We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Hydrogenation of Fullerene C₆₀: Material Design of Organic Semiconductors by Computation

Ken Tokunaga

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/48534>

1. Introduction

1.1. Motivation

Carrier mobility [1] in organic semiconductors is one of the most important properties in the performance of organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells, which are expected to be used in next-generation technologies [2]. Organic semiconductors have the advantages of lightness, flexibility, and low cost. Therefore, research and development of new materials with chemical and thermal stability has recently been very active [3–6]. However, the wide variety of organic materials, which is generally a major advantage of these materials, has hindered the systematic research and development of novel materials. Thus, the establishment of design guidelines for new organic materials is a matter of great urgency.

Up till now, much effort has been made to understand theoretically the relationship between the structure and the carrier-transport properties of these materials [7–10]. Theoretical investigations can give reliable guidelines for the development of such new organic semiconductors. We have also been studying the quantum-chemical design of organic semiconductors based on fullerenes from both scientific and technological viewpoints [11–19]. C₆₀ derivatives (Figure 1) are very interesting from the viewpoint of practical use. Some types of C₆₀ derivatives are shown in the figure, and C₆₀ derivatives of types (a) and (b) have already been studied in our research group [11–19].

It is well known that C₆₀ is chemically and thermally stable, and its method of synthesis is also established. Carrier mobility of amorphous silicon is about 1 cm²V^{−1}s^{−1}, so that a mobility above this value is desirable for organic semiconductors. However, hole mobility in C₆₀ film is in the order of 10^{−5} cm²V^{−1}s^{−1} [20], so that C₆₀ has not been used as a hole-transport material (p-channel semiconductor). Thus, the main purpose of our previous studies [11–14, 17–19] was to improve the hole mobility of C₆₀ by chemical methods. There is the possibility

Figure 1. Fullerene C₆₀ and some examples of C₆₀ derivatives.

that the addition of hydrogen to C₆₀ would result in a considerable modification of the C₆₀ materials. This possibility originates from the fact that C₆₀ has an electronic degeneracy in its cationic state because of its high symmetry I_h [21, 22], but C₆₀ hydrides usually do not because of the reduction in symmetry by the addition of hydrogen. Electron mobility in C₆₀ film is about $1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [20, 23, 24] so that C₆₀ is one of the most useful electron-transport materials. However, to achieve low-cost production and large-area devices, it is necessary for C₆₀ materials to have a solution-processable form, such as [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) [25]. Therefore, in organic electronics, the electronic properties of C₆₀ derivatives rather than those of the original C₆₀ are of much interest and importance.

Although ambipolar transport in [6,6]-phenyl-C₇₁-butyric acid methyl ester ([70]PCBM) was reported recently, its hole mobility ($2 \times 10^{-5}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) is much smaller than its electron mobility ($2 \times 10^{-3}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [26]. Therefore, the enhancement of hole mobility is necessary for the practical use of fullerene derivatives as ambipolar transistor materials. Very recently, conduction-type control of fullerene C₆₀ films from *n*- to *p*-type by doping with molybdenum(VI) oxide (MoO₃) was demonstrated [27]. Thus, analysis of the hole-transport properties of C₆₀ derivatives is very important for the practical use of C₆₀ materials.

1.2. Our previous publication: C₆₀X_n (*n* = 2, 4, and 6)

In our previous publication [11], the effect on carrier-transport properties of chemical addition of X (X=H, R, R-COOH, and R-SH, where R is an alkyl chain) to C₆₀ was systematically discussed from the viewpoint of reorganization energy (λ) using Marcus theory [28]. We focused on the C₆₀ derivatives of type (a) in Figure 1, C₆₀X_n, where X is the added group and *n* is the number of added X. There are many isomers for C₆₀X_n, so that the position of X was also a subject of investigation. The dependence of carrier-transport properties on the type or chemical nature of X was discussed from the results of C₆₀X₂. The dependence of carrier-transport properties on the number of added groups was discussed from the results

Figure 2. (a) Two addition patterns of CX_2 . (b) Open and closed structures of $C_{60}CX_2$.

of $C_{60}H_n$ ($n = 2, 4$, and 6). From these discussions, guidelines for effective design of carrier-transport materials were proposed:

- Carrier-transport properties of $C_{60}X_2$ are quite different from those of C_{60} [13–15, 18].
- Chemical addition can improve hole mobility of C_{60} for some isomers [13, 14, 18]. Conversely, electron mobility of C_{60} is not influenced or is decreased by the chemical addition [15].
- The values of reorganization energies of both hole transport and electron transport are almost independent of the type (chemical nature) of addition group X , but are strongly dependent on the position and the number of addition groups [15]. Therefore, reorganization energies of other types of $C_{60}X_2$ will be approximately estimated from the results of $C_{60}H_2$ [15].
- Hole and electron mobilities are closely related to the distribution patterns of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital), respectively [13–15]. Delocalized orbitals give high carrier mobility (small reorganization energy) and localized molecular orbitals produce a low carrier mobility (large reorganization energy).
- There is a clear linear relationship between the reorganization energy and the geometrical relaxation upon carrier injection.

These results will also be applied to other types of X , and give us a guideline for efficient design of novel materials based on C_{60} from both experimental and theoretical approaches. For example, in the experimental viewpoint, we can freely select an X that is appropriate for thin-film formation and is easily synthesized without considering the influence of X on the electronic properties. From the theoretical viewpoint, this result enables us to save computation time and resources in the material design because various types of $C_{60}X_2$ can be simplified to $C_{60}H_2$ in the prediction and discussion of these properties.

1.3. Our previous publication: $C_{60}CX_2$

In another of our publications [12], the effect of methylene bridging of C_{60} by $-CX_2$ ($X = H$, halogen, R, R-COOH, and R-SH, where R is an alkyl chain) on carrier-transport properties was systematically discussed. There are two isomers for $C_{60}CX_2$, I and II (Figure 2). Systematic

analyses of reorganization energies of methylene-bridged fullerenes $C_{60}CX_2$ give us very important knowledge for the efficient design of useful C_{60} materials:

- Hole mobility of C_{60} is strongly influenced by methylene bridging. $C_{60}CBr_2$ (**II**) has the smallest reorganization energy (93 meV). On the other hand, $C_{60}CX_2$ (**I**) isomers with R, R-COOH, and R-SH chains have very large reorganization energies of about 500 meV.
- Electron mobility of C_{60} is not influenced or is decreased by methylene bridging [16].
- Values of reorganization energies of both hole transport and electron transport are dependent on the type (chemical nature) of X. Therefore, especially for the case of hole transport, reorganization energies of other types of $C_{60}CX_2$ will not be easily predicted from the results of $C_{60}CH_2$. This result is quite different from the case of $C_{60}H_2$ and $C_{60}X_2$.
- There is a clear linear relationship between the reorganization energy and the change in the distance between bridged C $\cdots$ C atoms.
- Hole and electron mobilities are closely related to the distribution patterns of the HOMO and the LUMO between bridged carbon atoms, respectively [16]. Small carrier mobility and large reorganization energy result from strong antibonding character between bridged carbon atoms.

One of the important findings in this work is that the properties of $C_{60}CX_2$ are dependent on the type (chemical nature) of X. This is because CX_2 addition directly changes the carbon network around the addition position. The possibility of a transformation between a *closed* structure and an *open* structure upon carrier injection is one of the reasons why the reorganization energy of $C_{60}CX_2$ is strongly dependent on the type of X. Therefore, the molecular design of type (b) molecules is a little more difficult compared with the molecular design of type (a) molecules, $C_{60}X_2$.

We also found that electron-transport properties are little influenced by the methylene bridging, so that we can freely select an X that is appropriate for thin-film formation and is easily synthesized without considering the effect of X on the electronic properties. On the other hand, when constructing high-mobility hole-transport materials, the use of isomer **I** of $C_{60}CX_2$, which includes an alkyl chain with $-CH_3$ and $-COOH$ terminals, should be avoided.

1.4. This chapter

In this chapter, the effect of further hydrogenation of C_{60} on hole-transport properties is systematically discussed from the viewpoint of reorganization energy. We again focus on the C_{60} derivatives of type (a) in Figure 1. The dependence of hole-transport properties on the number and the position of hydrogen atoms is discussed from the results of $C_{60}H_n$ ($n = 2, 4, 6, 8, 52, 54, 56, 58$, and 60). From these discussions, guidelines for the effective design of high-performance carrier-transport materials of type (a) are proposed.

This chapter is organized as follows: In Section 2, the definition of λ and computational details of λ are presented. Synthesis methods of hydrogenated C_{60} are reviewed in Section 3. Structures of hydrogenated C_{60} molecules studied in this chapter are shown in Section 4. In Section 5, calculated results of λ for hole transport are shown. λ for electron transport is not

Figure 3. Schematic reaction diagram of a hole-transfer reaction $M^+(A) \cdots M(B) \rightarrow M(A) \cdots M^+(B)$.

discussed because it is expected that λ for electron transport is independent of the position and the number of hydrogen atoms. From the systematic discussion of these results, the dependence of λ on the position and the number of hydrogen atoms is shown in Section 6. Summarizing these discussions, simple guidelines for the efficient design of useful C₆₀H_n semiconductors are proposed in Section 7.

2. Hole-transport mechanism

2.1. Hopping mechanism

The hole mobility of single-crystal C₆₀ is around $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at a maximum. Materials having a mobility of $0.1\text{--}1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are categorized in the boundary region between the hopping and the band-transport mechanisms [29–31]. Therefore, in this chapter, only the hopping mechanism is considered because the hole mobility of C₆₀ is much smaller than $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

A schematic picture of hole hopping in an organic solid is shown in Figure 3. C₆₀ and C₆₀H_n molecules are represented by spheres in Figure 3. In the treatment of the hopping mechanism, two neighboring molecules are chosen from the solid. Then, a hole hopping between these two molecules, that is, the hole-transfer reaction, is considered. Repeating such a hopping between neighboring molecules, a carrier travels from one edge to the other edge of the organic solid. The initial and final states of a hole-transfer reaction are represented as $M^+(A) \cdots M(B)$ and $M(A) \cdots M^+(B)$. The system is fluctuating around the bottom of the potential curve as a result of molecular vibrations in its initial state. When the system occasionally reaches the transition state at which energies of the initial state and the final state are the same, the system jumps from the initial state to the final state with a rate constant k . This reaction is written as

Figure 4. Schematic potential energy surfaces of molecules related to the hole-transfer reaction. Q_0 and Q_+ mean the nuclear coordinates of stable structures in neutral and cationic states, respectively. Subscripts on the right-hand side of E mean the geometrical structure of the molecule and superscripts on the right-hand side of E mean the charge on the molecule.

A localized hole on one molecule (A) jumps to the neighboring molecule (B). From the Marcus theory [28], the hole-transfer rate constant k of a homogeneous carrier-transfer reaction can be estimated from two parameters, the reorganization energy (λ), and the electronic coupling element (H) between adjacent molecules:

$$k = \frac{4\pi^2}{h} \frac{H^2}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{\lambda}{4k_B T}\right), \quad (2)$$

where k_B is the Boltzmann constant, h is the Planck constant, and T is the temperature of the system. We can see that a small λ , large H , and high temperature T result in a fast hole hopping.

2.2. Reorganization energy

From Figure 3, we can see that the reorganization energy is the difference between "the energy in the final state of the system with a stable nuclear configuration in the *final* state" and "the energy in the final state of the system with a stable nuclear configuration in the *initial* state". For the calculation of λ , potential energy diagrams of the hole-transfer reaction are shown in Figure 4. The values of λ are obtained by the following procedure: First, the geometries of neutral C_{60} and $C_{60}H_n$ were fully optimized, giving a nuclear coordinate Q_0 and energy E_0^0 . At Q_0 , single-point energy calculations of cations give E_0^+ . Next, the structures were fully optimized in their cationic states, giving Q_+ and E_+^+ . Single-point energy calculations of the neutral states with geometry Q_+ give E_+^0 . The reorganization energy of the hole-transfer reaction (λ_h) is defined as the sum of λ_h^+ and λ_h^0 :

$$\lambda_h = \lambda_h^+ + \lambda_h^0, \quad (3)$$

where λ_h^+ and λ_h^0 are relaxation energies in the cationic and neutral states, respectively, estimated from

$$\lambda_h^+ = E_0^+ - E_+^+, \quad (4)$$

$$\lambda_h^0 = E_+^0 - E_0^0. \quad (5)$$

2.3. Rate constant

In this chapter, the calculation and analysis of λ_h are focused on. The electronic-coupling element for hole transport (H_h) can be approximated by one half of the molecular orbital energy splitting between the HOMO and the next HOMO of the neutral dimer [3, 32]. However, the values of H_h are dependent on both the distance and the relative orientation between the two molecules. Therefore, H_h is assumed to be the same for C₆₀ and all C₆₀H_{*n*} for ease of discussion in this work [33]. Therefore, we cannot know the numerical values of the rate constants k_h . Instead, we define k'_h as a ratio of the rate constant of C₆₀H_{*n*} to that of C₆₀ at $T = 300$ K. The values of k'_h for hole transport are calculated as

$$\begin{aligned} k'_h &= \frac{k_h^{C_{60}H_n}}{k_h^{C_{60}}} \\ &= \left(\frac{H_h^{C_{60}H_n}}{H_h^{C_{60}}} \right)^2 \cdot \sqrt{\frac{\lambda_h^{C_{60}}}{\lambda_h^{C_{60}H_n}}} \cdot \exp \left(-\frac{\lambda_h^{C_{60}H_n} - \lambda_h^{C_{60}}}{4k_B T} \right) \\ &\approx \sqrt{\frac{\lambda_h^{C_{60}}}{\lambda_h^{C_{60}H_n}}} \cdot \exp \left(-\frac{\lambda_h^{C_{60}H_n} - \lambda_h^{C_{60}}}{4k_B T} \right) \end{aligned} \quad (6)$$

on the supposition that $H_h^{C_{60}H_n} \approx H_h^{C_{60}}$. Hereafter, we regard k'_h as the hole mobility. The values of k'_h are usually calculated using Equation 6 in this chapter.

All calculations (geometrical optimizations and self-consistent field (SCF) energy calculations) necessary to obtain the values of the energies in Figure 4 were performed by a quantum-chemical method, namely, density functional theory (DFT) using the B3LYP functional. For the calculation of λ_h , the 6-311G(*d*, *p*) basis set was adopted. All neutral (ionic) systems were calculated in singlet (doublet) states. Calculations were performed using the GAUSSIAN 03 [34] program package.

3. Hydrogenation of fullerene

Although the main topic of this chapter is a theoretical discussion of hydrogenated fullerenes, synthesis methods of hydrogenated fullerenes are also important for practical use. Up to now, many types of hydrogenated fullerenes have been synthesized. Hydrogenated fullerenes, C₆₀H₂, C₆₀H₄, and C₆₀H₆, have been prepared by hydroboration [35, 36], hydrozirconation [37], rhodium-catalyzed hydrogenation [38], diimide [39] and hydrazine [40] reduction, dissolving metal reduction [41, 42], photoinduced-electron-transfer

reduction with 10-methyl-9,10-dihydroacridine [43, 44], and ultrasonic irradiation in decahydronaphthalene [45]. In many cases, a mixture of C_{60} , $C_{60}H_2$, and $C_{60}H_n$ ($n > 2$) is obtained [46]. Birch reduction [47] and transfer hydrogenation [48] of C_{60} produce $C_{60}H_{18}$ and $C_{60}H_{36}$. In the ruthenium-catalyzed hydrogenation, other types of $C_{60}H_n$ ($n = 10, 12, 34, 36, 38$, and 40) were observed using a field-desorption (FD) mass spectrometer [49]. Direct hydrogenation of C_{60} was achieved without the use of a catalyst by exposing solid-phase fullerenes to high-pressure hydrogen gas, and many types of $C_{60}H_n$ ($n = 2-18$) were identified by laser-desorption Fourier-transform mass spectrometry [50]. Unfortunately, highly hydrogenated fullerenes discussed in this chapter, $C_{60}H_{52} - C_{60}H_{60}$, have not been synthesized.

4. Isomers of hydrogenated fullerenes

4.1. Low hydrogenation: $C_{60}H_2 - C_{60}H_8$

There are 23 isomers for $C_{60}H_2$ [51]. 11 isomers of Figure 5(a) with a small formation energy were selected to consider the possibility of synthesis. The ground state of these isomers is the singlet state. Other isomers that are not considered in this chapter have triplet ground states in semiempirical calculations [51]. The initial hydrogen atom of $C_{60}H_2$ is already shown in the figure. The second hydrogen atom is added to one of the carbon atoms labeled 1–11. These isomers are named **1–11** in boldface. As predicted by Matsuzawa *et al.* [51] from quantum-chemical calculations, two isomers, **1** from 1,2-addition and **5** from 1,4-addition, have been synthesized [35, 39]. Furthermore, isomer **1** has been synthesized by many different methods [52].

Although there are a total of 4190 isomers for $C_{60}H_4$ [53], we consider eight isomers originating from two H_2 additions to [6,6]-ring fusions (see Figure 5 (b)) [54]. In other words, these isomers result from 1,2-addition to $C_{60}H_2$ -**1**. In Figure 5 (b), the second H_2 pair is added to one of the carbon atom pairs labeled 1–8 and these isomers are named **1–8**. Experimentally, some of the eight isomers have been synthesized, and four isomers (**1**, **4**, **6**, and **8**) among them were identified [36, 39–41, 55–57].

Among a total of 418470 isomers of $C_{60}H_6$ [53], we consider only 16 isomers in Figure 5 (c) originating from one H_2 addition to $C_{60}H_4$ -**1** at a [6,6]-ring fusion. One hydrogen pair is added to one of the carbon atom pairs labeled 1–16 and these isomers are named **1–16**.

We consider only six isomers of $C_{60}H_8$ in Figure 5 (d) originating from H_2 addition to $C_{60}H_6$ -**1** at a [6,6]-ring fusion. One hydrogen pair is added to one of the carbon atom pairs labeled 1–6 and these isomers are named **1–6**.

4.2. High hydrogenation: $C_{60}H_{52} - C_{60}H_{60}$

As highly hydrogenated fullerenes, we consider $C_{60}H_{52}$, $C_{60}H_{54}$, $C_{60}H_{56}$, $C_{60}H_{58}$, and $C_{60}H_{60}$. $C_{60}H_{60}$ has I_h symmetry. We consider 11, 8, 16, and 6 isomers for $C_{60}H_{58}$, $C_{60}H_{56}$, $C_{60}H_{54}$, and $C_{60}H_{52}$, respectively. For these highly hydrogenated isomers, hydrogenated carbon atoms in Figure 5 are to be considered the nonhydrogenated carbon atoms.

Figure 5. Isomers of (a) C₆₀H₂, (b) C₆₀H₄, (c) C₆₀H₆ (2 figures), and (d) C₆₀H₈. Hydrogen atoms are bonded to the labeled carbon atoms. Figures (a), (b), (c), and (d) also correspond to isomers of C₆₀H₅₈, C₆₀H₅₆, C₆₀H₅₄, and C₆₀H₅₂, respectively.

5. Reorganization energies and rate constants

5.1. C₆₀

The electronic structure of C₆₀⁺ has been investigated both experimentally and theoretically because of its electronic degeneracy [58, 59]. C₆₀⁺ has an *H_u* degenerate electronic state so that symmetry lowering because of the Jahn–Teller effect [21] stabilizes C₆₀⁺. The most stable structure of C₆₀⁺ was calculated as having *D_{5d}* symmetry, and its λ_h^+ is 95 meV in our calculation. The result of λ_h^+ is qualitatively consistent with previous works based on the static Jahn–Teller effect [60–62] in which the values of λ_h^+ were calculated as 351 [60], 35 [61], and 71 meV [62]. The value of λ_h^0 of C₆₀⁺(*D_{5d}*) was calculated as 74 meV. Thus, the reorganization energy of the hole transport, λ_h , is 169 meV. It should be noted that the value of λ_h^+ is much larger than that of λ_h^0 . This result comes from the fact that geometrical relaxation in the ionic state is very large because of Jahn–Teller distortion [21]. The potential curves of the ionic states are expected to have larger curvature around the minima than that of the neutral state.

5.2. C₆₀H₂ – C₆₀H₈

On average, λ_h^+ of C₆₀H₂ is 84 meV, which is smaller than that of C₆₀ by 11 meV and λ_h^0 of C₆₀H₂ is 90 meV, which is larger than that of C₆₀ by 16 meV [12, 13]. The average value of λ_h of C₆₀H₂ (174 meV) is almost as large as that of C₆₀ (169 meV). However, only the addition of two H atoms leads to the large difference in λ_h , 101–257 meV. It is interesting that six isomers of C₆₀H₂ (**1**, **4**, **5**, **6**, **8**, and **9**) have a smaller λ_h than C₆₀. In particular, isomer **6** has the smallest λ_h (101 meV), which is over 40% less than that of C₆₀. In addition, the k_h' of **6** is about 2.5 times as large as that of C₆₀. From the viewpoint of practical use, it should be noted that the values of λ_h for the two synthesized isomers, **1** and **5**, are 133 and 142 meV, respectively, which are about 20% smaller than that of C₆₀. The values of k_h' for these isomers are about 1.5 times as large as that of C₆₀. These results indicate that hydrogenation can be an effective method for modifying the hole-transport properties of C₆₀. Two synthesized isomers of C₆₀H₂, **1** and **5**, have potential utility as hole-transport materials. For almost all isomers of C₆₀H₂, λ_h^+ is almost equal to λ_h^0 . This means that the potential curves of the ionic and neutral states have almost the same curvature around the minima because the hydrogenation removes the electronic degeneracy in ionic states of C₆₀.

On average, λ_h^+ of C₆₀H₄ is 65 meV, which is smaller than that of C₆₀ by 30 meV and λ_h^0 of C₆₀H₄ is 68 meV, which is smaller than that of C₆₀ by 6 meV [12, 14]. The average value of λ_h of C₆₀H₄ (134 meV) is much smaller than that of C₆₀ (169 meV) and is almost as large as that of C₆₀H₂-**1** (133 meV). The addition of two H atoms to C₆₀H₂-**1** results in the large difference in λ_h , 83–183 meV. Seven isomers of C₆₀H₄ (**1**, **3**, **4**, **5**, **6**, **7**, and **8**) have smaller λ_h than C₆₀. Remarkably, the major product **1** has the smallest λ_h (83 meV), which is over 50% less than that of C₆₀. In addition, k_h' of **1** is 3.28 times as large as that of C₆₀, and more than twice as large as that of the synthesized C₆₀H₂-**1** [13]. Isomer **7** with the second smallest λ_h has a value for k_h' that is 2.83 times as large as that of C₆₀. Other identified isomers **4**, **6**, and **8** also have small λ_h (138, 150, and 126 meV, respectively), and k_h' of these isomers are respectively 1.49, 1.26, and 1.74 times larger than that of C₆₀. Synthesized isomers of C₆₀H₄, especially the major product **1**, have potential utility as useful hole-transport materials.

On average, λ_h^+ of C₆₀H₆ is 61 meV, which is much smaller than that of C₆₀ by 34 meV and λ_h^0 of C₆₀H₆ is 66 meV, which is smaller than that of C₆₀ by 8 meV [12]. The average value of λ_h for C₆₀H₆ (127 meV) is much smaller than that for C₆₀ (169 meV); however, it is much larger than that for C₆₀H₄-**1** (83 meV). Further addition of two H atoms to C₆₀H₄-**1** leads to a large difference in λ_h , 71–182 meV. 14 of the 16 isomers have smaller λ_h than C₆₀. Isomer **1** has the smallest λ_h (71 meV), which is about 60% less than that of C₆₀. In addition, k_h' of **1** is 3.94 times as large as that of C₆₀. Isomer **4** with the second smallest λ_h has a value of k_h' that is 3.22 times as large as that of C₆₀.

λ_h and k_h' of C₆₀H₈ are shown in Table 1. On average, λ_h^+ of C₆₀H₈ is 51 meV, which is much smaller than that of C₆₀ by 44 meV, and λ_h^0 of C₆₀H₈ is 62 meV, which is smaller than that of C₆₀ by 12 meV. The average value of λ_h for C₆₀H₈ (113 meV) is much smaller than that for C₆₀ (169 meV); however, it is much larger than that for C₆₀H₆-**1** (71 meV). Further addition of two H atoms to C₆₀H₆-**1** leads to a large difference in λ_h , 81–175 meV. Five of the six isomers have smaller λ_h than C₆₀. Isomer **5** has the smallest λ_h (81 meV), and k_h' of **5** is 3.39 times as large

C ₆₀ H ₈	λ_h^+	λ_h^0	λ_h	k'_h
(C ₆₀)	95	74	169	1.00
1	57	72	128	1.69
2	37	50	86	3.09
3	81	94	175	0.92
4	55	68	123	1.82
5	36	45	81	3.39
6	41	42	84	3.23
Average	51	62	113	2.09

Table 1. Reorganization energies (λ_h in meV) and rate constants (k'_h) for hole transport in C₆₀H₈. Values for the original C₆₀ and an averaged value over the six C₆₀H₈ isomers are also shown.

as that of C₆₀. Isomer **6** with the second smallest λ_h has a value of k'_h that is 3.23 times as large as that of C₆₀.

5.3. C₆₀H₅₂ – C₆₀H₅₈

λ_h and k'_h of C₆₀H₅₂ are shown in Table 2. On average, λ_h^+ of C₆₀H₅₂ is 122 meV, which is much larger than that of C₆₀ by 27 meV, and λ_h^0 of C₆₀H₅₂ is 132 meV, which is much larger than that of C₆₀ by 58 meV. The average value of λ_h of C₆₀H₅₂ (254 meV) is much larger than that of C₆₀ (169 meV). Hydrogenation leads to a large difference in λ_h , 175–441 meV. Isomer **6** has λ_h as large as C₆₀.

C ₆₀ H ₅₂	λ_h^+	λ_h^0	λ_h	k'_h
1	163	174	337	0.14
2	204	237	441	0.04
3	100	104	204	0.65
4	86	94	180	0.87
5	92	96	188	0.78
6	86	89	175	0.92
Average	122	132	254	0.36

Table 2. Reorganization energies (λ_h in meV) and rate constants (k'_h) for hole transport in C₆₀H₅₂. The average value over six C₆₀H₅₂ isomers is also shown.

Values of λ_h and k'_h for C₆₀H₅₄ isomers are shown in Table 3. On average, λ_h^+ of C₆₀H₅₄ is 176 meV, which is much larger than that of C₆₀ by 81 meV, and λ_h^0 of C₆₀H₅₄ is 181 meV, which is much larger than that of C₆₀ by 107 meV. The average value of λ_h of C₆₀H₅₄ (357 meV) is much larger than that of C₆₀. It is interesting that the values of λ_h are in the range 254–397 meV and there is not so large a difference.

Values of λ_h and k'_h for C₆₀H₅₆ isomers are shown in Table 4. On average, λ_h^+ of C₆₀H₅₆ is 140 meV, which is much larger than that of C₆₀ by 45 meV, and λ_h^0 of C₆₀H₅₆ is 154 meV, which is much larger than that of C₆₀ by 80 meV. The average value of λ_h for C₆₀H₅₆ (294 meV) is

$C_{60}H_{54}$	λ_h^+	λ_h^0	λ_h	k_h'
1	122	132	254	0.36
2	182	190	372	0.09
3	192	196	388	0.08
4	187	177	363	0.10
5	182	187	368	0.10
6	214	184	397	0.07
7	174	186	360	0.11
8	176	180	356	0.11
9	158	170	328	0.15
10	188	194	382	0.08
11	183	187	369	0.10
12	178	187	364	0.10
13	164	174	338	0.14
14	160	185	345	0.13
15	184	179	363	0.10
16	179	188	367	0.10
Average	176	181	357	0.12

Table 3. Reorganization energies (λ_h in meV) and rate constants (k_h') for hole transport in $C_{60}H_{54}$. The average value over 16 $C_{60}H_{54}$ isomers is also shown.

much larger than that for C_{60} . The values of λ_h are in the range 230–501 meV. Isomer **2** has the largest λ_h of more than 500 meV.

$C_{60}H_{56}$	λ_h^+	λ_h^0	λ_h	k_h'
1	180	186	366	0.10
2	217	284	501	0.02
3	126	141	267	0.31
4	128	121	249	0.38
5	119	123	242	0.41
6	123	129	252	0.37
7	107	123	230	0.47
8	118	124	242	0.41
Average	140	154	294	0.23

Table 4. Reorganization energies (λ_h) and rate constants (k_h') for hole transport in $C_{60}H_{56}$. The average value over eight $C_{60}H_{56}$ isomers is also shown.

λ_h and k_h' of $C_{60}H_{58}$ are shown in Table 5. On average, λ_h^+ of $C_{60}H_{58}$ is 606 meV, which is much larger than that of C_{60} by 511 meV and λ_h^0 of $C_{60}H_{58}$ is 468 meV, which is much larger than that of C_{60} by 394 meV. The average value of λ_h of $C_{60}H_{58}$ (1074 meV) is much larger than that of C_{60} . It is interesting that the values of λ_h are in the range 392–2411 meV. Isomers **1**, **2**, and **4** have smaller λ_h .

C ₆₀ H ₅₈	λ_h^+	λ_h^0	λ_h	k_h'
1	205	263	467	0.03
2	196	214	409	0.06
3	1323	1089	2411	0.00
4	184	208	392	0.08
5	1235	607	1842	0.00
6	704	478	1182	0.00
7	693	513	1206	0.00
8	585	463	1049	0.00
9	543	458	1001	0.00
10	444	366	810	0.00
11	556	488	1044	0.00
Average	606	468	1074	0.00

Table 5. Reorganization energies (λ_h) and rate constants (k_h') for hole transport in C₆₀H₅₈. The average value over 16 C₆₀H₅₈ isomers is also shown.

These results mean that highly hydrogenated C₆₀H₅₂ – C₆₀H₅₈ are generally not suited for hole-transport materials.

5.4. C₆₀H₆₀

C₆₀H₆₀⁺ has nine electrons in fivefold degenerate h_u orbitals. Thus, C₆₀H₆₀⁺ has an H_u degenerate electronic state, and symmetry lowering because of the Jahn–Teller effect [21] stabilizes C₆₀H₆₀⁺. The most stable structure of C₆₀⁺ was calculated as having D_{3d} symmetry, and its λ_h^+ is 101 meV in our calculation. The value of λ_h^0 for C₆₀⁺(D_{3d}) was calculated as 40 meV. Thus, the reorganization energy for hole transport, λ_h , is 140 meV. Similar to C₆₀, λ_h^+ is much larger than λ_h^0 because of the Jahn–Teller effect. k_h' of C₆₀H₆₀⁺ is 1.44 times as large as that of C₆₀.

5.5. Summary

Figure 6 shows minimum and average values of λ_h for C₆₀H_{*n*}. C₆₀ and C₆₀H₆₀ have only one isomer so that the minimum values are equal to the average values. From the systematic discussion through C₆₀H_{*n*} (*n* = 2, 4, 6, and 8), it was found that hydrogenation has a large effect on the improvement of hole-transport properties (λ_h). The minimum values of λ_h decrease as the number of hydrogen atoms increases: C₆₀ (169 meV) → C₆₀H₂-6 (101 meV) → C₆₀H₄-1 (83 meV) → C₆₀H₆-1 (71 meV). However, λ_h increases for C₆₀H₈-5 (81 meV). The average values of λ_h change as C₆₀ (169 meV) → C₆₀H₂ (174 meV) → C₆₀H₄ (134 meV) → C₆₀H₆ (127 meV) → C₆₀H₈ (113 meV). The average λ_h of C₆₀H₄ (134 meV) is almost as large as that of C₆₀H₂-1 (133 meV), but the average λ_h of C₆₀H₆ (127 meV) is much larger than that of C₆₀H₄-1 (83 meV), and the average λ_h of C₆₀H₈ (113 meV) is much larger than that of C₆₀H₆-1 (71 meV). Highly hydrogenated C₆₀H_{*n*} generally has large λ_h . The average λ_h is C₆₀H₅₂ (254 meV), C₆₀H₅₄ (357 meV), C₆₀H₅₆ (294 meV), C₆₀H₅₈ (1074 meV), and C₆₀H₆₀ (140 meV). Only C₆₀H₆₀ has a smaller λ_h than C₆₀.

Figure 6. Dependence of minimum and average values of λ_h on the degree of hydrogenation. The average value of λ_h for $C_{60}H_{58}$ is very large (1074 meV), therefore it is not shown in the figure.

6. Analysis for molecular design

6.1. Geometrical relaxation

The reorganization energy is a stabilization energy by geometrical relaxation originating from the change in electronic structure [64–66]. The strong forces on the nuclei generally result in large λ and geometrical relaxation. In our previous publications, we defined parameters Δr that characterize the geometrical relaxation as

$$\Delta r = \sum_i |\Delta r_i|, \quad (7)$$

where Δr_i is the difference in the i th bond length between neutral and cationic states. The summation is taken over all bonds. It has already been shown that there is an almost linear relationship between Δr and λ_h for $C_{60}H_n$ ($n = 2, 4$, and 6) [11]. Figure 7 shows the relationship between λ and Δr for hole transport in $C_{60}H_8$, $C_{60}H_{52}$, $C_{60}H_{54}$, $C_{60}H_{56}$, $C_{60}H_{58}$, and $C_{60}H_{60}$. A linear relationship between Δr and λ_h is observed for $C_{60}H_8$ and $C_{60}H_{58}$. A clear linear relationship is not found for $C_{60}H_{52}$, $C_{60}H_{54}$, and $C_{60}H_{56}$ because the values of the reorganization energy for these species are almost the same. When the values of Δr are the same, $C_{60}H_8$ has a smaller reorganization energy but $C_{60}H_{58}$ has a larger reorganization energy.

6.2. Molecular orbital pattern

It is well known that the electronic properties of the HOMO have a close relation to hole-transport properties. Therefore, we focus on the distribution of the HOMOs of $C_{60}H_n$. The HOMO of C_{60} , which is originally fivefold degenerate, splits because of the interaction between C_{60} and the H atoms. The distribution of the HOMO easily changes depending on the interaction between C_{60} and the H atoms.

Figure 7. Relationship between reorganization energy (λ) and geometrical relaxation (Δr) for hole transport in $C_{60}H_n$ ($n = 8, 52, 54, 56, 58$, and 60).

The HOMOs of isomer-1 of $C_{60}H_n$ are shown in Figure 8. The HOMOs of $C_{60}H_8$ -1 and other lowly hydrogenated fullerenes [11, 13, 14] are distributed over the whole molecule. In

Figure 8. HOMOs of isomer-1 of $C_{60}H_n$.

contrast, the HOMOs of $C_{60}H_{52}-1$, $C_{60}H_{54}-1$, $C_{60}H_{56}-1$, and $C_{60}H_{58}-1$ are localized around the nonhydrogenated C atoms. Therefore, highly hydrogenated C_{60} has a large reorganization energy. In particular, the HOMO of $C_{60}H_{58}-1$ is localized on two carbon atoms, therefore the reorganization energy is very large. The HOMO of $C_{60}H_{60}$ is delocalized over the whole molecule because $C_{60}H_{60}$ has high symmetry, so that the value of λ_h is smaller than that for other highly hydrogenated fullerenes.

7. Summary

Systematic analyses of reorganization energies of hydrogenated fullerenes $C_{60}H_n$ ($n = 2, 4, 6, 8, 52, 54, 56, 58$, and 60) give us very important knowledge for efficient design of useful C_{60} materials:

- Considering only 1,2-addition, $C_{60}H_6-1$ has the smallest reorganization energy (71 meV). Further hydrogenation does not reduce the reorganization energy.
- Highly hydrogenated fullerenes, especially $C_{60}H_{58}$, have very large reorganization energies because the HOMOs are localized around nonhydrogenated carbon atoms. Therefore, these C_{60} derivatives are not suited for hole-transport materials.
- However, $C_{60}H_{60}$ has a smaller reorganization energy than other highly hydrogenated fullerenes and C_{60} because the HOMO of $C_{60}H_{60}$ is distributed over the whole molecule.
- There is a linear relationship between the reorganization energy and the geometrical relaxation. When the values of Δr are the same, lowly hydrogenated fullerenes have smaller reorganization energies than highly hydrogenated fullerenes.

Acknowledgments

This work was supported by Grant-in-Aid for Scientific Research on Innovation Areas from the Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 20118007) and Grant-in-Aid for Scientific Research (C) from Japan Society for Promotion of Sciences (No. 24560930). The author would like to thank Dr. Shigekazu Ohmori of the National Institute of Advanced Industrial Science and Technology (AIST) and Dr. Hiroshi Kawabata of Hiroshima University for collaboration in this research theme and helpful comments on this chapter. Theoretical calculations were mainly carried out using the computer facilities at the Research Institute for Information Technology, Kyushu University.

Author details

Ken Tokunaga
Division of Liberal Arts, Kogakuin University, Tokyo, Japan

8. References

- [1] Fong HH, Lun KC, So SK (2002) Chem. phys. lett. 407: 353.
- [2] Tang CW, VanSlyke SA (1987) Appl. phys. lett. 51: 913.
- [3] Brédas JC, Beljonne D, Coropceanu V, Cornil J (2004) Chem. rev. 104: 4971.
- [4] Murphy AR, Fréchet JMJ (2007) Chem. rev. 107: 1066.

- [5] Coropceanu V, Cornil J, da Silva Filho DA, Olivier Y, Silbey R, Brédas JL, Chem. rev. 107: 926.
- [6] Mori T (2008) J. phys.: condens. matter 20: 184010.
- [7] Sakanoue K, Motoda M, Sugimoto M, Sakaki S (1999) J. phys. chem. A 103: 5551.
- [8] Sancho-García JC, Horowitz G, Brédas JL, Cornil J (2003) J. chem. phys. 119: 12563.
- [9] Hutchison GR, Ratner MA, Marks TJ (2005) J. am. chem. soc. 127: 16866.
- [10] Pan JH, Chiu HL, Chen L, Wang BC (2006) Comput. mater. sci. 38: 105.
- [11] Tokunaga K (2011) In: Velasquez MA editor. Organic Semiconductors: Properties, Fabrication and Applications. New York: Nova Science Publishers.
- [12] Tokunaga K (2012) In: Verner RF, Benvegnu C, editors. Handbook on Fullerene: Synthesis, Properties and Applications. New York: Nova Science Publishers.
- [13] Tokunaga K, Ohmori S, Kawabata H, Matsushige K (2008) Jpn. j. appl. phys. 47: 1089.
- [14] Tokunaga K, Kawabata H, Matsushige K (2008) Jpn. j. appl. phys. 47: 3638.
- [15] Tokunaga K (2009) Chem. phys. lett. 476: 253.
- [16] Tokunaga K, Ohmori S, Kawabata H (2009) Thin solid films 518: 477.
- [17] Tokunaga K, Ohmori S, Kawabata H (2011) Jpn. j. appl. phys. 50: 01BA03.
- [18] Tokunaga K, Ohmori S, Kawabata H (2011) Mol. cryst. liq. cryst. 539: 252(592).
- [19] Tokunaga K, Ohmori S, Kawabata H (2012) Jpn. j. appl. phys. accepted.
- [20] Könenkamp R, Priebe G, Pietzak B (1999) Phys. rev. B 60: 11804.
- [21] Jahn HA, Teller E (1937) Proc. r. soc. London, ser. A 161: 220.
- [22] Ceulemans A, Fowler PW (1990) J. chem. phys. 93: 1221.
- [23] Singh TB, Marjanović M, Matt GJ, Günes S, Sariciftci NS, Ramil AM, Andreev A, Sitter H, Schwödiauer R, Bauer S (2005) Org. electron. 6: 105.
- [24] Kitamura M, Kuzumoto Y, Kamura M, Aomori S, Arakawa Y (2007) Appl. phys. lett. 91: 183514.
- [25] Singh TB, Marjanović M, Stadler P, Auinger M, Matt GJ, Günes S, Sariciftci NS, Schwödiauer R, Bauer S (2005) J. appl. phys. 97: 083714.
- [26] Anthopoulos TD, de Leeuw DM, Cantatore E, van't Hof P, Alma J, Hummelen JC (2005) J. appl. phys. 98: 054503.
- [27] Kubo M, Iketani K, Kaji T, Hiramoto M (2011) Appl. phys. lett. 98: 073311.
- [28] Marcus RA (1956) J. chem. phys. 24: 966.
- [29] Horowitz G (1998) Adv. mater. 10: 365.
- [30] Nelsona SF, Lin YY, Gundlach DJ, Jackson TN (1998) Appl. phys. lett. 72: 1854.
- [31] Dimitrakopoulos CD, Mascaró DJ (2001) IBM j. res. dev. 45: 11.
- [32] Li XY, Tang XS, He FC (1999) Chem. phys. 248: 137.
- [33] Wu Q, Van Voorhis T (2006) J. chem. phys. 125: 164105.
- [34] Frisch, MJ *et al.* (2003) Gaussian 03 (Revision C. 02) Pittsburgh: Gaussian, Inc.
- [35] Henderson CC, Cahill PA (1993) Science 259: 1885.
- [36] Henderson CC, Rohlfing CM, Gillen KT, Cahill PA (1994) Science 264: 397.
- [37] Ballenweg S, Gleiter R, Krätschmer W (1993) Tetrahedron lett. 34: 3737.
- [38] Becker L, Evans TP, Bada J (1993) J. org. chem. 58: 7630.
- [39] Avent AG, Darwish AD, Heimbach DK, Kroto HW, Meidine MF, Parsons JP, Remars C, Roers R, Ohashi O, Taylor R, Walton DRM (1994) J. chem. soc., perkin trans. 2: 15.
- [40] Billups WE, Luo W, Gonzalez A, Arguello D, Alemany LB, Marriott T, Saunders M, Jiménez-Vázquez HA, Khong A (1997) Tetrahedron lett. 38: 171.
- [41] Meier MS, Corbin PS, Vance VK, Clayton M, Mollman M, Poplawska M (1994) Tetrahedron lett. 35: 5789.

- [42] Meier MS, Bergosh RG, Laske Cooke JA, Spielmann HP, Weedon BR (1997) *J. org. chem.* 62: 7667.
- [43] Fukuzumi S, Suenobu T, Kawamura S, Ishida A, Mikami K (1997) *Chem. commun.* 291.
- [44] Fukuzumi S, Suenobu T, Patz M, Hirasaka T, Itoh S, Fujitsuka M (1998) *J. am. chem. soc.* 120: 8060.
- [45] Mandrus D, Kele M, Hettich RL, Guiochon G, Sales BC, Boatner LA (1997) *J. phys. chem. B* 101: 123.
- [46] Wang GW, Li YJ, Li FB, Liu YC (2005) *Lett. org. chem.* 2: 595.
- [47] Haufler RE, Conceicao J, Chibante LPF, Chai Y, Byrne NE, Flanagan S, Haley MM, O'Brien SC, Pan C, Xiao Z, Billups WE, Ciufolini MA, Hauge RH, Margrave JL, Wilson LJ, Curl RF, Smalley RE (1990) *J. phys. chem.* 94: 8634.
- [48] Ruchardt C, Gerst M, Ebenhoch J, Beckhaus H, Campbell E, Tellgmann R, Schwarz H, Weiske T, Pitter S (1993) *Angew. chem.* 32: 584.
- [49] Shigematsu K, Abe K, (1992) *Chem. express* 7: 905.
- [50] Jin C, Hettich R, Compton R, Joyce D, Blencoe J, Burch T (1994) *J. phys. chem.* 98: 4215.
- [51] Matsuzawa N, Dixon DA, Fukunaga T (1992) *J. phys. chem.* 96: 7594.
- [52] Nossal J, Saini RK, Alemany LB, Meier M, Billups WE (2001) *Eur. j. org. chem.*: 4167.
- [53] Shao Y, Jiang Y (1995) *Chem. phys. lett.* 242: 191.
- [54] Cahill PA, Rohlfing CM (1996) *Tetrahedron* 52: 5247.
- [55] Cross RJ, Jiménez-Vázquez HA, Li Q, Saunders M, Schuster DI, Wilson SR, Zhao H (1996) *J. am. chem. soc.* 118: 11454.
- [56] Bergosh RG, Meiser MS, Cooke JAL, Spielmann HP, Weedon BR (1997) *J. org. chem.* 62: 7667.
- [57] Alemany LB, Gonzalez A, Billups WE, Willcott MR, Ezell E, Gozansky E (1997) *J. org. chem.* 62: 5771.
- [58] Canton SE, Yencha AJ, Kuk E, Bozek JD, Lopes MCA, Snell G, Berrah N (2002) *Phys. rev. lett.* 89: 045502.
- [59] Manini N, Gattari P, Tosatti E (2003) *Phys. rev. lett.* 91: 196402.
- [60] Bendale RD, Stanton JF, Zerner MC (1992) *Chem. phys. lett.* 194: 467.
- [61] Boese AD, Scuseria GE (1998) *Chem. phys. lett.* 294: 233.
- [62] Manini N, Corso AD, Fabrizio M, Tosatti E (2001) *Philos. mag. B* 81: 793.
- [63] Devos A, Lannoo M (1998) *Phys. rev. B* 58: 8236.
- [64] Sato T, Tokunaga K, Tanaka K (2006) *J. chem. phys.* 124: 024314.
- [65] Tokunaga K, Sato T, Tanaka K (2006) *J. chem. phys.* 124: 154303.
- [66] Sato T, Tokunaga K, Tanaka K (2008) *J. phys. chem. A* 112: 758.