Synthesis, isolation, and X-ray structural characterization
of trifluoromethylated \( C_{78} \) fullerenes:
\( C_{78}(2)(CF_3)_{10/12} \) and \( C_{78}(3)(CF_3)_{12/14} \)

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Four CF \(_3\) derivatives of \( C_{78}, \ C_{78}(2)(CF_3)_{10/12} \) and \( C_{78}(3)(CF_3)_{12/14} \), have been isolated via HPLC from the products of high-temperature trifluoromethylation of a \( C_{76}–C_{96} \) fullerene mixture or a \( C_{78} \) fraction. Their molecular structures were determined by single crystal X-ray crystallography using synchrotron radiation. The addition patterns of the new compounds are compared with each other and with the previously known \( C_{78}(2)(CF_3)_{10} \) and \( C_{78}(3)(CF_3)_{12} \).

**Keywords:** higher fullerenes, \( C_{78} \), trifluoromethylation, HPLC, structure elucidation.

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1. Introduction

Higher fullerenes are characterized by the existence of multiple cage isomers and relatively lower abundance compared to those of \( C_{60} \) and \( C_{70} \), and thus their isolation and further study of their structure and properties are much more difficult. Among the family of higher fullerenes, \( C_{78} \) is present in moderate abundance in fullerene soot because it, along with \( C_{84}, \ C_{90}, \) and \( C_{96} \), belongs to the group of \( C_{6n} \) fullerenes, which have richer isomeric distribution and have been more comprehensively investigated [1]. The \( C_{78} \) fullerene possesses five topologically-distinct isolated pentagon rule (IPR) isomers, \( D_3h-C_{78}(1), \ C_{2v}-C_{78}(2), \ C_{2v}-C_{78}(3), \ D_{3h}-C_{78}(4), \) and \( D_{3h}-C_{78}(5) \) [2]. The \( C_{78}(2) – C_{78}(5) \) isomers can be converted into each other by Stone – Wales rearrangements (SWR) of the pyracylene type, whereas \( C_{78}(1) \) cannot be transformed into other isomers of \( C_{78} \) by SWRs. The abundances of \( C_{78}(1) – C_{78}(3) \) isomers in the fullerene soot are comparable, being dependent on the method of fullerene synthesis [3,4]. The \( D_3-C_{78}(1) \) and \( C_{2v}-C_{78}(2) \) isomers were isolated chromatographically and their cage structures were confirmed by \( ^{13}C \) NMR spectroscopy [3]. At the same time, isomer \( D_{3h}-C_{78}(5) \) is elusive because of a small band gap resulting in a very low solubility; its presence in the fullerene soot could be unambiguously confirmed by the structural study of a CF \(_3\) derivative, \( C_{78}(5)(CF_3)_{12} \) [5]. The \( D_{3h}-C_{78}(4) \) isomer possesses the lowest stability; it has never been found in the fullerene soot. These differences are satisfactorily explained by the differences in the relative formation energies of the \( C_{78}(1) – C_{78}(5) \) isomers [3].

The chemical reactivity of \( C_{78} \) fullerene was studied in cyclopropanation, halogenation, trifluoromethylation, and other reactions [6–14]. Structural characterization of the derivatives was carried out by \(^1H, \ ^{13}C, \) and \(^{19}F \) spectroscopy as well as by X-ray crystallography. Among the most structurally investigated compounds are the bromides, \( C_{78}(2,3)Br_{18} \) [8], chlorides, \( C_{78}(2,3,5)Cl_{18} \) [9–11] and \( C_{78}(1,2)Cl_{30} \) [12,13], and several trifluoromethylated derivatives, \( C_{78}(CF_3)_{2n} \) [14]. For the latter group, structural data obtained by \(^{19}F \) NMR spectroscopy and/or X-ray studies are available for compositions \( C_{78}(3)(CF_3)_{8}, \ C_{78}(1,2)(CF_3)_{10}, \)
and $C_{78}(3,5)(CF_3)_{12}$. The only structural X-ray study of a pentafluoroethyl derivative concerns the compound $C_{78}(2)(C_2F_5)_{10}$ [15]. Investigations of the structural chemistry of CF$_3$ derivatives have been restricted to only several examples, which hampers a comprehensive comparison, even within the derivatives of a distinct isomer of $C_{78}$. The aim of the present study is to expand the chemistry of trifluoromethylated $C_{78}$ derivatives for different isomers. The synthesis, HPLC isolation, and X-ray crystallographic study was performed for several CF$_3$ derivatives of $C_{78}(2)$ and $C_{78}(3)$ with 10 – 14 CF$_3$ groups, which enables comparison with previously known $C_{78}(2,3)(CF_3)_n$ isomers. Addition patterns are discussed in terms of the partial of full occupation of 12 pentagons and formation of aromatic substructures and isolated double C=C bonds on the fullerene cage.

2. Results

Two different starting higher fullerene mixtures were used for trifluoromethylation with gaseous CF$_3$I in quartz ampules following a previously described procedure [16–18]. The mixture of higher fullerenes $C_{76} - C_{96}$ (45 mg; MER Corp.) was trifluoromethylated at 560 °C for 1 h, whereas a $C_{78}$ fraction (60 mg) obtained by HPLC from the $C_{76} - C_{90}$ mixture (Suzhou Dade Carbon Nanotechnology Co.) was reacted at 450 °C for 1.5 h. In both cases, the trifluoromethylation products were sublimed into the colder parts of the ampoules and were collected from there. The products obtained from the $C_{76} - C_{90}$ mixture contained a complex mixture of fullerene(CF$_3$)$_{2n}$ compounds with $2n$ in the range of 12 – 20 according to MALDI TOF mass spectrometric analyses, whereas CF$_3$ derivatives of $C_{78}$ were represented by $C_{78}(CF_3)_{10–16}$ with the maximum abundance of $C_{78}(CF_3)_{12}$ species. Thifluoromethylation of the $C_{78}$ fraction gave a mixture of $C_{78}(CF_3)_{12–18}$ with the highest abundance of $C_{78}(CF_3)_{14}$ and $C_{78}(CF_3)_{16}$. It can be concluded that the lower reaction temperature (450 vs. 560 °C) somewhat shifts the composition in the mixture to the compounds with a large number of CF$_3$ groups. This effect can be explained by the increase of the compound volatility with the increasing number of CF$_3$ groups which influences the kinetics of sublimation in the reaction ampoule [19].

Both products were dissolved in toluene and subjected to HPLC separation in toluene (Buckyprep column, 10 mm i.d. × 250 mm, Nacalai Tesque Corp.) with a flow rate of 4.6 mL·min$^{-1}$ monitored at 290 nm. A typical HPLC trace for the $C_{76–96}(CF_3)_{n}$ product is shown in Fig. 1a. The fractions obtained were further separated by HPLC using toluene/n-hexane mixtures or pure n-hexane. The second-step separation of the toluene fraction, which eluted at 6.4 min, was carried out in a toluene/hexane mixture with $v/v = 1/1$ and a subfraction eluted at 20.2 min gave a compositionally pure $C_{78}(CF_3)_{10}$ compound. Recrystallization from o-dichlorobenzene and p-xylene afforded small crystals which were then investigated by X-ray diffraction with the use of synchrotron radiation, thus revealing molecular structures of $C_{78}(2)(CF_3)_{10}$ in the form of solvates with o-dichlorobenzene and p-xylene, respectively. HPLC separation of the toluene fraction eluted at 6.8 min was performed in a toluene/hexane ($v/v = 1/1$) eluent and a subfraction eluted at 23.1 min afforded a compositionally pure $C_{78}(CF_3)_{12}$ compound. Slow evaporation of solvent gave small crystals which were studied by X-ray crystallography revealing the molecular structure of $C_{78}(2)(CF_3)_{12}$.

Trifluoromethylation products of the $C_{78}$ fraction were also separated by two-step HPLC using the same Buckyprep column. The second-step HPLC of the first toluene fraction in a toluene/hexane 15/85 $v/v$ mixture (not shown) gave a compositionally pure $C_{78}(CF_3)_{12}$ fraction according to MALDI TOF mass-spectrometry. Recrystallization from toluene afforded small crystals of $C_{78}(3)(CF_3)_{12} · 1.5$ (toluene). Finally, the second-step HPLC separation of the first toluene fraction in hexane at flow rate of 1.5 mL·min$^{-1}$ allowed the isolation of several $C_{78}(CF_3)_{12–18}$ compounds (Fig. 1b). A fraction eluted at 17.7 min (indicated by the arrow),
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Fig. 1. HPLC trace of a fullerene$(CF_3)_{2n}$ mixture in toluene (a) and of a $C_{78}(CF_3)_{2n}$ mixture in hexane (b). The collected $C_{78}(CF_3)_{2n}$ fractions are indicated by arrows. The compositions of $C_{78}(CF_3)_{2n}$ derivatives are given as $78(N)/2n$, where $N$ denotes the number of a $C_{78}$ isomer according to the spiral algorithm which contained predominantly $C_{78}(CF_3)_{14}$ admixed by small amount of $C_{78}(CF_3)_{16/18}$, afforded crystals after recrystallization from $p$-xylene. X-ray diffraction revealed the structure of a solvate, $C_{78}(3)(CF_3)_{14} \cdot 2.5 \cdot p$-xylene. Most other peaks of this separation also gave crystals which were shown to be CF$_3$ derivatives of $C_{78}(1)$ with 12 – 18 attached groups. These data will be presented in a separate publication elsewhere later.

Synchrotron X-ray data for the obtained crystals 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 presented in Table 1. The structures were solved with SHELXD and anisotropically refined with SHELXL [20]. All crystal structures except $C_{78}(2)(CF_3)_{12}$ show disordering phenomena, most of which concern disorder of solvent molecules and CF$_3$ groups. The latter was caused by the librational movement of CF$_3$ groups around the C–CF$_3$ bonds or due to statistical overlap of similar molecules in the same crystallographic site. In the crystal structure of $C_{78}(2)(CF_3)_{10} \cdot 0.5 \cdot (o$-dichlorobenzene), one CF$_3$ group and the solvated molecule of $o$-dichlorobenzene are disordered over two positions each. In the crystal structure of $C_{78}(2)(CF_3)_{10} \cdot p$-xylene, the molecule of solvation is strongly disordered over several positions. In the crystal structure of $C_{78}(3)(CF_3)_{12} \cdot 1.5$ (toluene), there is a disorder of two CF$_3$ groups and one toluene molecule. In the crystal structure of $C_{78}(3)(CF_3)_{14} \cdot p$-xylene, there is an overlap of the main molecule with its enantiomer (ca. 16 %) and the molecule of an epoxide, $C_{78}(3)(CF_3)_{14}O$ (ca. 33 %), in the same crystallographic site, which is accompanied by a disorder of seven CF$_3$ groups. Crystallographic data are deposited under CCDC 1408116 – 1408120.

3. Discussion

Mass spectrometric MALDI TOF analyses of the raw trifluoromethylation products demonstrate the presence of $C_{78}(CF_3)_{2n}$ species with $2n$ ranging from 10 to 18, however, without information concerning $C_{78}$ cage connectivity and CF$_3$ addition patterns. HPLC separation supported by subsequent MALDI MS analyses of separated fractions indicated the presence of several different $C_{78}(CF_3)_{2n}$ isomers of the same composition, whereas their assignment to specific $C_{78}$ frameworks remained unknown. Crystal growth from separated fractions, followed by
<table>
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<tr>
<th>Compound</th>
<th>C_{78}(2)(CF_3)_{10}</th>
<th>C_{78}(2)(CF_3)_{12}</th>
<th>C_{78}(3)(CF_3)_{12}</th>
<th>C_{78}(3)(CF_3)_{14}</th>
<th>C_{78}(5)(CF_3)_{14}</th>
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<td>Solvate</td>
<td>0.5 o-C_6H_4Cl_2</td>
<td>p-C_6H_4(CH_3)_2</td>
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<td>1.5 C_6H_4(CH_3)</td>
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<td>Mr</td>
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<td>1733.04</td>
<td>1764.90</td>
<td>1903.10</td>
<td>2174.44</td>
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<td>Space group</td>
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<td>a [Å]</td>
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<td>11.218(1)</td>
<td>11.490(1)</td>
<td>11.878(1)</td>
<td>21.280(2)</td>
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<td>19.022(1)</td>
<td>26.243(1)</td>
<td>12.374(1)</td>
<td>17.637(1)</td>
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<td>c [Å]</td>
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<td>28.842(2)</td>
<td>19.154(1)</td>
<td>24.267(2)</td>
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<td>3259.1(5)</td>
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<td>D_c [g·cm^{-3}]</td>
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<td>87675 / 0.025</td>
<td>91568 / 0.028</td>
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<td>13634 / 1252</td>
<td>18585 / 1463</td>
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<tr>
<td>R_1[I ≥ 2σ(I)]/ wR_2 (all)</td>
<td>0.087 / 0.233</td>
<td>0.048 / 0.114</td>
<td>0.054 / 0.135</td>
<td>0.077 / 0.174</td>
<td>0.116 / 0.290</td>
</tr>
<tr>
<td>Δρ(max / min)[e Å^{-3}]</td>
<td>0.90 / –0.49</td>
<td>0.57 / –0.44</td>
<td>0.56 / –0.39</td>
<td>0.55 / –0.55</td>
<td>0.67 / –0.50</td>
</tr>
</tbody>
</table>

¹The crystal structure contains ca. 30 % admixture of an epoxide, C_{78}(3)(CF_3)_{14}O, localized in the same crystallographic site.

Single crystal X-ray structure determination using synchrotron radiation was successful for only some cases of C_{78}(CF_3)_{10–14}, which are additional examples of unambiguous structural characterization of CF_3 derivatives for the most abundant isomers 1 – 3 of C_{78} fullerene (Fig. 2). CF_3 derivatives of the elusive C_{78}(5) have not been detected, most probably, due to its very low content (or perhaps very low solubility), whereas the isolation of CF_3 derivatives of C_{78}(4) was not even expected because of its obvious absence in the fullerene soot.

Two of the three CF_3 derivatives of C_{78}(2) isolated and structurally characterized in this work contain the same C_{8s}-C_{78}(2)(CF_3)_{10} molecule, which is known from Ref. [14] and designated there as 78-10-2. The differences concern only the solvate molecules, o-dichlorobenzene,
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The addition pattern of 12 CF_3 groups in the structure of C_{2v}-C_{78}(2)(CF_3)_{12} is interesting in several aspects. Importantly, the structure of C_{2v}-C_{78}(2)(CF_3)_{12} retains the symmetry of the pristine C_{2v}-C_{78}(2) cage (Fig. 3). Its addition pattern contains the addition patterns of both C_{s}-C_{78}(2)(CF_3)_{10} and C_{2}-C_{78}(2)(CF_3)_{10} as substructures. Most probably, both molecules serve as precursors of C_{2v}-C_{78}(2)(CF_3)_{12} in the course of trifluoromehylation. The attachment of two CF_3 groups transforms the p^9 ribbon into a p^{12} loop. At the same time, two nearly isolated benzenoid rings become fully isolated and one carbon-carbon bond becomes an isolated double C=C bond, both acting as additional stabilizing factors. It should be noted that the addition pattern of C_{2v}-C_{78}(2)(CF_3)_{12} exhibits an extremely rare example of a fullerene(CF_3)_{12} structure.
where not all pentagons are occupied by CF₃ groups. In fact, two pentagons remain unsubsti-
tuted in the experimentally determined structure. If the addition of two more groups occurs in
these pentagons (for example, in the left-most and right-most positions of free pentagons), the
hypothetical C₅₋C₇₈(2)(CF₃)₁₂ molecule with all 12 pentagons occupied by CF₃ groups would
contain two groups attached in isolated positions, which can be considered as a destabilizing
feature. Indeed, DFT calculations of the formation energies of the hypothetical and the exper-
imentally determined C₇₈(2)(CF₃)₁₂ molecules revealed that the former is 10.1 kJ·mol⁻¹ less
stable than the latter.

Structural relations between C₇₈(2)(CF₃)₁₀ and C₇₈(2)(CF₃)₁₂ molecules are very similar
to those reported for C₈₄(18)(CF₃)₁₀ and C₈₄(18)(CF₃)₁₂ [18]. The addition pattern of C₅₋C₈₄(18)(CF₃)₁₀ contains a single p⁹ ribbon which is very similar to that in C₅₋C₇₈(2)(CF₃)₁₀.
Though the experimentally determined structure of C₅₋C₈₄(18)(CF₃)₁₂ is characterized by the
attachment of twelve CF₃ groups in all pentagons (with two additional groups in a separate
p-C₆(CF₃)₂ hexagon), a theoretically predicted structure with a p¹² loop (8₄(18)/12 − 3 in [18]),
i.e., an analog of C₇₈(2)(CF₃)₁₂, is only 6 kJ·mol⁻¹ less stable so that in its presence in the
 trifluoromethylation products of C₈₄(18) cannot be excluded. In fact, the only example of
addition-free pentagons in the molecule with more than 12 addends on a fullerene cage has
been reported for C₈₈(17)Cl₁₆ containing two such pentagons [21]. The stabilizing factors of
this structure include the formation of one isolated benzenoid ring and three isolated C=C bonds
on the fullerene C₈₈(17) cage.

The crystal structure of C₇₈(3)(CF₃)₁₂ · 1.5(toluene) contains the C₁₋C₇₈(3)(CF₃)₁₂ mole-
cule, which is known from the previous structure determination for a solvate with bromobenzene
(7₈-12-2) [14]. Its asymmetric addition pattern of 12 CF₃ groups occupying all 12 pentagons
is characterized by the presence of a short p⁹ ribbon and a longer p⁶mp ribbon (m for a
meta-C₆(CF₃)₂ hexagon) on the fullerene cage (Fig. 3). Thus, it differs considerably from the
additions pattern of C₇₈(2)(CF₃)₁₂ which comprises a loop of exclusively para additions
in C₆(CF₃)₂ hexagons (p¹₂) and containing two unoccupied pentagons. For comparison, the
addition pattern of C₂₋C₇₈(5)(CF₃)₁₂ [5] contains a single p¹₁ ribbon of 12 CF₃ groups on the
C₇₈(5) cage which differs from the C₇₈(3) cage by the position of only one C–C bond.

The molecular structure of C₇₈(3)(CF₃)₁₄ was determined for the first time. Its addition
pattern consists of a short pmp ribbon and a long p¹₀ ribbon of edge-sharing C₆(CF₃)₂ hexagons
(Fig. 3). There is an isolated double C=C bond and an isolated triphenylene-like substructure on
the fullerene cage. 13 of 14 CF₃ groups are arranged mirror-symmetrically on the cage. This
feature explains the existence of packing errors with a number of enantiomeric molecules located in
the same crystallographic sites as the main molecules in the crystal structure. C₁₋C₇₈(3)(CF₃)₁₄
and C₁₋C₇₈(3)(CF₃)₁₂ possess only seven CF₃ groups attached in common positions. Therefore,
the latter cannot be regarded as a precursor of the former.

4. Conclusions

Trifluoromethylation of a higher fullerenes mixture and a C₇₈ fraction followed by HPLC
separation, crystallization, and X-ray diffraction studies resulted in structure determination of
several CF₃ derivatives, C₇₈(2,3)(CF₃)₁₀−₁₄. Although the carbon cages of C₂₋C₇₈(2) and C₂₋C₇₈(3) differ by the position of only one C–C bond [2], the addition patterns of the derivatives
with equal numbers of CF₃ groups, C₇₈(2,3)(CF₃)₁₂, differ significantly. A similar phenomenon
has also been found for (CF₃)₁₂ derivatives of isomers C₈₄(22) and C₈₄(23), which also differ
by the position of one bond on the carbon cages [16,17]. In contrast, the addition patterns of
C₇₈X₁₈ (X = Cl, Br) are the same for isomers C₇₈(2), C₇₈(3), and even C₇₈(5) [8–11] which
give rise to co-crystallization phenomena for these halides [8,11] thus demonstrating the
levelling effect for a large number of addends on the addition patterns of fullerene derivatives with similar carbon cages. The existence of similar effects for CF$_3$ derivatives of isomers of C$_{78}$ could be clarified by structural study of compounds with 16 – 18 attached groups.

Acknowledgements

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