Crystal structures of chloroform solvates of fullerenes

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The chloroform solvates of C_{60} and C_{70} fullerenes and of the C_{60}/C_{70} mixture were synthesized and investigated by X-ray powder diffraction.

Key words: C_{60} and C_{70} fullerenes, C_{60}/C_{70} mixture, chloroform, solvate, X-ray powder diffraction study.

Donor-acceptor solvates are often formed upon extraction of fullerenes from soots and in other chemical processes involving fullerenes and organic solvents. Since soots contain fullerenes of several types (C_{60}, C_{70}, *etc.*), the products can consist of mixed compounds with different fullerene ratios.

In the present work, we synthesized three chloroform crystal solvates, *viz.*, $C_{60}(CHCl_3)_2$ (**1**), $(C_{60})_{0.83}(C_{70})_{0.17}(CHCl_3)_2$ (**2**), and $C_{70}(CHCl_3)_2$ (**3**), and studied them by the X-ray powder diffraction method. Compound **1** has been structurally characterized; in particular, the data on the parameters of the hexagonal unit cell (a = 10.08, c = 10.11 Å) and the space group $P6/mmm$ are availbale in the literature.[1]

Experimental

Compound **2** was synthesized with the use of a fullerene-containing carbon condensate prepared in a plasma-chemical reactor in a helium stream (2 L min^{-1}) at atmospheric pressure.[2,3] Under these conditions, a mixture of fullerenes with a high C_{70} content (15—30%) was formed.[4,5] The fullerene mixture was extracted with benzene followed by the removal of the solvent *in vacuo* on a VUP-5 apparatus.

Crystal solvates **1** and **3** were synthesized from pure C_{60} (99.8%) and C_{70} (98%) prepared at the Kurchatov Institute of Atomic Energy of the Russian Academy of Sciences. Fullerenes C_{60} and C_{70} and a C_{60}/C_{70} mixture were dissolved in chloroform and dried in a vacuum evaporator at 300 K.

The C_{60}/C_{70} ratio in compound **2** was determined based on a comparison of the unit-cell volumes of pure C_{60} and C_{70} and crystal solvates **1** and **2** on the assumption that this ratio linearly depends on the volume. The calculated value agrees with the data of mass spectrometry (83% of C_{60}, 16% of C_{70}, and 1% of higher fullerenes), IR spectroscopy (82% of C_{60} and 18% of C_{70}), and electronic absorption spectroscopy (82.5% of C_{60} and 17.5% of C_{70}).

The crystal structures of the compounds were studied by the X-ray powder diffraction method on a DRON-4 diffractometer. The samples were deposited on planar silicon plates, which were cut perpendicular to a nonreflecting direction. We employed Cu-Kα radiation monochromatized with a planar graphite monochromator using a reflected beam. The X-ray diffraction patterns were scanned using the θ—2θ techniques with a step of 0.02° and accumulation at a point during 5 s.

The unit cell parameters were determined from the positions of the peaks using the ITO program.[6] The structures were determined and refined with the use of a modified and improved version of the DBWS-9006PC program[7] (Table 1).

The crystal structures were established based on analysis of X-ray powder patterns by the full-profile method. The integrated intensities of reflections were estimated from the profile using a known algorithm.[8] There is one fullerene molecule per unit cell as follows from its volume. The coordinates of independent atoms of C_{60} fullerene for compound **1** were determined by comparing the molecular symmetry ($\bar{3}m$) with the symmetry of the unit cell, the space group ($P\bar{3}1m$) being

Table 1. Crystallographic characteristics of the compounds

Parameter	$C_{60}(CHCl_3)_2$	$(C_{60})_{0.83}(C_{70})_{0.17}(CHCl_3)_2$	$C_{70}(CHCl_3)_2$
Space group	$P6/mmm$	$P6/mmm$	$P6/mmm$
Z	1	1	1
a/Å	10.099(2)	10.169(3)	10.55(1)
c/Å	10.099(2)	10.228(3)	10.70(1)
V/Å^3	892.0(3)	916.0(5)	1031(2)
d_{calc}/mg m^{-3}	1.786	1.776	1.738
R_{Bragg}	0.081	0.067	—

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chosen. The atoms were located using the idealized model of C_{60} with equal C—C bond lengths.

The positions of the chloroform molecules were found from the difference electron density synthesis. We revealed 10 peaks whose mutual arrangement corresponds closely to the possible positions of the Cl atoms of two $CHCl_3$ molecules adopting three different orientations in the unit cell. The position of the C atom of the $CHCl_3$ molecule was calculated geometrically based on the positions of the Cl atoms. The subsequent refinement of the crystal structure confirmed the proposed model.

The preliminary search for and the refinement of the structure were performed in the space group $P\bar{3}1m$, which corresponds most closely to the symmetry of the C_{60} molecule. However, the better agreement between the calculated and experimental profiles of the X-ray diffraction pattern was achieved within the higher-symmetry space group $P6/mmm$, which is attributable to the presence of orientational disorder in the structure.

Preliminary analysis of the crystal structures of compounds **2** and **3** demonstrated that the modes of packing of the fullerene and chloroform molecules in all three compounds are analogous. The structure of **1** was refined by the Rietveld method,[9] only the atomic coordinates of the $CHCl_3$ molecule being varied (Table 2). The molecular packing is shown in Fig. 1. Selected interatomic distances in $C_{60}(CHCl_3)_2$ (the symmetrically related position (*i*): $y, x-y, z$) are given below:

Bond	C(7)—Cl(1)	C(7)—Cl(2)	Cl(1)—C(2)^i
Interatomic distance/Å	1.68(5)	1.76(4)	3.486(4)

The experimental and calculated X-ray patterns are shown in Fig. 2. The small peak with the maximum at $2\theta = 21.48°$, which is absent in the calculated curve, belongs to an impurity phase.

Results and Discussion

Unlike the close molecular packing in the crystals of pure C_{60} and C_{70}, the arrangements of the fullerene molecules in the chloroform solvates are described by the primitive hexagonal lattice. The cavities in the crystal packing are filled with $CHCl_3$ molecules. Analogous arrangements of the molecules have also been found in the series of other solvates of fullerene, for example, in

Table 2. Atomic coordinates for $C_{60}(CHCl_3)_2$

Atom	*x*	*y*	*z*	*B*/Å^2
C(1)	0.08210	−0.08210	0.32240	3.7(6)[a]
C(2)	0.13350	−0.16410	0.24060	3.7(6)
C(3)	0	−0.30440	0.19250	3.7(6)
C(4)	−0.27000	−0.35300	0.15800	3.7(6)
C(5)	0.13350	0.40540	0.02410	3.7(6)
C(6)	0	−0.35300	0.05770	3.7(6)
Cl(1)	1/3	2/3	0.370(1)	2.4(7)
Cl(2)	0.449(1)	0.898(1)	1/2	2(1)
C(7)	0.273(6)	0.726(6)	1/2	2[b]

[a] The thermal parameters of the C(1)—C(6) atoms were fixed in the course of the refinement.
[b] The thermal parameter of the C(7) atom was not refined.

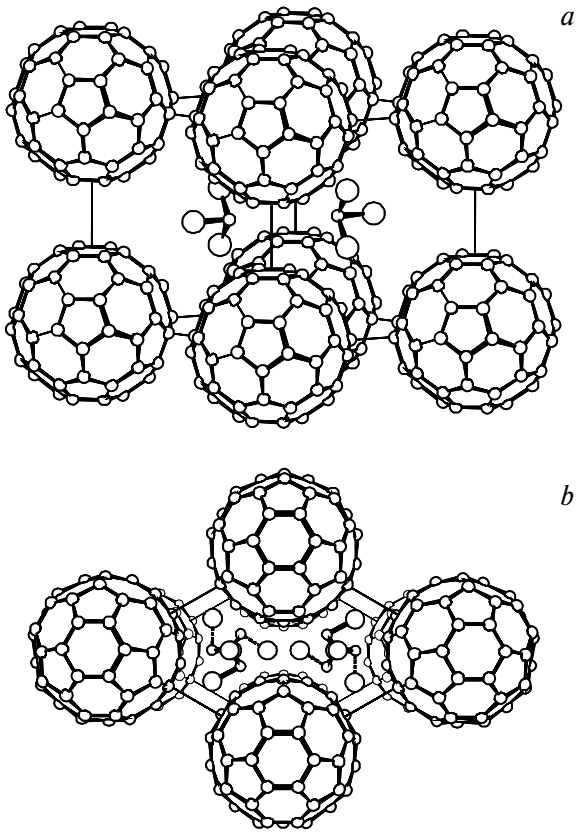

Fig. 1. Crystal structure of $C_{60}(CHCl_3)_2$: *a*) overall view; and *b*) the perspective view along the *c* axis (alternative orientations of the $CHCl_3$ molecules are indicated by dashed lines).

$C_{60}(CHBr_3)_2$ (a = 10.212, c = 10.209 Å)[1] and $C_{60}(CCl_4)_2$ (a = 10.10, c = 10.75 Å).[10] A distorted type of the same packing is typical of compounds crystallized in the triclinic system, *viz.*, of $C_{60}(C_{10}H_{16}N_2)$ (a = 10.124, b = 10.224, c = 10.544 Å, α = 78.24, β = 84.07,

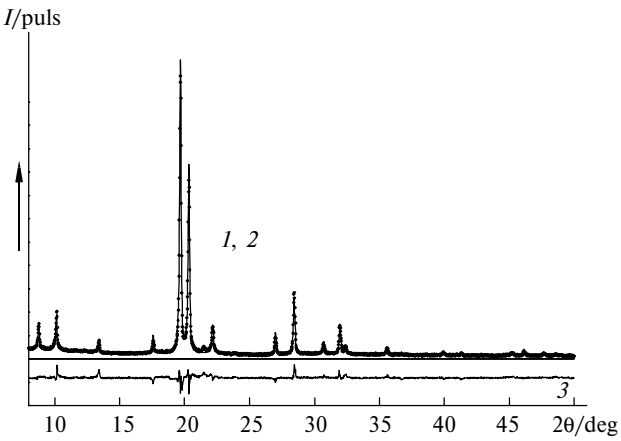

Fig. 2. Experimental (*1*), calculated (*2*), and difference (*3*) profiles of the X-ray diffraction pattern of $C_{60}(CHCl_3)_2$ (the profile *R* factors were R_p = 0.086 and R_{wp} = 0.119). The dotted and solid curves correspond to the experimental and calculated data, respectively.

$\gamma = 59.60°$)[11] and $C_{60}(C_{10}H_{10}Fe)_2$ ($a = 10.084$, $b = 10.528$, $c = 11.306$ Å, $\alpha = 95.29$, $\beta = 90.65$, $\gamma = 118.47°$).[12]

Two of three Cl atoms of the $CHCl_3$ molecule occupy fixed positions in the unit cell. The third Cl(2) atom is disordered over three positions, which are equivalent in the local environment. Taking into account two different positions of the C atom with respect to the Cl_3 plane, it can be concluded that each chloroform molecule has six alternative equivalent orientations in the unit cell (see Fig. 1, *b*). Since the regular packing of the chloroform molecules in the crystal is contradictory to the hexagonal symmetry of the lattice, the molecules adopting different orientations are, apparently, statistically distributed over the unit cells. The fact that the use of the high-symmetry space group *P6/mmm* in the structure refinement has the above-described advantage is also indicative of the orientational disorder of the fullerene molecule. This fact has been noted previously in the study of single crystals of $C_{60}(CHBr_3)_2$.[1]

The distances between the Cl(1) atom and the C atoms of three adjacent C_{60} molecules are smaller than the sum of the van der Waals radii of the Cl and C atoms (3.6 Å), which is indicative of a rather strong intermolecular interaction between the fullerene and chloroform molecules. The shortest distance between the C_{60} molecules in the structure of **1** is 0.07 Å larger than that in pure C_{60}, which bears witness to a weak interaction between the fullerene molecules in the chloroform solvates.

In the crystals of **2** and **3**, the C_{70} molecules occupy positions identical to those occupied by the C_{60} molecules in the crystals of **1**. In the case of crystal solvate **1**, the unit cell parameters *a* and *c* are virtually equal (to within 0.006 Å), whereas the *c* parameters of the crystal lattices of **2** and **3** are noticeably larger than the *a* parameters. Hence it follows that the C_{70} molecules in the crystal solvates are arranged so that their longest axes are oriented along the [001] direction in the crystals. As mentioned above, all three compounds of the series under consideration are characterized by the similar molecular packings. Generalizing the results of the present study, it can be concluded that the crystal solvates $(C_{60})_x(C_{70})_{1-x}(CHCl_3)_2$ ($x = 0...1$) form a continuous series of molecular solid solutions characterized by the primitive hexagonal packing of the fullerene molecules.

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