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Characterization of reactions of fullerene C_{60} with bromine. Crystal structures of bromofullerenes $C_{60}Br_6$, $C_{60}Br_6 \cdot CS_2$, $C_{60}Br_8 \cdot CHBr_3 \cdot 2Br_2$, and $C_{60}Br_{24} \cdot C_6H_4Cl_2 \cdot Br_2$

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Results of research on bromination of [60]fullerene in organic solvents and liquid bromine are summarized. The conditions of the synthesis of bromofullerenes $C_{60}Br_6$ and $C_{60}Br_8$ were optimized. The formation of bromide $C_{60}Br_{14}$ was detected. A model was proposed for the description of the processes involved in bromination of C_{60} in organic solvents. The crystal and molecular structures of $C_{60}Br_6$, $C_{60}Br_6 \cdot CS_2$, $C_{60}Br_8 \cdot CHBr_3 \cdot 2Br_2$, and $C_{60}Br_{24} \cdot C_6H_4Cl_2 \cdot Br_2$ were established by X-ray diffraction analysis.

Key words: fullerene C_{60}, bromination, bromofullerenes, X-ray diffraction analysis.

Earlier,[1] the reaction of C_{60} with liquid bromine has been found to afford bromofullerene $C_{60}Br_{24}$. Bromination of fullerene in organic solvents gave $C_{60}Br_6$ and $C_{60}Br_8$.[2,3] It was difficult to reproduce the synthesis of bromofullerenes because the experimental procedures were virtually lacking in the publications.[2,3] Hence, we carried out extensive investigation of bromination of fullerene under various conditions, developed convenient procedures for the synthesis of bromofullerenes $C_{60}Br_6$ and $C_{60}Br_8$,[4] and obtained reliable data on the molecular and crystal structures of bromides of fullerene C_{60}.[5]

In the present paper, we summarized the results of research on the reactions of C_{60} with Br_2 and established the crystal structures of bromofullerene $C_{60}Br_6$ and solvates $C_{60}Br_6 \cdot CS_2$, $C_{60}Br_8 \cdot CHBr_3 \cdot 2Br_2$, and $C_{60}Br_{24} \cdot C_6H_4Cl_2\text{-}o \cdot Br_2$.

Results and Discussion

Bromination of [60]fullerene. *Reaction with liquid bromine*. Earlier,[1] bromination of C_{60} with liquid bromine has been demonstrated to afford bromofullerene $C_{60}Br_{24}$ as the final product. However, data on the possible intermediates were lacking. We studied the course of direct bromination of fullerene by IR spectroscopy. It was found (see also Ref. 4) that the addition of solid C_{60} to liquid bromine is accompanied by rapid dissolution of fullerene and the almost simultaneous (1—2 min) formation of the crystalline solvate $C_{60}Br_8 \cdot nBr_2$ (n = 1 or 2), whose precipitation was completed in 15—20 min. The solvates $C_{60}Br_8 \cdot nBr_2$ gradually react with bromine to give products with the molecular formula $C_{60}Br_{14-16}$, which appeared to be rather resistant to further bromination and can be isolated. Small amounts of $C_{60}Br_{24}$ were detected in the reaction mixture only within 1 h after the beginning of reaction, and the transformation of $C_{60}Br_{14-16}$ into $C_{60}Br_{24}$ was completed in 6—12 h. No intermediates were detected in the pathway from $C_{60}Br_{14-16}$ to $C_{60}Br_{24}$.

When $C_{60}Br_{14-16}$ is kept at room temperature for 1—2 days, bromine is partially eliminated due, apparently, to decomposition of the solvate $C_{60}Br_{14} \cdot Br_2$ into $C_{60}Br_{14}$ and bromine. This was also confirmed by the fact that the IR spectrum of freshly prepared $C_{60}Br_{14-16}$ is completely identical to the IR spectrum of $C_{60}Br_{14}$ (decomposition product). The results of thermogravimetry and differential scanning calorimetry provided evidence that thermal decomposition of $C_{60}Br_{14}$ occurs in one step. Hence, it is highly probable that all 14 bromine atoms are covalently bound to the C_{60} carbon cage.

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Therefore, the sequence of transformations involved in the reaction of C_{60} with liquid bromine can be represented by Scheme 1.

Scheme 1

$$C_{60} \xrightarrow[10\text{—}20\text{ min}]{Br_2} C_{60}Br_8 \cdot nBr_2 \downarrow \xrightarrow[30\text{—}50\text{ min}]{Br_2}$$

$$\longrightarrow C_{60}Br_{14} \xrightarrow[6\text{—}12\text{ h}]{Br_2} C_{60}Br_{24}$$

The IR spectrum of $C_{60}Br_{14}$ differs from the spectra of $C_{60}Br_8$ and $C_{60}Br_{24}$ [2] in that it has a very intense band at 857 cm^{-1} and several less intense bands, which are absent from the spectra of $C_{60}Br_8$ and $C_{60}Br_{24}$. The position of the most intense band (842 cm^{-1}) differs from those observed in the spectra of both $C_{60}Br_8$ (847 cm^{-1}) and $C_{60}Br_{24}$ (849 cm^{-1}) by a few inverse centimeters (Fig. 1). These data confirm that $C_{60}Br_{14}$ is a previously unknown bromo derivative, *viz.*, an intermediate in the pathway from $C_{60}Br_8$ to $C_{60}Br_{24}$.

When kept at room temperature for 2 months, $C_{60}Br_{14}$ completely decomposed into $C_{60}Br_8 \cdot nBr_2$ (n = 1, 2). Dissolution of $C_{60}Br_{14}$ in organic solvents (chloroform, benzene, carbon disulfide) also leads to its decomposition. This fact did not allow us to use ^{13}C NMR spectroscopy for determining the molecular structure of this compounds and to prepare single crystals suitable for X-ray diffraction study. Attempts to crystallize $C_{60}Br_{14}$ from liquid bromine also failed because this compound gradually reacts with bromine to give $C_{60}Br_{24}$.

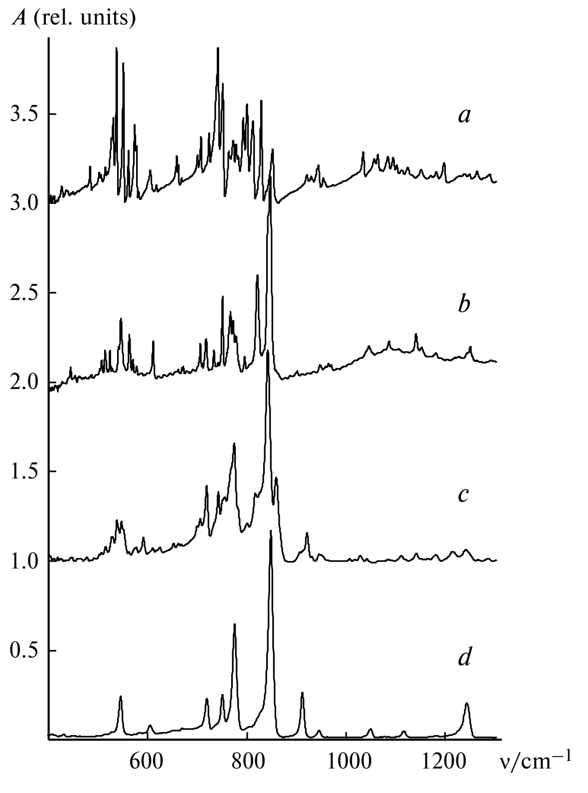


Fig. 1. IR spectra of bromofullerenes $C_{60}Br_6$ (*a*), $C_{60}Br_8$ (*b*), $C_{60}Br_{14}$ (*c*), and $C_{60}Br_{24}$ (*d*).

Bromination in organic solvents. Earlier,[2,3] it has been reported that the reaction of fullerene with bromine in chloroform, carbon tetrachloride, carbon disulfide, and benzene is accompanied by precipitation of either $C_{60}Br_6$ or $C_{60}Br_8$ depending on the solvent nature. In the present study, we systematically studied bromination of C_{60} in a series of solvents, which are nearly almost or completely resistant to bromine, and revealed the following.

1. Solvents in which the solubility of C_{60} is lower than 1.5—2 mg mL^{-1}, such as benzene, carbon tetrachloride, choroform, fluorobenzene, and iodobenzene, are unsuitable for the synthesis of $C_{60}Br_6$ and $C_{60}Br_8$. The addition of bromine to saturated C_{60} solutions in these solvents in amounts corresponding to the concentration of 0.0005—20 mol Br_2 L^{-1} is not accompanied by precipitation of products for 2 weeks. After the reaction mixtures are concentrated *in vacuo* (or Br_2 and the solvents are frozen out), either pure fullerene or $C_{60}Br_{24}$ are obtained as residues depending on the reagent ratio used in the reaction.

2. Addition of Br_2 to C_{60} solutions at a concentration higher than 2 mg mL^{-1} (in 1,2- and 1,3-dichlorobenzene, 1,2-dibromobenzene, 1,2,4-trichlorobenzene, chlorobenzene, bromobenzene, bromoform, and carbon disulfide) can result in precipitation of either the starting fullerene (apparently, as a solvate with bromine) or bromides $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Br_{24}$ (Table 1). In this case, the concentration of bromine in the reaction mixture is the main factor determining the composition of the reaction products. For example, crystallization of $C_{60}Br_6$ occurs at a bromine concentration of 1.2—2.5 mol L^{-1}; $C_{60}Br_8$ is formed at $[Br_2]$ = 5.3—8.3 mol L^{-1}, whereas the synthesis of $C_{60}Br_{24}$ requires $[Br_2] > 10$ mol L^{-1}. The reagent ratios (Br_2 : C_{60}) optimal for the synthesis of each particular bromide depends on the solvent nature and are always substantially larger than the stoichiometric values (see Table 1).

3. Mother liquors obtained after separation of crystalline precipitates of $C_{60}Br_6$ or $C_{60}Br_8$ contain only fullerene and Br_2, whereas no bromides were detected. Dissolution of $C_{60}Br_6$ in organic solvents (chloroform, dichloromethane, 1,2-dichlorobenzene) is accompanied by decomposition of bromide into C_{60} and Br_2. Analogous decomposition of $C_{60}Br_8$ was observed upon heating to 70—80 °C. By contrast, $C_{60}Br_{24}$ remained intact even upon prolonged reflux in 1,2-dichlorobenzene (180 °C).

These results suggest that bromination of fullerene in organic solvents is reversible, the position of equilibrium in the reactions being substantially shifted toward the reagents. That is why the addition of a small amount of

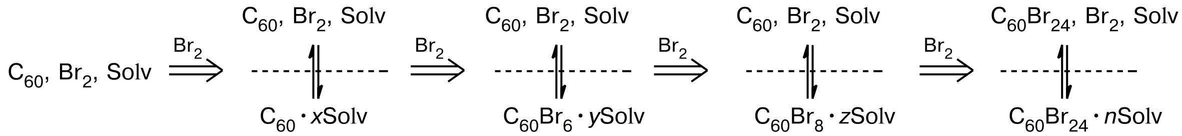
Table 1. Optimal conditions for the synthesis of $C_{60}Br_6$ and $C_{60}Br_8$ in organic solvents

Solvent	$S(C_{60})$* /mg mL^{-1}	$C_{60}Br_6$			$C_{60}Br_8$		
		$[Br_2]$ /mol L^{-1}	$Br_2 : C_{60}$**	Yield (%)	$[Br_2]$ /mol L^{-1}	$Br_2 : C_{60}$**	Yield (%)
1,2-Dichlorobenzene	27	1.35	39	95	8.20	430	96
1,2-Dibromobenzene	13.8	2.0	100	65	8.10	405	70
1,2,4-Trichlorobenzene	10.4	1.60	120	90	6.70	780	79
Carbon disulfide	7.9	2.35	250	80	6.25	910	86
Chlorobenzene	7.0	2.40	290	90	7.90	1550	75
Bromoform	4.97	1.10	160	20	5.40	780	60
1,3-Dichlorobenzene	3.8	1.20	250	40	5.35	1490	65
Bromobenzene	2.8	2.55	770	15	8.25	4180	63

* Solubility of fullerene C_{60} according to the results of the study.[6]

** The molar ratio is given.

Scheme 2



Solv is solvent

bromine ($[Br_2]$ = 0.05—0.2 mol L^{-1}) to a C_{60} solution does not lead to the formation of the products. An increase in the bromine concentration ($[Br_2]$ = 0.2—0.7 mol L^{-1}) results in partial precipitation of fullerene as solvates with the solvent or bromine, and only fullerene and Br_2 are still present in the solution. At an even higher bromine concentrations in the solution ($[Br_2]$ > 1—1.2 mol L^{-1}), fullerene bromide ($C_{60}Br_6$ or $C_{60}Br_8$) rather than solvated fullerene precipitates, but no noticeable amounts of bromo derivatives are present in the liquid phase. Only at a very high bromine concentration ($[Br_2]$ > 10 mol L^{-1}), a precipitate of $C_{60}Br_{24}$ is formed, the liquid phase containing bromine and dissolved $C_{60}Br_{24}$ (Scheme 2).

The solid phase is in dynamic equilibrium with the liquid phase. Hence, the addition of bromine to a system containing a precipitate of the solvate $C_{60}Br_6$ is accompanied by gradual dissolution of crystals of hexabromofullerene to form $C_{60}Br_8$ (or even $C_{60}Br_{24}$ at high concentrations of Br_2).

A comparison of Figs 2 and 3 demonstrates that the arrangement of the Br atoms in hexabromofullerene-60 differs substantially from that in octabromofullerene-60. The mechanism of formation of $C_{60}Br_8$ from $C_{60}Br_6$ proposed earlier[7] involves the 1,3-shift of Br atoms followed by the addition of the Br_2 molecules. However, according to the description of the process proposed in our study (see Scheme 2), the $C_{60}Br_6$ molecule with the C_s symmetry does not, apparently, serve as a precursor of $C_{60}Br_8$ (C_{2v}), and the formation of both bromofullerenes from fullerene C_{60} can occur through different pathways. Since the reaction is under thermodynamic control, only the most stable isomers of bromofullerenes are produced. Interestingly, only four [60]fullerene bromides ($C_{60}Br_6$, $C_{60}Br_8$, $C_{60}Br_{14}$, and $C_{60}Br_{24}$) out of various possible bromides were isolated as bromination products of fullerene C_{60}. Compounds with other compositions are, ap-

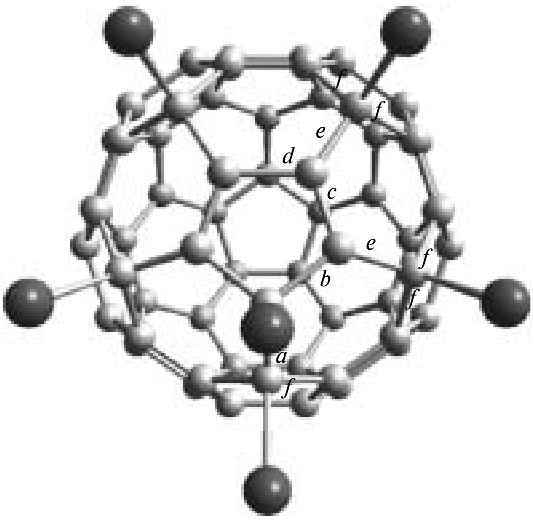


Fig. 2. Structure of the $C_{60}Br_6$ molecule with the C_s symmetry in the solvate $C_{60}Br_6 \cdot CS_2$.

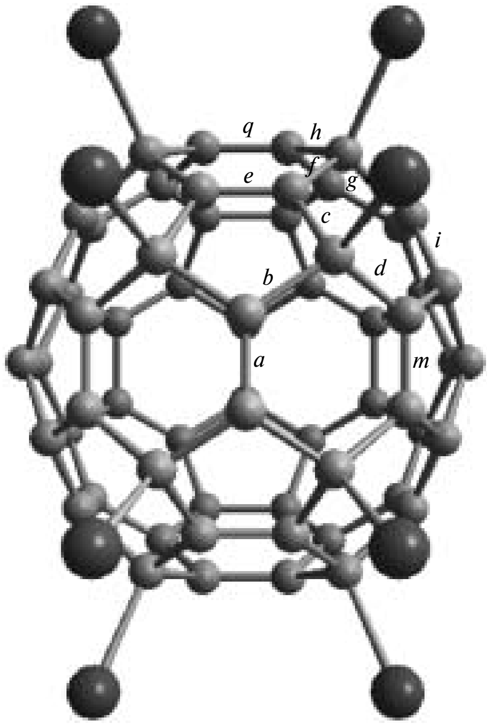


Fig. 3. Structure of the $C_{60}Br_8$ molecule with the C_{2v} symmetry in the solvate $C_{60}Br_8 \cdot CHBr_3 \cdot 2Br_2$.

parently, kinetically unstable, *i.e.*, are subjected to further bromination at a rate higher than the rate of their formation.

Molecular and crystal structures of bromofullerenes. In most cases, well-faceted single crystals of bromofullerenes are formed directly during the synthesis. Some of the crystals are stable in air for months, which allowed us to study the crystal structures of these compounds by X-ray diffraction (Table 2). Crystals of other compounds rapidly decompose already at room temperature with a loss of the solvated bromine and solvent, and, very often, with elimination of bromine bound to the fullerene cage.

For hexabormide $C_{60}Br_6$, the crystal structures of both the unsolvated compound (**1**) and the solvate $C_{60}Br_6 \cdot CS_2$ (**2**) were established. The molecular structure of $C_{60}Br_6$ having a mirror plane (C_s) is shown in Fig. 2. In the crystal of $C_{60}Br_6$, all atoms occupy general positions, whereas the hexabromofullerene molecule in the crystal solvate is located on a symmetry plane *m*. The accuracy of determination of the structures of **1** and **2** suffices to compare the bond lengths in these molecules with the corresponding parameters for the solvate $C_{60}Br_6 \cdot 0.5C_6H_5Cl \cdot 0.5Br_2$ studied earlier.[5] The average C—Br bond lengths (2.013 and 2.010 Å) are only slightly larger than the values found earlier[5] (1.99—2.00). The changes in the carbon—carbon bond lengths in the $C_{60}Br_6$ molecule com-

Table 2. Crystallographic data, characteristics of X-ray data collection, and details of the structure refinement of bromofullerenes **1—4**

Parameter	**1**	**2**	**3**	**4**
Molecular formula	$C_{60}Br_6$	$C_{60}Br_6 \cdot CS_2$	$C_{60}Br_8 \cdot CHBr_3 \cdot 2Br_2$	$C_{60}Br_{24} \cdot C_6H_4Cl_2 \cdot Br_2$
Molecular weight	1200.06	1276.19	1932.27	2945.25
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2_1/n$	*Pnma*	*Imm*2	$P\bar{1}$
a/Å	11.225(3)	19.044(4)	12.640(3)	12.963(4)
b/Å	16.899(3)	13.596(3)	16.625(3)	13.004(4)
c/Å	19.197(5)	14.625(3)	11.434(2)	13.113(4)
α/deg	90	90	90	79.48(3)
β/deg	102.40(3)	90	90	61.83(3)
γ/deg	90	90	90	60.49(3)
V/Å^3	3556.6(2)	3786.7(2)	2402.7(8)	1692.2(9)
Z	4	4	2	1
d_{calc}/g cm^{-3}	2.241	2.239	2.671	2.890
μ (Mo-K$_\alpha$)/mm^{-1}	68.26	65.24	125.44	154.89
Crystal dimensions/mm	0.4×0.3×0.16	0.5×0.12×0.08	0.3×0.25×0.2	0.2×0.12×0.08
T/K	180	170	150	180
θ_{max}/deg	27.5	28.0	26.4	28.1
Number of measured /independent reflections	32691/8118	22407/3840	8479/2636	12638/6010
Number of reflections with $F^2 > 2\sigma(F^2)$	4650	2484	2046	3147
Number of reflections /parameters in least-squares	8103/605	3836/326	2632/190	5994/451
R_1/wR_2	0.0412/0.0875	0.0348/0.0779	0.0451/0.1120	0.0662/0.1581
Residual electron density/e · Å^3, $\Delta\rho_{min}/\Delta\rho_{max}$	0.743/−0.918	0.844/−0.972	1.448/−1.254	1.497/−1.554

pared to those in C_{60} (1.453 and 1.383 Å for two types of predominantly single and double bonds[8]) are essential only for the brominated hemisphere. The largest elongation was observed for the bonds involving the sp^3-hybridized C atoms (*i.e.*, bearing Br atoms). The bond lengths of the types *a* (sp^3—sp^3), *b*, *e*, and *f* (sp^3—sp^2) are, respectively, 1.558, 1.530, 1.494, and 1.528 Å (in the structure of **1**) and 1.559, 1.532, 1.486, and 1.524 Å (in **2**). In the butadiene fragment, the bonds of the types *c* and *d* are double and intermediate in character, respectively, and their lengths are 1.356 and 1.462 Å (**1**), 1.352 and 1.476 Å (**2**).

The structure of the solvate $C_{60}Br_8 \cdot CHBr_3 \cdot 2Br_2$ (**3**) determined in the present study supplements the data for four solvates of $C_{60}Br_8$ obtained earlier.[2,5] In the structure of **3**, the crystallographic symmetry of the $C_{60}Br_8$ molecule (*mm*2) corresponds to the molecular C_{2v} symmetry (see Fig. 3). The C—Br bond lengths are 1.992 and 2.008 Å. The arrangement of the Br atoms is responsible for the presence of isolated carbon—carbon double bonds of the types *a* and *e* with lengths of 1.333—1.339 Å and the presence of the predominantly carbon—carbon double bonds of the types *i*, *m*, and *q* with lengths of 1.370—1.374 Å. The average length of the predominantly carbon—carbon single bonds (sp^3—sp^2) of the types *c*, *b*, *d*, *f*, *g*, and *h* is 1.510 Å. The carbon—carbon bond lengths in the unbrominated hemisphere differ only slightly from those in the C_{60} molecule. On the whole, the data for the structure of **3** agree well with the geometric parameters of the bonds in the structure of the solvate $C_{60}Br_8 \cdot 0.5C_6H_5Br \cdot 0.5Br_2$, which has been determined most precisely.[5]

Earlier, the molecular structure of $C_{60}Br_{24}$ has been established by single-crystal X-ray diffraction analysis[1,5] and powder X-ray diffraction[9] for various solvates with bromine. In the solvate $C_{60}Br_{24} \cdot C_6H_4Cl_2$-*o* $\cdot Br_2$ (**4**) prepared in the present study, the $C_{60}Br_{24}$ molecule has only a center of symmetry, although the idealized structure should have the T_h symmetry with three types of carbon—carbon single bonds (*a*—*c*) and two types of (*d*, *e*) carbon—carbon double bonds (Fig. 4) Since the crystal structure of compound **4** was determined with low accuracy, it is reasonable to consider the average bond lengths of only three types: C—Br, 2.002 Å; C—C, 1.512 Å (bond types *a*—*c*); and C=C, 1.347 Å (bond types *d* and *e*). These bond lengths are in rather good agreement with the corresponding average bond lengths observed in the solvates with bromine: 1.993, 1.500, and 1.339 Å ($C_{60}Br_{24} \cdot Br_2$ [1]), 1.994, 1.510 and 1.346 Å ($C_{60}Br_{24} \cdot 2\ Br_2$).[5]

Hence, the reaction of solid C_{60} with liquid bromine proceeds stepwise to give successively $C_{60}Br_8$, $C_{60}Br_{14}$, and $C_{60}Br_{24}$ (the latter is the final bromination product). The precise control over the bromination time enables one to prepare each bromide in the pure state.

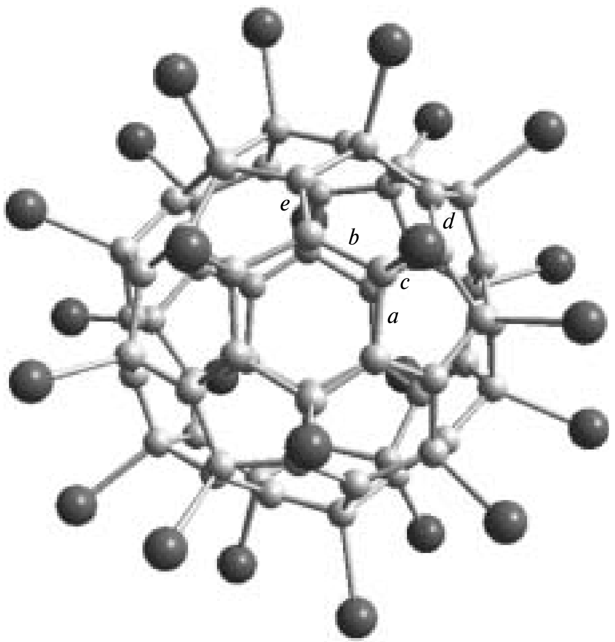


Fig. 4. Structure of the $C_{60}Br_{24}$ molecule with the idealized T_h symmetry in the solvate $C_{60}Br_{24} \cdot C_6H_4Cl_2 \cdot Br_2$.

In the reactions of fullerene with bromine in organic solvents, the position of thermodynamic equilibrium is shifted toward the starting compounds. Hence, to synthesize bromofullerenes, it is necessary to use an amount of bromine substantially larger than that corresponding to the stoichiometry of the expected products. For a series of solvents, we found the optimal bromine concentrations for the preparation of $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Br_{24}$.

Single-crystal X-ray diffraction study allowed us to refine the molecular structures of bromofullerenes $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Br_{24}$.

Experimental

Apparatus and reagents. All solvents were purified according to standard procedures. The IR spectra were recorded on a Bruker Vector-22 Fourier-transform IR spectrometer. Thermogravimetry and differential scanning calorimetry were performed on a Mettler TA-3000 thermoanalyzer.

Bromination of C_{60} in organic solvents. A necessary amount of bromine (see Table 1) was added to a saturated C_{60} solution. The reaction mixture was allowed to stand without stirring at room temperature for 1—10 days. The crystals of bromofullerene that formed were filtered off or decanted and then washed with hexane. In some cases, washing led to partial or complete decomposition of the bromofullerene solvates (due to removal of the solvent molecule or bromine), which makes them unsuitable for X-ray diffraction study.

Synthesis of $C_{60}Br_8 \cdot nBr_2$ (n = 1, 2) by the reaction of C_{60} with bromine. Fullerene C_{60} (50—150 mg) was added to bromine (5—10 mL). The mixture was allowed to stand without stirring at room temperature for 5—20 min. Then black crystals of

$C_{60}Br_8 \cdot 2Br_2$ were filtered off and dried in air to remove adsorbed bromine. The crystals of $C_{60}Br_8 \cdot 2Br_2$ rapidly lost one bromine molecule to form $C_{60}Br_8 \cdot Br_2$. Found (%): C, 42.86; Br, 57.14. $C_{60}Br_8 \cdot 2Br_2$. Calculated (%): C, 42.88; Br, 56.89. IR (KBr), ν/cm^{-1}: 444, 501, 514, 523, 542, 545, 561, 569, 575, 609, 706, 720, 733, 750, 766, 768, 774, 794, 820, 846.

Synthesis of $C_{60}Br_{14} \cdot Br_2$ by the reaction of C_{60} with bromine. A mixture of fullerene C_{60} (100 mg) and bromine (10 mL) was stirred for 30 min. Then the solution was filtered from unreacted $C_{60}Br_8 \cdot 2Br_2$, and the filtrate was concentrated *in vacuo* using a water-jet pump to give an orange-red compound ($C_{60}Br_{14} \cdot Br_2$) in 87% yield. Found (%): C, 36.38; Br, 63.65. $C_{60}Br_{14} \cdot Br_2$. Calculated (%): C, 36.00; Br, 64.00. IR (KBr), ν/cm^{-1}: 418, 528, 537, 546, 550, 590, 604, 609, 623, 651, 668, 698, 717, 742, 748, 753, 764, 773, 779, 796, 815, 817, 823, 842, 857, 920.

X-ray diffraction study. X-ray diffraction data sets for single crystals of **1—4** were collected at 150—180 K on an IPDS (Stoe) single-crystal diffractometer equipped with a two-coordinate detector using Mo-Kα monochromated radiation (λ = 0.71073 Å). The absorption correction was applied numerically taking into account the real crystal shape. The structures were solved and the atomic coordinates and displacement parameters were refined by the least-squares method using the SHELXS[10] and SHELXL[11] program packages. The crystallographic data, characteristics of X-ray data collection, and details of structure refinement of compounds **1—4** are given in Table 2. The crystallographic data for compounds **1—4** were deposited with the Cambridge Structural Database (CSD deposition numbers 230207—230210).

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