

Optimized geometries and electronic structures of graphyne and its family

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The optimized geometries of carbon allotropes related to graphite, called graphyne, graphdiyne, graphyne-3, and graphyne-4, as well as their electronic band structures were calculated using a full-potential linear combination of atomic orbitals method in the local-density approximation. These carbon allotropes consist of hexagons connected by linear carbon chains. The bond length of a hexagon is a little longer than that of the bond that links a hexagon to the outside carbon. Furthermore, part of the linear carbon chain is composed of acetylenic linkages ($\text{—C}\equiv\text{C—}$) rather than cumulative linkages (=C=C=). The binding energies are 7.95 eV/atom for graphyne and 7.78 eV/atom for graphdiyne, and the optimized lattice lengths are 6.86 Å for graphyne and 9.44 Å for graphdiyne. These materials are semiconductors with moderate band gaps. The band gap occurs at the M point or Γ point depending on the number of acetylenic linkages that are contained between the nearest-neighbor hexagons. The effective masses are very small for both conduction and valence bands. [S0163-1829(98)07939-9]

I. INTRODUCTION

There exist many carbon allotropes such as graphite, diamond, and carbon black in the natural world. The continuous efforts on synthesis and discovering new carbon allotropes have been made. As a result, fullerene,¹ nanotube,² carbyne,³ and carbolite⁴ have been added to the numbers of new carbon allotropes. In this paper we deal with some new members in carbon allotropes.

First we mention graphyne, which was predicted by Baughman, Eckhardt, and Kertesz⁵ as one of the new carbon allotropes. This material consists of layered carbon sheets containing sp and sp^2 carbon atoms shown in Fig. 1. The name ‘‘graphyne’’ results from its structure, namely, the layers can be constructed by replacing one-third of the carbon-carbon bonds in graphite with acetylenic linkages ($\text{—C}\equiv\text{C—}$). They calculated the structure and heat of formation for graphyne using the modified neglect of differential overlap (MNDO) quantum chemical method and an atom-atom potential method. They found the lattice lengths of the unit cell for the energy-minimized graphyne structure are $a=6.86$ Å, $c=6.72$ Å, and $\gamma=120^\circ$. The unit cell contains two sheets. This carbon allotrope was predicted to have high-temperature stability and similar mechanical properties to graphite. It was also shown that this material might be a semiconductor ($E_g=1.2$ eV) rather than a metal or semimetal.

Recently, another synthetic research on planar polymeric networks comprising sp and sp^2 carbon atoms has been developed, and the new carbon allotrope that is called graphdiyne was proposed by Haley, Brand, and Pak.⁶ The structure is shown in Fig. 2. The name ‘‘graphdiyne’’ comes from the name graphyne, as well as containing two acetylenic (di-

acetylenic) linkages between carbon hexagons. We can see that graphdiyne belongs to the same family as graphyne. This material was supposed to exhibit similar properties to graphyne.

The binding energies for graphyne and graphdiyne are expected to be much less than graphite. However, these materials have been tried to form. The reason is considered as follows: These materials contain both sp^2 and sp carbon atoms, while the only crystalline forms with well-established structures contain either all sp^3 or all sp^2 carbon atoms. The formation energies of these materials are estimated as 12.4

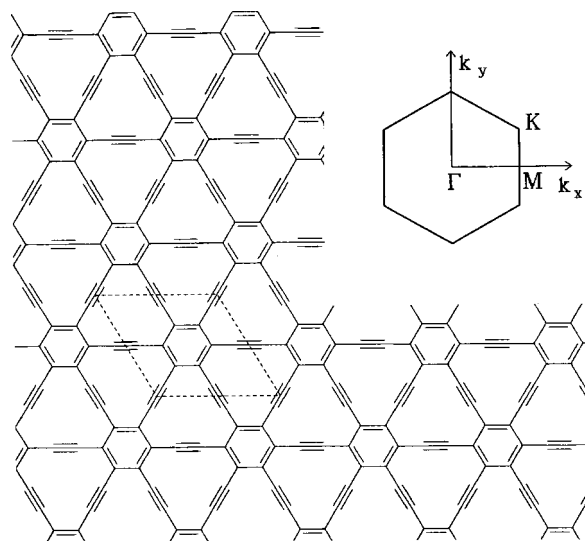


FIG. 1. The structure of graphyne. The parallelogram drawn with a broken line represents a unit cell. The Brillouin zone is shown on the upper side.

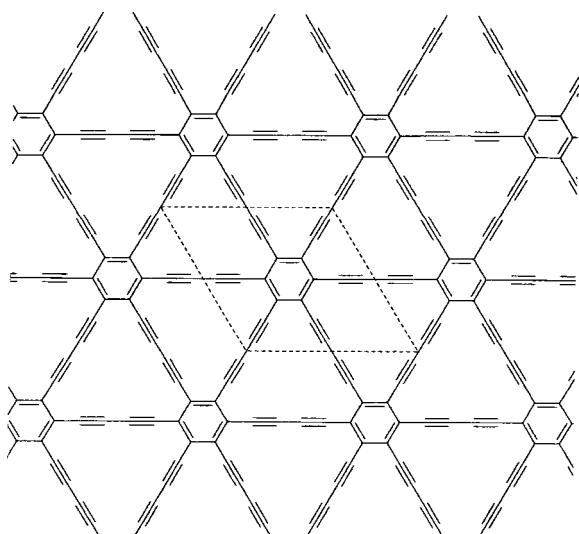


FIG. 2. The structure of graphdiyne. The parallelogram drawn with a broken line represents a unit cell.

kcal/mol carbon for graphyne and 18.3 kcal/mol carbon for graphdiyne. These values are much lower than for any carbon allotrope containing acetylenic linkages.^{5,6} Furthermore, some substructures of graphyne and graphdiyne, as shown in Fig. 3, have been already synthesized.⁶⁻⁸ A typical approach to synthesize graphyne and graphdiyne is presently in progress in two different ways. That is to say, one is the trimerization of cyclocarbon, and another is the polymerization of hexaethynylbenzene.⁹ We can expect that graphyne and graphdiyne will be synthesized in the near future.

Under these circumstances we have started the first-principles study of these attractive materials, graphyne and its family. In this paper we present the results of geometry optimization and the electronic structures of two-dimensional graphyne and its family. We hope our present paper triggers great progress of the study on these materials.

We give a brief explanation of the calculation method in Sec. II and show the crystal structures in Sec. III. In Sec. IV we present the results of geometry optimization and the electronic structures of graphyne and its family. Section V is devoted to conclusions.

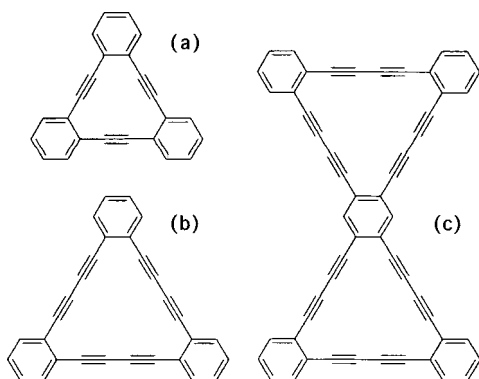


FIG. 3. Substructures of graphyne and graphdiyne. These substructures have been already synthesized. (a) TBC (1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne). (b) and (c) Derivatives of these compounds are synthesized.

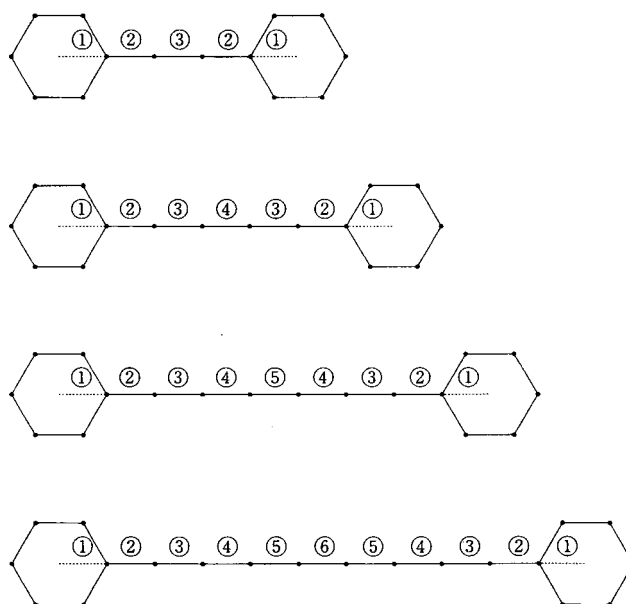


FIG. 4. Assignment for bonds.

II. CALCULATION METHOD

The calculation was carried out using the full potential linear combination of atomic orbitals (LCAO) method,¹⁰ which is based on the density-functional theory within the local-spin-density approximation.^{11,12} The full-potential approach, in which any shape approximation is not introduced in the calculation of the electrostatic potential, is indispensable for the geometry optimization. We used the results of Ceperley and Alder,¹³ which were parametrized by Perdew and Zunger¹⁴ for the exchange-correlation potential and energy density. Furthermore, we performed the calculation of the forces acting on the atoms, which consist of the Hellman-Feynman forces and the Pulay corrections.¹⁵

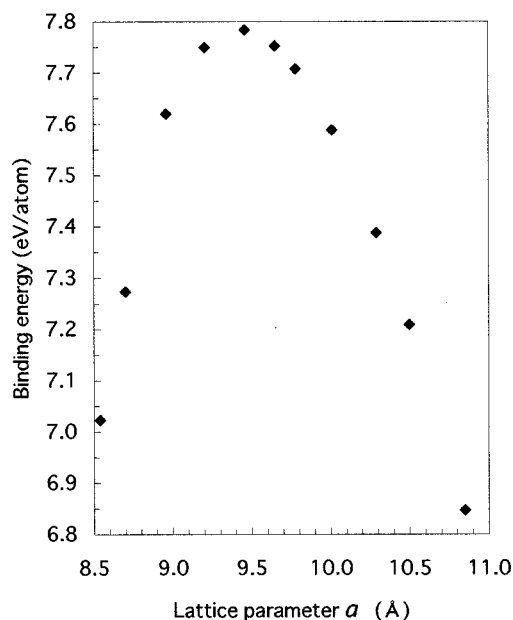


FIG. 5. Plot of the binding energy vs the lattice parameter for graphdiyne.

TABLE I. The optimized lattice length and the binding energy are given.

	Lattice length (Å)	Binding energy (eV/atom)
Graphyne	6.86	7.95
Graphdiyne	9.44	7.78
Graphyne-3	12.02	7.70
Graphyne-4	14.60	7.66

In the present study we used numerical-type orbitals for the basis sets, which were obtained by solving the Kohn-Sham equations of the atoms. The merit of this type of atomic orbital is the perfect description of the dissociated limit of the constituent atoms within local-spin-density approximation. For the numerical-type orbitals $1s$, $2s$, and $2p$, orbitals of a neutral carbon atom and $2s$ and $2p$ orbitals of a carbon ion C^{2+} were adopted. The reason why we used two kinds of orbitals, $2s$ and $2p$ orbitals of a neutral carbon atom and a carbon ion C^{2+} , is to give variational flexibility.¹⁶

For the geometrical optimization we chose to use 13 k points in the Brillouin zone, which are generated by the good-lattice-point method.¹⁷ To confirm the accuracy of the calculation we examined the results of the electrostatic potential for several cases by using 89 k points in the Brillouin zone, which were also generated by the same method. As a result, the numerical difference in the binding energy between them was about 0.002 eV/atom. This difference is very small, and it does not give significant effect to the electronic band structures. The calculation was continued until the force among the atoms converges within 0.2 eV/Å atom.

Thus the band calculation was performed using the obtained self-consistent potential with the optimized geometry.

III. CRYSTAL STRUCTURE

Two-dimensional structures of graphyne and graphdiyne are shown in Figs. 1 and 2, respectively. On the analogy of

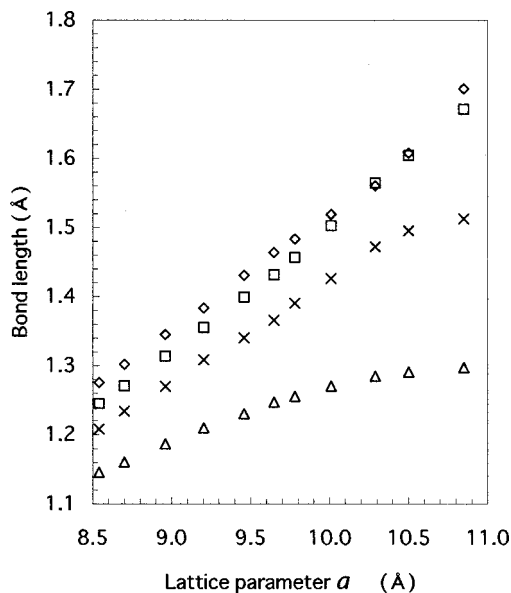


FIG. 6. Plot of the bond length vs the lattice parameter for graphdiyne. \diamond , 1; \square , 2; \triangle , 3; \times , 4.

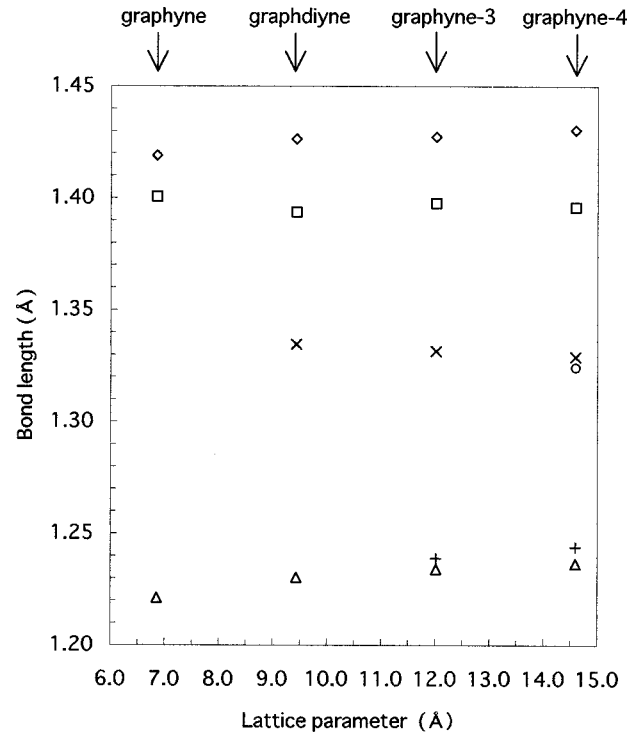


FIG. 7. Plot of the bond length vs the optimized lattice parameter for graphyne, graphdiyne, graphyne-3, and graphyne-4. \diamond , 1; \square , 2; \triangle , 3; \times , 4; $+$, 5; \circ , 6.

these structures we can expect the possibility of materials that contain three or more acetylenic linkages between carbon hexagons. For the sake of convenience we distinguish these materials ($n \geq 3$) by the number of acetylenic linkages between carbon hexagons; the graphyne- n represents the material that contains n -acetylenic linkages between the nearest-neighbor carbon hexagons.

We deal with two-dimensional structures of graphyne, graphdiyne, graphyne-3, and graphyne-4. Though the bonds between hexagons are drawn as acetylenic linkages ($-C \equiv C-$) in Figs. 1 and 2, it might be cumulative linkages ($=C=C=$). Then we must solve for which bond is more stable.

The unit cell of graphyne (graphdiyne, graphyne-3, and graphyne-4 are similar to graphyne) is drawn with a broken line in Fig. 1. The lattice lengths are a and b ($a=b$), and the

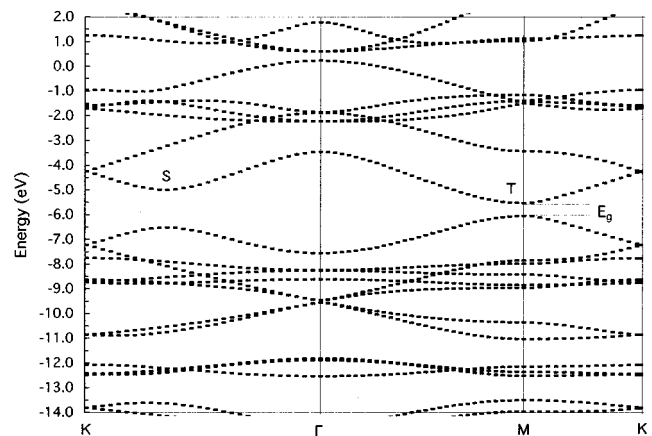


FIG. 8. Electronic band structure of graphyne.

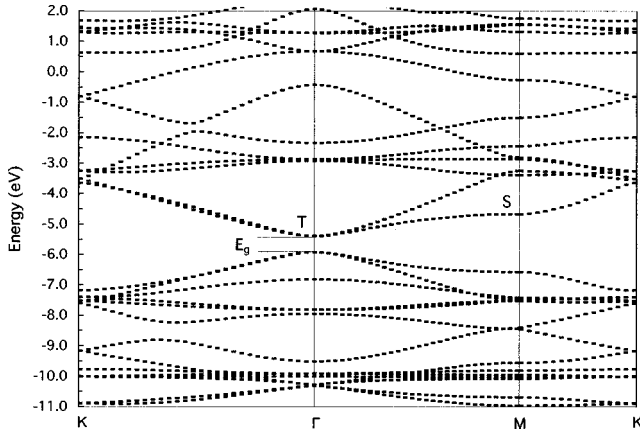


FIG. 9. Electronic band structure of graphdiyne.

angle between them is $\gamma=120^\circ$. A unit cell contains 12 carbon atoms. The Brillouin zone for this structure is a equilateral hexagon shown on the upper side in Fig. 1.

IV. RESULTS AND DISCUSSION

A. Optimized geometry

First we assign the number for each bond as shown in Fig. 4. The distance between the centers of two hexagons is equal to the lattice length a of each material. When we fix the length a we get the optimized lengths of each assigned bond for such a . Since the most stable structure of the material has the maximum binding energy, we tried to find the maximum binding energy changing the lattice length of the lattice. As an initial condition for this calculation we set all bond lengths equal and all bond angles are set (not fixed) at either 120° or 180° . Here the lattice length is determined by the type of bonds. As for the bond lengths, we change them between two limiting values: one is 1.20 \AA of a triple bond ($\text{C}\equiv\text{C}$) and another is 1.55 \AA of a single bond ($\text{C}-\text{C}$). The former gives the minimum value of the lattice length and the latter gives the maximum value. In practice we calculated some points as an initial condition that all of the bonds are not always equivalent, because we feared that other stable states of the structures might exist. However, we got the same convergence.

The change of the binding energy with the lattice parameter a for graphdiyne is shown in Fig. 5. It is certain that the binding energy gets the maximum at somewhere within $a=9.2-9.5 \text{ \AA}$. The calculation was carried out closely to search the maximum point in this region, and the maximum binding energy for graphdiyne was obtained at 7.78 eV/atom at $a=9.44 \text{ \AA}$. In a similar way the calculation was carried out

for graphyne, graphyne-3, and graphyne-4. All of the optimized lattice lengths and the binding energies of graphyne and its family are given in Table I. The optimized length of graphyne is consistent with the results of Baughman, Eckhardt, and Kertesz.⁵

The values of the binding energy for graphyne and graphdiyne are compared with the calculated values of 8.66 eV/atom for graphite and 8.22 eV/atom for fullerene C_{60} in the local-density approximation. The difference of the binding energy seemed to depend on whether sp carbon atoms are contained in the material.

Furthermore, the change of each bond length with the lattice parameter a for graphdiyne is shown in Fig. 6. We can see from Fig. 6 that each bond is stable and does not change to another type of bond immediately, even if the lattice parameter changes a little. We also carried out the calculation and obtained similar results for graphyne, graphyne-3, and graphyne-4 to that for graphdiyne. These data are very useful to study in case pressure is applied to these materials, because we can see how each bond changes from these figures.

Now we can show all of the optimized bond lengths. They are given in Fig. 7. The bond lengths 1 and 3 are gradually increasing as the lattice parameter increases, while the bond lengths 2 and 4 are slightly decreasing as the lattice parameter increases. This is considered to be mainly caused by the effect of the conjugated bonds. However, the difference of each bond length is very small. Therefore, it is considered that each bond has the same character for the graphyne and its family. The bond lengths such as 4 and 6 that appear for graphdiyne, graphyne-3, and graphyne-4 would be almost equivalent. Thus, the bonds with length 4 or 6 have the same bond character, because the relative position of the nearest-neighbor atoms is the same. In the same consideration the bonds with length 3 or 5 have the same bond character, too.

The mean bond lengths 1, 2, 3, (5 is included), and 4 (6 is included) are $1.43, 1.40, 1.23, \text{ and } 1.33 \text{ \AA}$, respectively. The bond length 1 is a little longer than 2 for these materials. The type of the bonds with the former length is to be $\text{C}(sp^2)-\text{C}(sp^2)$ as seen in graphite ($=1.42 \text{ \AA}$), and the type of bonds with the latter length is not a typical single bond such as toluene ($=1.53 \text{ \AA}$) and diphenyl ($=1.50 \text{ \AA}$) but is to be $\text{C}(sp^2)-\text{C}(sp)$ considering that the neighboring bond length 3 is nearly equal to the acetylenic bond length 1.20 \AA . The type of the bonds with the bond length 3 is $\text{C}(sp)\equiv\text{C}(sp)$ and the small difference is probably due to the effect of the conjugated bond as mentioned above. The tendency of the order of bond lengths for graphyne is consistent with the results of Baughman, Eckhardt, and Kertesz, using the MNDO method.⁵

TABLE II. The band gap E_g and effective mass in the conduction band (m_c) and valence band (m_v) are given. Effective masses are anisotropic for graphyne and graphyne-3. m_0 is an electron mass, and ($\Gamma \rightarrow M$) means the approach to the gap point M from the ΓM side.

	E_g (eV)	m_c/m_0		m_v/m_0	
Graphyne	0.52 at M	0.15($\Gamma \rightarrow M$)	0.063($M \leftarrow K$)	0.17($\Gamma \rightarrow M$)	0.066($M \leftarrow K$)
Graphdiyne	0.53 at Γ		0.073		0.075
Graphyne-3	0.60 at M	0.099($\Gamma \rightarrow M$)	0.081($M \leftarrow K$)	0.12($\Gamma \rightarrow M$)	0.085($M \leftarrow K$)
Graphyne-4	0.59 at Γ		0.081		0.080

The bond lengths 4 and 6 are about 10% larger than the acetylenic bond length. These bond lengths are close to the typical double bond length of 1.34 Å, and then judging only from the bond length, carbons seem to form the bond such as $C(sp^2)=C(sp^2)$ or $C(sp^2)=C(sp)$. However, these bonds are considered as follows: The bonds that have the length 3 or 5 are mainly triple bonds. These carbons form $C(sp)\equiv C(sp)$, and also contain some characteristics of the single bond. And the bonds that have the length 4 or 6 are single bonds between two triple bonds $C(sp)\equiv C-C\equiv C(sp)$. This is the same type of bond as seen in diacetylene. The single bond length of diacetylene is 1.38 Å, and it is extremely shorter than the ordinary single bond length. In this case it is explained by the conjugated multiple bond. Thus, the single bond between two triple bonds has the character of the double bond. In the same consideration the single bonds with length 4 or 6 interact with each other through the triple bond situated between them, hence we get the character of a double bond.

Thus the carbon chains constructing graphyne and its family are composed of acetylene linkages ($-C\equiv C-$). It is very difficult to accept that the bonds are composed of cumulative linkages ($=C=C=$) in these carbon chains as the bond lengths are considerably different from one another.

B. Electronic band structure

We calculated the electronic band structures of graphyne, graphdiyne, graphyne-3, and graphyne-4 by use of each self-consistent potential with the optimized geometry. The electronic band structures of graphyne and graphdiyne are shown in Figs. 8 and 9, respectively. As seen in the figures, both graphyne and graphdiyne are semiconductors with moderate energy band gaps. The similar electronic band structures were obtained for graphyne-3 and graphyne-4. The energy gaps are given in Table II. The energy gaps occur at the M point or Γ point alternately by the number of acetylenic linkages ($-C\equiv C-$), which are contained between two hexagons. Both the highest valence band and the lowest conduction band consist of mainly $2p_z$ orbitals. The characteristics included mainly in some bands which lie above and below the gap are given for graphyne and graphdiyne in Table III.

Graphyne and its family are very promising for the use of intercalation compounds. It is very convenient to intercalate the alkali metal into the voids. Then the distance between adjacent layers is extremely shorter than that of the graphite intercalation compound. We are going to investigate the stability of alkali-doped interlayer sheets. There are further interesting points for graphyne and its family in relation to the intercalation. As seen in Figs. 8 and 9, the values of energy at the bottoms of the lowest conduction bands are -5.5 eV for graphyne and -5.4 eV for graphdiyne, and are almost equal to the energy at the K point for graphite, -5.5 eV. Therefore, we can expect for graphyne and its family to exhibit the same property as graphite by doping alkali metal to these materials. Furthermore, the difference of the energy between the saddle point S on the lowest conduction band ($\frac{2}{3}$ point from the Γ point to the K point) and its lowest point T is small ($=0.53$ eV) for graphyne in Fig. 8, and the difference of the energy between S and T on the lowest conduction band is 0.72 eV for graphdiyne in Fig. 9. The peculiar prop-

TABLE III. The characters that are mainly included in the conduction and valence bands near the gaps. The characters at the M point for graphyne and at the Γ point for graphdiyne are given. s represents nondegenerated and d represents doubly degenerated.

Graphyne		Graphdiyne			
Conduction band	Band (s)	$2s, 2p_x, 2p_y$	Conduction band	Band (s)	$2p_z$
	Band (s)	$2s, 2p_x, 2p_y$		Band (s)	$2p_z$
	Band (s)	$2s, 2p_x, 2p_y$		Band (d)	$2p_z$
	Band (s)	$2p_z$		Band (s)	$2p_x, 2p_y$
	Band (s)	$2p_z$		Band (d)	$2p_z$
Gap at M point		Gap at Γ point			
Valence band	Band (s)	$2p_z$	Valence band	Band (d)	$2p_z$
	Band (s)	$2p_z$		Band (s)	$2p_x, 2p_y$
	Band (s)	$2p_x, 2p_y$		Band (d)	$2s, 2p_x, 2p_y$
	Band (s)	$2p_x, 2p_y$		Band (s)	$2p_z$
	Band (s)	$2s, 2p_x, 2p_y$		Band (s)	$2p_z$

erty such as superconductivity is expected to come out if we can dope the alkali metal to graphyne and its family and make the density of states at the Fermi energy diverge.

The effective masses in the conduction band (m_c) and valence band (m_v) were estimated as given in Table II. The effective masses are very small compared with typical semiconductors. The curvatures of these bands around the gaps are independent of direction, and the effective masses are isotropic for graphdiyne and graphyne-4, while the curvatures dependent on directions for graphyne and graphyne-3, and the effective masses are extraordinarily anisotropic.

V. CONCLUSIONS

The optimized geometry and electronic band structures of new carbon allotropes, graphyne, graphdiyne, graphyne-3, and graphyne-4 were calculated using a full potential LCAO method.

As a result of the geometry optimization, hexagons are equilateral and all bond angles are either 120° or 180° . The binding energy and the lattice parameter are 7.95 eV and 6.86 Å for graphyne and 7.78 eV and 9.44 Å for graphdiyne, respectively. The bond length of a hexagon is almost equal to that of graphite and it is a little longer than the bond length that extends outside a hexagon, and the carbon chain between hexagons is not composed of cumulative linkages ($=C=C=$), but is composed of acetylenic linkages ($-C\equiv C-$). The effect of conjugated multiple bond is very important for graphyne and its family.

The electronic band structures of these materials were obtained using the potentials with the optimized geometries. As a result, these compounds are semiconductors with gaps of 0.5 – 0.6 eV. The effective masses for these materials are considerably small compared with typical semiconductors.

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