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Preparation and crystal structure of D_{2d}-$C_{84}(23)Cl_{24}$ chlorofullerene

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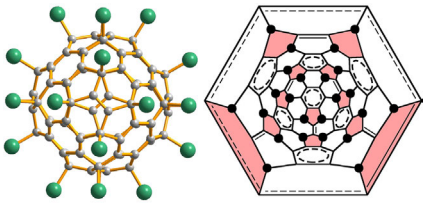
Chlorofullerene D_{2d}-$C_{84}(23)Cl_{24}$ was prepared by chlorination of D_{2d}-$C_{84}(23)$ with VCl_4 or $SbCl_5$ at 320–350 °C. An X-ray crystallographic study with the use of synchrotron radiation revealed the addition pattern of 24 Cl atoms stabilized by the formation of isolated C=C bonds and benzenoid rings on the carbon cage.



D_{2d}-$C_{84}(23)Cl_{24}$

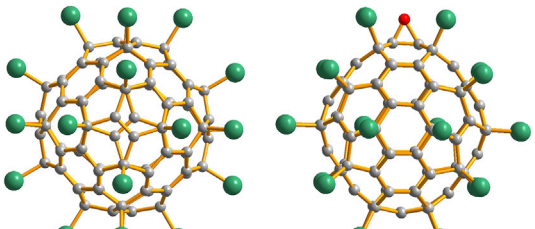
Keywords: higher fullerenes, C_{84}, chlorination, IPR isomers, structure elucidation.

In spite of the discovery of fullerenes about four decades ago, the chemistry of higher fullerenes (above C_{70}) still remains in its enfancy. The studies are hampered by the low abundance of higher fullerenes in the fullerene soot, the existence of numerous structural isomers, and difficulties of their separation.[1] The mostly studied compound classes are halogeno and perfluoroalkyl derivatives of higher fullerenes up to C_{108} and C_{98}, respectively.[2,3] The most abundant higher fullerene, C_{84}, has 24 topologically possible isomers obeying the Isolated-Pentagon-Rule (IPR).[1,4–8] Several IPR isomers of C_{84} nos. 4, 5, 11, 16, 18, 22, 23, and 24 (the numbering according to the spiral code[1]) have been reported as perfluoroalkyl derivatives.[9–14] At the same time, structural data on chlorinated C_{84} are available only for two minor IPR isomers in $C_{84}(5)Cl_{20,32}$ and $C_{84}(11)Cl_{20,22}$,[12,15] whereas no data for the major isomers, $C_{84}(22)$ and $C_{84}(23)$, were reported so far.

In this communication, the data on the synthesis and X-ray crystal structure of a chlorofullerene, D_{2d}-$C_{84}(23)Cl_{24}$, are reported. The chlorination pattern featuring the formation of stabilizing substructures on the carbon cage are discussed in detail. The structure of the oxidation product, $C_{84}(23)OCl_{24}$, is presented as well.

Experimentally, the main chromatographic HPLC fraction of C_{84}, containing primarily isomers $C_{84}(23)$ admixed with $C_{84}(22)$ was chlorinated with an excess of $SbCl_5$ or VCl_4 in glass ampoules at 320–350 °C for 3–5 days. After cooling, the ampule was opened and the excess of $SbCl_5/VCl_4$ and $SbCl_3/VCl_3$ formed were removed by washing, sequentially, with conc. HCl, dilute HCl, and water, leaving orange-colored crystalline phase of chlorofullerene. Its composition, $C_{84}(23)Cl_{24}$, and crystal structure were determined by the single crystal X-ray diffraction study with the use of synchrotron radiation. Remarkably, the same compound was obtained by chlorination of the separately prepared sample of $C_{84}(CF_3)_n(C_2F_5)_n$ with $SbCl_5$ under the conditions described above.[11] In some experiments using $SbCl_5$ not fully purified from antimony oxochlorides, similar crystalline phase of $C_{84}(23)OCl_{24}$ was obtained as proven by single crystal X-ray diffraction study.

The molecular structures of D_{2d}-$C_{84}(23)Cl_{24}$ and C_{2v}-$C_{84}(23)OCl_{24}$ are shown in Figure 1.† The crystallographic symmetry of both molecules, S_4, is lower. The idealised point symmetry of D_{2d}-$C_{84}(23)Cl_{24}$ corresponds exactly to the point symmetry of the starting D_{2d}-$C_{84}(23)$ fullerene because of the symmetric arrangement of 24 Cl atoms. In contrast, an oxygen atom in $C_{84}(23)OCl_{24}$ is attached in an epoxide mode to only one C–C bond thus lowering D_{2d} symmetry of the molecule. In fact, the molecule of epoxide, $C_{84}(23)OCl_{24}$, adopts C_{2v} or C_2 symmetry depending on the addition site of O atom. In the disordered crystal structure, the distribution of one O atom over six partially occupied positions imitates a more symmetric, S_4, arrangement.



D_{2d}-$C_{84}(23)Cl_{24}$ C_{2v}-$C_{84}(23)OCl_{24}$

Figure 1 Molecular structures of D_{2d}-$C_{84}(23)Cl_{24}$ and C_{2v}-$C_{84}(23)OCl_{24}$. The projection of D_{2d}-$C_{84}(23)Cl_{24}$ is given along the main D_2 axis. In the projection of the C_{2v}-$C_{84}(23)OCl_{24}$ molecule parallel to the mirror plane, only one epoxide O atom is shown whereas it is distributed over six positions in the disordered crystal packing.

† *Crystal data.* Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2/3, PSF, Germany) using a MAR225 CCD detector (λ = 0.8856 or 0.8950 Å). The crystal structures were solved by SHELXS and refined with SHELXL. $C_{84}Cl_{24}$, tetragonal, $I\bar{4}$, a = 13.912(1) and c = 16.184(2) Å, V = 3132.3(6) Å^3, Z = 2. The refinement with 3563 reflections and 262 parameters converged to wR_2 = 0.167 and R_1 = 0.060 for 2909 reflections with $I > 2\sigma(I)$. $C_{84}OCl_{24}$, tetragonal, $I\bar{4}$, a = 13.948(1) and c = 16.052(2) Å, V = 3122.9(6) Å^3, Z = 2. The refinement with 3428 reflections and 255 parameters converged to wR_2 = 0.175 and R_1 = 0.063 for 2654 reflections with $I > 2\sigma(I)$.

CCDC 2323029 and 2323030 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

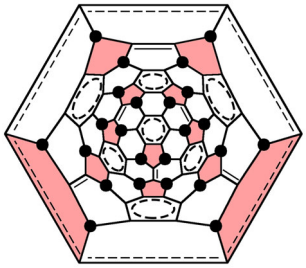


Figure 2 Schlegel diagram of D_{2d}-$C_{84}(23)Cl_{24}$. Cage pentagons are shown red. Black circles denote the attachment positions of chlorine atoms. Isolated C=C bonds and benzenoid rings are indicated with solid double lines and dashed ovals, respectively. All six C=C bonds are possible epoxidation sited in the molecule of $C_{84}(23)OCl_{24}$.

The chlorination pattern of D_{2d}-$C_{84}(23)Cl_{24}$ is presented as a Schlegel diagram in Figure 2. The arrangement of 24 Cl atoms is highly symmetric, thus retaining D_{2d} symmetry of the starting fullerene molecule. Each of 12 cage pentagons is occupied by two chlorine addends at the average C–Cl distance of 1.813 Å which is a typical value for IPR chlorofullerenes.[2] The groups of four C–Cl attachments isolate altogether six sp^2–sp^2 C=C bonds (*av*. bond length is 1.338 Å) which is a strong stabilizing factor of the whole molecule. An additional stabilization occurs due to the formation of aromatic substructures, eight benzenoid rings, on the carbon cage. Thus, a remarkable feature of the chlorine arrangement is the participation of each Cl attachment in the isolation of one C=C bond and two benzenoid rings, which has not been observed previously in the molecules of chlorofullerenes.

Theoretical DFT calculations[16,17] confirmed a high relative stability of D_{2d}-$C_{84}(23)Cl_{24}$ among chlorofullerenes. In the absence of structural data on isomeric $C_{84}Cl_{24}$ chlorofullerenes, we calculated the chlorination enthalpy per one Cl atom, E(Cl), and the values of ΔE(Cl) relative to E(Cl) of D_{3d}-$C_{60}Cl_{30}$ taken as a standard, for which the formation enthalpy is determined experimentally. The previous formation energy calculations for a wide range of multi chlorinated fullerenes revealed that, as a rule, the chlorination enthalpy decreases monotonously with increasing number of attached Cl atoms, regardless of the carbon cage size. The ΔE(Cl) value of D_{2d}-$C_{84}(23)Cl_{24}$, 9.6 kJ mol^{-1}, is significantly higher than those of $C_{84}(5)Cl_{20}$ and $C_{84}(11)Cl_{22}$, 2.8 and 7.5 kJ mol^{-1}, respectively, despite the lower number of attached Cl atoms in the latter. A comparison with other known IPR chlorofullerenes with 24 attached Cl atoms (ΔE(Cl) in kJ mol^{-1}) of T_h-$C_{60}Cl_{24}$ (–1.6), C_2-$C_{76}(1)Cl_{24}$ (3.4), C_S-$C_{90}(35)Cl_{24}$ (4.5), and four isomeric $C_{96}Cl_{24}$ (0.2–4.5) clearly demonstrates an outstanding stability of D_{2d}-$C_{84}(23)Cl_{24}$ in the family of chlorofullerenes.[2]

The product of a partial oxidation, $C_{84}(23)OCl_{24}$, is a monoepoxide with one O atom attached to the isolated C–C bond (see Figure 1), the position of which is statistically disordered in the crystal structure over six orientations. Note that the attachment of oxygen as an epoxide in $C_{84}(23)OCl_{24}$ is fully different to the case of C_{2h}-$C_{60}Cl_{30}O_2$ where both O atoms are inserted across C–C bonds, resulting in the formation of an intramolecular diether.[18]

In summary, a chloro derivative of the highly abundant C_{84} isomer, D_{2d}-$C_{84}(23)Cl_{24}$, was synthesized and structurally characterized. The addition pattern of 24 attached Cl atoms features the formation of six isolated C=C bonds and eight benzenoid rings on the carbon cage, which contribute to the enhanced stability among other multi chlorinated fullerenes.

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