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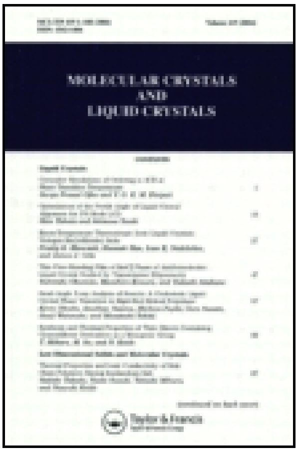

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Published online: 11 Sep 2013.

To cite this article: Tetsuji Iyama & Hiroto Tachikawa (2013) Density Functional Theory (DFT) Study on Interaction of Carbon Free Radicals with Graphene Surface, Molecular Crystals and Liquid Crystals, 579:1, 10-16, DOI: 10.1080/15421406.2013.804793

To link to this article: http://dx.doi.org/10.1080/15421406.2013.804793

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Mol. Cryst. Liq. Cryst., Vol. 579: pp. 10–16, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.804793

Density Functional Theory (DFT) Study on Interaction of Carbon Free Radicals with Graphene Surface

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The interaction of carbon free radicals (CH and CCH) with a graphene surface has been investigated by means of density functional theory (DFT) method in order to elucidate the radical scavenge mechanism of graphene surface. These radicals are highly reactive and the radical plays an important part of materials chemistry. The DFT calculation showed that the CH and CCH radicals bind to the bond center of C-C carbon atoms as a carbon bridge and a strong C-CH-C bond (or C-C_2H-C bond) is formed. The binding energies of CH and CCH radicals to the graphene were calculated to be 48.2 and 46.2 kcal/mol at the B3LYP/6-31G(d) level of theory. The mechanism of CH radical addition was discussed on the basis of theoretical results.

Keywords addition reaction; CH radical; DFT; graphene

1. Introduction

Graphene is a single layer sheet composed of carbon backbone with benzene-ring structure. The ideal and infinite graphenes act as a semimetal or zero-gap semiconductor. The graphene can be applied to an electronic device and an electronic circuit because it shows the electronic conductivity that is higher than the three-dimensional silicon [1–3]. Experimental results from transport measurements show that the graphene has a remarkably high electron mobility at room temperature, with reported values in excess of 15,000 cm^2/Vs. Additionally, the symmetry of the experimentally measured conductance indicates that the mobility for hole and electron are nearly the same. The mobility is nearly independent of temperature between 10 and 100 K [4,5].

The mono-hydrogenated carbon radicals (CH and CCH radicals) are the reactive species and have some potential biological effects, e.g. inhibition of HIV protease, antiviral activity, specific cleavage of DNA and photodynamic therapy [6]. Also, the radicals are generated in flame of combustion process. The interaction of the reactive carbon species with carbon materials is important to trap the reactive intermediate by the carbon materials.

In the present study, the reactions of carbon radicals (CH and CCH radicals) with the graphene flake are investigated by means of DFT method. To elucidate the mechanism

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of CH addition to the surface, two carbon radicals, CH and CCH were examined as the reactive radicals.

2. Method of Calculation

A graphene flake composed of eight hexagonal rings was examined in the present study. It was assumed that the CH and CCH radicals interact with a carbon atom near center region of the graphene flake. The structures of the interaction systems were fully optimized at the B3LYP/6-31G(d) level of theory [7–10]. The atomic charges were calculated using the natural bond population analysis (NPA) method. All calculations were carried out using Gaussian 03 package [11].

3. Results

3.1. Structures of Graphene and CH Added Graphene

The optimized structure of the graphene flake used in the present study is given in Fig. 1. The structure of graphene showed a planar form. The C—C bond length is 1.452 Å at the central region.

The binding structure of CH to the graphene flake is illustrated in Fig. 2, and the geometrical parameters are also given in Table 1. The C—H distance was calculated to be 1.089 Å. The C_1—C_2 bond length of the addition site is significantly elongated from 1.452 to 2.173 Å after the CH binding to the graphene. It was found that the radicals are added to the C—C center, and C—CH—C bridge structure is formed.

3.2. Spin Density

Figure 3 depicts a special distribution of spin density of CH added graphene. The unpaired electron is widely distributed over the CH-graphene. The hyperfine coupling constant of

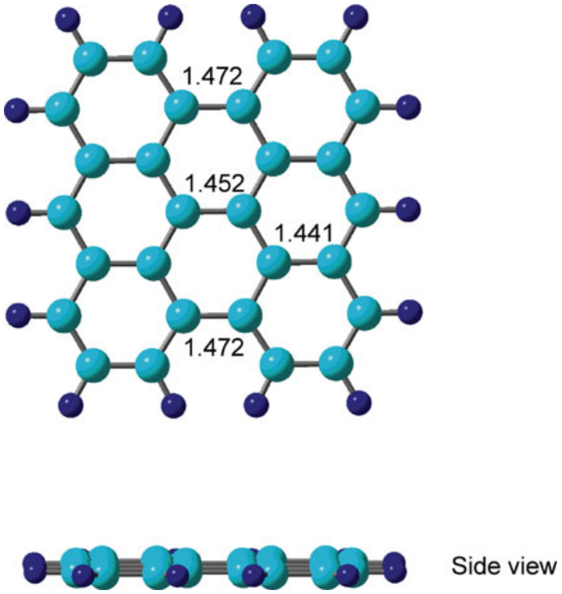

Figure 1. Structure of graphene flake used in the present calculation. Structure was optimized at the B3LYP/6-31G(d) level. The values indicate the bond distances in Å.

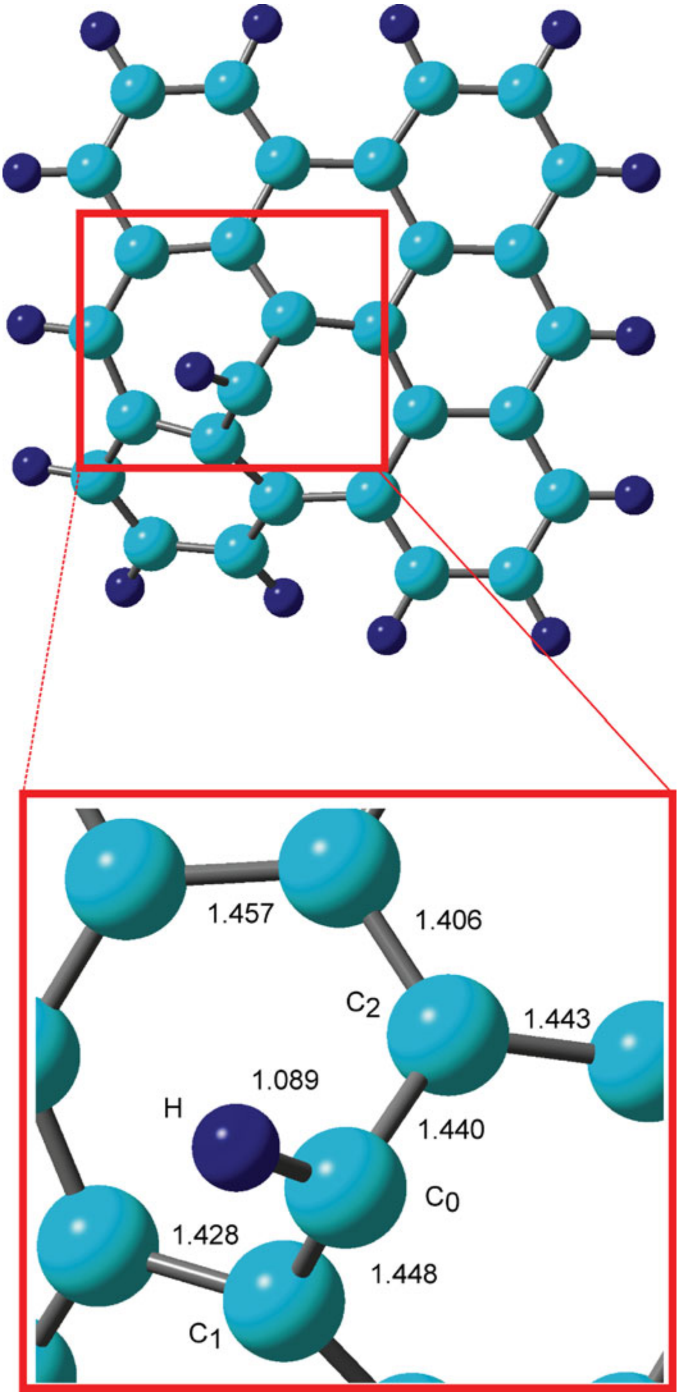

Figure 2. Binding structure of CH to the graphene flake optimized at the B3LYP/6-31G(d) level. The values indicate the bond distances in Å. Expanded view of binding site is given in lower panel.

Table 1. Excitation energies (E_{ex} in eV) and configuration state functions (CSFs) of CH-graphene calculated at the TD-DFT(B3LYP)/6–31G(d) level.

state	CSF and CI vector	E_{ex}/eV
D_1	$-0.803\phi(\text{a: SOMO} \rightarrow \text{LUMO}) + 0.700\phi(\text{b: HOMO} \rightarrow \text{SOMO})$	1.63
D_2	$-0.482\phi(\text{a: SOMO} \rightarrow \text{LUMO}) + 0.583\phi(\text{b: HOMO} \rightarrow \text{SOMO})$	1.80
D_3	$0.800\phi(\text{b: HOMO} \rightarrow \text{LUMO})$	1.80

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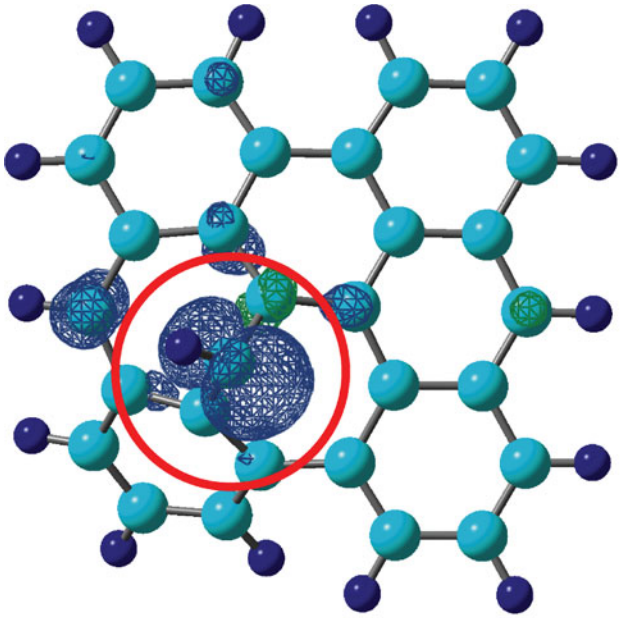
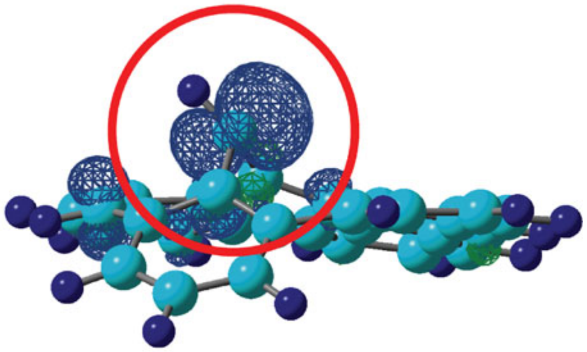


top view



side view

Figure 3. Spin densities on carbon atoms around the binding site of CH radical.

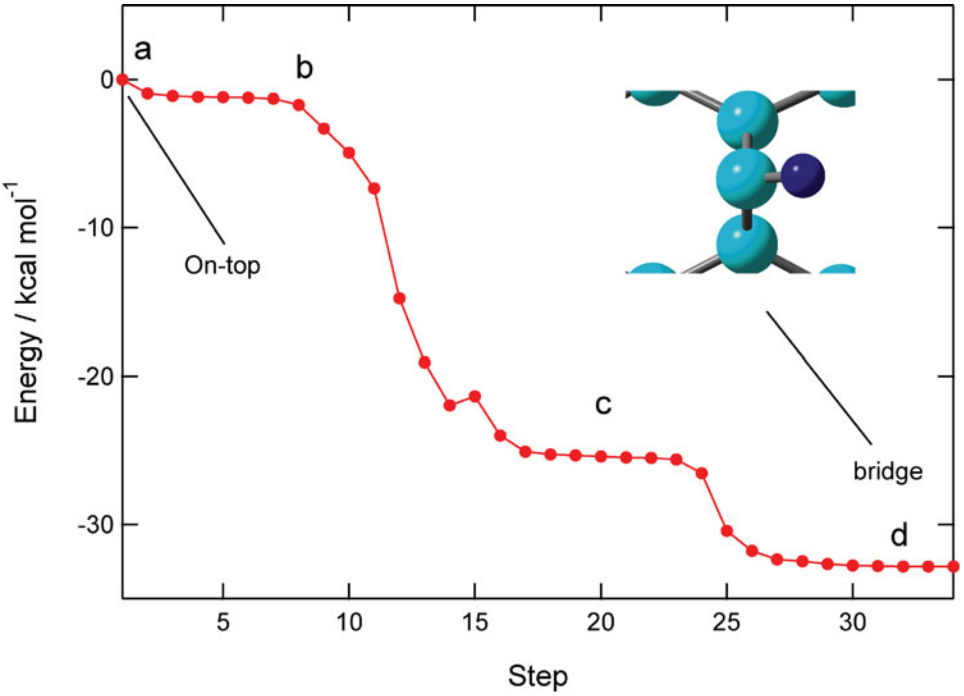


Figure 4. Potential energy curve along the CH radical addition to graphene flake.

the hydrogen atom of C—CH—C bridge site is calculated to be −7.96 G at the B3LYP/6-311G(d,p) level, which is significantly smaller than that of free CH radical.

3.3 Addition of CH Radical to the Graphene Surface

The potential energy curve (PEC) along the CH radical addition to the graphene surface is given in Fig. 4. The initial structure of CH radical addition is assumed to the on-top site of graphene surface (i.e. CH radical is put over the carbon atom of graphene surface). PEC shows the shape of addition is composed of a downhill type: CH radical can bind the surface without activation barrier. First, CH radical moves from the on-top to C—C bridge site, which is expressed by the PEC from points **a** to **b**). The energy difference is 2.0 kcal/mol. This is a parallel transfer above the surface. The energy is suddenly changed from points **b** to **c**. This energy change is caused by the approaches of CH radical to the surface. At point **d**, the addition of CH radical is completed and a C-CH-C bridge is formed. The energy difference is calculated to be 33.0 kcal/mol. Before addition (point a), the C—C bond distance is 1.452 Å, which is a normal bond length of graphene. By the approaching of CH radical, the C—C bond distance is gradually elongated.

3.4. Simulated UV-VIS Spectra

To elucidate the electronic states of CH-added graphene, TD-DFT calculation was carried out at the B3LYP/6-31G(d) level. The simulated absorption spectrum of CH-added graphene is given in Fig. 5. One peak is found with a peak maximum at Eex = 1.89 eV. However, this peak is composed of 16 electronic transitions. The transition is assigned using configuration

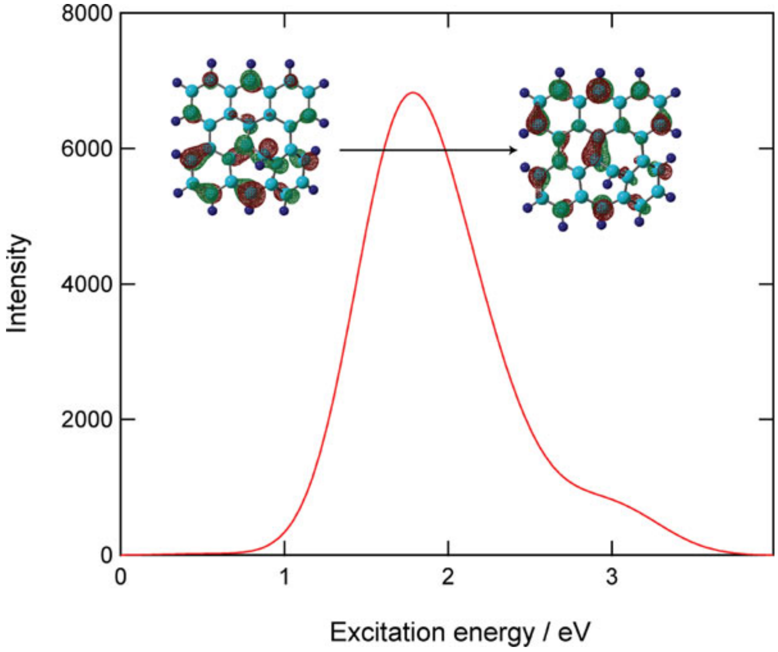


Figure 5. Simulated absorption spectrum of the CH added graphene flake.

state functions, as shown in Table 1. The lowest transition is assigned to be SOMO-LUMO transition (1.63 eV) which is assigned to a transition from a localized CH site to delocalized surface.

4. Discussion

4.1. Interaction Between Graphene and Radicals

The present calculations showed that the CH radical can bind to the graphene surface without activation barrier. On the other hand, addition of hydrogen atom and methyl radical need activation barrier. In case of hydrogen and methyl, sp^2 -> sp^3 hybridization is important in the addition. This process needs an activation energy. On the other hand, CH radical has a $^2\Pi$ state and the un-paired electron is occupied in 2p-orbital. This orbital interacts with $\sigma^*_{C=C}$ orbital of graphene surface. Thus, the unpaired electron is transferred into the $\sigma^*_{C=C}$ orbital. Therefore, the C—C bond is clevaraged smoothly without activation barrier.

4.2 Summary

1) The CH radical can react with a graphene surface and binds to a carbon atom (C_0), and C_0-OOH strong bond is formed. The binding energy is in the range 18–25 kcal/mol.
2) It was found that the radicals are added to the C—C center and C—CH—C bridge is formed. The reaction proceeds without activation barrier.
3) The spin density of CH is mainly localized around CH addition site.

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