7/0.344	874.8/3.960	11.5	340 (3)	51.3	54.2	25.9	131.4
5	118.0/0.164	1303.6/5.899	36.0	340 (2)	–	53.2	2.8	56.0

[a] Weight of the combined sublimates. [b] The conversion of C_{60} was too low and sublimation of the crude products was not performed. [c] The sublimation time was 30 min.

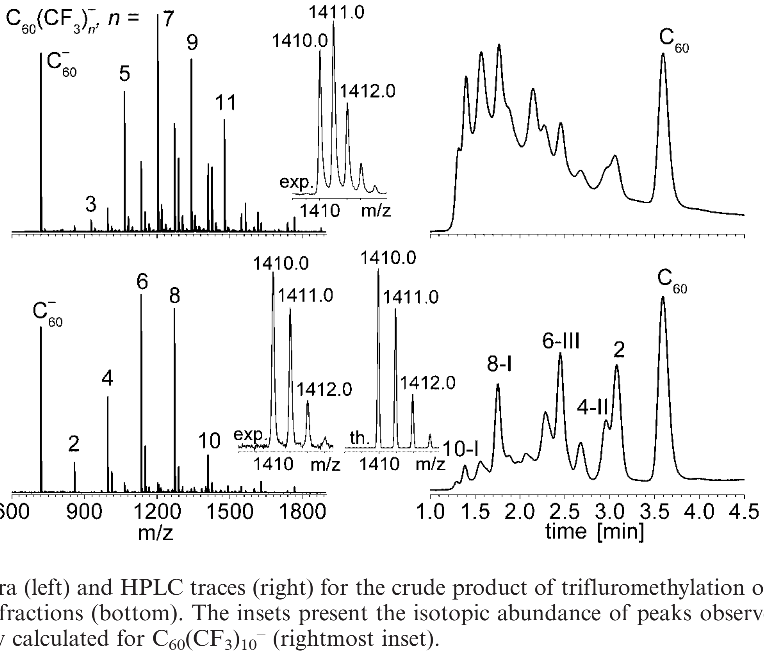

Figure 1. MALDI mass spectra (left) and HPLC traces (right) for the crude product of trifluromethylation of C_{60} with CF_3COOAg (top) and the mixture of sublimed fractions (bottom). The insets present the isotopic abundance of peaks observed at about m/z = 1410 (top and bottom) and theoretically calculated for $C_{60}(CF_3)_{10}^-$ (rightmost inset).

$C_{70}(CF_3)_8$ was prepared in 30% yield [together with small amounts of other $C_{70}(CF_3)_n$ isomers (n = 2–10)] and structurally characterized.[7,10] This approach made possible the isolation of a number of $C_{60}(CF_3)_n$ compounds (n = 2–8), but none of them was crystallographically characterized.[4]

In this work, the finely ground mixtures of C_{60} and from 3- up to 36-fold molar excess of CF_3COOAg were heated at 300–340 °C in a closed reactor for 1–3 h (see Table 1). The crude reaction product was analyzed by MALDI mass spectrometry and HPLC. It was found that the use of a 36- instead of a 14-fold excess of CF_3COOAg did not improve the results, whereas a low CF_3COOAg/C_{60} molar ratio of 3.4:1 led to a sharp decrease in the efficiency of the trifluoromethylation reaction. Large-scale syntheses (150–250 mg of C_{60}, experiments 2–4) were carried out with an optimal 12–14-fold molar excess of CF_3COOAg.

The MALDI mass spectrum and HPLC trace of the crude mixture of the trifluoromethylation products are shown in the Figure 1 (top). As one can see, fragment ions $C_{60}(CF_3)_n^-$ with odd values of n (n = 3–13) prevail and distortion of isotopic abundance for even-numbered $C_{60}(CF_3)_n^-$ peaks also takes place (see top inset, Figure 1). These two facts point to the presence of the hydrogenated species $C_{60}(CF_3)_nH$ with odd values of n giving no molecular ions. Probably, their fragmentation is due to the loss of hydrogen (most likely) or CF_3. Our previous MALDI experiments with trifluoromethylated fullerenes indicated that the loss of CF_3 should not be important and fragment peaks do not prevail.[32]

Similar compounds [$C_{60}(CF_3)_nH_m$, where n = 1–13, m = 1–30] have already been reported among the trifluoromethylated derivatives of C_{60} in the presence of hydrocarbons.[1] $C_{60}(CF_3)_5H$ and $C_{60}(CF_3)_nH_2$ (n = 4, 6, 8) were also isolated as byproducts of trifluoromethylation by CF_3COOAg or the Scherer radical C_9F_{19}.[6] In our case, hydrogenation could occur directly in the course of the trifluoromethylation reaction as well as during sample preparation for MALDI analysis. Hydrogen sources in the former case may be solvent (toluene or benzene) contained in the pristine fullerene sample, the CF_3COOH admixture, or traces of water. In the latter case, the crude product contains highly reactive particles that are able to abstract hydrogen from the DCTB matrix or the toluene used for sample preparation. The possible candidates are radical particles, similar, for example, to the allylic $C_{60}R_3^{\cdot}$ and cyclopentadienyl $C_{60}R_5^{\cdot}$ (R = $C_6H_4CH_2$) radical adducts which were proven by ESR spectroscopy as stable products even above 50 °C.[33]

The presence of $C_{60}(CF_3)_nH_m$ compounds, a complex isomeric composition of the prepared crude mixture, and strong overlap of most HPLC peaks (see Figure 1, top HPLC trace) resulted in inefficient HPLC separation. Therefore, it was subjected to vacuum sublimation at 420, 480, and 520 °C.

The sublimation fractions were collected and analyzed by MALDI mass spectrometry and HPLC (see Figure 2). The MALDI mass spectra of the sublimation products differ from the spectra of the crude products. The domination of even-numbered $C_{60}(CF_3)_n^-$ peaks and the agreement between experimental and theoretical isotopic abundances for all peaks (see inset in the bottom spectrum of Figure 1) point to the complete absence of hydrogenated species in the sublimed fractions.

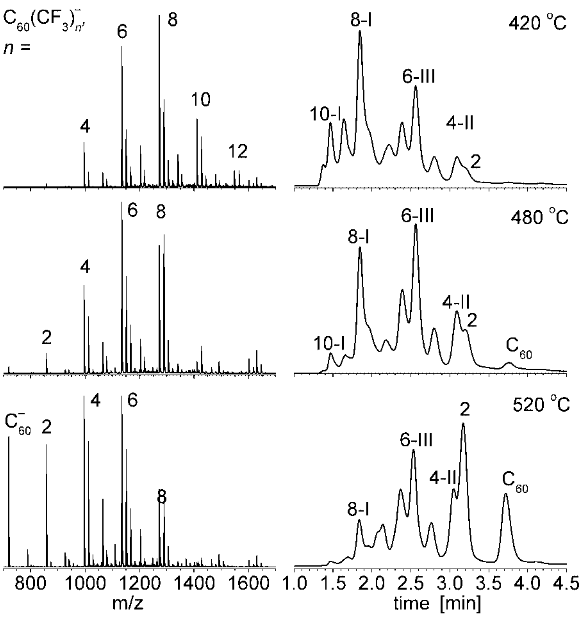

Figure 2. MALDI mass spectra (left) and HPLC traces (right) of the sublimed fractions (at 420, 480, and 520 °C) of the product from the experiment No. 2 (Table 1).

Sublimation led to partial separation. Namely, the 420 °C sublimate contained more “higher” $C_{60}(CF_3)_n$ derivatives (with n = 6–10) while the 520 °C sublimate was characterized by larger amounts of the “lower” derivatives with n = 2–8 and the initial C_{60}. Nevertheless, the differences were not significant and we found it more efficient to work with a mixture of fractions. The HPLC trace and MALDI mass spectrum of the combined sublimation fractions are shown in Figure 1. One can see that the HPLC trace is better resolved than that of the crude reaction product (Figure 1). Thus, the sublimation procedure results in a simplification of the isomeric composition and, probably, the decomposition of aforementioned hydrogenated species. The obtained mixture was subjected to further purification by HPLC.

HPLC Separation

In the first step of the HPLC separation of the combined mixture with toluene as eluent, 13 chromatographic fractions were isolated. However, none of these isolated fractions contained a single compound according to the MALDI mass spectra and HPLC analyses. Therefore, the second and third stages of the HPLC purification were performed with hexane [for $C_{60}(CF_3)_{10}$-I] or toluene/hexane mixtures as eluent. Finally, we obtained 18 chromatographic fractions of trifluoromethylated fullerenes, 13 of which predominantly contained a single isomer. The molec-

Table 2. HPLC isolated compounds and their retention times [min].

No.	Compounds[a]	Eluent, toluene/hexane volume ratio[b]							
		10:0		8:2	5:5	3:7	2:8	1:9	0:10
1	$C_{60}(CF_3)_{12/14}$, $C_{60}(CF_3)_{12}O$[c]		1.29	1.31	–	–	–	–	1.6–2.74
2	$\mathbf{C_{60}(CF_3)_{10}}$	**10-I**[19]	1.40	1.44	–	–	2.63	–	7.47
3	$C_{60}(CF_3)_{10}$	10-II	1.56	1.68	–	–	5.14	–	–
4	$C_{60}(CF_3)_{8/10}$[c]		1.59	1.68	–	–	5.76	–	–
5	$C_{60}(CF_3)_8$	8-I[d]	1.77	1.99	3.07	5.86	9.81	19.23	–
6	$C_{60}(CF_3)_8$	8-II	1.83	2.05	3.10	6.26	–	–	–
7	$C_{60}(CF_3)_{6/8}$[c]		1.88	2.16	3.49	7.38	–	–	–
8	$C_{60}(CF_3)_8$	8-III	1.90	–	3.38	6.99	–	–	–
9	$C_{60}(CF_3)_6$	6-I	1.91	–	3.65	7.75	–	–	–
10	$C_{60}(CF_3)_{6/8}$[c]		1.94	–	3.83	8.46	–	–	–
11	$\mathbf{C_{60}(CF_3)_6}$	**6-II**	1.99	2.37	4.17	9.52	–	–	–
12	$C_{60}(CF_3)_{4/6}$[c]		2.28	–	4.7–6.5	–	–	–	–
13	$\mathbf{C_{60}(CF_3)_6}$	**6-III**	2.46	3.15	6.42	–	–	–	–
14	$\mathbf{C_{60}(CF_3)_6}$	**6-IV**	2.68	–	6.67	–	–	–	–
15	$\mathbf{C_{60}(CF_3)_4}$	**4-I**	2.70	–	7.27	–	–	–	–
16	$\mathbf{C_{60}(CF_3)_4}$	**4-II**	2.96	3.99	8.79	–	–	–	–
17	$\mathbf{C_{60}(CF_3)_2}$	**2-I**	3.06	4.22	9.24	–	–	–	–
18	$\mathbf{C_{60}(CF_3)_4O}$	**4O**[23]	3.06	4.22	10.56	–	–	–	–
19	C_{60}		3.62	5.09	–	–	–	–	–

[a] Molecular composition given in accord with MALDI MS data. The formulae of the compounds investigated in this study by means of X-ray crystallography are marked **bold**. Roman numerals denote various isomers. [b] 4.6 mm × 25 cm Cosmosil Buckyprep column (dead volume 2.58 mL); eluent flow rate 2 mL min^{-1}, 25 °C. [c] The mixture was not subjected to HPLC separation. [d] The crystal structure of this isomer of $C_{60}(CF_3)_8$ has been published recently.[17]

ular composition and retention times of the isolated fractions are given in Table 2. In contrast to the polyfluorofullerenes, $C_{60}F_n$ with n = 2–20,[34] the retention times of the $C_{60}(CF_3)_n$ compounds increase with decreasing degree of trifluoromethylation and their chromatographic behavior is similar to that of other perfluoroalkylated compounds.[35]

As a result of the HPLC separation, the following isomers were isolated: a single isomer of $C_{60}(CF_3)_2$, $C_{60}(CF_3)_4$ (two isomers), $C_{60}(CF_3)_4O$ (one isomer), $C_{60}(CF_3)_6$ (four isomers), $C_{60}(CF_3)_8$ (three isomers), and $C_{60}(CF_3)_{10}$ (two isomers). Some $C_{60}(CF_3)_n$ derivatives were not separated from fractions 1, 4, 7, 10, and 12. Therefore, the total isomeric composition of the combined mixture of sublimation fractions can be estimated as follows: n = 2 (one isomer), 4 (≥ three isomers), 6 (≥ seven isomers), 8 (≥ six isomers), and 10 (≥ three isomers).

The relative amounts of the $C_{60}(CF_3)_n$ isomers were estimated by integration of the HPLC peaks (290 nm). It was found that in spite of the many isomers only a few of them dominate in the mixture, namely $C_{60}(CF_3)_4$-II, $C_{60}(CF_3)_6$-III, $C_{60}(CF_3)_8$-I, and $C_{60}(CF_3)_2$.

$C_{60}(CF_3)_2$

$C_{60}(CF_3)_2$ is present as a single isomer. The HPLC fraction eluted in toluene (hereinafter the eluent flow rate 2 mL min^{-1}, Cosmosil Buckyprep 4.6 mm × 25 cm column, 25 °C) with a retention time of 3.06 min contains $C_{60}(CF_3)_4$-II and $C_{60}(CF_3)_4O$ as admixtures. The satisfactory separation of these compounds was achieved in a 1:1 (v/v) mixture of toluene/hexane as eluent. The MALDI mass spectrum and UV/Vis spectrum of the isolated fraction (R_T = 9.24 min; toluene/hexane, 1:1, v/v) of $C_{60}(CF_3)_2$ are shown in Figure 3a. The UV/Vis spectrum of $C_{60}(CF_3)_2$ (toluene, peaks at 326 and 446, and weak broad absorptions at 600 and 692 nm) exhibits the characteristic absorption pattern, that is, a rather broad absorption at 446 nm, which appears to be typical for *para*-$C_{60}R_2$, in contrast to a sharp peak at 430 nm, characteristic of *ortho*-$C_{60}R_2$.[36,37]

$C_{60}(CF_3)_4O$

This oxo derivative coelutes with $C_{60}(CF_3)_2$ in toluene. Therefore, isolation of the compound was carried out with a 1:1 (v/v) mixture of toluene/hexane with a retention time of 10.6 min. The $C_{60}(CF_3)_4OH^-$ ion as well as its complexes with DCTB are observed in the MALDI mass spectrum of the obtained fraction (Figure 3b). The formation of $C_{60}(CF_3)_4OH^-$ probably occurs in the course of the ionization of $C_{60}(CF_3)_4O$ and following abstraction of the hydrogen atom from the matrix or solvent molecules. The UV/Vis spectrum [toluene, λ = 294 (sh.), 334 (sh.), 390, 436 (sh., w.), 472 (sh., w.), 506 (sh., w.) nm] of the compound agrees well with that recently reported for (C_s)-$C_{60}(CF_3)_4O$.[23]

$C_{60}(CF_3)_4$

Two isomers of $C_{60}(CF_3)_4$ (1:4 ratio) were eluted at 7.27 [$C_{60}(CF_3)_4$-I] and 8.79 min [$C_{60}(CF_3)_4$-II, major isomer] by using a toluene/hexane mixture (1:1, v/v). A few isomers of $C_{60}(CF_3)_4$ were also observed in fraction 12; however, they were not isolated as individual compounds. The $C_{60}(CF_3)_4^-$ molecular ion dominates the MALDI mass spectra of both separated fractions (Figure 3c). The UV/Vis spectra of $C_{60}(CF_3)_4$-I (toluene, λ = 316 with shoulders at 368, 492, and 566 nm) and $C_{60}(CF_3)_4$-II (toluene, λ = 320 nm with shoulders at 370, 436, and 518 nm) are shown in Figure 3c.

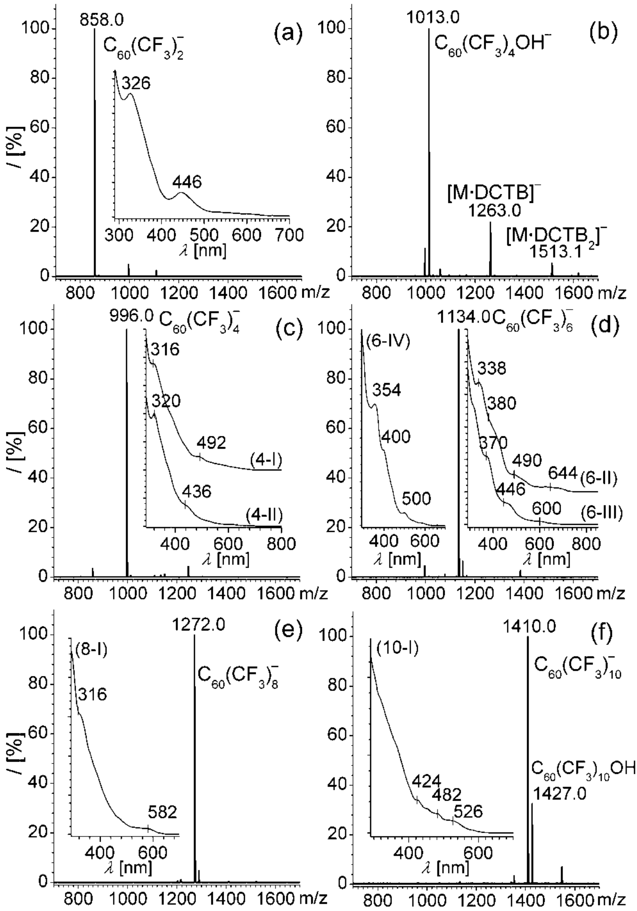

Figure 3. MALDI mass spectra of $C_{60}(CF_3)_2$ (a), $C_{60}(CF_3)_4O$ (b), $C_{60}(CF_3)_4$-II (c), $C_{60}(CF_3)_6$-IV (d), $C_{60}(CF_3)_8$-II (e), and $C_{60}(CF_3)_{10}$-I (f). UV/Vis spectra (in toluene; arbitrary units versus nm) of some of the isolated compounds are shown on the insets.

$C_{60}(CF_3)_6$

Four isomers, $C_{60}(CF_3)_6$-I, -II, -III, and -IV (1:3:33:7 ratio), were isolated by HPLC using toluene/hexane mixtures (3:7 and 1:1) as eluent; their retention times were 3.65, 4.17, 6.42, and 6.67 min (toluene/hexane, 1:1), respectively. Few $C_{60}(CF_3)_6$ isomers were observed as mixtures with $C_{60}(CF_3)_8$ in fractions 7 and 10. $C_{60}(CF_3)_6$-III was the major isomer among the four isolated. The $C_{60}(CF_3)_6^-$ molecular ion dominates the MALDI mass spectra of the $C_{60}(CF_3)_6$-I–IV isomers (Figure 3d). The UV/Vis spectra of the $C_{60}(CF_3)_6$-II, -III, and -IV isomers are shown in the insets of Figure 3d. The principal UV/Vis data are as follows: $C_{60}(CF_3)_6$-I: toluene, λ = 320, 434 (sh.), 588 nm, see the Supporting Information; $C_{60}(CF_3)_6$-II: toluene, λ = 338, 380 (sh.), 488 (sh.), 644 nm; $C_{60}(CF_3)_6$-III: toluene, λ = 310 (sh.), 370, 438, 600 nm; $C_{60}(CF_3)_6$-IV: toluene, λ: 354, 400 (sh.), 500 nm.

$C_{60}(CF_3)_8$

Isomers of $C_{60}(CF_3)_8$-I, -II, and -III (ratio 17:5:2) were isolated among at least six observed $C_{60}(CF_3)_8$ isomers. The $C_{60}(CF_3)_8^-$ ion is dominant in the MALDI mass spectra of the isolated fractions; a typical mass spectrum is shown in Figure 3e. The retention times of the dominating $C_{60}(CF_3)_8$-I isomer, eluting at 1.77 min in toluene and at 9.81 min in a toluene/hexane mixture (1:4), are close to the previously reported values (R_T = 1.76 and 9.75 min at the same HPLC conditions, respectively) for 1,6,11,16,18,24,27,36-$C_{60}(CF_3)_8$ obtained by trifluoromethylation of C_{60} with CF_3I.[18] The identities of these compounds were also confirmed by comparison of their UV/Vis spectra (toluene, shoulder at 316 nm and a broad shoulder at 582 nm, Figure 3e). The $C_{60}(CF_3)_8$-II and -III isomers elute at 3.10 and 3.38 min in a toluene/hexane (1:1) mixture. The UV/Vis spectra of $C_{60}(CF_3)_8$-II (toluene, λ = 316 nm, shoulders at 400, 450, 522, and 626 nm) and $C_{60}(CF_3)_8$-III (toluene, shoulders at 308, 348, 422, and 584 nm) are given in the Supporting Information.

$C_{60}(CF_3)_{10}$

$C_{60}(CF_3)_{10}$-I and -II isomers (3:2 ratio) were isolated by HPLC from the reaction products. The $C_{60}(CF_3)_{10}$-I isomer was purified by HPLC separation by using hexane as eluent [R_T = 7.47 min with hexane and R_T = 2.63 min with toluene/hexane (1:4) as eluents]. The MALDI mass spectrum of the isolated fraction of $C_{60}(CF_3)_{10}$-I contains the oxo derivative $C_{60}(CF_3)_{10}O$ [it is observed as the pseudomolecular ion $C_{60}(CF_3)_{10}OH^-$, as described above for $C_{60}(CF_3)_4O$]. HPLC purification of a $C_{60}(CF_3)_{10}O$ admixture was not successful. Furthermore, the accumulation of this admixture due to slow oxidation by atmospheric oxygen was observed. The second fraction eluted at 5.14 min with toluene/hexane (1:4) as the eluent contained $C_{60}(CF_3)_{10}$-II. The UV/Vis spectrum of $C_{60}(CF_3)_{10}$-I (hexane, shoulders at 272, 424, 454, 482, and 526 nm) are shown in the inset in Figure 3f. The UV/Vis spectrum of $C_{60}(CF_3)_{10}$-II (toluene, shoulder at 338 nm) does not reveal any significant features.

Crystal and Molecular Structures

As one can see from Table 2, crystals suitable for X-ray crystallographic investigation were obtained for only eight fractions. Moreover, in all cases, except for $C_{60}(CF_3)_2 \cdot C_6H_5(CH_3)$, crystals of a very small size were formed and synchrotron radiation was used to obtain X-ray data.

We determined the crystal and molecular structures of six trifluoromethylated [60]fullerenes containing two, four, and six CF_3 groups for the first time (Figure 4 and Figure 5a,c–f,h). Six other structures are also shown in Figure 5 to discuss their possible precursors among lower derivatives. The structures of $C_{60}(CF_3)_8$ (Figure 5k and j) have been published recently[17,18] and, therefore, are not presented here in much detail. The structure of $C_{60}(CF_3)_{10}$ (Figure 5l), known from the literature,[19] was determined in this work for the second time. It has been included for completeness as this compound was obtained by another synthetic approach. In addition, the structure of $C_{60}(CF_3)_4O$ (Figure 5b) was determined as a toluene solvate and compared with the structure of solvated m-C_6H_4-$(CH_3)_2$.[23] The structures of the two isomers of $C_{60}(CF_3)_6$ shown in Figure 5g and i were established on the basis of

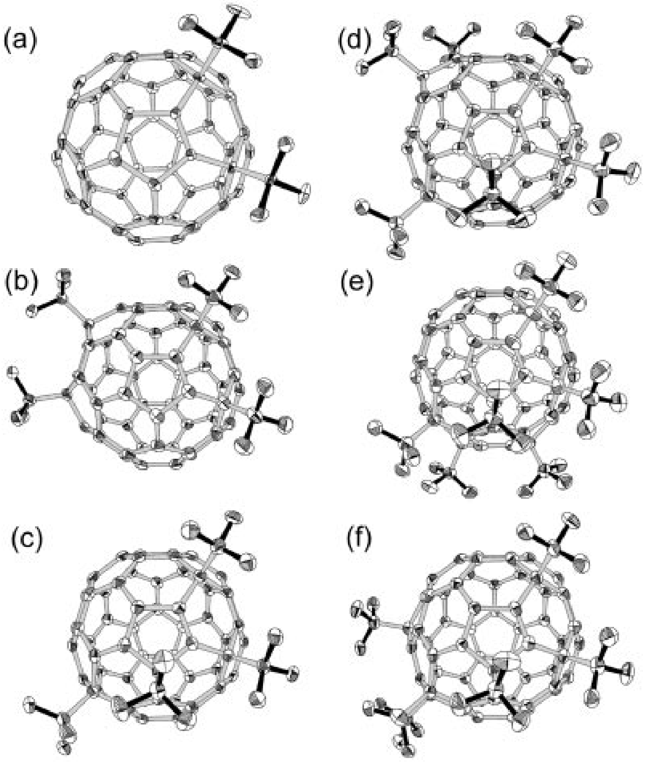

Figure 4. ORTEP views of $C_{60}(CF_3)_2$ (a), $C_{60}(CF_3)_4$-I and -II (b, c), and $C_{60}(CF_3)_6$-II, -III, and -IV (d–f). Thermal elepsoids are given at the 50% probability level.

the NMR spectra of some isolated chromatographic fractions which were first reported (but ambiguously interpreted) by Taylor and co-workers[6] and later reassigned[4,23] (isomer from Figure 5i only). Selected data on the C–C and C–F bond lengths are presented in Table 3 and the crystallographic data are summarized in Table 5 (see Exp. Sect.).

Each addition of a CF_3 group to the fullerene cage creates an sp^3-carbon atom instead of a sp^2 one and is accompanied by a nonuniform expansion of the surrounding bonds. For example, the C–C bonds of 6:6 junctions almost always remain a bit shorter than those of 5:6 junctions. There are no completely isolated double bonds, but some C–C bonds are nearly isolated (by three sp^3 neighbors instead of four) which imparts on them double-bond character, for example, the C4–C5 bonds in the molecular structures of $C_{60}(CF_3)_4$ (Figure 5c) and all the characterized isomers of $C_{60}(CF_3)_6$. The positions of the CF_3 groups relative to the three C–C bonds of the cage tend to be staggered due to mutual repulsion of the fluorine atoms from the nearest cage carbon atoms. The two CF_3 groups of the *para*-$C_6(CF_3)_2$ hexagons are distant enough for the fluorine atoms not to be in contact with each other; so such CF_3 groups are in perfect staggered positions. However, in *meta*-$C_6(CF_3)_2$ hexagons the F···F contacts are closer so that such groups are partly eclipsed. It is known that through-space contacts between fluorine atoms of neighboring CF_3 groups provide observable J_{FF} values in the ^{19}F NMR spectra. The extreme case of an eclipsed conformation of the CF_3 group is energetically unfavorable (by ca. 12 kJ mol^{-1} per CF_3 group). Below, characteristic features of molecules together with their IUPAC notations are presented.

Table 3. Selected (averaged) C–C and C–F bond lengths [Å] in $C_{60}(CF_3)_n$ molecules.

Bond type	$C_{60}(CF_3)_2$	$C_{60}(CF_3)_4$ I	II	$C_{60}(CF_3)_6$ II	III	IV
C–C (sp^2–sp^2)[a]	1.344	1.352	1.356	1.344	–	–
C–C (sp^3–sp^2)[b]	1.514	1.514	1.510	1.513	1.511	1.512
C–C (sp^3–sp^2)[c]	1.535	1.541	1.538	1.543	1.540	1.539
C–CF_3	1.530	1.528	1.545	1.532	1.539	1.533
C–F	1.335	1.336	1.332	1.333	1.338	1.332

[a] Nearly a C–C double bond of the C4–C5 type (with two or three sp^3 neighbors; see Schlegel diagrams in Figure 5). [b] C–C bond at a 6:6 junction. [c] C–C bond at a 5:6 junction.

$C_{60}(CF_3)_2$

1,7-Isomer (Figure 5a). The molecule possesses noncrystallographic C_s symmetry with both CF_3 groups in perfectly staggered positions relative to the three C–C bonds of the fullerene cage.

$C_{60}(CF_3)_4$-I

1,7,16,36-Isomer (Figure 5d). There are two isolated *para*-$C_6(CF_3)_2$ hexagons with each CF_3 group in a nearly perfect staggered conformation. Averaged sp^2–sp^2 C–C bond lengths in the $C_6(CF_3)_2$ hexagons are 1.367 Å, that is, they have a pronounced double-bond character.

$C_{60}(CF_3)_4$-II

1,6,11,18-Isomer (Figure 5c). The molecule contains three "connected" or "edge-sharing" $C_6(CF_3)_2$ hexagons in the sequence *pmp*. Owing to the presence of two CF_3 groups in *meta* positions, one CF_3 group (at C1) is somewhat skewed relative to the staggered conformation; the corresponding C–CF_3 bond (1.556 Å) is slightly longer than the other three (therefore, the average distance is somewhat longer). A nearly isolated C4–C5 "double" bond is very short, 1.344 Å.

$C_{60}(CF_3)_6$-II

1,6,11,18,33,51-Isomer (Figure 5e). The orientation of four CF_3 groups relative to the cage is very similar to that in the 1,6,11,18-$C_{60}(CF_3)_4$ isomer, that is, with only one CF_3 group skewed relative to the ideal staggered position. However, the skewed group is attached to C6, whereas it is attached to C1 in $C_{60}(CF_3)_4$. A C4–C5 bond is nearly a double bond in character with a length of 1.352 Å.

$C_{60}(CF_3)_6$-III

1,6,11,18,24,27-Isomer (Figure 5f). The orientation of the CF_3 groups relative to the cage is similar to that in the 1,6,11,18-$C_{60}(CF_3)_4$ isomer but the two CF_3 groups that are in a *meta* position are slightly skewed from the staggered positions.

$C_{60}(CF_3)_6$-IV

1,6,11,18,28,31-Isomer (Figure 5h). There are two *meta*-$C_6(CF_3)_2$ hexagons in the addition pattern. The most

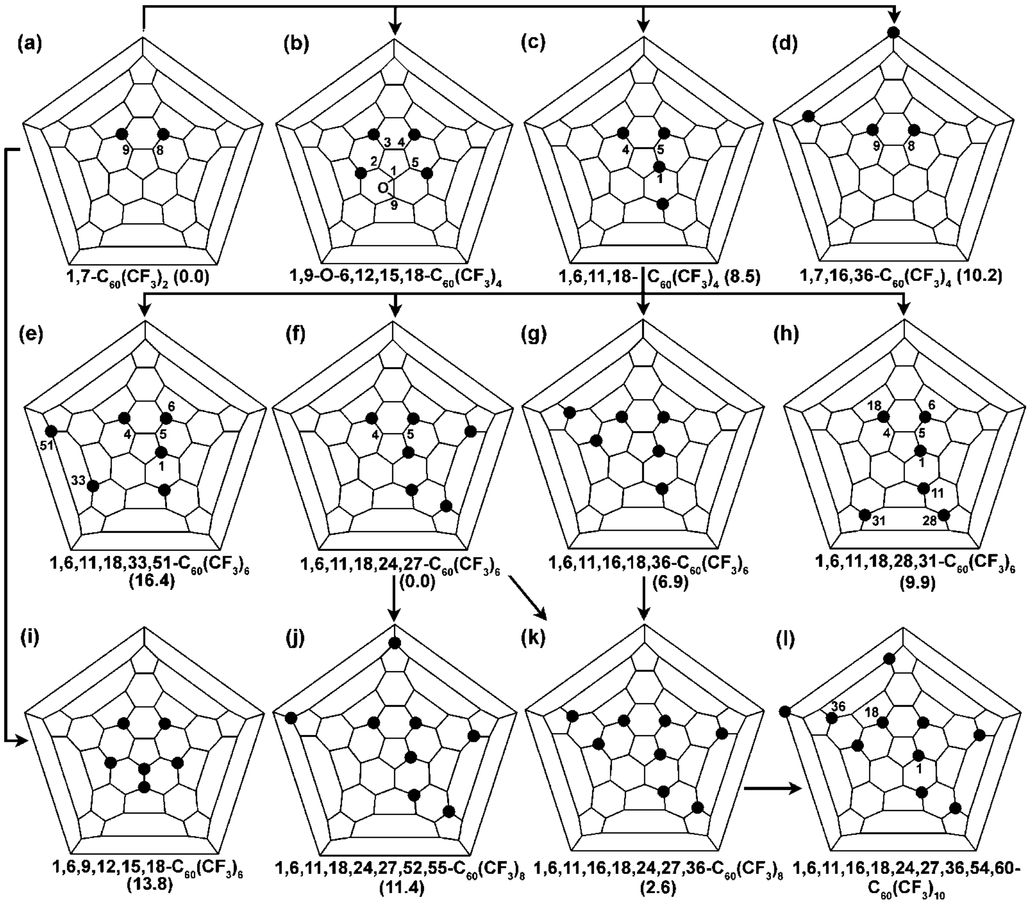

Figure 5. Schlegel diagrams, IUPAC lowest-locant abbreviations, and DFT-predicted relative energy values [kJ mol^{-1}] for experimentally observed isomers.

skewed CF_3 groups are those attached to C1 and C11, both having *meta* neighbors. Less skewed are the CF_3 groups attached to C6 and C28, whereas those at C18 and C31 are nearly perfectly staggered.

$C_{60}(CF_3)_{10}$

1,6,11,16,18,24,27,36,54,60-Isomer (Figure 5l). The structure of this isomer has been previously determined but an incorrect IUPAC name was assigned.[19] There are three *meta*-$C_6(CF_3)_2$ hexagons in a $p^3(mp)^3$ ribbon. Therefore three CF_3 groups (at C1, C18, and C36) are significantly skewed relative to the staggered conformations. The averaged C–C and C–F bond lengths are very close to values typical of the lower $C_{60}(CF_3)_n$: sp^2–sp^2 (double) 1.348 Å (the corresponding average distance in ref.[19] is 1.356 Å), sp^2–sp^3 (6:6) 1.513 Å, sp^2–sp^3 (6:6) 1.540 Å, C–CF_3 1.538 Å, and C–F 1.332 Å.

$C_{60}(CF_3)_4O$

See Figure 5b. The structure of this tetrakis(trifluoromethyl)oxo derivative as the solvate in *m*-xylene has been previously determined.[23] We were able to determine the crystal structures of pure (not solvated) compounds (two crystalline modifications) and toluene solvate. Our structure determination for the latter resulted in the same addition pattern; the estimated standard deviations of the bond lengths (0.003–0.004 Å) and angles are a bit smaller than those in ref.[23], whereas the data for the former (not presented here) are less accurate. The $C_{60}(CF_3)_4O$ molecular geometry is very similar in the crystals of both toluene and *m*-xylene solvates. C_s symmetry should be valid for this molecule as a result of the nearly perfectly staggered positions of all the CF_3 groups relative to the C–C bonds of the fullerene cage. However, some unexpected asymmetry (possibly due to some interaction with toluene in the crystal packing) was found for C–C bonds in the central C1–C5 pentagon: 1.488 and 1.544 Å for C1–C2 and C1–C5 bond lengths, respectively, and 1.387 and 1.350 Å for C2–C3 and C4–C5 bonds, respectively. In ref.[23] the same C–C bonds have lengths that are closer within the pairs. In addition, the asymmetry of the C–O bonds is the same (C1–O 1.448 and C9–O 1.476 Å), as predicted by the DFT method, but the absolute values are larger by around 0.03 Å. However, the C1–C9 distance (1.496 Å) is closer to the calculated one (1.512 Å) than to that in the *m*-xylene solvate (1.488 Å). Interestingly, some of the intermolecular F···F contacts (for example, 2.660 and 2.851 Å) are as short as the intramolecular F···F contacts (2.660, 2.549, and 2.629 Å). However, this is not expected to be the reason for the asymmetry of the central pentagon. Four C–CF_3 distances lie in the range 1.531–1.598 Å.

Apparent genetic connections between isomers characterized in this work and some others are marked by arrows in Figure 5. In order to understand whether the synthetic products observed can be rationalized by kinetic arguments that do not require the consideration of rearrangements of addends, we carried out extensive quantum chemical calculations on the possible molecular and radical products on the sequential addition pathway.

Mechanistic Considerations

Though it can hardly be disputed that the basic route of trifluoromethylation involves radical addition of CF_3 groups, specific details of this process are still in question. While high-temperature hydrogenation and halogenation of fullerenes generally results in a very limited number of isomers and are supposed to be thermodynamically controlled by some sort of rearrangement (e.g., "fluorine dance"),[38] the addition of CF_3 groups provides a wealth of isomers for any degree of addition (see, for example, refs.[6,15]). On the one hand, this could reflect a higher number of structures of comparable stability due to steric unavailability of the most compact addition patterns that prove to be most preferable for smaller addends.[39] On the other hand, there is always a possibility of kinetic control in the process of trifluoromethylation. In order to understand whether the synthetic products observed in the present study and detected in earlier NMR work[4,6] can be rationalized with the use of kinetic arguments that do not require consideration of the rearrangements of addends, we have carried out extensive quantum chemical calculations (see Exp. Sect. for details) on the possible molecular and radical products on the sequential addition pathway.

Various approaches to the prediction of regiochemical effects in organic molecules are known, such as the consideration of boundary orbitals and charge distribution, and Fukui functions. Unfortunately, these approaches do not seem that reliable, in our experience, in the case of fullerene derivatives with their quasi-degenerate HOMOs and LUMOs and small atomic charges due to delocalization over a large number of atoms. Instead, we decided to choose an approach based on the Bell–Evans–Polanyi (BEP) principle that postulates a correlation between the reaction rate and reaction enthalpy for groups of sufficiently similar reactions. The BEP principle thus makes it possible to find the most probable addition sites for the $(n + 1)$th CF_3 group on a given $C_{60}(CF_3)_n$ cage by calculation of the relative stability of all possible $C_{60}(CF_3)_{n+1}$ products of attachment. When considering the addition to a certain set of $C_{60}(CF_3)_n$ structures, one would thus need to compare the highest attachment energies observed for these different precursors.

An alternative approach that can be useful in the case of addition to radical intermediates is based on the spin-density criterion. In spite of strong delocalization of the electron density over the fullerene cage, the unpaired electron is generally found to be delocalized only in the proximity of the attached CF_3 groups, providing sufficiently high and, consequently, meaningful atomic spin populations. The spin-density approach requires, unfortunately, the imposition of some additional restrictions on adjacent attachment, such as the exclusion of sterically hindered *ortho* positions in spite of the fact that they are generally characterized by the highest spin density. However, this exclusion cannot be absolute because of the existence of the skew pentagonal isomer of $C_{60}(CF_3)_6$ with an *ortho* contact,[16,23] so the BEP considerations seem to be more reliable.

It should be mentioned that analogous approaches have already been successfully tested in fullerene chemistry. Detailed theoretical analysis of sequential fluorination of C_{60} from the thermodynamic and magnetic points of view[24] have revealed possible pathways to some of the experimentally characterized fullerene fluorides and thus explained their formation. However, this analysis, having been confined within the continuous *S* and *T* motifs of addition, has led to some compounds like $C_{60}F_8$ with two isolated fluorine atoms being overlooked.[40] Another interesting example is the application of the BEP principle to a sort of "inverse problem", that is, the estimation of enthalpies and activation energies as a function of the degree of fluorination on the basis of time-resolved analysis of synthetic products.[25,41,42] It has been confirmed experimentally that changes in the above enthalpies due to different choices of fluorinating agents can, indeed, result in drastic changes in the major products that agree with predictions based on the enthalpy–activation-energy linear correlation. In particular, it has been shown how to switch the C_{60}/solid fluorinating agent system between producing $C_{60}F_{18}$ and $C_{60}F_{36}$.

That said, we used the following algorithm to model kinetic pathways. Addition of the first two CF_3 groups to the C_{60} cage is likely to provide only the experimental *para*-$C_{60}(CF_3)_2$ isomer. This structure is separated by at least 33 kJ mol^{-1} from all other possible isomers and its formation is also favored by the spin-density criterion. Further addition can be treated as follows: It is stated that only *para*-$C_{60}(CF_3)_2$-based $C_{60}(CF_3)_3^{\cdot}$ isomers can form that are characterized by the highest relative energy of attachment of the third CF_3 group, that is, the thermodynamically most stable isomers within some given energy range. Selection of these isomers makes it possible to proceed to $C_{60}(CF_3)_4$ by consideration of all the products of addition of the fourth CF_3 group to any of the selected $C_{60}(CF_3)_3^{\cdot}$ precursors. In their turn, the isomers of $C_{60}(CF_3)_4$ thus obtained are ranged according to the calculated relative attachment energy of the fourth CF_3 group and the leading structures are selected in a similar way as possible precursors of $C_{60}(CF_3)_5^{\cdot}$ intermediates. This selection procedure can be repeated both for radical and closed-shell compounds until one covers the desired range of degrees of addition in order to predict all those closed-shell $C_{60}(CF_3)_{2n}$ structures that form during the sequential addition process. It should be noted, however, that some of these structures will undergo further addition more rapidly than others and thus will not accumulate in the synthetic mixture. Prediction of the composition of the synthetic mixture by using the kinetic assumptions mentioned above may thus require comparison of the absolute energies of attachment in the $C_{60}(CF_3)_{2n}$–$C_{60}(CF_3)_{2n+1}^{\cdot}$ pairs. Lower attachment energy values indi-

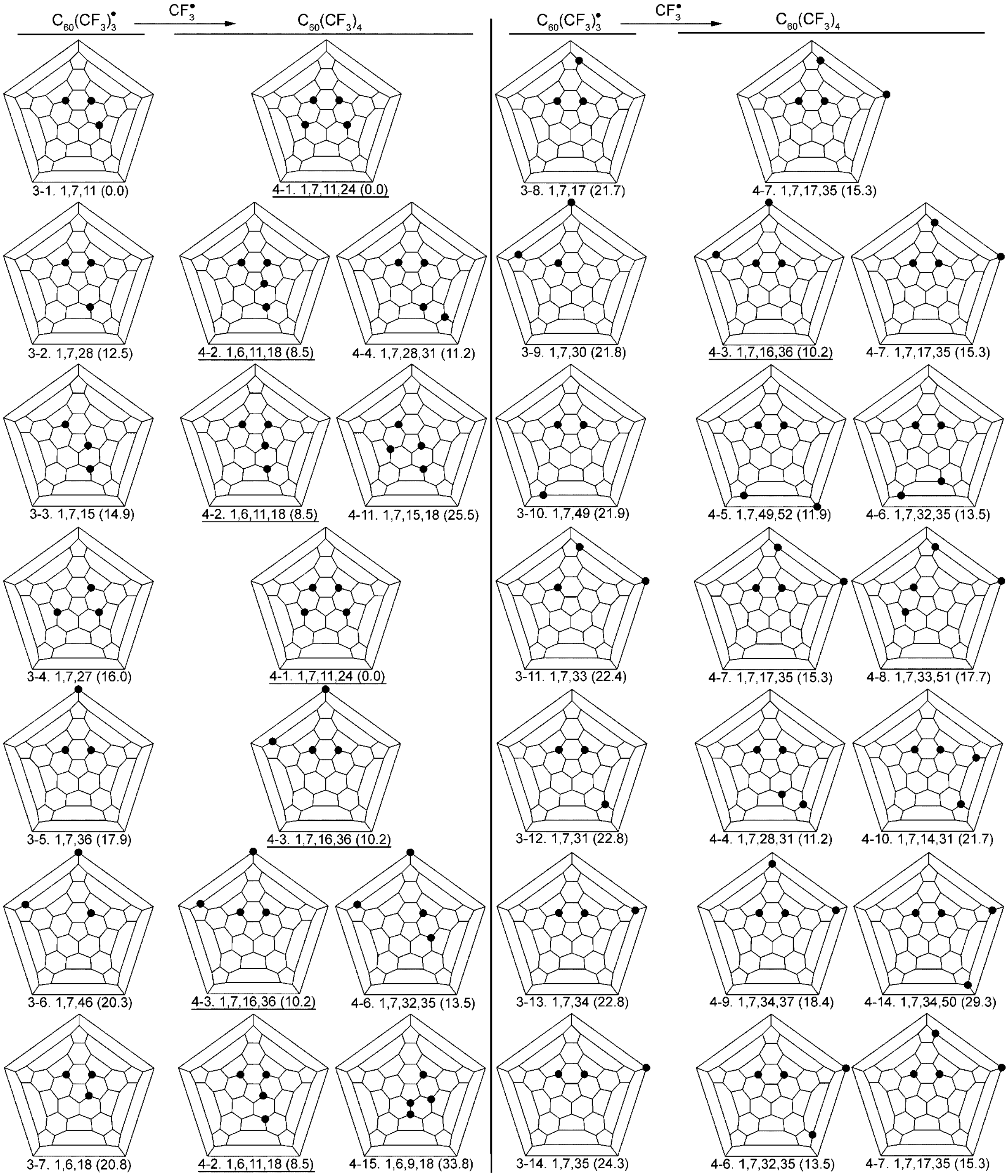

Figure 6. DFT energies [kJ mol^{-1}], IUPAC lowest-locant abbreviations of the lowest $C_{60}(CF_3)_3^{\cdot}$ precursors and their most probable $C_{60}(CF_3)_4$ products. Isomers are denoted with two Arabic numbers, the first one for the number of CF_3 groups and the second one for the sequential number of the isomer given in the order of relative stability. The experimentally observed isomers are underlined.

cate a greater chance of surviving further trifluoromethylation. Much faster barrier-free recombination of CF_3 and $C_{60}(CF_3)_{2n+1}^{\cdot}$ radicals to give $C_{60}(CF_3)_{2n+2}$ should not contribute to the rate of trifluoromethylation, the addition energies of this stage being responsible for regiochemical aspects only.

Even the initial survey of the $C_{60}(CF_3)_3^{\cdot}$ and $C_{60}(CF_3)_4$ isomers reveals promising results that evidence the workability of the approach employed. As shown in Figure 6, the experimentally observed isomers of $C_{60}(CF_3)_4$ [isomers 4-2 (II) and 4-3 (I)] and $C_{60}(CF_3)_4O$, clearly arising from the easily oxidized (C_s-p^3)-$C_{60}(CF_3)_4$ (4-1) isomer (the latter involves a fulvene motif possessing high reactivity),[37,43] can be formed from the most stable $C_{60}(CF_3)_3^{\cdot}$ precursors that lie within only 20 kJ mol^{-1}. Moreover, each of them can be formed by two or more pathways and, prior to considering further trifluoromethylation, are predicted to be the most abundant, followed, perhaps, by isomers 4-4, 4-6, 4-7, and, maybe, 4-5. These seven compounds are likely to be among the eight isomers of $C_{60}(CF_3)_4$ detected by HPLC–EIMS.[6] It should be noted that the three NMR patterns of $C_{60}(CF_3)_4$ reported in ref.[6] are consistent with the structures of isomers 4-2, 4-3, and 4-4, taking into account the proper interpretation of the observed spin–spin interactions as 1,3 and 1,4 couplings.[4] Although it is harder to locate these eight compounds among the rest of the isomers, it seems likely that consideration of $C_{60}(CF_3)_3^{\cdot}$ precursors within the range 20–25 kJ mol^{-1} provides all the relevant candidates. Thus, the energy range of 25 kJ mol^{-1} seems sufficient to search for possible precursors.

The most important pathways of the $C_{60}(CF_3)_4 \rightarrow C_{60}(CF_3)_5^{\cdot} \rightarrow C_{60}(CF_3)_6$ transformations that start from the above-mentioned isomers 4-4, 4-6, 4-7, and 4-11 of $C_{60}(CF_3)_4$ are given, owing to their extensive size, in the Supporting Information. The highest-energy addition of the 5th CF_3 group to the above $C_{60}(CF_3)_4$ isomers was found to differ insignificantly. We would prefer to refrain from quantitative estimation of the competitive rates of their trifluoromethylation on the basis of the number of pathways, as listed in the Supporting Information, and to restrict ourselves to the analysis of the likely addition products. The isomers of $C_{60}(CF_3)_6$ structurally characterized herein are given in Figure 5e,f,h. These isomers are also likely to follow from the NMR patterns published previously[4,6] together with the other two structures of $C_{60}(CF_3)_6$ shown in Figure 5g,i. As one can see, all five compounds are, indeed, accessible by the most probable pathways listed in the Supporting Information, together with a number of other $C_{60}(CF_3)_6$ isomers. It can be expected that the listed isomers overlap considerably with those 13 isomers of $C_{60}(CF_3)_6$ detected previously.[6]

It would be of particular interest to trace subsequent trifluoromethylation up to $C_{60}(CF_3)_{10}$ and $C_{60}(CF_3)_{12}$ and to rationalize the formation of such isomers as 1,6,12,15,18,23,25,41,45,57-$C_{60}(CF_3)_{10}$ with two *mpppm* loops of CF_3 groups, with isomers 6-2, 6-3, 6-4, 6-13, and 6-14 of $C_{60}(CF_3)_6$ acting as precursors, or (S_6)-$C_{60}(CF_3)_{12}$, with isomer 6-6 of $C_{60}(CF_3)_6$ as a possible precursor. The determination of sufficiently probable pathways that yield these compounds would be an important test of validity of our model. As one can see, however, the results of our approach look very promising even in the present state.

Conclusions

A set of $C_{60}(CF_3)_n$ compounds with n = 2–10 have been successfully synthesized and isolated. This enabled the first molecular structure characterization of six of the synthesized compounds by single-crystal X-ray diffraction. In addition to filling in some gaps in our knowledge of trifluoromethylated fullerenes, this allowed a kinetic model to be proposed for the sequential trifluoromethylation of fullerenes based on the BEP principle. Further structural examination of the isolated lower CF_3 derivatives of C_{60} will be of considerable importance for definitive verification of the first promising results of our model approach.

Experimental Section

Reagents and Solvents: The fullerene C_{60} (99.95%) was a product of Term-USA. HPLC-grade toluene and hexane (99.8%), silver(I) trifluoroacetate (AgTFA, Acros Organics, 98%), 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB, Fluka, ≥99%) were used as received.

Mass Spectrometry: Negative-ion MALDI mass spectrometry was used to analyze reaction products, sublimation fractions, and HPLC fractions. A Bruker AutoFlex II reflectron time-of-flight mass spectrometer equipped with an N_2 laser (337 nm, 1 ns pulse) was used. DCTB was chosen as the matrix, the matrix-to-analyte ratio being 1000–4000. Sample preparation was performed with the use of toluene as solvent. Each mass spectrum was the sum of at least 300 laser shots.

High-Performance Liquid Chromatography: HPLC analyses were carried out with the use of an Agilent Technologies System Model 1100 instrument equipped with a diode-array detector (DAD) and a temperature-controlled Cosmosil Buckyprep 4.6 mm × 25 cm column (Nacalai Tesque Inc.). Further HPLC separation was carried out with the use of a Waters 1500 chromatographic system equipped with a dual wavelength UV/Vis detector and a 10 mm × 25 cm column (Nacalai Tesque Inc.). Toluene (99.8%, Khimmed, Russia), hexane (99.7%, Khimmed, Russia), and their mixtures were used as eluents. The UV/Vis spectra of toluene solutions were obtained with a DAD in the 290–950 nm range with 2 nm resolution.

Preparation and Purification of $C_{60}(CF_3)_n$ (n = 2, 4, 6, 8, 10): A mixture of C_{60} and CF_3COOAg (C_{60}/AgTFA molar ratio varied from 1:3.4 to 1:36.0) was thoroughly ground and placed in a glass tube that was subsequently transferred to a closed copper tube. The copper container was then heated at 300–340 °C in a tube furnace for 1–3 h. The reaction product was subjected to step-by-step sublimation under vacuum (10^{-2} Torr) at 420, 480, and 520 °C (see Table 1). Each sublimation fraction collected in the cold zone was weighed and analyzed by using MALDI mass spectrometry and HPLC. The sublimed fractions were combined and the resulting mixture was separated by HPLC (Cosmosil Buckyprep 10 mm × 25 cm column, either toluene or toluene/hexane mixtures as eluents with a flow rate of 4.6 mL min^{-1} and monitored at

290 nm). Finally, 19 chromatographic fractions, each predominantly containing a single compound (except fractions 1, 4, 7, 10, and 12, see Table 2) were isolated. The total yields of the isolated $C_{60}(CF_3)_n$ isomers and the isomeric ratios are given in Table 4.

Table 4. Total yields and isomeric ratios of some $C_{60}(CF_3)_n$ compounds isolated by HPLC.

$C_{60}(CF_3)_n$	Yield [%]	Isomeric ratio
$C_{60}(CF_3)_2$	12	1 isomer
$C_{60}(CF_3)_4$	7	2 isomers, 4:1 ratio
$C_{60}(CF_3)_6$	11	4 isomers, 1:3:33:7 ratio
$C_{60}(CF_3)_8$	5	3 isomers, 17:5:2 ratio
Recovered C_{60}	35	–

X-ray Crystallography: The fractions obtained after HPLC separation (each ca. 10–30 mL) were reduced by concentration to 2–3 mL and then transferred into vessels for further slow concentration to give crystalline material. Data collection for the crystal of $C_{60}(CF_3)_2\cdot C_6H_5(CH_3)$ was carried out with an image plate diffractometer (IPDS2, Stoe, Mo-K_α, λ = 0.71073 Å, 150 K). The crystals of all the other compounds were too small to use this laboratory equipment. Data collection for these crystals was performed with a MAR345 image plate (or a MAR225 with a CCD detector) at 100 K using synchrotron radiation at the BESSY storage ring (λ = 0.9100 Å), PSF BL 14.2 (or 14.1), of the Free University of Berlin, Germany. Crystallographic data for the eight trifluoromethylated [60]fullerenes along with details of data collection and structure refinement are given in Table 5. Owing to the presence of only light elements in the crystal structures and the small size of the crystals, absorption correction was not applied in all cases. Crystal structures were solved by direct methods (SHELXS-97)[44] or by the use of the shake-and-bake program SHELXD[45] [for $C_{60}(CF_3)_6$-IV]. The structures were then extended and refined with SHELXL-97.[46] The crystals of $C_{60}(CF_3)_2\cdot C_6H_5(CH_3)$ contain an ordered toluene molecule of solvation, whereas the toluene molecules in the crystals of $C_{60}(CF_3)_4O\cdot 0.5C_6H_5(CH_3)$ and $C_{60}(CF_3)_6\cdot 0.5C_6H_5(CH_3)$ (isomer IV) are statistically disordered around an inversion center. The accuracy of the latter structure is somewhat worse [the estimated standard deviations (esd's) of the C–F and C–C bond lengths are 0.011–0.016 Å] than that of $C_{60}(CF_3)_6$-IV (esd's 0.008–0.010 Å) and, especially, of the other structures investigated in this work which have esd's of the C–F and C–C bond lengths of between 0.002 and 0.005 Å. CCDC-646060 to -646067 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum Chemical Calculations: Molecular structures were calculated at the DFT level of theory by using the PRIRODA package[47] and the PBE functional.[48] The TZ2P-quality basis set was used for both carbon and fluorine atoms. The quantum chemical code employed expansion of the electron density in an auxiliary basis set to accelerate the evaluation of the coulomb and exchange-correlation terms. Preliminary geometries were obtained from AM1 calculations (PC GAMESS).[49]

Supporting Information (see footnote on the first page of this article): UV/Vis spectra of $C_{60}(CF_3)_6$-I–IV and $C_{60}(CF_3)_8$-I–III isomers, calculation details and the DFT energies of lowest

Table 5. Crystallographic data and some details of data collection and structure refinement for trifluoromethylated [60]fullerenes.

Compound Isomer (Solvent)	$C_{60}(CF_3)_2$ (toluene)	$C_{60}(CF_3)_4$ I	$C_{60}(CF_3)_4$ II	$C_{60}(CF_3)_4O$ (0.5 toluene)
Crystal dmns [mm]	0.5 × 0.5 × 0.25	0.04 × 0.04 × 0.01	0.05 × 0.05 × 0.01	0.03 × 0.03 × 0.02
Symmetry	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [Å]	12.282(1)	19.8146(9)	9.9144(2)	12.9972(6)
b [Å]	10.1464(5)	9.8860(7)	11.5544(3)	16.5253(6)
c [Å]	14.615(1)	17.396(1)	15.8102(4)	18.4792(7)
α [°]	90	90	87.997(1)	90
β [°]	103.748(7)	94.372(4)	81.087(1)	107.607(3)
γ [°]	90	90	71.279(1)	90
V [Å]^3	1769.1(2)	3397.7(3)	1694.39(7)	3783.1(3)
Z	2	4	2	4
$N_{\text{refl.}}/N_{\text{param.}}$	11959/677	5585/685	4865/686	6569/740
R_1/wR_2	0.055/0.140	0.058/0.152	0.059/0.162	0.051/0.143
Compound Isomer (Solvent)	$C_{60}(CF_3)_6$ II	$C_{60}(CF_3)_6$ III	$C_{60}(CF_3)_6$ IV (0.5toluene)	$C_{60}(CF_3)_{10}$ I
Crystal dmns [mm]	0.1 × 0.01 × 0.01	0.1 × 0.03 × 0.03	0.05 × 0.05 × 0.03	0.05 × 0.05 × 0.02
Symmetry	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	9.9382(2)	10.0850(7)	9.964(1)	21.1725(2)
b [Å]	20.4433(5)	12.363(1)	12.188(1)	11.1778(1)
c [Å]	19.2406(5)	15.776(2)	18.961(1)	39.4419(5)
α [°]	90	91.050(6)	91.54(1)	90
β [°]	103.326(1)	98.009(7)	103.04(1)	99.0521(6)
γ [°]	90	99.201(6)	113.24(1)	90
V [Å]^3	3803.9(2)	1921.1(3)	2043.9(3)	9218.1(2)
Z	4	2	2	8
$N_{\text{refl.}}/N_{\text{param.}}$	5732/757	3540/758	4900/803	7831/902
R_1/wR_2	0.042/0.108	0.058/0.143	0.097/0.303	0.045/0.123

$C_{60}(CF_3)_4$ precursors and their most probable $C_{60}(CF_3)_5$ and $C_{60}(CF_3)_6$ products.

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