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Halogenated Fullerenes

Connectivity Patterns of Two C_{90} Isomers Provided by the Structure Elucidation of $C_{90}Cl_{32}$**

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Since the discovery and characterization of fullerenes C_{60} and C_{70}, isolation and characterization of the stable isomers of higher fullerenes have been the subject of much research. Owing to a very low content of higher fullerenes in the fullerene soot, isolation of most of the higher fullerenes requires the use of a multistep HPLC process. Their characterization, though not always unambiguous, proceeds typically through ^{13}C NMR spectroscopy supported in most cases by theoretical calculations of their relative stability.[1] Another method to characterize higher fullerenes is based on their derivatives which, as a rule, are much easier to separate. In the last few years, some isomers of C_{74},[2] C_{76},[3] C_{78},[2,4] C_{80},[5] and C_{84},[6] have been structurally investigated in form of their halogenated, trifluoromethylated, or other derivatives.

For still higher fullerenes an additional problem arises from the growing number of cage isomers obeying the isolated pentagon rule (IPR).[7] In the case of C_{90}, which has a "magic" $6n$ number of carbon atoms and 46 possible IPR isomers,[7,8] there were ambiguities in the assignments of the ^{13}C NMR spectral lines of isomer mixtures.[9–11] Recently, a probable addition pattern of 12 CF_3 groups to the C_{90} cage (suggested as isomer 32) was proposed based on the ^{19}F NMR spectrum of $C_{90}(CF_3)_{12}$.[4e] Herein we report the isolation and X-ray crystallographic study of $C_{90}Cl_{32}$ that allowed us to establish the cage structure of two C_{90} isomers, one of which was not expected to be found in a synthetic mixture.

A mixture (15 mg, MER Corp.) containing higher fullerenes from C_{76} to C_{96} (with the exception of C_{80}) and small amounts of C_{60} and C_{70} was treated with excess $SbCl_5$ (0.5 mL) in a glass ampoule at 350 °C for one to two weeks. After cooling, the ampoule was opened and $SbCl_5$ was washed out by treatment with several portions of concentrated HCl and water. Crystalline $C_{90}Cl_{32}$ together with some other crystalline fullerene chlorides (for example, D_{3d}-$C_{60}Cl_{30}$ primarily obtained by the same method[12]) was present in the dried product mixture as thin rhombus-like pale-yellow plates. Its composition and crystal structure were determined by single crystal X-ray diffraction with the use of synchrotron radiation.[13]

It is worth noting that the formation of different crystalline phases in the form of well distinguishable and separable single crystals was observed by us several times in the course of the halogenation of fullerene mixtures. For example, bromination of 98.5 % C_{70} containing approximately 1 % of C_{60} and small amounts of higher fullerenes as admixtures yielded well-shaped crystals of $C_{78}Br_{18}$ thus resulting in the first X-ray structure determination for higher fullerene halides.[4a] In the recent work, chlorination of C_{70} of approximately the same purity with a $TiCl_4/Br_2$ mixture yielded, along with $C_{70}Cl_{10}$, separate phases of $C_{60}X_{24}$ (X = Cl, Br) and $C_{78}Cl_{18}$ in form of single crystals.[4c]

Two crystalline modifications of $C_{90}Cl_{32}$ were found; however, both contain essentially the same $C_{90}Cl_{32}$ molecules which are characterized by the same formal disorder of one C–C bond. In fact, there are two slightly different $C_{90}Cl_{32}$ molecules at the same crystallographic site which correspond to chlorides of different cage isomers of C_{90}. The main component with a site occupation of approximately 80 % will be described first. As can be seen in Figure 1, the whole $C_{90}Cl_{32}$ molecule has noncrystallographic C_s symmetry with a mirror plane passing through the middle of the C–C bonds connecting the left and right sides of the C_{90} cage. This cage of idealized C_{2v} symmetry can be unambiguously identified as isomer No. 46 among 46 possible IPR isomers of C_{90} according to the classification based on their spiral codes.[7] The earlier NMR spectroscopic data for a sample containing the mixture of C_{90} isomers were indicative for the presence of five different species, especially, isomers 36 (C_{2v}) and a C_2 isomer for the major fraction according to the interpretation reported.[9] Isomer 45 (C_2) was shown by quantum-chemical

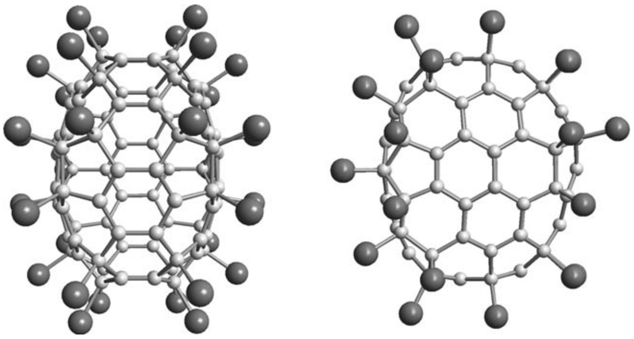

Figure 1. Two projections of the $C_{90}Cl_{32}$ molecule with the C_{90} (46) fullerene cage.

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computations to be the most stable species followed by isomer 46 (C_{2v}) and 35 (C_s).[10,11,14] On this basis, the published experimental NMR data for the major fraction were reevaluated, thus resulting in an alternative interpretation which assumes the presence of isomers 46 and 35 in the mixture.[10,11]

Therefore, the isolation of $C_{90}Cl_{32}$ as chloro derivative of isomer C_{2v}-C_{90} (46) is not very surprising. However, our crystallographic data indicate the presence of a $C_{90}Cl_{32}$ molecule originating from another C_{90} isomer. In structural determinations of the both crystalline modifications as well as the crystals obtained by chlorination of different higher fullerene batches, a formal disorder of two C atoms was found arising from an overlap of two C_{90} cages. This results in a rotation of one C–C bond by 90° resembling a Stone–Wales pyracyclene transformation (Figure 2).[15] A close inspection of the connectivity in the second carbon cage clearly identifies it as the isomer C_s-C_{90} (34). The carbon cage of C_{90} (46) has only one hexagon surrounded by six adjacent hexagons (the most distant one from the viewer in the left projection in Figure 1 and the largest limiting hexagon on the Schlegel diagram in Figure 2). The cage of C_{90} (34) has three such hexagons (two of them are marked with crosses on the Schlegel diagram in Figure 2), whereas the cage of C_s-C_{90} (35) has none.[7]

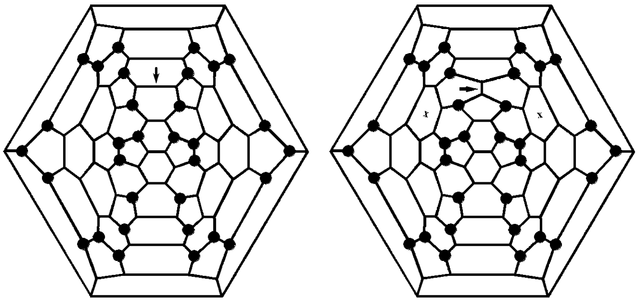

Figure 2. Schlegel diagrams of two $C_{90}Cl_{32}$ molecules present in the same crystal which contain C_{90} (46, left) and C_{90} (34, right) cages. Arrows indicate the C–C bonds which are oriented differently in the two cages. See main text for further details.

A refinement of the relative occupancies of disordered C atoms gave an estimated content of 28(4) % for the $C_{90}Cl_{32}$ molecule with the carbon cage of isomer 34 for structure I and 17(2) % for structure II. It is therefore clear that the C_s isomer of C_{90} (34) was present in the initial fullerene mixture, though its relative content not necessarily corresponds to that found in crystals of $C_{90}Cl_{32}$. Isomer 34 has a relatively high heat of formation (80–93 $\mathrm{kJ\,mol^{-1}}$ according to different computational data),[10,11] but, at the same time, it is characterized by a relatively high HOMO–LUMO gap of approximately 2.0 eV that may contribute to its high kinetic stability. From this point of view, the presence of isomer 34 instead of isomer 35 in the isomeric mixture investigated by high-resolution ^{13}C NMR spectroscopy[9] cannot be excluded.

The $C_{90}Cl_{32}$ molecule represents an example of the richest chloro derivative of the highest fullerene investigated to date by single-crystal X-ray diffraction. The use of hot $SbCl_5$ as chlorinating agent ensures a maximum degree of chlorination for a given fullerene. By this method, C_{60} and C_{70} were chlorinated to $C_{60}Cl_{30}$ and $C_{70}Cl_{28}$, respectively.[12,16] In addition, liquid $SbCl_5$ as chlorination media provides suitable conditions for crystal growth. The addition pattern of 32 Cl atoms on the C_{90} cage can be rationalized in terms of the maximum use of the pentagon–hexagon–hexagon (PHH) junctions as suitable sites for chlorination. All known structures of higher chlorides of fullerenes demonstrate that, while triple Cl contacts are definitively avoided, 1,2 contacts of attached Cl atoms are possible under simultaneous formation of extended aromatic systems. Therefore, longer chains of attached Cl atoms are present in the molecules of $C_{60}Cl_{28}$,[17] $C_{60}Cl_{30}$,[12,17] $C_{70}Cl_{28}$,[16] and $C_{76}Cl_{18}$.[3]

In both experimentally found C_s-$C_{90}Cl_{32}$ molecules there are two nine-membered chains of Cl atoms attached in 1,2 positions and two three-membered chains. The other eight Cl atoms occupy isolated positions on the C_{90} cage. As a result, four isolated quasi-aromatic systems are present in both $C_{90}Cl_{32}$ molecules, one antracene-like and two phenanthrene-like fragments together with one benzenoid ring. They are characterized by averaged C–C distances of 1.40, 1.40, and 1.38 Å, respectively, the values for the molecules from different crystalline modifications being practically the same. Among five isolated double C–C bonds, one is disordered and the remaining four bonds have average bond length of 1.34 Å. As expected, the most elongated C–C bonds are those between two sp^3 carbon atoms both bearing Cl atoms. It is possible to distinguish between bonds common to two hexagons (6:6 bonds) with average bond lengths of 1.54 Å and those shared by a hexagon and a pentagon (6:5 bonds) which are elongated, average 1.60 Å. The average C–Cl distance is 1.80 Å being close to the values for D_{3d}-$C_{60}Cl_{30}$ (1.78 Å),[12] $C_{60}Cl_{24}$ (1.82 Å),[18] and $C_{76}Cl_{18}$ (1.81 Å).[3] The shortest intramolecular Cl···Cl distances (3.02 Å) are between chlorine atoms attached to the C atoms forming 6:6 bonds.

The same addition pattern of 32 Cl atoms to the C_{90} fullerene isomeric cages 46 and 34 enables a co-crystallization of the two similar $C_{90}Cl_{32}$ species. The molecular packing diagrams in two crystalline modifications of $C_{90}Cl_{32}$ are shown in Figure 3. Both monoclinic (I) and triclinic (II) modifications have packing motifs consisting of two layer systems which are nearly orthogonal to one another in I and somewhat inclined in II. The relative positions of adjacent molecules within vertical layers are parallel in the modification I and antiparallel in II. Both packings are characterized by rather short intermolecular Cl···Cl contacts (3.10–3.35 Å) that are typical for all structures of crystallographically characterized solvent-free fullerene chlorides.[3,4b,c,12] The existence of special but not clearly defined Cl···Cl interactions has been postulated to explain this phenomenon.[3,4b] In our opinion, short Cl···Cl contacts are possible because Cl atoms do not bear any significant negative charge in fullerene chlorides. This was quantitatively confirmed in an electron-density study of D_{3d}-$C_{60}Cl_{30}$ in which the charges on three different types of Cl atoms were found to be −0.13, −0.08, and even + 0.06 e.[19] Such charge distribution might be caused by high electron affinity of fullerenes as shown, for example, by

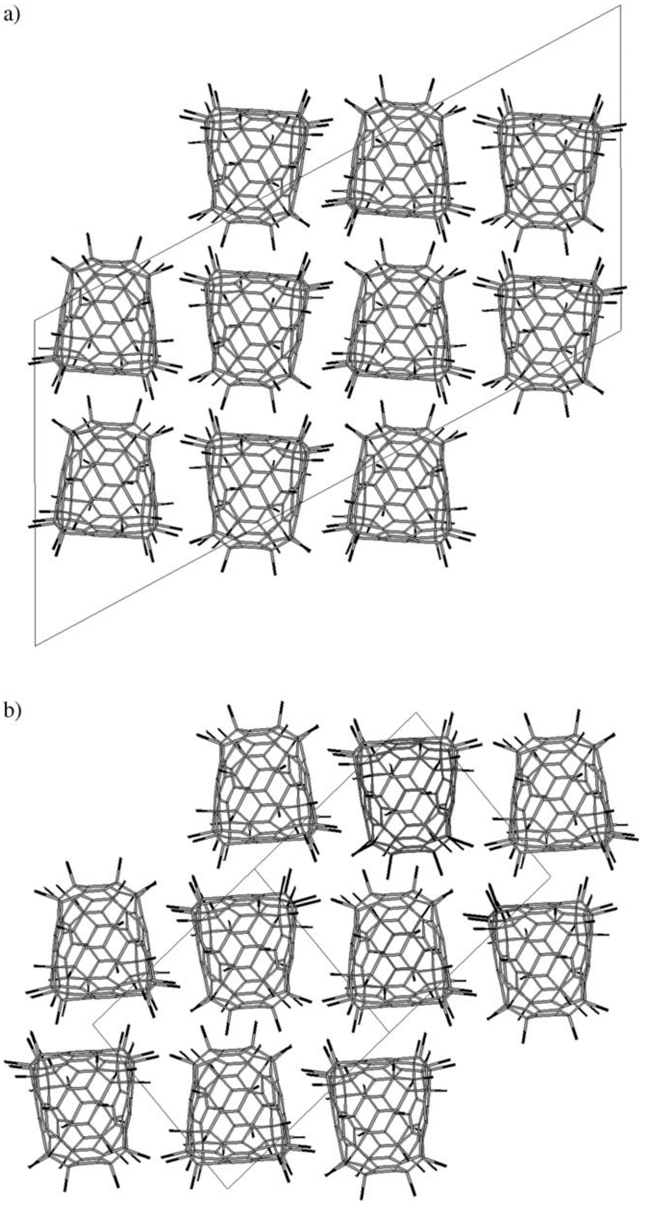

Figure 3. Packing of $C_{90}Cl_{32}$ molecules in crystal modifications I (a) and II (b).

their enhanced ability to form multiply charged anions. Therefore, for fullerene chlorides, mutual repulsion of Cl atoms caused by Coulomb interactions should be reduced thus allowing shorter intra- and intermolecular Cl···Cl contacts.

In summary, the chlorination of a higher fullerene mixture with $SbCl_5$ resulted in the formation of $C_{90}Cl_{32}$, which is the maximum degree of chlorination achieved for fullerenes. The addition pattern of 32 Cl is characterized by the presence of linear chains of 1,2-attached Cl atoms as well as isolated Cl atoms resulting in the formation of aromatic systems and isolated C−C double bonds on the C_{90} fullerene cage. The first XRD study of a C_{90} derivative revealed the presence of C_{90} (46) and C_{90} (34) carbon cage isomers as major and minor components, respectively. The isomer 34 of C_{90} has been experimentally confirmed for the first time indicating a need to reinterpret the NMR spectroscopy data for C_{90} reported earlier.

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[13] Data collection was performed on a MAR225 image plate at 100 K using synchrotron radiation at the BESSY storage ring ($\lambda = 0.9050$ Å, BL14.2, PSF of the Free University of Berlin, Germany). Structure solution and refinement with SHELXS97 and SHELXL97, respectively. $C_{90}Cl_{32}$-I: $M_r = 2215.30$, mono-

clinic, $C2/c$, $a = 47.5533(2)$, $b = 14.9608(1)$, $c = 23.2785(1)$ Å, $\beta = 118.2182(3)^\circ$, $V = 14\,592.9(1)$ Å^3, $Z = 4$, $wR_2 = 0.210$ (for 15042 reflections and 1118 parameters), $R_1 = 0.079$ (for 14286 reflections with $I > 2\sigma(I)$). $C_{90}Cl_{32}$-II: triclinic, $P\bar{1}$, $a = 14.8335(1)$, $b = 15.2243(1)$, $c = 16.0550(1)$ Å, $\alpha = 94.6749(4)$, $\beta = 90.1735(3)$, $\gamma = 93.7615(4)^\circ$, $V = 3605.72(4)$ Å^3, $Z = 2$, $wR_2 = 0.122$ (for 13168 reflections and 1108 parameters), $R_1 = 0.045$ (for 11431 reflections with $I > 2\sigma(I)$). In the both crystal modifications of $C_{90}Cl_{32}$, two C atoms occupy two different positions each indicating the presence of the second $C_{90}Cl_{32}$ isomer in the same crystal. CCDC 713663 and CCDC 713664 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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