Physical Chemistry

Crystal and molecular structures of fluorinated derivatives of C_{60} fullerene

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Two solvates of fluorinated derivatives of C_{60} fullerene were studied by single-crystal X-ray diffraction analysis. The crystals of fluorinated fullerene solvate $C_{60}F_{18}\cdot C_6H_5Me$ belong to the monoclinic system with the unit cell parameters $a = 11.532(2)$ Å, $b = 21.501(3)$ Å, $c = 16.261(2)$ Å, $\beta = 101.798(5)°$. The fluorinated fullerene molecule with the approximate symmetry C_{3v} occupies a general position. The crystals of fluorinated fullerene solvate $C_{60}F_{48}\cdot 2C_6H_3Me_3$ belong to the cubic system ($a = 23.138(2)$ Å). The $C_{60}F_{48}$ molecule occupies the special position with the S_6 symmetry. The experimental molecular geometry agrees with the results of quantum-chemical calculations.

Key words: fluorinated fullerenes, X-ray diffraction analysis, *ab initio* calculations.

Extensive studies of fullerenes[1] by various physical methods, including X-ray diffraction analysis, were started after Kratchmer has developed procedures for the preparation of these compounds in macroscale amounts.[2] However, X-ray diffraction studies of fullerenes and their derivatives are hampered due to a low quality of crystals and commonly occurring orientational disorder of the carbon cluster.

Chemical modifications of fullerenes can lead to lowering of the symmetry and ordering of the molecules in the crystals. A number of recent reviews concerned the molecular structures of fullerene derivatives, including donor-acceptor complexes and radical ion salts,[3—5] metallofullerenes,[6,7] π-complexes,[8] polyhydrogenated fullerenes,[9] and polyfluorinated fullerenes.[10] Fluorinated derivatives of buckminsterfullerene, *viz.*, $C_{60}F_{18}$ [11] and $C_{60}F_{48}$,[12] were synthesized in 1996 and 1994, respectively. However, their molecular structures were studied only by IR and NMR spectroscopy[11] and quantum-chemical methods.[13] The X-ray powder data are available for hydrides $C_{60}H_n$ ($n = 36$ [14] and 42 [15]) and solvates of $C_{60}F_n$ ($n = 44$—48) with different solvents.[16,17] Brominated fullerenes $C_{60}Br_6$, $C_{60}Br_8$,[18] and $C_{60}Br_{24}$ [19] were studied as solvates with molecular bromine by X-ray diffraction analysis. Apparently, the molecular structure of $C_{60}Br_{24}$ is to a large extent determined by steric repulsions between the bromine atoms due to which neither two of the bromine atoms can be bound to the adjacent C atoms. In the $C_{60}Br_6$ and $C_{60}Br_8$ molecules, the bromine atoms are compactly arranged on the surface of the fullerene skeleton thus forming an "island".

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In recent years, complete X-ray diffraction studies of fluorinated derivatives of buckminsterfullerene, *viz.*, $C_{60}F_{18}$,[20] $C_{60}F_{18}O$,[21] $C_{60}F_{17}CF_3$,[22] and $C_{60}F_{48}$,[23,24] were carried out. In spite of the fact that the crystal chemistry of these unusual compounds, which are characterized by high polarity of the C—F bonds, is of considerable interest, it has been little investigated. In the present study, we report the molecular and crystal structures of two arene-solvated fluorinated fullerenes, *viz.*, toluene solvate (1 : 1) $C_{60}F_{18} \cdot C_6H_5Me$ (**1**) and mesitylene solvate (1 : 2) $C_{60}F_{48} \cdot 2[1,3,5\text{-}C_6H_3Me_3]$ (**2**), which were established by X-ray diffraction analysis, and discuss the factors responsible for their molecular packings. Earlier, we have presented the results of preliminary X-ray diffraction studies of compounds **1** [20] and **2**.[23]

Experimental

The X-ray diffraction data sets for crystals of **1** and **2** were collected on a single-crystal Bruker SMART diffractometer equipped with a coordinate detector at the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences). Single crystals of **1** and **2** were supplied by O. V. Boltalina and P. A. Troshin (Laboratory of Thermochemistry, Department of Chemistry, M. V. Lomonosov Moscow State University). The crystallographic data and the details of X-ray diffraction studies are given in Table 1.

Table 1. Details of X-ray diffraction studies

Parameter	**1**	**2**
Molecular formula	$C_{60}F_{18} \cdot C_6H_5Me$	$C_{60}F_{48} \cdot 2C_6H_3Me_3$
$2\theta_{max}$/deg	60	45
Crystal system	Monoclinic	Cubic
Space group	$P2_1/n$	$Ia\bar{3}$
Unit cell parameters		
a/Å	11.532(2)	23.138(2)
b/Å	21.501(3)	
c/Å	16.261(2)	
β/deg	101.798(5)	
V/Å^3	3947	12386
Z	4	8
ρ_{calc}/g cm^{-3}	1.943	2.009
k (packing coefficient)	0.73	0.70
μ/mm^{-1}	0.17	0.22
T/K	100	110
Wavelength/Å	0.7107	0.7107
Number of reflections	49263	27973
independent	11565	1346
observed ($F > 4\sigma$)	6426	1115
Number of refinable parameters	798	219
$R(F > 4\sigma)$	0.0494	0.160
wR_2	0.1178	0.357
GOF	0.916	1.053

Toluene solvate **1** crystallizes in the monoclinic system (space group $P2_1/c$). The fluorinated fullerene and solvent molecules are completely ordered and occupy general positions. The structure of **1** was solved by direct methods and refined by the full-matrix least-squares method based on F^2. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were revealed from a series of difference electron density syntheses. The final R factor was 0.049 for 6426 independent observed reflections (see Table 1).

The mesitylene solvate of highly fluorinated fullerene **2** belongs to the cubic system (space group $Ia\bar{3}$). The $C_{60}F_{48}$ molecule occupies a special position with the symmetry $\bar{3}$ (S_6). The solvent molecule is located on a $\bar{3}$ axis. The structure of **2** was solved by direct methods and refined by the full-matrix least-squares method based on F^2. A difference Fourier synthesis showed the orientational disorder of the $C_{60}F_{48}$ molecules and revealed the positions of the C(1′) and C(7′) atoms of the carbon skeleton and of the exopolyhedral F(2′), F(7′), F(8′), F(9′), and F(10′) atoms belonging to the second orientation of the molecule. In this case, the positions of the C(1), C(7), F(1), F(2), and F(8)—F(10) atoms correspond to the predominant orientation of the molecule in the crystal (the occupancy ratio was 35 : 65), whereas the positions of the remaining carbon atoms in the fullerene core and of the F(3)—F(5) atoms for both orientations were not separated and were refined with the occupancy of 1. The positions of the atoms belonging to the less occupied orientation were refined isotropically and the remaining atoms were refined anisotropically. In the final stage of the refinement, the difference synthesis revealed the hydrogen atoms of the mesitylene molecule, which were placed in geometrically calculated positions and refined using the riding model because of the insufficiently large number of the independent observed reflections. The final R value was 0.160. The accuracy of determination did not allow us to discuss the effects of redistribution of the bond lengths in the $C_{60}F_{48}$ molecule. However, the molecular structure and molecular packing in crystal solvate **2** were unambiguously established.

Quantum-chemical calculations were carried out using the GAUSSIAN-98 program package.[25]

Results and Discussion

Solvate of fluorinated fullerene $C_{60}F_{18} \cdot C_6H_5Me$ (1). According to the NMR data,[11] all fluorine atoms in the $C_{60}F_{18}$ molecule are symmetrically bound to one hemisphere of the fullerene core around the C(1)—C(6) face with the noncoordinated C(sp^2) atoms occupying the vertices. The resulting "zone" consisting of 18 sp^3-hybridized carbon atoms separates the nonfluorinated six-membered ring from the π-system of the remaining part of the molecule (Fig. 1). This arrangement of 18 exopolyhedral F atoms has been predicted previously based on the results of semiempirical calculations of the model hydrogenated fullerene[13] and was found recently in the structure of $C_{60}F_{18}O$ established by X-ray diffraction analysis.[21] It should be noted that quite a different structure of fluoride $C_{60}F_{20}$ was proposed based on the

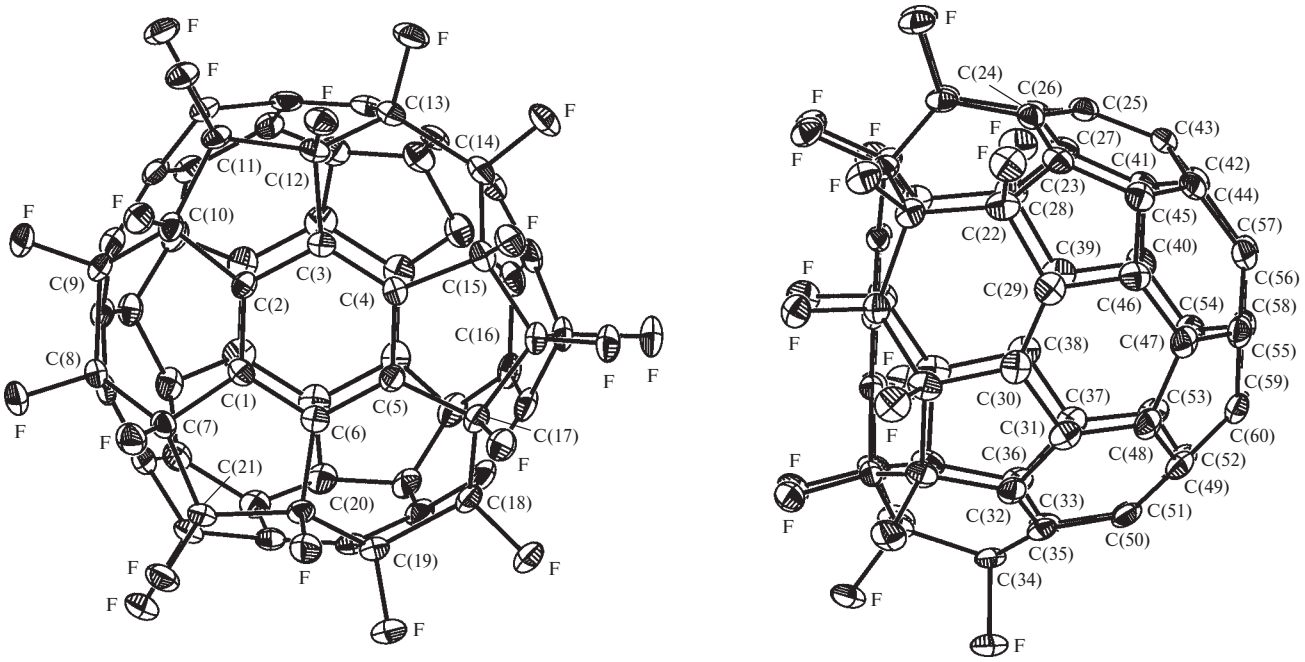

Fig. 1. Overall view of the $C_{60}F_{18}$ molecule and the numbering scheme for the C atoms (two projections). The F atoms are numbered in accordance with the carbon atoms to which they are bound.

^{19}F NMR data. The latter can be described as two coranullene fragments linked through a fluorinated zone.[26] In solvate **1**, the $C_{60}F_{18}$ molecule has the noncrystallographic symmetry C_{3v} with an accuracy of 0.003 Å for the equivalent bond lengths. The residual electron density map (Fig. 2) contains maxima at the midpoints of the C—C bonds, which confirm the high quality of the experimental data.

Previously, the distribution of the attached fragments over the perimeter of the five-membered carbon ring in the C_{60} core has been revealed by NMR spectroscopy in hexachloride $C_{60}Cl_6$ [27] and in products of the replacement of the Cl atoms in this molecule by the phenyl[28] and methyl[29] groups (in the last cited study, the structure of $C_{60}Me_5O_2OH$ was established by X-ray diffraction analysis). Among other derivatives of this series, which reflect the tendency to the formation of a delocalized aromatic π-system in the isolated five-membered ring, we refer to the $C_{60}Ph_5^-Tl^+$ complex with the predominantly ionic structure[30] and the first π-complex in which fullerene is η^5-coordinated through the cyclopentadienyl fragment, *viz.*, $(CO)_2Rh(\eta^5\text{-}C_{60}Me_5)$.[31] Hence, the delocalized "arene" π-electron system would be expected to appear in the isolated six-membered ring of the C_{60} core.[20]

The bond lengths in the $C_{60}F_{18}$ molecule are given in Table 2. We use the Δ_i and ϕ_i parameters (the distance from a particular atom to the center of the molecule and the spherical excess of the carbon atom, respectively) for the description of distortions of the carbon skeleton. The latter parameter is the amount by which the sum of three C—C—C bond angles at a particular carbon atom is smaller than 360° and characterizes the nonplanarity of the environment of the carbon atom in the fullerene cage. In the case of structure **1**, the center of the nondistorted fullerene molecule, which was fitted by least-squares to the carbon skeleton of $C_{60}F_{18}$ taking into account only the back nonfluorinated portion of the molecule (21 carbon atoms), was taken as the center of the cage. In the case of structure **2**, the geometric center of

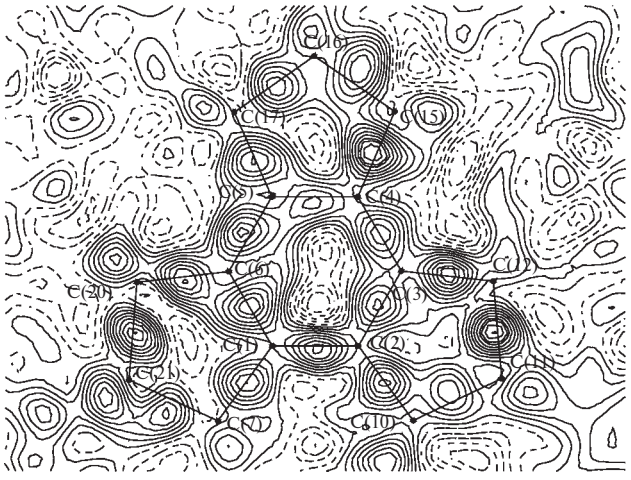

Fig. 2. Final difference electron density synthesis for the $C_{60}F_{18}$ molecule (section in the plane of the aromatic six-membered ring).

Table 2. Bond lengths (d) in the $C_{60}F_{18}$ molecule

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
C(1)—C(6)	1.373(3)	C(16)—C(34)	1.554(3)	C(33)—C(34)	1.520(3)	C(52)—C(60)	1.455(3)
C(1)—C(2)	1.375(3)	C(16)—C(17)	1.620(3)	C(34)—C(35)	1.525(3)	C(53)—C(54)	1.433(3)
C(1)—C(7)	1.475(3)	C(17)—C(18)	1.553(3)	C(35)—C(36)	1.366(3)	C(54)—C(55)	1.455(3)
C(2)—C(3)	1.374(3)	C(18)—C(36)	1.505(3)	C(35)—C(51)	1.436(3)	C(55)—C(56)	1.388(3)
C(2)—C(10)	1.474(3)	C(18)—C(19)	1.677(3)	C(36)—C(37)	1.424(3)	C(55)—C(60)	1.446(3)
C(3)—C(4)	1.369(3)	C(19)—C(38)	1.493(3)	C(37)—C(53)	1.384(3)	C(56)—C(57)	1.445(3)
C(3)—C(12)	1.477(3)	C(19)—C(20)	1.568(3)	C(37)—C(38)	1.432(3)	C(57)—C(58)	1.394(3)
C(4)—C(5)	1.372(3)	C(20)—C(21)	1.624(3)	C(38)—C(39)	1.358(3)	C(58)—C(59)	1.450(3)
C(4)—C(15)	1.481(3)	C(21)—C(22)	1.564(3)	C(39)—C(40)	1.430(3)	C(59)—C(60)	1.380(3)
C(5)—C(6)	1.372(3)	C(22)—C(23)	1.522(3)	C(40)—C(54)	1.393(3)	F(7)—C(7)	1.384(2)
C(5)—C(17)	1.474(3)	C(22)—C(39)	1.533(3)	C(40)—C(41)	1.435(3)	F(8)—C(8)	1.376(2)
C(6)—C(20)	1.476(3)	C(23)—C(24)	1.365(3)	C(41)—C(42)	1.386(3)	F(9)—C(9)	1.383(2)
C(7)—C(8)	1.555(3)	C(23)—C(41)	1.435(3)	C(42)—C(43)	1.438(3)	F(10)—C(10)	1.384(2)
C(7)—C(21)	1.623(3)	C(24)—C(25)	1.420(3)	C(42)—C(56)	1.454(3)	F(11)—C(11)	1.365(2)
C(8)—C(24)	1.504(3)	C(25)—C(43)	1.386(3)	C(43)—C(44)	1.433(3)	F(12)—C(12)	1.390(2)
C(8)—C(9)	1.667(3)	C(25)—C(26)	1.428(3)	C(44)—C(45)	1.381(3)	F(13)—C(13)	1.373(2)
C(9)—C(26)	1.496(3)	C(26)—C(27)	1.361(3)	C(44)—C(57)	1.455(3)	F(14)—C(14)	1.376(2)
C(9)—C(10)	1.553(3)	C(27)—C(45)	1.434(3)	C(45)—C(46)	1.437(3)	F(15)—C(15)	1.383(2)
C(10)—C(11)	1.625(3)	C(27)—C(28)	1.520(3)	C(46)—C(47)	1.390(3)	F(16)—C(16)	1.362(2)
C(11)—C(28)	1.557(3)	C(28)—C(29)	1.523(3)	C(47)—C(48)	1.435(3)	F(17)—C(17)	1.388(2)
C(11)—C(12)	1.621(3)	C(29)—C(30)	1.363(3)	C(47)—C(58)	1.447(3)	F(18)—C(18)	1.377(2)
C(12)—C(13)	1.562(3)	C(29)—C(46)	1.438(3)	C(48)—C(49)	1.434(3)	F(19)—C(19)	1.377(2)
C(13)—C(30)	1.502(3)	C(30)—C(31)	1.437(3)	C(49)—C(50)	1.383(3)	F(20)—C(20)	1.382(2)
C(13)—C(14)	1.671(3)	C(31)—C(48)	1.389(3)	C(49)—C(59)	1.449(3)	F(21)—C(21)	1.356(2)
C(14)—C(32)	1.498(3)	C(31)—C(32)	1.429(3)	C(50)—C(51)	1.440(3)	F(22)—C(22)	1.395(2)
C(14)—C(15)	1.552(3)	C(32)—C(33)	1.364(3)	C(51)—C(52)	1.386(3)	F(28)—C(28)	1.398(2)
C(15)—C(16)	1.625(3)	C(33)—C(50)	1.437(3)	C(52)—C(53)	1.440(3)	F(34)—C(34)	1.394(2)

the fullerene molecule was used. For the initial buckminsterfullerene in which all atoms are symmetrically equivalent, the above-mentioned parameters are $\Delta_i = 3.57$ Å and $\phi_i = 12°$.

Based on analysis of the Δ_i and ϕ_i parameters, four regions can be distinguished on the surface of the $C_{60}F_{18}$ molecule:

(a) the planar ($\phi_i = 0.1°$) isolated six-membered C(1)—C(6) ring located closer to the center of the molecule ($\Delta_i = 2.97$ Å);

(b) the zone containing 18 fluorinated pyramidal C(sp^3) atoms far remote from the center ($3.8 < \Delta_i < 4.0$ Å; $26.4 < \phi_i < 29.9°$);

(c) the region consisting of 12 C(sp^2) atoms with a flattened environment, which are adjacent to the fluorinated zone ($\phi_i = 3$—$6°$, the Δ_i values differ slightly from those for nondistorted C_{60});

(d) the remaining portion of the molecule (similar to the initial C_{60} molecule).

The isolated six-membered C(1)—C(6) ring of the $C_{60}F_{18}$ molecule in structure **1** is planar to within 0.003 Å. The C—C bond lengths in this ring are equalized (see Table 2), which indicates that the ring is aromatic. Due to the strong electron-withdrawing effect of the fluorinated zone, the average C(sp^2)—C(sp^2) bond length in the ring (1.372 Å) is close to the average C—C bond length in hexafluorobenzene (1.368 Å) calculated from the data available in the Cambridge Structural Database (see Ref. 20). By contrast, the 6—6 and 6—5 bonds in the C(55)—C(60) ring located on the opposite side of the fullerene cage alternate and their average lengths (1.387 and 1.447 Å, respectively) are typical of nondistorted buckminsterfullerene.[32]

The C(sp^3) atoms bound to the arene ring (the average C(sp^2)—C(sp^3) bond length is 1.476 Å) deviate from the mean plane toward the nonfluorinated hemisphere by only 0.055—0.075 Å, whereas the adjacent C(sp^3) atoms in the fluorinated zone are substantially bent away from the plane of the ring. As a result, the five- and six-membered rings adjacent to the arene ring are nonplanar and adopt envelope and boat conformations, respectively. The flattened carbon rings, which are located in the next environment of the arene ring and composed of the sp^3- and sp^2-hybridized carbon atoms, have envelope and half-chair conformations, respectively. In the back hemisphere of the fullerene cage, three symmetrically equivalent five-membered rings containing one C(sp^3) atom each adopt a flattened envelope conformation. The remaining rings are planar to within 0.02 Å.

In the fluorinated zone, the C(sp^3)—C(sp^3) bond lengths are in the range of 1.552(4)—1.677(4) Å. Such an elongation of the C—C bonds is typical of cage

polyfluorinated derivatives.[33] Interestingly, alternation of the *single* 6—6 and 6—5 carbon—carbon bond lengths in the fullerene cage is retained. The $C(sp^3)—C(sp^3)$ distances of the 6—6 type averaged within the noncrystallographic symmetry C_{3v} are 1.557 and 1.558 Å for the C(12)—C(13) and C(21)—C(22) bonds, respectively. The single 6—5 bonds are elongated to 1.623 Å (C(11)—C(12)) and 1.672 Å (C(8)—C(9); all bonds equivalent to these bonds within the space group C_{3v} are also elongated. The most elongated C—C bonds possess high reactivities. Thus, these bonds readily undergo the cleavage with the insertion of the ether oxygen atom to form a series of isomers of $C_{60}F_{18}O$ [21] and $C_{60}F_{18}O_2$.[34]

The C—F distances in solvate **1** are in the range of 1.363—1.398 Å (Table 2). The average lengths of four independent bonds (within the symmetry group C_{3v}) differ substantially (1.385 Å for C(7)—F(7), 1.377 Å for C(8)—F(8), 1.361 Å for C(11)—F(11), and 1.396 Å for C(22)—F(22) and the equivalent bonds). Hence, the C—F bonds at the C(11), C(16), and C(21) atoms, which are opposite to the arene core in the three adjacent five-memebred rings, are somewhat shortened, whereas the C—F bonds at the three most remote fluorinated C(22), C(28), and C(34) atoms are elongated. The elongated C—F bonds can be involved in the Friedel—Crafts reaction. Thus, prolonged storage of $C_{60}F_{18}$ in a benzene solution of $FeCl_3$ led to the replacement of the F atoms by the phenyl fragments to give *symm*-$C_{60}F_{15}Ph_3$.[35] Apparently, the highest lability of the fluorine atoms is attributable to the smallest steric hindrances upon their replacement. The $C(sp^3)—C(sp^3)—F$ bond angle involving these bonds (the average value is 107.5°) is somewhat smaller than the tetrahedral angle (109.45°), whereas the average $C(sp^3)—C(sp^3)—F$ bond angle with the participation of the single 6—6 bond is increased to 111.3°.

The average FCCF torsion angles at the 6—5 bonds are 22.3° (F(7)C(7)C(21)F(21) and the symmetrically equivalent fragments) and 32.5° (F(7)C(7)C(8)F(8) and the symmetrically equivalent fragments). The analogous fragments at the 6—6 bonds in the 15-membered C(7)—C(21) macrocycle surrounding the arene ring and at the three such bonds, which are directed away from the C(11), C(16), and C(21) atoms toward the equatorial carbon zone, have an exact eclipsed configuration (the average torsion angles are 0.3° and 0.6°, respectively). In the last three-mentioned fragments, the vicinal intramolecular F...F contacts (2.40 Å) are substantially shorter than the remaining corresponding contacts (2.48—2.53 Å). The observed distribution of the bond angles and torsion angles reveals the tendency to grouping of the F atoms in the fluorinated zone of the molecule around the arene ring.

In crystal solvate **1**, the $C_{60}F_{18}$ molecules are related by inversion centers to form antiparallel zigzag chains along the (**101**) direction (Fig. 3). The angle between this direction and the threefold symmetry axis of the fullerene molecule is 16.4°. The chains with the same direction are arranged in layers perpendicular to the *b* axis. In the adjacent layers, the chains have the opposite direction. Each fluorinated fullerene molecule forms contacts with two adjacent molecules from the same chain and with eight molecules from the adjacent chains. Hence, the molecular coordination number[36] for $C_{60}F_{18}$ is 10. The shortest contacts between the molecules from differ-

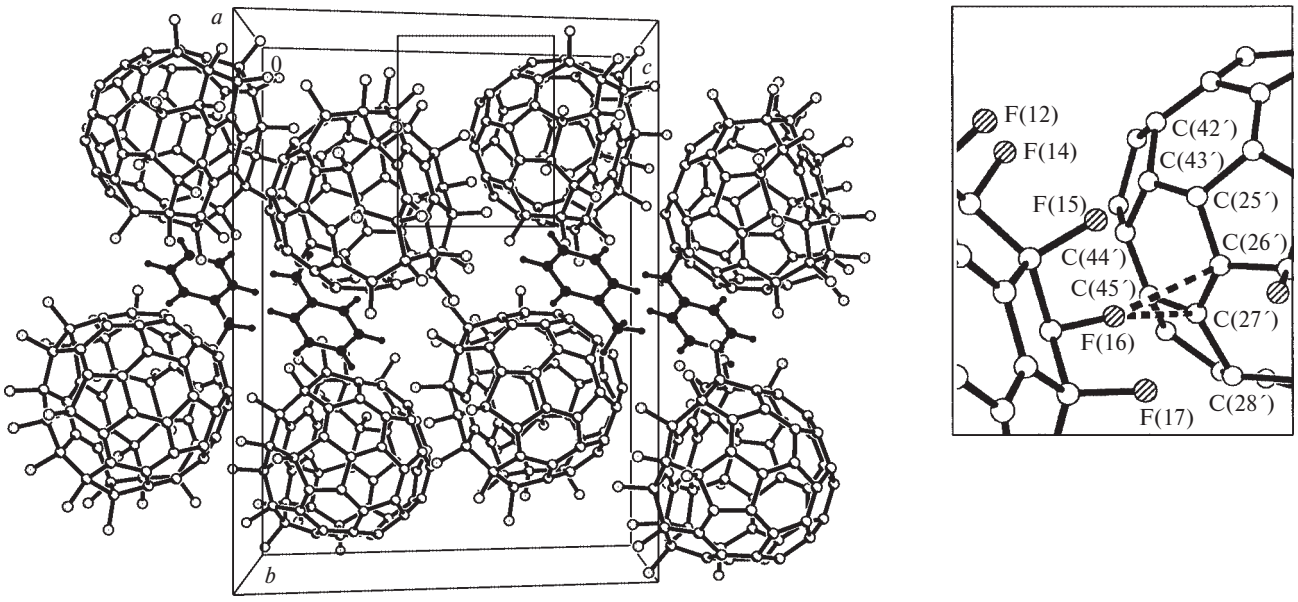

Fig. 3. Molecular packing in crystal solvate **1** and its fragment with short F...C contacts (at the top right). The toluene molecules located within the unit cell are shown in black.

ent chains are formed by the fluorine atoms, on the one hand, and the carbon atoms of the flattened zone of the fullerene cage, on the other hand. According to the quantum-chemical calculations (see below), these C atoms bear substantial positive charges. Apparently, the shortest F(16)...C(26′)* and F(16)...C(27′) contacts (2.747 and 2.915 Å, respectively) are forced and caused by repulsions between the above-mentioned atoms. This is indicated by the fact that the coordination environments about the C(26′) and C(27′) atoms are most flattened (the ϕ_i parameters are 3.5° and 4.4°, respectively) of all the atoms in the "planar" carbon zone of the molecule.

The toluene molecules in solvate **1** are located one by one between the adjacent chains of the fluorinated fullerene molecules. The shortest intermolecular C...C (3.3—3.5 Å), C...F (3.1—3.4 Å), and H...F (2.6—2.9 Å) contacts correspond to the sums of the van der Walls radii.[37]

Solvate of fluorinated fullerene $C_{60}F_{48} \cdot 2C_6H_3Me_3$ (2). Polyfluorinated fullerene $C_{60}F_{48}$ is the terminal fluorination product of buckminsterfullerene that retains the carbon cage.[12] In the crystal of **2**, the $C_{60}F_{48}$ molecule occupies a special position with the symmetry S_6. Its symmetrically independent part contains ten carbon atoms and eight fluorine atoms. The C_{60} carbon skeleton has a substantially distorted spherical shape (Fig. 4), which is indicative of a substantial redistribution of the bond lengths in the cage due to fluorination. The molecule has six double C—C bonds of the 5—6 type located approximately in the vertices of the octahedron and "forced down" into the fullerene sphere (ϕ_i = −2—−9°, Δ_i = 2.96—3.04 Å).** Apparently, this arrangement of the C=C bonds results in the fact that they are inaccessible to the further attack by the fluorine atoms. The overall molecular structure of $C_{60}F_{48}$ including the arrangement of the double bonds, which is untypical of buckminsterfullerene, is identical to that proposed previously based on the ^{13}C NMR data.[12] For the fluorinated sp^3-hybridized carbon atoms, the geometric parameters of the cages are ϕ_i = 12.5—34.7° and Δ_i = 3.57—3.93 Å. However, the accuracy of determination of the crystal structure of **2** does not allow us to quantitatively analyze these parameters.

The six-membered rings containing one sp^2-hybridized carbon atom each are most nonplanar and adopt an envelope conformation (the sp^2-hybridized carbon atom is bent inward). The five- and six-membered rings containing the double bond have envelope and boat conformations, respectively. The five-membered ring separated from the double bond adopts a half-chair conformation. The six-membered ring located on the $\bar{3}$ axis is planar.

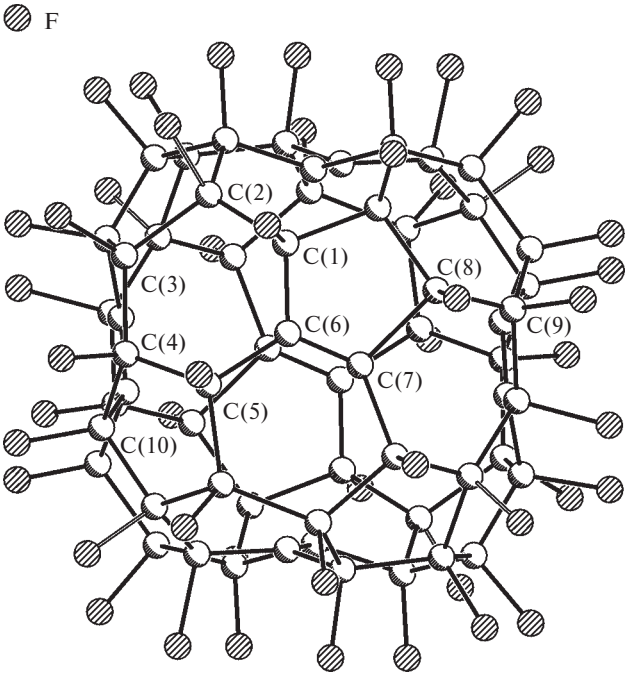

Fig. 4. Overall view of the $C_{60}F_{48}$ molecule and the numbering scheme for the C atoms of the symmetrically independent portion. The numbering scheme of the F atoms is identical with that presented in Fig. 1.

In the crystal of solvate **2**, the $C_{60}F_{48}$ molecules are disordered over two independent orientations with the occupancy ratio of approximately 2 : 1. Both orientations (Fig. 5) are related by a pseudosymmetry plane. The addition of this symmetry element changes the point symmetry group from S_6 to D_{3d}. In the alternative orientations, the disordered positions in the carbon skeleton are occupied by the $C(sp^3)$ and $C(sp^2)$ atoms, whereas five of eight independent fluorine atoms in the environment of the cage are disordered (see the Experimental section). The distances between the corresponding atoms belonging to the molecules in different orientations are in the range of 0.6—0.8 Å. Hereinafter, the interatomic distances under consideration correspond to the predominant orientation of the $C_{60}F_{48}$ molecules in structure **2**.

The fluorinated fullerene molecules in solvate **2** occupy the vertices and the center of the unit cell, the centers of the faces, and the midpoints of the edges. Hence, the centers of the fullerene molecules form a simple cubic packing. Pairs of the solvent molecules related by inversion centers occupy the cavities of the packing (Fig. 4). The fullerene cores present the double bonds to each other. However, contacts between the $C_{60}F_{48}$ molecules are formed exclusively by the fluorine atoms due to the fact that the double bonds are forced down into the fullerene cages. The intermolecular F...F con-

* Atoms with primed numbers belong to the adjacent molecule in the crystal.

** Negative spherical excesses correspond to the trigonal-pyramidal environment of the C atoms with the vertex directed *inside* the C_{60} cage.

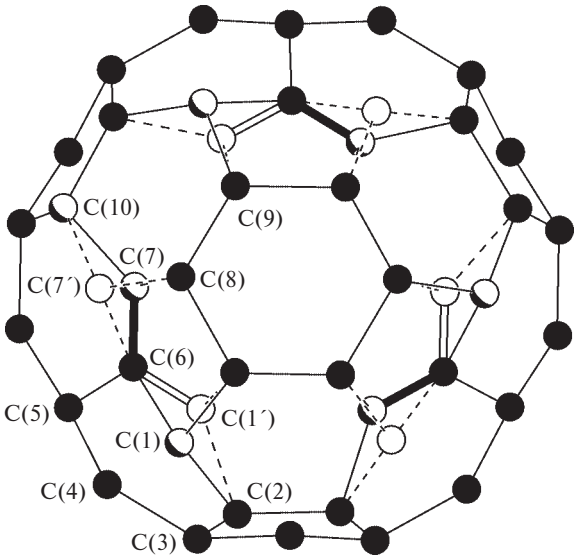

Fig. 5. Disorder of the $C_{60}F_{48}$ molecules in the crystal of **2**. A hemisphere of the carbon core is shown. The C atoms common to both orientations are completely hatched, the atoms belonging to the molecule in the predominant orientation are partially blackened, and the atoms belonging to the molecule in the second orientation are represented by empty circles. The numbering scheme for the C atoms in the symmetrically independent portion of the molecule is given.

tacts correspond to the usual van der Waals distances (2.88—3.22 Å). The mesitylene molecules form the C...F contacts (3.43—3.83 Å) with the fluorinated fullerene molecules. There are also C...C contacts between the mesitylene molecules with the distances of 3.82 Å and longer, which are larger than the sums of the van der Waals radii. The H...F contacts involving the hydrogen atoms in the calculated positions are in the range of 2.58—2.79 Å.

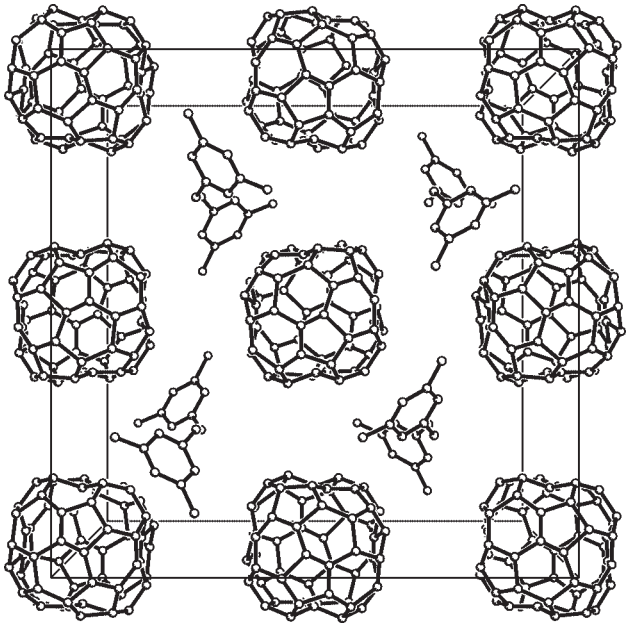

Fig. 6. Cubic packing of the fluorinated fullerene and mesitylene molecules in the crystal of **2**. The F atoms are omitted.

Figure 7 gives the histograms of the distributions of the intermolecular F...F and C...F contacts in crystal solvates **1** and **2** in comparison with the analogous distributions for typical polyfluorinated aromatic compounds, *viz.*, perfluorohexamethylbenzene[38] and perfluoroindacene.[39] A comparison of the histograms revealed that the $C_{60}F_{18}$ molecules in solvate **1** are located at distances smaller than the sums of the van der Waals radii (in Fig. 7, the distances corresponding to these sums are indicated by thin vertical strokes), unlike the $C_{60}F_{48}$ molecules in the crystal of **2**. In solvate **2**, the carbon core is completely sterically shielded. Hence, the packing of the

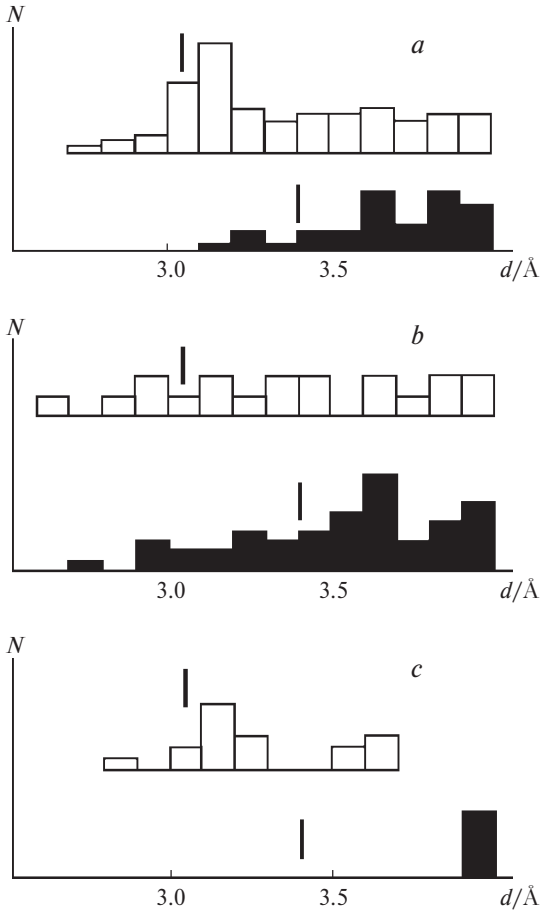

Fig. 7. Overall histograms of the distances corresponding to the intermolecular C...F (shaded bars) and F...F (empty bars) contacts (Å) in the crystals of perfluorohexamethylbenzene[37] and perfluoroindacene[38] (*a*); between the $C_{60}F_{18}$ molecules in solvate **1** (*b*); between the $C_{60}F_{48}$ molecules in the crystal of **2** (*c*). The distances corresponding to the sums of the van der Waals radii of the corresponding pairs of atoms are indicated by thin vertical strokes; *N* is the number of the contacts (arbitrary units).

fluorinated fullerene molecules in solvate **2** is looser than that in solvate **1** in spite of the lower density of the crystals of the latter (see Table 1). This fact is also confirmed by the smaller coefficient of molecular packing[35] in **2** compared to that in **1** (0.70 and 0.73, respectively; Table 1).

Table 3. Calculated Mulliken atomic charges in molecule **1** taking into account the symmetry C_{3v}

Atom	PM3	3-21G*	6-31G	6-31G DFT
C(1)	−0.078	0.041	0.029	0.083
C(7) (sp^3)	0.145	0.254	0.319	0.175
C(8) (sp^3)	0.161	0.316	0.323	0.189
C(21) (sp^3)	0.075	0.397	0.394	0.251
C(22) (sp^3)	0.230	0.276	0.309	0.155
C(23)	−0.067	0.005	0.010	0.045
C(24)	−0.083	−0.003	0.009	0.041
C(25)	0.011	0.064	0.093	0.080
C(41)	0.012	0.028	0.027	0.024
C(42)	0.007	0.008	0.018	0.010
C(43)	0.008	0.018	0.022	0.008
C(56)	0.010	0.006	0.014	0.012
F(7)	−0.089	−0.337	−0.379	−0.268
F(8)	−0.089	−0.349	−0.391	−0.279
F(21)	−0.087	−0.353	−0.386	−0.274
F(22)	−0.094	−0.340	−0.390	−0.282

Table 4. Average bond lengths (d) in molecule **1** taking into account the symmetry C_{3v}

Bond	d/Å				
	X-ray analysis	PM3	3-21G*	6-31G	6-31G DFT
C(1)—C(2)	1.372	1.372	1.349	1.361	1.376
C(1)—C(6)	1.372	1.395	1.354	1.362	1.381
C(1)—C(7)	1.476	1.496	1.470	1.475	1.480
C(7)—C(8)	1.557	1.590	1.547	1.557	1.565
C(8)—C(9)	1.672	1.701	1.674	1.659	1.679
C(7)—C(21)	1.623	1.653	1.616	1.616	1.631
C(21)—C(22)	1.558	1.582	1.551	1.559	1.568
C(22)—C(23)	1.524	1.539	1.526	1.522	1.529
C(8)—C(24)	1.500	1.510	1.501	1.502	1.506
C(23)—C(24)	1.363	1.359	1.340	1.349	1.371
C(24)—C(25)	1.428	1.437	1.427	1.428	1.436
C(23)—C(41)	1.435	1.446	1.438	1.437	1.444
C(40)—C(41)	1.437	1.446	1.441	1.440	1.449
C(41)—C(42)	1.387	1.383	1.366	1.373	1.396
C(25)—C(43)	1.386	1.386	1.368	1.375	1.398
C(42)—C(43)	1.436	1.446	1.436	1.435	1.443
C(42)—C(56)	1.453	1.459	1.454	1.452	1.459
C(55)—C(56)	1.387	1.384	1.371	1.378	1.401
C(56)—C(57)	1.447	1.457	1.447	1.446	1.454
F(7)—C(7)	1.385	1.364	1.383	1.393	1.423
F(8)—C(8)	1.361	1.358	1.377	1.388	1.416
F(21)—C(21)	1.377	1.358	1.371	1.377	1.401
F(22)—C(22)	1.396	1.365	1.390	1.403	1.437

Table 5. Atomic charges in the independent portion of the $C_{60}F_{48}$ molecule

Atom	Charge		Atom	Charge	
	PM3	3–21G		PM3	3–21G
C(1) (sp^3)	0.141	0.301	C(10) (sp^3)	0.145	0.289
C(2) (sp^3)	0.091	0.347	F(1)	−0.087	−0.312
C(3) (sp^3)	0.092	0.334	F(2)	−0.086	−0.323
C(4) (sp^3)	0.092	0.360	F(3)	−0.088	−0.317
C(5) (sp^3)	0.141	0.274	F(4)	−0.086	−0.322
C(6)	−0.130	−0.030	F(5)	−0.084	−0.308
C(7)	−0.129	−0.015	F(8)	−0.087	−0.314
C(8) (sp^3)	0.140	0.293	F(9)	−0.083	−0.326
C(9) (sp^3)	0.101	0.376	F(10)	−0.083	−0.308

Quantum-chemical calculations. The results of semiempirical and *ab initio* quantum-chemical calculations of the charge distributions in the $C_{60}F_{18}$ and $C_{60}F_{48}$ molecules with geometry optimization are given in Tables 3—6 where the lengths of the symmetrically independent bonds determined experimentally are also presented. The geometric distortions of the $C_{60}F_{18}$ molecule are quantitatively reproduced by the *ab initio*

Table 6. Bond lengths (d) in the independent portion of the $C_{60}F_{48}$ molecule

Bond	d/Å		
	Experiment	PM3	3–21G
C(1)—C(2)	1.54(3)	1.574	1.545
C(2)—C(3)	1.63(2)	1.596	1.579
C(3)—C(4)	1.60(2)	1.608	1.602
C(4)—C(5)	1.53(2)	1.575	1.539
C(1)—C(6)	1.57(3)	1.515	1.492
C(5)—C(6)	1.48(2)	1.490	1.471
C(6)—C(7)	1.20(3)	1.332	1.295
C(7)—C(8)	1.65(3)	1.515	1.490
C(8)—C(9)	1.51(2)	1.556	1.529
C(4)—C(10)	1.59(2)	1.580	1.546
C(1)—C(9A)*	1.58(3)	1.620	1.580
C(8)—C(9A)	1.58(2)	1.593	1.556
C(3)—C(5B)	1.60(2)	1.591	1.556
C(2)—C(10B)	1.48(2)	1.579	1.542
C(7)—C(10C)	1.54(3)	1.492	1.471
C(1)—F(1)	1.31(4)	1.369	1.379
C(2)—F(2)	1.43(2)	1.368	1.374
C(3)—F(3)	1.37(2)	1.368	1.375
C(4)—F(4)	1.36(2)	1.368	1.373
C(5)—F(5)	1.38(2)	1.371	1.380
C(8)—F(8)	1.29(2)	1.372	1.381
C(9)—F(9)	1.40(2)	1.363	1.369
C(10)—F(10)	1.29(2)	1.371	1.379

* The notations A, B, and C correspond to the symmetrically equivalent atoms of the independent portion of the molecule.

calculations with the 3-21G* and 6-31G basis sets (GAUSSIAN-98 program package). The differences between the positions of the atoms are no higher than 0.12 Å and the bond lengths are identical to within 0.045 Å (Table 4). The results of calculations confirmed the aromaticity of the six-membered C(1)—C(6) ring and agree with the results of the recent quantum-chemical calculations[40] for the structurally similar $C_{60}H_{18}$ and $C_{60}F_{18}$ molecules. The results of our theoretical study for $C_{60}F_{18}$ have partially been reported previously.[20]

The calculated geometry of the $C_{60}F_{48}$ molecule is in somewhat poorer agreement with the experimental data (the discrepancies in the atomic positions are as high as 0.21 Å) due, apparently, to the lower accuracy of determination of the crystal structure of **2** as compared to that of **1**. However, the quantum-chemical calculations reproduced all principal geometric characteristics of the carbon skeleton revealed by X-ray diffraction analysis, *viz.*, the fact that the sp^2-hybridized carbon atoms are forced down into the C_{60} core (the calculated spherical excess is −4°), the elongation of the C—C bonds, and the shortening of the double C=C bond in the carbon cage as compared to the standard values caused by the effect of the electron-withdrawing exopolyhedral F atoms (see Table 6). The calculated lengths of the substantially disordered C—F bonds, which were experimentally determined with a low accuracy, are in the standard range (1.363—1.372 and 1.369—1.380 Å according to the PM3 and *ab initio* calculations, respectively), which is identical with the range of the calculated bond lengths in $C_{60}F_{18}$. The above-mentioned effect of alternation of the single 5—6 and 6—6 bonds in solvate **1** is absent in the crystal structure of **2**.

A comparison of the calculated atomic charges in $C_{60}F_{18}$ and $C_{60}F_{48}$ (Table 5) demonstrates that the semiempirical methods substantially underestimated polarization of the bonds in the molecule as compared to the *ab initio* calculations. The semiempirical calculations also assigned noticeable negative charges to the nonfluorinated carbon atoms. Interestingly, the calculations by all methods predicted narrow ranges of the charges on the exopolyhedral fluorine atoms. Hence, the major portion of the carbon cage is shielded by a dense negatively charged shell of the F atoms (Fig. 8). In the case of the $C_{60}F_{18}$ molecule, the arene ring is accessible to an attacking agent with the atomic radius of <1.5 Å (for example, Li^+ in a weak solvating medium), which opens up a principal way for the synthesis of π-complexes of fluorinated fullerenes of the arene type.[20] At the same time, the C=C double bonds in $C_{60}F_{48}$ are efficiently shielded by the F shell (Fig. 8, *b*).

The dipole moments of the $C_{60}F_{18}$ molecule calculated by the *ab initio* quantum-chemical methods are very large (12.4—15.7 D depending on the size of the basis set). This allows us to attribute the short contacts

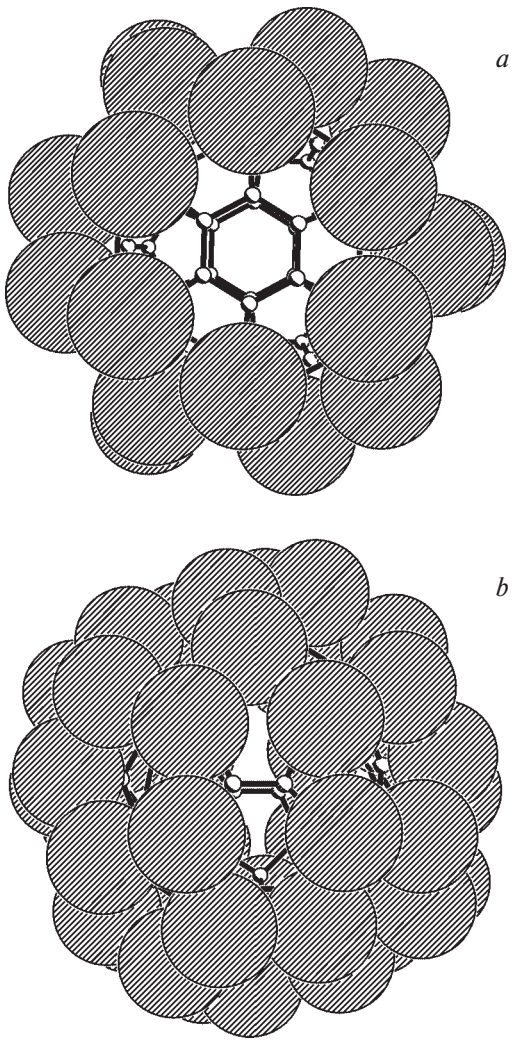

Fig. 8. Steric shielding of the $C_{60}F_{18}$ (*a*) and $C_{60}F_{48}$ (*b*) molecules by the exopolyhedral fluorine atoms represented by the van der Waals spheres.

and the tight molecular packing observed in crystal solvate **1** to intermolecular Coulomb attraction. In the crystal, the mutual attraction of the centrosymmetrical $C_{60}F_{48}$ molecules possessing zero dipole moments occurs primarily through van der Waals interactions as evidenced by the absence of shortened intermolecular contacts and the lower packing coefficient in solvate **2**.*

* In the independent X-ray diffraction study of solvate **2**,[24] the space group $Pa\bar{3}$ with the pseudocentered unit cell was established and different occupancies of the rotationally disordered $C_{60}F_{48}$ molecules in two independent positions on the $\bar{3}$ axis were revealed. This allowed the authors[24] to achieve a substantially higher accuracy of structure determination of **2**. However, in our opinion, the assumption that the crystal of **2** contains a mixture of isomers with the symmetry groups D_3 and S_6[24] did not follow directly from the X-ray diffraction data (including those obtained within the space group $Pa\bar{3}$) and called for additional data, which were lacking in the cited study.

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