New polymorphic varieties of graphyne formed on the basis of 5-7b graphene: Ab initio calculations

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Abstract: The crystal and electronic structure of 16 new polymorphic varieties of sp+sp² graphyne layers was calculated by the density functional theory method in the gradient approximation. The primary structure of the graphyne layers was constructed by replacing the interatomic bonds in the graphene layers 5-7b with carbyne chain fragments. Ab initio calculations have shown that out of 29 modeled structures only sixteen are stable: 14 β-type layers and one α- and γ-type layer each. During optimization 13 graphyne layers were transformed into graphene layers or into graphyne layers with a smaller relative number of sp-hybridized atoms. The electronic properties of most of the new graphyne layers are metallic, since the density of electronic states at the Fermi energy level for them is different from zero. There are forbidden zones in the electronic structure of the seven layers, but their value is small and varies from 0.05 to 0.20 eV.

1. Introduction
Carbon compounds can have different crystal structures and exist in the form of allotropic varieties polymorphs or polytypes [1]. Allotropic varieties differ in that carbon atoms in their structure are in different coordinated states, as a consequence of which they have different hybridization of electronic orbitals (sp, sp² or sp³) [2]. Carbyne, graphite and diamond are the three main allotropic varieties of carbon [3-6]. Each of the structures belonging to the corresponding allotropes can exist as different polymorphs. For example, the existence of many polymorphs of graphene [7] or diamond [8] is possible. The next type of structural forms of carbon compounds is polytypes. In polytypes the coordination of atoms and correspondingly the allotropy and polymorphic structure are the same [1]. Polytypes differ in the order of alternation of molecular layers in three-dimensional crystals. Examples of polytypes are rhombohedral and hexagonal graphite or cubic and hexagonal diamond [3]. The different structure of carbon compounds causes differences in their properties. Except for carbon compounds which can be referred to one of three basic allotropic varieties the existence of various hybrid carbon structures which consist of carbon atoms with different hybridization of orbitals - sp+sp², sp+sp³, sp²+sp³ or sp+sp²+sp³ is possible [2]. For practical applications it is important to understand how variations in the structure of carbon materials can change the properties. From this point of view, the most interesting are hybrid compounds whose properties can vary significantly with changes in the proportion of atoms in different hybridized states. Hybrid sp+sp² compounds have a
layered structure. Some of these compounds called graphynes have been synthesized experimentally [9-12]. Even more graphyne structural forms have been predicted theoretically [13-18]. Theoretically the structure of all possible graphyne compounds can be constructed on the basis of graphene layers according to the algorithm proposed in [14,16]. Various polymorphs of graphene can be used as the basis for the construction of the graphyne structural varieties. Earlier the graphyne structures modeled from the graphene layers L_6, L_4-8, L_3-12 and L_4-6-12 were theoretically investigated [16]. The properties of graphyne polymorphs change significantly depending on the fraction of carbon atoms in sp and sp² hybridized states. To find statistically significant regularities describing the relationship between the structural characteristics and various properties of graphyne polymorphs, further research is needed. In this paper the structure and electronic properties of the new polymorphs of the graphyne modeled on the basis of the 5-7b graphene layer are investigated.

2. Algorithm for modelling graphyne structures and calculation methods

The primary structure of the new graphyne layers was theoretically constructed using the algorithm proposed in [14,16]. According to this algorithm the graphene layer should be used as the initial structure. In [7] the possibility of the stable existence of the three main polymorphic varieties of 5-7 graphene was established (figure 1). In this work the 5-7b graphene layer was chosen as the initial layer for the construction of the graphyne structures. The structure of the graphyne layers was obtained by replacing all or part of the carbon-carbon bonds with carbyne chains. Each carbon atom in the graphene layer is connected by covalent bonds with three neighboring atoms, so it is possible to replace one, two or three bonds with a carbyne chain. If each three-coordinated atom has all bonds with neighboring atoms replaced with a carbyne chain, then α-graphene layers are formed. Replacing two or one bond formed the structure of β and γ graphyne varieties, respectively.

![Figure 1. Structure of optimized graphene layers L_5-7a (a), L_5-7b (b), L_5-7c (c) [7].](image)

The geometric optimization of the modeled structures and calculation of their electron properties were performed by the Density Functional Theory (DFT) [19] in Generalized Gradient Approximations (GGA) [20]. The DFT-GGA parallel calculations were performed using the Quantum ESPRESSO software package [21]. The temperature was assumed to be 0.01 K. A 12 × 12 × 12 grid of k-points was used. The cutoff energy for the plane wave basis was 816 eV. The calculations were performed for stacked parallel graphyne layers, with a distance of 10 Å between layers, at which the influence of neighboring layers on each other can be neglected.

3. Calculation results and discussion

As a result of the model construction of graphyne structures based on layer 5-7b, fourteen initial graphyne layers γ and β of structural varieties each were constructed, as well as one α structure.
Figure 2. Structure of geometrically optimized graphyne layers with a stable structure: (a) $\alpha$-L$_{5.76}$; (b) $\beta$L$_{1}$-L$_{5.76}$; (c) $\beta$2-L$_{5.76}$; (d) $\beta$3-L$_{5.76}$; (e) $\beta$4-L$_{5.76}$; (f) $\beta$5-L$_{5.76}$; (g) $\beta$6-L$_{5.76}$; (h) $\beta$7-L$_{5.76}$; (i) $\beta$8-L$_{5.76}$; (j) $\beta$9-L$_{5.76}$; (k) $\beta$10-L$_{5.76}$; (l) $\beta$11-L$_{5.76}$; (m) $\beta$12-L$_{5.76}$; (n) $\beta$13-L$_{5.76}$; (o) $\beta$14-L$_{5.76}$; (p) $\gamma$1-L$_{5.76}$. 
DFT-GGA calculations of the geometrically optimized structure of the graphyne layers showed that only \( \alpha \) layer, one \( \gamma \) layer, and fourteen structural varieties of \( \beta \) layers retained their original graphyne structure. Images of the structure of these stable layers are shown in Figure 1. The structure of the unstable \( \gamma \)-type layers was transformed into the structure of graphene layers or into the structure of graphyne layers with a smaller relative number of \( \text{sp}^2 \) hybridized atoms in the process of optimization.

Numerical values of structural parameters characterizing the graphyne layers 5-7b are shown in Table 1. The unit cells of the layers are orthorhombic and monoclinic, containing 32 to 64 atoms. The values of translation vectors \( a \) and \( b \) range from 0.80 to 2.59 nm (Table 1). The number of different structural positions of the atoms in the unit cells is minimal for the \( \gamma \)-type layer (\( P = 8 \)), the maximum value is observed in the \( \beta8-L_{5.7b} \) layer (\( P = 48 \)). This is a characteristic difference of the graphyne layers formed on the basis of 5-7 graphene layers from the graphene layers constructed from the main polymorphic varieties of graphene in which the number of different structural positions of atoms is only two. The ratio of the number of atoms in the \( \text{sp} \) and \( \text{sp}^2 \) hybridization states changes from 1:1 in the \( \gamma1-L_{5.7b} \) graphyne layer to 2:1 in the \( \beta \)-type layers and 3:1 in the \( \alpha-L_{5.7b} \) graphyne layer (Table 1).

**Table 1.** Parameters of the structure of the graphyne layers built on the basis of \( L_{5.7b} \) graphene, calculated by the DFT-GGA method (\( P \) - the number of non-equivalent structural positions of atoms; \( N \) - the number of atoms in the unit cell; \( a, b \) - vectors of elementary translations; \( \gamma \) - angle between translation vectors; Crystal family - \( m \) (monoclinic) or \( o \) (orthorhombic) for calculations of three-dimensional crystals consisting of graphyne layers packed in a stack with a distance between layers of 1 nm).

| Graphyne layer | \( P \) | \( N \) | \( a, \text{nm} \) | \( b, \text{nm} \) | \( \gamma, ^\circ \) | \( \text{sp}:\text{sp}^2 \) | Crystal family |
|----------------|--------|--------|----------------|----------------|---------------|----------------|----------------|
| \( \alpha-L_{5.7b} \) | 16     | 64     | 2.59           | 1.35           | 90            | 3:1            | o              |
| \( \beta1-L_{5.7b} \) | 12     |        | 2.06           | 1.23           | 126.8         | m              | m              |
| \( \beta2-L_{5.7b} \) | 24     |        | 2.33           | 1.04           | 120           | m              | m              |
| \( \beta3-L_{5.7b} \) | 24     |        | 2.03           | 1.04           | 83.3          | m              | m              |
| \( \beta4-L_{5.7b} \) | 24     |        | 1.83           | 1.12           | 90            | o              | m              |
| \( \beta5-L_{5.7b} \) | 24     |        | 1.93           | 1.12           | 110.1         | m              | o              |
| \( \beta6-L_{5.7b} \) | 24     |        | 2.29           | 0.92           | 101.3         | m              | m              |
| \( \beta7-L_{5.7b} \) | 12     | 48     | 2.25           | 0.92           | 90            | 2:1            | o              |
| \( \beta8-L_{5.7b} \) | 48     |        | 2.14           | 0.98           | 101.8         | m              | m              |
| \( \beta9-L_{5.7b} \) | 24     |        | 2.09           | 0.97           | 90            | o              | m              |
| \( \beta10-L_{5.7b} \) | 10     |        | 2.06           | 1.00           | 103.6         | m              | m              |
| \( \beta11-L_{5.7b} \) | 10     |        | 2.00           | 1.00           | 90            | o              | m              |
| \( \beta12-L_{5.7b} \) | 12     |        | 2.42           | 0.92           | 112.6         | m              | m              |
| \( \beta13-L_{5.7b} \) | 24     |        | 2.32           | 0.96           | 114.8         | m              | m              |
| \( \beta14-L_{5.7b} \) | 10     |        | 2.24           | 1.00           | 116.6         | m              | o              |
| \( \gamma1-L_{5.7b} \) | 8      | 32     | 0.80           | 1.27           | 90            | 1:1            | o              |

The results of calculations of some properties of 5-7b are shown in Table 2. The layer density is minimum for layer \( \alpha-L_{5.7b} \) - 0.36 mg/m², the maximum density value - 0.62 mg/m² is observed for the graphyne layer \( \gamma1-L_{5.7b} \). For the \( \beta \)-type graphyne layers, the density is about 0.47 mg/m². The layer density of the graphene layers is below 0.74 mg/m² - the values of the layer density for hexagonal graphene. The total specific bonding energy \( E_{\text{total}} \) per atom varies from -156.34 to -156.10 eV/atom. The energy \( \Delta E_{\text{total}} \) calculated as the difference of specific energies in the graphene layers and the hexagonal graphene layer varies from 0.98 to 1.22 eV/atom. This indicates a lower stability of the graphyne layers compared to the graphene layers. However, the sublimation energies of 6.66 ÷ 6.78 eV/atom 5-7b graphyne layers have values falling within the interval characteristic of carbon compounds stably existing under normal conditions. The maximum sublimation energy is observed for \( \beta10-L_{5.7b} \), \( \beta11-L_{5.7b} \) and \( \beta14-L_{5.7b} \) layers (Table 2). These graphyne layers should be the most stable.
Ab initio DFT-GGA calculations of the band structure and electron density of $\alpha$, $\beta$, and $\gamma$-L$_{5.7b}$ graphyne layers have shown that for nine layers, at an energy equal to the Fermi energy, the density of electron states is non-zero. The remaining seven layers have a small band gap ($\Delta$) which varies from 0.05 to 0.20 eV. The Fermi energy ($E_F$) varies in the range from -4.99 to -4.24 eV (table 2).

| Graphyne layer | $E_{\text{total}}$, eV/atom | $\Delta E_{\text{total}}$, eV/atom | $E_{\text{sub}}$, eV/atom | $\Delta$, eV | $E_F$, eV | $\rho$, mg/m$^2$ |
|----------------|-----------------------------|-----------------------------------|----------------------------|-------------|----------|-------------|
| $\alpha$-L$_{5.7b}$ | -156.22                     | 1.10                              | 6.66                       | -4.64       | 0.36     |             |
| $\beta$1-L$_{5.7b}$ | -156.29                     | 1.03                              | 6.73                       | -4.58       | 0.47     |             |
| $\beta$2-L$_{5.7b}$ | -156.22                     | 1.10                              | 6.66                       | -4.60       | 0.46     |             |
| $\beta$3-L$_{5.7b}$ | -156.10                     | 1.22                              | 6.54                       | -4.55       | 0.46     |             |
| $\beta$4-L$_{5.7b}$ | -156.31                     | 1.01                              | 6.75                       | 0.17        | 0.47     |             |
| $\beta$5-L$_{5.7b}$ | -156.31                     | 1.01                              | 6.75                       | 0.08        | 0.47     |             |
| $\beta$6-L$_{5.7b}$ | -156.24                     | 1.08                              | 6.68                       | -4.57       | 0.46     |             |
| $\beta$7-L$_{5.7b}$ | -156.27                     | 1.05                              | 6.71                       | 0.11        | 0.47     |             |
| $\beta$8-L$_{5.7b}$ | -156.28                     | 1.04                              | 6.72                       | 0.18        | 0.47     |             |
| $\beta$9-L$_{5.7b}$ | -156.28                     | 1.04                              | 6.72                       | 0.20        | 0.47     |             |
| $\beta$10-L$_{5.7b}$ | -156.34                    | 0.98                              | 6.78                       | -4.91       | 0.48     |             |
| $\beta$11-L$_{5.7b}$ | -156.34                    | 0.98                              | 6.78                       | -4.99       | 0.48     |             |
| $\beta$12-L$_{5.7b}$ | -156.22                    | 1.10                              | 6.66                       | -4.59       | 0.46     |             |
| $\beta$13-L$_{5.7b}$ | -156.29                    | 1.03                              | 6.73                       | 0.05        | 0.47     |             |
| $\beta$14-L$_{5.7b}$ | -156.34                    | 0.98                              | 6.78                       | -4.91       | 0.48     |             |
| $\gamma$1-L$_{5.7b}$ | -156.29                    | 1.03                              | 6.73                       | -4.24       | 0.62     |             |

4. Conclusion

Thus, 29 new graphyne layers based on the 5-7b graphene layer were theoretically constructed using a specially developed algorithm. As a result of ab initio DFT-GGA calculations it was found that only 16 layers have a stable structure: $\alpha$-L$_{5.7b}$, $\gamma$1-L$_{5.7b}$ and 14 graphyne layers $\beta$-L$_{5.7b}$. The structure of 13 $\gamma$-type layers turned out to be unstable under geometric optimization. These layers consisting of sp+sp$^2$ hybridized atoms in the ratio 1:1 tend to transform their structure transforming into graphene layers consisting only of sp$^2$ hybridized atoms. The band gap width is zero for most of the stable graphene layers, and for the rest does not exceed 0.2 eV. Experimental synthesis of new polymorphic graphyne varieties seems to be possible with polymerization of molecular structures having carbon framework structure close to the structure of corresponding graphyne layers [22]. Practical use of new graphyne compounds is possible as hydrogen power, in lithium batteries and as molecular sieves [23-25].

5. References

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