Inorganic Chemistry
Communication

Inorg. Chem. **2010**, *49*, 3089–3091 **3089**
DOI: 10.1021/ic902442p

$C_{76}Cl_{34}$: High Chlorination of the Inherent Chiral Fullerene with a Helical Configuration

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Received December 8, 2009

As the smallest chiral fullerene in conformity with the Isolated Pentagon Rule (IPR), D_2-symmetric C_{76} has been chlorinated with iodine monochloride to form $C_{76}Cl_{34}$, a highly chlorinated derivative. Its structure with the chiral cage enwrapped by a helical chlorine pattern has been established using single-crystal X-ray diffraction analysis. The high chlorination and its implication for constructing novel chiral fullerene-based materials are discussed.

As the first available chiral fullerene, D_2-symmetric C_{76} (no. 19150, the numeration is specified with a spiral algorithm[1]) is the most representative member in the growing family of chiral fullerenes.[2-4] This inherent chiral fullerene, isolated and characterized just 1 year after the macroscopic synthesis of the notable C_{60} and C_{70}, is the smallest all-carbon cage that satisfies both the inherent chirality and the famous Isolated Pentagon Rule (IPR).[5] In principle, this species can serve as a "chiral superatom", from which a huge number of chiral fullerene-based derivatives can be synthesized through bonding with any addends. Previously reported derivatives of C_{76} (the molecular formula of C_{76} in this article is referred to as $^{\#19150}C_{76}$ if there is no specific notation) include the monoadducts with bis[(*S*)-1-phenylbutyl] 2-bromomalonate,[6] 3,4-dimethoxy-*o*-quinodimethane,[7] 1,1,2,2-tetramesityldisilirane,[8,9] and osmium tetroxide,[10,11] as well as methylate and methylenate,[12,13] respectively. By contrast, multiaddends to the chiral C_{76} core, which are expected to bring in a great variety of bonding geometries with chirality, have rarely been reported in the literature. Preliminary experiments for fluorination and hydrogenation with C_{76} were conducted by Taylor and co-workers to yield tiny amounts of multiaddend mixtures of $C_{76}H_{2m}$ (m = 23−25)[14] or $C_{76}F_{2n}$ (n = 16−22),[15] but full identification of their structures was fruitless. A family of $C_{76}(CF_3)_{2n}$ (n = 3−6) derivatives were isolated from the products of the reaction involving C_{76} with CF_3I at 520 °C under an argon atmosphere.[16] Their structures have been studied by mass spectrometry, ^{19}F NMR spectroscopy, and density functional theory calculations,[16] but X-ray crystallography seems necessary to confirm their geometries. Chlorination of C_{76} with $Br_2/TiCl_4$ (1:100, v/v) in an glass ampule gave $C_{76}Cl_{18}$ at 150 °C.[17] Following a similar chlorination method but with $SbCl_5$ at higher reaction temperature (340 °C), remarkably, a non-IPR $^{\#18917}C_{76}Cl_{24}$ was synthesized from the IPR-satisfying C_{76}.[18] Here we report a higher chlorination of C_{76} to afford $C_{76}Cl_{34}$ featuring a diverse derivatization pattern. X-ray crystallography reveals a cake-shaped geometry with the unchanged chiral C_{76} core enwrapped by two helically patterned chains of chlorine atoms.[19] Such

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(19) Crystal data: $C_{76}Cl_{34}$, fw = 2118.06, T = 273(2) K, λ = 0.71073 Å, monoclinic, $P2_1/n$, a = 13.821(7) Å, b = 19.569(9) Å, c = 25.085(12) Å; α = 90.00°, β = 91.879(11)°, γ = 90.00°, V = 6781(6) Å^3, Z = 4, reflections collected 24816, independent 12124, D_{calcd} = 2.075 g cm^{-3}, μ = 1.411 cm^{-1}, R1 = 0.0845, wR2 = 0.1973 [$I > 2\sigma(I)$]; R1 = 0.2119, wR2 = 0.2865 (all data).

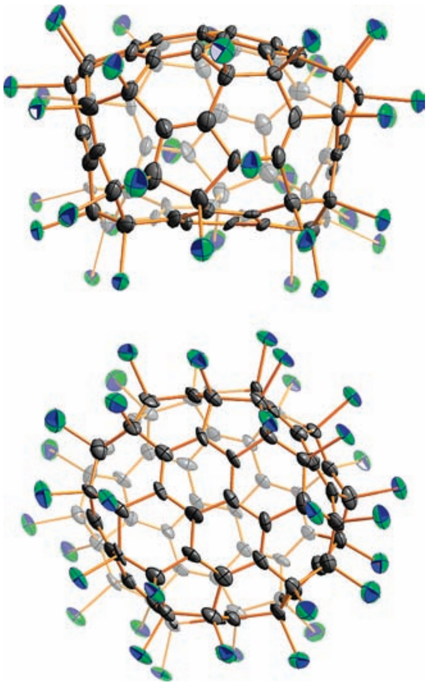

Figure 1. Structure of $C_{76}Cl_{34}$ in the form of an ORTEP drawing with thermal ellipsoids at the 50% probability level. The C_2 symmetry can be recognized in the structure below.

a highly chlorinated pattern is informative for understanding the reactivity of this representative inherent chiral all-carbon cage.

C_{76} was isolated and purified from the fullerene soot of graphite arc discharge by multistage high-performance liquid chromatography (HPLC) using toluene as the eluting solvent. Reacting with excess ICl at 180 °C for 24 h in a sealed glass ampule, C_{76} was chlorinated to produce $C_{76}Cl_{34}$ in the form of a platelike crystal. A UV−vis spectrum of the compound in toluene exhibits two distinct absorbing peaks at 405 and 457 nm, respectively. The details about the experiments are described in the Supporting Information.

The structure of $C_{76}Cl_{34}$ was determined by means of single-crystal X-ray diffraction. As showed in Figure 1, the cage of C_{76} is deformed into a cakelike shape in order to satisfy the tetrahedral geometric requirement of the sp^3-hybridized carbon atoms linking to chlorine atoms. The pattern for chlorination involves the carbon atoms of C17−C20, C22, C23, C26−C31, C33, C34, C37, C38, C43−C49, C54, C55, C57−C63, and C68−C70 (the numeration is shown in Figure 2). Such a chlorination pattern results in an interesting structure with a spiral configuration of chlorine atoms wrapping on the surface of the fullerene cage (Figure 3).

The residual sp^2-hybridized carbon skeletons are aromatic or conjugated. They include a pyrene of C1−C16, a naphthalene of C64−C67 and C71−C76, two butadiene fragments of C39−C42 and C50−C53, as well as four ethene parts of C24 and C25, C21 and C45, C32 and C56, and C35 and C36 (Figure 2). These aromatic or π-conjugated fragments in the fullerene derivative contribute to the overall stability of $C_{76}Cl_{34}$. The characteristic local aromaticity is also the common feature of the chloro derivatives of non-IPR fullerenes such as the non-IPR $^{\#18917}C_{76}Cl_{24}$.[18,20]

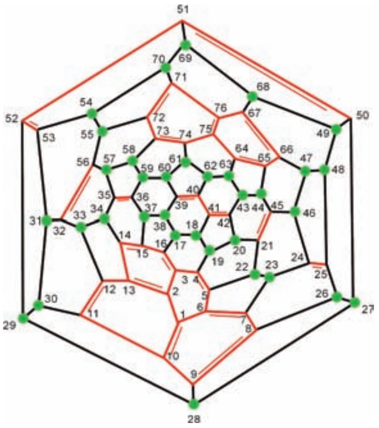

Figure 2. Schlegel diagram of $C_{76}Cl_{34}$, in which the chlorine atoms are indicated by green dots. The local aromatic or conjugated regions are highlighted in red.

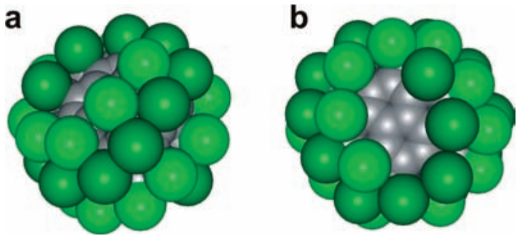

Figure 3. Side view (a) and top view (b) of the cage of C_{76} enwrapped by two helically patterned chlorine chains. The structures are plotted in the form of CPK mode (at 100% van der Waals radius). The color of the chlorine atom is classified as dark or light green for clarifification of the spiral chlorine pattern.

There are four long $C(sp^3)-C(sp^3)$ bonds (1.65 Å) in the $C_{76}Cl_{34}$ molecule, i.e., C30−C31, C38−C17, C60−C61, and C54−C70. In comparison with the longest $C(sp^3)-C(sp^3)$ bonds of C24−C25 and C52−C53 (1.71 Å) in $C_{76}Cl_{18}$,[17] however, the bonds in $C_{76}Cl_{34}$ are much shorter. The torsion angles of Cl−C−C−Cl involved in the longest $C(sp^3)-C(sp^3)$ bonds in $C_{76}Cl_{34}$ are −22.52°, 37.42°, −37.17°, and 42.79° respectively, while in $C_{76}Cl_{18}$, the corresponding torsion angles are nearly zero (−0.59° and 0.73°, respectively), which leads to strong repulsion between the vicinal chlorine atoms and sequentially results in elongated $C(sp^3)-C(sp^3)$ bonds. In addition, the C−Cl distances (1.76−1.83 Å) in $C_{76}Cl_{34}$ are on average shorter than those in $C_{76}Cl_{18}$ (1.82−1.85 Å). Both of the bond lengths of $C(sp^3)-C(sp^3)$ and C−Cl possibly suggest a higher stability of $C_{76}Cl_{34}$ as compared with the previously reported $C_{76}Cl_{18}$, just like the comparable case of $C_{60}Cl_{30}$ versus $C_{60}Cl_{24}$.[21,22]

In the crystal packing, as shown in Figure 4, the pyrene rings of $C_{76}Cl_{34}$ are opposite to each other in two neighboring layers through the so-called $C-Cl\cdots\pi$-type interactions[23] between a chlorine atom in one molecule and a neighboring hexagon in another mirror molecule symmetrically (as marked in Figure 4). In the same layer, the cakelike molecules are laid up side by side through the intermolecular chlorine interactions. As shown in Figure 4, marked with the

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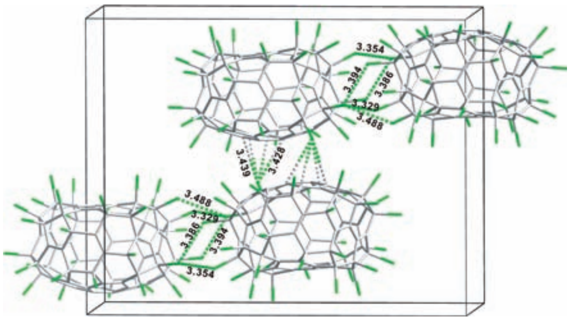

Figure 4. Crystal packing motif of $C_{76}Cl_{34}$. The short intermolecular Cl···Cl contacts are indicated by green dashed lines, and the short C−Cl···π-type contacts are labeled by green-gray dashed lines.

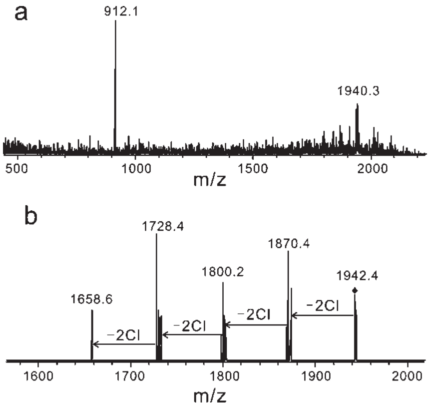

Figure 5. Mass spectra of $C_{76}Cl_{34}$: (a) APCI; (b) MS/MS. Note that the amounts of ions seem to be insufficient to give the present mass spectra with flawed isotopic distribution.

intermolecular distances of Cl···Cl in detail, the average short distance within intermolecular chlorine is about 3.39 Å. This bond length is shorter than the average of the van der Waals radii of Cl···Cl (3.6 Å), with implication of an attractive interaction between the chlorine atoms involved.

The mass spectrum in negative mode was performed on a Bruker Esquire HCT mass spectrometer with an ion source of atmospheric pressure chemical ionization (APCI) in the range of *m*/*z* 50−3000. The APCI furnace temperature was 350 °C. The molecular ion peak of $C_{76}Cl_{34}$ is hard to observe because of facile loss of chlorine atoms in such APCI heating conditions. As shown in Figure 5a, only $C_{76}Cl_{29}^-$ (corresponding to the peaks around *m*/*z* 1940.3) and C_{76}^- (corresponding to the peaks around *m*/*z* 912.1) are observed in the spectrum, likely implying the relative stability of the negative ion of $C_{76}Cl_{29}^-$. A Bruker HCT mass spectrometer equipped with an ion trap allows selection of any target ions for further fragmentation—by collision of the selected ions in vacuo with high-energy helium—to generate an offspring mass spectrum. Such a procedure could be repeated several times (could be up to 11 times as long as enough ions survive in the ion trap) so as to give a series of offspring mass spectra, i.e., multistage mass spectra (MS^n, $n = 2, 3, ...$). MS/MS is defined as MS^n with $n = 2$. Shown in Figure 5b is the MS/MS spectrum of the selected mother ion around *m*/*z* 1940−1943, whereby stepwise detachment of two chlorine atoms is observed. The progressive loss of two chlorine atoms in $C_{76}Cl_x^-$ ($x = 29, 27, 25, 23, ...$) is similar to the previous observation about the chlorofullerene $^{\#913}C_{56}Cl_{10}$.[24] Together with the fact that no molecular ion peak of $C_{76}Cl_{34}$ is detected in the APCI condition, it is reasonable to speculate the facile reaction involving dechlorination of $C_{76}Cl_{34}$, followed by substitution. This implies that $C_{76}Cl_{34}$ can be further derivatized by substituting chlorine atoms with desired functional groups for the construction of novel chiral fullerene-based materials.

The clarified stereochemical pattern of the polyaddition derivatization of $C_{76}Cl_{34}$ provides basic insights into the fundamental chemical properties of the chiral C_{76}. Most previously synthesized derivatives of C_{76} are limited in monoaddition.[6−13] The monoaddends afford only the information regarding the preliminary reaction involving C_{76}. To our knowledge, $C_{76}Cl_{34}$ represents the highest polyaddition derivative of the chiral C_{76} cage experimentally identified so far. In comparison with the chlorinated pattern of $C_{76}Cl_{18}$ in which the chlorine atoms are located at the carbon atoms of C13, C16, C19, C22−C27, C50−C55, C58, C61, and C64 (the numeration is the same as those shown in Figure 2), the structure of $C_{76}Cl_{34}$ is completely incompatible on the fashion of chlorine addition. This may preclude the possibility of the origin of $C_{76}Cl_{34}$ from $C_{76}Cl_{18}$ because the former cannot be derived by the simple addition of chlorine over the residual double bonds of the lower chlorinated one. However, it seems impractical to determine the intermediates for the formation of $C_{76}Cl_{34}$ at this stage.

In conclusion, $C_{76}Cl_{34}$, a highly chlorinated fullerene has been synthesized by chlorination of the inherent chiral fullerene D_2-symmetric C_{76} with iodine monochloride. As identified by single-crystal X-ray diffraction, the chlorination pattern with the chiral cage enwrapped by a spiral configuration of chlorine atoms is dissimilar to the structures previously reported and promises the construction of novel chiral fullerene-based polyaddition derivatives.

Acknowledgment. We thank Professor Yu-Qi Feng from Wuhan University for HPLC support. This work was supported by the NNSF of China (Grants 20525103, 20531050, and 20721001) and the 973 Program (Grant 2007CB815301).

Supporting Information Available: Crystallographic data in CIF format, experiments for the synthesis of $C_{76}Cl_{34}$, HPLC isolation of C_{76}, X-ray diffraction analysis of $C_{76}Cl_{34}$, and UV spectra of C_{76} and $C_{76}Cl_{34}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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