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Hydrogenation Effect on Hole-Transport Properties of Fullerene C_{70}: A Density Functional Theory Study on $C_{70}H_4$, $C_{70}H_6$, and $C_{70}H_8$

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*Reorganization energies λ of isomers of hydrogenated fullerenes, $C_{70}H_n$ (n = 4, 6, 8), are investigated by the density functional theory (B3LYP/6–311G**). The smallest value of λ (λ_{min}) of $C_{70}H_4$ is 74 meV and is smaller than those of $C_{70}H_2$ (79 meV) and $C_{60}H_4$ (83 meV). λ_{min} of $C_{70}H_6$ and $C_{70}H_8$ are 72 meV and 74 meV, respectively. Addition of H atoms to [6,6]-ring fusion generally gives smaller λ than that to [5,6]-ring fusion. Hydrogenation can reduce λ_{min} of C_{70} materials and the result that $C_{70}H_6$ has the smallest λ_{min} is same with the result of hydrogenation of C_{60}.*

Keywords DFT; fullerene; hole transfer; hydrogenation; Marcus theory; reorganization energy

1. Introduction

Organic materials have been used as essential parts of organic light-emitting devices (OLEDs), organic field-effect transistors (OFETs), and organic solar cells which are expected to be used in next-generation technologies [1] because of variety, lightness, and flexibility. Carrier mobility [2] in the material is one of the most important properties in the performance of these devices. Therefore, new organic carrier-transport materials with high mobility, chemical, and thermal stability are desirable.

Theoretical investigations can give reliable guidelines for the development of such new organic hole-transport materials. Up to now, much effort has been made to theoretically understand the relationship between the structure and the carrier-transport properties of the materials [3–6]. We are also studying quantum-chemical design of carrier transport materials based on fullerenes from both scientific and technological viewpoints [7–16]. From the calculations of C_{59} [7], $C_{60}H$ [8], $C_{60}H_2$ [9], $C_{60}H_4$ [10] $C_{60}H_6$ [11], $C_{60}H_n$

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(n = 8, 52, 54, 56, 58, 60) [12], $C_{60}X_2$ (X = H, C_3H_6COOH, C_4H_8SH) [13], $C_{60}(CF_2)_n$ (n = 1, 2) [14], $C_{60}CX_2$ [15], C_{69} [7], $C_{70}H$ [8], and $C_{70}H_2$ [16], we have already obtained very important knowledge for efficient design of useful C_{60} materials.

In the present paper, we focus on hydrogenation effect on reorganization energy of hole-transport of $C_{70}H_2$. There are many reasons why we study the hydrogenation of C_{70} materials: (i) Hydrogenation dramatically changes electronic structure of C_{70} because it removes electronic degeneracy [17] of C_{70}^+. (ii) C_{70} is chemically and thermally stable, and its synthesis method has been established. Additionally, C_{70} and C_{70} derivatives are often used as hole-transport materials for organic devices [18–21]. (iii) Ambipolar transport in [6,6]-phenyl-C_{71}-butylic acid methyl ester ([70]PCBM) was reported [19]. From these points, the enhancement of hole mobility is necessary for the practical use of C_{70} derivatives [22]. We focus on the calculations of reorganization energy (λ) of $C_{70}H_4$, $C_{70}H_6$, and $C_{70}H_8$ and the values of λ are discussed from the viewpoints of the geometrical and electronic structures.

2. Theory and Computational Details

In non-crystal organic materials, it is known that hole transfer takes place in the hopping mechanism. Therefore, localized holes jump from one molecule (A) to the next (B) as

$$M^+(\mathrm{A}) + M(\mathrm{B}) \xrightarrow{k} M(\mathrm{A}) + M^+(\mathrm{B})$$

From Marcus theory [23], the hole-transfer rate constant k of a homogeneous hole-transfer reaction can be estimated from two parameters, reorganization energy (λ) and the electronic coupling element (H_{AB}) between adjacent molecules,

$$k = \frac{4\pi^2}{h}\frac{(H_{\mathrm{AB}})^2}{\sqrt{4\pi\lambda k_{\mathrm{B}}T}}e^{-\lambda/4k_{\mathrm{B}}T}$$

where k_{B} is the Boltzmann constant and T is the temperature. A small λ results in large k and fast hole transport.

$C_{70}H_2$ isomer with the smallest λ (λ_{min}) is shown in Fig. 1 (a) [16]. There are two candidates to add two H atoms at neighboring two C atoms of $C_{70}H_2$, the one is [5,6]-addition in which two H atoms are added at two C atoms of the fusion of 5- and 6-membered rings,

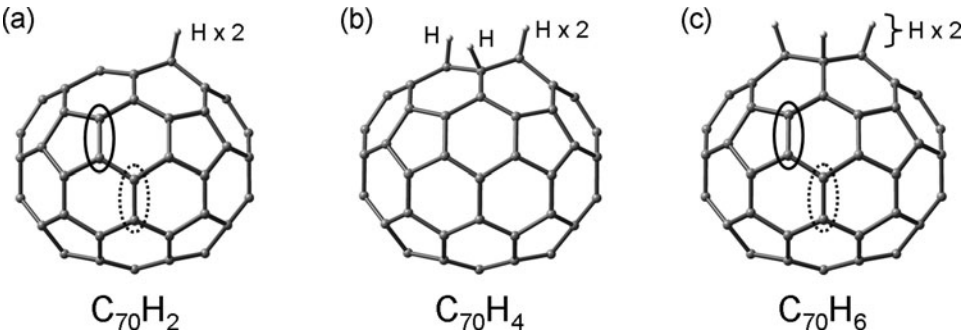

Figure 1. (a) Structure of $C_{70}H_2$ with λ_{min} and two kinds of ring fusions, [5,6]-ring fusion (solid circle) and [6,6]-ring fusion (dot circle). (b) Structure of $C_{70}H_4$ with λ_{min}. (c) Structure of $C_{70}H_6$ with λ_{min} and two kinds of ring fusions.

and the other is [6,6]-addition at two C atoms of the fusion of two 6-membered rings. The number of isomers of $C_{70}H_4$ produced by [5,6]-addition is 29 and that of [6,6]-addition is 24.

All DFT calculations were carried out at the B3LYP/6–311G(*d*,*p*) level of theory using the Gaussian 03 [24] program package. Neutral molecules and cations are calculated using RB3LYP and UB3LYP functionals, respectively. Reorganization energies are calculated following the method used in our previous works [7–16].

3. Results and Discussion

3.1. Reorganization Energy

Λ of C_{70} is 120 meV and λ_{min} of $C_{70}H_2$ (Fig. 1(a)) is 79 meV [16]. Averaged value of λ (λ_{avg}) of $C_{70}H_4$-[5,6] is 156 meV and λ_{avg} of $C_{70}H_4$-[6,6] is 109 meV. Therefore, in average, both [5,6]- and [6,6]-additions to $C_{70}H_2$ lead to the increase of λ. $C_{70}H_4$ with λ_{min} is shown in Fig. 1 (b). λ_{min} of $C_{70}H_4$ is 74 meV and is obtained by [6,6]-addition. This value is smaller than λ_{min} of $C_{70}H_2$ (79 meV). Therefore, further hydrogenation of $C_{70}H_2$ reduces λ_{min}. Same with the case of $C_{60}H_4$ [10], the isomer with four H atoms on the same 6-membered ring gives λ_{min}.

To produce $C_{70}H_6$, two H atoms were added to $C_{70}H_4$ with λ_{min}. We have already reported that the isomer with six H atoms on the same 6-membered ring gives λ_{min} in the case of $C_{60}H_6$ [11]. Therefore, we considered all three $C_{70}H_6$ isomers in which six H atoms were added on the same 6-membered ring. λ_{min} of $C_{70}H_6$ is 72 meV. This isomer is shown in Fig.1(c) and is obtained by [6,6]-addition to $C_{70}H_4$ with λ_{min}.

Lastly, we calculated λ of $C_{70}H_8$. Two H atoms were added to $C_{70}H_6$ with λ_{min}. Similar to the addition to $C_{70}H_2$, there are two candidates, [5,6]- and [6,6]-additions. The number of isomers of $C_{70}H_8$ originated from [5,6]-addition is 14 and that of isomers of $C_{70}H_8$ originated from [6,6]-addition is 12. λ_{avg} of $C_{70}H_8$-[5,6] is 169 meV and λ_{avg} of $C_{70}H_8$-[6,6] is 120 meV. Therefore, in average, both [5,6]- and [6,6]-additions to $C_{70}H_6$ result in the increase of λ. λ_{min} of $C_{70}H_8$ is 74 meV and is obtained by [6,6]-addition. This value of λ_{min} is larger than that of $C_{70}H_6$ (72 meV) so that the further hydrogenation to $C_{70}H_6$ does not reduce λ_{min}. This result is similar to the result about $C_{60}H_6$ and $C_{60}H_8$ [12].

From these results, we found that the further hydrogenation of $C_{70}H_2$ can decrease λ and one isomer of $C_{70}H_6$ has the smallest λ, 72 meV. The result that addition of six H atoms leads to the smallest λ among $C_{70}H_n$ (n = 2, 4, 6, 8) isomers is similar to the

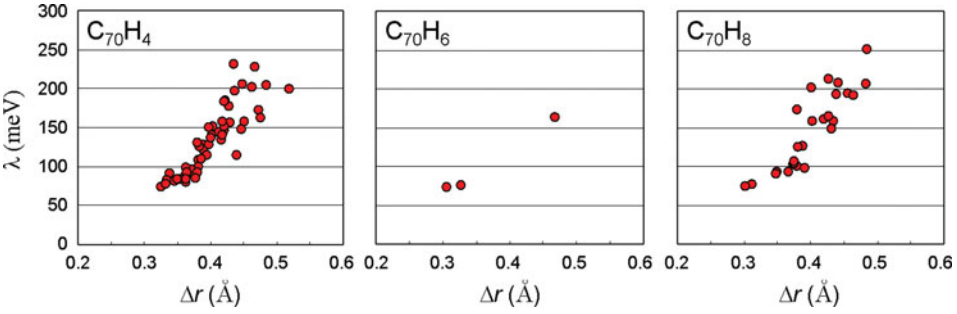

Figure 2. The relationship between geometrical relaxation (Δr) and reorganization energy (λ) of $C_{70}H_n$ (n = 4, 6, 8).

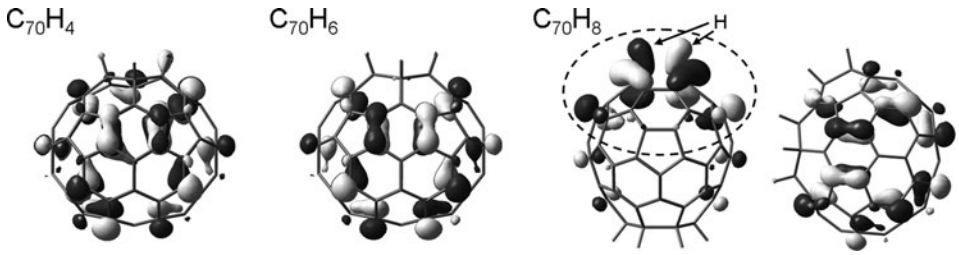

Figure 3. HOMOs of $C_{70}H_4$ and $C_{70}H_6$ with λ_{min}, and HOMOs of $C_{70}H_8$ with λ_{min} (left) and the second λ_{min} (right).

result of hydrogenation of C_{60} [9–12]. In average, [6,6]-addition results in smaller λ than [5,6]-addition, and λ_{min} is obtained by [6,6]-addition.

3.2. Geometrical and Electronic Structures

It is expected that there is a relationship between the geometrical relaxation by carrier injection and reorganization energy because the reorganization energy is the stabilization energy by the geometrical relaxation due to the force on nuclei by the change in molecular charge [25–28]. Here, we define Δr as the sum of the absolute differences of bond lengths between $C_{70}H_n$ and $C_{70}H_n{}^+$ ($n = 4, 6, 8$),

$$\Delta r = \sum_{i}^{\text{allbonds}} |\Delta r_i| = \sum_{i}^{\text{allbonds}} |r_i \text{ (neutral)} - r_i \text{ (cation)}|$$

where Δr_i means the difference in bond length for ith pair of bonds. The relations between the values of Δr and the values of λ for all isomers are shown in Fig. 2. It is found that there is almost linear relationship between Δr and λ. Smaller Δr results in smaller λ.

Hole-transport properties are often discussed from the distribution of the highest occupied molecular orbital (HOMO). HOMOs of $C_{70}H_4$ and $C_{70}H_6$ with λ_{min} are shown in Fig. 3. HOMOs of $C_{70}H_8$ with λ_{min} (left) and the second λ_{min} (right) are also shown. HOMOs of $C_{70}H_4$, $C_{70}H_6$, and $C_{70}H_8$ with the second λ_{min} are delocalized on the whole molecule. This result is same with our previous results about other fullerene materials. On the other hand, HOMO of $C_{70}H_8$ with λ_{min} is localized at the top of the molecule. In our previous works, fullerene derivatives with localized HOMO tend to have large λ. Therefore, HOMO of $C_{70}H_8$ with λ_{min} seems to be contradictory to previous results. However, HOMO of this isomer has large coefficients on two H atoms. Upon carrier injection, injected carrier localized on H atoms does not contribute to the relaxation of molecule. Thus, this $C_{70}H_8$ isomer has the smallest λ in spite of the localized HOMO.

4. Conclusions

The smallest values of λ of $C_{70}H_4$, $C_{70}H_6$, and $C_{70}H_8$ are 74 meV, 72 meV, and 74 meV, respectively. These values are smaller than the value of C_{70} (120 meV) and the smallest value of $C_{70}H_2$ (79 meV) so that further hydrogenation of $C_{70}H_2$ can reduce the smallest value of λ. Hydrogenation at the [6,6]-ring fusion generally results in small λ and the smallest values are obtained by the [6,6]-addition. Similar to the case of C_{60} hydrides, $C_{70}H_6$ with six H atoms on the same 6-membered ring gives the smallest λ. These results

indicate that the hydrogenation of all carbon atoms of the same 6-membered ring gives the smallest reorganization energy for fullerene materials. It was also found that there is a close relationship between λ, geometrical relaxation, and the distribution of HOMO of $C_{70}H_n$ ($n = 4, 6, 8$).

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