The stability, frontier orbitals, bond character, and static linear polarizability of the fluorinated fullerene $H_{20}@C_{80}F_{60}$*

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(Received 3 February 2009; revised manuscript received 13 April 2009)

This paper uses the density functional theory under generalised gradient approximation to analyse the stability, frontier orbitals, bond character, and static linear polarizability of $H_{20}@C_{80}F_{60}$, which has not been isolated, as well as those of the synthesised $H_{20}@C_{80}H_{60}$. The $H_{20}@C_{80}F_{60}$ should be considerably stable by analysing its energy and aromaticity. The inside H and outside X will play different role in the chemical reaction involving $H_{20}@C_{80}X_{60}$ (X = H and F). The covalence of C–H bond is in the order that the inside C–H bond of $H_{20}@C_{80}F_{60}$> the inside C–H bond of $H_{20}@C_{80}H_{60}$> the outside C–H bond of $H_{20}@C_{80}H_{60}$, whereas the C–F bond of $H_{20}@C_{80}F_{60}$ have both the covalent and ionic characters. The static linear polarizabilities of C_{80} and $H_{20}@C_{80}X_{60}$ (X = H and F) are all isotropic.

Keywords: C_{80}, $H_{20}@C_{80}H_{60}$, $H_{20}@C_{80}F_{60}$, density functional theory

PACC: 3640B, 7500, 7115M

1. Introduction

Recent predictions of hydrogenated fullerenes, as well as their realization in the laboratory, are currently of great interest due to their potential application in the hydrogen storage materials. As we know, aside from perhydrogenated $C_{20}H_{20}$, C_{60} has only partially been hydrogenated.[1] The failure in perhydrogenation of C_{60} can be understood in terms of strain energy. The fullerenes as hollow spherical molecules, have space for hydrogenation from the inside, as well. This 'in–out' isomerism was first postulated by Saunders in 1991 for $C_{60}H_{60}$.[2] They found that the strain energy reaches its minimum when ten hydrogen atoms point inwards the cage centre, making the more optimal adaptation of sp^3 hybridization for the hexagons. Hence, the 'in–out' isomerism requires compromises in the case of $H_{10}@C_{60}H_5$.[3]

Linnolahti *et al.*[3] have studied the hydrogenation of the next smallest I_h-symmetric fullerene C_{80}. They find that hydrogenation of twenty inside interconnecting carbons and the remaining outside sixty carbons produces I_h symmetric $H_{20}@C_{80}H_6$, which is essential in the 'in–out' isomerism. This species is remarkably stable, its energy per CH unit is even lower than that of $C_{20}H_{20}$, a molecule previously considered as the least strained $(CH)_n$ cage.[3,4] As we know, many fluorinated fullerenes such as $C_{20}F_{20}$[5] and $C_{74}F_{38}$[6] have been experimentally observed. If C_{80} could also be fully fluorinated outward to produce I_h symmetric $H_{20}@C_{80}F_{60}$, it would provide an alternative ultimate-lubricant of $C_{60}F_{60}$.[3] While $C_{60}F_{60}$ is unobtainable due to overcrowding of C_{60},[7] this obstacle should not present in $H_{20}@C_{80}F_{60}$.[3] Hence, there are two aims in this paper. One is performing a comprehensive first principles study on the stability and properties of $H_{20}@C_{80}F_{60}$. The other is researching into the properties of $H_{20}@C_{80}H_{60}$.

2. Computational details

All the calculations were performed by using the generalised gradient approximation based on density functional theory,[8,9] The Becke–Lee–Yang–Parr correlation exchange functional (Becke gradient exchange functional[10] together with Lee, Yang and Parrcorrelation functional[11]) and the double Numerical plus d-functions (DND) were used for the optimiza-

*Project supported by the Research Starting Foundation of Hohai University (Grant No. 2084/40801130), the Natural Science Foundation of Hohai University (Grant Nos. 2008431211 and 2008430311), the Excellent Innovation Personal Support Plan of Hohai University, the Basic Scientific Research Foundation of National Central, and the Special Foundation of the Natural Natural Science (Grant No. 10947132).

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tion. The electronic structure was obtained by solving the Kohn–Sham[12] equations self-consistently under the spin unrestricted condition. Mulliken population analysis was made to obtain both the charge and net spin populations on each atom. Self-consistent field procedures are done with a convergence criterion of 10^{-5} a.u. on the energy and electron density. Geometrical optimizations were performed using the Broyden–Fletcher–Goldfarb–Shanno algorithm[12] with a convergence criterion of 10^{-2} a.u. on the displacement and 10^{-4} a.u. on the energy. The finite-field approach used in our calculations has been verified to produce reliable static polarizability. The calculated static polarizability components were the eigenvalues of the matrix, which is composed of the dipole moment vector respectively under the electronic fields with the strength of 0.005 a.u. along three different Cartesian axes. Our calculated average length of C–C bond (1.56Å, 1 Å = 0.1 nm) and the C–H bond length (1.10Å) for $C_{20}H_{20}$ are close to the experimental value of 1.55 Å[13] and the computed value of 1.10 Å by Chen *et al.*[14] respectively. The total energy of $C_{20}H_{20}$ is –774.04 eV, close to the –774.18 eV gotten by Chen *et al.*[14]

3. Results and discussion

3.1. The stability

We first discuss the inclusion energy, defined as the energy sum of C_{80} and 80 additional atoms minus the total energy of $H_{20}@C_{80}X_{60}$ (X = H and F). The positive inclusion energy means that the reaction is exothermic. The higher positive inclusion energy leads to the greater stability of the resultant.[15] The computed inclusion energies of $H_{20}@C_{80}H_{60}$ and $H_{20}@C_{80}F_{60}$ are respectively 284.42 and 291.99 eV. It reveals the binding between 80 additional atoms and carbon atoms can release much of the strain of I_h–C_{80}. As a result, $H_{20}@C_{80}X_{60}$ (X = H and F) is more stable than its parent compound I_h–C_{80}. The larger positive value of $H_{20}@C_{80}F_{60}$ indicates that its formation is more exothermic and more energetically favoured than $H_{20}@C_{80}H_{60}$.

Since the easily calculated nucleus independent chemical shift (NICS) value at the cage centre normally agrees well with the endohedral ^{3}He nuclear magnetic resonance (NMR) chemical shift, it has been proved to be a simple criterion of aromaticity theoretically.[16] Therefore, the calculated NICS value has been employed to characterise fullerenes instead of ^{3}He NMR. According to the so-called NICS characterization, the aromatic and antiaromatic are associated with negative and positive NICS values, respectively. It is calculated that the NICS value is –1.09 and –4.82 ppm (1 ppm = 1 mg/L) respectively for $H_{20}@C_{80}H_{60}$ and $H_{20}@C_{80}F_{60}$. Therefore, both $H_{20}@C_{80}H_{60}$ and $H_{20}@C_{80}F_{60}$ show aromatic character like C_{60}.[17] Generally, there is a correlation between the energy gap (E_g) and aromaticity.[18] For the structures with the same E_g, the larger NICS value results in the higher stability. For the structures with the same NICS value, the stability could be improved due to the wide E_g.[18] The E_g is 3.57 eV and 5.15 eV respectively for $H_{20}@C_{80}F_{60}$ and $H_{20}@C_{80}H_{60}$, both much larger than that of C_{60} 1.66 eV.[19] Since $H_{20}@C_{80}F_{60}$ possesses large E_g and NICS value, we expect that $H_{20}@C_{80}F_{60}$ is a stable compound.

Therefore, $H_{20}@C_{80}F_{60}$ can be easily obtained by analysing its energy and aromaticity.

3.2. The frontier orbitals

The frontier orbital theory states that the reactivity of a molecule mainly relates to its frontier orbital,[13] so the frontier orbitals will be analysed in detail as follows. Figure 1(a) shows the iso-density surfaces of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of $H_{20}@C_{80}X_{60}$ (X = H and F). Commonly, the atom occupied by more densities of HOMO should have stronger ability for detaching electrons, whereas the atom with more occupation of LUMO should be easier to gain electrons.[8] As shown in Fig. 1(a) the LUMOs of $H_{20}@C_{80}X_{60}$ (X = H and F) are mainly occupied by the H atoms inside of the cage, indicating that the electron attachment of $H_{20}@C_{80}X_{60}$ (X = H and F) will occur on the inside H atoms. On the other hand, the densities on the HOMOs of $H_{20}@C_{80}X_{60}$ (X = H and F) distribute partly on the outside X atoms, suggesting that the electron detachment will partially take place on the outside X atoms. Therefore, the inside H and outside X will play different roles in the chemical reaction involving $H_{20}@C_{80}X_{60}$ (X = H and F). Taking $H_{20}@C_{80}H_{60}$ and $H_{20}@C_{80}H_{60}^+$ as examples, we found that the electron obtained by $H_{20}@C_{80}H_{60}$ almost distribute on the inside twenty H, whereas the one electron detached mainly comes from the outside H. This strongly confirms our conclusion.

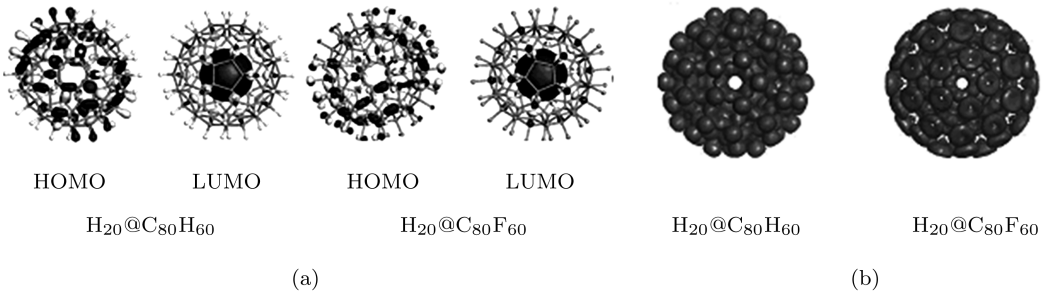


Fig. 1. (a) The iso-density surfaces of HOMOs and LUMOs. (b) The difference charge density of $H_{20}@C_{80}X_{60}$ (X = H and F).

3.3. The bond character

The computed C–H bond lengths outside and inside of $H_{20}@C_{80}H_{60}$, and inside of $H_{20}@C_{80}F_{60}$ are respectively 1.10 Å, 1.09 Å, and 1.10 Å, close to that of $C_{20}H_{20}$[14] and either as same as or 0.1 Å smaller than the sum of the radii of C and H, 1.10 Å. Thus, C–H bond should contain covalent character. Figure 1(b) shows the difference charge density distribution of these two molecules obtained from the total density with the density of the isolated atoms subtracted.[20] Usually, it makes sense to discuss the difference charge density distribution, because the bond character can also be determined from it.[15] If there is difference charge density distribution between X and C, the C–X bond should contain covalent character. The more difference charge densities result in the more covalence of the C–X bond. It is obvious from Fig. 1(b) that the C–H bond should be covalent. Moreover, it is meaningful to distinguish whether the bond characters of the outside and inside C–H bond are the same or different. As calculated, the average Mulliken charge of the carbons hydrogenated inside and outside of $H_{20}@C_{80}H_{60}$ as well as that of the inside hydrogenated carbons of $H_{20}@C_{80}F_{60}$ is respectively 0.10, 0.07, and 0.17 e, indicating their strong covalence, while, the average densities at nucleus of them are 126.55, 126.99, and 127.35 a.u. respectively. Therefore, the bond covalence of the C–H bond is in the order that the inside C–H bond of $H_{20}@C_{80}F_{60}$> the inside C–H bond of $H_{20}@C_{80}H_{60}$> the outside C–H bond of $H_{20}@C_{80}H_{60}$. As to C–F bond, it is 1.38 Å in $H_{20}@C_{80}F_{60}$ cage, almost the same as the C–F bond length in many other fullerene cages, such as $C_{70}F_{38}$.[20] Because the C–F bond length is 0.12 Å smaller than the sum of radii of C and F, 1.49 Å, it should contain covalent character. On the other hand, the average Mulliken charge of the fluorinated carbon is about 0.30 e and there is a little difference charge density distribution between C and F, indicating its ionic character. Thus, the C–F bond in $H_{20}@C_{80}F_{60}$ have both the covalent and ionic characters, similar to that of $C_{74}F_{38}$.[20]

3.4. The static linear polarizability

Table 1 presents the calculated results of α tensors, the average linear static polarizability $\langle\alpha\rangle$, and the static linear polarizability anisotropies $\Delta\alpha$ for C_{80}, $H_{20}@C_{80}H_{60}$, and $H_{20}@C_{80}F_{60}$. The mean polarizability was calculated from the polarizability components as $\langle\alpha\rangle = [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}]/3$.[21] The static linear polarizability anisotropy is defined as $\Delta\alpha = \sqrt{\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2\right]}/2$.[22] Table 1 shows that the components of α are the same in x, y and z directions for C_{80} and $H_{20}@C_{80}X_{60}$ (X = H and F), indicating that the static linear polarizabilies of them are all isotropic. It is well known that the static linear polarizabily is indeed relative to the shape of the molecule.[21] Therefore, the isotropic static linear polarizabily of all three molecules may be due to the fact that they are all I_h symmetric. The calculated static linear polarizabily of $H_{20}@C_{80}F_{60}$ is 42.49Å^3 larger than that of $H_{20}@C_{80}H_{60}$. We hope the experiment will prove our results in the future.

Table 1. The α tensors, the average linear static polarizability $\langle\alpha\rangle$, and the static linear polarizability anisotropies $\Delta\alpha$ of C_{80}, $H_{20}@C_{80}H_{60}$, and $H_{20}@C_{80}F_{60}$ with the unit in Å^3.

	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	$\Delta\alpha$
C_{80}	257.49	257.49	257.49	257.49	0
$H_{20}@C_{80}H_{60}$	334.17	334.17	334.17	334.17	0
$H_{20}@C_{80}F_{60}$	376.66	376.66	376.66	376.66	0

4. Conclusions

$H_{20}@C_{80}F_{60}$ should be considerably stable by analysing its energy and aromaticity. The inside H and outside X will play different roles in the chemical reaction involving $H_{20}@C_{80}X_{60}$ (X = H and F). The bond covalence is in the order that the inside C–H bond of $H_{20}@C_{80}F_{60}$> the inside C–H bond of $H_{20}@C_{80}H_{60}$> the outside C–H bond of $H_{20}@C_{80}H_{60}$; the C–F bond in the $H_{20}@C_{80}F_{60}$ have both the covalent and ionic characters. The static linear polarizabilies of $C_{80}$and $H_{20}@C_{80}X_{60}$ (X = H and F) are all isotropic.

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