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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 mixtures 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_3-$C_{78}(1)$, 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, halogenations, 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_3I 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_{96} 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 $\mathrm{mL{\cdot}min^{-1}}$ 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 $C_{78}(3)(CF_3)_{12} \cdot 1.5$ (toluene). Finally, the second-step HPLC separation of the first toluene fraction in hexane at flow rate of 1.5 $\mathrm{mL{\cdot}min^{-1}}$ 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),

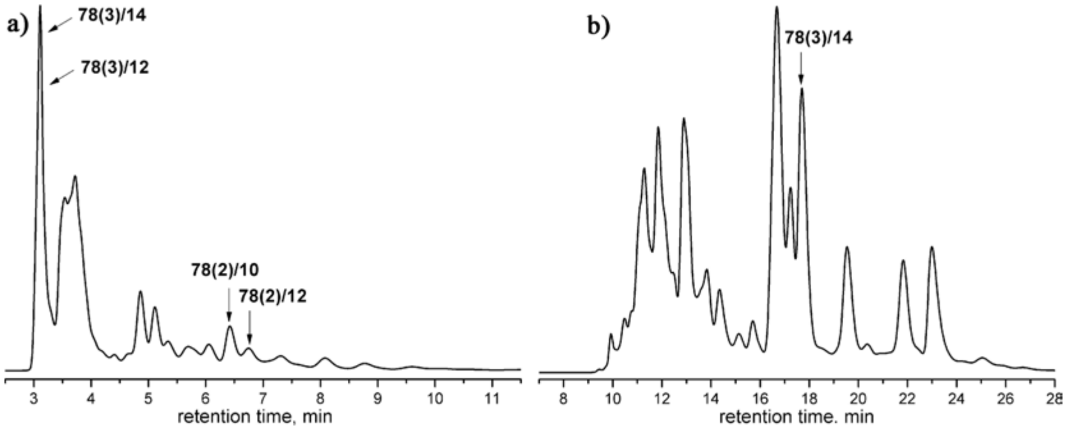

FIG. 1. HPLC trace of a fullerene$(CF_3)_{2n}$ mixture in toluene (a) and of a $C_{78}(CF_3)_{2n}$ mixture in hexane (b). The collected $C_{78}(CF_3)_{2n}$ fractions are indicated by arrows. The compositions of $C_{78}(CF_3)_{2n}$ derivatives are given as $78(N)/2n$, where N denotes the number of a C_{78} 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, $C_{78}(3)(CF_3)_{14} \cdot 2.5$ (*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 $C_{78}(2)(CF_3)_{10} \cdot 0.5$ (*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 1. Crystallographic data and details of data collection and refinement for $C_{78}(CF_3)_{2n}$ compounds

Compound	$C_{78}(2)(CF_3)_{10}$	$C_{78}(2)(CF_3)_{10}$	$C_{78}(2)(CF_3)_{12}$	$C_{78}(3)(CF_3)_{12}$	$C_{78}(3)(CF_3)_{14}$[1]
Solvate	0.5 o-$C_6H_4Cl_2$	p-$C_6H_4(CH_3)_2$	–	1.5 $C_6H_5(CH_3)$	2.5 p-$C_6H_4(CH_3)_2$
Mr	1700.38	1733.04	1764.90	1903.10	2174.44
Crystal system	triclinic	orthorhombic	monoclinic	triclinic	monoclinic
Space group	$P\,\bar{1}$	$P2_12_12_1$	$P2_{1/n}$	$P\,\bar{1}$	$C2/c$
a [Å]	11.537(1)	11.218(1)	11.490(1)	11.878(1)	21.280(2)
b [Å]	14.421(1)	19.022(1)	26.243(1)	12.374(1)	17.637(1)
c [Å]	18.038(1)	28.842(2)	19.154(1)	24.267(2)	42.567(3)
α [°]	85.60(1)	90	90	89.485(9)	90
β [°]	84.155(9)	90	91.409(10)	86.869(8)	90.02(1)
γ [°]	73.83	90	90	66.236(8)	90
V [Å^3]	2863.7(4)	6174.6(8)	5773.8(6)	3259.1(5)	15976(2)
Z	2	4	4	2	8
D_c [g·cm^{-3}]	1.972	1.870	2.030	1.939	1.807
Crystal size [mm]	0.02×0.02 ×0.01	0.03×0.03 ×0.01	0.03×0.02 ×0.01	0.03×0.03 ×0.01	0.03×0.03 ×0.01
λ [Å]	0.9050	0.8434	0.8434	0.8434	0.8551
Temperature [K]	100	100	100	100	100
θ(max)[deg]	36.66	33.70	34.21	34.74	34.75
Refls collected/R(int)	37547 / 0.064	87675 / 0.025	91568 / 0.028	51625 / 0.026	84029 / 0.073
Data / parameters	10391 / 11148	14259 / 1144	13460 / 1135	13634 / 1252	18585 / 1463
$R_1[I \geq 2\sigma(I)]$/ wR_2 (all)	0.087 / 0.233	0.048 / 0.114	0.054 / 0.135	0.077 / 0.174	0.116 / 0.290
$\Delta\rho$(max / min)[e Å^{-3}]	0.90 / –0.49	0.57 / –0.44	0.56 / –0.39	0.55 / –0.55	0.67 / –0.50

[1] The 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_s-$C_{78}(2)(CF_3)_{10}$ molecule, which is known from Ref. [14] and designated there as 78-10-2. The differences concern only the solvate molecules, o-dichlorobenzene,

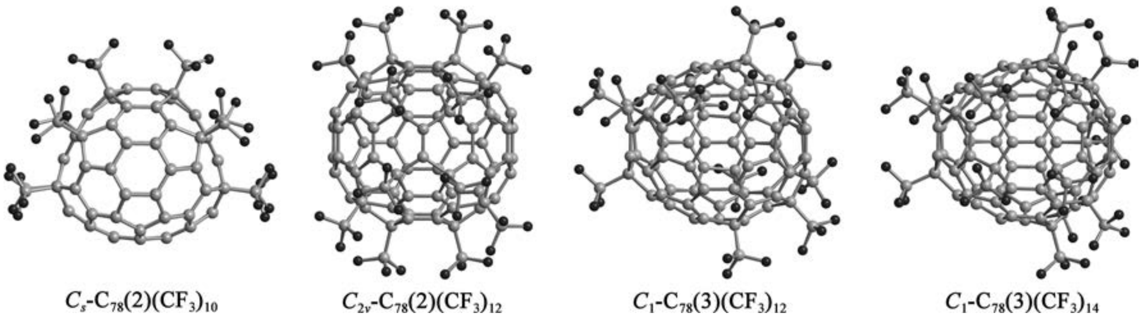

FIG. 2. Projection of the C_s-$C_{78}(2)(CF_3)_{10}$ molecule parallel to the mirror plane; the C_{2v}-$C_{78}(2)(CF_3)_{12}$ molecule is shown along the C_2 axis, whereas the C_1-$C_{78}(3)(CF_3)_{12}$ and C_1-$C_{78}(3)(CF_3)_{14}$ molecules are presented along the C_2 axes of the $C_{78}(3)$ carbon cages

p-xylene, and toluene in [14]. The formation of a toluene solvate with similar unit cell parameters and the space group $P2_1/m$ was also observed in one of our crystallization experiments. The addition pattern of 10 CF_3 groups contains a single ribbon of *para* attachments in nine edge-sharing p-$C_6(CF_3)_2$ hexagons, which is designated as p^9 (Fig. 3). This addition pattern is additionally stabilized by the formation of two nearly isolated benzenoid substructures on the fullerene cage. An isomeric p^4, p^4 structure of C_2 symmetry (78-10-3), which differs by the position of only one CF_3 group (in the same pentagon near the C_2 axis), has been proposed in [14] based on ^{19}F NMR spectroscopy data. Note that the proposed 78-10-3 also contains two stabilizing nearly isolated benzenoid substructures. According to DFT calculations, C_s-$C_{78}(2)(CF_3)_{10}$ is 21.3 kJ·mol^{-1} more stable than the isomer with C_2 symmetry.

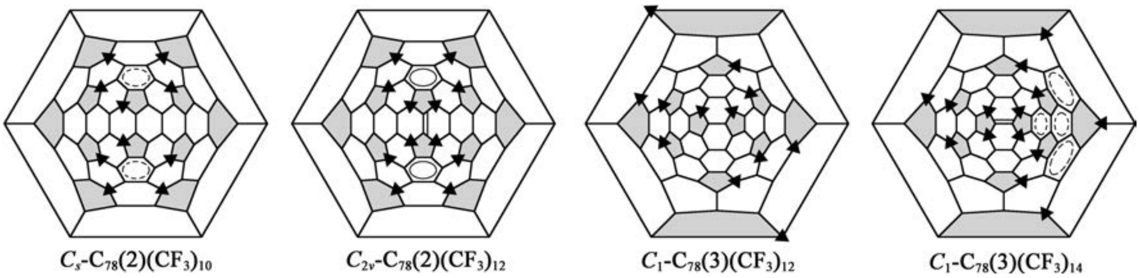

FIG. 3. Schlegel diagrams of C_s-$C_{78}(2)(CF_3)_{10}$, C_{2v}-$C_{78}(2)(CF_3)_{12}$, C_1-$C_{78}(3)(CF_3)_{12}$, and C_1-$C_{78}(3)(CF_3)_{14}$ molecules. Cage pentagons are highlighted with gray. Black triangles denote the positions of attached CF_3 groups. The isolated C=C bonds are denoted by double lines. Aromatic nearly isolated and isolated benzenoid as well as triphenylene substructures are also indicated

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 CF_3 groups. In fact, two pentagons remain unsubstituted 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 C_s-$C_{78}(2)(CF_3)_{12}$ molecule with all 12 pentagons occupied by CF_3 groups would contains 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 experimentally determined $C_{78}(2)(CF_3)_{12}$ molecules revealed that the former is 10.1 $kJ{\cdot}mol^{-1}$ less stable than the latter.

Structural relations between $C_{78}(2)(CF_3)_{10}$ and $C_{78}(2)(CF_3)_{12}$ molecules are very similar to those reported for $C_{84}(18)(CF_3)_{10}$ and $C_{84}(18)(CF_3)_{12}$ [18]. The addition pattern of C_s-$C_{84}(18)(CF_3)_{10}$ contains a single p^9 ribbon which is very similar to that in C_s-$C_{78}(2)(CF_3)_{10}$. Though the experimentally determined structure of C_s-$C_{84}(18)(CF_3)_{12}$ is characterized by the attachment of twelve CF_3 groups in all pentagons (with two additional groups in a separate p-$C_6(CF_3)_2$ hexagon), a theoretically predicted structure with a p^{12} loop ($84(18)/12-3$ in [18]), i.e., an analog of $C_{78}(2)(CF_3)_{12}$, is only 6 $kJ{\cdot}mol^{-1}$ less stable so that its presence in the trifluoromethylation products of $C_{84}(18)$ 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 $C_{88}(17)Cl_{16}$ 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 $C_{88}(17)$ cage.

The crystal structure of $C_{78}(3)(CF_3)_{12} \cdot 1.5$(toluene) contains the C_1-$C_{78}(3)(CF_3)_{12}$ molecule, which is known from the previous structure determination for a solvate with bromobenzene (78-12-2) [14]. Its asymmetric addition pattern of 12 CF_3 groups occupying all 12 pentagons is characterized by the presence of a short p^3 ribbon and a longer p^5mp ribbon (m for a *meta*-$C_6(CF_3)_2$ hexagon) on the fullerene cage (Fig. 3). Thus, it differs considerably from the additions pattern of $C_{78}(2)(CF_3)_{12}$ which comprises a loop of exclusively *para* additions in $C_6(CF_3)_2$ hexagons (p^{12}) and containing two unoccupied pentagons. For comparison, the addition pattern of C_2-$C_{78}(5)(CF_3)_{12}$ [5] contains a single p^{11} ribbon of 12 CF_3 groups on the $C_{78}(5)$ cage which differs from the $C_{78}(3)$ cage by the position of only one C–C bond.

The molecular structure of $C_{78}(3)(CF_3)_{14}$ was determined for the first time. Its addition pattern consists of a short *pmp* ribbon and a long p^{10} ribbon of edge-sharing $C_6(CF_3)_2$ hexagons (Fig. 3). There is an isolated double C=C bond and an isolated triphenylene-like substructure on the fullerene cage. 13 of 14 CF_3 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. C_1-$C_{78}(3)(CF_3)_{14}$ and C_1-$C_{78}(3)(CF_3)_{12}$ possess only seven CF_3 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 C_{78} fraction followed by HPLC separation, crystallization, and X-ray diffraction studies resulted in structure determination of several CF_3 derivatives, $C_{78}(2,3)(CF_3)_{10-14}$. Although the carbon cages of C_{2v}-$C_{78}(2)$ and C_{2v}–$C_{78}(3)$ differ by the position of only one C–C bond [2], the addition patterns of the derivatives with equal numbers of CF_3 groups, $C_{78}(2,3)(CF_3)_{12}$, differ significantly. A similar phenomenon has also been found for $(CF_3)_{12}$ derivatives of isomers $C_{84}(22)$ and $C_{84}(23)$, which also differ by the position of one bond on the carbon cages [16, 17]. In contrast, the addition patterns of $C_{78}X_{18}$ (X = Cl, Br) are the same for isomers $C_{78}(2)$, $C_{78}(3)$, and even $C_{78}(5)$ [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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