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The Way of Stabilizing Non-IPR Fullerenes and Structural Elucidation of C₅₄Cl₈*

XINGFA GAO,^{1,2} YULIANG ZHAO^{1,2,3}

¹Laboratory for Bio-Environmental Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, People's Republic of China

²Department of Chemistry and Chemical Engineering, Graduate University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

³National Center for Nanoscience and Technology of China, Beijing 100080, People's Republic of China

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Abstract: Recently, a new non-IPR chlorofullerene C₅₄Cl₈ was isolated experimentally (Science 2004, 304, 699). To explore the ways to stabilize non-IPR fullerenes, the authors studied all of the possible isomers of C₅₄ fullerene and some of the C₅₄Cl₈ isomers at PM3, B3LYP/3-21G, and B3LYP/6-31G* levels. Combined with analysis of pentagon distributions, bond resonance energies, and steric strains, C₅₄:540 with the least number of 5/5 bonds was determined to be the thermodynamically best isomer for the C₅₄Cl₈. Based on C₅₄:540, the most probable structure of the experimental C₅₄Cl₈ was elucidated. The results suggested one of the necessary conditions of stabilizing non-IPR fullerenes: chemical derivatizations of either endohedral complexation or exohedral addition need to sufficiently stabilize all of the kinetically unstable 5/5 bonds of the cages.

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Key words: C₅₄Cl₈; fullerenes; nanostructures; non-IPR; stabilities

Introduction

Except for I_h-C₆₀,¹ all possible isomers of fullerenes with less than 70 carbons disobey the “isolated pentagon rule (IPR)”² and can be called non-IPR fullerenes. Since the discovery of C₆₀,¹ the structures of non-IPR fullerenes have attracted considerable experimental and theoretical interest because as ineluctable intermediates for the growth of the stable C₆₀, the study of these would provide fundamental and indispensable knowledge for understanding the long-pending mechanism of fullerene formation.^{3–8} However, because of enhanced steric strain and resonance destabilization pertaining to adjacent pentagons, non-IPR fullerenes are always unstable, so chemical derivatizations become important to stabilize them for experimental investigations. The presently known stabilizing reactions and the attained non-IPR products can fall into two categories (1): *endo* complexation to achieve endohedral metal fullerenes,^{9–12} and (2) *exo* addition to achieve exohedral adducts.^{13–17} Among these products, the structures of C₅₀Cl₁₀,^{15,18} Sc₂@C₆₆,^{9,19,20} and Sc₃N@C₆₈^{10,21,22} have been definitely determined by experiments; those of La₂@C₇₂,^{12,23} Sc₂@C₇₂,²³ Sc₂C₂@C₆₆,¹¹ C₃₆H₆,^{24–26} and C₅₀Cl₁₂¹⁸ have also been elucidated, but for a wide range of adducts the structures remain unclear.^{15–17} For example, using the graphite arc-discharge process modified by introducing a small amount of carbon tetrachloride (CCl₄) in the helium

atmosphere, Su-Yuan Xie and Lan-Sun Zheng et al. have isolated a series of non-IPR chlorofullerenes C₅₀Cl₁₀, C₅₄Cl₈, and C₅₆Cl₁₀, etc.¹⁵ Among them, only the structure of the most abundant C₅₀Cl₁₀ has been explicitly identified in the experiments. It is worthy noting that the cages of these chlorofullerenes are close in size, and this characteristic is of particular interest because the comparative study of their structures may provide valuable information for the growth process of fullerenes. Molecular modeling has been demonstrated to be an important complementary tool for identification and prediction of fullerene structures.^{27,28} In this work, we explored the structures, stabilities, and reactivities of the newly isolated non-IPR chlorofullerene C₅₄Cl₈ using theoretical approaches. As some unambiguous rules for screening the stable isomers of non-IPR fullerene derivatives can be established from the existing knowledge of fullerenes, in the present paper, we summarized

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Correspondence to: Y. L. Zhao; e-mail: zhaoyuliang@ihep.ac.cn

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Table 1. Point Group Symmetry, Relative Energies (E_{rel} , in kJ/mol) at the B3LYP/3-21G Level, Number of Fused Pentagon Pairs (N_{55}), and Pentagon Distribution Pattern (p.d.p.) for Each C_{54} Isomer.

Isomer	E_{rel}	p.d.p.	N_{55}	Isomer	E_{rel}	p.d.p.	N_{55}
540 (C_{2v})	0.00	$2 \times \mathbf{B}$	4	532 (C_1)	155.70	$2 \times \mathbf{A} + 2 \times \mathbf{B}$	6
537 (C_1)	59.02	$3 \times \mathbf{A} + 1 \times \mathbf{B}$	5	535 (C_1)	156.45	$2 \times \mathbf{A} + 2 \times \mathbf{B}$	6
541 (C_1)	68.10	$1 \times \mathbf{A} + 2 \times \mathbf{B}$	5	415 (C_2)	165.24	$2 \times \mathbf{D}$	6
369 (C_s)	126.82	$3 \times \mathbf{A} + 1 \times \mathbf{C}$	6	580 (D_3)	174.19	$6 \times \mathbf{A}$	6
579 (C_2)	134.39	$6 \times \mathbf{A}$	6	348 (C_1)	176.11	$1 \times \mathbf{A} + 1 \times \mathbf{B} + 1 \times \mathbf{C}$	6
539 (C_s)	135.54	$2 \times \mathbf{A} + 2 \times \mathbf{B}$	6	562 (C_2)	176.13	$2 \times \mathbf{A} + 2 \times \mathbf{B}$	6
546 (C_1)	149.44	$4 \times \mathbf{A} + 1 \times \mathbf{B}$	6	417 (C_s)	176.89	$2 \times \mathbf{D}$	6
542 (C_1)	150.42	$4 \times \mathbf{A} + 1 \times \mathbf{B}$	6	342 (C_1)	181.82	$1 \times \mathbf{A} + 1 \times \mathbf{B} + 1 \times \mathbf{C}$	6
551 (C_1)	153.58	$4 \times \mathbf{A} + 1 \times \mathbf{B}$	6	574 (C_s)	191.18	$4 \times \mathbf{A} + 1 \times \mathbf{B}$	6
345 (C_1)	155.29	$3 \times \mathbf{A} + 1 \times \mathbf{C}$	6	536 (C_1)	204.25	$3 \times \mathbf{B}$	6

these rules, applied them to help identify the structure of $C_{54}Cl_8$ in addition to molecular modeling. The results indicate that to fully stabilize and the species of C_{54} via exohedral additions, the reaction needs to sufficiently saturate all of the kinetically unstable 5/5 bonds (C—C bonds shared by two pentagonal rings) of the cage, and that the additions of at least eight chlorines are required. This interprets the experimental observation and predicts the structure for the $C_{54}Cl_8$.

Isomers of C_{54}

Both experiments and theoretical calculations have shown that carbon clusters larger than C_{32} prefer to form classical fullerenes, i.e., polyhedral carbon cages made up entirely of 12 pentagonal and various numbers of hexagonal rings.^{29–32} For the structure of the $C_{54}Cl_8$, the only information we knew is that it is likely analogous to its sister molecule, $C_{50}Cl_{10}$.¹⁵ To elucidate the structure, one first needs to consider the structures of the parent fullerene C_{54} . In accordance with *the spiral algorithm*,³³ there exist 580 isomers of C_{54} fullerene in total. First, we explored all of the 580 isomers and obtained the energy sequence for them via theoretical calculations. All of them contain fused pentagons. Because abutting pentagons play critical roles in determining both the thermodynamic and kinetic properties of the fullerenes,^{33,34} we hence analyzed the distribution patterns of pentagons for the 580 isomers. Finally, the stabilities of nonclassical C_{54} isomers, those containing other sizes of ring such as square or heptagon, were also investigated to demonstrate their unstabilities.

Stabilities of the 580 C_{54} Isomers

The initial geometrical coordinates of the 580 C_{54} isomers were generated using *the spiral computer program*.³³ The simultaneously generated sequence numbers were used as their unique denotations. Here, each isomer was fully geometrically optimized using the PM3 method.³⁵ It has been recognized that the number of pentagon adjacencies governs the stability of non-IPR fullerenes: stable non-IPR fullerenes prefer to minimize the number of pentagon adjacencies (N_{55}).³⁶ For fullerenes C_n ($n < 60$ and $60 < n < 70$) it is impossible for the pentagons to be fully isolated from each other; therefore, the N_{55} for each isomer was also

calculated (Table 1 and Table S-1 of supplementary information) (Calculation of the N_{55} and analysis of the pentagon distributions were realized by manipulating the corresponding fullerene dual adjacency matrix **D** of *the spiral computer program*; see ref. 33). The correlation between the PM3 energies and the N_{55} is illustrated in Figure 1, where the generally linear shape is consistent with the minimal N_{55} rule.³⁶

However, C_{54} :540 with the least 5/5 bonds was not predicted to be the energetically lowest isomer in these PM3 calculations; eight isomers were predicted to be energetically lower than C_{54} :540 such as C_{54} :537 and C_{54} :541 (Table S-1 of supplementary information). The density functional hybrid method B3LYP has been widely used in fullerene computations. Especially, the combination of B3LYP and the basis set 6-31G* possesses a good balance between accuracy and computational cost in calculating structures and total energies of fullerenes. For example, the B3LYP/6-31G* treatment has been successfully used in the study of small fullerene C_{36} ³¹ and fullerene chloride $C_{50}Cl_{10}$,¹⁸ whose accuracy has been demonstrated therein. To find the most stable C_{54} , the 20 isomers of lower PM3 energies were further geometrically optimized using the B3LYP/3-21G method.³⁵ C_{54} :540 of the least N_{55} was revealed to be the lowest-energy isomer (Table 1). Geometry reoptimizations at the higher level of theory, B3LYP/6-31G*,³⁵

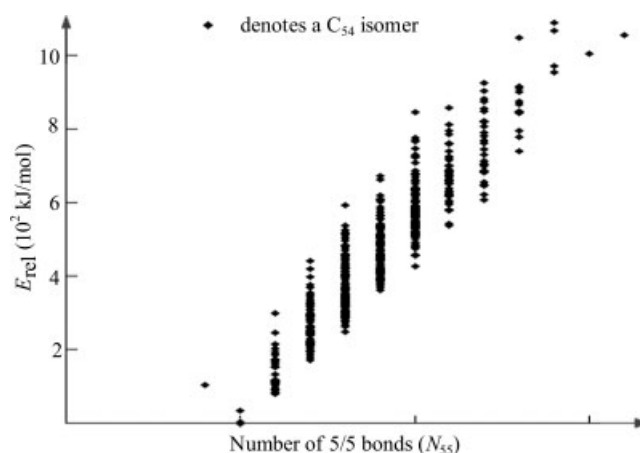
**Figure 1.** The correlation of the PM3 energies with N_{55} of the 580 C_{54} isomers.

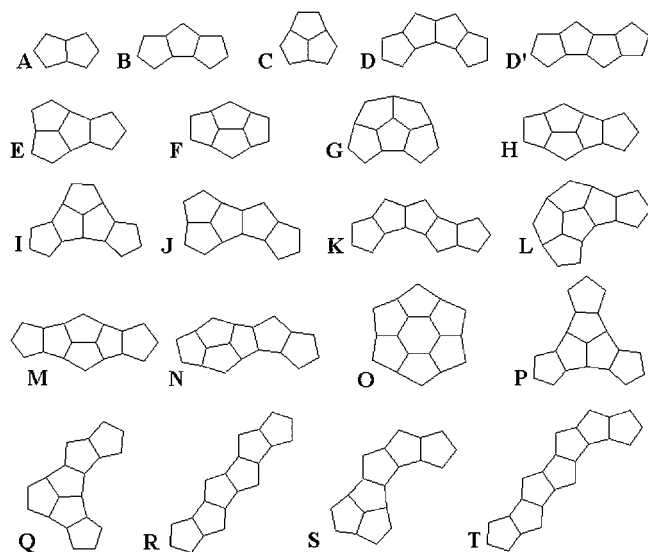
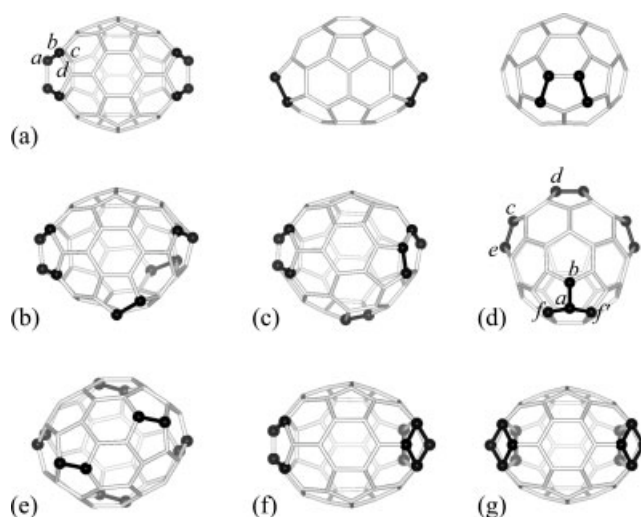
Table 2. Relative Energies (E_{rel} , kJ/mol), HOMO-LUMO Gap Energies (eV) Computed at Singlet States with B3LYP/6-31G* Method.

Isomer	E_{rel}	Gap	Isomer	E_{rel}	Gap
$C_{54}:540$	0	1.31	$C_{54}:579$	122.13	1.50
$C_{54}:537$	53.17	1.44	$C_{54}:540(1S)$	137.02	1.74
$C_{54}:541$	62.96	1.33	$C_{54}:540(2S)$	312.66	1.77
$C_{54}:369$	121.41	1.63	I_h-C_{60}		2.75

were then conducted for $C_{54}:540$ and the four less stable isomers of Table 1. The results confirmed $C_{54}:540$ to be energetically lowest-lying C_{54} and gave the stability order as $C_{54}:540 > C_{54}:537 > C_{54}:541 > C_{54}:369 > C_{54}:579$ (Table 2). These showed $C_{54}:540$ to be the thermodynamically best isomer among the 580 that is subject to be accumulated and captured by chlorines in the arc discharge chamber. In addition, these DFT results suggested that the semiempirical PM3 method would not be accurate enough in predicting the relative energies of isomers with small structural differences. As a less computationally cost method, the PM3 can be used in preliminary study regarding the total energy calculation; however, when reaching a conclusion, calculations with a higher level of theory must be supplemented.

Distribution Patterns of Pentagons in the 580 C_{54} Isomers

Of all of the 580 C_{54} isomers, the fused pentagons are distributed in a total of 20 types of patterns that are shown in Figure 2 and denoted as A, B ... and T, respectively. The geometries of the best isomer, $C_{54}:540$ and four neighboring less stable ones, $C_{54}:537$, $C_{54}:541$, $C_{54}:369$, and $C_{54}:579$ are given in Figures 3a–3e; the pentagon–pentagon shared bonds are shown as dark balls and sticks. On the surface of $C_{54}:540$ (Fig. 2A), one can see that

**Figure 2.** Twenty types of pentagon distributing patterns in the 580 classical C_{54} isomers. The variants like D and D' are sorted into the same category of D. Similarly, patterns K, Q, R, S, and T contain also more than one variants.**Figure 3.** Ground state geometries of $C_{54}:540$ (a), $C_{54}:537$ (b), $C_{54}:541$ (c), $C_{54}:369$ (d), $C_{54}:579$ (e), $C_{54}:540(1S)$ (f), and $C_{54}:540(2S)$ (g) computed at B3LYP/6-31G* level. 5/5 bonds and the squares are shown as dark balls and sticks. $C_{54}:540$ (a) is showed from one top view (along the C_2 molecular axis) and two side views.

there are two sets of three fused pentagons sharing two C—C bonds. In other words, $C_{54}:540$ contains two pentagon patches of pattern B ($2 \times B$). Analogously one can find $C_{54}:537$ (Fig. 3b) contains three patches of pattern A and one of pattern B ($3 \times A + 1 \times B$), and $C_{54}:541$ (Fig. 3c) contains one of A and two of B ($1 \times A + 2 \times B$), etc. The pentagon-patch components for the 20 isomers are given in Table 1, and those for the entire 580 isomers are given in Table S-1 of supplementary information (Calculation of the N_{55} and analysis of the pentagon distributions were realized by manipulating the corresponding fullerene dual adjacency matrix D of the spiral computer program; see ref. 33).

C_{54} Isomers Containing Squares or Heptagons

It has been suggested that introduction of square faces, with consequent loss of two pentagons per square, could turn out to be energetically favorable in the ranges ($n < 60$ and $60 < n < 70$) where classical isolated-pentagon fullerenes are impossible.³⁷ Accordingly, $C_{54}:540(1S)$ (Fig. 3f) with one square and $C_{54}:540(2S)$ (Fig. 3g) with two squares can be derived via single and double pyraclyene rearrangements (see Fig. 4), respectively.³⁸ We then explored the stabilities of these two nonclassical fullerene structures and compared them with the five classical ones, $C_{54}:540$, $C_{54}:537$, $C_{54}:541$, $C_{54}:369$, and $C_{54}:579$. Full geometry optimizations performed at B3LYP/6-31G* level indicated that neither $C_{54}:540(1S)$ nor

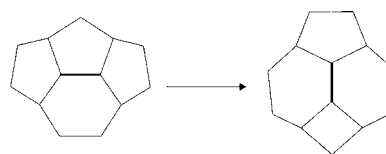
**Figure 4.** Pyraclyene rearrangement to introduce a square.

Table 3. BREs of the Symmetrically Distinct C—C Bonds of C₅₄:540.

Bond	Bond type	BRE/ $ \beta $	Bond	Bond type	BRE/ $ \beta $	Bond	Bond type	BRE/ $ \beta $	Bond	Bond type	BRE/ $ \beta $
1–3	5/5	−0.312	10–12	5/6	−0.048	8–15	5/6	0.073	8–9	5/6	0.110
1–2	5/6	−0.144	17–22	5/6	−0.035	19–24	5/6	0.082	14–22	6/6	0.149
3–7	5/6	−0.085	19–26	5/6	−0.002	15–21	5/6	0.086	7–14	6/6	0.164
22–32	5/6	−0.071	5–12	5/6	0.001	24–30	5/6	0.092	15–24	6/6	0.188
3–10	5/6	−0.067	17–27	5/6	0.042	26–27	6/6	0.105	5–8	6/6	0.192
1–5	5/6	−0.049	10–17	6/6	0.068	12–19	6/6	0.108	21–34	6/6	0.203

C₅₄:540(2S) is more stable than the best classical isomer (Table 2). In contrast, the introduction of squares into C₅₄:540 remarkably increases the total energy, indicating a larger destabilizing effect of one square than two pentagons in C₅₄. Heptagons are also energetically unfavorable in C₅₄:540, because when a heptagon is inserted into it, a square always accompanies it. In the other C₅₄ isomers of Table 1, such two carbon rings are also unfavorable. Therefore, the following discussion is focused on the classical isomers of C₅₄.

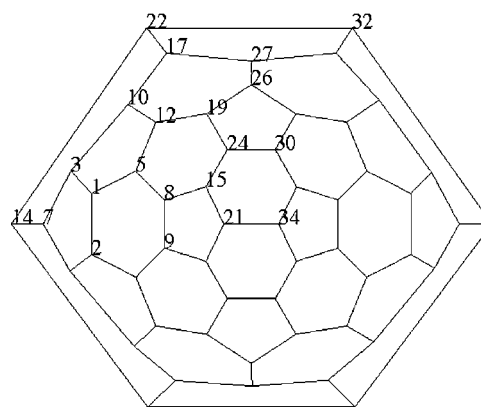
Structure of the C₅₄Cl₈

The C₅₄Cl₈ was formed through annealing of carbon plasm that contains a little CCl₄.¹⁵ At a plasm temperature of about 3000–4000 K, a large number of reactive carbon dimers (C₂) exist,⁸ and meanwhile the introduction of CCl₄ provided an appropriate situation for the generation of other free radicals like Cl, C₂Cl, etc., which are also highly reactive. So, the chemical conditions in the fullerene reactor were extremely harsh and thereby required that all of the surviving molecules therein had considerable kinetic stabilities without labile sites; otherwise, they would decompose or be transformed to other stable forms.³⁴ This requirement gives us a valuable criterion for selecting the most likely experimental structures: only those C₅₄Cl₈ isomers that have no kinetically unstable sites on the parent cage C₅₄ could be isolated and deserve further consideration.

The next problem is identifying the labile sites in C₅₄. Before probing into this, we reviewed the experimentally isolated non-IPR fullerene derivatives that have been reported so far. The structures of non-IPR fullerene derivatives C₅₀Cl₁₀,^{15,18} Sc₂@C₆₆,^{9,19} Sc₃N@C₆₈,^{10,21,22} and C₆₄H₄³⁹ have been definitely determined by experiments; those of La₂@C₇₂,^{12,23} Sc₂@C₇₂,²³ Sc₂C₂@C₆₆,¹¹ C₃₆H₆,^{24–26} and C₅₀Cl₁₂¹⁸ have also been elucidated. Among them, except for C₃₆H₆ that tends to form the so-called “spheriphane” because of its peculiar π electronic structure,^{24–26} the others have a feature in common: the reactive regions of the non-IPR cages are located at the 5/5 bonds. For example, on the surface of the C₆₆, there are two 5/5 bonds with two Sc atoms closely situated thereby^{9,19}; on the surface of the C₆₈, there are three 5/5 bonds beside which are three metal atoms^{11,35}; on the surface of the C₇₂, there are two 5/5 bonds with two La atoms located proximately^{10,21,22}; the C₅₀ contains five 5/5 bonds, so there are exactly 10 chlorines bonded exteriorly to them.^{15,18} Theoretical calculation also predicted that the most stable Ca@C₇₂ owns the non-IPR cage structure containing a 5/5 bond that is stabilized by the closely situated La atom.⁴⁰ These independent experimental and theoretical

results revealed common rules: (1) 5/5 bonds serve as the chemically most reactive (kinetically most unstable) sites of non-IPR fullerenes; (2) If non-IPR fullerenes are capable of being experimentally isolated their labile 5/5 bonds should be fully stabilized via chemical derivatizations (endohedral complexation or exohedral addition).

As early as 1995, Aihara developed a theoretical model for this rule.³⁴ Starting from the Hückel molecular orbital theory, Aihara defined bond resonance energy (BRE), the quantity of which represents the contribution of a given bond in a cyclic π system to aromaticity. The BRE was then supposed to be an indicator of kinetic stability: When the minimum BRE of an aromatic hydrocarbon is less than $-0.100 |\beta|$, the molecule is usually very reactive. The 5/5 bonds of most non-IPR fullerenes have large negative BREs ($< -0.100 |\beta|$) and thus are highly antiaromatic and chemically reactive.^{34,41} Within this model, the IPR becomes a necessary precondition for kinetically stable fullerenes and therefore satisfactorily interprets the IPR. As the BRE model has also provided a good understanding of the stabilization of metallofullerenes,^{42,43} we therefore applied it to explore the chemically labile sites for C₅₄ isomers. The BREs for the 24 symmetrically distinct C—C bonds of C₅₄:580 were calculated and are listed in Table 3. The BRE of the 5/5 bond (bond “1–3” in Fig. 5) is $-0.312 |\beta|$, far less than $-0.100 |\beta|$. In accordance with the BRE scheme, these 5/5 bonds of C₅₄:580 are hence highly antiaromatic and chemically reactive. We then calculated the BREs for C₅₄:537, C₅₄:541, and C₅₄:369. The results indicated that all of their 5/5 bonds have largely negative BREs (Table S-2 of supplementary information). They suggested that all the 5/5 bonds of these isomers are reactive.

**Figure 5.** Labeling system for C₅₄:540.

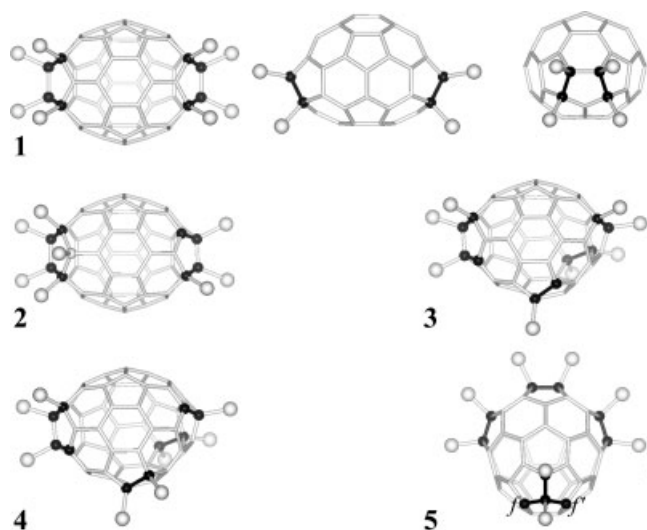


Figure 6. Ground state geometries of C₅₄Cl₈ isomers computed at B3LYP/6-31G* level. Structures **1** and **2** are based on C₅₄:540; **3** and **4** are based on C₅₄:537; **5** is based on C₅₄:369. Carbon–Carbon bonds in dark gray are 5/5 bonds. Structure **1** is showed from one top view (along the C₂ molecular axis) and two side views.

More important, the results revealed the crucial fact that the number of such reactive 5/5 bonds in C₅₄:540, C₅₄:537, C₅₄:541, and C₅₄:369 are 4, 5, 5, and 6, respectively. These numbers determine the minimal number of chemical addends that are required to fully stabilize the non-IPR cages. They determined that to stabilize C₅₄ fullerene, at least eight single-valent chemical addends are needed. This result was perfectly consistent with the experimental observation that C₅₄Cl₈ was indeed isolated. So, it was natural to conclude that **1** (Fig. 6) is the most appropriate structure for the experimental C₅₄Cl₈. In **1**, the eight chlorines stabilize the four 5/5 bonds and **1** keeps the symmetry of C_{2v}. In fact, by analyzing the geometries for all the 580 C₅₄ isomers, **1** was found to be the exclusive chlorofullerene that is fully stabilized without retaining reactive carbons.

In addition to the BRE, steric effect is another important factor that underlies the reactivity of fullerenes. We therefore performed π -orbital axis vector⁴⁴ analysis to calculate the pyramidalization angles (θ_p) of different carbons of C₅₄:540 (Table 4). The carbons of 5/5 bonds have a large θ_p (16.0°), larger than the most strained carbons of D_{5h}-C₅₀ (15.5°). In fullerenes, a large θ_p corresponds to a large local reactivity.⁴⁴ So, this result suggested that the eight

Table 4. Calculated Pyramidalization Angles (θ_p , °) for C₅₄:540, C₅₄:369, C₅₀, and C₆₀ on the Geometries Optimized at B3LYP/6-31G* Level.

Entity ^a	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	Others
C ₅₄ :540	16.0	16.0	13.3	13.1			12.4–9.8
C ₅₄ :369	22.6	17.5	16.0	15.4	15.1	15.1	13.5–8.1
D _{5h} -C ₅₀ ^b	15.5						12.8–10.7
I _h -C ₆₀	11.6						

^aFor labeling of C₅₄:540 and C₅₄:369, see **1** and **5** of Figure 3, respectively; for D_{5h}-C₅₀, *a* is the most strained carbon of 5/5 bond.

^bSee also ref. 18.

chlorines should be surely added to the 5/5 bonds, yielding the structure of **1** (Fig. 6). In **1**, the strains are relieved as the carbons are changed into nearly strain-free *sp*³-hybrid state. However, all of the other C₅₄Cl₈ isomers still have *sp*²-C-atoms (usually carbons of 5/5 bonds) with a large θ_p and therefore are unstable. For example, in **5** (Fig. 6), carbons labeled by *f* and *f'* are the reactive sites. For the same reason, the intermediates of **1**, i.e., other chlorides of C₅₄:540 such as C₅₄Cl₂ and C₅₄Cl₆, or free radical species like C₅₄Cl₁, C₅₄Cl₃ and C₅₄Cl₇ are reactive and unstable.

Thermodynamics of C₅₄Cl₈

The above results indicated that **1** is the one and only appropriate structure for the experimentally isolated C₅₄Cl₈. The only question remaining is regarding the steric repulsion of the exohedral addends. As the eight chlorines in **1** are concentratively distributed in two groups, if this brings a high repulsion force between chlorines, it would increase the energy and hence lower the thermodynamic stability. To clarify this issue, we explored the relative stabilities for a variety of C₅₄Cl₈ isomers and found out the energetically lowest-lying one. Then we made further effort to estimate the chlorine-repulsion in **1** and its possible influence on the formation of C₅₄Cl₈.

It is too burdensome to calculate all of the possible isomers of C₅₄Cl₈. To overcome this difficulty, we took the following approach. The carbons of 5/5 bonds are the energetically preferable addition sites; accordingly, the stable C₅₄Cl₈ are those whose chlorines are attributed entirely to 5/5 bonds with large separations (low repulsions). We considered C₅₄ cages that have fewer 5/5 bonds and meanwhile wider distributions of the 5/5 bonds. Isomers based on C₅₄:540, C₅₄:537, C₅₄:369, and C₅₄:579 were hence investigated. They contain pentagon patches of **A**, **B**, and **C**, and also represent the geometric categories. C₅₄:541 was not considered because its 5/5 bonds are more crowded than C₅₄:537 although their *N*₅₅ are equal. Table 1 shows that some C₅₄ isomers containing pentagon patch **D** also have relatively lower energies, but they were not considered because **D** has a higher density of 5/5 bonds. Similarly, other C₅₄ isomers that have higher energies and more condensed pentagons were not considered.

The detailed results are in S-3 of supplementary information. They show that **1** is more stable than most of the other C₅₄Cl₈ isomers. Nevertheless, there are four isomers (i.e., **2**, **3**, **4**, and **5**, Fig. 6) having slightly lower energies (Table 5). **5** has a dispersed

Table 5. Relative Energies (*E*_{rel}, kJ/mol) of the C₅₄Cl₈ Isomers with Respect to **1**, and of the Isostructural C₅₄H₈ with Respect to **1'**.

C ₅₄ Cl ₈ ^a	<i>E</i> _{rel}	C ₅₄ H ₈	<i>E</i> _{rel}
1	0 ^b (0.00) ^c	1'	(0.00) ^c
2	−17.03 ^b (−13.29) ^c		
3	−58.45 ^b		
4	−72.16 ^b		
5	−94.10 ^b (−106.61) ^c	5'	(−55.21) ^c

^aSee Figure 6 for the entities.

^bCalculated with the B3LYP/3-21G method.

^cCalculated with the B3LYP/6-31G** method.

chlorine-distribution with the reactive carbons quite efficient eliminated and is the lowest $C_{54}Cl_8$. To estimate the chlorine-repulsions of **1** and **5**, we calculated the energies of their isostructural $C_{54}H_8$ isomers (denoted as **1'** and **5'**). Geometry optimization at B3LYP/6-31G** showed that the energy difference between **1'** and **5'** is remarkably lower than that between **1** and **5** (106.61 vs. 55.21 kJ/mol, Table 5). The reason is that the smaller steric volume of hydrogens causes smaller repulsions. So, this comparative study revealed that it is indeed chlorine-repulsions that cause the energy enhancement of **1** than **5**. But as the synthesis of $C_{54}Cl_8$ was at a very high temperature of several thousand degrees and far from the chemical equilibrium,^{45,46} the influence of such a steric effect will be tiny and will not prevent the formation of **1**.

Conclusion

5/5 bonds of fullerenes have large negative BREs ($< -0.100 |\beta|$) and high steric strains; they serve as kinetically unstable (chemically reactive) sites of non-IPR fullerenes. Since C_{54} fullerenes contain not fewer than four 5/5 bonds, they are unstable in nature. However, they are experimentally isolable when all of their reactive 5/5 bonds are stabilized by exohedral additions. Among the possible C_{54} isomers, $C_{54}:540$ has the lowest relative energy, and is the thermodynamically best isomer that is subject to be accumulated in the arc-discharge reactor. It is also the only isomer containing four 5/5 bonds, and can be fully stabilized by exohedral additions of eight chlorines. So, from this view, **1** is the exclusively appropriate structure for the experimental $C_{54}Cl_8$. **1** has an architecturally unique structure of C_{2v} symmetry, and is energetically lower than most of the other $C_{54}Cl_8$ isomers. However, because of its relatively large chlorine-repulsions, there exist $C_{54}Cl_8$ isomers with slightly lower energies than **1**. This is interpreted by the fact that the synthetic conditions of the $C_{54}Cl_8$ is extremely harsh and deviated from chemical equilibrium, so kinetic aspects also play a key role in determining the survival possibility of the resultants.

We conclude that to stabilize non-IPR fullerenes, the derivatization reactions should firstly stabilize all of the 5/5 bonds on the cages. This rule is tested by almost all of the non-IPR fullerene derivatives that have been experimentally isolated and studied so far. This finding will open a large possibility for synthesizing novel carbon nanomaterials and also help identify structures of non-IPR fullerene derivatives themselves.

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Note Added in Proof

A recent paper that computationally studied the structure and reactivity of some selected neutral and cationic C_{54} isomers

(Diaz-Tendero, S.; Martin, F.; Alcamí, M. *Phys Chem Chem Phys* 2005, 7, 3756.) should be cited in the introduction of this manuscript.

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