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SYNTHESIS, ISOLATION, AND X-RAY STRUCTURAL CHARACTERIZATION OF TRIFLUOROMETHYLATED C_{90} FULLERENES: $C_{90}(30)(CF_3)_{18}$ AND $C_{90}(35)(CF_3)_{14}$

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Two CF_3 derivatives of C_{90}, $C_{90}(30)(CF_3)_{18}$ and $C_{90}(35)(CF_3)_{14}$, have been isolated via HPLC from the products of a high-temperature trifluoromethylation of a C_{76}–C_{96} fullerene mixture with CF_3I. Their molecular structures were determined by single crystal X-ray crystallography using synchrotron radiation. The addition patterns of the new compounds are discussed in comparison with those of the corresponding chlorinated C_{90}.

Keywords: Fullerenes, C_{90}, Trifluoromethylation, HPLC, Structure elucidation.

1. Introduction

Compared to C_{60} and C_{70}, the investigation of higher fullerenes has been hampered by their relatively low abundance in fullerene soot and due to the existence of cage isomers [1]. Structural characterization of pristine higher fullerenes is typically accomplished by means of ^{13}C NMR spectroscopy, which provides information on molecular symmetries. However, identification of higher fullerenes by this conventional method is not unambiguous in many cases since several isomers may exhibit the same molecular symmetry [2,3]. An efficient alternative is chemical derivatization of higher fullerenes followed by isolation and structural characterization of the derivatives thus obtained, as exemplified by several examples for C_{76}–C_{96} [4-12].

C_{90} belongs to the group of higher fullerenes with magic ($6n$) number of carbon atoms, which usually possess higher abundance and richer isomerism compared to their neighboring members [13]. For C_{90}, there are 46 topologically possible isomers obeying the Isolated Pentagon Rule (IPR) [1]. Experimentally, ^{13}C NMR spectra of chromatographic C_{90} fractions were interpreted as showing the existence of five isomers of C_{2v}, C_s, C_2, C_1, and C_2 symmetry [14,15]. A comparison between the experimental and theoretically predicted ^{13}C NMR shifts allowed the establishment of most probable carbon cages, 28 (C_2), 30 (C_1), 32 (C_1), 35 (C_s), 40 (C_2), 45 (C_2) and 46 (C_{2v}), which are present in the C_{90} fractions [16]. X-ray crystallographic study of co-crystals of C_{90} from three HPLC fractions (obtained from arc-discharge of Sm_2O_3-doped graphite rods) with Ni^{II}(OEP) (OEP - octaethylporphirin) resulted in the structural confirmation of three isomers of pristine C_{90}, 1 (D_{5h}), 30, and 32 [17,18].

A trifluoromethylated derivative of C_{90}, $C_{90}(CF_3)_{12}$, was suggested to contain C_1-$C_{90}(32)$ cage on the basis of its ^{19}F NMR spectrum [19]. X-ray crystallographic investigation of $C_{90}Cl_n$(n = 22, 24, 28, and 32) unambiguously confirmed the C_{90} cages nos. 28, 30, 32, 34 (C_s), 35, and 46 and significantly contributed to the study of their reactivity towards inorganic chlorides [20,21].

Herein, we report the synthesis, HPLC isolation, and X-ray structure elucidation of trifluoromethylated derivatives of two C_{90} isomers, $C_{90}(30)(CF_3)_{18}$ and $C_{90}(35)(CF_3)_{14}$. Addition patterns are discussed and compared with those of the corresponding chlorinated C_{90}.

2. Results

A starting higher fullerene mixture (35-45 mg; MER Corp.) contained C_{76}–C_{96} fullerenes with the highest abundance of C_{84} and small admixtures of C_{60} and C_{70} [22]. The reaction with CF_3I was performed at 420 °C in a glass ampoule for 48 h, whereas the reaction at 560 °C (in a quartz ampoule) lasted only 1 h (see [23] for more details). In both cases, the trifluoromethylation products sublimed in the colder parts of the ampoules contained mixtures of fullerene$(CF_3)_{2n}$ derivatives with $2n$ in the range of 12 – 20 according to MALDI TOF mass spectrometric analyses (fig. 1).

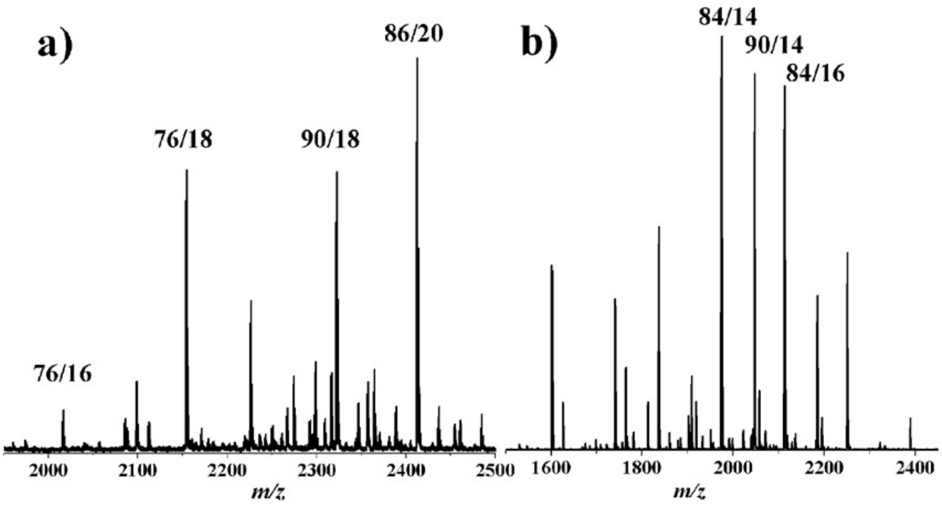

FIG. 1. Mass spectra of trifluoromethylation products. (a) reaction at 420 °C; (b) reaction at 560 °C. The compositions of $C_{2m}(CF_3)_{2n}$ derivatives are given as $2m/2n$.

The product obtained at 420 °C was subjected to a two-step HPLC separation in hexane (Buckyprep column, 10 mm i.d. × 250 mm, flow rate 4.6 mL min^{-1}, monitored at 290 nm). The fraction collected at 13.5 min in the second HPLC step contained mainly a $C_{90}(CF_3)_{18}$ species. Slow concentration of the solution afforded small orange crystals of $C_{90}(CF_3)_{18}\cdot 1.5$ Hexane, which have been investigated by singe crystal X-ray diffraction using synchrotron radiation.

The sublimation product from the synthesis at 560 °C was first separated by HPLC in toluene at the same chromatographic conditions; the fraction eluted between 6.3 and 6.6 min was further separated using a toluene/hexane (1/1) mixture as the eluent. The fraction eluted at 19.4 min contained $C_{90}(CF_3)_{14}$ species (fig. 2). Recrystallization from *o*-dichlorobenzene (*o*-DCB) afforded small red crystals. The crystal structure of $C_{90}(CF_3)_{14}\cdot 2.5$ (o-DCB) was determined by X-ray single crystal crystallography using synchrotron radiation.

Synchrotron X-ray data were collected at 100 K at the BL14.2 at the BESSY storage ring (PSF at the Free University of Berlin, Germany) using a MAR225 CCD detector. Crystallographic data along with some details of data collection and structure refinements are

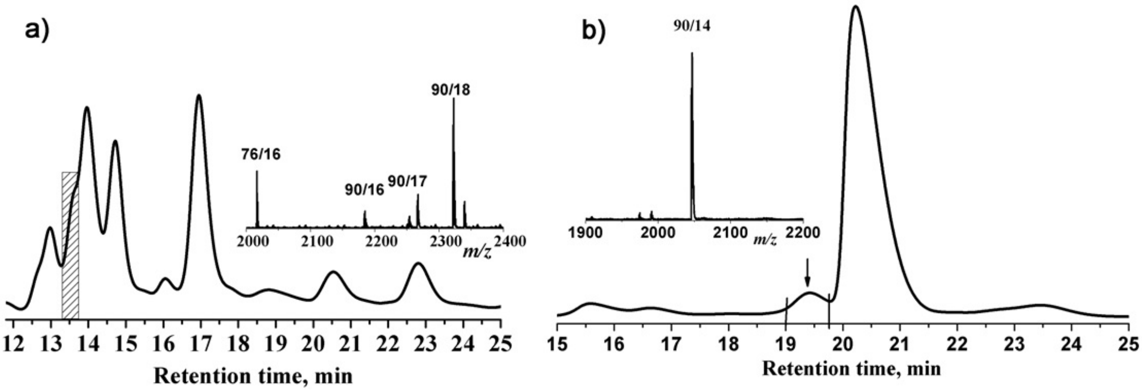

FIG. 2. Chromatographic isolation $C_{90}(CF_3)_{18}$ (a) and $C_{90}(CF_3)_{14}$ (b). The fractions collected are indicated by hatching (a) or arrow (b). Insets show mass spectra of the collected fractions. The compositions of $C_{2m}(CF_3)_{2n}$ derivatives are given as $2m/2n$.

TABLE 1. Crystallographic data and some details of data collection and refinement for $C_{90}(CF_3)_{18}\cdot1.5$Hexane and $C_{90}(CF_3)_{14}\cdot2.5(o\text{-}C_6H_4Cl_2)$

Compound	**$C_{90}(CF_3)_{18}\cdot1.5$Hexane**	**$C_{90}(CF_3)_{14}\cdot2.5(o$-DCB)**
M_r	2452.34	2427.41
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a [Å]	47.661(4)	14.206(1)
b [Å]	22.404(2)	24.343(2)
c [Å]	16.352(1)	25.359(2)
α [$^\circ$]	90	93.312(3)
β [$^\circ$]	97.516(6)	99.786(8)
γ [$^\circ$]	90	102.104(3)
V [Å^3]	17311(2)	8410.0(11)
Z	8	4
D_c [g cm^{-3}]	1.882	1.907
Crystal size [mm]	0.02×0.02×0.01	0.05×0.02×0.01
Detector; λ [Å]	MAR225 / 0.9050	MAR225 / 0.8856
Temperature [K]	100	100
θ(max) [deg]	36.94	36.67
Refls collected / R(int)	121922 / 0.051	122394 / 0.191
Data / parameters	17704 / 1712	33354 / 3099
R_1 [$I \geqslant 2\sigma(I)$] / wR_2 (all)	0.060 / 0.160	0.090 / 0.216
$\Delta\rho$ (max / min) [e Å^{-3}]	1.107 / -1.265	0.391 / -0.426

presented in Table 1. The structures were solved with SHELXD and anisotropically refined with SHELXL. In the crystal structure of $C_{90}(CF_3)_{18}\cdot1.5$Hexane, seven CF_3 groups and solvated hexane molecules are strongly disordered. In the crystal structure of $C_{90}(CF_3)_{14}\cdot2.5(o\text{-}C_6H_4Cl_2)$, there are two crystallographically independent $C_{90}(CF_3)_{14}$ molecules. One CF_3 group and three of six independent dichlorobenzene molecules are disordered. Crystallographic data are deposited under CCDC-917604 and -917603, respectively.

3. Discussion

Mass spectrometric MALDI analyses of trifluoromethylation products demonstrate the presence of $C_{90}(CF_3)_{2n}$ species with $2n$ ranging from 12 to 20, however, without information concerning the C_{90} cage connectivity and CF_3 addition patterns. HPLC separation supported by subsequent MALDI MS analyses of separated fractions indicates the occurrence of several different $C_{90}(CF_3)_{2n}$ isomers of the same composition whereas their assignment to specific C_{90} cages remained unknown. Growing crystals from separated fractions followed by X-ray crystallographic structure determination using synchrotron radiation was successful in only two cases of $C_{90}(CF_3)_{14}$ and $C_{90}(CF_3)_{18}$, which are the first examples of unambiguous structural characterization of CF_3 derivatives of C_{90} fullerene (fig. 3).

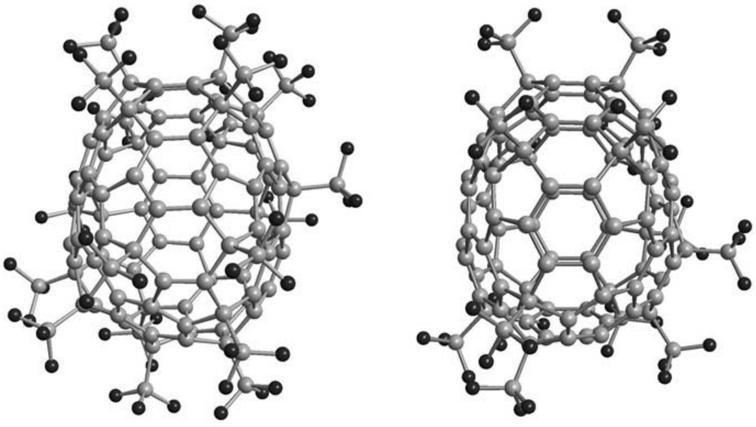

FIG. 3. Projections of the $C_{90}(30)(CF_3)_{18}$ (left) and $C_{90}(35)(CF_3)_{14}$ (right) molecules.

An analysis of the carbon cage connectivities in two molecules reveals that they contain different C_{90} cages, C_s-$C_{90}(35)$ and C_1-$C_{90}(30)$, respectively, i.e., the C_{90} isomers, which have been already confirmed previously either in a pristine form (disordered C_{90} (30) cage in co-crystals with Ni^{II}(OEP) [18]) or as chlorinated derivatives (both 30 and 35 isomers [21]). The description of molecular structures, their addition patterns, and comparison with corresponding chloro derivatives are convenient to perform using Schlegel diagrams (figs. 4 and 5).

In the C_1-$C_{90}(30)(CF_3)_{18}$ molecule, 18 CF_3 groups are attached to a C_1-C_{90} cage exclusively in positions of double hexagon junctions (DHJs), whereas positions of triple hexagon junctions (THJs) remain unoccupied (fig. 4). All cage pentagons contain one or two attached CF_3 groups. The stabilization of the addition pattern is achieved due to the formation of five isolated or partially isolated C=C bonds (av. bond length 1.33 Å) and one partially isolated benzenoid ring (av. C-C bond length 1.39 Å).

The previous X-ray crystallographic characterization of $C_{90}(30)$ fullerene derivative has been performed on the crystal, which contained both $C_{90}(30)Cl_{22}$ and $C_{90}(28)Cl_{24}$ molecules in the unit cell [20,21]. A comparison of the addition patterns of $C_{90}(30)(CF_3)_{18}$

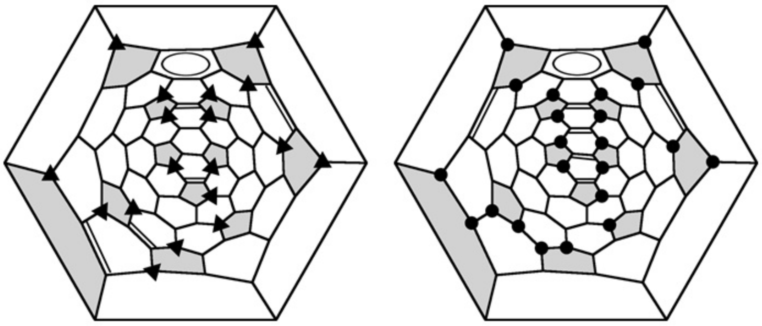

FIG. 4. Schlegel diagrams of $C_{90}(30)(CF_3)_{18}$ (left) and $C_{90}(30)Cl_{22}$ (right). Cage pentagons are highlighted with gray. Black triangles and circles denote attached CF_3 groups and Cl atoms, respectively. The isolated or partially isolated C=C bonds and benzenoid rings are also indicated.

and $C_{90}(30)Cl_{22}$ shows their rather close similarity because of 16 of 18 attachments positions in the former molecule are also occupied in the chlorinated molecule. This results in the same location of three C=C bonds and the benzenoid ring on the $C_{90}(30)$ carbon cage. The differences in the addition patterns concern the attachment of some Cl atoms in adjacent (*ortho*) positions, which are less favourable for bulkier CF_3 groups. For the same reason, the maximum number of CF_3 groups attached to fullerene cages is only 20 (structurally confirmed for C_{70}, C_{84}, C_{88}, and C_{94}) [23-26], whereas several fullerene chlorides with 32-34 Cl atoms are known [27,28].

The addition pattern of $C_{90}(35)(CF_3)_{14}$ of both crystallographically independent (but chemically identical) molecules is characterized by CF_3 attachment exclusively in positions of DHJs and the occupation of all twelve pentagons with CF_3 groups, while two additional CF_3 groups contribute to the formation of an isolated C=C bond (av. bond length 1.32 Å in two independent molecules) on the fullerene C_s-$C_{90}(35)$ cage (fig. 5). Three partially isolated benzenoid rings are also present on the cage (av. C−C bond length 1.40 Å).

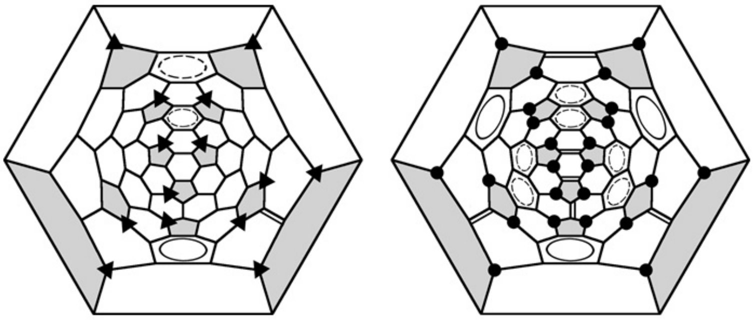

FIG. 5. Schlegel diagrams of $C_{90}(35)(CF_3)_{14}$ (left) and $C_{90}(35)Cl_{24}$ (right). Cage pentagons are highlighted with gray. Black triangles and circles denote attached CF_3 groups and Cl atoms, respectively. The isolated or partially isolated C=C bonds and aromatic substructures are also indicated.

The first crystallographic confirmation of the cage connectivity of $C_{90}(35)$ was reported for $C_{90}(35)Cl_{24}$ and $C_{90}(35)Cl_{28}$, which possess rather similar chlorination patterns [20,21]. A comparison of the addition patterns in C_1-$C_{90}(35)(CF_3)_{14}$ and C_s-$C_{90}(35)Cl_{24}$ demonstrates their similarity due to 12 common attachment positions. However, due to a large number of attached Cl atoms, several additions in *ortho* positions are present in the

$C_{90}(35)Cl_{24}$ molecule. Furthermore, all unoccupied carbon atoms on the C_{90} cage are involved into isolated aromatic substructures or isolated C=C bonds. Usually, CF_3 and chloro derivatives of fullerenes show rather different addition patterns as can be exemplified by the comparison in pairs of $C_{70}(CF_3)_{16}$ [29] and $C_{70}Cl_{16}$ [30] or $C_{76}(CF_3)_{18}$ [31] and $C_{76}Cl_{18}$ [5].

4. Conclusions

Trifluoromethylation of a higher fullerenes mixture followed by HPLC separation, crystallization, and X-ray crystallographic structure determination resulted in the first molecular structures of CF_3 derivatives of C_{90} fullerene, $C_{90}(30)(CF_3)_{18}$ and $C_{90}(35)(CF_3)_{14}$. The comparison of the addition patterns with those of the chlorides of the corresponding C_{90} isomers revealed their close similarities, whereas some differences can be attributed to different sizes of CF_3 group and Cl atom as well as to different numbers of attached groups/atoms. It should be noted that C_{90} isomers 30 and 35 belong to the energetically rather stable isomers according to theoretical calculations [16,32,33]. However, the cage connectivity of the most stable C_2-C_{90} (45) still remains unconfirmed in any experimental report.

Acknowledgments

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