Bromination of C_{70}: $C_{70}Br_{10}$

The First X-ray Crystal Structures of Halogenated [70]Fullerene: $C_{70}Br_{10}$ and $C_{70}Br_{10}\cdot 3Br_2$**

Sergey I. Troyanov, Alexey A. Popov,*
*Nadezhda I. Denisenko, Olga V. Boltalina,**
Lev N. Sidorov, and Erhard Kemnitz

In the past decade halogenated fullerenes have been intensely studied as versatile synthons in fullerene chemistry.[1] X-ray structural data were reported for various halo[60]fullerenes, including fluorides ($C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$) and bromides: $C_{60}Br_6$,[2,3] $C_{60}Br_8$,[2,3] and $C_{60}Br_{24}$.[2,4] In addition, the structure of $C_{60}Cl_6$ has been suggested on the basis of NMR spectroscopy.[5]

In contrast, only modest progress has been made in the regioselective synthesis and structural characterization of halo[70]fullerenes. Fluorination of C_{70} has yielded complex mixtures of highly fluorinated products.[8] The most probable addition pattern in $C_{70}Cl_{10}$ was proposed based on its ^{13}C NMR spectrum.[9] The situation for bromo[70]fullerenes is even less clear; two theoretical studies have been published, each predicted a different addition pattern for bromo[70]fullerenes.[6,7] In one synthetic study, the direct bromination of C_{70} was claimed to yield $C_{70}Br_{24}$.[2] In another synthetic study, the product of C_{70} bromination with liquid Br_2 (as well as with Br_2 dissolved in CS_2 or $C_2H_2Cl_4$) was proposed to be $C_{70}Br_{14}$.[10] In our recent study, the available experimental evidence suggested that the product of C_{70} bromination was $C_{70}Br_{10}$.[11]

Herein, we confirm that the bromination of C_{70} produces $C_{70}Br_{10}$ and not $C_{70}Br_{14}$ or $C_{70}Br_{24}$. The evidence is the single-crystal X-ray structures of $C_{70}Br_{10}$ (**1**) and $C_{70}Br_{10}\cdot 3Br_2$ (**2**).

The bromination of C_{70} in neat bromine, in *o*-dichlorobenzene, or in carbon disulfide yielded crystalline $C_{70}Br_{10}$ or its crystalline dibromine solvates. The IR spectra of all crystalline products were similar and were in good agreement with the DFT-calculated spectrum shown in Figure 1. Thermogravimetric analysis reveals a two-step mass loss for the solvates formed by the direct bromination of C_{70}: the first step

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[*] Dr. S. I. Troyanov, Dr. O. V. Boltalina, A. A. Popov, N. I. Denisenko,
Prof. Dr. L. N. Sidorov
Chemistry Department
Moscow State University
119992 Moscow (Russia)
Fax: (+7) 095-9391-240
E-mail: troyanov@thermo.chem.msu.ru
ovbolt@lamar.colostate.edu

Prof. Dr. E. Kemnitz
Institut für Chemie
Humboldt-Universität Berlin
12489 Berlin (Germany)

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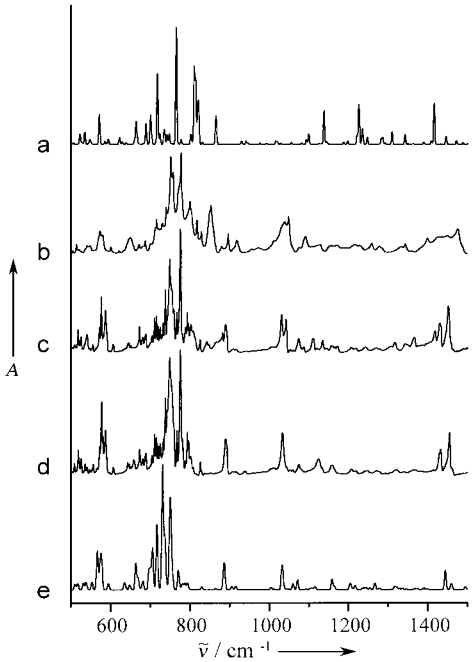

Figure 1. IR spectra of the bromo[70]fullerenes: a) simulated spectrum of $C_{70}Br_{14}$ with meridianal arrangement; b) experimental spectrum of "$C_{70}Br_{14}$" from reference [10] presented in absorbance units; experimental spectra of $C_{70}Br_{10}$ c) synthesized in neat bromine, d) in 1,2-dichlorobenzene, and e) simulated spectrum of $C_{70}Br_{14}$ with equatorial arrangement. A = relative absorbance (arbitary units).

(40–70 °C) was assigned to the release of the Br_2 solvate molecules leaving $C_{70}Br_{10}$; the second step (130–144 °C) was assigned to the decomposition of $C_{70}Br_{10}$ to C_{70} and Br_2. The formation of the bromine solvate was confirmed additionally by the X-ray single crystal structure of $C_{70}Br_{10}\cdot 3\,Br_2$ (**2**) synthesized by brominating dilute *o*-dichlorobenzene solutions of C_{70}. Probably, the putative compound $C_{70}Br_{14}$ [10] corresponds to the bromine solvate of $C_{70}Br_{10}$. The IR spectrum of "$C_{70}Br_{14}$"[13] (Figure 1 b) is close to that of $C_{70}Br_{10}$ reported herein and differs drastically from the simulated spectrum for $C_{70}Br_{14}$ with meridianal bromine arrangement (Figure 1 a).

The molecular structure of $C_{70}Br_{10}$ in **1** has an idealized C_s symmetry (Figure 2). There are five pairs of symmetry-related Br atoms. The brominated sp^3 carbon atoms are located in a closed belt of ten hexagons around the C_{70} equator. Nine of the ten hexagons contain a pair of Br atoms in 1,4-positions; the remaining hexagon has a 1,2-addition pattern of Br atoms (Figure 3). This is the same addition pattern that was deduced from the NMR spectra for $C_{70}Cl_{10}$,[9] $C_{70}Ph_{10}$,[12] and $C_{70}H_{10}$.[13] The observed structure had been predicted in two theoretical studies[7,11] and was also considered as the most stable for the case of ten bulky groups attached to C_{70}.[14] The stabilizing factors of the observed addition pattern are the retention of conjugation in both hemispheres of the C_{70} cage and the absence of double bonds in pentagons. Note that the equatorial addition pattern in $C_{70}Br_{10}$ differs significantly from the meridianal pattern predicted earlier[6] for the still-unknown molecule $C_{70}Br_{14}$.

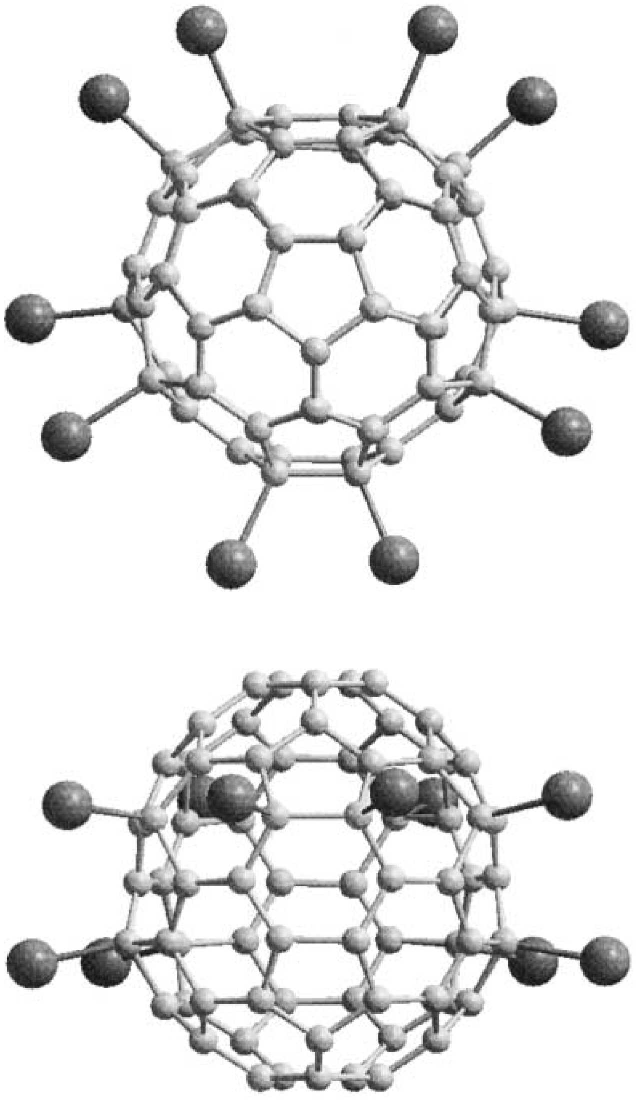

Figure 2. The top and side views of the $C_{70}Br_{10}$ molecule.

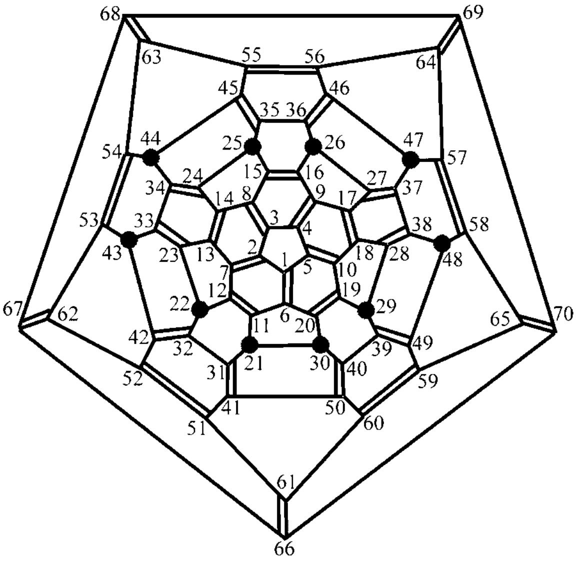

Figure 3. The Schlegel diagram and labeling Scheme for the $C_{70}Br_{10}$ molecule.

The geometry parameters in the polar regions of $C_{70}Br_{10}$ remain substantially the same as those in the parent C_{70}. The averaged lengths for "single" and "double" C–C bonds are 1.44 Å and 1.40 Å, respectively, (Table 1) consistent with the values for C_{70}, 1.45 Å and 1.38 Å.[15] As expected, the most considerable perturbations of the carbon cage occur around the bromine-bearing carbon atoms. Significant bond lengthening was found for sp^2–sp^3 C–C (1.48(2)–1.54(2) Å; the analogous bonds in C_{70} 1.42–1.45 Å) and, in particular, for the unique sp^3–sp^3 C21–C30 bond (1.59(2) Å cf. 1.44 Å in C_{70}). The experimental $C_{70}Br_{10}$ molecular structure was found to be in a comparatively good agreement with the results of our DFT calculations (Table 1).

Additionally, a small (by 0.05 Å) shortening of the long axis of the ellipsoidal C_{70} molecule takes place upon bromination. The sp^3 C atoms are displaced from the geometric center of the molecule on average by 0.37 Å, whereas some adjacent sp^2 C atoms (C23, C24, C27, C28, C41, C42, C45, C46, C49, and C50) are further from the center by only 0.10 Å as compared with the analogous averaged distances in C_{70}.[15] C–Br bonds lie within a narrow range of 1.99–2.03(1) Å, in good agreement with data for three known C_{60} bromides, 1.99–2.01 Å.[3,4]

The X-ray single-crystal structure determination for the bromine solvate, $C_{70}Br_{10}{\cdot}3Br_2$ (**2**), revealed the same molecular structure as that of the $C_{70}Br_{10}$ moiety, but with higher standard deviations for C–C (0.05 Å) and C–Br bonds (0.03 Å).

The packing in the crystal structures of **1** and **2** is shown in Figure 4. The shortest intermolecular separations in **1** are: C···C, 3.14–3.49 Å, C···Br, 3.26–3.31 Å, and Br···Br, 3.31–3.61 Å. In contrast to the dense packing in **1**, the structure of **2** has channels parallel to the *a* axis, in which Br_2 molecules are situated. The longer carbon cage axes of the $C_{70}Br_{10}$ molecules are oriented nearly parallel to the channels. Therefore, the shortest C···C separations, 3.36–3.54 Å, are between the top and bottom pentagons.

In summary, we have determined the first X-ray structures of halogenated [70]fullerene, containing $C_{70}Br_{10}$ molecule, which has a prominent beltlike arrangement of Br atoms in the equatorial region and is the most stable product of the C_{70} bromination.

Table 1: C–C and C–Br bonds (Å) in $C_{70}Br_{10}$ according to the averaged X-ray data for structure **1** and DFT calculations.

Bond	X-ray	Calc.	Bond	X-ray	Calc.
	North pole, C–C			South pole, C–C	
C(1)–C(2)	1.45(2)	1.438	C(31)–C(32)	1.44(2)	1.437
C(2)–C(3)	1.46(2)	1.455	C(35)–C(36)	1.49(2)	1.441
C(3)–C(4)	1.48(2)	1.439	C(41)–C(50)	1.48(2)	1.471
C(6)–C(11)	1.42(2)	1.430	C(41)–C(51)	1.42(2)	1.427
C(7)–C(12)	1.44(2)	1.431	C(42)–C(52)	1.40(2)	1.416
C(7)–C(13)	1.44(2)	1.445	C(45)–C(55)	1.42(2)	1.415
C(8)–C(14)	1.43(2)	1.447	C(51)–C(61)	1.44(2)	1.445
C(8)–C(15)	1.45(2)	1.433	C(52)–C(62)	1.43(2)	1.446
C(13)–C(23)	1.42(2)	1.414	C(53)–C(62)	1.44(2)	1.435
C(14)–C(24)	1.41(2)	1.415	C(54)–C(63)	1.44(2)	1.435
C(33)–C(34)	1.44(2)	1.441	C(55)–C(63)	1.45(2)	1.445
			C(66)–C(67)	1.48(2)	1.453
			C(67)–C(68)	1.43(2)	1.440
			C(68)–C(69)	1.42(2)	1.456
	North pole, C=C			South pole, C=C	
C(1)–C(6)	1.39(2)	1.411	C(31)–C(41)	1.42(2)	1.396
C(2)–C(7)	1.39(2)	1.398	C(32)–C(42)	1.42(2)	1.399
C(3)–C(8)	1.38(2)	1.401	C(35)–C(45)	1.37(2)	1.395
C(11)–C(12)	1.44(2)	1.379	C(51)–C(52)	1.42(2)	1.402
C(13)–C(14)	1.40(2)	1.401	C(53)–C(54)	1.38(2)	1.376
C(15)–C(16)	1.39(2)	1.377	C(55)–C(56)	1.43(2)	1.402
C(23)–C(33)	1.40(2)	1.395	C(61)–C(66)	1.38(2)	1.396
C(24)–C(34)	1.40(2)	1.396	C(62)–C(67)	1.40(2)	1.403
			C(63)–C(68)	1.38(2)	1.399
		Equatorial region, C(Br)–C(Br), C–C(Br), and C–Br			
C(11)–C(21)	1.43(2)	1.502	C(25)–C(35)	1.51(2)	1.504
C(21)–C(30)	1.59(2)	1.636	C(33)–C(43)	1.49(2)	1.504
C(21)–C(31)	1.52(2)	1.515	C(34)–C(44)	1.50(2)	1.504
C(12)–C(22)	1.48(2)	1.508	C(42)–C(43)	1.52(2)	1.526
C(15)–C(25)	1.52(2)	1.511	C(43)–C(53)	1.54(2)	1.510
C(22)–C(23)	1.52(2)	1.526	C(44)–C(45)	1.54(2)	1.527
C(22)–C(32)	1.52(2)	1.501	C(44)–C(54)	1.50(2)	1.510
C(24)–C(25)	1.53(2)	1.527	C(21)–Br(1)	2.03(1)	2.016
C(22)–Br(2)	2.01(1)	2.036	C(25)–Br(5)	1.99(1)	2.034
C(43)–Br(3)	2.00(1)	2.036	C(44)–Br(4)	2.00(1)	2.035

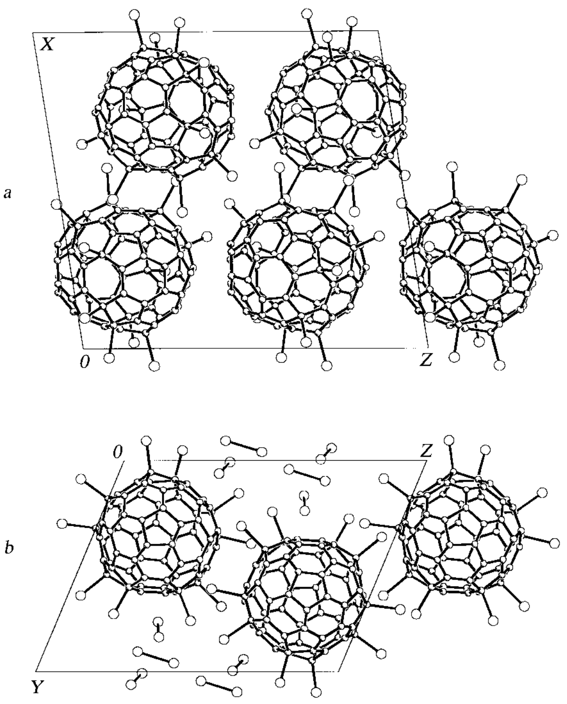

Figure 4. The packing in the crystal structure of a) $C_{70}Br_{10}$ and b) $C_{70}Br_{10}{\cdot}3\,Br_2$.

Experimental Section

Two synthetic routes were used for the preparation of $C_{70}Br_{10}$. In the first procedure, a reaction of C_{70} (98.5 %, TERMUSA) with an excess of liquid bromine was carried out at room temperature with a variation of the reaction time ranging from 5 min to several weeks. The orange solid separated by filtration had poor crystallinity. Alternatively, saturated solution of C_{70} in 1,2-dichlorobenzene (or in CS_2) reacted with excess bromine during 20–50 h. The fine crystalline orange product was stable in air for some weeks.

Small needles crystals of $C_{70}Br_{10}$ (**1**) were grown in glass ampoules by diffusion of Br_2 into concentrated solution of C_{70} in 1,2-dichlorobenzene during two months. Small crystals of $C_{70}Br_{10}{\cdot}3\,Br_2$ (**2**) were precipitated in a similar ampoule after two weeks when a dilute solution of C_{70} was used.

Thermal properties were investigated with 3–5 mg samples by using differential scanning calorimetry (DSC) and thermogravimetric methods with METTLER TA300. IR spectra were recorded in KBr pellets on a Bruker IFS-113v FT spectrometer with an average of 128 scans and a resolution of 0.5 cm^{-1}.

Data collection for crystals of **1** ($0.16\times0.03\times0.03$ mm^3) and **2** ($0.30\times0.08\times0.02$ mm^3) was carried out on an IPDS diffractometer (Stoe) at 153 K and 170 K, respectively (graphite monochromatized $Mo_{K\alpha}$-radiation, $\lambda = 0.71073$ Å). $C_{70}Br_{10}$, **1**: monoclinic, $P2_1/c$, $a = 18.579(4)$, $b = 12.313(2)$, $c = 19.680(4)$ Å, $\beta = 98.64(3)°$, $V = 4451.0(15)$ Å^3, $Z = 4$. Reflections collected 35754, independent 9654. Structure solution with SHELXS-97. LS refinement (SHELXL-97) with anisotropic Br and isotropic C for 7563 reflections and 371 parameters converged to $wR_2 = 0.1115$ and $R_1 = 0.0553$. $C_{70}Br_{10}{\cdot}3\,Br_2$, **2**: triclinic, $P\bar{1}$, $a = 11.400(3)$, $b = 13.973(4)$, $c = 18.165(5)$ Å, $\alpha = 111.78(4)$, $\beta = 93.19(4)$, $\gamma = 96.42(4)°$, $V = 2655.3(13)$ Å^3, $Z = 2$. Reflections collected 23593, independent 11828. LS refinement with anisotropic Br and isotropic C for 7946 reflections and 425 parameters gave the final values of $wR_2 = 0.3184$ and $R_1 = 0.1388$.[16]

The geometry optimization and vibrational spectra calculation were performed with the PRIRODA program[17] at the DFT level of theory employing PBE exchange-correlation functional[18] and a Gaussian-type basis set of TZ2P quality with effective core potential for bromine atoms.

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Keywords: bromination · fullerenes · structure elucidation

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[16] CCDC-200994 (**1**) and -200995 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
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