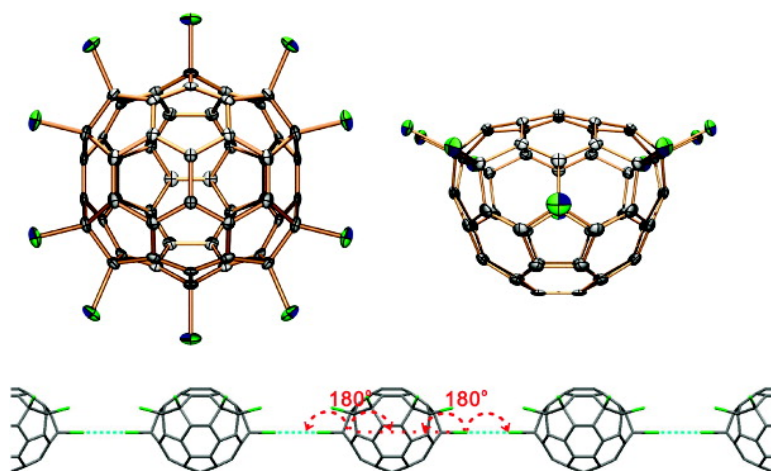


An Entrant of Smaller Fullerene: C Captured by Chlorines and Aligned in Linear Chains

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An Entrant of Smaller Fullerene: C₅₆ Captured by Chlorines and Aligned in Linear Chains

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Since the first celebrated fullerene, C₆₀(I_h), was macroscopically synthesized in 1990,¹ a growing family of fullerenes has come into reality. The number of novel fullerenes is still increasing even at the present time. However, most of the synthesized fullerenes are larger cages containing carbon atoms more than 60. The fullerenes smaller than C₆₀ are predicted to have unusual electronic properties because of their geometric structures with higher curvature, and have aroused the long-attention of chemists in either theoretic computations or experimental investigations.^{2,3} These smaller fullerenes, however, inevitably consist of structural abutting pentagons and violate the well-known isolated pentagon rule (IPR),⁴ leading to their instability and elusion in standard laboratory conditions under ambience atmosphere. Recent experiments have demonstrated the IPR-violating fullerenes could be stabilized either by endohedral encapsulation of metal clusters^{3a,5} or exohedral derivatization.^{3c–g,6} By the latter method, three kinds of smaller fullerenes are stabilized and unambiguously characterized heretofore, that is, C₂₀Br_nH_{20–n},^{3e,f} C₅₀Cl₁₀,^{3c,g} and C₅₈F₁₈.^{3d} Among them, only C₅₀Cl₁₀ was the species directly captured during the fullerene growth in carbon arc plasma, so as to be helpful for understanding fullerene formation. In the paper about C₅₀Cl₁₀,^{3c} we mentioned the mass spectrometry observation of another smaller chlorofullerene, C₅₆Cl₁₀, as one of the byproducts. Following this observation, some theoretical predictions about the structures of C₅₆Cl₁₀ and pristine C₅₆ (#913)⁷ have been reported.⁸ However, authentic structure, assembly, and properties of this new entrant of smaller fullerene will need to be experimentally investigated. In this Communication we focus our efforts on isolation and characterization of the C₅₆Cl₁₀. Its structure, with implications on stabilization, chemical reactivity, and alignment in crystal has been unambiguously identified by X-ray diffraction.

C₅₆Cl₁₀ was produced in a modified Krätschmer–Huffman arc-discharge reactor.^{1b,9} Crude soot was extracted with toluene in a supersonic bath, followed by separation and purification using multistage recyclic high performance liquid chromatography (HPLC) on Shimadzu LC-6AD HPLC instrument with a Cosmosil Buckyprep column (10 i.d. × 250 mm) eluted by toluene at a flow of 4.0 mL/min under the temperature of 40 °C (The chromatograms for C₅₆Cl₁₀ isolation are shown in Supporting Information). The purified C₅₆Cl₁₀ is soluble in carbon disulfide, chloroform, and toluene with absorption around 304, 364, 444, and 509 nm (Supporting Information). By solvent evaporation from its carbon disulfide solution, its dark red single crystals suitable for X-ray diffraction were obtained.

As revealed by X-ray diffraction (Figure 1), the overall symmetry of C₅₆Cl₁₀ is C_{2v}, the same as its parent cage. The most outstanding feature of the C₅₆ structure is the existence of four pairs of adjacent pentagons, that are respectively bonded with eight of the chlorines. For a spherical carbon cage, the local surface strain can be defined

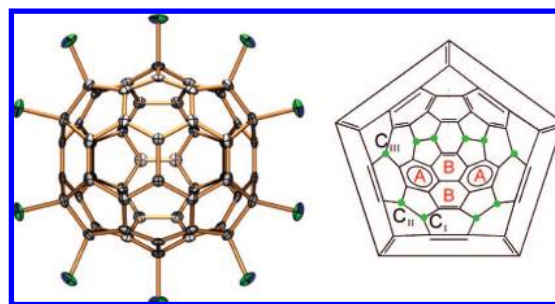


Figure 1. Structures of C₅₆Cl₁₀: ORTEP drawing with thermal ellipsoids at 50% probability level (left) and Schlegel diagram with chlorines indicated by green dots (right).

in terms of pyramidalization angle, that is, the π -orbital axis vector (POAV), at the involved carbon atom.¹⁰ The POAVs of the two sets of carbon atoms (i.e., C_I and C_{II} in Figure 1) at the adjacent pentagons of the pristine C₅₆ cage are 14.63 and 16.32°,^{8b} respectively, sharply higher than that of the regular POAV in I_h-C₆₀ cage (11.64°). Such higher POAVs lead to the significantly reduced angles between the mean planes of the involved rings and subsequently the high reactivity of the bare C₅₆ cage. However, the enhanced curvature strain can be released as the result of chlorination to transfer the carbon atoms at the pentagon adjacencies as sp³-hybridized. As shown in the structural data of C₅₆Cl₁₀ (Supporting Information), the average C–C_I–Cl and C–C_{II}–Cl bond angles are respectively 3.72° and 4.43° deviated from the regular tetrahedron (109.48°). Therefore, adding chlorines at adjacent-pentagons sites is well favorite geometrically, so as to stabilize this IPR-violating smaller fullerene.

Another factor in contributing to the overall stability of the C₅₆ is the aromaticity of the remaining carbon skeletons after chloro-derivatization. Besides the eight chlorines bonded at the abutting-pentagons sites, the remainder of the chlorines are linked at two hexagon–hexagon–pentagon vertexes (i.e., the C_{III} in Figure 1) to complete a close “belt” of chlorine-bonded sp³-carbons cutting the cage into two aromatic fragments of C₁₆ and C₃₀. The chlorination pattern in C₅₆Cl₁₀ agrees well with proposed principles for fullerene reactivity.¹¹ In the pyrene portion of C₁₆ there are two sorts of hexagons, rings A and B (Figure 1). Ring A with fairly equalized C–C bond lengths ranging from 1.395 to 1.411 Å suggests a good electronic delocalization, whereas ring B is less aromatic with the alternating C–C/C=C bond lengths ranging from 1.363 to 1.455 Å. This fits well with our theoretical computations about the nucleus-independent chemical shifts (NICS) values at the centroids of the hexagons, with values of –14.36 and –8.87 ppm for ring A and B, respectively. The larger segment of C₃₀ is just a half of I_h-C₆₀ with alternating single-double bonds ranging from 1.350 to 1.446 Å.

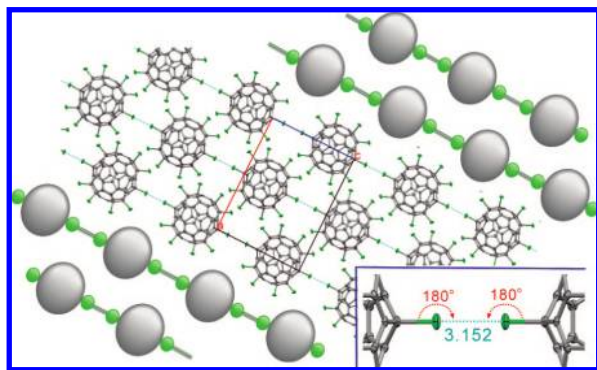


Figure 2. Alignment of $C_{56}Cl_{10}$ molecules along c axis. The skeletons of the $C_{56}Cl_{10}$ molecule on both sides are indicated as gray/green balls for a clearer view of the pearl-necklace-shaped alignment. Inset shows the distance and angles of the short $C-Cl\cdots Cl-C$ contact.

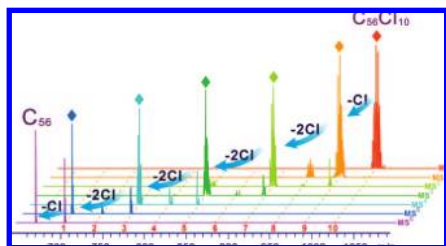


Figure 3. Dechlorination of $C_{56}Cl_{10}$. Multistage mass spectrometry (MS^n , $n = 1-6$) showing the formation of C_{56} by progressive dechlorination of $C_{56}Cl_m$ ($m = 1-10$) (m value is indicated as number in red on the bottom line, and the species selected for next stage of MS fragmentation are marked with colored rhombus).

Of interest is the assembly of the $C_{56}Cl_{10}$ molecule in the crystal. There are three kinds of intermolecular contacts among $C_{56}Cl_{10}$ molecules in the crystal: $\pi-\pi$, $C\cdots Cl$, and $Cl\cdots Cl$ contacts (see Supporting Information). The most intriguing intermolecular interaction is the linear $C-Cl\cdots Cl-C$ short contact along the c axis in the crystal of $C_{56}Cl_{10}$ (Figure 2). According to the symmetry, $C_{56}Cl_{10}$ has three different $C-Cl$ bonds (1.779, 1.785, and 1.810 Å). Interestingly only Cl atoms which are involved in the highly elongated $C-Cl$ bonds form short $Cl\cdots Cl$ contacts, although strong repulsive forces are expected due to accumulation of negative charge on the corresponding Cl atoms.¹² This $Cl\cdots Cl$ distance is rather short (3.152 Å), which is, to our knowledge, one of the shortest $Cl\cdots Cl$ contacts observed in the chlorofullerenes family.¹³ Unexpectedly, the $C_{56}Cl_{10}$ molecules in the crystal are aligned as entirely straight chains with the angle of $C-Cl\cdots Cl-C$ being 180°, just like pearl necklaces (Figure 2).

Suggested by regioselectivity of IPR-violating $C_{60}Cl_8$ (#1809) in Friedel-Crafts-type and nucleophilic reactions where the substitution reactions prefer to take place for the chlorines in longer $C-Cl$ bonds of 1.81 Å (the unreacted chlorines are located in the $C-Cl$ bond with distance of 1.78 Å),¹⁴ linear fullerene polymers of C_{56} are expected to be synthesized because the two chlorines involved in the linear chains have longer $C-Cl$ distance (1.81 Å vs the others of 1.78 Å) and are sterically ready for reaction with bidentate donors to construct one-dimensional architectures. Such kind of one-dimensional fullerene polymer may be applicable as electronic or mechanical materials.

Dechlorination of $C_{56}Cl_{10}$ was conducted by multistage mass spectrometry (MS^n), where stepwise dissociation of chlorine was achieved by collision of $C_{56}Cl_m$ ($m = 1-10$) molecules with helium

buffer gas in ion trap (Figure 3). The eventual formation of bare C_{56} units suggests the possibility of studying electronic properties of its bare cages by, for example, photoelectron spectroscopy.

In summary, our experiments have demonstrated the existence of C_{56} (#913), a new entrant in the family of smaller fullerenes. The otherwise unstable IPR-violating C_{56} has been macroscopically stabilized by chlorination as $C_{56}Cl_{10}$, and thus provides significant experimental opportunities into the new world of fullerenes smaller than C_{60} . The crystallographic data of $C_{56}Cl_{10}$ reveal an unusual $Cl\cdots Cl$ short contact and the alignment of pearl-necklace-like molecular chains, which can be potentially converted into a class of useful one-dimensional fullerene polymer through previously established regioselective reactions.

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Supporting Information Available: Crystallographic information file (CIF), intermolecular contacts in $C_{56}Cl_{10}$ crystal, HPLC chromatograms, and UV-Vis-NIR spectrum of $C_{56}Cl_{10}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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