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Energetics and electronic structures of three-dimensional covalent networks of hydrocarbon molecules

Electronic properties of carbon allotropes and hydrocarbon materials are sensitive to the topological arrangement of sp^2 C atoms in their covalent networks. According to the zero gap semiconducting electronic structure of graphene, for instance, nanoscale structures of graphene are known to exhibit interesting electronic structures which strongly depend on the local atomic arrangement and on the boundary condition imposed on graphene. Besides materials consisting only of sp^2 C atoms, nanoscale materials containing sp^3 C atoms have further variation in their geometries and electronic properties which are absent in the nanoscale graphene derivatives. Triptycene is a representative hydrocarbon molecule containing sp^3 atoms at its molecular axis, leading to form two- and three-dimensional covalent networks as its polymeric forms. According to weak itineracy of π electrons through the networks, the polymeric forms of triptycene possess peculiar electronic structure in their both valence and conduction bands. In the present work, we focus on tetraphenylmethane, which consists of a methane core with four phenyl substituents, and diphenylmethane, which consists of a methane with two phenyl substituents, as for the other constituent unit for constructing three-dimensional covalent networks because of their tetrahedrally arranged phenyl substituents. Therefore, an aim of this work is to clarify the energetics and electronic structures of the three-dimensional covalent networks of C assembling and polymerizing diphenylmethane or tetraphenylmethane, using the density functional theory (DFT) with the generalized gradient approximation (GGA).

Figure 1 shows optimized structures of three-dimensionally polymerized diphenylmethane [Fig. 1(a)], in which tetrahedrally arranged sp^3 C atoms are connected via phenyl, and of the polymerized tetraphenylmethane [Fig. 1(b)], in which sp^3 C atoms are connected via biphenyl. According to the choice of the constituents and their arrangements, they could be regarded as the extended diamond networks in which the methane and phenyl or biphenyl mimic the atom and bonds, respectively. These polymers are energetically stable with the total energy of 90 and 65 meV/atom for polymeric diphenylmethane and tetraphenylmethane, respectively, with respect to that of diamond. We also estimate the formation energies of polymers from polymeric reactions of diphenylmethane and tetraphenylmethane. The calculated formation energies are 1.62 and 0.68 eV/molecule for the polymerized diphenylmethane and tetraphenylmethane, respectively. Although these reactions are endothermic, the formation energies are small enough to overcome the polymerization reaction, leading to the three-dimensional covalent networks of sp^2 and sp^3 C atoms.

Figures 2(a) and 2(b) show the electronic structure of the polymerized diphenylmethane and tetraphenylmethane, respectively. These polymeric structures are semiconductors with an indirect band gap of 3.38 and a direct gap of 3.02 eV for diphenylmethane and tetraphenylmethane polymers, respectively. Furthermore, they have peculiar band structures in both valence and conduction states: Each energy band consists of four branches, two of which have finite dispersion of about 0.5 eV forming a Dirac cone at the W point while the remaining two show flat band or less dispersive natures throughout the Brillouin zone. For both cases, the highest branches of the valence band and the third lowest branches of the conduction band show flat band nature. Thus, the polymers may exhibit the strong absorption or emission between these states in UV region. In addition to the flat band states, although the π electron networks are segmented in each phenyl or biphenyl and are terminated by sp^3 C atoms situated at the network vertexes, the Dirac cone with the band width of 0.5 eV indicates that π electrons could itinerate through the covalent network with different hopping probabilities between and within sp^2 moieties.

References

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- [2] Y. Fujii, M. Maruyama, and S. Okada, *Jpn. J. Appl. Phys.* **57** (2018) 125203.

Figures

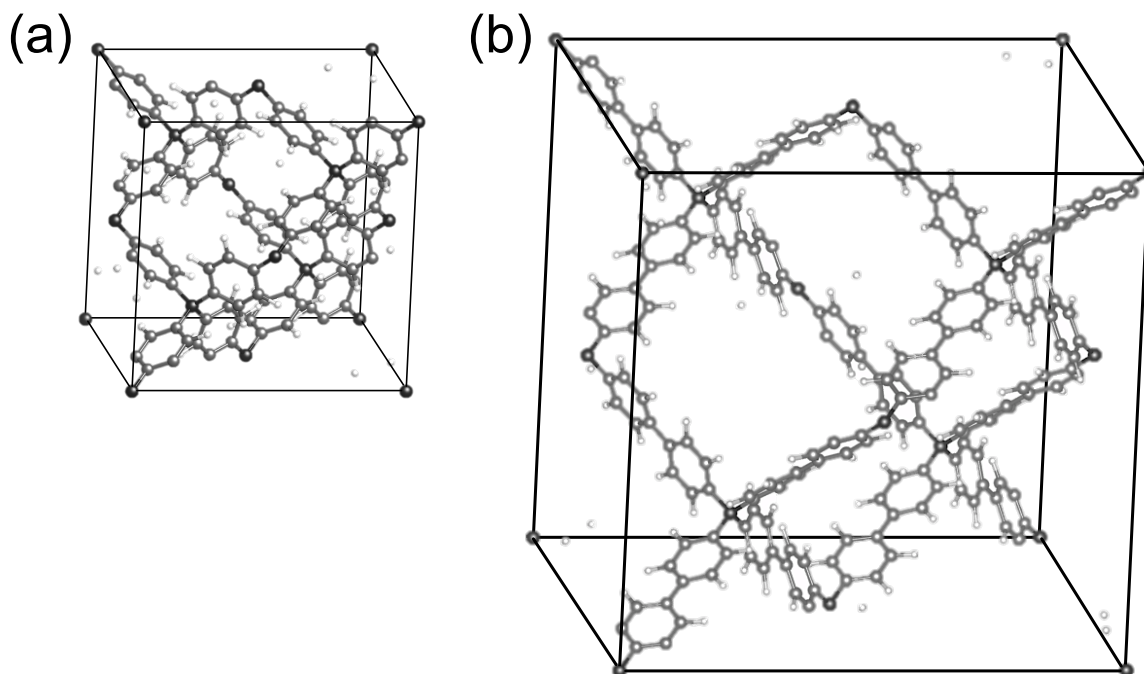


Figure 1: Optimized geometric structures of the (a) diphenylmethane and (b) tetraphenylmethane polymers. The black, gray and white ball indicate the sp^3 C, sp^2 C, and H atom, respectively.

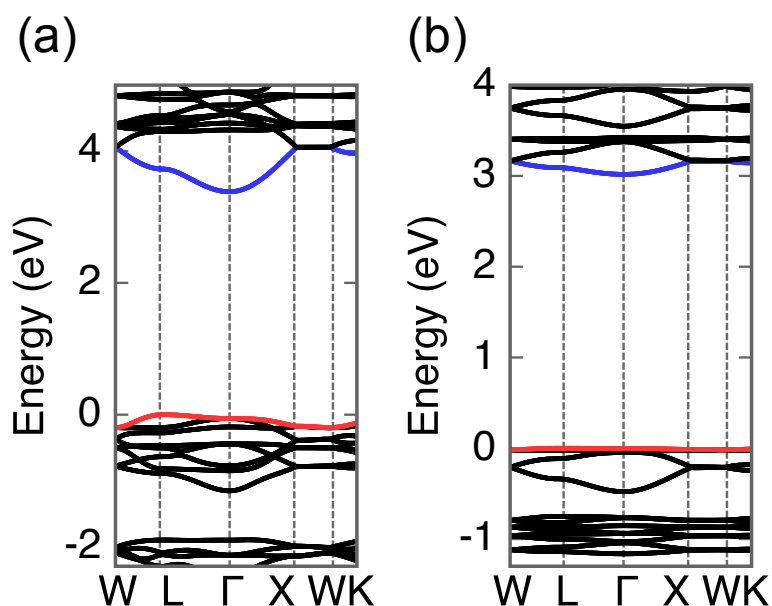


Figure 2: Electronic energy band of (a) the diphenylmethane and (b) tetraphenylmethane polymers along the high symmetries points in the fcc Brillouin zone. The energies are measured from that of the valence band top.