First-principles electronic structure calculations for peanut-shaped C_{120} molecules

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Abstract

Using the first-principles real-space finite-difference method, we have theoretically examined optimized structures and electronic energy levels of three peanut-shaped C_{120} molecules (C_{60} dimers), namely, P55-, P56-, and P66-C_{120} molecules. Our calculations show that as the number of eight-membered rings included in each C_{120} molecule increases, the total energy becomes large and the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gap becomes small. For the P56-C_{120} molecule, the LUMO is found to be localized at one C_{60} component, while for the other molecules, the LUMOs are extended over the entire molecule. This fact is understood from the symmetry/asymmetry in the atomic configuration of the three C_{120} molecules.

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1. Introduction

Recently, increasing attention has been focused on polymerized C_{60} in terms of its application to building blocks of nanoscale devices. Since the first report on the polymerization of C_{60} using photolirradiation [1], polymerization has been induced using various techniques, e.g., high-pressure and high-temperature application [2], alkali-metal doping [3], mechanochemical reaction [4], and electron-beam (EB) irradiation [5]. In particular, there is an interesting study reported by Onoe et al., in which a C_{60} film polymerized by EB irradiation is found to consist of peanut-shaped C_{60} polymer with negative curvature [6]. They also measured the resistivity of the polymerized film to be 7 Ω cm which is considerably smaller than that of solid C_{60} (10^8–10^{14} Ω cm). This surprising transition from an insulator to a conductor of the C_{60} film would be useful for developing carbon-based nanodevices. To date, a few theoretical studies on the optimized geometries and IR analyses of peanut-shaped C_{60} dimers as a basic unit of the polymer have been carried out using the tight-binding, MNDO, and AM1 methods [7–9]. However, details regarding the change of electronic structures upon coalescence of two C_{60} molecules have not been sufficiently discussed and clarified.

In this paper, we direct our attention to three types of peanut-shaped C_{120} molecules (C_{60} dimers), P55-, P56-, and P66-C_{120} molecules (see Fig. 1), and investigate the electronic structures of their ground states on the basis of first-principles structural optimizations within the framework of the density functional theory. The P55-C_{120} molecule is found to have the lowest total energy among the three molecules. We also find that the lowest unoccupied molecular orbital (LUMO) of the P56-C_{120} molecule is localized at one C_{60} component with eight-membered rings, while those of P55- and P66-C_{120} molecules extend over the entire molecule. Such localization of electronic orbital is not seen in the highest occupied molecular orbital (HOMO) of the three peanut-shaped C_{120} molecules.

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2. Calculation method and models

All the computations presented here were carried out using the calculation package based on the real-space finite-difference method, which enables us to determine electronic ground states and optimized atomic structures self-consistently with a high degree of accuracy by the timesaving double-grid technique [10]. The electron–ion interactions for carbon atoms are described in the norm-conserving pseudopotentials [11,12], and the exchange-correlation effects are treated by the local-density approximation (LDA) [13]. We take a cutoff energy of 91 Ry (1 Ry = 13.6 eV), which corresponds to a real-space grid width of 0.33 a.u. (1 a.u. = 0.529 Å).

The geometrical structures of the three peanut-shaped C₁₂₀ molecules are illustrated in Fig. 1. These peanut-shaped molecules can be modeled by (i) making a hexagon of one C₆₀ molecule face to a hexagon of another C₆₀ molecule, (ii) breaking three of the six bonds composing each hexagon for the creation of dangling bonds, and (iii) combining the dangling bonds of one C₆₀ molecule with those of the other C₆₀ molecule. There are two kinds of bonds within a C₆₀ molecule; one is the bond shared by two hexagons (h–h bond), and another is the bond shared by a hexagon and a pentagon (h–p bond). Then, in step (ii), there are two ways of cutting the three bonds of a hexagon in each C₆₀ molecule, namely, by breaking three h–h bonds and by breaking three h–p bonds. When the h–p bonds in both of the two C₆₀ molecules are broken to form a dimer, six seven-membered rings consequently appear in the junction region with negative curvature. As shown in Fig. 1, we define this peanut-shaped product as P₅₅-C₁₂₀ molecule. There is twofold symmetry with respect to the z axis. In the case of coalescence of one C₆₀ molecule with broken h–h bonds and another one with broken h–p bonds, three eight-membered rings and three seven-membered rings are formed in the junction region. This peanut-shaped product is called P₅₆-C₁₂₀ molecule, which has no symmetry with respect to the z axis. When a peanut-shaped molecule is formed from two C₆₀ molecules with broken h–h bonds, one can see six eight-membered rings in the junction region. This coalescence product is defined as P₆₆-C₁₂₀ molecule, and it also has twofold symmetry the same as the P₅₅-C₁₂₀ molecule. In all computations, the unit cell containing a C₁₂₀ molecule has the dimensions of 24, 15, and 15 a.u. in the directions of x, y, and z, respectively (see Fig. 1). To determine the optimized geometries of the three C₁₂₀ molecules, structural relaxations have been carried out until the remaining forces acting on the atoms are less than 0.004 Ry/A.

3. Results and discussions

The electronic and geometrical properties of P₅₅-, P₅₆-, and P₆₆-C₁₂₀ molecules are listed in Table 1. Here, total energies E₀ of the C₁₂₀ molecules are measured from the total energy of two C₆₀ molecules separated infinitely. The trend of the total energy is in agreement with the results of a tight-binding study by Esfarjani et al. [7]; the total energy of three C₁₂₀ molecules increases as the number of eight-membered rings included in the molecules increases, and the P₆₆-C₁₂₀ molecule is higher in energy than two isolated C₆₀ molecules. However, the dispersion of the total energies determined by our calculations is smaller than that determined by the tight-binding calculations reported previously.

![Fig. 1. Atomic geometries of P₅₅- (top), P₅₆- (middle), and P₆₆-C₁₂₀ (bottom) molecules. The numbers of atoms composing some rings are indicated in figures.](image-url)
Energy gap, $E_{\text{gap}}$, is given by the difference in energy between HOMO and LUMO shown in Fig. 2. In comparison with the isolated C$_{60}$ molecule, the three coalescent C$_{120}$ molecules show smaller $E_{\text{gap}}$, as shown in Table 1. Since LDA generally underestimates the energy gap, we do not present a more detailed discussion on the absolute values of the energy gaps in this paper.

Also shown in Table 1 are intersphere distances $d_0$ in the peanut-shaped C$_{120}$ molecules, that is, the distance between the centers of mass of the respective C$_{60}$ components. All the intersphere distances for P55-, P56-, and P66-C$_{120}$ molecules are approximately 8.6 Å, which are about 14% shorter than the center-to-center distance of 10.0 Å in a face-centered-cubic (fcc) C$_{60}$ crystal [14]. This suggest that polymerization of C$_{60}$ in an fcc crystal causes a decrease in volume. Moreover, the reduction rate of the volume is found to be negligibly dependent on the difference in atomic geometry around the junction regions (see Fig. 1).

Fig. 2 shows electronic energy levels of the three C$_{120}$ molecules. In all cases of the C$_{120}$ molecules, the fivefold-degenerated HOMO of an isolated C$_{60}$ molecule is decomposed into a doubly degenerated HOMO and other states as two C$_{60}$ molecules coalesce. For the LUMO of the C$_{120}$ molecules, we can see a difference between the P55-C$_{120}$ molecule and others: In the case of the P55-C$_{120}$ molecule, the threefold-degenerated LUMO of an isolated C$_{60}$ molecule is decomposed into a nondegenerated LUMO and other states, and in the cases of P56- and P66-C$_{120}$ molecules, the LUMO of the C$_{60}$ molecule is found to be decomposed into a twofold-degenerated LUMO and other states.

Fig. 3 shows spatial density distributions of HOMO and LUMO of the peanut-shaped C$_{120}$ molecules. Electrons are seen to distribute on the cage surface of each molecule. In the figures of HOMO (Fig. 3b, d and f), we can observe that the HOMO expands over the entire molecule. While for P55- and P66-C$_{120}$ molecules, the HOMOs are found to have twofold symmetry with respect to the $z$ axis, for the P56-C$_{120}$ molecule, the HOMO is not found to have such a symmetry. This tendency is also observed in the figures of LUMO (Fig. 3a, c and e), and is considered to reflect the respective atomic geometries of the molecules. It is interesting to point out that the degenerated LUMO of the P56-C$_{120}$ molecule is completely localized at one C$_{60}$ component while the LUMO of the other molecule is delocalized over the molecule. If we consider a linear chain of P56-C$_{120}$ molecules, and if the observed localization in the P56-C$_{120}$ molecule is retained even after the formation of the linear chain, the LUMO of the molecule will be a single electron state of the C$_{60}$ component.
of the chain, we would expect poor conductivity along the chain. On the other hand, linear chains formed by P55- or P66-C_{120} molecules are expected to be conductive upon electron doping to the LUMO-derived conduction band.

4. Conclusions

Employing the first-principles real-space finite-difference method, we have calculated and analyzed the optimized geometries and electronic structures of three types of peanut-shaped C_{120} molecules. Our calculations of the total energies and electronic energy levels for the molecules show that the P55-C_{120} molecule has the lowest total energy, and that the P66-C_{120} molecule has the smallest HOMO–LUMO energy gap. Energy gaps of the three C_{120} molecules are also shown to be small in comparison with that of an isolated C_{60} molecule. We observe the clear localization of LUMO only for the P56-C_{120} molecule, whereas the LUMO for the other two molecules and the HOMO for all the molecules are extended over the entire molecule. We surmise that the linear chain of peanut-shaped C_{120} molecules may exhibit conductivity depending on the atomic geometry of C_{120} molecules composing the chain.

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