ORGANIC LETTERS

2008
Vol. 10, No. 12
2573−2576

Tube and Cage $C_{60}H_{60}$: A Comparison with $C_{60}F_{60}$

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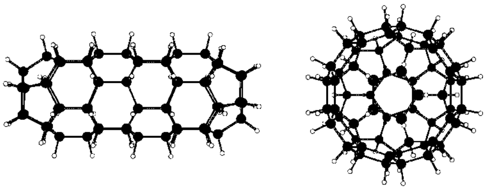
Received April 15, 2008

ABSTRACT



Tube $C_{60}H_{60}$ (5) with fused five-membered rings is more stable than the cage isomer (1) with isolated five-membered rings. Introduction of *endo* C−H bonds into structure 5 results in further stabilization, but the most stable tube structure with four *endo* C−H bonds (7) is higher in energy than the most stable cage structure with ten *endo* C−H bonds (3) by 74.2 kcal/mol. A comprehensive comparison of $C_{60}H_{60}$ with $C_{60}F_{60}$ has been made.

Very soon after the availability of C_{60} fullerene in gram scale,[1] hydrogenation of C_{60} has become the subject of extensive experimental studies.[2–5] The most abundant hydrogenation products are $C_{60}H_{18}$ and $C_{60}H_{36}$.[2,3] The isolable derivative with the largest number of hydrogen atoms is actually $C_{60}H_{44}$,[4] and $C_{60}H_{52}$[5] has been only observed in mass spectroscopy. For $C_{60}H_{60}$, there is no experimental information available, and the best information is from computation.[6–11]

On the basis of empirical potential analysis, Dunlap et al.[7] suggested that $C_{60}H_{60}$ with *endo* C−H bonds is energetically more favored over the all-*exo* isomer. Molecular mechanics calculations by Saunders[9] showed that taking one C−H bond of the all-*exo* $C_{60}H_{60}$ isomer inside can reduce the energy for about 53 kcal/mol, and the minimum energy isomer with ten C−H bonds inside ($H_{10}@C_{60}H_{50}$) is more stable than the all-*exo* isomer by 400 kcal/mol. Doduiuk et al.[10] also showd that *endo* $H_{10}@C_{60}H_{50}$ in D_5 symmetry is more stable than the all-*exo* isomer and other *endo* isomers on the basis of molecular mechanics calculation. Recently Zdetsis[11] reported a more stable isomer with ten inside C−H bonds in D_{5d} symmetry over the all-*exo* isomer at B3LYP/TVZP. That

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inside C−H bonds can reduce the strain and stabilize the cage structures also has been found in large $C_{80}H_{80}$ and $C_{180}H_{180}$ cages with twenty ($H_{20}@C_{80}H_{60}/I_h$) and sixty ($H_{60}@C_{180}H_{120}/I_h$) inside C−H bonds,[12] respectively.

Recently, we[13] have found that a tube $C_{60}F_{60}$ (D_{5d}) with fused five-membered rings located at the ends of the tube is more stable than the all-*exo* cage isomer by 446.2 kcal/mol at B3LYP/6-31G*. Furthermore, the tube structure with four *endo* C−F bonds ($F_4@C_{60}F_{56}$, C_2) is more stable than the most stable cage isomer with eight *endo* C−F bonds ($F_8@C_{60}F_{52}$, D_2) by 22.6 kcal/mol. Due to the structural similarity of $C_{60}H_{60}$ and $C_{60}F_{60}$, it is interesting to know if $C_{60}H_{60}$ also has the same structural and energetic scheme as $C_{60}F_{60}$.

All structures have been optimized at the HF/6-31G(d) and B3LYP/6-31G(d,p) levels of theory. These structures are characterized at HF/6-31G(d) as energy minimums. The relative energies in Table 1 for discussion and comparison are obtained at B3LYP/6-31G(d,p). All calculations have been done with Gaussian 03 program.[14]

Table 1. Relative Energies (E_{rel}, kcal/mol) of $C_{60}H_{60}$ and $C_{60}F_{60}$

$C_{60}H_{60}$	E_{rel}	$C_{60}F_{60}$	E_{rel}[13]
$C_{60}H_{60}/I_h$ (**1**)	0.0	$C_{60}F_{60}/I_h$ (**1**)	0.0
$H_8@C_{60}H_{52}/D_2$ (**2**)	−353.9	$F_8@C_{60}F_{52}/D_2$ (**2**)	−575.6
$H_{10}@C_{60}H_{50}/C_2$ (**3**)	−374.2	$F_{10}@C_{60}F_{50}/C_2$ (**3**)	−522.7
$H_{12}@C_{60}H_{48}/C_i$ (**4**)	−359.4	$F_{12}@C_{60}F_{48}/C_i$ (**4**)	−409.7
$C_{60}H_{60}/D_{5d}$ (**5**)	−232.0	$C_{60}F_{60}/D_{5d}$ (**5**)	−446.2
$H_2@C_{60}H_{58}/C_{2h}$ (**6**)	−275.8	$F_2@C_{60}F_{58}/C_{2h}$ (**6**)	−543.4
$H_4@C_{60}H_{56}/C_2$ (**7**)	−300.0	$F_4@C_{60}F_{56}/C_2$ (**7**)	−598.2
$H_6@C_{60}H_{54}/C_2$ (**8**)	−294.6	$F_6@C_{60}F_{54}/C_2$ (**8**)	−440.8

Figure 1 shows the cage structures (**1−4**) of $C_{60}H_{60}$. Isomer **1** is the reported structure with all-*exo* C−H bonds in I_h symmetry.[6−8] Isomers **2**, **3,** and **4** have cage structures with eight ($H_8@C_{60}H_{52}$), ten ($H_{10}@C_{60}H_{50}$), and twelve ($H_{12}@C_{60}H_{48}$) *endo* C−H bonds, respectively. At B3LYP/6-31G(d,p), isomer **3** ($H_{10}@C_{60}H_{50}$, actually in C_2 symmetry) reported by Saunders is more stable than the D_5 structure by Doduiuk[10] and the D_{5d} structure by Zdetsis[11] by 22.0 and 120.9 kcal/mol, respectively. The reported energetic order[10] of the cage isomers has been reproduced at B3LYP/6-31G(d,p). For example, the cage isomer of $C_{60}H_{60}$ with ten *endo* C−H bonds (**3**) is the energy minimum structure and lower in energy than the all-*exo* isomer (**1**) by 374.2 kcal/mol and the cage isomers **2** and **4** by 20.3 and 14.8 kcal/mol, respectively.

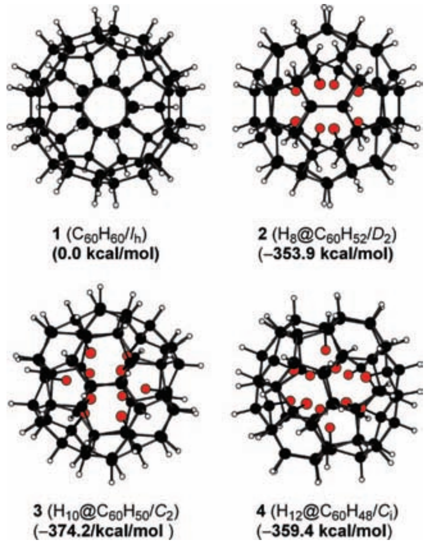
1 ($C_{60}H_{60}/I_h$) (0.0 kcal/mol)
2 ($H_8@C_{60}H_{52}/D_2$) (−353.9 kcal/mol)
3 ($H_{10}@C_{60}H_{50}/C_2$) (−374.2/kcal/mol)
4 ($H_{12}@C_{60}H_{48}/C_i$) (−359.4 kcal/mol)

Figure 1. B3LYP/6-31G(d,p) $C_{60}H_{60}$ cage structures (**1−4**) with inside hydrogen atoms in red.

Figure 2 shows the tube structures (**5−8**) of $C_{60}H_{60}$. Tube $C_{60}H_{60}$ isomer (**5**) has all-*exo* C−H bonds and the twelve five-membered rings fused at the ends of the tube, whereas isomers **6**, **7**, and **8** have tube structures with two ($H_2@C_{60}H_{58}$), four ($H_4@C_{60}H_{56}$), and six ($H_6@C_{60}H_{54}$) *endo* C−H bonds, respectively.

As shown in Table 1, tube isomer **5** is lower in energy than cage isomer **1** by 232.0 kcal/mol. Both **1** and **5** have all-*exo* C−H bonds and the same numbers of five- and six-membered rings, and they differ only in the distribution of the five-membered rings. Therefore, the fused five-membered rings should be the decisive factor for the stability of **5**, while the five-membered rings in **1** are perfectly isolated. This is in full agreement with $C_{60}F_{60}$.[13] Recent experimental and theoretical studies also imply that carbon cages with fused five-membered rings, in opposition to the isolated pentagon rule for the stability of carbon fullerenes,[15] can be essentially stabilized by either exohedral or endohedral derivatization. For example, Wang et al.[16] have reported a $C_{64}H_4$ (C_{3v}) cage with one triquinancene unit containing three fused five-membered rings. Popov et al.[17] found that some endohedral

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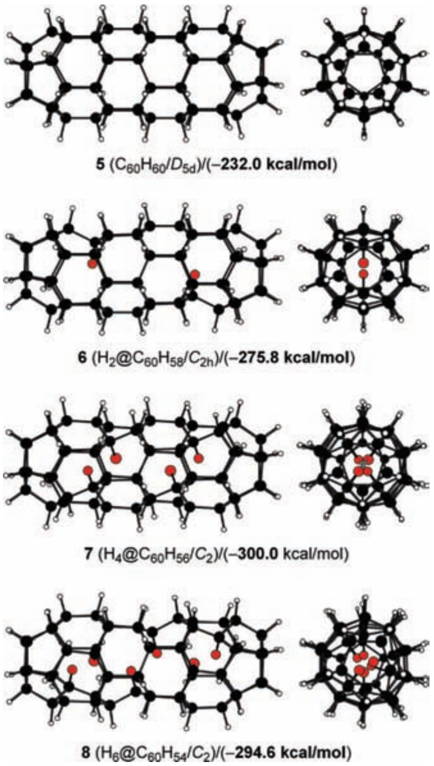

Figure 2. B3LYP/6-31G(d,p) $C_{60}H_{60}$ tube isomers (**5**−**8**) with inside hydrogen atoms in red.

$(M_3N)@C_{2n}$ (M = Sc, Y; 2*n* = 68−84) fullerenes with fused five-membered ring pairs (pentalene like unit) are more stable than those with isolated five-membered rings.

It is obvious that the fused five-membered rings are planar or nearly planar and the six-membered rings have boat conformation in **5**. In contrast, **1** has not only planar five-membered rings but also planar six-membered rings. In **1**, the distances of the nonbonded hydrogen atoms are 1.982 and 2.020 Å. In **5**, the distances of the nonbonded hydrogen atoms of the five-membered rings are 2.329 and 2.306 Å, and those of the six-membered rings are 2.146, 2.117, 2.083, 2.120, and 2.086Å. Longer distances of nonbonded hydrogen atoms and boat-like six-membered rings of isomer **5** imply that the torsional strain in **5** is less than that in **1**.

To model the stability of the five- and six-membered rings in **1** and **5**, the unique five- and six-membered rings are cut from **1** and **5** and then optimized at B3LYP/6-31G(d,p) by saturating them with hydrogen atoms (C_5H_{10} and C_6H_{12}) and keeping all bond angles fixed. The calculated results show that two unique five-membered rings in **5** are more stable than that in **1** by 27.2 and 23.0 kcal/mol, and the two unique six-membered rings in **5** are more stable than that in **1** by 18.1 and 12.9 kcal/mol, respectively. Both the five- and six-membered rings in **5** are more stable than those in **1**, with the five-membered rings being more remarkable.

All carbon atoms in $C_{60}H_{60}$ are tetrahedral and should prefer sp^3 hybridization. Detailed inspection of structures **1** and **5** indicates that the distortion of the angles with respect to sp^3 hybridization at the carbon vertices in **1** is stronger than that in **5**. Therefore, we define angle distortion (*AD*) of a carbon vertex according to eq 1, where α and *β* are the CCC and HCC angles at the carbon atom, respectively. Their reference values of 111.47° and 107.39° are obtained from a fully optimized perhydrogenated graphite single sheet at the B3LYP/6-31G(d,p) level by imposing periodic boundary condition[18] on a two-dimensional hexagonal unit cell with two carbon atoms and two hydrogen atoms (Figure 3).

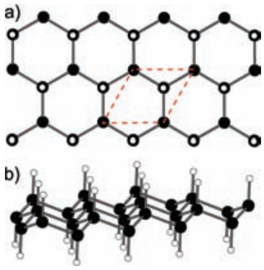

Figure 3. Unit cell of perhydrogenated graphite in top (a) and side view (b).

$$AD = \Sigma(111.47^\circ - \alpha) + \Sigma(107.39^\circ - \beta) \qquad (1)$$

In **1**, the *AD* for each carbon vertex is 37.7°. In **5**, the *AD*s of the carbon vertice rounded by three five-membered rings are 20.0°, and those by two five-membered rings and one six-membered ring and by one five-membered ring and two six-membered rings are 23.2° and 24.5°, respectively, whereas those by three six-membered rings are 31.4°, 31.1°, and 31.3°, respectively. The *AD*s of all carbon vertices in **5** are smaller than that in **1**, indicating lower angle strains in **5** compared with those in **1**. Moreover, all vertices of five-membered rings have small *AD*s, revealing that fusion of five-membered rings in perhydrogenated fullerene can reduce the angle strains.

Inspired by the results of $C_{60}F_{60}$,[13] that introduction of *endo* C−F bonds of the tube structure further reduces the strain, we are interested to know the similarity between $C_{60}H_{60}$ and $C_{60}F_{60}$. Starting from **5**, the most stable isomer with two *endo* C−H bonds is **6** ($H_2@C_{60}H_{58}/C_{2h}$), as expected, which is more stable than **5** by 43.8 kcal/mol. Further, the most stable tube isomer with four *endo* C−H bonds is **7** ($H_4@C_{60}H_{56}/C_2$), which is more stable than **5** by 68.0 kcal/mol. However, further increase of *endo* C−H bonds from four to six raises the energy, and the most stable tube isomer with six *endo* C−H bonds is **8** ($H_6@C_{60}H_{54}/C_2$), which is more stable than **5** by 62.6 kcal/mol but less stable than **7** by 5.4 kcal/mol.

Although *endo* isomers **6**, **7**, and **8** are more stable than **5**, they are less stable than the cage *endo* isomers **2**, **3**, and **4**. The most stable tube isomer **7** is higher in energy than the most stable cage *endo* isomer **3** by 74.2 kcal/mol, whereas for $C_{60}F_{60}$, on the contrary, the most stable tube *endo* isomer **7** is more stable than the most stable cage *endo* isomer **2** by 22.6 kcal/mol.[13]

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Now, it is interesting to compare **3** and **7** in detail. Due to the narrow inner space of tube $C_{60}H_{60}$, **7** can adopt much fewer *endo* C−H bonds than **3**. The shortest nonbonded hydrogen distances of **7** are 1.678 and 2.051 Å, and those of **3** are 1.914 and 2.139 Å. Further introduction of *endo* C−H bonds in **7** will raise the nonbonded hydrogen repulsive interactions considerably, as shown in **8** with the shortest H−H distances of 1.456 Å.

In **7**, each *endo* C−H bond connects with three six-membered rings. Detailed analysis of the structure shows that each *endo* C−H bond changes one boat-like six-membered ring into chair-like conformation, and another two boat-like six-membered rings change from *eclipsed* to *gauche* conformation. It reveals that *endo* C−H bonds can further decrease angle strains. This is confirmed by the change of the average *AD*, which of **7** is 20.7°, and less than that of **5** by 6.2°. In **3**, each *endo* C−H bond connects with one five-membered ring and two six-membered rings. Compared with **1**, not only do the shortest distances of the *exo* nonbonded hydrogen atoms of **3** become longer (>2.051 vs 1.982 and 2.020 Å), but also the average *AD* changes from 37.7° to 18.6°, which is also less than that of **7** (20.7°). This explains the higher stability of **3** over **7**.

It is also interesting to compare the relative stability of $C_{60}H_{60}$ and $C_{60}F_{60}$ on the basis of homodestomic reaction equations 2 and 3. These negative reaction energies (−836.6 and −622.4 kcal/mol, respectively) show clearly that $C_{60}H_{60}$ in both cage and tube configurations are much less strained than their $C_{60}F_{60}$ counterparts.

$$C_{60}F_{60}(\mathbf{1})+60(H_3C)_3C\text{-}H=C_{60}H_{60}(\mathbf{1})+60(H_3C)_3C\text{-}F \quad \Delta E(2)=-836.6\text{kcal/mol} \qquad (2)$$

$$C_{60}F_{60}(\mathbf{5})+60(H_3C)_3C\text{-}H=C_{60}H_{60}(\mathbf{5})+60(H_3C)_3C\text{-}F \quad \Delta E(3)=-622.4\text{kcal/mol} \qquad (3)$$

$$C_{20}F_{20}(\mathbf{1})+20(H_3C)_3C\text{-}H=C_{20}H_{20}(\mathbf{1})+20(H_3C)_3C\text{-}F \quad \Delta E(4)=-162.5\text{kcal/mol} \qquad (4)$$

Further comparison has been made for dodecahedron ($C_{20}H_{20}$) with its perfluorinated counterpart $C_{20}F_{20}$[19] in eq 4. The negative reaction energy (−162.5 kcal/mol) shows that $C_{20}F_{20}$ is much more strained than $C_{20}H_{20}$, which has been considered strain-free.[20]

For estimating the strength of the nonbonded fluorine repulsive interaction in $C_{60}F_{60}$ and $C_{20}F_{20}$, we have analyzed the effect of fluorine substitution in ethane. Our example is the *eclipsed cis*-1,2-difluoroethane (*cis*-FH_2C-CH_2F), along with ethane and fluoroethane as reference counterparts in the same conformation. The effect of fluorine substitution can be estimated on the basis of homodesmotic reaction eq 5.

$$cis\text{-}FH_2C\text{-}CH_2F+CH_3\text{-}CH_3=2FCH_2\text{-}CH_3 \quad \Delta E(\text{eclipsed})=-5.69\text{kcal/mol} \qquad (5)$$

The negative reaction energy reveals a repulsive or destabilizing effect of two C−F bonds in *cis*-1,2-difluoroethane by 5.69 kcal/mol. This is relatively a large number for only one nonbounded fluorine pair.

On the basis of this quantity, it is interesting to compare the strain in $C_{20}F_{20}$ as well as in the tube (**5**) and cage (**1**) structures of $C_{60}F_{60}$. For $C_{20}F_{20}$, there are thirty nonbonded fluorine pairs, and the expected repulsive interaction should be 170.7 kcal/mol, which is very close to the estimated value of 162.5 kcal/mol from eq 4. This shows roughly an additivity of the strain effects and reveals that the strain in $C_{20}F_{20}$ is solely originated from the repulsive interaction of the nonbonded fluorine atoms. It is indeed not surprising since the distance of the nonbonded fluorine atoms in *cis*-1,2-difluoroethane is close to that in $C_{20}F_{20}$ (2.498 vs 2.531 Å, respectively).

For **1** and **5** with ninety nonbonded fluorine pairs, the excepted repulsive interaction should be 512.1 kcal/mol, and this value is much smaller than those from eqs 2 and 3 (836.6 and 622.4 kcal/mol, respectively). Such large discrepancies are due to the much shorter distances of the nonbonded fluorine atoms in **1** (2.177 and 2.146 Å) and in **5** (2.506 and 2.473 Å for the five-membered rings, and 2.317, 2.267, 2.291 and 2.318 Å for the six-membered rings). Thus, nonbonded fluorine repulsive interaction is the driving force for the instability of $C_{20}F_{20}$ and $C_{60}F_{60}$, in agreement with the analysis of Cioslowski.[6]

We conclude that, as for $C_{60}F_{60}$, the tube $C_{60}H_{60}$ (**5**) is more stable than cage $C_{60}H_{60}$ with all-*exo* C−H bonds (**1**), and the driving force is the fused five-membered rings, which reduce not only the angle strain but also the torsional strain. Introduction of *endo* C−H bonds further reduce the strains, but in much less extent, and the cage isomer with ten *endo* C−H bonds (**3**) is more stable than the tube isomer with four *endo* C−H bond (**7**). This is in opposition to the stability of $C_{60}F_{60}$. Compared with $C_{60}H_{60}$ and $C_{20}H_{20}$, $C_{60}F_{60}$ and $C_{20}F_{20}$ are more highly strained, and the reason for that is the repulsive interaction of the nonbonded fluorine atoms.

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

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

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