The First Crystal Structure of a Halogenated Higher Fullerene, $C_{78}Br_{18}$, Obtained by Bromination of a Fullerene Mixture

Sergey I. Troyanov*[a] and Erhard Kemnitz[b]

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Simple bromination of a fullerene mixture allowed the separation of C_{78} from other fullerenes in form of crystalline $C_{78}Br_{18}$. The first X-ray single-crystal structure of a halogenated higher fullerene, $C_{78}Br_{18}$, revealed that the addition pattern of 18 bromine atoms on the C_{78} cage corresponds to a partial retention of the conjugated double bond systems and the formation of isolated C–C double bonds. Evidently, even a separation of the C_{2v} and D_3 isomers of C_{78} occurred in the course of bromination and precipitation.

Since the discovery of fullerenes, their chemistry has developed very rapidly. Most experimental work was performed with C_{60}, yet only a small fraction of the investigations have been devoted to the chemistry of C_{70}. Higher fullerenes are obtained during fullerene formation as a minor admixture with C_{60} and C_{70}. Their separation from C_{60} and C_{70} is achieved by multi-step, high-pressure liquid chromatography (HPLC). This results in a mixture of higher fullerenes,[1] which makes further separation a difficult but challenging task. Limited studies on individual higher fullerenes show that the existence of several isomers complicates their investigation drastically.[2]

Among halogenated fullerenes, which are important synthons for further derivatization of fullerenes, some fluorides, from $C_{60}F_2$ to $C_{60}F_{48}$,[3] one chloride, $C_{60}Cl_6$,[4] and three bromides, $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Br_{24}$,[5] were isolated. Among C_{70} halides, many fluorides (from $C_{70}F_{34}$ to $C_{70}F_{44}$),[6] $C_{70}Cl_{10}$,[7] $C_{70}Br_{14}$,[8] and $C_{70}Br_{10}$,[9] have been reported, the latter was the only studied crystallographically. Fluorinated higher fullerenes with C_{76}, C_{78}, C_{82}, and C_{84} were isolated and characterised to varying extents by MS, NMR, and IR spectra.[10] Here, we report that bromination of fullerenes results in a separation of one of the higher fullerenes, C_{78}, from its mixture with C_{70} and several higher fullerenes. The X-ray single-crystal structure of $C_{78}Br_{18}$ showed that a partial separation of C_{78} isomers occurred even during bromination.

A CS_2 solution of C_{70} (94.70%, TERMUSA) containing 1.90% C_{60} and 3.40% of higher fullerenes (0.24% C_{76}, 0.67% C_{78}, and 2.49% C_{84}) was brominated in a glass ampoule by slow diffusion of gaseous Br_2. In several independent experiments, small dark-red crystals (**I**) were precipitated at the first stage of bromination. The next bromination step led to the deposition of orange-coloured crystalline $C_{70}Br_{10}$ (**II**).[9] X-ray single-crystal structure investigation of **I** revealed the presence of the $C_{78}Br_{18}$ molecule, the first structurally characterized halide of a higher fullerene.[11] The high molecular D_{3h} symmetry of $C_{78}Br_{18}$ in the crystal results most probably from statistical disordering of two $C_{78}Br_{18}$ isomers, both with C_{2v} symmetry (Figure 1). Among five possible C_{78} isomers obeying the isolated pentagon rule, the two isomers possessing C'_{2v} and C_{2v} symmetry should be more stable according to theoretical calculations.[12] Two C_{2v} isomers and the third one with D_3 symmetry were detected by NMR in the C_{78} sample in 5:2:2 [13] or 1.8:3.0:5.2 ratios.[14] Only two C_{78} isomers, C'_{2v} and D_3, were found in an earlier study.[15] Such remarkable deviations may arise from differences in the methods used for fullerene preparation. We believe that $C_{78}Br_{18}$ in **I** is formed from the two C_{78} isomers: C'_{2v} (major part) and C_{2v} (minor part). Other combinations of the starting C_{78} isomers are conceivable, but less probable, because they would involve the C'_{3h} isomer expected to have the lowest stability.[12] In contrast, the C_{78} cage corresponding to the C'_{3h} isomer has been found in the endohedral $Sc_3N@C_{78}$ fullerene.[16]

As can be seen from Figure 1 and the Schlegel diagrams (Figure 2), both isomeric $C_{78}Br_{18}$ molecules possess C_{2v} symmetry and differ only in the position of some C−C bonds parallel or perpendicular to the equatorial mirror plane (which appears horizontal in the top views in Figure 1). In the $C_{78}Br_{18}$ molecule disordered around the threefold axis, superposition of carbon atoms C8 and C8a has been found with relative site occupancies of 0.61:0.39, which corresponds to a C'_{2v}/C_{2v} ratio of about 80:20, close

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[a] Chemistry Department, Moscow State University,
Vorobjevy Gory, 119992 Moscow, Russia
Fax: (internat.) + 7-095/9391240
E-mail: troyanov@thermo.chem.msu.ru
[b] Institut für Chemie, Humboldt-Universität zu Berlin,
Brook-Taylor-Str. 2, 12489 Berlin, Germany

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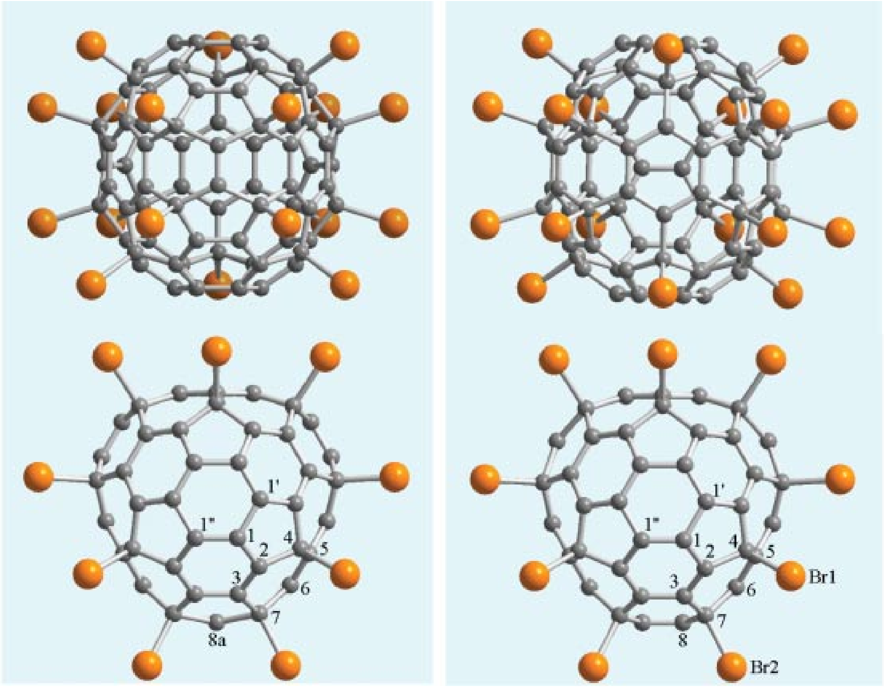

Figure 1. $C_{78}Br_{18}$ molecules with C'_{2v} (left) and C_{2v} (right) symmetry shown along their C_2 axes (top projections); the bottom projections are along the trigonal axis of the disordered molecule in the crystals of **I**

to that reported in ref.[13] A similar type of disordering is also present in the crystal structure of the iridium derivative of C_{84}, which, so far, was the only exohedral derivative of a higher fullerene characterized by X-ray single-crystal diffractometry.[17] A possible bromination product of the D_3-C_{78} isomer is definitely absent in the crystals of **I**. Due to a very small quantity of **I** available, the IR spectrum of a single crystal was recorded with an FT-IR microscope (Mattison Galaxy 5020, MCT detector) with a resolution of 4 cm^{-1} and 256 scans (Figure 3). Comparison of experimental and simulated spectra for the brominated C'_{2v}-C_{78} isomer (DFT level of theory with PBE exchange-correlation functional) demonstrates their relatively close similarity.[18]

The first X-ray single-crystal structure of a higher fullerene bromide, $C_{78}Br_{18}$, revealed that the highly symmetrical addition pattern of eighteen bromine atoms on the C_{78} cage corresponds to a partial retention of the conjugated double-bond systems in both isomeric $C_{78}Br_{18}$ molecules (C5/C6 and C1/C2/C3) and the formation of isolated C−C double bonds (C8 or C8a). The formation of three benzenoid rings (C5/C6) and the absence of double bonds in pentagons contribute to the stability of the molecules. The interatomic distances for the $C_{78}Br_{18}$ molecule are presented in Table 1. There is a distinct gradation in the C−C bond lengths dependent on a presumably single- (av. 1.433 Å) or double-bond (av. 1.387 Å) character (depicted in Figure 2 as single and double bonds). Due to superposition of two isomeric structures, the C5−C6 and C6−C6′ bonds are of approximately equal length, 1.403(6) and 1.414(8) Å. Much shorter are the isolated double bonds, C8−C8′ and C8a−C8a′ (on average 1.33 Å). As expected, the sp^2-sp^3 C−C bonds are substantially longer (av. 1.525 Å). Two C−Br bonds have virtually the same length (av. 2.000 Å). The geometrical parameters for C−C and C−Br bonds in $C_{78}Br_{18}$ correspond well to those found earlier for bromides of C_{60} [5,19] and C_{70} (**II**).[9]

A partial separation of C_{84} isomers was achieved by the selective formation of an iridium derivative.[17] C_{2v} and D_3 isomers of C_{78} could also be separated in the course of a silylation reaction with disilirane due to a greater reactivity of the C_{2v} isomers.[20] However, pure C_{84} and C_{78} fullerenes were used as the starting material in ref.[17] and ref.[20], respectively. In our case, a surprisingly high selectivity of bromination resulted in the precipitation of **I** as an individual phase, although a mixture of several fullerenes was used. It is known that bromination of C_{60} and C_{70} proceeds easily, only if a large excess of bromine is present in the system.[5] It seems that such limitation does not exist for C_{78} so that bromination of C_{78} occurs at lower Br_2 concentrations. A possible high reactivity of the C_{2v} and D_{3h} isomers of C_{78} was discussed earlier on the basis of double-/single-bond distribution patterns.[21] Deposition of crystals from a very dilute C_{78} solution (ca. 10^{-5} mol/L) seems to occur because of extremely low solubility of **I** in carbon disulfide.

In conclusion, simple bromination of a fullerene mixture with only 0.67% C_{78} content led to the isolation of crystals containing $C_{78}Br_{18}$. X-ray single-crystal structure showed a highly symmetrical addition pattern of eighteen Br atoms characterized by the presence of conjugated double-bond systems and isolated double bonds in the carbon cage. Partial separation of fullerene isomers also occurred in the co-

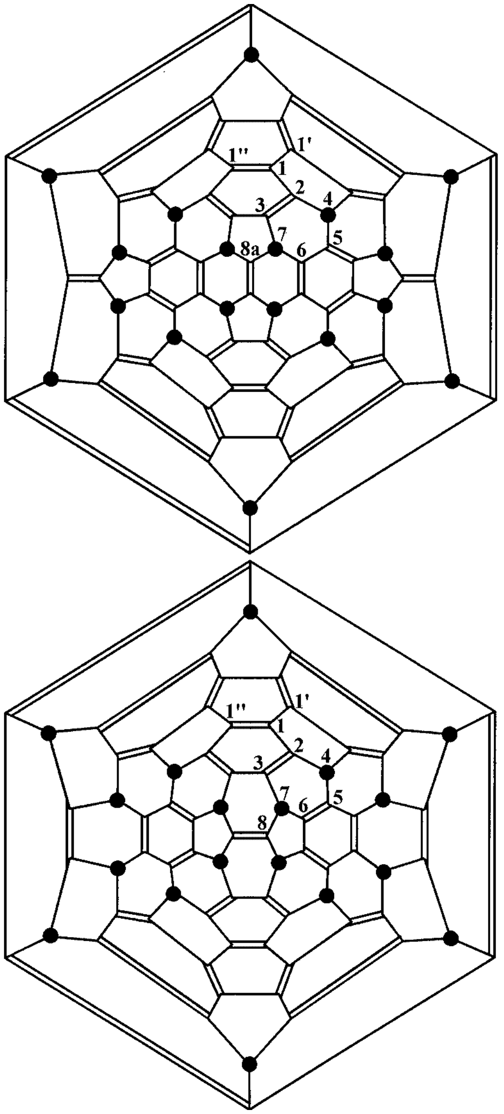

Figure 2. Schlegel diagrams for two isomeric $C_{78}Br_{18}$ molecules with C_{2v}' (top) and C_{2v} (bottom) symmetry: the horizontal symmetry planes correspond to the molecule equators; the labels of independent C atoms for the averaged structure in the crystal are given

urse of bromination and precipitation. The bromination reaction described above could be used for a separation of fullerenes or even their isomers. Due to a generally low thermal stability of fullerene bromides, any specific fullerene can be easily recovered from its bromide by simple heating to 130−160 °C. Such addition/elimination processes were discussed earlier as a possible way to separate the higher fullerenes.[22]

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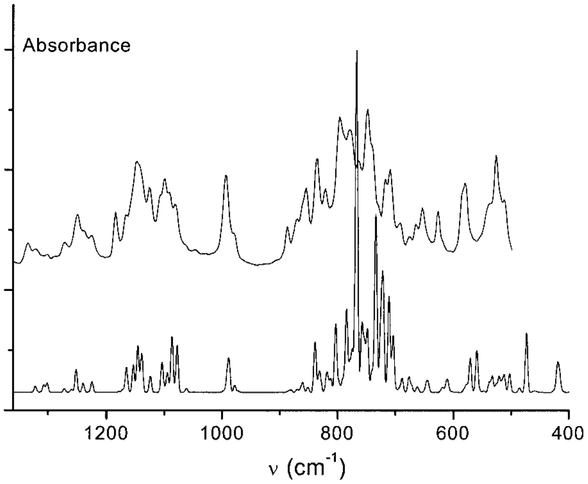

Figure 3. Comparison between experimental (top) and calculated (bottom) IR spectra of $C_{78}Br_{18}$ with C_{2v}' symmetry; the calculated spectrum is slightly shifted to lower wavenumbers due to an imperfect scaling

Table 1. Bond lengths [Å] in the $C_{78}Br_{18}$ molecule

Bond	Length	Bond	Length
C−C		C−C(Br)	
C1−C1′	1.466(9)	C2−C4	1.528(6)
C1−C2	1.406(9)	C5−C4	1.528(6)
C3−C3′	1.427(9)	C3−C7	1.504(6)
C5−C6[a]	1.403(6)	C6−C7	1.506(7)
C=C		C8−C7	1.528(6)
C1−C1′′	1.388(9)	C8a−C7	1.577(8)
C2−C3	1.386(6)	C−Br	
C6−C6′[a]	1.414(8)	C4−Br1	1.996(6)
C8−C8′	1.33(2)	C7−Br2	2.003(4)
C8a−C8a′	1.32(3)		

[a] Superposition of single and double bonds due to disorder.

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[11] Crystal data for **I**: dark-red hexagonal prism, data collection with an IPDS (Stoe) at 160(2) K with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Hexagonal, space group $P6_3/mmc$, a = 17.877(3), c = 15.370(3) Å, V = 4254(1) Å^3, Z = 2; 27284 reflections collected; numerical absorption correction with min/max transmission = 0.317/0.426; 1711 independent reflections (R_{int} = 0.120) included in the full-matrix least-square refinement with 131 parameters (SHELXL-97), R_1 = 0.0334, wR_2 = 0.0731. Within the $C_{78}Br_{18}$ molecule, one independent C8 atom was found to be disordered with a site occupancy ratio of 0.61:0.39 for C8/C8a. Besides the $C_{78}Br_{18}$ molecule, **I** contains one small and one larger disordered region with some partial occupied sites. In the smaller disordered region, CS_2 or HBr molecules are most likely present. EDX analysis of the crystals weathered during ca. 4 months showed the presence of ca. 1 mol-% S (less, than expected). The larger disordered region contains a highly disordered nonidentified molecule of solvation. CCDC-210174 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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