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Crystal Structures of Saturn-Like $C_{50}Cl_{10}$ and Pineapple-Shaped $C_{64}Cl_4$: Geometric Implications of Double- and Triple-Pentagon-Fused Chlorofullerenes**

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Fullerenes are spherical cage carbon molecules constructed from hexagons and exactly 12 pentagons.[1,2] Theoretically, according to the so-called Isolated Pentagon Rule (IPR),[3] fullerenes with isolated pentagons are relatively stable and synthesizable. This same rule predicts that fullerenes with fused pentagons are too reactive to be isolated. IPR-violating fullerenes, however, have been reported to be stabilized by either encapsulation with metal atoms (or their carbide/nitride clusters)[4,5] or external derivatization.[6a,7] Fullerenes featuring fused pentagons have been characterized by computationally corroborated ^{13}C NMR spectroscopy.[6–8] Detailed information regarding their geometries and inter-molecular interactions, however, requires single-crystal X-ray characterization, as in the case of $Sc_3N@C_{68}$.[9] The crystal structures of two double-fused-pentagon endohedral metallofullerenes, namely $La@C_{72}(C_6H_3Cl_2)$[10] and $Tb_3N@C_{84}$,[11] have also been determined. Highly accurate structural parameters established by X-ray crystallography are rare for exohedral derivatives of IPR-violating fullerenes. Prinzbach et al., for example, have recently reported the crystal structures of polybrominated dodecahedrane,[12] which is the smallest IPR-violating fullerene derivative known to date. Herein we report two crystal structures of IPR-violating fullerenes (C_{50} (no. 271) and C_{64} (no. 1911))[2,13] stabilized by exohedral chlorination. The former is the smallest fullerene

for which a cage can be constructed without triplets of directly or sequentially fused pentagons,[3,6,14] while the latter is a triple-fused-pentagon fullerene.[7] The crystallographic data reported herein provide unequivocal structural information for these IPR-violating fullerene derivatives (e.g., detailed geometric parameters, molecular curvature, pyramidalization angles,[15] aromaticity, intermolecular interactions) and the property implications thereof.

The X-ray structures[16] of $C_{50}Cl_{10}$ (**1**) and $C_{64}Cl_4$ (**2**) are shown in Figure 1. The symmetries of these IPR-violating chlorofullerenes are identical to those of their carbon cage parents, in other words D_{5h}-C_{50} (**1a**) for **1** and C_{3v}-C_{64} (**2a**) for **2**. The former is a Saturn-like chlorofullerene molecule constructed symmetrically from five pairs of two fused pentagons whose fused edges are covalently bound by ten chlorines in a manner that resembles the rings around Saturn (another Saturn-like halogenated molecule is $C_{60}F_{20}$, which was synthesized by Taylor[17]). In contrast, **2** has a pineapple-shaped structure with four chlorine atoms covalently attached
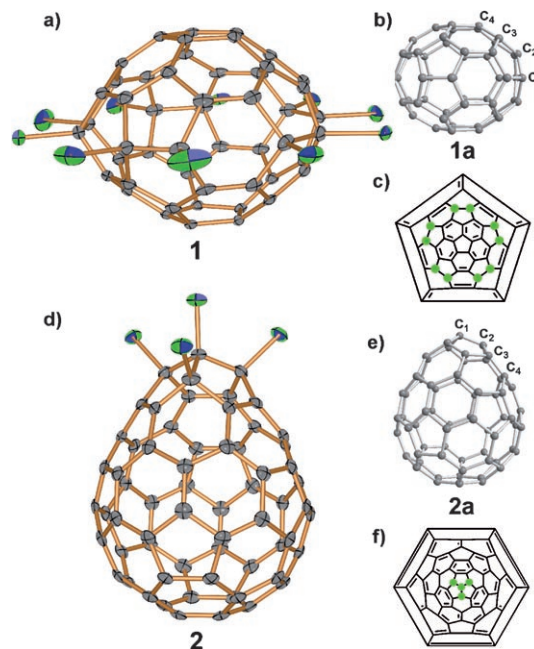
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Figure 1. ORTEP structures (a, d) and Schlegel diagrams (c, f) of $C_{50}Cl_{10}$ (**1**) and $C_{64}Cl_4$ (**2**), and theoretically optimized structures (b, e) of C_{50} and C_{64}. The ORTEP structures are plotted with thermal ellipsoids at 50% probability. The chlorine atoms in the Schlegel diagrams (c, f) are indicated as green dots.

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to the fused edges of three fused pentagons like "pineapple leaves". These crystallographic studies confirm our previously reported structure for $C_{50}Cl_{10}$, which was deduced mainly by ^{13}C NMR spectroscopy and theoretical calculations,[6a] and support the structural identification of the recently isolated $C_{64}H_4$.[7]

The most notable feature of these IPR-violating fullerenes is the existence of fused pentagons (two in **1a** and three in **2a**), which lead to enhanced strain of the cage surfaces. The degree of strain is reflected in terms of the pyramidalization angles (θ_p)[15] at the relevant carbon atoms. θ_p for an sp^2-hybridized carbon is defined as the angle of $\theta_{\sigma\pi}$ minus 90.0°, where $\theta_{\sigma\pi}$ is the angle between the π-orbital and its three adjacent C−C bonds (Figure 2a). This θ_p concept can be
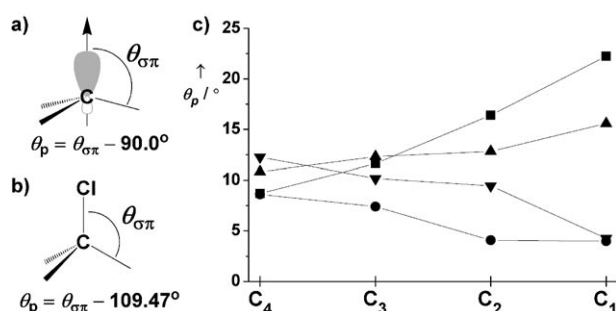

Figure 2. Pyramidalization angles (θ_p) for a) sp^2 and b) sp^3 carbon atoms in chlorofullerenes. c) The θ_p values of the first four carbon atoms in C_{50}, $C_{50}Cl_{10}$, C_{64}, and $C_{64}Cl_4$. ■ C_{64}, ● $C_{64}Cl_4$, ▲ C_{50}, ▼ $C_{50}Cl_{10}$. The carbon labels are defined in Figure 1.

extended to a single sp^3 carbon in chlorofullerenes by subtracting 109.47°, the regular tetrahedral angle, from the average angle of the three adjoining Cl−C−C bonds (Figure 2b). θ_p for the I_h-symmetric fullerene C_{60}, which lacks a fused pentagon, is approximately 11.64°. The θ_p values of the carbon atoms at the edges of the fused pentagons for these IPR-violating fullerenes are calculated to be 15.58° for C_1 in **1a**, 16.41° for C_2 in **2a**, and 22.23° for C_1 in **2a** (Figures 1b and 1e). The curvature-induced pyramidalization therefore apparently depends on the multiplicity of pentagon fusions while the relative reactivity dramatically increases progressively from I_h-C_{60} (no pentagon fusion) to **1a** (two fused pentagons) and **2a** (three fused pentagons).

The reactive carbon atoms at the fused pentagon edges can be stabilized by exohedral addends, in the present case chlorines, which change the carbon hybridization from sp^2 to sp^3 and thus relieve strain.[6,7] The θ_ps values for the carbon atoms at, and adjacent to, the fusion sites in parent and chlorinated C_{50} and C_{64} are shown in Figure 2c. These data highlight the extraordinary stabilities of the chlorinated fullerenes in comparison to all-carbon cages.

Another prominent structural feature is the aromaticity of the sp^2-hybridized carbon framework of **1** and **2**. Ten equatorial sp^3 C−Cl bonds split molecule **1** into two distinct sp^2 C_{20} fragments (Figure 1c) which are similar to the carbon skeleton seen in corannulene $C_{20}H_{10}$.[18] Although the C_{20} fragments in **1** are necessarily more curved than in the

bowl-shaped $C_{20}H_{10}$ in order to maintain a closed cage structure (θ_p at C_4 is 12.27° in the C_{20} fragments of **1** vs. 8.39° in $C_{20}H_{10}$), X-ray structure analyses reveal that the alternations of C−C/C≡C single/double bonds in the C_{20} fragments of **1** are much less prominent than those in $C_{20}H_{10}$ (average C−C/C≡C bond lengths are 1.423/1.397 Å in the C_{20} caps of **1** and 1.433/1.379 Å in $C_{20}H_{10}$,[18] respectively). These geometric properties are linked to the electron delocalization and aromaticity of these C_{20} components and undoubtedly contribute to the stability of **1**. For species **2**, removal of the chlorine and carbon atoms from the three fused pentagons gives an open-cage C_{60} species containing a 15-membered-ring orifice (Figure 1 f). This enlarged C_{60} cluster is analogous to the previously synthesized complex $[(C_5H_5)Co(C_{64}H_4)]$,[19] and is aromatic with I_h-C_{60} symmetry and alternate single/double bond lengths of 1.445/1.385 Å, on average. Such aromaticity retention in the remaining non-pentagon-fused fragments may be another essential requirement for stabilization of IPR-violating fullerenes by exohedral derivatization.

Among isomers containing only hexagons and pentagons, both **1a** and **2a** have the minimum number of carbon atoms at their pentagon-fused edges,[2] that is, 10 for **1a** and 4 for **2a**. A single C_{50} (no. 271) isomer with ten reactive pentagon-fused carbon atoms is the theoretical precursor for $C_{50}Cl_{10}$. In the case of $C_{64}Cl_4$, however, there are four possible C_{64} candidates with four active carbons, namely C_{64} nos. 1911, 3451, 3452, and 3457. Although C_{64} (no. 1911) is not itself the energetically most favorable species among C_{64} fullerenes, quantum chemical computations predict that the other three $C_{64}Cl_4$ isomers are low band-gap species with HOMO–LUMO gaps of less than 0.9 eV and are at least 31.9 kcal mol^{-1} less stable than **2** (see Supporting Information). These values explain why none of the other $C_{64}Cl_4$ isomers, which are thermodynamically and kinetically unstable, have been detected experimentally.[20]

The sp^2-hybridized portions of **2** are close to each other in the crystal packing cell of **2** (Figure 3), whereas the chlorinated parts are remotely orientated. The intermolecular interactions in **2** are dominated by π-π stacking. There are 16 C···C distances shorter than 3.27 Å around the surfaces of each $C_{64}Cl_4$ cage. The four shortest intermolecular C···C distances are 3.107 Å, which is about 0.24 Å shorter than the usual π-π stacking distance (3.35 Å) seen in layered graphite or multiwall carbon nanotubes.[4,21] Such strong C···C interactions have potential implications for applications in molecular electronics because of the easier electron transfer between neighboring fullerene cages in the crystal.

Two sets of disordered $C_{50}Cl_{10}$ molecules share approximately identical chlorine positions in the crystal structure of **1**. In addition to the much shorter intermolecular C···C distances, which indicates stronger π–π stacking, a short intermolecular Cl···Cl contact (3.167 Å) is also observed in the $C_{50}Cl_{10}$ crystal (Figure 4). This Cl···Cl distance, which is comparable to those observed in polychlorinated IPR fullerenes such as $C_{60}Cl_{30}$, $C_{60}Cl_{28}$, $C_{70}Cl_{16}$, and $C_{76}Cl_{18}$,[22] can be explained in terms of both n-type Cl···Cl−C halogen bonding and π-type aromatic-C_{20}···Cl−C bonding.[23] These intriguing intermolecular interactions, together with the short and
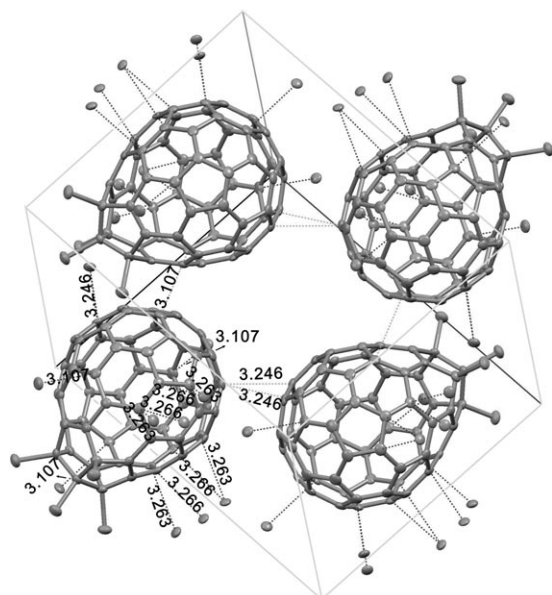
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Figure 3. The crystal packing motif of $C_{64}Cl_4$. Short intermolecular C···C contacts (less than 3.27 Å) inside and outside the crystal cell are indicated by dashed lines. The C···C distances around a representative molecule are given in angstroms.
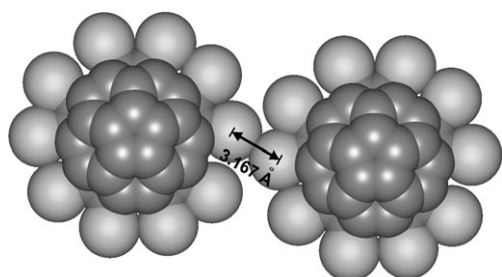

Figure 4. Two adjacent $C_{50}Cl_{10}$ molecules (CPK model) in the crystal structure of **1**. Carbon atoms and chlorine atoms are in dark gray and light gray, respectively.

equidistant intramolecular Cl···Cl contacts, imply that the smaller chlorinated fullerene $C_{50}Cl_{10}$ might be an ideal nanoscale "molecular gear" with promising applications.[24]

In conclusion, the detailed geometries of D_{5h}-$C_{50}Cl_{10}$ and C_{3v}-$C_{64}Cl_4$ have been reported. The highly reactive double- or triple-pentagon-fusion sites in these IPR-violating fullerenes can be stabilized by exohedral derivatization. The resulting stability is additionally enhanced by the aromaticity of the residual sp^2-hybridized carbon skeletons. Hence, the difficulties in synthesizing IPR-violating fullerenes can be overcome by means of external functionalization, and additional fullerenes with fused pentagon may be realized in the future. The X-ray crystallographic data of these molecules also reveal strong π-π stacking in $C_{64}Cl_4$ and short Cl···Cl contacts in $C_{50}Cl_{10}$, thereby suggesting potential applications in molecular electronics and nano-devices.

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