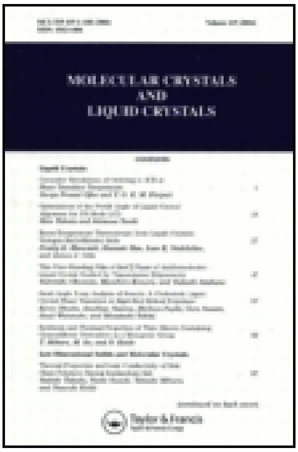

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Mono-Hydrogenation of Fullerene Materials: A Density Functional Theory Study on the Properties of Fullerene Mono-Hydrides $C_{60}H$ and $C_{70}H$

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Mono-Hydrogenation of Fullerene Materials: A Density Functional Theory Study on the Properties of Fullerene Mono-Hydrides $C_{60}H$ and $C_{70}H$

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Mono-hydrogenation effect on the properties of fullerenes C_{60} and C_{70} was investigated by the density functional theory (B3LYP/6-311G(d, p)). One isomer of $C_{60}H$ and five isomers of $C_{70}H$ were examined, comparing with C_{60} and C_{70}. Energies of fullerene mono-hydrides (FMH) are smaller than the summation of energy of the fullerene and that of hydrogen atom. Dipole moments of cationic FMH (μ^+) are much larger than those of neutral FMH radicals (μ^0). Mono-hydrogenation decreases frontier energy gap (ΔE_g) and excitation energy (E_{ex}) by about 0.9 eV. The hyperfine coupling constant (a_H), spin density (ρ_H, ρ_C), and reorganization energy (λ) are strongly dependent on the addition position of hydrogen atom.

Keywords Energy gap; excitation energy; fullerene; hydrogenation; hyperfine coupling constant; reorganization energy

1. Introduction

Chemical modification of carbon materials such as carbon nanotube, graphene, graphite, and fullerene continues to attract immense interest. The simplest way of such modification is the addition of one atomic hydrogen to the carbon materials [1,2]. Hydrogenation has great influence on the geometric and electronic structures of carbon materials so that the elucidation of the properties of hydrogenated carbon materials is the important theme in the development of high-performance carbon materials.

Recently, atomic hydrogen chemisorbed on carbon nanotubes have been studied and the formation of C–H sp^3 chemical bonds were confirmed by a variety of experimental techniques including infrared [3], ultraviolet [4], and scanning tunneling microscopy [5]. It was also found by the theoretical research [6] that attaching a single hydrogen atom is always exothermic. Hydrogenation of graphene is also studied by both theoretical [7,8] and experimental [9–11] methods. The highly conductive graphene is converted from a semimetal into an insulator by hydrogenation [11].

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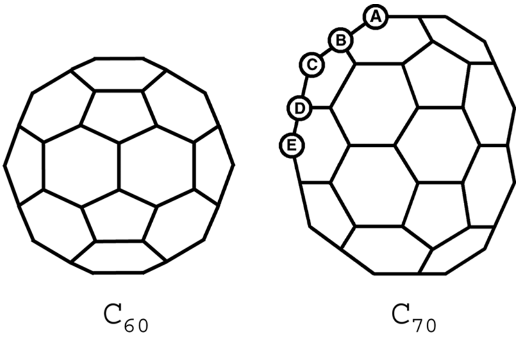

Figure 1. Structures of C_{60} and C_{70}. The hydrogen atom is bound to one of the carbon atoms labeled **A**–**E**.

In the present work, we focus on mono-hydrogenation effect on the properties of fullerene C_{60} and C_{70}. Both C_{60} and C_{70} have degenerate orbitals due to the high symmetry. Therefore, there is a possibility that the hydrogenation dramatically changes the properties of these fullerenes.

This paper is organized as follows: In Section 2, the research method and selected isomers of $C_{60}H$ and $C_{70}H$ are presented. Calculated results of C−H bond length (r_{C-H}), C−H binding energy (E_{C-H}), dipole moment (μ^0, μ^+), atomic charge (q), frontier orbital energy (ε), frontier energy gap (ΔE_g), and excitation energy (E_{ex}) of fullerenes (referred as "F" hereafter) and fullerene mono-hydrides (referred as "FMH" hereafter) are shown in Section 3. Hyperfine coupling constant (a_H) of hydrogen atom, spin density (ρ_H and ρ_C) of hydrogen and carbon atoms, and reorganization energies (λ) are also tabulated. Finally, we conclude this paper in Section 4.

2. Computational Method

There is only one isomer for $C_{60}H$ since all carbon atoms are equivalent in I_h symmetry. On the other hand, C_{70} has five kinds of carbon atoms so that there are five isomers for $C_{70}H$. Carbon atoms of C_{70} are labeled **A**–**E** (See Fig. 1) and one atomic hydrogen is added to one of carbon atoms to produce five kinds of isomers **a**–**e**.

All DFT calculations were carried out at the B3LYP/6-311 G (*d, p*) level of theory using the Gaussian 03 [12] program package. Neutral radicals and cations are calculated using UB3LYP and RB3LYP functionals, respectively. It was confirmed by frequency calculations that there is no mode with imaginary frequency at the optimized structures of neutral radicals and cations. Reorganization energies are calculated following the method used in our previous works [13–16].

3. Results and Discussion

3.1. *Relative Energy (E_{rel}) and C−H Bond Characters (r_{C-H}, E_{C-H})*

C−H bond length (r_{C-H}) and C−H binding energy (E_{C-H}) are given in Table 1, where E_{C-H} is defined as

$$E_{\text{C-H}} = -(E_{\text{FMH}\cdot} - E_{\text{F}} - E_{\text{H}\cdot}) \tag{3.1}$$

Table 1. Optimized C–H bond length (r_{C-H}), binding energy of hydrogen atom (E_{C-H}), and relative values (E_{rel}) of neutral radicals, $C_{60}H$ and $C_{70}H$

	Isomers	r_{C-H} (Å)	E_{C-H} (kcal/mol)	E_{rel} (kcal/mol)
$C_{60}H$		1.101	48.7	
$C_{70}H$	**a**	1.101	47.7	0.0
	b	1.101	46.9	+0.8
	c	1.102	46.7	+1.0
	d	1.101	47.7	+0.1
	e	1.105	35.3	+12.4

Values of r_{C-H} (1.101–1.105 Å) and E_{C-H} (35.3–48.7 kcal/mol) of FMH are near to those of C–H bonds at the edge region of finite-sized graphene (1.101 Å and 36.8, 42.9 kcal/mol) [8]. This means that sp^3 hybrid orbitals are completely formed in all hydrogen-added sites of FMH. All values of E_{C-H} are positive so that the atomic hydrogen addition to F is exothermic reaction. E_{C-H} of $C_{70}H$ is strongly dependent on the position of hydrogen atom. There is clear relation between E_{C-H} and r_{C-H} that isomers with short r_{C-H} tend to have large E_{C-H}.

From the values of relative energy (E_{rel}), isomer **a** is most stable among five isomers of $C_{70}H$ in our calculation. Reid *et al.* reported in 1994 that isomer **c** is the most stable by using semiempirical AM1 method [17]. On the other hand, in 1996, Borghi *et al.* found that isomers **c** and **a** are the most stable at the semiempirical MNDO/PM3 and the NLDFT level, respectively [18]. Very recently, in 2009, Sun *et al.* have reported that isomer **a** is most stable at the B3LYP/6-31 G (*d*) level [19]. Our result by B3LYP/6-311 G (*d, p*) is consistent with the result of Sun *et al.* by B3LYP/6-31 G (*d*).

3.2. *Dipole Moment (μ) and Atomic Charge (q)*

Dipole moments and natural population analysis (NPA) charges of neutral and cationic states are shown in Table 2. C_{60} and neutral C_{70} have no dipole moment

Table 2. Dipole moment of neutal radicals (μ^0) and those of cations (μ^+). NPA charge of carbon and hydrogen atoms of C–H bonds is also shown for both neutral (q_C^0, q_H^0) and cationic states (q_C^+, q_H^+)

	Isomers	q_C^0 (e)	q_H^0 (e)	q_C^+ (e)	q_H^+ (e)	μ^0 (D)	μ^+ (D)
C_{60}		–	–	–	–	0.00	0.00
$C_{60}H$		−0.282	0.260	−0.308	0.311	1.55	3.57
C_{70}		–	–	–	–	0.00	1.28
$C_{70}H$	**a**	−0.284	0.261	−0.314	0.316	1.80	4.11
	b	−0.283	0.262	−0.308	0.312	1.83	3.77
	c	−0.284	0.261	−0.309	0.311	1.57	3.36
	d	−0.271	0.260	−0.293	0.305	1.64	2.97
	e	−0.286	0.259	−0.326	0.332	1.26	3.51

due to their symmetries. Neutral FMH has μ^0 in range of 1.26–1.83 D, but cationic FMH has very large μ^+ in range of 2.97–4.11 D. Direction of moments is from the center of F to hydrogen atom.

In both states, carbon and hydrogen atoms have negative and positive charges, respectively. Therefore, dipole moment of C−H bond is from a hydrogen atom to a carbon atom. Inversely, negative charge of the carbon atom of C−H bond leads to the polarization of fullerene part which is anti-parallel to that of C−H bond. Dipole moment is linearly proportional to the distance between separated charges, so that fullerene part with large molecular size tends to has larger dipole moment than C−H bond. Therefore, the direction of dipole moment of FMH is from fullerene part to H atom in total (See Fig. 2).

Total charge of C−H bonds is almost zero in both states, so that extra one positive charge is distributed on fullerene part except for the carbon atom of C−H bond in the cationic state. This results in the increase of dipole moment from fullerene part to the carbon atom (negative charge) of C−H bond in cationic state. Therefore, removal of one electron from FMH radical results in the increase of the dipole moment.

3.3. *Hyperfine Coupling Constant (a) and Spin Density (ρ)*

The hyperfine coupling constant, a_H, of hydrogen atom and the NPA spin densities, ρ_C and ρ_H, of $C_{60}H$ and $C_{70}H$ are given in Table 3. ρ_C and ρ_H were calculated from the NPA population of α spin electron minus NPA population of β spin electron.

All carbon atoms of C−H bonds have excess β spin electron and all hydrogen atoms have excess α spin electron. Therefore, spin polarization occurs on all C−H bonds. The values of a_H are almost proportional to those of ρ_H ($a_H/\rho_H \approx 800$) since the α spin electron on a hydrogen atom strongly couples to the nuclear spin of the hydrogen core by Fermi contact interaction.

a_H were calculated to be 29.1–56.5 (G) and are strongly dependent on the position of hydrogen atom. These values show good agreement with the experimental values [20–22]. Except for the value of isomer **e** of $C_{70}H$, the values of a_H of FMH are near to those of hydrogen atom at the edge region of finite-sized graphene (23.1–33.4 G) [8].

3.4. *Frontier Energy Gap (ΔE_g) and Excitation Energy (E_{ex})*

Orbital energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of F, ε_H and ε_L, and those of the singly

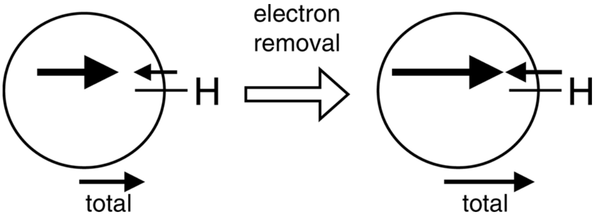

Figure 2. Schematic pictures which explain the change of dipole moment by electron removal.

Table 3. Hyperfine coupling constant (a_H) of hydrogen atom and NPA spin density (ρ_H and ρ_C) of hydrogen and carbon atoms of FMH. ρ_H and ρ_C are calculated from the NPA population of α spin electron minus NPA population of β spin electron. Experimental values of a_H are also shown

	Isomers	a_H (Expt.) (G)	a_H (Calc.) (G)	ρ_H (e)	ρ_C (e)	a_H/ρ_H (G/e)
$C_{60}H$		33.1[20]	33.6	0.042	−0.024	809
$C_{70}H$	**a**	36.8[21]	36.8	0.045	−0.025	818
	b	36.0[22]	37.3	0.046	−0.026	809
	c	34.5[22]	35.5	0.044	−0.023	806
	d	27.9[22]	29.1	0.037	−0.019	793
	e	(37.2)[22]	56.5	0.070	−0.034	803

occupied alpha molecular orbital (SOMO) and the next singly occupied alpha molecular orbital (SOMO + 1) of FMH, ε_S and ε_{S+1}, are shown in Table 4. It is found that values of ε_L are almost same to those of ε_{S+1}, but those of ε_S are larger than those of ε_H by about 0.9 eV. Therefore, frontier energy gaps (ΔE_g) of FMH are about 0.9 eV smaller than those of F. Absorption spectrum is expected to be red-shifted by mono hydrogenation.

Excitation energies to nth excited state ($E_{ex}^{(n)}$) from ground state calculated by time-dependent (TD) DFT are also shown in Table 4. Excitation which corresponds to HOMO – LUMO transition for F and SOMO – (SOMO + 1) transition for FMH is underlined. Underlined values of E_{ex} are generally smaller than those of ΔE_g by about 0.7 eV and the ordering of underlined E_{ex} is qualitatively consistent with that of ΔE_g. These results are qualitatively same with the results about graphene [8].

Table 4. Calculated HOMO and LUMO energies of F (ε_H and ε_L) and SOMO and (SOMO + 1) energies of FMH (ε_S and ε_{S+1}). HOMO – LUMO energy gap and SOMO – (SOMO + 1) energy gap (ΔE_g) calculated by B3LYP/6–311G (*d, p*) and nth excitation energy ($E_{ex}^{(n)}$, $n \leq 3$) calculated by time-dependent (TD) – B3LYP/6-311 G (*d, p*) are also shown. Excitation energies which correspond to HOMO – LUMO or SOMO – (SOMO + 1) transitions are underlined

	Isomers	ε_H or ε_S (eV)	ε_L or ε_{S+1} (eV)	ΔE_g (eV)	$E_{ex}^{(1)}$ (eV)	$E_{ex}^{(2)}$ (eV)	$E_{ex}^{(3)}$ (eV)
C_{60}		−6.38	−3.64	2.74	$\underline{2.08}$	2.08	2.08
$C_{60}H$		−5.51	−3.59	1.92	1.20	$\underline{1.24}$	1.44
C_{70}		−6.32	−3.63	2.68	2.10	$\underline{2.11}$	2.16
$C_{70}H$	**a**	−5.60	−3.57	2.02	1.22	1.34	$\underline{1.34}$
	b	−5.36	−3.55	1.81	$\underline{1.12}$	1.17	1.37
	c	−5.44	−3.57	1.87	$\underline{1.17}$	1.29	1.43
	d	−5.33	−3.59	1.74	$\underline{1.07}$	1.19	1.39
	e	−5.42	−3.64	1.78	$\underline{1.07}$	1.20	1.31

3.5. *Reorganization Energy (λ) and Rate Constant (k_{ht})*

From Marcus theory [23], the hole-transfer rate constant k_{ht} of a homogeneous hole-transfer reaction can be estimated from reorganization energy (λ),

$$k_{\mathrm{ht}} = \frac{4\pi^2}{h}\frac{H_{\mathrm{AB}}^2}{\sqrt{4\pi\lambda k_{\mathrm{B}}T}}e^{-\lambda/4k_{\mathrm{B}}T} \tag{3.2}$$

where k_{B} is the Boltzmann constant, T is the temperature, and H_{AB} is the electronic coupling element. A small λ results in effective hole transport [24]. Calculated results of λ are all shown in Table 5. The values of k_{ht} are calculated using Eq. (3.2.) Be careful that the tabulated values are (rate constant of FMH, $k_{\mathrm{ht}}^{\mathrm{FMH}}$)/(rate constant of F, $k_{\mathrm{ht}}^{\mathrm{F}}$).

Stable structure of C_{60} has I_h symmetry (A_g electronic state). On the other hand, C_{60}^{+} has H_u electronic state with electronic degeneracy so that its symmetry lowers to D_{5d} (A_{1u} electronic state) due to Jahn-Teller distortion [25]. Considering the Jahn-Teller effect, the value of λ of C_{60} is calculated to be 169 meV. λ of $C_{60}H$ is calculated to be 161 meV which is a little smaller than that of C_{60}.

Stable structure of C_{70} has D_{5h} symmetry (A_g electronic state). Similar to C_{60}^{+}, C_{70}^{+} also has electronic degeneracy (E_1'' electronic state). Therefore, stable symmetry of C_{70} is lowered to C_{2v} (B_1 electronic state) due to the Jahn-Teller effect. The value of λ of C_{70} was calculated to be 121 meV. λ of $C_{70}H$ were calculated to be 140, 174, 152, 111, and 161 meV for **a, b, c, d**, and **e** isomers, respectively. Only one isomer **d** has smaller λ and larger k_{ht} than the original C_{70} so that faster hole-transfer between **d** isomers is expected.

Here, we define Δr as the sum of the absolute differences of bond lengths between neutral and cationic species,

$$\Delta r = \sum_{i}^{\text{all bonds}} |\Delta r_i| = \sum_{i}^{\text{all bonds}} |r_i(\text{neutral}) - r_i(\text{cation})| \tag{3.3}$$

where Δr_i means the difference in bond length for one pair of bonds, i. Values of Δr are shown in Table 5. In our previous works about fullerene derivatives [13–16],

Table 5. Geometrical difference between neutral radical and cation (Δr), reorganization energy (λ), and ratio of the hole-transfer rate constant of FMH to the hole-transfer rate constant of F ($k_{\mathrm{ht}}^{\mathrm{FMH}}/k_{\mathrm{ht}}^{\mathrm{F}}$)

	Isomers	Δr (Å)	λ (meV)	$k_{\mathrm{ht}}^{\mathrm{FMH}}/k_{\mathrm{ht}}^{\mathrm{F}}$
C_{60}		0.459	169	1.00
$C_{60}H$		0.263	161	1.10
C_{70}		0.391	121	1.00
$C_{70}H$	**a**	0.235	140	0.76
	b	0.369	174	0.49
	c	0.319	152	0.65
	d	0.253	111	1.14
	e	0.181	161	0.58

there was clear relationship between λ and Δr. However, such a relation can not be found for FMH.

4. Conclusions

Mono-hydrogenation effect on the properties of fullerenes C_{60} and C_{70} was investigated by the density functional theory (B3LYP/6-311G (*d, p*)). One isomer of $C_{60}H$ and five isomers of $C_{70}H$ were examined, comparing with C_{60} and C_{70}. Energies of FMH are smaller than the summation of energy of the F and that of hydrogen atom. The binding energies of C–H bond (E_{C-H}) were calculated to be 35.3–47.7 kcal/mol. Dipole moments of cationic FMH (μ^+) are much larger than those of neutral FMH radicals (μ^0). Mono-hydrogenation decreases the frontier energy gap (ΔE_g) and excitation energy (E_{ex}) by about 0.9 eV.

There is large difference in hyperfine coupling constant (a_H) between $C_{70}H$ isomers, 29.1–56.5 G. The values of a_H are clearly proportional to the spin density (ρ_H) of hydrogen atom and show good agreement with experimental values. Reorganization energies (λ) of FMH are strongly dependent on the position of hydrogen atom.

These results show that the addition of atomic hydrogen strongly affects the properties of fullerenes and mono hydrogenation can be used as efficient method to modify these properties.

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