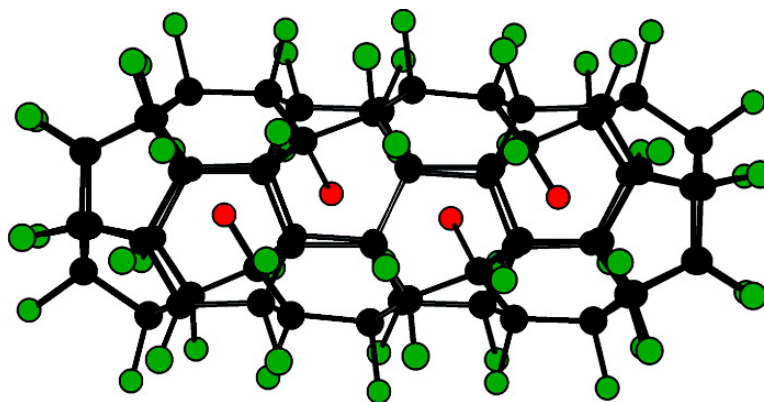


Fused Five-Membered Rings Determine the Stability of CF

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Fused Five-Membered Rings Determine the Stability of C₆₀F₆₀Jianfeng Jia,[†] Hai-Shun Wu,^{*,†} Xiao-Hong Xu,[†] Xian-Ming Zhang,[†] and Haijun Jiao^{*,†}

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Abstract: The structure and stability of a set of (CF)₆₀ isomers have been computed at the B3LYP/6-31G(d) density functional theory level. The most stable isomer (**6**, F₄@C₆₀F₅₆) has tube-like structure with four endo C–F bonds and fused five-membered rings at the end of the tube, while the reported most stable cage structure (**2**, F₈@C₆₀F₅₂) with eight endo C–F bonds is higher in energy by 22.6 kcal/mol. This is in contrast to the isolated pentagon rule for the stability of fullerenes. The mean bond dissociation energy of **6** is larger than those of the experimental known C₆₀F₃₆, C₆₀F₄₈, and graphite fluoride. The relative energy per CF unit of **6** to graphite fluoride (CF)_n is 3.7 kcal/mol, which is smaller than that of C₆₀ fullerene per carbon to graphite (about 9–10 kcal/mol).

Introduction

Because of the practical importance of perfluorocarbons,¹ fluorination of fullerene has attracted considerable attention since the discovery of C₆₀ fullerene.² The strong electron-withdrawing character of the fluorine atom compared to carbon and hydrogen atoms changes the physical and chemical properties of these carbon materials drastically and in turn makes them promising compounds for materials science.

The possible formation of C₆₀F₆₀ via C₆₀ fluorination was reported by Holloway et al. in 1991 on the basis of a single-line ¹⁹F NMR spectrum.³ However, the detailed information about the structure and stability of C₆₀F₆₀ is still elusive despite increased experimental evidence.^{4,5} The best known examples are partially fluorinated C₆₀F_x, and the isolable derivative with the largest number of fluorine atom is actually C₆₀F₄₈.⁶ In addition, fluorination of higher fullerenes⁷ and carbon nanotubes^{8,9} has also been reported.

Parallel to the experimental activities, theoretical studies on the structure and stability of C₆₀F₆₀ have also been carried out. On the basis of C₆₀, C₆₀F₆₀ (**1**) has been computed to have a

cage structure with 60 exo C–F bonds in I_h symmetry,¹⁰ and a strong nonbonded interaction between the fluorine atoms has been found.¹¹ Similar to C₆₀H₆₀¹² as well as C₈₀H₈₀ (H₂₀@C₈₀H₆₀/I_h) and C₁₈₀H₁₈₀ (H₆₀@C₁₈₀H₁₂₀/I_h),¹³ C₆₀F₆₀ with endo C–F bonds has been found to be more stable than the all exo isomer (**1**),^{14,15} and the most stable isomer has eight endo C–F bonds (F₈@C₆₀F₅₂, **2**) using the AM1 semiempirical method.^{14,16} It should also be noted that fluorinated single-wall carbon nanotubes with endo C–F bonds can be more stable than isomers with all exo C–F bonds on the basis of the tube diameters.¹⁷

In this article we report more stable C₆₀F₆₀ isomers with fused five-membered rings, and this is in contrast to the isolated pentagon rule (IPR) for the stability of carbon fullerenes,¹⁸ i.e.,

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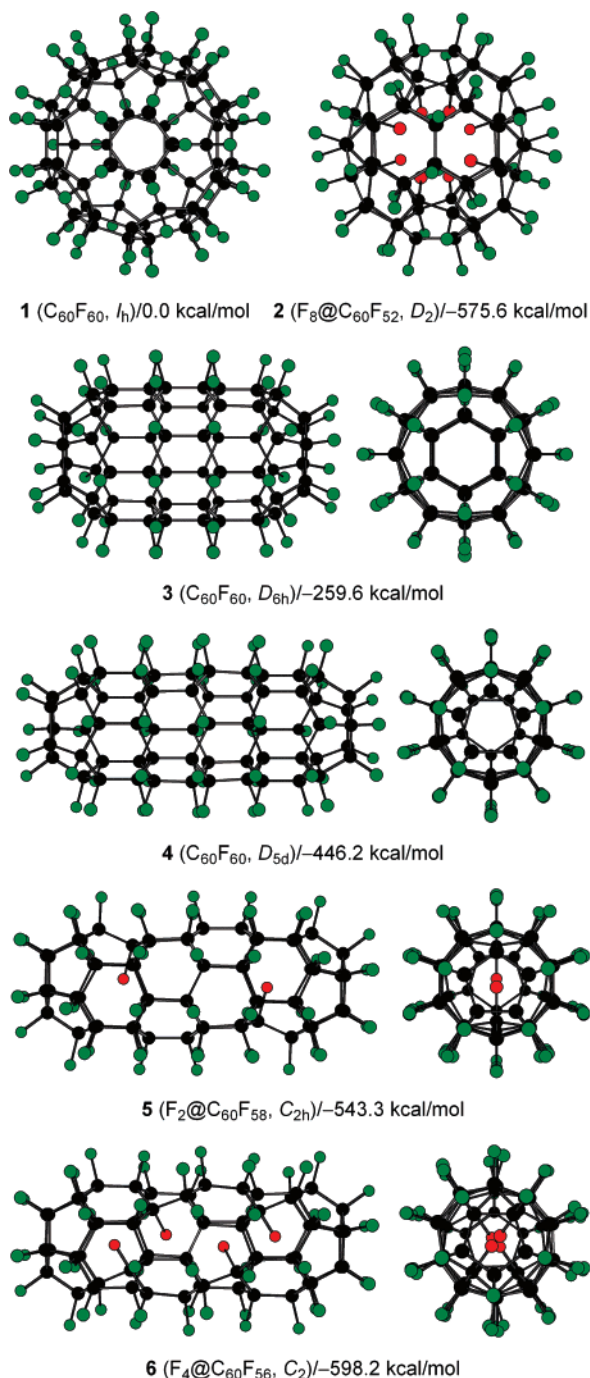


Figure 1. B3LYP/6-31G(d)-optimized (CF)₆₀ isomers (1–6), and the computed relative energies (the endo fluorine atoms are shown in red).

maximal and perfect separation of the strained pentagons. The thermodynamic stability of these selected isomers has also been analyzed and discussed.

Computational Details

All (CF)₆₀ isomers were optimized at the B3LYP/6-31G(d) level of density functional theory with the Gaussian 03 program.¹⁹ Due to the large size of the structures, we carried out frequency calculations only on selected most stable isomers at HF/6-31G(d). The selected structures (1–6) in Figure 1 are energy minimum structures at the HF/6-31G(d) level. The monocyclic (CFH)₅ and (CFH)₆ reference molecules were

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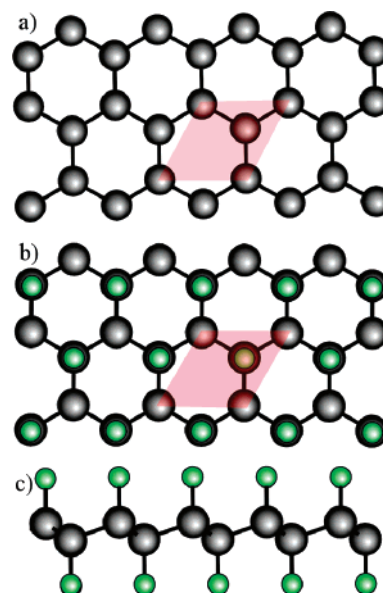


Figure 2. Unit cells for graphite (a) and graphite fluoride (CF)_n (b, top view; c, side view).

computed at the B3LYP/6-31G(d) level of theory for estimating the ring strain energies.

To estimate the thermodynamic stability of these (CF)₆₀ isomers, a graphite sheet and graphite fluoride sheet (CF)_n were computed by imposing periodic boundary conditions (PBC).²⁰ The unit cells for PBC calculation are shown in Figure 2. The graphite fluoride sheet (CF)_n has a unit cell comprised of six-membered rings in chairlike conformation. These are the same models used by Bettinger et al. for carbon nanotubes.²¹ The PBC calculations were carried out at the B3LYP/6-31G(d) level (PBC-B3LYP/6-31G(d)). Integration in the first Brillouin zone was performed using a k -point mesh of 142×142 for both graphite and graphite fluoride sheet (CF)_n.

For direct comparison with the available reference data for carbon nanotubes by Bettinger et al.,²⁰ the selected isomers were also calculated using gradient-corrected density functional of Perdew, Burke, and Ernzerhof (PBE) and the 3-21G basis set (PBE/3-21G). The computed energetic data and Cartesian coordinates for all isomers are given in the Supporting Information.

Results and Discussion

(a) Structure and Stability of $C_{60}F_{60}$. Inspired by the finding that large (BCO)_n structures favor tube instead of cage conformations,²² we calculated two tube-like $C_{60}F_{60}$ structures with all exo C–F bonds for searching more stable isomers. The first one (3) has D_{6h} symmetry with 12 five-membered rings located at the ends of the tube. The second one (4) has D_{5d} symmetry with 12 five-membered rings fused and located at the ends of the tube. At the B3LYP/6-31G(d) level, both two tube-like isomers (3 and 4) are more stable than the cage isomer (1) by 259.6 and 446.2 kcal/mol, respectively. The major difference between 4 (or 3) and 1 is the location of the five-membered rings. Since the stability of C_{60} fullerene is governed by the isolated pentagons, the stability of the tube-like isomer 4 (or 3) is governed by the fused five-membered rings, i.e., the more fused the five-membered rings, the more stable the isomers. This also explains the higher stability of isomer 4 over isomer

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3 by 186.6 kcal/mol, since **4** has more fused five-membered rings than **3**.

Detailed inspection into structure **4** shows that the fused five-membered rings are planar or nearly planar, and the six-membered rings have boat conformation. In contrast, **1** has not only planar five-membered rings but also planar six-membered rings. To model the stability we used the planar structures of (CHF)₅ and (CHF)₆ with all fluorine atoms on the same side in C_{5v} and C_{6v} symmetries, respectively; it shows that the relative energy per CHF unit of (CHF)₅ is lower than that of (CHF)₆ by 2.66 kcal/mol, indicating the higher stability of the five-membered ring.

In **4**, the boat-like six-membered rings reduce not only the strain of the rings but also the nonbonded interaction of the fluorine atoms. In **1**, for example, the distances of the nonbonded fluorine atoms are 2.177 and 2.146 Å. In **4**, the distances of the nonbonded fluorine atoms of the five-membered rings are 2.506, 2.473, and 2.317 Å, and those of the six-membered rings are 2.267, 2.291, and 2.318 Å. In addition, C–F bonds of the boat-like six-membered rings in **4** have gauche rather than eclipsed conformations, and this reduces the torsion strain additionally. This is shown by the relative energies per CHF of the boat-like and twisted boat-like structures of (CHF)₆ in C_{2v} and C₂ symmetries, which are lower than that of the planar structure (C_{6v}) by 4.63 and 5.14 kcal/mol, respectively.

At B3LYP/6-31G(d), however, cage isomer **2** with eight endo C–F bonds is more stable than tube-like isomer **4** by 129.4 kcal/mol and the cage isomer **1** by 575.6 kcal/mol. On the basis of these energetic data, it is expected that introduction of endo C–F bonds into tube-like structure **4** will further reduce the ring and torsion strains and therefore lead to more stable isomers than **2**.

Starting from **4**, we computed 13 isomers with two endo C–F bonds (F₂@C₆₀F₅₈, see Supporting Information). They are more stable than **4** but higher in energy than **2**. The most stable F₂@C₆₀F₅₈ structure is isomer **5**, which is higher in energy than **2** by 32.3 kcal/mol. This indicates that two endo C–F bonds reduce the strain energy by about 97 kcal/mol.

Further, we computed five isomers with four endo C–F bonds (F₄@C₆₀F₅₆, see Supporting Information). It is worth noting that all five isomers are more stable than **2**! The most stable isomer is **6**, which is more stable than **2** by 22.6 kcal/mol. This indicates that four endo C–F bonds in the tube-like structure reduce the strain considerably and revise the energetic order. However, a further increase of endo C–F bonds from four to six raises the energy considerably, and the isomers become strongly less stable by at least 157 kcal/mol, as compared to isomer **6**.

It is now interesting to compare structures **2** and **6** for detail. Due to its larger cage size, **2** can adopt more endo C–F bonds than **6**. The shortest nonbonded distances of **2** are 2.268 and 2.278 Å, and those of **6** are 2.224 and 2.411 Å. Therefore, further introduction of endo C–F bonds in **6** might reduce the angle and torsion strains but raise nonbonded repulsive interaction of these bonds, as shown above.

In **2**, the endo C–F bonds connect both five- and six-membered rings, and these reduce the torsion strain of the exo C–F bonds. Compared to **1**, not only the shortest distances of the exo nonbonded fluorine atoms of **2** become longer (>2.327 vs 2.177 and 2.146 Å) but also the torsion angles deviate strongly from 0.0°; this reduces the torsion strain. In

Table 1. Mean Bond Dissociation Energies (BDE, kcal/mol) per Fluorine Atom, and Relative Energies of CF to Graphite Fluoride ($\Delta E_{\text{rel}}/\text{CF}$, kcal/mol)

isomer	BDE ^a	BDE ^b	$\Delta E_{\text{rel}}/\text{CF}^a$	$\Delta E_{\text{rel}}/\text{CF}^b$
1	55.3	61.4	13.7	15.0
2	64.9	71.2	4.1	5.1
3	64.4	69.5	9.3	10.9
4	71.6	76.2	6.2	7.6
5	73.2	78.3	4.6	5.6
6	74.1	79.8	3.7	4.1
C ₆₀ F ₃₆	69.5 (70.5 ± 0.2 ²⁴)	74.8		
C ₆₀ F ₄₈	64.3 (68.8 ± 0.8 ²⁵)	71.5		
(CF) _n	c	68.2	0.0	0.0

^a At B3LYP/6-31G(d). ^b At PBE/3-21G. ^c Unstable wave function at B3LYP/6-31G(d).

addition, the bond angles of the five- and six-membered rings deviate strongly from those of the planar structures (108.0° and 120.0°), and therefore, these raise and reduce the angle strain of the five- and six-membered rings, respectively.

In **6**, however, the endo C–F bonds are found only in the six-membered rings, and these reduce not only the torsion but also the angle strains of the six-membered rings. On the other hand, the fused five-membered rings are nearly planar, and no significant strain changes can be expected. Therefore, the enhanced stability of **6** should be ascribed to the fused five-membered rings. Compared to C₆₀ with the perfect isolated pentagons, the tube structures with fused pentagons (the carbon frameworks of **3** and **4**, considered as unconventional fullerene isomer) are much less stable by 286.5 and 527.4 kcal/mol, respectively. The difference in fluorination energy of **2** and **6** starting from the corresponding carbon clusters (the carbon frameworks of **1** and **4**) is 550.0 kcal/mol. Compared to the cage isomers, therefore, the higher stability of the tube-like structures is governed by the fused five-membered rings, and this is in sharp contrast to the isolated pentagon rule for the stability of carbon fullerenes. That fused pentagons stabilize highly strained unconventional fullerenes explains the stability of the recently prepared C₆₄H₄ (C_{3v}) with one triquinacene unit containing three fused five-membered rings.²³

(b) Thermodynamic Stability of C₆₀F₆₀. To derive the mean C–F bond dissociation energy (BDE) of the (CF)₆₀ isomers, we employed theisodesmic equation used by Bettinger et al.²⁰ for fluorinated nanotubes. The difference in heat of formation between C₆₀F₆₀ and C₆₀ can be estimated from eq 1 using the heats of formation of ethene (+12.54 kcal/mol²⁴) and 1,2-difluoroethane (−102.7 kcal/mol²⁵). With the experimental heat of formation of the fluorine atom (+18.97 kcal/mol²²), the mean C–F BDE of C₆₀F₆₀ can be calculated according to eq 2

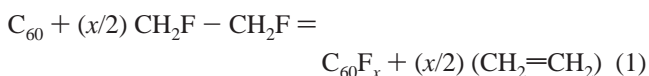


Table 1 lists the calculated BDE at the B3LYP/6-31G(d) and PBE/3-21G levels. It shows clearly that the calculated BDE for C₆₀F₃₆ and C₆₀F₄₈ at both levels are in reasonable agreement

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with the available experimental values.^{26,27} Therefore, the B3LYP/6-31G(d) results are used for discussion, and the PBE/3-21G data are used for comparison.

As expected, the all exo cage isomer **1** has the lowest C–F BDE, indicating its high thermodynamic instability. At B3LYP/6-31G(d), the C–F BDE of **1** is lower than those of C₆₀F₃₆ and C₆₀F₄₈ by 14.2 and 9.0 kcal/mol, respectively, and these reveal the difficulty of experimental realization of **1**,^{3–5} while both C₆₀F₃₆²⁸ and C₆₀F₄₈^{6,29} are well studied experimentally. It is worth noting that the C–F BDE (64.9 kcal/mol) of the cage structures with eight endo C–F bonds (**2**) is close to that of C₆₀F₄₈ (64.3 kcal/mol), and this indicates the enhanced thermodynamic stability of structures with endo C–F bonds.

The C–F BDE increases from the cage structure (**1**) to the tube structure (**4**) by 16.3 kcal/mol, and the largest C–F BDE (74.1 kcal/mol) is found for the most stable tube structure with four endo C–F bonds (**6**). Apart from **1**, isomers **2–6** have larger C–F bond DBEs than the graphite fluoride (CF)_n (Table 1, second entry, at PBE/3-21G), and the largest difference (11.6 kcal/mol) is found between **6** and (CF)_n.

At PBE/3-21G, the C–F BDE (79.8 kcal/mol) of the most stable isomer **6** is close to those of the fluorinated armchair (3,3) and (4,4) nanotubes (83.1 and 74.4 kcal/mol, respectively) and greater than those with larger tube diameters, e.g., 68.5 kcal/mol of armchair (5,5), as reported by Bettinger et al.²⁰

In addition to C–F BDE, it is also interesting to compare the relative energy per CF unit. Taking graphite fluoride (CF)_n as reference (Table 1), the relative energy per CF unit of **6** is the smallest (3.7 kcal/mol), while that of **1** is the largest (13.7 kcal/mol). It is worth noting that C₆₀ is higher in energy than graphite

sheet by about 9–10 kcal/mol per carbon atom determined both by theoretical calculations³⁰ and experiments.³¹

Conclusion

Both B3LYP/6-31G(d) and PBE/3-21G density functional theory calculations were carried out to study the structure and stability of a set of (CF)₆₀ isomers. It is found that the most stable isomer (**6**, F₄@C₆₀F₅₆) is tube-like and has a structure with fused five-membered rings at the end of the tube and four endo C–F bonds. In contrast, the reported cage structure (**2**, F₈@C₆₀F₅₂) with eight endo C–F bonds and isolated pentagons is less stable by 22.6 kcal/mol. In addition, the tube-like structure (**4**, C₆₀F₆₀) with fused five-membered rings at the end of the tube is also more stable than the cage structure (**1**, C₆₀F₆₀) with isolated pentagons by 446.2 kcal/mol. This behavior is in sharp contrast to the isolated pentagon rule for the stability of carbon fullerenes. Indeed, the carbon framework of **4** with fused five-membered rings at the end of the tube is higher in energy than C₆₀ with isolated pentagons by 527.4 kcal/mol.

It is also found that the mean bond dissociation energy (79.8 kcal/mol) of the most stable isomer (**6**) is larger than those (74.8, 71.5, and 68.2 kcal/mol, respectively) of the experimentally known C₆₀F₃₆, C₆₀F₄₈, and graphite fluoride (CF)_n. It is also interesting to note that the mean bond dissociation energy of **6** is comparable to those of the fluorinated armchair (3,3) and (4,4) carbon nanotubes (83.1 and 74.4 kcal/mol, respectively). It is finally noted that the relative energy of **6** per CF unit to graphite fluoride is smaller than that of C₆₀ to graphite.

Acknowledgment. This work was supported by the Natural Science Foundations of China (20673070).

Supporting Information Available: Computed energetic data and optimized Cartesian coordinates for all isomers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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