The density functional study of the stabilities, bond characters, static linear polarisabilities, and aromaticities of the 'in-out' isomerism $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74)*

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This paper uses the density functional theory to analyse the stabilities, bond characters, static linear polarisabilities, and aromaticities of the 'in-out' isomerism $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74). The binding energies, C–H bond energies, and energy gaps explore that the 'in-out' isometric perhydrogenation of C_n (n = 70, 72, 74) can remarkably improve the stabilities. The static linear polarisabilies of $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) are indeed relative to their shapes, while they show almost nonaromatic character. This study can suggest that the 'in-out' isometric perhydrogenation of fullerenes could lead to the invention of entirely novel potential hydrogen storage nanomaterials.

Keywords: C_nH_n, $C_{70}H_{70}$, $C_{72}H_{72}$, density functional
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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 dodecahedrane $C_{20}H_{20}$, the abundant buckminsterfullerene C_{60} has only partially been hydrogenated outside.[1] The failures in perhydrogenation of C_{60} can be understood in terms of strain energy.[2,3] Fullerenes, as hollow spherical molecules, have space for hydrogenation from the inside, as well. This 'in-out' isomerism was first postulated in 1991 for $C_{60}H_{60}$ by Saunders *et al.*,[4] who have calculated that taking one C–H bond of the all-exo $C_{60}H_{60}$ isomer inside could reduce the energy for about 53kcal/mol, and the minimum energy isomer with ten C–H bonds inside ($H_{10}@C_{60}H_{50}$) was more stable than the all-exo isomer by 400 kcal/mol (1 cal=4.19 J),[4] which is agree well with the conclusion of Linnolahtl *et al.*[2]

Linnolahti *et al.*[2] have considered the hydrogenation of the I_h-symmetric fullerene C_{80}. They found that the hydrogenation of 12 pentagons outside and the remaining twenty carbons inside could produce an I_h symmetric $H_{20}@C_{80}H_{60}$ structure, which was essential in the 'in-out' isomerism. The energy per CH unit being lower than that for dodecahedrane, previously considered as the least strained $(CH)_n$ cage.[5] Linnolahti *et al.*[2] also have studied the hydrogenation of the next I_h-symmetric fullerene C_{180}, in which each pair of pentagons was connected via two fused hexagons, and each set of three pentagons via a hexagon. They found that the alternate hydrogenation of the hexagons inside and outside combined with hydrogenation of the pentagons outside produced an I_h-symmetric $H_{60}@C_{180}H_{120}$, which had even lower energy per CH unit than its smaller $H_{20}@C_{80}H_{60}$ counterpart.

It is inspired that, if all the pentagons in the fullerene cage larger than C_{68} that abide the isolated pentagon rule(IPR) are hydrogenated outside and the remaining carbons are hydrogenated inside, then can it produce a lower energy structure, such as the IPR-satisfied D_{5h}–C_{70}, D_{6d}–C_{72}, and D_{3h}–C_{74} structures? Hence, in this paper, a comprehensive density functional study on the 'in-out' isomerism $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) is carried out to test whether they are more stable. The theoretical study can give the structural characterization at the molecular level, which

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could lead to the invention of entirely novel materials.

2. Computational details

All the calculations are performed by using the generalized gradient approximation based on density functional theory.[6] The Becke–Lee–Yang–Parr correlation exchange functional (Becke gradient exchange functional[7] together with Lee, Yang and Parrcorrelation functional[8]) and the double numerical plus polarisation (DNP) basis sets are used. The DNP basis set uses double-numerical basis functions together with polarisation functions. The electronic structure is obtained by solving the Kohn–Sham[9] equations self-consistently under the spin unrestricted condition. Mulliken population analysis is made to obtain the charge on each atom. Self-consistent field procedures are done with a convergence criterion of 10^{-5} a.u. on the energy. Geometrical optimisations are performed by using the Broyden–Fletcher–Goldfarb–Shanno algorithm[10] with a convergence criterion 10^{-2} a.u. on the displacement and of 10^{-4} a.u. on the energy.

3. Results and discussion

3.1. The stability

Table 1 presents the binding energies (BEs), C–H bond energies (ΔEs) and the $E_{\rm HOMO}-E_{\rm LUMO}$ energy gaps ($E_{\rm g}$s) of C_nH_n and $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74).

Table 1. The BEs/eV, ΔEs/eV, $E_{\rm g}$/eV, the outside and inside C–H bond lengths (Å(1 Å=0.1 nm)) of C_nH_n and $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74).

	$C_{70}H_{70}$	$H_{10}@C_{70}H_{60}$	$C_{72}H_{72}$	$H_{12}@C_{72}H_{60}$	$C_{74}H_{74}$	$H_{14}@C_{74}H_{60}$
BE	671.50	675.15	690.04	704.17	708.14	719.47
ΔE	2.41	2.43	2.43	2.63	2.33	2.53
$E_{\rm g}$	4.48	3.53	4.37	4.84	4.53	4.55
C–H (outside)	1.09	1.10	1.09	1.09	1.09	1.10
C–H (inside)	–	1.07	–	1.08	–	1.08

Commonly, BE is defined as an absolute value of the difference between the total energy of the molecule and the energy sum of all free atoms constituting the molecule. The larger BE means the higher thermodynamic stability of the molecule.[11] The ΔE is defined as $\Delta E = \frac{1}{n}(E_{C_n} + nE_{\rm H} - E_{C_nH_n})$ or $\Delta E = \frac{1}{n}(E_{C_n} + nE_{\rm H} - E_{H_{n-60}@C_nH_{60}})$. The higher positive ΔE leads to the greater stability of the resultant.[12] The computed BEs of $H_{n-60}@C_nH_{60}$ are 3.65, 14.13, and 11.33 eV larger than those of C_nH_n respectively, while, the ΔEs of $H_{n-60}@C_nH_{60}$ are separately 0.02, 0.2, and 0.2 eV larger than those of C_nH_n. Therefore, the 'in-out' isomerism $H_{n-60}@C_nH_{60}$ should be more thermodynamically stable than the all-exo isomer C_nH_n. As calculated, the ΔEs of $H_{n-60}@C_nH_{60}$ are smaller than that of CH_4 and many other fullerenes, such as $C_{64}H_n$,[13] this fact indicates that the C–H bond should have weaker covalent character than them and H could be easily dissociated along the following approaches:

$$H_{n-60}@C_nH_{60} \longrightarrow C_n + nH, \tag{1}$$

$$nH \longrightarrow \frac{n}{2}H_2. \tag{2}$$

Next, we will pay attention to the $E_{\rm g}$s, because they are often correlated with the kinetic stabilities.[14] The calculated $E_{\rm g}$s of C_{70}, C_{72}, and C_{74} are 1.77, 1.27, and 0.09 eV respectively, while those of C_nH_n and $H_{n-60}@C_nH_{60}$ are obvious larger than their parent structures and many other isolated fullerenes, such as C_{60} and C_{70},[15] implying that the hydrogenation can remarkably improve the stabilities of the pure structures. Another point should be noticed here, that is, $H_{10}@C_{70}H_{60}$ has an $E_{\rm g}$ about 0.95 eV smaller than that of $C_{70}H_{70}$, however, the $E_{\rm g}$s of $H_{12}@C_{72}H_{60}$ and $H_{14}@C_{74}H_{60}$ are about 0.47 and 0.02 eV larger than those of $C_{72}H_{72}$ and $C_{74}H_{74}$ respectively. Obviously, the BEs of two isomers did not exactly correlate with the $E_{\rm g}$s. This feature indirectly indicated a question of the kinetic stability. It should be noticed that the thermodynamic and kinetic stabilities of the fullerene were not necessarily the same as Slanina *et al.* stated.[16] It is explored from BE, $E_{\rm inc}$, and $E_{\rm g}$ that the 'in-out' isomerism $H_{n-60}@C_nH_{60}$ (n = 70,

72, 74) may become a new class of entirely novel potential hydrogen storage nanomaterials, so the detail properties of them will be analysed in the following.

3.2. The bond character

The average lengths of the outside C–H bonds of C_nH_n (n = 70, 72, 74) are all 1.09 Å, while those of the outside C–H bonds of $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) are respectively 1.10, 1.09, and 1.10 Å, close to those of $C_{20}H_{20}$.[17] The inside C–H bond lengths of $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) are separately 1.07, 1.08, and 1.08 Å, about 0.3 or 0.2 Å smaller than those of the outside one, indicating that the smaller space in the fullerene leads to the more shortened C–H bond inside. It is worth noticing that the C–H bond here is either as same as or 0.1 Å smaller than the radius sum of C and H, 1.10 Å. Thus, C–H bond should contain covalent character. Figure 1 shows the different charge density distributions of these three molecules, obtained from the total density with the density of the isolated atoms subtracted.[10] If there is different charge density distributions between H and C, the C–H bond should contain covalent character. It is obvious from Fig. 1 that the C–H bond should be covalent.

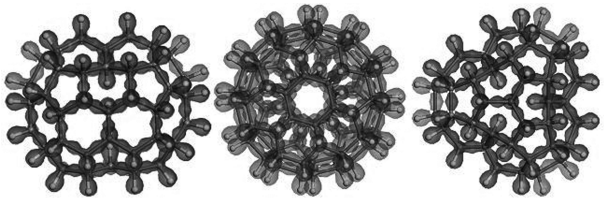


Fig. 1. The different charge densities of $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74).

The calculated average Mulliken charges of the carbons hydrogenated inside of $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) are respectively −0.04, −0.08, and −0.04e, while those of the outside hydrogenated carbons are all −0.03e, which is somewhat smaller. Meanwhile, the average densities at nucleus of the carbons hydrogenated inside of $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) are respectively 127.02, 126.98, and 126.99 a.u., those of the outside hydrogenated carbons are 127.04, 127.02, and 127.03 a.u., becoming a little larger. Therefore, by analysing both the average Mulliken charge and average density at nucleus, we can conclude that, in the $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) molecules, the bond covalence of the outside C–H bond is slightly larger than that of the inside C–H bond.

3.3. The static linear polarisability and aromaticity

The mean polarisability is calculated from the polarisability components as $\langle\alpha\rangle = \frac{1}{3}[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}]$.[18] The static linear polarisability anisotropy $\Delta\alpha$ is defined as $\Delta\alpha = \sqrt{\frac{1}{2}[(\alpha_{xx}-\alpha_{yy})^2 + (\alpha_{xx}-\alpha_{zz})^2 + (\alpha_{yy}-\alpha_{zz})^2]}$.[19] The components are obviously different in the x, y and z directions for $H_{10}@C_{70}H_{60}$, 313.88, 382.87, and 301.71 Å^3, producing the 75.81 Å^3 static linear polarisabily anisotropic value. However, $H_{14}@C_{74}H_{60}$ is oriented with its permanent dipole moment only along the z axis, 353.24 Å^3, similar to the case for C_{74} and $Ba@C_{74}$,[20] while $H_{12}@C_{72}H_{60}$ has the same static linear polarisabily in the x and y directions, 327.39 Å^3, and a smaller value in the z direction, 277.67 Å^3. As we know, $H_{10}@C_{70}H_{60}$ is D_{5h} symmetric, while $H_{14}@C_{74}H_{60}$ together with C_{74} and $Ba@C_{74}$ are the lower D_{3h} symmetric. Obviously, the static linear polarisabilies of $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) are indeed relative to their shapes, as Kobayashi *et al.* concluded.[19] We hope that the experiment will prove our results in the future.

The nucleus independent chemical shift (NICS) has been demonstrated to be a useful criterion for aromaticity of a molecule. The degree of electron delocalization is evaluated by using the calculated value of NICS at the cage center. The aromatic and antiaromatic are associated with the negative and positive NICS values, respectively. The more negative the NICS value is, the higher the aromaticity is. The NICS values for $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) at the cage center are only −2.02, −1.89, and −1.21 ppm. Therefore, $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) shown almost nonaromatic character.

4. Conclusion

The binding energies, bond energies, and energy gaps of the 'in-out' isomerism $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) explore that the 'in-out' hydrogenation of the pure clusters can remarkably improve their stabilities and to achieve synthesis of them. The static linear polarisabilies of $H_{n-60}@C_nH_{60}$ (n = 70, 72, 74) are indeed relative to their shape, while they show almost nonaromatic character. This study can suggest that the 'in-out' isometric perhydrogenation of fullerenes could lead to the invention of entirely novel potential hydrogen storage nanomaterials.

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