Radical spin interaction in one-dimensional chains of decamethyl C₆₀

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Abstract

Based on density functional theory, we examine the energetics and electronic structure of chains of decamethyl C₆₀ with two stacking conformations. The decamethyl C₆₀ chains possess various spin configurations arising from the combinations of intramolecular and intermolecular spin interactions. The antiparallel spin arrangement within and between molecules is the ground state, and the intramolecular spin interaction is four times larger than the intermolecular interaction. These decamethyl C₆₀ chains possess small dispersion bands near the Fermi level arising from the π states distributed on pentagonal rings, which are well separated from each other because of segmentation by the attached methyl groups.

Keywords: Decaorgano C₆₀, Electronic structure, One-dimensional chain, Spin polarization

1. Introduction

Fullerenes [1, 2] are used as starting materials to design various derivatives which often possess unusual geometric and electronic properties owing to their hollow-cage structure with nanometer diameter [3, 4]. For example, it has been pointed out that the nanoscale space inside fullerenes is capable of accommodating foreign atoms and molecules [5], leading to various com-

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plexes with interesting physical and chemical properties. Indeed, following the macroscopic production of C_{60} [6] and other fullerenes [7, 8, 9, 10, 11, 12], higher fullerenes containing metal atoms (metallofullerenes) were synthesized by laser evaporation of carbon rods containing metal atoms [13, 14, 15, 16]. In addition to the encapsulation of atoms and molecules, chemical modification of the fullerene cages by functional groups leads to various fullerene derivatives with unique geometries and interesting physical properties [17, 18, 19, 20, 21, 22]: C_{60} derivatives with nanometer-scale badminton shuttlecock shape have been synthesized under controlled modifications of C_{60} by the attachment of five aromatic functional groups [17, 18, 19]. Further selective multiple additions of organic molecules onto pentaorgano C_{60} results in decaorgano C_{60} , in which the attached organic groups divide the spherical π -electron system of C_{60} into two pentagonal π rings and a cyclophenanthrene π network. Because of this segmentation of spherical π networks into one or two pentagonal π rings, these fullerene derivatives possess radical spins on the pentagonal π rings [20, 23, 24]. In our previous work, the decamethyl C_{60} was shown to possess various spin states that are tunable by applying an external electric field [24].

Fullerenes and their derivatives are known to form condensed phases in which the molecules act as atom-like constituent units similar to atoms in conventional solids [25]. In the solid phase, the molecules are weakly bound to each other and retain their hollow-cage covalent network. In these condensed phases, because of their structural hierarchy, the electronic properties of the solid phase reflect the characteristic features of each constituent. For example, a face-centered cubic C_{60} possesses small dispersion band corresponding with its molecular states, leading to the superconductivity by injecting additional electrons into unoccupied t_{1u} states [26, 27, 28, 29]. In our previous calculation, we demonstrated that the stacked pentaorgano C_{60} possesses an antiferromagnetic spin arrangement in its ground state, rather than the ferromagnetic state [20].

In this work, we aim to investigate the spin states of one-dimensional chains of decamethyl C_{60} with respect to their inter- and intra-molecular radical spin arrangement using first-principles total-energy calculations based on density functional theory. Our calculations show that an antiparallel spin arrangement between two radical spins, not only in each molecule but also between adjacent molecules, is the most energetically favorable among five possible spin states studied here. Energetics of these spin states revealed that the spin-spin interactions are 48 meV and 11 meV for within and between

molecules, respectively, indicating that the intramolecular spin interaction dominates the spin-spin interaction in one-dimensional chains of decamethyl C_{60} . Furthermore, the intermolecular radical spin interaction depends on the mutual molecular arrangement in the chains. Our finding clearly shows the possible spin conformations of the decamethyl C_{60} chain and their energetics, which are important to consider for practical applications employing these molecules in spin electronic devices in the near future.

2. Calculation methods and structural model

All calculations were performed using density functional theory [30, 31] as implemented in the Simulation Tool for Atom TEchnology (STATE) package [32]. We use the local spin density approximation to treat the exchange-correlation energy of interacting electrons [33, 34] to account for the spin degree of freedom of the system and to simulate the weak intermolecular interaction to investigate the radical spin interaction under the equilibrium molecular spacing. Ultrasoft pseudopotentials generated using the Vanderbilt scheme were used to describe the interaction between electrons and ions [35]. The valence wave functions and charge density were expanded by the plane-wave basis set with cutoff energies of 25 and 225 Ry, respectively.

In this work, to investigate the molecular orientation dependence of the spin interaction in the decamethyl C_{60} chains, we consider two different intermolecular conformations: the side-to-side conformation in which the highest symmetry molecular axis is normal to the chain direction, and the head-to-head arrangement in which the molecular axis is parallel to the chain. To investigate long-range modulation in the spin arrangements, the unit cell contains two molecules with the same molecular orientation. The atomic structures and intermolecular spacing were optimized until the force acting on each atom was less than 5 mRy/Å. Each molecular chain is separated from its adjacent chains by 12 Å-vacuum spacing to exclude the effect arising from the periodic images. Integration over the one-dimensional Brillouin zone was carried out using an equidistance mesh of two k-points which allow us to make qualitative discussion on relative total energy of C_{60} chain [36]. Under the equilibrium arrangement of decamethyl C_{60} chains with these molecular conformations, we investigate the total energy of various spin states.

(a)

(b)

Figure 1: Structural models of decamethyl C₆₀ chains with (a) the head-to-head and (b) side-to-side molecular conformations.

(a)

(b)

Figure 2: (Color online) Total energies of decamethyl C₆₀ chains with the (a) head-to-head and (b) side-to-side conformations as a function of the intermolecular distance. The energies are relative to the total energy of an isolated decamethyl C₆₀ molecule.

3. Results and Discussion

Figure 2 shows the total energy of the decamethyl C_{60} chains with the side-to-side and head-to-head molecular conformations as a function of the intermolecular distance, **which corresponds to the distance between the center of mass of adjacent molecule.** The chains have energy minima at an intermolecular distance of 10.2 and 11.1 Å for the side-to-side and head-to-head conformations, respectively, indicating that the equilibrium intermolecular distance strongly depends on the molecular conformations. The conformation dependence is caused by the steric hindrance of the methyl group attached to the C_{60} . In the case of the side-to-side conformation, the methyl groups are alternately arranged between adjacent decamethyl C_{60} leading to a small distance which is almost the same at the intermolecular distance of conventional solid C_{60} . In this case, the methyl groups do not affect the intermolecular distance. In contrast, for the head-to-head conformation, the methyl groups act as the steric hindrance between the two molecules, resulting in the remarkable elongation of the intermolecular distance.

At the equilibrium intermolecular distance, the total energies of the decamethyl C_{60} chains are lower than that of an isolated decamethyl C_{60} by 188 and 318 meV per molecule for the side-to-side and head-to-head conformations, respectively. Furthermore, the total energy of the chain with intermediate arrangements between the head-to-head and side-to-side arrangements, in which the molecules are tilted by 30 and 60 degree with respect to the chain direction, are 136 and 101 meV, indicating that the conformations are less stable than the head-to-head conformation. Thus, the head-to-head conformation is the ground state molecular conformation for one-dimensional chains of decamethyl C_{60} . Note that the intermolecular interaction per molecular coordination number is stronger than that of the solid C_{60} by about 20 meV. More interestingly, the interaction for the head-to-head conformation is larger than those for the side-to-side and for the pristine C_{60} , although the intermolecular distance is the largest among these three. This fact indicates that the methyl groups attached to C_{60} play a decisive role in stabilizing the system. Since the methyl groups possesses CH bonds, interactions between the CH bonds and π systems of the molecule decreases the total energy of the chains. In particular, in the case of the head-to-head conformation, electrostatic interaction between pentagonal rings and H atoms substantially stabilizes the chain structure, in which the pentagonal rings and H atoms tend to be negatively and positively charged, respectively, compared with

Figure 3: (Color online) Isosurfaces of polarized electron spins of five spin arrangements of decamethyl C_{60} chains with (a) the head-to-head and (b) side-to-side molecular conformations. **Pink and green isosurfaces denote the polarized electrons with majority and minority spin components.**

the C atoms in the hexagonal networks [37]. Therefore, this large binding energy is ascribed to a cooperative effect between the weak intermolecular interactions and CH/π interactions between adjacent decamethyl C_{60} [38, 39].

At the equilibrium intermolecular distance, we investigate the possible spin arrangements of four radical spins distributed on pentagonal rings in the side-to-side and head-to-head conformations. Figure 3 shows possible spin arrangements on decamethyl C_{60} chains with the side-to-side and head-to-head conformations: We consider antiparallel and parallel spin arrangements between and within the molecules, and find that these five spin arrangements are energetically metastable.

In the case of the head-to-head conformation, among these five spin configurations, the spin state with antiparallel intramolecular and intermolecular spin arrangements (AaAa state) is the ground state in which the polarized electron spins on pentagonal rings are antiferromagnetically aligned along the chain direction. In contrast, the spin state with parallel intramolecular and intermolecular spin arrangements (PpPp state) is the least stable

state among the five, in which the polarized radical spins are ferromagnetically aligned through the molecular chain. The remaining three arrangements have stabilities in between the AaAa and PpPp states. These are described as follows: The chains have antiparallel intramolecular and parallel intermolecular spin configurations (ApAp), one of two molecules possesses a parallel spin arrangement with antiparallel and parallel intermolecular spin arrangement (PpAa), and the chains have a parallel intramolecular and an antiparallel intermolecular spin configuration (PaPa). The relative stability of the spin state decreases with increasing amount of parallel spin pairs both within and between molecules. Thus, the radical spins on the decamethyl C₆₀ chains prefer antiparallel over the parallel spin coupling within each molecule and between adjacent molecules.

In the case of the side-to-side conformation, the AaAa is also the ground state. In addition, the ApAp state, in which the spins in each molecule are antiparallely aligned while the spin between molecules are parallely aligned, is of the same energy within the numerical error. The result indicates that the intermolecular spin-spin interaction is negligible in decamethyl C₆₀ chains with this molecular conformation. Indeed, the least stable state is also doubly degenerate: both the PaPa and PpPp states have equal energies and are the least stable.

Table 1: Relative total energies per unit cell and the number of polarized electron spins ($\Delta N = \int [n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})] dV$) of decamethyl C₆₀ with the side-to-side and head-to-head conformations. Energies are relative to the state with antiparallel intermolecular and intramolecular spin arrangements (AaAa state in Fig. 3).

Spin state	ΔN	Energy (meV)	
		head-to-head	side-to-side
AaAa	0	0	0
ApAp	0	22	0
PpAa	2	57	48
PaPa	0	88	96
PpPp	4	118	96

To introduce a more quantitative discussion of the energetics of spin states of the decamethyl C₆₀ chains, we present the relative total energies of the spin states in Table 1. By comparing the total energies of the AaAa and ApAp states in the head-to-head conformation, we find that the energy cost

to flip the antiparallel spin arrangement between molecules into the parallel spin arrangement is 22 meV per unit cell, which corresponds to twice the intramolecular spin-spin interaction energy or the exchange interaction J_{inter} . As we reported in our previous work, spin-spin interactions within the molecule are $J_{intra}=42$ meV. Thus the intermolecular spin interaction is about a fourth of the intramolecular spin-spin interaction, although the distance between adjacent radical spins is smaller by 3 Å than that within the molecule. **It is plausible that the large spin-spin interaction within molecules is caused by valence electrons mediating the spin-spin interaction as the case of RKKY interaction [40, 41, 42], because of the substantial electron transfer between not only the nearest neighbor but also the next-nearest neighbor atomic sites in sp^2 C network materials.** Therefore, the decamethyl C_{60} chain with the head-to-head conformation is described using a spin chain model containing two exchange interactions J_{intra} and J_{inter} . By combining the J_{intra} and J_{inter} , we can quantitatively examine the relative stabilities of all spin states.

In the case of the chain with the side-to-side conformation, we find unusual spin-spin interaction between adjacent molecules. The antiparallel and parallel spin arrangements between molecules are degenerate with each other to within the numerical error because of the large separation between the two radical spin sites (10 Å). Thus the energetics of the spin states is mainly determined by the individual spin states of each decamethyl C_{60} .

Figure 4 shows the electronic energy bands of the decamethyl C_{60} chains with the side-to-side and head-to-head conformations in the AaAa ground state spin configuration. In both cases, we find that the electronic states near the Fermi level have dispersion of about 100 meV which is narrower than that of the fcc C_{60} (~ 0.5 eV). This small band dispersion is ascribed to the small π - π overlap between adjacent molecules due to the localized nature of the states near the E_F leading to the intermolecular spin ordering (Fig. 5). In both molecular conformations, methyl groups attached to C_{60} act as a steric hindrance preventing substantial π - π overlap between adjacent molecules. Furthermore, in the case of the head-to-head conformation, the segmentation of the π network by the methyl groups also causes the small dispersion bands near the Fermi level. Since the state near the Fermi level is localized on the pentagonal rings surrounded by methyl groups, the pentagonal rings are separated from each other by 3 and 7 Å between and within the molecules, respectively.

In the real system, decamethyl C_{60} is expected to form bulk condensed

Figure 4: (Color online) Electronic structure of decamethyl C_{60} chains with (a) head-to-head and (b) side-to-side molecular conformation in the AaAa ground state spin configuration. The energies are relative to the vacuum level. The highest occupied state is denoted by HO.

Figure 5: Squared wave function at Γ point of the highest occupied and the lowest unoccupied states of decamethyl C_{60} chains with (a) the head-to-head and (b) side-to-side molecular conformations. In each panel, HO and LU denote the wave function of the highest occupied and the lowest unoccupied states, respectively.

phases in which the molecules are three-dimensionally packed in an appropriate manner. In such a solid, because of anisotropic interactions between molecules, the condensed phases may also possess structural anisotropy; it is plausible that the stable condensed phase possesses bundle structures of columns, each of which consists of one-dimensional chains of decamethyl C_{60} with the head-to-head stacking conformation. Thus, an unusual spin ordering is expected to occur because of the delicate balance among the three antiferromagnetic spin exchange interactions J for the intramolecular, intermolecular, and intercolumnar spin interactions.

4. Summary

We studied the energetics and electronic structures of decamethyl C_{60} chains using density functional theory with the local spin density approximation. Our calculations show that the chain with the head-to-head molecular arrangement is more stable than that with the side-to-side conformation because of the substantial CH- π interaction cooperating with the weak intermolecular interaction. At equilibrium intermolecular distances, we investigate the possible spin configurations for these chains and found five possible

spin arrangements in the head-to-head conformation, AaAa, ApAp, PpAa, PaPa, and PpPp where A(P) and a(p) denote the antiparallel (parallel) spin coupling within each molecule and between molecules, respectively. Among these spin configurations, the AaAa state is the ground state where all radical spins are antiferromagnetically aligned within and between molecules. On the other hand, a parallel spin coupling has higher total energy than that with the antiparallel spin coupling. Detailed energetics showed that the spin-spin interaction between adjacent molecules is smaller than that within molecule by about a quarter. In contrast, in the case of the side-to-side conformation, because radical spins between adjacent molecules are sufficiently separated, the intermolecular spin interaction is almost negligible compared with the intramolecular interactions. Electronic structures of these decamethyl C₆₀ chains possess small dispersion bands near the Fermi level arising from the π states being distributed on pentagonal rings, which are well separated from each other due to segmentation by the methyl groups. These small dispersion bands are the physical origin leading to various spin states on the chains.

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