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Preparation and crystal structure of $C_{84}(11)Cl_{20,22}$, chloro derivatives of a C_{84} minor isomer

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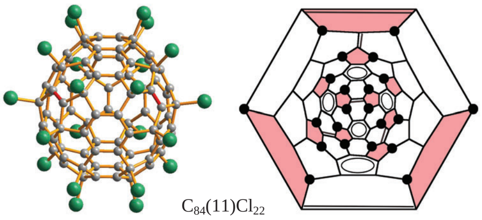
Chlorofullerenes $C_{84}(11)Cl_{20}$ and $C_{84}(11)Cl_{22}$ were prepared by chlorination of C_2–$C_{84}(11)$ with VCl_4 at 340–360 °C. An X-ray crystallographic study with the use of synchrotron radiation revealed the chlorination patterns featuring only *para* additions in C_6Cl_2 hexagons.


$C_{84}(11)Cl_{22}$

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Since the discovery of fullerenes, the chemistry of C_{60} and C_{70} has been studied intensively whereas that of higher fullerenes remains essentially unexplored.[1] The main restrictions are a low abundance of higher fullerenes in the fullerene soot and the existence of numerous structural isomers. Fullerene C_{84} is the most abundant in the arc-discharge fullerene soot and the number of topologically possible Isolated–Pentagon–Rule (IPR) isomers is 24.[2] The existence of ten C_{84} isomers has been confirmed experimentally either by ^{13}C NMR spectroscopy of chromatographically isolated fractions[3–5] or by structural studies of derivatives.[6–8] There are two major isomers, D_2-$C_{84}(22)$ and D_{2d}-$C_{84}(23)$, and several minor ones, from which isomer C_2-$C_{84}(11)$ possesses the higher abundance (isomer numbering in the parentheses is according to the spiral algorithm[2]).[3,4] Up to recently, the chemistry of C_2-$C_{84}(11)$ was limited to perfluoroalkyl derivatives, one isomer of $C_{84}(11)(C_2F_5)_{12}$ and several isomers of $C_{84}(11)(CF_3)_n$ with n ranging from 10 to 14.[8–10] The presence of C_2-$C_{84}(11)$ cage along with isomeric C_s-$C_{84}(14)$ and C_s-$C_{84}(16)$ has been yet assumed in chlorinated C_{84}.[11]

Herein, the preparation and X-ray crystal structure of two chlorofullerenes, $C_{84}(11)Cl_{20}$ and $C_{84}(11)Cl_{22}$ are reported. The discussion concerns the addition patterns of Cl atoms on the carbon cages and the origin of Stone–Wales crosses due to the disorder in the crystal packing.

Experimentally, a C_{84} subfraction of recycling HPLC containing predominately C_2-C_{84} isomer (*ca.* 0.1 mg) was chlorinated with an excess of VCl_4 in a thick-walled glass ampoule at 340 °C for 3 weeks. After cooling and ampoule opening, excess of VCl_4 and VCl_3 was removed by washing with water affording tiny, yellow-coloured crystals. In another experiment, a similar C_{84} sample (0.2 mg) reacted with VCl_4 to which a drop of $SbCl_5$ was added. The reaction at 360 °C lasted ten days till small yellow crystals have appeared which were isolated by washing with conc. HCl, dilute HCl, and, finally, with water. The crystals from both experiments were studied by X-ray diffraction with the use of synchrotron radiation revealing the structures of $C_{84}(11)Cl_{20}$ and $C_{84}(11)Cl_{22}$, respectively.[†]

The isolation of two compositionally different chlorofullerenes under essentially similar reaction conditions can be attributed to the presence of $SbCl_5$ in the reaction mixture which generally shows a stronger chlorination power at high temperature as compared with VCl_4. It should be, however, noted that the long total heating was needed not only for chlorination itself but also for the crystal growing process, often demanding considerable time. It is worth to mention that the excess of chlorinating agent, pure VCl_4 or a $VCl_4/SbCl_5$ mixture, proved to be a suitable media for growing crystals of chlorofullerenes.

The molecular structures of $C_{84}(11)Cl_{20}$ and $C_{84}(11)Cl_{22}$ are shown in Figure 1 whereas the cage connectivity and the addition patterns are presented as Schlegel diagrams in Figure 2. It can be seen in Figure 1 that the arrangement of 20 or 22 Cl atoms on the carbon cage is mirror-symmetric whereas two C–C bonds of the carbon cage (highlighted red) do not obey the mirror symmetry. The same differences in the arrangement symmetry of Cl atoms and C–C bonds are evident on Schlegel diagrams of both

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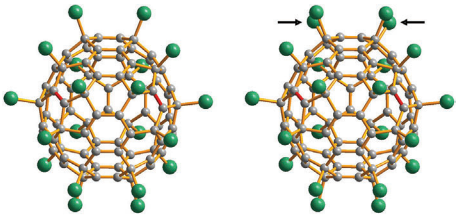
[†] *Crystal data.* Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2/3, PSF, Germany) using a MAR225 CCD detector (λ = 0.8950 or 0.8793 Å). The crystal structures were solved by SHELXD and refined with SHELXL.

$C_{84}Cl_{20}$, monoclinic, $P2_1/m$, a = 12.7810(8), b = 18.8981(7) and c = 13.4809(8) Å, β = 114.353(4)°, V = 2966.4(3) Å^3, Z = 2. The refinement with 6625 reflections and 232 parameters converged to wR_2 = 0.096 and R_1 = 0.075 for 5082 reflections with $I > 2\sigma(I)$.

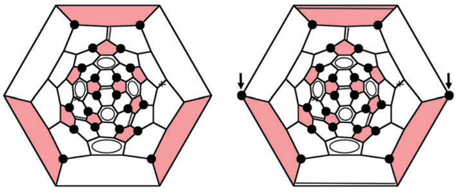
$C_{84}Cl_{22}\cdot 0.025\,Cl_2$, monoclinic, $P2_1/m$, a = 12.8271(7), b = 18.3229(5) and c = 13.3990(8) Å, β = 94.190(5)°, V = 3140.7(3) Å^3, Z = 2. Anisotropic refinement with 6062 reflections and 507 parameters converged to wR_2 = 0.037 and R_1 = 0.037 for 5936 reflections with $I > 2\sigma(I)$.

CCDC 2166076 and 2166077 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.



C_1-C_{84}(11)Cl_{20} C_1-C_{84}(11)Cl_{22}

Figure 1 Projections of the C_{84}(11)Cl_{20} and C_{84}(11)Cl_{22} molecules. The arrangements of all Cl and most C atoms are mirror-symmetric. Two C–C bonds violating the mirror symmetry are highlighted by red colour. Two added Cl atoms in the C_{84}(11)Cl_{22} molecule are indicated with arrows.



C_1-C_{84}(11)Cl_{20} C_1-C_{84}(11)Cl_{22}

Figure 2 Schlegel diagrams of C_{84}(11)Cl_{20} and C_{84}(11)Cl_{22}. Cage pentagons are shown red. Black circles denote the positions of chlorine attachments. The position of two added Cl atoms in the structure of C_{84}(11)Cl_{22} are pointed out by arrows. Isolated C=C bonds and isolated or nearly isolated benzenoid rings are shown with double lines and ovals, respectively. Two small crosses indicate the position of a two-fold axis of the C_2-C_{84}(11) carbon cage.

molecules. In the chlorination pattern of C_{84}(11)Cl_{20}, the attachment of Cl atoms occurs exclusively in *para* positions in C_6Cl_2 hexagons thus isolating four double C–C bonds and five benzenoid rings on the carbon cage. The attachment of two more Cl atoms in C_{84}(11)Cl_{22} results in the formation of two additional isolated C=C bonds. A comparison of the chlorination patterns of both molecules demonstrates clearly that C_{84}(11)Cl_{22} contains the pattern of C_{84}(11)Cl_{20} as a substructure.

In fact, the identification of C_{84} isomeric carbon cage in both rather similar crystal structures was not fully straightforward. The space group $P2_1/m$ implies the existence of a mirror plane bisecting the whole molecule which is not intrinsic to the C_2-C_{84}(11) carbon cage possessing only two-fold symmetry. A distinctive feature of both structure determinations was the presence of two so-called Stone–Wales crosses (SWCs), *i.e.*, two crossing C–C bonds on the place of a single C–C bond on the carbon cage. This phenomenon occurs in the structural chemistry of fullerene derivatives as a consequence of disorder in crystal packing when two molecules with symmetric outer form but asymmetric inner structure occupy statistically the same crystallographic site. In the case of C_{84}(11)Cl_{20} or C_{84}(11)Cl_{22}, the outer shape of both molecules is mirror-symmetric because of the symmetric arrangement of Cl atoms (see Figures 1 and 2). Therefore, there exists an equal probability for a molecule or its enantiomer to be included into the crystal packing in a given position which results in a higher symmetry and a formal overlap of two molecules manifested as the appearance of SW crosses. Thus, an individual molecule of C_{84}(11)Cl_{20} or C_{84}(11)Cl_{22} is slightly asymmetric whereas the presence of two half-occupied, overlapped molecules appears as being mirror-symmetric.

The overlap of C_{84}(11)Cl_{20} or C_{84}(11)Cl_{22} molecules with their enantiomers should result in equal (0.5/0.5) occupancies of two crossing C–C bonds in SWCs which was the case in the present crystallographic study. In the previously reported structure of $C_{84}Cl_{22}$ obtained by chlorination of non-separated C_{84} fraction with VCl_4, the appearance of similar, but asymmetric SWCs (with an occupancy ratio of 0.68/0.32) was interpreted as the presence of different isomeric C_{84} carbon cages, C_s-C_{84}(16), C_s-C_{84}(14), and, supposedly, C_2-C_{84}(11).[11] The latter suggestion could not be proven at that study because a C_{84} fraction with mixed (but unknown) isomeric composition has been used for chlorination. In general, a phenomenon of SWCs is documented in many reported cases of chlorofullerenes exemplified in the crystal structures of non-IPR $^{1810}C_{60}Cl_{24}$,[12] $C_{96}Cl_{24}$,[13] $C_{98}Cl_{20/22}$,[14] and $C_{104}Cl_{24}$.[15]

In the more accurately determined molecular structure of C_{84}(11)Cl_{22}, C–C bond lengths range from the short (isolated) sp^2–sp^2 C=C (*av*. 1.327 Å) over aromatic sp^2–sp^2 C–C in benzenoid rings (*av*. 1.396 Å) to the longest sp^2–sp^3 C–C(Cl) (*av*. 1.510 Å). The lengths of C–Cl bonds are 1.807–1.820(2) Å, *i.e.*, in a typical range for the most IPR chlorofullerenes. Theoretically DFT calculated[16,17] chlorination enthalpy (per one Cl atom) of C_{84}(11)Cl_{20} and C_{84}(11)Cl_{22} is +8.2 and +7.5 kJ mol^{-1}, respectively, relative to the value for D_{3d}-$C_{60}Cl_{30}$ which serves as a standard. The higher chlorination enthalpy of both C_{84} chlorofullerenes is due to the smaller than 30 numbers of bound Cl atoms which corresponds well to the typical dependences found previously for IPR chlorofullerenes irrespective of the cage sizes.[15]

In summary, high-temperature chlorination of C_2-C_{84}(11), the third abundant isomer of C_{84} fullerene, resulted in the isolation of C_{84}(11)Cl_{20} and C_{84}(11)Cl_{22}. An X-ray diffraction study revealed the molecular structures with similar chlorination patterns, featuring the presence of stabilizing substructures on the carbon cages such as isolated benzenoid rings and isolated C=C bonds.

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