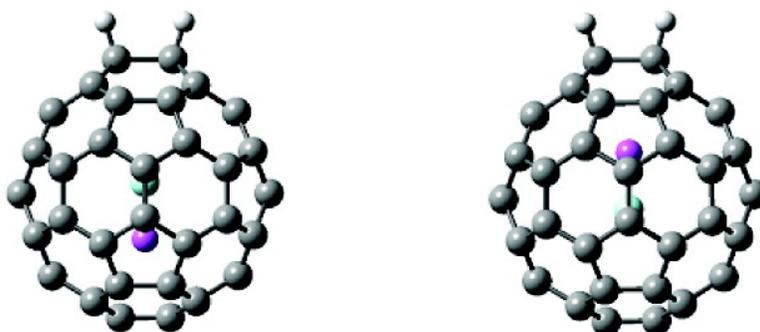


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Endohedral Chemistry of C₆₀-Based Fullerene Cages

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Abstract: Fullerenes have unique chemistry owing to their cage structure, their richness in π -electrons, and their large polarizabilities. They can trap atoms and small molecules to generate endohedral complexes as superconductors, drug carriers, molecular reactors, and ferroelectric materials. An important goal is to develop effective methods that can affect the behavior of the atoms and small molecules trapped inside the cage. In this paper, the quantum chemical density functional theory was employed to demonstrate that the stability and position of a guest molecule inside the C₆₀ cage can be changed, and its orientation controlled, by modifying the C₆₀ cage shell. The outside attachment of two hydrogen atoms to two adjacent carbon atoms located between two six-membered rings of the C₆₀ cage affects the orientation of the LiF molecule inside and increases the stability of LiF inside the cage by 45%. In contrast, when 60 hydrogen atoms were attached to the outside surface of the C₆₀ cage, thus transforming all C=C double bonds into single bonds, the stability of the LiF inside was reduced by 34%. If two adjacent carbon atoms were removed from C₆₀, the stability of LiF inside this defect C₆₀ was reduced by 41%.

1. Introduction

The discovery of fullerenes is one of the most important developments in chemistry and material sciences. The most prominent representative of fullerenes is C₆₀,¹ which is the smallest fullerene that satisfies the isolated pentagon rule. The cage structure, richness in π -electrons, and large polarizabilities constitute unique characteristics of fullerenes. Their cages can trap atoms and small molecules to generate endohedral complexes, which have potential applications as superconductors, drug carriers, ferroelectric materials, and molecular reactors. Soon after the discovery of C₆₀, the Kroto, Smalley, and Curl group suggested the possibility of encapsulating La atoms inside its cage.² Endohedral fullerene complexes with metals³ and noble gases⁴ have been also prepared, but very few fullerene complexes with molecules contained inside have been reported.⁵ A stimulating challenge for synthetic chemists was to develop

efficient synthetic approaches to prepare endohedral fullerene complexes with molecules inside.⁶ An obvious choice was to generate a wider opening in the fullerenes by increasing the distance between the carbon atoms to allow an atom or a small molecule to pass through.⁷ Recently, chemical "surgery" methods have been successfully developed to open windows that allow the preparation of endohedral complex of C₆₀ with small molecules.^{5a,8,9}

Fullerene complexes have also attracted attention in theoretical areas. Cioslowski's group carried out pioneering theoretical research regarding the endohedral chemistry of fullerenes.¹⁰⁻¹³ Cioslowski and Fleischmann performed ab initio HF electronic structure calculations for C₆₀ endohedral complexes with F⁻, Ne, Na⁺, Mg²⁺, and Al³⁺.¹⁰ They found that location of ions at the center of the cage resulted in a net stabilization and that the ionic guest either decreased (F⁻) or increased (Na⁺, Mg²⁺, and Al³⁺) the cage radius. However, the Ne@C₆₀ complex was destabilized by about 0.4 kcal/mol relative to the separate components. Furthermore, Cioslowski's ab initio HF calculations demonstrated that the C₆₀ cage acts as a polarizable sphere that stabilizes polar molecules (such as LiF and LiH) and destabilizes

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nonpolar ones (such as H₂ and N₂).¹¹ By use of the Hartree–Fock (HF), density functional theory (DFT), and second-order Möller–Plesset perturbation (MP2) methods, Scuseria's^{14–16} and Thiel's^{17–20} groups have made significant contributions regarding equilibrium geometries and binding energies, as well as the mechanisms of formation of endohedral complexes. In recent years, other researchers have published papers regarding various endohedral complexes.^{21–29}

With regard to the molecular design of practical endohedral materials, effective methods to control the characteristics (such as stability, position, and orientation) of the guest molecule inside the cage are necessary. However, no such experimental or theoretical work has been carried out. This situation prompted us to investigate, using DFT, how the outside modifications of the C₆₀ cage shell can change the position and stability of a LiF guest molecule inside and control its orientation in the endohedral complex.

2. Calculation Details

The C₆₀ structure has been examined theoretically using semiempirical,³⁰ ab initio HF,³¹ local density-functional (LDF),³² and MP2 methods.³³ All these calculations have revealed that the C₆₀ cluster has a unique icosahedral structure, consisting of only five- and six-membered rings, in which all the atoms are equivalent, with short bonds between the six- and six-membered rings and longer bonds between the five- and six-membered rings. Compared with experiment (single bond, 1.458 Å; double bond, 1.401 Å),^{34,35} the best theoretical predictions for the bond lengths in C₆₀, 1.446 and 1.406 Å, were obtained using the MP2 method with a large orbital basis set.³³ From the viewpoint of quantum chemical calculations, the fullerenes are challenging molecules because of their size. The steep increase of computational cost with

the molecular size has prohibited the application of the most sophisticated ab initio methods to the ordinary fullerenes.³⁶ In the past few years, progress has been achieved for large molecular systems^{37,38} with the HF and the DFT methods, which are the least expensive ab initio methods. Furthermore, it has been found that a major improvement over the standard DFT can be achieved by combining the HF and DFT methods, leading to the so-called self-consistent hybrid (SCH) approaches. The B3LYP, which is a combination of HF with a DFT based on the Becke three-parameter exchange coupled with the Lee–Yang–Parr (LYP) correlation potential,³⁹ is one of the most popular hybrid density functional methods. In our previous paper,⁴⁰ it was shown that the bond lengths of C₆₀ predicted by the B3LYP hybrid DFT calculations are in very good agreement with experiment. Furthermore, the B3LYP method provided relatively accurate results for the La₂@C₈₀ endohedral complex.⁴¹ For this reason, in this paper the interaction between fullerene and its internal guest, the LiF molecule, is calculated using the B3LYP hybrid DFT method with the 6-31G(d) orbital basis set for the geometry optimization and the larger orbital basis set 6-311G(d) for the energy and the polarizability calculations.

Furthermore, the basis set superposition error (BSSE),^{15,42–44} which corrects for the fact that the practical quantum chemical calculations are restricted to the use of finite basis sets, is taken into account for the endohedral complexes. The Boys–Bernardi counterpoise (CP) procedure^{45–47} is employed, using the so-called “ghost orbitals” method, for the BSSE correction.

To evaluate the electron overlapping between the guest molecule and the cage, the electron density is calculated. Furthermore, to take into account the electron clouds, the molecular volume is calculated as the volume inside a contour with a 0.001 electrons/bohr³ density.⁴⁸

All these calculations are carried out using the Gaussian 94 program.⁴⁸

3. Results and Discussion

3.1. Polarizabilities of Modified C₆₀ Cages. One of the most important characteristics of fullerenes is their large polarizabilities. The polarizability of C₆₀ has been investigated experimentally and theoretically.^{49,50} Accurate experimental results⁴⁹ show that the static polarizability of C₆₀ is 76.5 ± 8.0 Å³. To examine the effect of the modification of the C₆₀ cage shell on its polarizability, we employed the B3LYP/6-311G(d) method to calculate the polarizabilities of C₆₀, defect C₆₀ with two neighboring vacancies, C₆₀H₂, and C₆₀H₆₀. The average polarizabilities(α), which are defined by eq 1, are listed in Table 1.

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (1)$$

The structure of C₆₀, which possesses 12 five-membered rings and 20 six-membered rings with two kinds of bonds (short double-bonds between the six- and six-membered rings and

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Table 1. Results for Non-Endohedral Molecules Obtained from B3LYP Calculations

| molecule ^a | dipole (D) | polarizability (Å ³) | HOMO (eV) | LUMO (eV) | HOMO–LUMO GAP (eV) |
|---------------------------------|------------|----------------------------------|-----------|-----------|--------------------|
| LiF | 5.7195 | 1.2 | −7.3967 | −1.3954 | 6.0013 |
| C ₆₀ | 0 | 73.8 | −6.4070 | −3.6719 | 2.7351 |
| C _{60−2} | 0.3354 | 73.6 | −5.7944 | −4.2578 | 1.5366 |
| C ₆₀ H ₂ | 2.7045 | 74.7 | −6.0617 | −3.5683 | 2.4934 |
| C ₆₀ H ₆₀ | 0 | 77.9 | −6.4872 | −0.4172 | 6.0700 |

^a See Figure 1.

longer single-bonds between the five- and the six-membered rings) is given in Figure 1a.^{30–35,40} As shown in Table 1, although C₆₀ is nonpolar, it has the high static polarizability of 73.8 Å³, in good agreement with the experimental value of 76.5 ± 8.0 Å³.⁴⁹

When two neighboring carbon atoms were removed from the C₆₀ cage to generate a defect C₆₀ cage with two vacancies (denoted C_{60−2}), the most stable isomer consisted of 13 five-membered rings, 17 six-membered rings, and 1 seven-membered ring.⁴⁰ Furthermore, it was found that, for the defect C_{60−2}, the singlet structure has a lower energy than the triplet one. Consequently, C_{60−2} possesses a singlet electronic ground state. The formation of one seven-membered ring and 6-abutting five-membered rings in this stable defect cage leads to a partial loss of symmetry (Figure 1b), resulting in the small permanent dipole moment of 0.3354 D (Table 1). However, C_{60−2} has a high static polarizability of 73.6 Å³, which is almost the same as that of the C₆₀ cage.

To annihilate two π -electrons of the C₆₀ cage, two hydrogen atoms were attached outside of two adjacent carbon atoms located between the six- and six-membered rings, generating a modified C₆₀ cage denoted C₆₀H₂. As a result, the length of the C=C bond, which was saturated with two hydrogen atoms, changed from 1.395 to 1.590 Å (Figure 1c), indicating that the C=C double bond was transformed into a C–C single bond. Furthermore, the calculation showed that the C₆₀H₂ cage still has the high polarizability of 74.7 Å³, which is somewhat larger than that of C₆₀ (Table 1). In contrast to C₆₀, C₆₀H₂ is a highly polar cage with a permanent dipole moment of 2.7045 D.

To annihilate all the π electrons of the C₆₀ cage, 60 hydrogen atoms were attached outside of the 60 carbon atoms, generating a C₆₀H₆₀ cage. In this manner, all the C=C double bond lengths changed from 1.395 to 1.571 Å (see parts a and d of Figure 1), indicating that all C=C double bonds became single bonds. The large HOMO–LUMO difference for C₆₀H₆₀ (Table 1), which constitutes a characteristic of the normal saturated hydrocarbons, confirms that C₆₀H₆₀ is a saturated hydrocarbon.⁵¹ The calculations showed that the C₆₀H₆₀ cage without any π electron still has a high polarizability of 77.9 Å³, which is the highest among the four fullerenes, C₆₀, C_{60−2}, C₆₀H₂, and C₆₀H₆₀ considered (see Table 1).

3.2. Stability of LiF in Fullerene Cages. The large polarizabilities of the cages generate a large dipole–induced dipole interaction when a polar small molecule is located in the cage to form an endohedral complex.¹¹ Let us examine how the

modifications of a C₆₀ cage, achieved by removing carbon atoms from or by attaching hydrogen atoms to a C₆₀ cage, affect the polar guest molecule. To perform such a calculation, we introduced a strongly polar LiF molecule (with a permanent dipole moment of 5.7195 D) into C₆₀, defect C₆₀ with two neighboring vacancies (C_{60−2}), C₆₀H₂, and the non- π -electron C₆₀H₆₀ cages. As shown in Table 2, all the above cages, with or without π electrons, stabilized LiF inside them. The stabilization energies are 9.8, 5.8, 14.2, and 6.5 kcal/mol for LiF@C₆₀, LiF@C_{60−2}, LiF@C₆₀H₂, and LiF@C₆₀H₆₀, respectively (Table 2). Consequently, the outside attachment of two hydrogen atoms to the C₆₀ cage increases the stability of the LiF inside by 4.4 kcal/mol (from 9.8 to 14.2 kcal/mol, 45%), whereas the external attachment of 60 hydrogen atoms to, or the removal of two neighboring carbon atoms from, the C₆₀ cage decreases the stability of the LiF inside by 3.3 kcal/mol (from 9.8 to 6.5 kcal/mol, 34%) and 4 kcal/mol (from 9.8 to 5.8 kcal/mol, 41%), respectively.

To evaluate the pure electrostatic interaction in the endohedral complexes, LiF was replaced by a two-point-charge-couple in the corresponding endohedral complex. The natural bond orbital (NBO) analysis indicated that the charges of Li and F are +0.899 and −0.899, respectively, in an individual LiF molecule. Therefore, a +0.899 and −0.899 point charge couple was used to replace LiF in LiF@C₆₀, LiF@C_{60−2}, LiF@C₆₀H₂, and LiF@C₆₀H₆₀ without any geometry change. As shown in Table 2, the stabilization energies due to the pure electrostatic interaction, provided by B3LYP/6-311G(d) calculations, were 18.1, 18.2, 17.8, and 25.3 kcal/mol for LiF@C₆₀, LiF@C_{60−2}, LiF@C₆₀H₂, and LiF@C₆₀H₆₀, respectively. This indicates that LiF@C₆₀, LiF@C_{60−2}, and LiF@C₆₀H₂ have almost the same electrostatic interaction, whereas LiF@C₆₀H₆₀ has a larger one.

By comparison of the interaction between LiF and cage to that between the corresponding two-point charge couple and cage, one can note that the interactions between LiF and cages are much smaller than their corresponding purely electrostatic attractive interactions obtained from the interactions of the two-point charge couple with the cages (Table 2). Therefore, another repulsive interaction between LiF and cages, besides the attractive electrostatic interactions, must be present. Such a possible repulsive interaction between LiF and cages might be provided by the overlap of electron clouds. To investigate this possibility, we calculated the electron densities of LiF, C₆₀, C_{60−2}, C₆₀H₂, C₆₀H₆₀, LiF@C₆₀, LiF@C_{60−2}, LiF@C₆₀H₂, and LiF@C₆₀H₆₀. Furthermore, to compare the diameters of the electron clouds, the electron cloud volume was defined as the volume inside a contour with a 0.001 electrons/bohr³ density.⁴⁸ As shown in Figure 2a, the electron cloud of the free LiF molecule has an apple shape with a diameter of 3.41 Å and length of 3.95 Å. Both dimensions are much larger than the bond length of 1.551 Å (based on the nuclear centers). Furthermore, the inside diameters of the electron clouds of the cages are from 2.46 to 3.82 Å (parts b, d, f, and h of Figure 2). Hence the inside diameters of the electron clouds of the cages (the empty cavities of the cages) are much smaller than the diameters of the cages (~6.37–7.76 Å) based on the nuclear centers. Because the size of the LiF electron cloud is larger than that of the empty cavity of the cage, the electron cloud of LiF overlaps with the electron cloud of the cage (parts c, e, g and i of Figure 2), generating a repulsive interaction. The total

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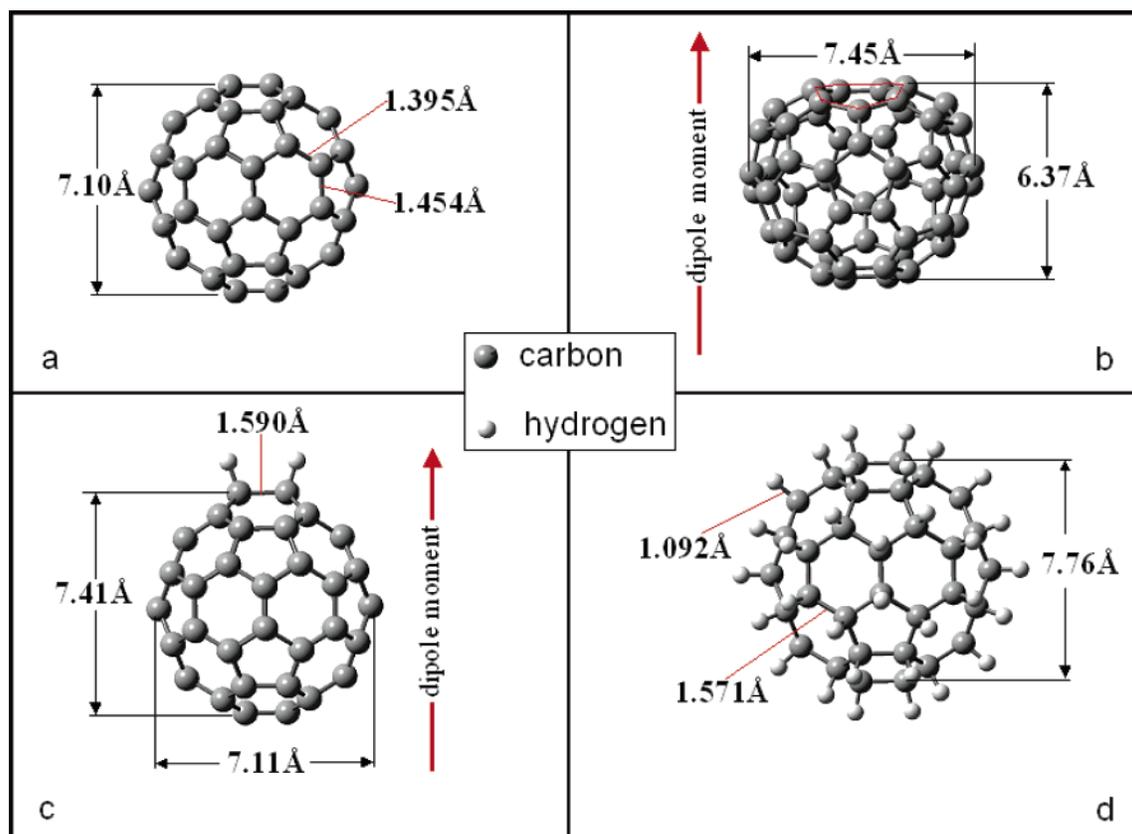


Figure 1. Optimized geometries: (a) C_{60} ; (b) defect C_{60} with two vacancies (denoted C_{60-2}) generated by removing two neighboring carbon atoms; (c) $C_{60}H_2$ generated by attaching two hydrogens to two neighboring carbons (located between the six- and six-membered rings) of C_{60} ; (d) $C_{60}H_{60}$ generated by attaching one hydrogen atom to each carbon of C_{60} .

Table 2. Results for Endohedral Complexes Obtained from B3LYP Calculations

| molecule | bond length of Li–F (Å) | BSSE-corrected stabilization energy (E_S^a) (kcal/mol) | pure electrostatic stabilization energy (E_{PS}^b) (kcal/mol) |
|---------------------|-------------------------|--|---|
| LiF | 1.5514 | | |
| LiF@ C_{60} | 1.5664 | 9.78 | 18.12 |
| LiF@ C_{60-2} | 1.5781 | 5.82 | 18.19 |
| LiF@ $C_{60}H_2$ | 1.5905 | 14.17 | 17.83 |
| LiF@ $C_{60}H_{60}$ | 1.5830 | 6.53 | 25.29 |

^a $E_S = E_A(AB) + E_B(AB) - E_{AB}(AB)$, where $E_{AB}(AB)$ is the total energy of the complex, and $E_A(AB)$ and $E_B(AB)$ are the energies of the cage and its inside molecule calculated using the whole complex basis set. In the equation, the subscripts denote the molecular species in the energy expression, and the symbol in the parenthesis refers to the basis set used in the calculations. ^b A +0.899 and –0.899 point-charge couple was used to replace LiF in the endohedral complexes without geometry change. $E_{PS} = E_A + E_B - E_{AB}$, where E_{AB} is the total energy of the complex, E_A is the cage energy, and E_B is the two-point charge couple energy.

interaction between LiF and C_{60} is a combination between the attractive electrostatic interaction and the repulsive electron cloud overlapping. This explains why the total stabilization energies of all four complexes are less than the corresponding attractive electrostatic interactions. Furthermore, to reduce the repulsive electron cloud overlap, the electron-rich end, F^- of LiF, has to be shifted away from the electron cloud shell of the cage in LiF@ C_{60} , LiF@ C_{60-2} , and LiF@ $C_{60}H_2$. In contrast, for LiF@ $C_{60}H_{60}$, the F end of LiF is shifted to be closer to the shell of the $C_{60}H_{60}$ cage. Whereas the shifting of the F end of LiF nearer to the shell of $C_{60}H_{60}$ cage generates a larger repulsive interaction between LiF and the $C_{60}H_{60}$ cage (because

of the larger overlap of their electron clouds), it also generates the largest attractive electrostatic interaction between them.

The bond length of LiF is longer in all four cages than that of the free individual LiF molecule (Table 2). This occurs because the polarized spherical cage acts back on the guest molecule through an effective electric field that perturbs the molecular electronic structure. This perturbation is significant for LiF inside a cage because of the high polarizability of F^- .⁵²

3.3. Orientations of LiF in $C_{60}H_2$ and Defect C_{60-2} Cages.

The removal of two adjacent carbon atoms from, or the external attachment of two hydrogen atoms to, the C_{60} cage destroys the perfect symmetry of the cage (parts b and c of Figure 1). The orientation of the polar LiF molecule inside such asymmetrical cages is dependent on two factors: the electrostatic interaction and the electron cloud overlap, the former stabilizing and the latter destabilizing the guest. In LiF@ C_{60-2} , a maximum attractive dipole–dipole interaction is obtained if the dipole moments of LiF and the cage are oriented in opposite directions. This direction is normal to the seven-membered ring with the F head of the LiF axis pointing toward the seven-membered ring. To achieve the smallest repulsive electron cloud overlap between the guest molecule and cage, the axis of LiF should be parallel to the face of the seven-membered ring because in that direction the cage is the longest and this minimizes the electron cloud overlap. As shown in Figure 2e, the most stable LiF molecular axis is almost normal to the face of the seven-membered ring of the C_{60-2} with the F head of the LiF axis

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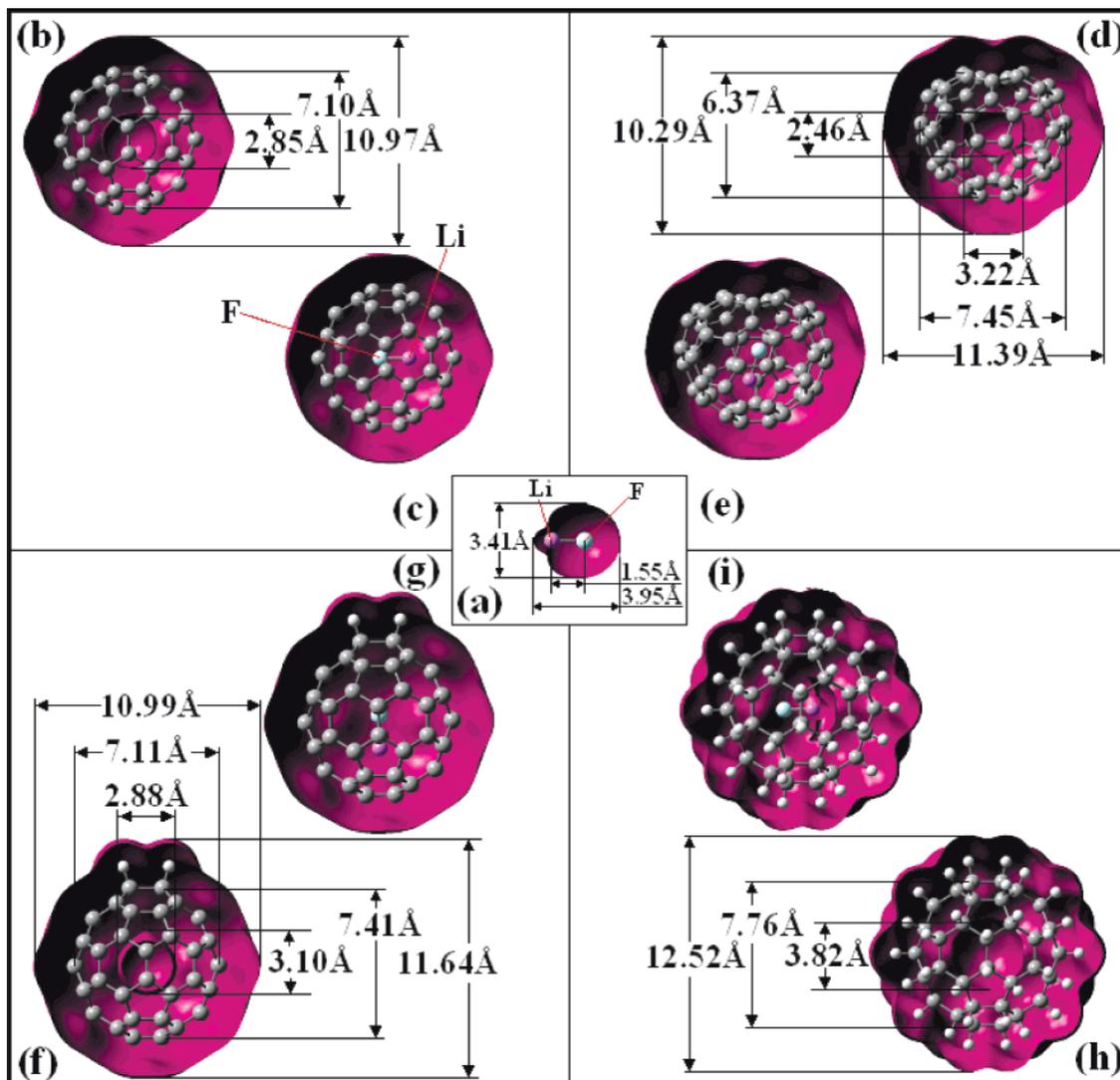


Figure 2. Electron clouds (cross section): (a) LiF, (b) C_{60} , (c) LiF@ C_{60} , (d) C_{60-2} , (e) LiF@ C_{60-2} , (f) $C_{60}H_2$, (g) LiF@ $C_{60}H_2$, (h) $C_{60}H_6$, and (i) LiF@ $C_{60}H_6$.

pointing toward this ring, indicating that the orientation of the polar molecule is mainly determined by the attractive dipole–dipole interaction. To examine how difficult is to rotate LiF inside the defect C_{60-2} cage, the opposite orientation of LiF inside the cage was compared with its most stable orientation. The energy difference between the two orientations is 1.4 kcal/mol (Table 3). In contrast, Cioslowski found that LiF can rotate freely with an energy barrier of only 0.02 kcal/mol in the C_{60} cage.¹¹ Hence, the rotation of LiF is achieved with higher difficulty in the defect C_{60-2} cage than in the C_{60} cage.

For LiF@ $C_{60}H_2$, there is an orientation of LiF for which the repulsive electron cloud overlapping between LiF and cage is the smallest and the attractive dipole–dipole electrostatic interaction is the largest. This orientation is normal to the defect C–C bond, and in the plane containing the two C–H bonds, with the F head of the LiF axis pointing toward the defect C–C bond (Figure 2g). When the LiF molecular axis is reoriented from this (most stable) direction to the opposite direction, its stabilization energy changes from 14.2 to 7.9 kcal/mol (Table 3). This indicates that the rotation of LiF is much more difficult in the $C_{60}H_2$ cage than in the defect C_{60-2} cage.

Table 3. Rotating LiF in C_{60-2} and $C_{60}H_2$ Cages

| endohedral complex | bond length of Li–F (Å) | BSE-corrected stabilization energy (E_S) ^a (kcal/mol) |
|---|-------------------------|--|
| LiF@ C_{60-2} ^b | 1.5781 | 5.82 |
| LiF@ C_{60-2} (reverse) ^c | 1.5771 | 4.40 |
| LiF@ $C_{60}H_2$ ^d | 1.5905 | 14.17 |
| LiF@ $C_{60}H_2$ (reverse) ^e | 1.5829 | 7.93 |

^a $E_S = E_A(AB) + E_B(AB) - E_{AB}(AB)$, where $E_{AB}(AB)$ is the total energy of the complex and $E_A(AB)$ and $E_B(AB)$ are the energies of the cage and its inside molecule calculated using the whole complex basis set. In the equation, the subscripts denote the molecular species in the energy expression, and the symbol in the parenthesis refers to the basis set used in the calculations. ^b The most stable LiF@ C_{60-2} (Figure 2e). ^c The LiF molecular axis is rotated from the most stable orientation to the reverse. ^d The most stable LiF@ $C_{60}H_2$ (Figure 2g). ^e The LiF molecular axis is rotated from the most stable orientation to the reverse.

4. Conclusions

In conclusion, the B3LYP hybrid DFT calculations demonstrated that the stability and position of a guest molecule inside the C_{60} cage can be changed and its orientation controlled by modifying the C_{60} cage shell. The external attachment of two hydrogen atoms to two adjacent carbon atoms located between two six-membered rings of the C_{60} cage can increase the stability

of LiF inside its cage by 45% (from 9.8 to 14.2 kcal/mol). Such an external attachment generates a relatively large permanent dipole moment, which determines the orientation of the LiF molecule inside. In contrast, when 60 hydrogen atoms are attached to the outside surface of the C_{60} cage, which transformed all C=C double bonds into single bonds, the stability of the inside LiF is reduced by 34% (from 9.8 to 6.5 kcal/mol).

If two adjacent carbon atoms are removed from C_{60} , the stability of LiF inside this defect C_{60} is reduced by 41% (from 9.8 to 5.8 kcal/mol).

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