

The studies on the aromaticity of fullerenes and their holmium endohedral compounds

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Received: 21 January 2010 / Accepted: 1 April 2010 / Published online: 5 May 2010
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Abstract Density functional theory BLYP/DNP was employed to optimize a series of fullerenes and their holmium endohedral compounds, including C_{20} , $Ho@C_{20}$, $Ho^{3+}@C_{20}$, C_{60} , $Ho@C_{60}$, $Ho^{3+}@C_{60}$, C_{70} , $Ho@C_{70}$, $Ho^{3+}@C_{70}$, C_{78} , $Ho@C_{78}$, $Ho^{3+}@C_{78}$, C_{82} , $Ho@C_{82}$ and $Ho^{3+}@C_{82}$. DFT semi core pseudopot approximation was taken into consideration in the calculations of the element holmium because of its particular electronic structure. Fullerenes and their holmium endohedral compounds' aromaticity were studied in terms of structural criteria, energetic criteria, and reactivity criteria. The results indicate that the aromaticity of fullerenes was reduced when a holmium atom was introduced into the carbon cage, and the endohedral fullerenes' reactive activity enhance; but the aromaticity of the carbon cage increased when a Ho^{3+} cation was encapsulated into a fullerene. Calculations of aromaticity and stability indicate that two paths can lead to the similar aim of preparing holmium endohedral fullerenes; that is, they can form from either a holmium atom or a holmium cation (Ho^{3+}) reacting with fullerenes, respectively, and the latter is more favorable.

Keywords Aromaticity · Endohedral · Fullerene · Holmium

Introduction

Hydrocarbons such as benzene, naphthalene, and pyridine, *etc.* have aromaticity, $\{\pi\}$ electrons in accordance with the Hückel rule, the direct exhibition is equalization of bond length, reflecting the extent of delocalization of $\{\pi\}$ electrons in a molecule. With further investigation of fullerene chemistry, some scholars proposed the concept of spherical aromaticity [1] and suggested some aromaticity criteria, such as “independent pentagon rule”(IPR), MO resonance energies of fullerenes, heat of hydrogenation, reactivity indices, magnetic criteria and the $2(N+1)^2$ rule of spherical aromaticity in Ih symmetrical fullerenes. Isodesmic equations [2, 3] provide energetic criteria for evaluating the decomposition of fullerenes, that is, fullerenes decomposing in an atmosphere of methane, ethylene and ethane molecule form and are equal in amount and type with the C-C and C=C bonds in a fullerene molecule. The higher the decomposition energy, the greater the aromaticity of a fullerene. Reactivity indices [4–6] mean aromaticity can be measured by chemical hardness, the bigger it is, the more aromatic the fullerene is.

Holmium is a metal of abnormal magnetism, usually used in a high magnetic field. Ho^{3+} also has high magnetism. Bis(Phthalocyaninato) holmium anion [7] is a kind of single-molecular magnet discovered in recent years. Holmium endohedral fullerenes have been found in the past decade to be novel materials. Isotope ^{166}Ho has the property of radioactivity, $^{165}Ho[n,\gamma]^{166}Ho$, with the half life of 26.8 h. Here n and $\{\gamma\}$ denotes neutron and $\{\gamma\}$ ray, respectively. ^{166}Ho can be a targeted drug of liver tumor [8–10], and the curative effect is unique. In

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order to control the radioactive effect both for suppressing tumor growth and for reducing bodily injury, ^{165}Ho must be encapsulated into a carbon cage first, and neutron irradiation on $^{165}\text{Ho}@C_n$ (usually $n=82$) is subsequently performed to produce $^{166}\text{Ho}@C_n$. For the Solubility in water, hydroxylation of the carbon cage [11] can be taken into consideration.

Therefore, the holmium endohedral fullerene is promising in medical use. To further study its characteristics, aromaticity of several fullerenes and their holmium endohedral compounds were studied by means of the computational method. The aim of this work is to explore the stability of holmium endohedral fullerenes in the course of preparation from the perspective of aromaticity.

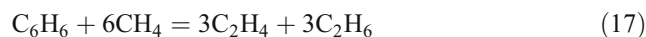
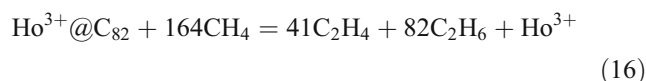
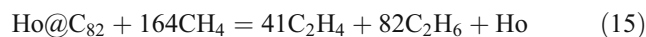
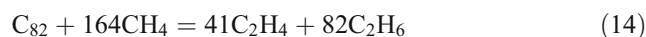
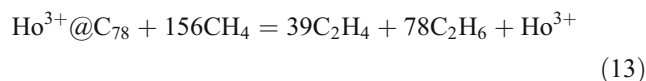
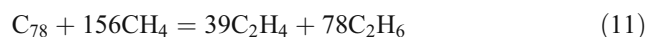
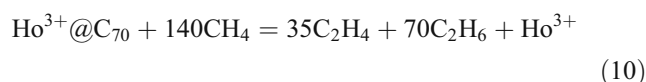
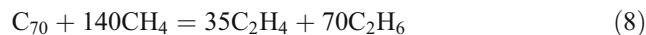
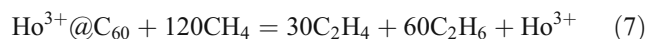
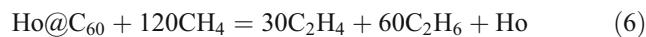
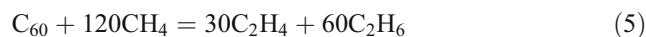
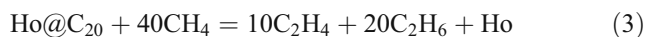
Computational methods

All of the electronic structure calculations were performed using the DMol3 [12, 13] numerical-based density-functional computer software implemented in the Materials Studio Modeling 3.0 package [14] distributed by Accelrys, Inc. Geometrical optimizations were obtained using the BLYP [15, 16] general-gradient potential approximation in conjunction with the double-numerical plus polarization basis set (DFT semi core pseudopot) that is denoted as DNP. Electronic configuration of Ho and Ho^{3+} are $[\text{Xe}]4f^{11}6s^2$ and $[\text{Xe}]4f^{10}$, respectively.

Structural criteria, isodesmic equations (energetic criteria) and reactivity criteria were employed to measure aromaticity of fullerenes and their Holmium endohedral compounds, and the expressions are in the form of (1) to (28).

$$A = 1 - \frac{225}{n} \sum_i^n \left(1 - \frac{R_i}{R}\right)^2 \quad (1)$$

A is an aromaticity criteria based on the molecular structure [17], and it is a relative value on the supposition of $A=1$ of benzene. n , R_i and R denote the number of C-C bonds, separate C-C bond length, and an average C-C bond length in fullerene and its holmium endohedral compound, respectively.



Equations 2–17 are a series of isodesmic equations (energetic criteria) based on various fullerenes and their holmium endohedral compound and benzene. Their decomposition energy can be expressed as $E_d = \sum E_P - \sum E_R$, energy changes of products to reactants on the bases of Eqs. 2–17. We also suggested stabilization energy to measure the difficulty level of formation of the holmium endohedral fullerene, $E_{\text{stab}} = \sum E_P - \sum E_R$, energy changes of products to reactants based on Eqs. 18–27.





As for reactivity criteria, η is on the basis of frontier molecular orbitals (HOMO and LUMO), expressed as Eq. 22. The more negative η is, the harder the compound behaves, and the more aromatic it is.

$$\eta = (\text{HOMO} - \text{LUMO})/2 \quad (28)$$

Results and discussion

On the structural criteria

The results are listed in Table 1. It indicates that when a holmium atom is encapsulated into the bulky fullerenes, the aromaticity index changes little. As for small fullerenes, such as C_{20} , aromaticity index increases more than the larger ones; the extent of the equalization trend of C-C bond length also enhances. Especially to $\text{Ho}^{3+}@\text{C}_{20}$, it entirely equalizes the C-C bond length, just a little longer than the usual C-C bond length. The structure and shape of holmium endohedral fullerenes are shown in Fig. 1. The holmium atom or holmium cation is located in the center of C_{20} . The rest are located at the side of the fullerenes, and the nearest distance between Holmium atom (or cation) and the carbon atoms range from 2.4 Å to 2.6 Å. Holmium endohedral fullerenes have lower symmetry than the primary ones.

The relationship between isodesmic equations and aromaticity

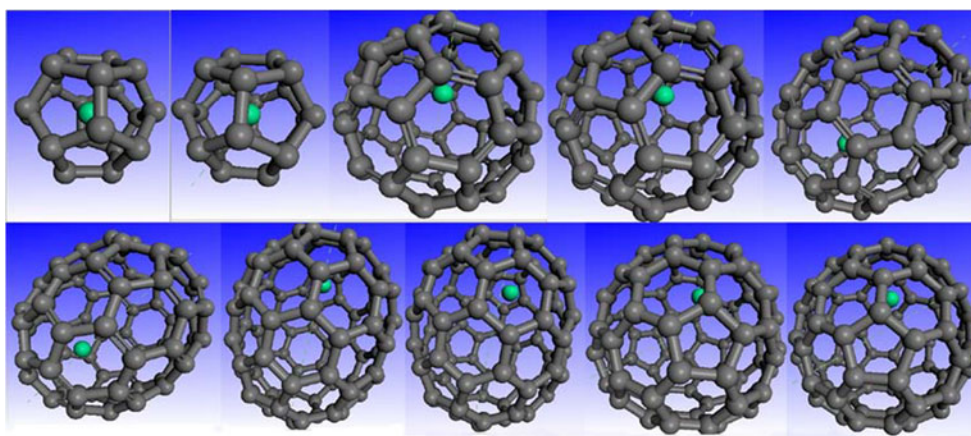
Decomposition energy (E_d) and average decomposition energy (\bar{E}_d) were calculated according to Eqs. 2–16, $\bar{E}_d = E_d/n$ (here n is the number of the C-C bond in a carbon cage). E_d and \bar{E}_d were also listed in Table 1. When the number of carbon atoms exceeds 60, average decomposition energy \bar{E}_d reduces if a holmium atom is introduced into the carbon cage, which leads to lower aromaticity. An interesting result is that the endohedral compound $\text{Ho}^{3+}@\text{C}_n$ ($n=60,70,78,82$) has a high average decomposition energy, (52.7 kJ mol^{-1} , $n=60$; 52.5 kJ mol^{-1} , $n=70$;

Table 1 Aromaticity index (A), symmetry, average C-C bond length decomposition energy (E_d), average decomposition energy (\bar{E}_d), and chemical hardness of fullerenes and their holmium endohedral compound

| Species | A | Symm. | $\bar{d}/\text{Å}^0$ | E_d (kJ/mol) | \bar{E}_d (kJ/mol) | $ \eta (\text{eV})$ |
|--------------------------------|------|-----------------|----------------------|----------------|----------------------|---------------------|
| C_{20} | 0.92 | Ih | 1.460 | -500.2 | -16.7 | 0.267 |
| $\text{Ho}@\text{C}_{20}$ | 0.99 | Ih | 1.540 | -1228.2 | -30.7 | 0.046 |
| $\text{Ho}^{3+}@\text{C}_{20}$ | 1.0 | Ih | 1.561 | -640.2 | -16.0 | 0.694 |
| C_{60} | 0.93 | Ih | 1.439 | 3067.0 | 34.1 | 0.830 |
| $\text{Ho}@\text{C}_{60}$ | 0.96 | Cs | 1.426 | 2953.7 | 32.8 | 0.290 |
| $\text{Ho}^{3+}@\text{C}_{60}$ | 0.93 | Cs | 1.444 | 4742.5 | 52.7 | 0.706 |
| C_{70} | 0.95 | D_{5h} | 1.438 | 3845.0 | 36.6 | 0.850 |
| $\text{Ho}@\text{C}_{70}$ | 0.96 | C_{5v} | 1.440 | 3641.0 | 34.7 | 0.270 |
| $\text{Ho}^{3+}@\text{C}_{70}$ | 0.91 | Cs | 1.441 | 5515.2 | 52.5 | 0.634 |
| C_{78} | 0.94 | D_3 | 1.438 | 4363.0 | 37.3 | 0.360 |
| $\text{Ho}@\text{C}_{78}$ | 0.95 | C_1 | 1.439 | 4153.0 | 35.5 | 0.170 |
| $\text{Ho}^{3+}@\text{C}_{78}$ | 0.93 | C_1 | 1.441 | 6070.3 | 51.9 | 0.584 |
| C_{82} | 0.95 | C_{3v} | 1.438 | 4646.0 | 37.8 | 0.510 |
| $\text{Ho}@\text{C}_{82}$ | 0.95 | Cs | 1.438 | 4492.0 | 36.5 | 0.340 |
| $\text{Ho}^{3+}@\text{C}_{82}$ | 0.95 | Cs | 1.437 | 6374.0 | 51.8 | 0.560 |

Symmetry group “Ih” denotes “Icosahedral”

Fig. 1 Structures and shapes of holmium endohedral fullerenes. From left to right, and from top to bottom, they are Ho@C₂₀, Ho³⁺@C₂₀, Ho@C₆₀, Ho³⁺@C₆₀, Ho@C₇₀, Ho³⁺@C₇₀, Ho@C₇₈, Ho³⁺@C₇₈, Ho@C₈₂ and Ho³⁺@C₈₂, respectively



51.9 kJ mol⁻¹, n=78; 51.8 kJ mol⁻¹, n=82), compared to average decomposition energy of benzene, calculated in terms of Eq. 17, 50.7 kJ mol⁻¹. This indicates that Ho³⁺@C_n(n=60,70,78,82) has a high aromaticity.

As for C₂₀ and its holmium endohedral compounds, their average decomposition energy is negative, which means they are unstable structures. It is easy to understand that the carbon cage is too small to encapsule a holmium atom or cation.

The relationship between chemical hardness and aromaticity

Chemical hardness was calculated in terms of Eq. 28, and the computational results were listed in Table 1. It shows that chemical hardness evidently reduces after the encapsulation of a holmium atom into a carbon cage, so the aromaticity also reduces. On the contrary, when a Ho³⁺ cation is encapsulated into a carbon cage, from Ho³⁺@C₂₀ to Ho³⁺@C₈₂, chemical hardness of the carbon cage increases evidently. Of course the aromaticity increases, too. In view of those fullerenes that violate the “independent pentagon rule” (IPR) may be stabilized *via* encapsulation of a (or more) metal cation.

Stabilization energy of endohedral fullerenes

Stabilization energy of endohedral fullerenes were calculated according to Eqs. 18–27, these results are listed in Table 2.

In general, the more negative the stabilization energy is, the more stable the product behaves. Table 2 shows that Ho@C₂₀ is lower in stability and the stability will be enhanced if the Ho³⁺ cation is used instead of the holmium atom. Stabilization energy is positive from Ho@C₂₀ to Ho@C₈₂. It indicates that the encapsulation of the holmium atom does not increase the stability of these fullerenes. In particular, Ho³⁺@C₆₀, Ho³⁺@C₇₀, Ho³⁺@C₇₈ and Ho³⁺@C₈₂ have large negative values. It shows that the encapsulation of the Ho³⁺ cation can stabilize the carbon cage, in accordance with the average decomposition energy (aromaticity criteria) analysis. Conversely, a carbon cage can stabilize the Ho³⁺ cation.

Conclusions

Structural criteria, energetic criteria and reactivity criteria were applied to measure the aromaticity of C₂₀, Ho@C₂₀, Ho³⁺@C₂₀, C₆₀, Ho@C₆₀, Ho³⁺@C₆₀, C₇₀, Ho@C₇₀, Ho³⁺@C₇₀, C₇₈, Ho@C₇₈, Ho³⁺@C₇₈, C₈₂, Ho@C₈₂ and Ho³⁺@C₈₂. Stabilization energy of Ho and Ho³⁺ endohedral fullerenes were also calculated by means of DFT/BLYP/DNP. This work makes clear that structural criteria has poor discrimination to be the forementioned fullerenes and their holmium endohedral compounds, but energetic criteria and reactivity criteria can quantifiably measure their aromaticity and distinguish them definitively.

Table 2 Stabilization energy of endohedral fullerenes

| | M ₁ | M ₂ | M ₃ | M ₄ | M ₅ | M ₆ | M ₇ | M ₈ | M ₉ | M ₁₀ |
|-----------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|
| <i>E</i> _{stab} (kJ/mol) | 780.0 | 140.1 | 112.3 | -1675.3 | 203.9 | -1670.2 | 209.6 | -1707.3 | 153.8 | -1728.5 |

M₁=Ho@C₂₀, M₂=Ho³⁺@C₂₀, M₃=Ho@C₆₀, M₄=Ho³⁺@C₆₀, M₅=Ho@C₇₀, M₆=Ho³⁺@C₇₀, M₇=Ho@C₇₈, M₈=Ho³⁺@C₇₈, M₉=Ho@C₈₂, M₁₀=Ho³⁺@C₈₂

Aromaticity decreased and reactive activity increased in the fullerene when a holmium atom was encapsulated into it, $\text{Ho}@C_n$ ($n=20, 60, 70, 78, 82$) may exhibit activity in chemical reactions. In $\text{Ho}^{3+}@C_{82}$, $\text{Ho}^{3+}@C_{78}$, $\text{Ho}^{3+}@C_{70}$, $\text{Ho}^{3+}@C_{60}$ and $\text{Ho}^{3+}@C_{20}$, the fullerene had a higher aromaticity and stability when a Ho^{3+} cation was introduced into the carbon cage in place of a holmium atom.

Acknowledgments This work were supported by “863” Program of China (2007AA03Z329), “973” Program of China (613830101-2), National Natural Science Foundations of China (50972122, 17876031), Concurrent Program of Institute of Laser Fusion Of China Academy of Engineering Physics (07zh0224, 06zh1145), and the Basic Research Program of the Department of Science and Technology in Sichuan Province (2008JY0117).

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