INTRODUCTION

Fullerenes that are formed by arc-discharge evaporation of graphite obey the isolated pentagon rule (IPR) [1]. Unlike the most well-known fullerenes (C_{60} and C_{70}), higher fullerenes composed of more than 74 atoms have several IPR isomers with different carbon cages. For example, 2, 9, 24, and 19 IPR isomers can exist for fullerenes C_{76}, C_{82}, C_{84}, and C_{86}, respectively. Studies of higher fullerenes are limited because they are available in small amounts, as well as due to the difficulties in isolating individual fullerenes from mixtures. High-performance liquid chromatography (HPLC) is often used for the separation of fullerenes [2]. However, in many cases, particularly for higher fullerenes that have a large number of isomers, this method is not sufficiently efficient.

Data on fullerenes can also be obtained by their functionalization followed by the separation and structure determination of their derivatives by single-crystal X-ray diffraction [3]. For example, the structures of several isomers of fullerene C_{64} have been determined for their metallated or perfluoroalkyl derivatives [4–6]. In these studies not only were the carbon cages determined, but also information on the reactivity of higher fullerenes and addition patterns for particular addends was obtained. The distinguishing feature of higher fullerenes C_{76} and C_{82} is that they are extracted from the fullerene soot as only one IPR isomer each. These isomers are denoted as D_2-C_{76} (1) [7] and C_2-C_{82} (3) [8], where the sequence number of the isomer (according to the classification proposed in [1]) is given in parentheses. The carbon cage connectivity of C_{60} (1) was additionally confirmed by X-ray diffraction studies of its derivatives. The molecular structures of the chlorides C_{76}Cl_{18} [9] and C_{82}Cl_{32} [10] and the trifluoromethyl derivatives of C_{76}(CF_3)_{14-18} [11] were determined. The carbon cage connectivity of fullerene C_{82} (3) was confirmed by X-ray diffraction studies of its trifluoromethyl derivatives C_{82}(CF_3)_{12} and C_{82}(CF_3)_{18} [12].

In this study we report the crystal and molecular structures of C_{76}(CF_3)_{16}, C_{76}(CF_3)_{18}, C_{82}(CF_3)_{16}, and C_{82}(CF_3)_{18}, which are trifluoromethyl derivatives of the fullerenes D_2-C_{76} (isomer 1) and C_2-C_{82} (isomer 3).

EXPERIMENTAL

Trifluoromethyl derivatives of fullerene were synthesized by the reaction of a mixture of higher fullerene C_{76}–C_{90} (Merck Corp.) with trifluoriodomethane CF_3I in ampoules at 400–420°C. The method for the synthesis of trifluoromethyl derivatives of fullerenes was described in detail in [13]. The reaction product containing trifluoromethyl derivatives of higher fullerenes was dissolved in hexane. The chromatographic separation was performed by HPLC with a 10 × 250-mm Cosmous Buckyprep column, hexane as the eluent, and the flow rate of 4.6 ml min^{-1}. The fractions were analyzed by MALDI mass spectrometry (DCTB matrix). Several fractions with retention times from 4 to 15 min, which were isolated at a flow rate of 4.6 ml min^{-1}, contained derivatives of fullerene C_{76} and C_{82} with 12–18 attached trifluoromethyl groups. The slow evaporation of the hexane fractions with retention times of 5.1 and 12.1 min afforded small single crystals of C_{76}(CF_3)_{16–II} and -III. Crystals of C_{76}(CF_3)_{18} · 0.74 C_6H_5(CH_3) were obtained from the fraction eluted at 4.2 min after recrystallization from...
toulene. Crystals of C_{82}(CF_3)_{16} \cdot 0.83C_6H_{14} were pre-
pipitated from the fraction with a retention time of 5.4 min, whereas the crystal solvate C_{82}(CF_3)_{16} \cdot 3.8C_7H_8 was obtained from the same fraction after recrystallization from toluene. For the fraction eluted at 4.4 min, crystals of C_{82}(CF_3)_{16} \cdot 0.5C_5H_4(CH_3)_2 were grown by recrystallization from para-xylene.

The X-ray diffraction data were collected at 100 K using synchrotron radiation at the beamline BL 14.2 (PSF, Free University of Berlin, BESSY, Germany) equipped with a CCD detector (MAR225, Bruker). No absorption corrections were applied. The structures were solved with the use of the SHELXS and SHELXD program packages and refined using the SHELXL program package with anisotropic displacement parameters for non-hydrogen atoms [14]. The hydrogen atoms of the ordered solvent molecules were included in the refinement in geometrically calculated positions. Crystallographic data and details of data collection and structure refinements for C_{76}(CF_3)_{16-18} and C_{82}(CF_3)_{16-18} are given in the table. The complete crystallographic data for six structures were deposited with the Cambridge Crystallographic Data Centre (CCDC 821346–821351).

In the crystal structures of C_{76}(CF_3)_{16}, there are asymmetric molecules with the ordered carbon cage and most of the CF_3 groups. In the molecules of the isomers C_{76}(CF_3)_{16-18} (denoted as 76-16-II and 76-16-III), two CF_3 groups and one CF_3 group, respectively, are disordered around the C–CF_3 axes; the occupancies of the major conformation are in the range of 0.83–0.91. The crystal structure of C_{82}(CF_3)_{16} \cdot 0.83C_6H_{14} (denoted as 82-16-I and 82-16-II) is characterized by the formal disorder of the cage in the form of two pairs of cross-intersecting C–C bonds. This type of disorder is analyzed in the Results and Discussion section. In addition, one of the CF_3 groups is disordered over two orientations around the C–CF_3 axis.

In the crystal structure of C_{82}(CF_3)_{16} \cdot 3.8C_7H_8, a more complex disorder is observed. One-half of the C_{82}(CF_3)_{16} molecule is a crystallographically independent unit in which two cage carbon atoms are disordered over four positions, each with half occupancy, so that their pairs form a cross consisting of two mutually perpendicular C–C bonds. The mirror symmetry of the whole molecule results in the presence of two crosses, i.e., in the formal disorder of two pairs of C–C bonds. In addition, two out of nine independent CF_3 groups attached to the fullerene cage of C_{82} have half-occupancies. Solvent (toluene) molecules, which are also characterized by partial occupancy, were located in the region of these two groups. Several CF_3 groups are orientationally disordered around the C–CF_3 bonds. Additional (ordered and disor-
dered) toluene molecules are present in the cavities of the packing of the fullerene molecules. The connectiv-
ity of the C_{82} cage and the addition patterns of the addends in the C_{82}(CF_3)_{16} and C_{82}(CF_3)_{18} molecules are analyzed in the next section.

**RESULTS AND DISCUSSION**

The MALDI mass-spectrometric analysis of the trifluoromethylation products of a mixture of higher fullerenes showed the presence of several compounds of the compositions C_{76}(CF_3)_n and C_{82}(CF_3)_n containing from 12 to 18 CF_3 groups. It should be noted that compounds with these numbers of attached groups can have numerous isomers due to different addition patterns. In this study we crystallographically characterized two isomers of C_{76}(CF_3)_{16} (76-16-II and 76-16-III) and one isomer of C_{76}(CF_3)_{18} as a crystal solvate with toluene, which are derivatives of fullerene D_{3d}–C_{76} (isomer 1). The structures of the molecules 76-16-II and 76-16-III are shown in Fig. 1. The molecular structures of the isomer 76-16-I, C_{76}(CF_3)_{14} (76-14-I), and two isomers of C_{76}(CF_3)_{18} (76-18-I and 76-18-II) were determined in [11]. The isomer of C_{76}(CF_3)_{18} investigated in the present study was identical to the isomer 76-18-II, but the crystal packings of these compounds are somewhat different due to the presence of different solvent molecules (toluene and hexane [11]).

Based on the similarity and difference in the addition patterns of CF_3 groups, the four isomers of C_{76}(CF_3)_{14-18} studied earlier were assigned to two fa-
milies. Two new isomers of C_{76}(CF_3)_{16} can be assigned to one of the two families based on the consideration of addition patterns of CF_3 groups to the C_{76} cage. It is convenient to compare the addition patterns with the use of Schlegel diagrams representing two-dimen-
sional schematic projections of the fullerene cage (graphs), where the addend positions are shown. Figure 2 presents the Schlegel diagrams for six C_{76}(CF_3)_{14-18} molecules whose molecular structures were determined by X-ray diffraction. In addition to the Schlegel diagrams, abbreviation codes for C_{76}(CF_3)_{14-18} according to the IUPAC rules [15] are given:

76-14-I: 5,20,28,34,37,44,47,51,53,56,58,60,68,71–C_{76}(CF_3)_{14}
76-16-I: 6,9,23,25,30,33,38,41,47,50,52,59,61,63,68,70–C_{76}(CF_3)_{16}
76-16-II: 5,20,28,34,37,44,47,51,53,56,58,60,63,68,71–C_{76}(CF_3)_{16}
76-16-III: 5,20,28,30,32,35,37,41,44,47,51,54,60,63,68,71–C_{76}(CF_3)_{16}
76-18-I: 6,9,14,23,25,30,33,36,38,39,41,47,50,52,57,63,68,70–C_{76}(CF_3)_{18}