

## Electronic structure of three-dimensional graphyne

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Graphyne is a hypothetical carbon allotrope with a layered structure. We calculated the optimized geometries and electronic structures of three-dimensional graphyne in some possible stacking arrangements from symmetry considerations. The optimized lattice constants and the binding energy of graphyne are given in comparison with graphite. The binding energy of graphyne is about 90% of that of graphite, and graphyne will be stable when it is synthesized. The electronic structures are classified into two types, metallic and semiconducting, according to the stacking arrangements. The most stable graphyne is expected to be a semiconductor with a moderate band gap.

### I. INTRODUCTION

Graphyne is a carbon allotrope predicted to have a high possibility of synthesis by Baughman, Eckhardt, and Kertesz in 1987.<sup>1</sup> The layer structure of graphyne is shown in Fig. 1. The characteristic of the structures is coexistence of  $sp^2$  and  $sp$  carbon atoms. We carried out optimization of the geometry and calculation of the electronic structure of two-dimensional graphyne using first principles in a previous paper.<sup>2</sup> The optimized bond lengths in the hexagonal rings (benzene rings) are all equal and the bonds between two hexagonal rings are not  $=C=C=$  linkages but  $-C\equiv C-$  linkages as shown in Fig. 1. This material is a semiconductor with an energy gap of 0.52 eV, and the binding energy is 7.95 eV/atom. This value is not small in comparison with the binding energy of graphite, 8.87 eV/atom. This fact shows that graphyne should be stable when it is synthesized.

In the present work we aim at obtaining the optimized structure and electronic structure of three-dimensional graphyne, and, in addition, the difference of electronic structure between two- and three-dimensional graphyne. In three-dimensional graphyne the electronic structure is influenced by both the intralayer and interlayer interactions, while in two-dimensional graphyne it is derived only from the intralayer interaction. Whether three-dimensional graphyne exhibits metallic, semimetallic, or semiconducting properties may depend on the strength of the interlayer interaction.

The stable layer arrangement of three-dimensional graphyne is not known. Thus we optimized the crystal structures for some possible cases of layer arrangement, and obtained the electronic structures for these optimized structures. The crystal structures that we dealt with are described in Sec. II, and the calculation method is given in Sec. III. The optimized geometries for these possible structures and their electronic structures are shown and discussed in Sec. IV.

### II. SUPPOSED CRYSTAL STRUCTURE

The structure of two-dimensional graphyne is shown in Fig. 1. The parallelogram drawn with a broken line repre-

sents a unit cell with the lattice constant  $a$ . It is not yet known what layer arrangement is stable for three-dimensional graphyne. Thus we need to determine stable stacking arrangements. We deal with four possible stacking arrangements from symmetry considerations. We show the projection of these structures onto a lattice plane. The AAA stacking arrangement structure  $\alpha$  is shown in Fig. 1 (it is equivalent to the figure for two-dimensional graphyne), and three different ABA stacking arrangement structures  $\beta 1$ ,  $\beta 2$ , and  $\beta 3$  are shown in Fig. 2. The A layer is drawn with dark and the B layer with light lines in order to see the structures clearly. We define  $d$  as the interlayer distance. In this study we have not considered other stacking arrangements such as ABC stacking, because the main purpose is to investigate the influence of the interlayer interaction on the electronic structure of three-dimensional graphyne.

In the calculation for the structures  $\alpha$  and  $\beta 3$  we chose a unit cell with double the volume (lattice constant  $a$  and double interlayer distance  $2d$ ) of the real one, in order that the same number of 24 carbon atoms are included in the unit cell for all the structures considered. Then each band structure obtained for  $\alpha$  and  $\beta 3$  is a folding of the real band structure in the direction perpendicular to the layer in the Brillouin zone, which is given in Fig. 3.

### III. METHOD OF CALCULATION

We used the first-principles full-potential linear combination of atomic orbitals method within the local-spin-density approximation (LSDA).<sup>3</sup> The details of the method are given in a previous paper.<sup>2</sup>

Here, we describe the method of finding the lattice constants that maximize the binding energy of three-dimensional graphyne. We must optimize the lattice constant  $a$ , the interlayer distance  $d$ , and bond lengths  $p$ ,  $q$ , and  $r$  assigned in Fig. 1. For this purpose we adopted the following method. Since the difference of the planar structure between two-dimensional graphyne and three-dimensional graphyne is considered to be small, we set the initial ratio of bond lengths  $p$ ,  $q$ , and  $r$  (that is to say, the initial sites of the

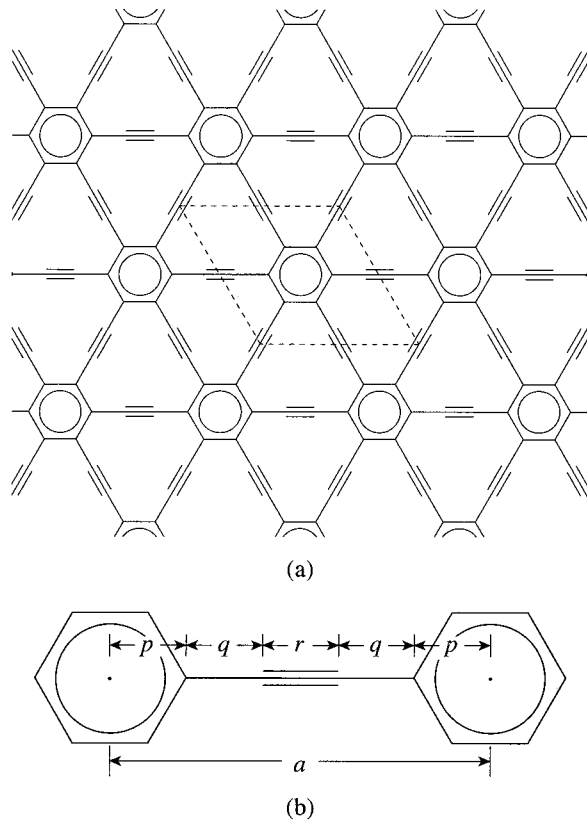


FIG. 1. (a) Layer structure of graphyne. The parallelogram drawn with a broken line shows a unit cell of two-dimensional graphyne. This figure represents also the projection of the AAA stacking arrangement (the crystal structure  $\alpha$ ) onto a lattice plane. (b) Assignment for each bond length.

carbon atoms) equal to that in two-dimensional graphyne. The lattice constant  $a$  is also not very different from that of two-dimensional graphyne ( $a_0$ ). Then we calculate the binding energy by varying the interlayer distance  $d$  for each  $a_1$  ( $=a_0 - \Delta$ ),  $a_0$ , and  $a_2$  ( $=a_0 + \Delta$ ), where  $\Delta$  is an arbitrary small value. Thus, we get the values of  $d_1$ ,  $d_2$ , and  $d_3$  that maximize the binding energy for  $a_1$ ,  $a_0$ , and  $a_2$ , respectively. We draw a quadratic curve that passes through  $(a_1, d_1)$ ,  $(a_0, d_2)$ , and  $(a_2, d_3)$ , and then try to find the  $(a_m, d_m)$  that maximize the binding energy in the direction along the curve. We try again to find the  $(a_m, d_m)$  that gives a much larger binding energy by varying both  $a$  and  $d$  along the curve. Further, we calculate the binding energy of the

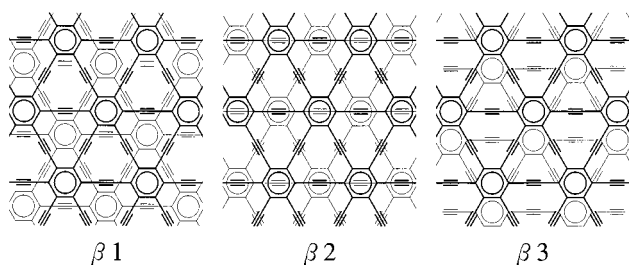


FIG. 2. The crystal structures  $\beta 1$ ,  $\beta 2$ , and  $\beta 3$  that are projections of the ABA stacking arrangement onto a lattice plane. The A and the B layer are drawn with dark and light lines, respectively.

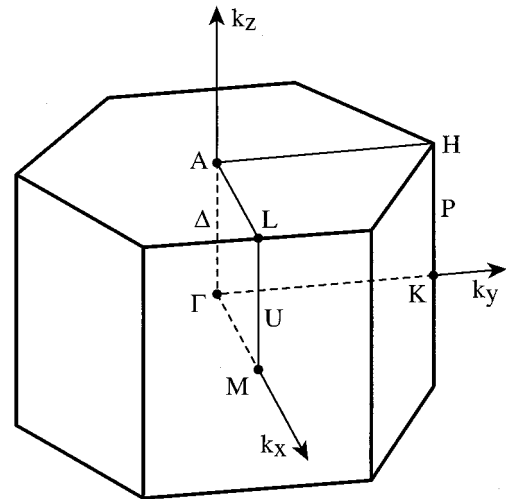


FIG. 3. Brillouin zone of all crystal structures dealt with in the text.

crystal around the point  $(a_m, d_m)$  in order to find the final  $(a_{\max}, d_{\max})$  that maximize the binding energy. Thus, we determine the optimized values of  $a$  and  $d$ . Finally we determined the lattice constant and interlayer distance to an accuracy of  $0.005 \text{ \AA}$  for  $a$  and  $0.01 \text{ \AA}$  for  $d$ . The optimization of bond lengths  $p$ ,  $q$ , and  $r$  (that is to say, the final sites of the carbon atoms) is performed at the same time by calculating the force acting on the atom.

## IV. RESULTS AND DISCUSSION

### A. Optimized geometry

We first tried to find the optimized structure  $\beta 1$  using the method described in Sec. III. The optimized lattice constant  $a$  was  $6.86 \text{ \AA}$ , which is equal to that of two-dimensional graphyne. From this result the planar structure of graphyne seems to be firm and does not change even if the stacking arrangements are different. Then we carried out the optimizing calculation for the other structures  $\alpha$ ,  $\beta 2$ , and  $\beta 3$  with  $a = 6.86 \text{ \AA}$ . The optimized values are given in Table I with the optimized values of two-dimensional graphyne. The optimized bond lengths are almost the same as those of two-dimensional graphyne, the bonds in the hexagonal rings are all  $sp^2$  as in graphite, and the bonds between two hexagonal rings are  $\text{—C}\equiv\text{C—}$  linkages. Our result for the bond lengths of graphyne is consistent with the result of Baughman, Eckhardt, and Kertesz.<sup>1</sup> In order to check whether the calculation was rightly carried out we optimized the geometry of graphite. The optimized values of graphite are also given in Table I.

As for the interlayer distance, it is known experimentally for graphite as  $3.35 \text{ \AA}$ . In our calculation the optimized value is  $3.17 \text{ \AA}$ , which is short by about 5%. Possibly this tendency will be similar in graphyne. Then the calculated interlayer distances for graphyne should be changed to the range from  $3.45$  and  $3.69 \text{ \AA}$ . Therefore the interlayer distance for graphyne is longer than that of graphite.

The structure with the smallest binding energy within the four arrangements of three-dimensional graphyne is  $\alpha$ . This binding energy is smaller than that of two-dimensional gra-

TABLE I. Optimized lattice constant, bond lengths, and binding energies for three-dimensional graphyne. The values for two-dimensional (2D) graphyne and three-dimensional graphite in our calculation are also given. Experimental lattice constant and interlayer distance of graphite are given in parentheses.  $d$ : Interlayer distance. BE is the binding energy.

	$a$ (Å)	$d$ (Å)	$p$ (Å)	$q$ (Å)	$r$ (Å)	BE (eV/atom)
$\alpha$	6.86	3.51	1.417	1.402	1.222	7.948
$\beta 1$	6.86	3.27	1.418	1.400	1.224	7.963
$\beta 2$	6.86	3.28	1.418	1.401	1.222	7.962
$\beta 3$	6.86	3.34	1.418	1.401	1.222	7.957
2D graphyne	6.86		1.419	1.401	1.221	7.951
Graphite	2.46 (2.46)	3.17 (3.35)				8.867

phyne. It is supposed that the nucleus-nucleus Coulomb repulsion acts strongly in the structure  $\alpha$  because all carbon atoms have neighbors just above and below them in adjacent layers in this structure. This is also suggested by the fact that the structure  $\alpha$  has the largest interlayer distance among the four structures examined. On the other hand, the binding energy of the structure  $\beta 1$  is the largest, as seen from Table I, although the binding energy of  $\beta 2$  is almost equal to that of  $\beta 1$ . We cannot determine which of these structures can stably exist in fact because a calculation error of 0.005 eV/atom is included in the binding energy. As the binding energy of graphite with the optimized structure is 8.867 eV/atom, the binding energies of graphyne are not small in comparison with that of graphite. In fact these binding energies are about 90% of that of graphite. This suggests that graphyne will be stable when it is synthesized.

Concerning the relative stability of the two- and three-dimensional structures, we cannot conclude that the proposed three-dimensional structures are stable or not relative to the isolated layer form. This is due to the fact that the

distribution of sampling points of the numerical integration for the two-dimensional structure is different from that for the three-dimensional structure in our calculation method, and thus the difference of the binding energies between the two- and three-dimensional structures is beyond the numerical error. It is noted, however, that the comparison among three-dimensional structures is still meaningful within a 0.005% error of the energy because the same distribution of sampling points was employed. For the case of graphite the interlayer bonding energy was found to be 0.020 eV/atom by Charlier, Gonze, and Michenaud.<sup>4</sup> The interlayer bonding energy of graphyne will be considerably smaller than that of graphite since the interlayer distance of graphyne is longer than that of graphite.

## B. Electronic structure

The electronic structures and densities of states for  $\alpha$ ,  $\beta 1$ ,  $\beta 2$ , and  $\beta 3$  calculated using the optimized potentials are shown in Figs. 4–7, respectively. The Fermi level ( $E_F$ ) is the

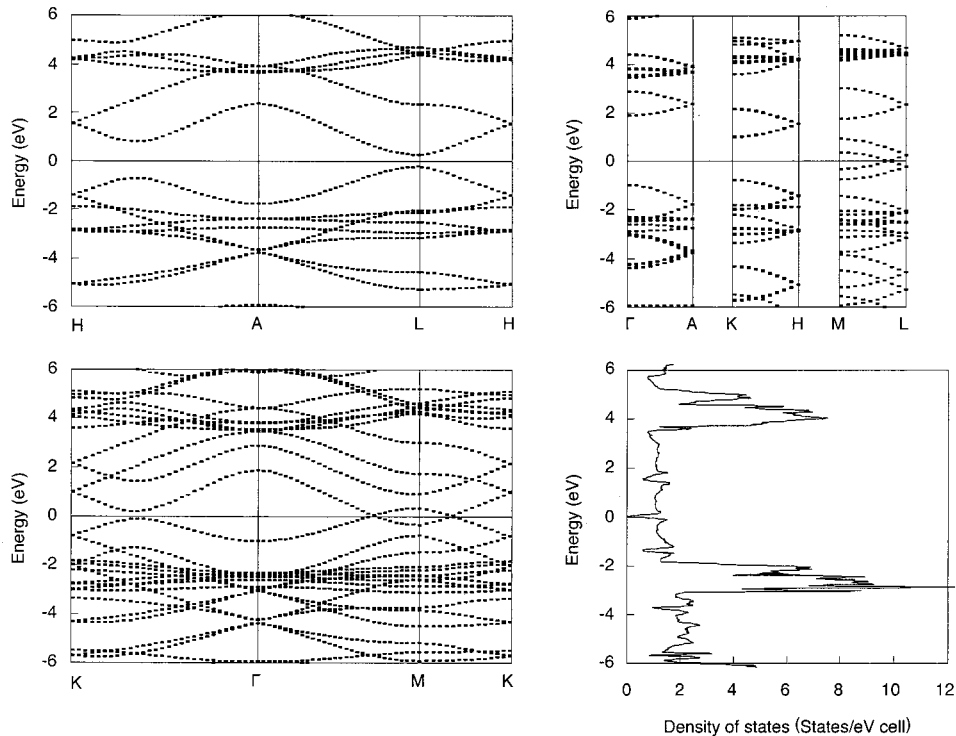


FIG. 4. Band structure and density of states of the crystal structure  $\alpha$ .

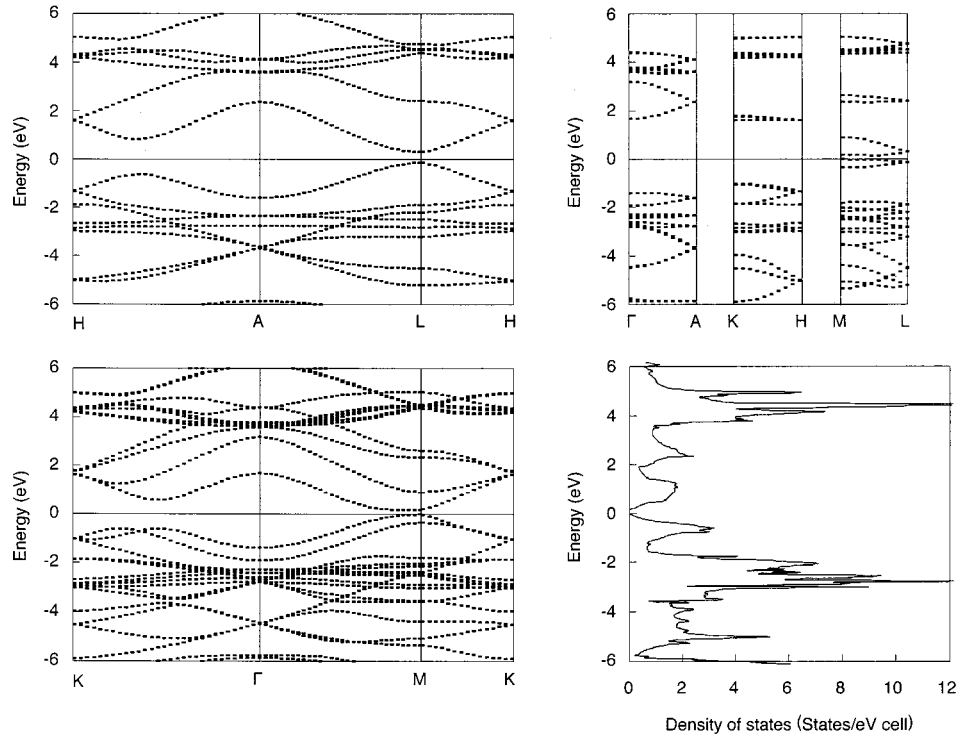


FIG. 5. Band structure and density of states of the crystal structure  $\beta_1$ .

line passing through the energy zero in each figure. Greatly undulating bands lying just above and below  $E_F$  include mainly the  $2p\pi$  component.

Reflecting the difference of stacking arrangements, the band structures are different from one another. Although the

band structures in the *HALH* plane have a strong resemblance for all the crystal structures, those in the *KGammaMK* plane show unique features according to the stacking arrangement. These band structures can be classified into two types by the different behaviors near  $E_F$ . In one type the bands cross  $E_F$ .

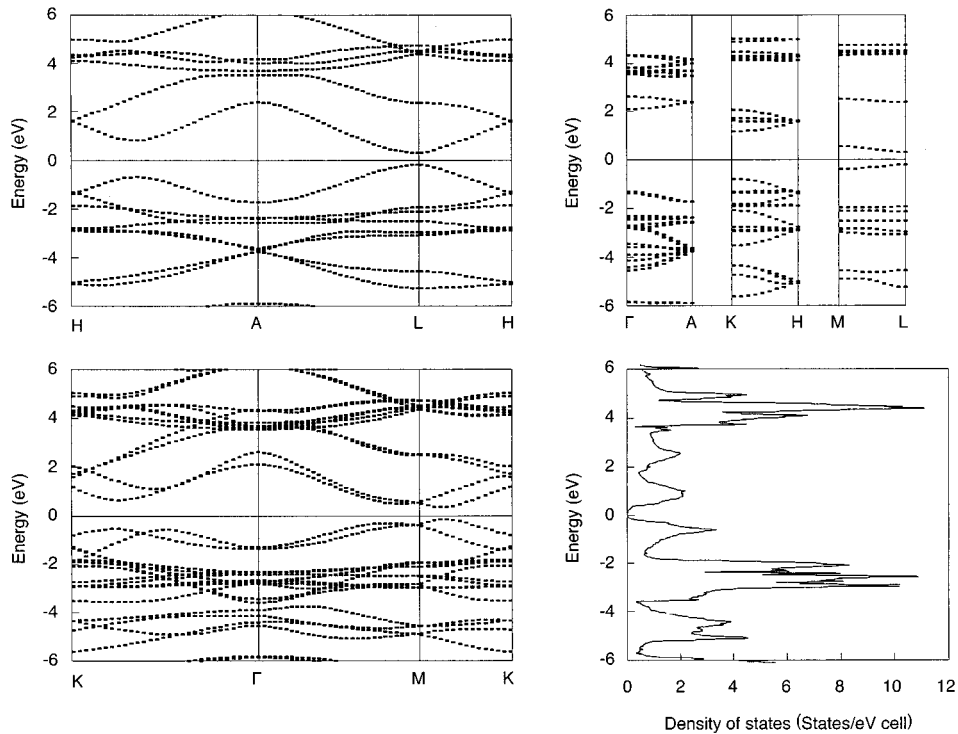
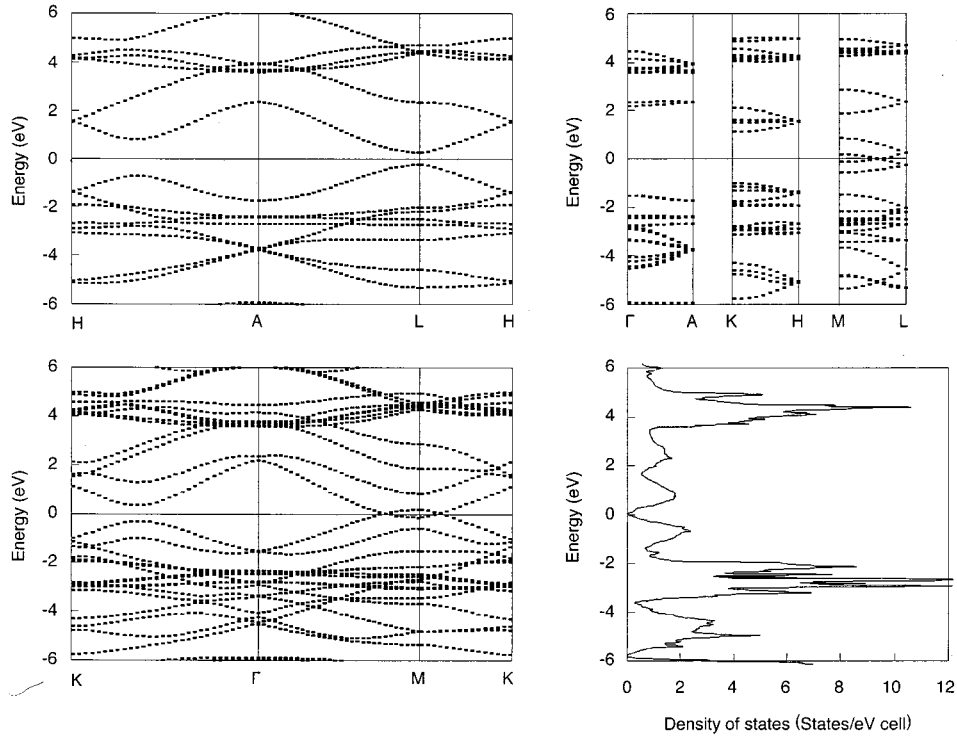


FIG. 6. Band structure and density of states of the crystal structure  $\beta_2$ .

FIG. 7. Band structure and density of states of the crystal structure  $\beta_3$ .

The band structures for  $\alpha$  (Fig. 4) and  $\beta_3$  (Fig. 7) are included in this type. In the other type the conduction band is separated by an energy gap from the valence band. The band structures for  $\beta_1$  (Fig. 5) and  $\beta_2$  (Fig. 6) are included in this type.

The former band structure is very interesting. Although the stacking arrangements  $\alpha$  and  $\beta_3$  are very different, their band structures on the  $K\Gamma MK$  plane and  $ML$  line resemble each other closely. These band structures are characteristic: from the viewpoint of the band structures these materials seem to be metallic, but their densities of states at  $E_F$  are zero. This zero-gap semiconducting feature is similar to that of two-dimensional graphite. We hope synthesis of the stackings  $\alpha$  and  $\beta_3$  with such attractive band structures will occur, although the stability of the structures  $\alpha$  and  $\beta_3$  will be inferior to that of  $\beta_1$  and  $\beta_2$ .

TABLE II. Energy gaps and effective masses in the valence ( $m_v$ ), and conduction bands ( $m_c$ ) for the stable structures  $\beta_1$  and  $\beta_2$ . The effective mass is given in units of the mass of the free electron. ( $M\leftarrow\Gamma$ ) means the component of the effective mass along the path from the  $\Gamma$  to the  $M$  points.  $U_{1/2}$ ,  $\Delta_{1/2}$ , and  $P_{1/2}$  are the midpoints of the  $U$ ,  $\Delta$ , and  $P$  lines.

	Energy gap (eV)	$m_v$	$m_c$
$\beta_1$	0.19	0.35 ( $M\leftarrow\Gamma$ )	0.79 ( $U_{1/2}\leftarrow\Delta_{1/2}$ )
		0.030 ( $M\leftarrow K$ )	0.031 ( $U_{1/2}\leftarrow P_{1/2}$ )
		10.5 ( $M\leftarrow L$ )	10.4 ( $U_{1/2}\leftarrow L$ )
$\beta_2$	0.50	0.16 ( $L\leftarrow A$ )	0.15 ( $L\leftarrow A$ )
		0.065 ( $L\leftarrow H$ )	0.064 ( $L\leftarrow H$ )
		1.14 ( $L\leftarrow M$ )	0.25 ( $L\leftarrow M$ )

The band structures of the more stable crystal structures  $\beta_1$  and  $\beta_2$  show that they are semiconductors. The energy gap of  $\beta_1$  is 0.19 eV at the midpoint between the  $M$  and  $L$  points. The top of the valence band is at the  $M$  point, and the bottom of the conduction band is the midpoint ( $U_{1/2}$ ) between the  $M$  and  $L$  points. The energy gap of  $\beta_2$  is 0.50 eV at the  $L$  point. As the energy gap is calculated to be a little smaller in the LSDA employed in the present method, it ought to be corrected to be a little larger. Thus, three-dimensional graphyne is expected to have the stacking arrangement  $\beta_1$  or  $\beta_2$  and to be a semiconductor with a moderate band gap.

Next, we consider the relation between the crystal structure and the electronic structure. In the structures  $\alpha$  and  $\beta_3$  some or all carbon atoms have neighbors just above or below them in adjacent layers, while in the structures  $\beta_1$  and  $\beta_2$  the carbon atoms have neighbors not just above or below but oblique to them in adjacent layers. Therefore, the interlayer interaction between  $2p\pi$  orbitals in  $\alpha$  and  $\beta_3$  is larger than that for  $\beta_1$  and  $\beta_2$ , resulting in a large splitting of these  $\pi$  bands, and the valence and conduction bands overlap each other in  $\alpha$  and  $\beta_3$ . However, the binding energies of  $\alpha$  and  $\beta_3$  are smaller than those of  $\beta_1$  and  $\beta_2$  because the core-core repulsion between adjacent layers in  $\alpha$  and  $\beta_3$  is stronger than that in  $\beta_1$  and  $\beta_2$ .

Finally we estimated the effective masses in the valence band ( $m_v$ ) and conduction band ( $m_c$ ). They are given in Table II. The curvatures of these bands around the energy gaps are dependent on direction, and the effective masses are extraordinarily anisotropic. The in-plane effective masses for  $\beta_1$  and  $\beta_2$  are almost equal to those of typical semiconductors. The effective masses of the conduction and valence bands in the direction perpendicular to the layer plane are considerably larger for  $\beta_1$ .

## V. CONCLUSION

The optimized geometry and electronic structure of three-dimensional graphyne were calculated using the first-principles full-potential linear combination of atomic orbitals method. The binding energy is sufficiently large and graphyne is expected to be stable when it is synthesized. The optimized plane lattice constant  $a$  and bond lengths are al-

most the same as in two-dimensional graphyne, the hexagonal rings are all  $sp^2$  like graphite, and the bonds between two hexagonal rings are  $\text{—C}\equiv\text{C—}$  linkages. The optimized interlayer distance  $d$  is a little longer than that of graphite. Graphyne will exhibit semiconducting properties with a moderate band gap. In addition, the interesting electronic structure showing a zero-gap semiconducting feature is found, although it occurs for less stable stacking arrangements.

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<sup>4</sup>J. C. Charlier, X. Gonze, and J. P. Michenaud, *Europhys. Lett.* **28**, 403 (1994).