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Pentagon-Fused Hollow Fullerene in C₇₈ Family Retrieved by ChlorinationYuan-Zhi Tan,[†] Jia Li,[†] Ting Zhou,[†] Yu-Qi Feng,[‡] Shui-Chao Lin,[†] Xin Lu,[†]
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Abstract: C₇₈ is one of the most widely investigated higher fullerenes. Among its huge isomer family, only one non-IPR (IPR = isolated pentagon ring) cage, the C₂-symmetric ^{#22010}C₇₈, was previously stabilized by endohedral derivatization. Here we report a new C₁-symmetric non-IPR hollow isomer, ^{#23863}C₇₈, which was captured as ^{#23863}C₇₈Cl₈ and then subjected to a regioselective substitution reaction with benzyl hydroperoxide to form ^{#23863}C₇₈(OOCH₂C₆H₅)Cl₇. The structural connectivity of ^{#23863}C₇₈, which contains a pair of fused pentagons, was confirmed by single-crystal X-ray diffraction analysis of the ^{#23863}C₇₈(OOCH₂C₆H₅)Cl₇ molecule, which shares the same fullerene core with ^{#23863}C₇₈Cl₈; support for the structure is provided by comparable IR measurements and computation. Theoretical studies suggest that the differences in C–Cl bond length, intermediate stability, and steric effects of the involved molecules account for the chemical regioselectivity of the substitution reaction.

Introduction

Higher fullerenes, the enlarged cagelike all-carbon clusters with more than 70 carbon atoms, are expected to have intriguing properties and afford more opportunities for application as novel carbon materials close to carbon nanotubes.^{1,2} Among them, C₇₈ is one of the most widely investigated higher fullerenes. In the huge family of 24 109 C₇₈ isomers, each of which is made of hexagons and exactly 12 pentagons, a total of five members faithfully satisfy the isolated pentagon ring (IPR) rule.³ As early as 1991, three soluble IPR-satisfying isomers, D₃-^{#24105}C₇₈, C_{2v}-^{#24106}C₇₈, and C_{2v}-^{#24107}C₇₈,⁴ were characterized by ¹³C NMR analysis.^{5,6} Recently, their structural connectivities, in the form of exohedral derivatives (e.g., chloride,^{7,8} bromide,⁹ trifluoro-

methyl,¹⁰ and perfluoroethyl derivatives¹¹), have been unambiguously disclosed by X-ray crystallographic characterization. The other two isomers, D_{3h}-symmetric ^{#24108}C₇₈ and ^{#24109}C₇₈, were predicted to be poorly soluble in common solvents,^{12,13} but the latter one has recently been isolated and crystallographically characterized as its trifluoromethyl,^{14,15} chloride,¹⁶ and endohedral derivatives.^{17–20} Thus, only one IPR-satisfying C₇₈

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isomer, D_{3h} - $^{24108}C_{78}$, remains a mystery to date.¹⁶ In contrast, more than 20 000 non-IPR isomers of C_{78} are still elusive. Heretofore, only one non-IPR cage, C_{2v} - $^{22010}C_{78}$, has been stabilized by the endohedral derivatization method, in which the metal nitride cluster Gd_3N was encapsulated.^{21,22} Intriguingly, when subjected to Diels–Alder reaction, the endohedral derivatives of the identified C_{78} exhibit regioselectivity due to the encapsulated clusters.^{23–27} In contrast to the non-IPR endofullerene, here we present an unprecedented hollow non-IPR C_{78} isomer, C_{1v} - $^{23863}C_{78}$, which was captured by exohedral chlorination and subjected to a substitution reaction with benzyl hydroperoxide to form C_{1v} - $^{23863}C_{78}(OOCH_2C_6H_5)Cl_7$ (**1**). This substitution reaction showed regioselectivity, as only one out of the eight chlorines in C_{1v} - $^{23863}C_{78}Cl_8$ (**2**) was selectively benzylperoxy-substituted. The chemical regioselectivity of this reaction was investigated by theoretical computations, which revealed that the factors of C–Cl bond length, intermediate stability, and steric hindrance effects result in the chemical regioselectivity.

Experimental Section

Synthesis and Analysis. Carbonaceous soot was produced under 0.1974 atm He and 0.0395 atm CCl_4 in a modified Krätschmer–Huffman arc-discharge reactor²⁸ equipped with two graphite electrodes, a cathode cylinder block [40 mm (diameter) \times 60 mm], and an anode rod [8 mm (diameter) \times 300 mm]. With a power input of 33 V and 100 A, an hourly production of ~ 3 g of soot was achieved.

The chlorofullerenes were extracted from the carbonaceous soot using toluene in a supersonic bath and then purified by a multistage high-performance liquid chromatography (HPLC) process using a pyrenebutyric acid-bonded silica column [20 mm (i.d.) \times 250 mm], a Cosmosil Buckyprep column [10 mm (i.d.) \times 250 mm], a 5PBB column [10 mm (i.d.) \times 250 mm], and a Cosmosil Buckyprep column [4.6 mm (i.d.) \times 250 mm] in turn [see the Supporting Information (SI)]. The HPLC chromatograms were obtained on a Shimadzu LC-6AD HPLC instrument. Mass spectrometry (MS) was performed on a Bruker HCT mass spectrometer. Crystallographic data were collected on an Oxford CCD diffractometer. FT-IR spectra were recorded on a Nicolet 330 FT-IR spectrometer. GC–MS analysis of toluene was performed on a Shimadzu GCMS-QP 2010 Plus instrument coupled with a Rtx-5MS chromatography column interfaced with an electron-impact ionization source. The 1H NMR spectrum of **1** was measured in CCl_2D_2 solution on a Bruker AV 400 NMR spectrometer.

Theoretical Calculations. Optimized geometries and electronic structures of all the involved compounds were calculated at the GGA/DNP level, in which the generalized gradient approximation

(GGA) in the Perdew–Burke–Ernzerhof (PBE)²⁹ form as well as a double numerical polarized (DNP) basis set were employed. Vibrational frequencies of $^{23863}C_{78}(OOCH_2C_6H_5)Cl_7$ and $^{23863}C_{78}Cl_8$ were calculated at the same level. Isomers of $^{23863}C_{78}Cl_8$ with different chlorine patterns were optimized using the semiempirical PM3 method,³⁰ and the low-lying isomers were further evaluated by density functional theory (DFT) calculations at the PBE/DNP level. All of the DFT computation was performed using the DMol³ code.^{31,32}

Results and Discussion

The fullerene soot was synthesized in a modified Krätschmer–Huffman arc-discharge reactor.²⁸ The soot was then extracted with toluene in a supersonic bath. In addition to the soluble IPR-satisfying isomers (i.e., D_{3h} - $^{24105}C_{78}$, C_{2v} - $^{24106}C_{78}$, and C_{2v} - $^{24107}C_{78}$),^{5,6} a new chloride of C_{78} with the molecular formula of $C_{78}Cl_8$ was isolated from the extraction by multistage-recycling HPLC (see the SI). The purified $C_{78}Cl_8$ sample was dissolved in a toluene solution and stored in a transparent glass flask, where it was partially transformed into a new species after exposure to sunlight for 3 days. As shown in Figure 1, this new component (retention at 12.9 min) in addition to the original $C_{78}Cl_8$ (retention at 20.4 min) could be readily isolated because of the different retention time.

Single crystals of **1** suitable for X-ray diffraction analysis were grown in toluene solution. By crystallographic measurement, the geometric structure of the monosubstituted chlorofullerene derivative **1** was unambiguously revealed (see the SI). The structure of **1** is depicted in Figure 2. In contrast to the four IPR hollow cages and one non-IPR endofullerene of C_{78} reported to date, $^{23863}C_{78}$ represents the first hollow pentagon-fused isomer in the C_{78} family. The pristine cage of $^{23863}C_{78}$ has C_1 symmetry, which makes it a useful building block for further chemical modification toward chiral supramolecular architectures. Topologically, the carbon cage of C_{1v} - $^{23863}C_{78}$ can be transformed into the previously reported IPR isomers C_{2v} - $^{24106}C_{78}$ and D_{3h} - $^{24105}C_{78}$ through the Stone–Wales transformation³³ (see the SI). In contrast to these IPR isomers, however, C_{1v} - $^{23863}C_{78}$ is inherently unstable and has higher energy due to its fused pentagons.³⁴ The unfavorable local strain at the vertexes of the pentagon fusion in **1** can be released through bonding to two chlorine atoms. In addition to the two chlorine atoms associated with the pentagon fusion, five chlorine atoms and a benzylperoxy group are bonded at six additional pentagon–hexagon–hexagon vertexes, resulting in a chain of sp^3 -hybridized carbon atoms (Figure 3a). This addition pattern, which obviously differs from those previously reported for $^{271}C_{50}Cl_{10}$ and $^{1911}C_{64}Cl_4$, in which only the fused-pentagon carbons are substituted,^{28,35} is in good accord with the so-called local-aromaticity principle,³⁴ which is one of the requirements for exohedral stabilization of non-IPR fullerenes.

In the crystalline state, the flexible benzylperoxy group bends to the carbon cage, with its phenyl group nearly parallel to the plane of the nearest conjugated fragment on the cage. The closest

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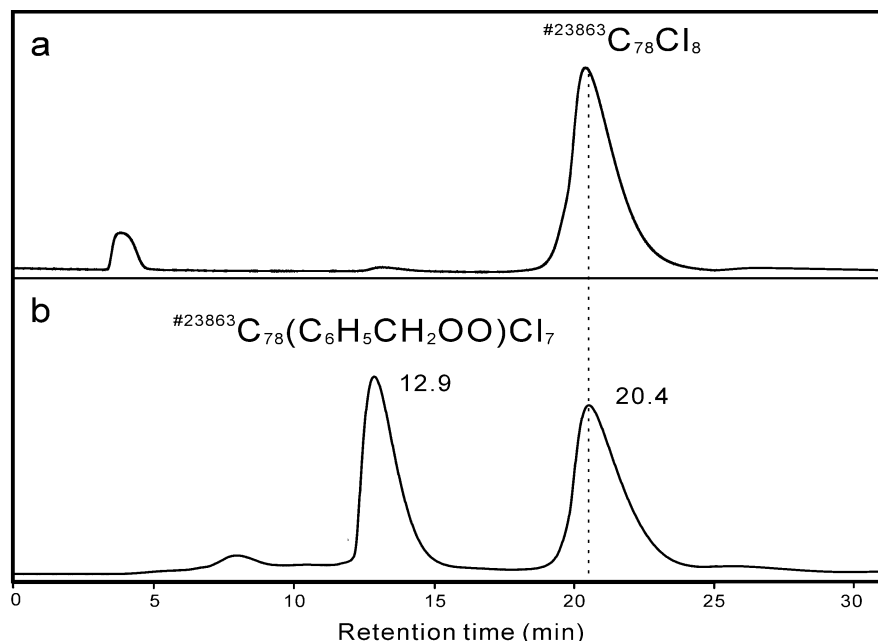


Figure 1. HPLC chromatograms for (a) purified and (b) sunlight-irradiated $C_{78}Cl_8$. The chromatograms were monitored at 330 nm and acquired on an analytical Buckyprep column [4.6 mm (i.d.) \times 250 mm] eluted using toluene at a flow rate of 1 mL/min. The peak at 4.3 min is due to an impurity in the solvent.

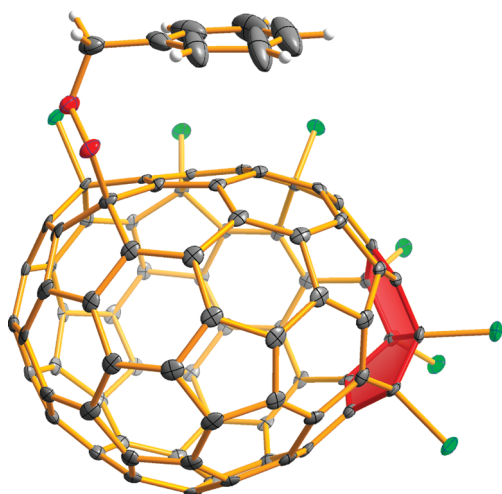


Figure 2. ORTEP structure of **1** with thermal ellipsoids at 50% probability. The fused pentagons are highlighted in red.

distance between the plane of the phenyl group and the cage is ~ 3.26 Å, implying an obvious π – π interaction. The presence of such a π – π interaction was also proved by means of 1H NMR analysis (see the SI), in which the 1H NMR signals of the benzyl group in **1** were shifted upfield by ~ 0.8 ppm (average of 7.28 ppm in benzyl hydroperoxide³⁶ vs 6.56–6.42 ppm in **1**). Apparently this is due to the shielding effect of the local aromatic π system from the C_{78} cage.^{37,38}

Despite laborious efforts, we failed to obtain a single crystal or perform NMR measurements on **2** (likely as a result of the poor solubility of **2** in common organic solvents used for fullerene research). In the absence of X-ray crystallographic data and a ^{13}C NMR spectrum, IR measurements coupled with DFT

calculations provide an alternative way to characterize fullerene structures.^{21,39} The IR spectra of both **1** and **2** were recorded for comparison (Figure 4). Except for the C–H stretching peaks at ~ 2900 cm^{-1} and the C–O stretching peak at ~ 980 cm^{-1} in the spectrum of **1**, the two spectra are quite similar to each other, which indicates that the two compounds share a similar core structure (see the SI). Additionally, theoretical IR spectra were computed for comparison with the experimental data as well. As shown in Figure 4a,b, the theoretical and experimental data match well for **1**, with the exception that the peaks in the computed spectrum are shifted by a few wavenumbers relative to the experimental ones (possibly as a result of the systemic error in the calculation methods). The validity of the theoretical computation is thus demonstrated, and it is apparently applicable to identify the structure of $C_{78}Cl_8$. Indeed, the calculated IR spectrum of the supposed $C_{78}Cl_8$ species is fairly identical with the experimental one (Figure 4c,d), with almost all of the peaks in the experimental spectrum corresponding to the computational ones with comparable intensities. Moreover, we were able to rule out the possibility of structural isomers of $C_{78}Cl_8$ with one rearranged chlorine atom. Some substitution reactions involving chlorofullerenes could lead to the rearrangement of added groups, but our computed results revealed that consistent with the IR spectrum analysis, the $C_{78}Cl_8$ species having an addition pattern identical to that of **1** is the most stable isomer (see the SI). On the basis of the analysis discussed above, the structure of **2** with the same core and addition pattern as compound **1** can be identified.

As shown in the HPLC chromatogram (Figure 1b), $C_{78}(OOCH_2C_6H_5)Cl_7$ was the dominant product of the substitution reaction, and only a few byproducts were formed. The residual $C_{78}Cl_8$ in the reaction, which could be isolated from the product mixture, underwent further substitution reaction to form **1** when it was stored in the same toluene solution under ambient conditions with sunlight irradiation, whereas it remained

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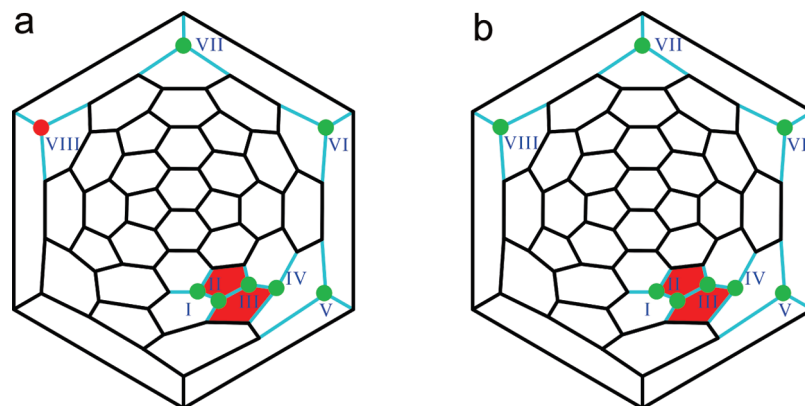


Figure 3. Schlegel diagrams of (a) **1** and (b) **2**. The chlorine atoms in the Schlegel diagrams are indicated as green dots. The benzylperoxy group is indicated as a red dot. Each adduct group is labeled with a Roman numeral. The fused pentagons are highlighted in red.

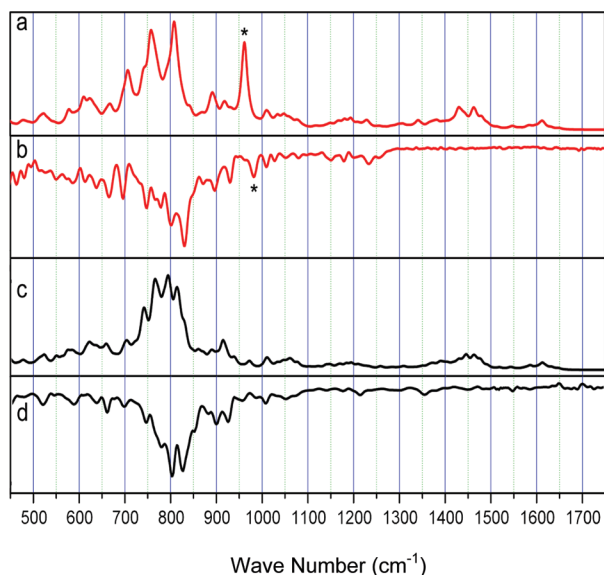


Figure 4. IR spectra of **1** and **2**. (a) Simulated IR spectrum of **1**. (b) Experimental IR spectrum of **1**. (c) Simulated IR spectrum of **2**. (d) Experimental IR spectrum of **2**. The peaks marked with asterisks in (a) and (b) are assigned to the stretching of the C–O bond between the benzylperoxy group and the cage in **1**.

intact in darkness or in the solid state. The formation of **1** is almost certainly due to the substitution reaction in which one of the eight chlorine atoms of the original $C_{78}Cl_8$ is substituted by a benzylperoxy group. In the present work, the hydroperoxide was not added by design but could have been produced by auto-oxidation of toluene. We assume that toluene is first oxidized into benzyl hydroperoxide, which then regioselectively reacts with the $C_{78}Cl_8$ to produce monosubstituted species sharing the same carbon cage and addition pattern. A number of previously reported works have discussed the possible production of benzyl hydroperoxide from toluene through auto-oxidation.^{40,41} Indeed, in the toluene solvent involved in the present experiment, a trace amount of benzyl hydroperoxide was detected by GC–MS (see the SI). To support the regioselective mechanism, a control experiment starting with cumene hydroperoxide was also conducted. The regioselective substitution reaction yielding monosubstituted product was thus corroborated. However, upon

Table 1. C–Cl Bond Lengths (Å) in **1** and **2** and Relative Energies (kcal/mol) of the $C_{78}Cl_7\cdot$ and $C_{78}Cl_7^+$ Intermediates

C–Cl bond ^a	bond length in 1 (exptl)	bond length in 1 (calcd) ^b	bond length in 2 (calcd) ^b	E_{rel}^b for $C_{78}Cl_7\cdot/C_{78}Cl_7^+$
C–Cl _I	1.816(3)	1.831	1.830	1.3/0.7
C–Cl _{II}	1.776(3)	1.793	1.792	12.2/16.0
C–Cl _{III}	1.786(3)	1.797	1.796	10.9/12.8
C–Cl _{IV}	1.806(3)	1.824	1.822	3.5/4.0
C–Cl _V	1.806(3)	1.839	1.834	5.3/10.0
C–Cl _{VI}	1.818(3)	1.842	1.838	5.5/6.5
C–Cl _{VII}	1.816(3)	1.848	1.844	5.4/4.5
C–Cl _{VIII}			1.855	0.0/0.0

^a See Figure 3 of the text for the numbering of the Cl atoms.

^b Calculated at the PBE/DNP level.

reaction with the smaller nucleophile methanol, polymethoxy-lated fullerenes were formed, similar to the solvolysis reaction involving non-IPR $^{271}C_{50}Cl_{10}$.²⁸ We tentatively assume that the steric effect could be an additional factor in directing the regioselectivity of the nucleophilic substitution (see below).

Theoretical computations of the geometry and electronic structure of the reactant were performed in order to understand the substitution reaction involving $C_{78}Cl_8$ (**2**). The HOMO–LUMO gap in **2** was predicted to be 1.65 eV, which is similar to that in **1** (1.64 eV) and comparable to those of typical chlorofullerenes, such as $^{271}C_{50}Cl_{10}$ (1.67 eV, at the same level).⁴² Table 1 summarizes the C–Cl bond lengths in the optimized geometry of **2** and compares them with the corresponding ones in **1**. Obviously, the C–Cl_{II} and C–Cl_{III} bonds at the vertexes of the pentagon fusion are shorter than the other C–Cl bonds in both the computationally optimized structure of **2** and the crystallographically determined structure of **1**, indicating that the C–Cl bonds at the fused pentagons are relatively stronger and more inert in the substitution reaction. In contrast, the longest C–Cl bond in **2** is just the C–Cl_{VIII} that was benzylperoxy-substituted in the present experiment. Because of such a difference in the C–Cl bonds, the substitution occurs favorably at the longest C–Cl bond, resulting in the remarkable chemical regioselectivity. Similar regioselective effects have also been found in other non-IPR chlorofullerenes, such as $^{1809}C_{60}Cl_8$ and $^{913}C_{56}Cl_{10}$,^{43,44} which makes the non-IPR chlorofullerenes better fullerene-based precursors for site-differentiated chemical modification.

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To further understand the chemical regioselectivity, the relative stabilities of the key intermediates involved in this substitution reaction from **2** to **1** were analyzed via DFT calculation as well. For a substitution starting from chlorofullerenes $C_{2n}Cl_m$, the radical $C_{2n}Cl_{m-1}\cdot$ or the cation $C_{2n}Cl_{m-1}^+$ formed by homolytic or heterolytic cleavage of C–Cl bond, respectively, is proposed as the key intermediate controlling the substitution.^{43,45,46} Listed in the last column of Table 1 are the relative energies of the intermediates $C_{78}Cl_7\cdot$ and $C_{78}Cl_7^+$ resulting from cleavage of different C–Cl bonds. Remarkably, both $C_{78}Cl_7\cdot$ and $C_{78}Cl_7^+$ from the cleavage of the longest C–Cl bond (i.e., C–Cl_{VIII}) are the most energy-favorable intermediates, sequentially resulting in the formation of the as-produced **1**. It should be noted that the energies of $C_{78}Cl_7\cdot$ and $C_{78}Cl_7^+$ formed by cleaving the C–Cl_I bond are higher than those of the most stable ones by only 1.3 and 0.7 kcal/mol, respectively, but the steric effect of the neighboring chlorine atom (Cl_{II}) hinders the attack of a foreign group at this site. Therefore, it is not surprising to see that the regioselective substitution reaction yields monosubstitution for benzyl and cumene hydroperoxides but multiple substitution for smaller groups such as methanol.

Conclusion

In conclusion, the first non-IPR hollow C_{78} fullerene, $^{#23863}C_{78}$, has been isolated by chlorination and unambiguously char-

acterized by X-ray crystallography. Its perchloro derivative $^{#23863}C_{78}Cl_8$ (**2**) was readily subjected to regioselective substitution to form a monosubstituted derivative, $^{#23863}C_{78}(OOCH_2C_6H_5)Cl_7$ (**1**). Theoretical computations have revealed that differences in C–Cl bond lengths, intermediate stability, and steric hindrance effects for the involved molecules account for the regioselectivity in the substitution reaction from **2** to **1**. Such chemical regioselectivity sheds new light on the synthesis and chemical properties of higher non-IPR fullerenes in the form of hollow cages and lends credence to the promise that chlorofullerenes can be useful chiral building blocks for construction of supramolecular fullerene-based architectures.

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Supporting Information Available: Chromatogram and mass spectrum of **2**, crystallographic information (CIF), π – π interactions and 1H NMR spectrum of **1**, GC–MS data for the solvent, MS analysis of the control experiment, Stone–Wales transformation diagram, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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