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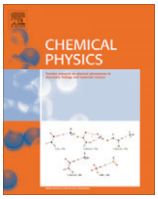

Ground state analysis of magnetic nanographene molecules with modified edge

Narjes Gorjizadeh [a,*], Norio Ota [b], Yoshiyuki Kawazoe [a]

[a] *Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*
[b] *Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8573, Japan*

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ABSTRACT

We study spin states of edge modified nanographene molecules with rectangular and triangular shapes by first principle calculations using density functional theory (DFT) and Hartree–Fock (HF) methods with Møller–Plesset (MP) correlation energy correction at different levels. Anthracene ($C_{14}H_{10}$) and phenalenyl ($C_{13}H_9$), which contain three benzene rings combined in two different ways, can be considered as fragments of a graphene sheet. Carbon-based ferromagnetic materials are of great interest both in fundamental science and technological potential in organic spintronics devices. We show that non-magnetic rectangular molecules such as $C_{14}H_{10}$ can become ferromagnetic with high-spin state as the ground state by dihydrogenization of one of the zigzag edges, while triangular molecules such as $C_{13}H_9$ become ferromagnetic with high-spin state by dehydrogenization of one of the zigzag edges.

1. Introduction

Carbon-based magnetism is a new emerging concept, which attracted the attention of theoretical and experimental scientists. Unlike conventional magnetic materials, whose magnetic properties are due to 3*d* orbital, in organic materials *p* orbitals are responsible for magnetization. The advantage of organic materials is their light weight, flexibility, low spin–orbit interaction and low cost compared to the conventional magnets, which make them promising candidates as organic ferromagnets and for organic spintronics. Room-temperature carbon-based magnetism is evidenced in experiments since 1991 [1–9]. Magnetism in π-conjugated systems is considered to be due to the number of unpaired electrons [10]. It was shown that graphite samples with certain defects have spontaneous magnetization [5]. Existence of ferromagnetism at the zigzag edges of graphene nanoribbons and graphene flakes due to localized edge states is also demonstrated in theoretical studies [11]. However, appearance of the edge states in graphene nanoflakes depends on the size of the structure. Depending on the shape of the nanographene, edge states appear at a critical size [12,13]. As the properties of the graphene nanoribbons and nanoflakes are associated with their edge states, modifications of the edge affect their electronic and magnetic properties to a significant value [14,15]. Kusakabe et al. [16,17] have shown that dihydrogenization of one of the edges of zigzag graphene nanoribbons can make them ferromagnetic. Ota et al. [18,19] have also shown by DFT calculations that edge modified asymmetric nanographenes with one dihydrogenated or dehydrogenated zigzag edge are ferromagnetic structures. The zigzag edges in these structures are large enough to have localized edge states and have singlet ground state before edge modification.

In this work we look for strong magnetism in small nanographene molecules by modifications of their zigzag edge. We seek the spin ground state of $C_{14}H_{7,10,13}$ and $C_{13}H_{7,9,11}$ using first-principle calculations by density functional theory (DFT) and Hartree–Fock (HF) method with MP*n* correlation energy corrections. $C_{14}H_{10}$ and $C_{13}H_9$ contain three benzene rings which are combined in two different ways to yield structures with different shapes and magnetic properties. $C_{14}H_{10}$ is a rectangular molecule with non-magnetic zigzag edges due to small size of the molecule. While $C_{13}H_9$ is a triangular molecule with one net spin, due to the difference in the number of the two subsets of site A and B, according to Lieb's rule [20]. Both of these structures can be considered as fragments of a graphene sheet [21,22] and their magnetic properties depend on their shape. We study the stable spin state of these molecules with modified edges by dihydrogenization and dehydrogenization of one of the zigzag edges. Energetically, dihydrogenization of all three carbon atoms of one zigzag edge in $C_{14}H_{13}$ is not the most stable structure, according to Clar's sextet rule [23]. The extra hydrogen atoms tend to attach the zigzag and armchair sites of one ring to preserve the sextet. The dihydrogenated structures presented in this study are physically and artificially modified structures which may be induced by artificial proton irradiation discussed in the experimental work by Esquinazi et al. [5].

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[*] Corresponding author.
E-mail address: gorjizadehn@ihpc.a-star.edu.sg (N. Gorjizadeh).

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We show that the rectangular molecules can become ferromagnetic by dihydrogenization, while triangular molecules become ferromagnetic by dehydrogenization of one the zigzag edges. Although different methods do not agree in the ground state of the structures between high-spin and low-spin states, we show that the DFT methods give the ground states in agreement with the counting rules for hydrogenated, dihydrogenated and dehydrogenated edges [20,24,25]. HF-based methods even with the higher accuracy of MP4 level do not lead to reliable results due to high spin contamination in at least one of the spin states. Using MP*n* correlation energy correction of the HF method up to the 4th order of approximation, we show that the C–C bond-length of the molecule can change due to exchange interaction in transition from low-spin to high-spin state, resulting in changing the sign of the exchange interaction and obtaining a different spin ground state, which does not agree with DFT methods.

2. Method

The structures are optimized for high spin and low spin states by DFT and HF methods, using Gaussian03 and Gaussian09 [26]. We compare the following methods and basis sets: DFT/UB3LYP/6-31+g, DFT/UPBE/6-31+g, UHF/6-31+g, UMP2/6-31+g, UMP2/6-311+g(d,p), UMP4/6-311+g(d,p). The spin contamination is zero or negligible for DFT (UPBE) and hybrid DFT (UB3LYP) calculations, but it is large for most of the structures for HF-based methods. All the structures with non-zero net spins are calculated with unrestricted orbitals to allow different spatial components for spin up and spin down orbitals.

3. Results

Starting from these molecules, $C_{13}H_9$ and $C_{14}H_{10}$, we study the ground state of the structures with different modified edges, i.e. the hydrogenated edge carbons, dehydrogenation and dihydrogenation of one of the zigzag edges, as depicted in Fig. 1. After optimizing the geometries for high-spin and low-spin states, the favored spin state and the energy gap between the two states are studied. Geometries are optimized with energy accuracy of $1 \times e^{-5}$ eV. The high spin and low spin states of the structures of Fig. 1(b)–(f) have total magnetic moment of 1 μB and 3 μB, respectively; while the structure of Fig. 1(a) has total magnetic moment of 0 and 2 μB. The two hydrogen atoms of the dihydrogenated carbons of Fig. 1(c) and (f) are out of plane, with similar angle with the plane of molecule. Table 1 shows the ground state and the absolute value of high-spin/low-spin energy gap (H/L gap) predicted by different methods. The spin-squared expectation value, $<s^2>$, for different methods is also reported at Table 2, to compare the spin contamination, i.e. the deviation from the exact value of $<s^2> = s(s+1)$, which is also shown in the table. UDFT methods have zero or negligible spin contamination, while UHF-based methods have significant spin contamination, which yields error in the ground state wavefunction and the calculated geometry. The problem of spin contamination is common for unrestricted orbitals in the UHF procedure, especially for the systems that the unpaired electrons are delocalized. Increasing electron correlation and size of the basis set may reduce the spin contamination. Hence, we used MP*n* correlation energy corrections up to the 4th level of approximation to reduce the spin contamination. Yet, The UMP4 method has small or negligible spin contamination for one of the spin states, while still large contamination is observed in the other spin state.

All methods find the ground state of $C_{14}H_{10}$ to be the low-spin state, i.e. non-magnetic, as also predicted by Lieb's rule [20]. However the energy gap is varied between 1.017 and 3.218 eV. But different methods do not agree with the ground state of $C_{14}H_7$, with three radical carbons. Disregarding UHF-based methods, which have large spin contamination in at least one of the spin states, the other methods, i.e. UB3LYP and UPBE, agree in the ground state and show that the low-spin state is the favored structure energetically. Higher stability of the low-spin state for $C_{14}H_7$ is in agreement with the prediction by the counting rule of radical carbons suggested by Ota et al. [24]. For this structure, the three unpaired σ bonds at the edge will have lower exchange energy in the anti-parallel configuration. Spin density of the $C_{14}H_7$ for the two spin states calculated by UB3LYP functional is sketched in Fig. 2(a) and (b). The parallel spin configuration in the high-spin state in this figure shows the high unfavorable exchange energy.

In case of $C_{14}H_{13}$, the structure did not converge for UMP2 and UMP4 methods, but the DFT methods predict the high-spin state to be the ground state. However, the structure of a smaller counterpart of the molecule ($C_{10}H_{10}$), which has two dihydrogenated edge carbon, is optimized with similar methods as Table 1 and the high-spin state is the ground state. In low-spin structure of this molecule calculated by UMP2 and UMP4 methods, most of the H atoms are distorted from the plane of the molecule, giving an untidy structure. The counting rule by Maruyama et al. [25] also predicts the high-spin state as the ground state of $C_{10}H_{10}$ and $C_{14}H_{13}$. Fig. 2(c) and (d) depicts the spin density of the $C_{14}H_{13}$ for the

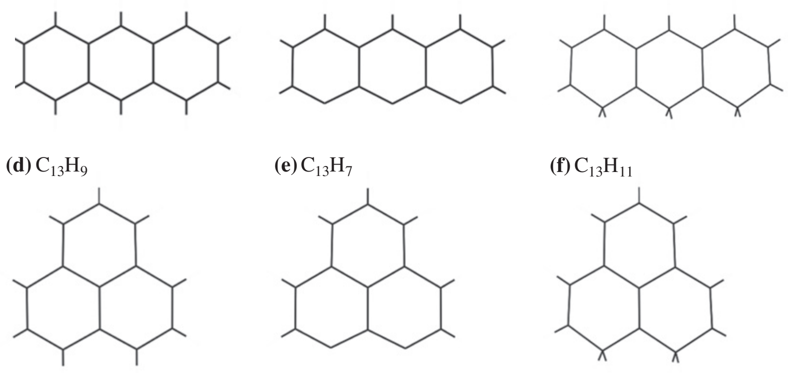

Fig. 1. Schematic picture of graphene molecules, showing connectivities and hydrogen counts on each carbon: (a) $C_{14}H_{10}$, with hydrogenated edge carbons (b) $C_{14}H_7$, with three dehydrogenated edge carbons (c) $C_{14}H_{13}$, with three dihydrogenated edge carbons (d) $C_{13}H_9$, with hydrogenated edge carbons (e) $C_{13}H_7$, with two dehydrogenated edge carbons (f) $C_{13}H_{11}$, with two dihydrogenated edge carbons. The two H atoms of the dihydrogenated edges in (c) and (f) are out of plane with the same angle with the plane of molecule.