Structural types of graphyne layers formed on the basis of 4-6-12 graphene

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Abstract. The structure of seven new polymorphic varieties of graphyne layers has been calculated using the density functional theory at the generalized gradient approximation. The model of graphyne layers is based on 4-6-12 graphene layer. For graphyne layers the sublimation energy varies in the range from 6.62 to 7.08 eV atom⁻¹, the band gap ranges from 0 to 0.643 eV. The structures of polymorphs of the graphyne are characterized by deformation parameter the value of which correlates well with the sublimation energy.

1. Introduction
Graphyne layers consist of carbon atoms in two- and three-coordinated (sp- and sp²-hybridized) states [1-9]. The structure of such compounds can be modeled on the basis of graphene layers in which the C-C bonds are substituted with fragments of carbyne chains [10-14]. The properties of graphyne layers can vary considerably depending on the ratio of different hybridized atoms and structural characteristics. The structure of graphyne polymorphs differs from the initial graphene layers by the degree of deformation, which may be the cause of the change in properties. In this work first-principle calculations of new structural varieties of graphyne were carried out to find the relationships between structural characteristics and properties.

2. Methods
The theoretical simulation of all the possible structural species of graphyne was performed according to the method described in [10, 14]. L₄₋₆₋₁₂ graphene was taken as the initial layer for the simulation. The structure of the graphyne layers can be characterized by deformation parameter (Def). Def was defined as a sum of absolute values of differences between the interbond angles observed in compounds of graphyne and corresponding angles in the hexagonal graphene (120°) for sp² atoms and chain of carbyne (180°) for sp atoms. The geometricaly optimized structure, sublimation energies, and electronic properties of graphynes were calculated by the density functional theory (DFT) method [15] in the generalized gradient approximation (GGA) [16]. Calculations of the graphyne layers were performed using the Quantum ESPRESSO software package [17]. The sublimation energy was found as the difference between the total energy per carbon atom in the graphyne layers and the energy of an isolated carbon atom.
3. Results and discussion

As a result of model calculation, seven main varieties of graphyne (α, β1, β2, β3, γ1, γ2, γ3) were obtained. Figure 1 presents the geometrically optimized structures of six layers, calculated by the DFT-GGA method. The structure of the γ3-graphyne was transformed into L4-6-8-12-graphene in the process of geometrical optimization (figure 2).

![Figure 1](image)

**Figure 1.** Geometrically optimized by the DFT-GGA method structures of α-, β1-, β2-, β3-, γ1- and γ2-graphyne layers on the basis of the L4-6-12-graphene.

The crystal lattices of graphyne layers are hexagonal syngony, their unit cells contain from 24 to 48 of carbon atoms (figure 1, table 1). All atoms with sp² hybridization of electronic orbitals in each graphyne layer of the different types are in equivalent structural positions. The number of unique structural positions of sp atoms for different layers is different: there are three such positions in the α-L4-6-12 layer, two in the β-L4-6-12 layers, and one in the γ-L4-6-12 layers. Therefore, the total quantity of different structural atomic positions (n) in graphyne layers varies from 2 to 4 (table 1). Different structural atomic positions in the graphyne layers correspond to different Wells ring parameters (Rng) (table 1).
Figure 2. The structure of the initial $\gamma_3$-graphene layer constructed on the basis of $L_{4.6-12}$-graphene previously optimized by the molecular mechanical method MM2 and after geometric optimization by the DFT-GGA method.

Table 1. Structural parameters and properties of graphyne layers (n is quantity of the atomic positions; Rng$_i$ are Wells ring parameters, where i is number of the atomic position; a, b are the lengths of the elementary translation vectors; N is the number of atoms in the unit cell; Def$_i$ is the deformation parameter, were j=1 for sp$^2$ atoms, j=2 for sp atoms; $E_{total}$ is the total energy; $\Delta E_{total}$ is the total difference energy; $E_{sub}$ is the sublimation energy; $\Delta$ is the band gap; $E_F$ is the Fermi energy; $\rho$ is layer density).

| Layer         | $\alpha$-$L_{4.6-12}$ | $\beta_1$-$L_{4.6-12}$ | $\beta_2$-$L_{4.6-12}$ | $\beta_3$-$L_{4.6-12}$ | $\gamma_1$-$L_{4.6-12}$ | $\gamma_2$-$L_{4.6-12}$ |
|---------------|-----------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| n             | 4                     | 3                       | 3                       | 3                       | 2                       | 2                       |
| Rng$_1$       | 12$^1$18$^3$36$^1$    | 12$^2$24$^1$            | 8$^1$18$^1$24$^1$      | 8$^1$12$^1$36$^1$      | 6$^1$8$^1$24$^1$      | 4$^1$12$^1$24$^1$      |
| Rng$_2$       | 12$^3$36$^1$         | 12$^4$24$^1$            | 8$^1$18$^1$24$^1$      | 8$^1$12$^1$36$^1$      | 6$^1$8$^1$24$^1$      | 4$^1$12$^1$24$^1$      |
| Rng$_3$       | 12$^1$18$^1$         | 12$^2$24$^1$            | 8$^1$18$^1$24$^1$      | 8$^1$12$^1$36$^1$      | 6$^1$8$^1$24$^1$      | 4$^1$12$^1$24$^1$      |
| Rng$_4$       | 18$^3$36$^1$         | -                       | -                       | -                       | -                       | -                       |
| sp:sp$^2$     | 3:1                   | 2:1                     | 2:1                     | 2:1                     | 1:1                     | 1:1                     |
| a, b (Å)      | 18.934                | 13.665                  | 14.156                  | 16.142                  | 10.901                  | 11.923                  |
| N (atom)      | 48                    | 36                      | 36                      | 36                      | 24                      | 24                      |
| Def$_1$ (°)   | 17.0                  | 22.6                    | 25.4                    | 11.2                    | 14.0                    | 60.0                    |
| Def$_2$ (°)   | 9.7                   | 10.2                    | 19.7                    | 13.9                    | 23.0                    | 8.0                     |
| $E_{total}$ (eV atom$^{-1}$) | -156.18              | -156.27                 | -156.18                 | -156.25                 | -156.64                 | -156.33                 |
| $\Delta E_{total}$ (eV atom$^{-1}$) | 1.14                  | 1.05                    | 1.14                    | 1.07                    | 0.68                    | 0.99                    |
| $E_{sub}$ (eV atom$^{-1}$) | 6.62                  | 6.71                    | 6.62                    | 6.69                    | 7.08                    | 6.77                    |
| $\Delta$ (eV) | 0.166                 | 0                       | 0                       | 0                       | 0.643                   | 0                       |
| $E_F$ (eV)    | -4.768                | -4.792                  | -4.732                  | -4.730                  | 4.670                   | -4.642                  |
| $\rho$, (mg m$^{-2}$) | 0.31                  | 0.44                    | 0.41                    | 0.32                    | 0.46                    | 0.39                    |

Graphyne layers have the different ratio of sp- and sp$^2$-hybridized atoms (table 1). For each atom in the $\alpha$-graphyne layer there are three two-coordinated atoms, in the $\beta$- and $\gamma$-type layers, the ratio is 2:1 and 1:1, respectively. The minimal sublimation energy is observed in $\alpha$-$L_{4.6-12}$- and $\beta_2$-$L_{4.6-12}$-graphyne, the maximal – in $\gamma_1$-$L_{4.6-12}$-graphyne (table 1). The deformation parameter Def$_i$, which characterizes the states of three-coordinated atoms, varies in the range from 11.2° to 60.0°. In the initial graphene layer $L_{4.6-12}$, the value of this parameter is 60°. Thus, when forming the structure of
graphyne layers, the stresses of the initial layer should decrease. This is due to the deformation of the carbyne chains. The degree of this deformation is characterized by the parameter Def, which is minimal for the γ2-L4-6-12 layer - 8.0° and maximum for the γ1-L4-6-12 layer - 23.0°. The deformation of the structure of the graphyne layer found as a weighted average of the deformation parameters of the two states is minimal for γ1-L4-6-12, the sublimation energy of which is maximum (table1).

The results of DFT-GGA calculations of the band structure and density of electronic states are shown in figures 3 and 4. For most graphene layers, the bandgap energy (Δ) at the Fermi level is zero that indicates on the metallic conductivity of these layers. For two layers α-L4-6-12 and γ1-L4-6-12, the bandgaps are not zero (0.166 and 0.643 eV, respectively) and the layers are semiconductors (table1).

Figure 3. Band structure of graphyne layers formed on the basis of graphene layer L4-6-12: (a) α-L4-6-12; (b) β1-L4-6-12; (c) β2-L4-6-12; (d) β3-L4-6-12; (e) γ1-L4-6-12; (f) γ2-L4-6-12.
Figure 4. Densities of electronic states (DOS) of graphyne layers formed on the basis of graphene layer $L_{4,6,12}$: (a) $\alpha-L_{4,6,12}$; (b) $\beta_1-L_{4,6,12}$; (c) $\beta_2-L_{4,6,12}$; (d) $\beta_3-L_{4,6,12}$; (e) $\gamma_1-L_{4,6,12}$; (f) $\gamma_2-L_{4,6,12}$ (zero on energy axis corresponds to the Fermi level).

4. Conclusion

Thus, in this work on the basis of the graphene layer $L_{4,6,12}$, seven new polymorphic varieties of graphyne were model-built. The calculations performed by the DFT-GGA method showed that the structure of only six layers of $\alpha$, $\beta_1$, $\beta_2$, $\beta_3$, $\gamma_1$, $\gamma_2$ types is stable. The angles between the bonds in the graphyne layers differ from the values characteristic for hexagonal graphite and ideal carbonyne, i.e. their structure can be considered as deformed. The sublimation energy of the graphyne layers varies in the range from 6.62 to 7.08 eV atom$^{-1}$ and correlates well with the value of the deformation parameters (the greater the strain, the less the energy of sublimation). Most graphyne layers have zero band gap at the Fermi energy level, however, two layers, $\alpha-L_{4,6,12}$ and $\gamma_1-L_{4,6,12}$, have a non-zero band gap and their properties must be semiconductor.

References

[1] Baughman R H, Eckhardt H and Kertesz M 1987 *J. Chem. Phys.* 87 6687
[2] Diederich F 1994 *Nature* 369 199
[3] Narita N, Nagai S, Suzuki S and Nakao K 1998 *Phys. Rev. B* 58 11009
[4] Bunz U H F, Rubin Y and Tobe Y 1999 *Chem. Soc. Rev.* 28, 107
[5] Marsden J A, Haley M M 2005 *J. Org. Chem.* 70 10213
[6] Tahara K, Yoshimura T, Sonoda M, Tobe Y and Williamst R V 2007 *J. Org. Chem.* 72, 1437
[7] Haley M M 2008 *Pure Appl. Chem.* 80 519–532
[8] Li G, Li Y, Liu H, Guo Y, Lia Y and Zhua D 2010 *Chem. Commun.* 46, 3256
[9] Enyashin A N and Ivanovskii A L 2011 *Phys. Status Solidi B* **248** 1879
[10] Belenkov E A, Mavrinskii V V, Belenkova T E and Chernov V M 2015 *J. Exp. Theor. Phys.* **120** 820
[11] Belenkova T, Chernov V and Mavrinskii V 2016 *Mater. Sci. Forum* **845** 239
[12] Belenkov E A and Mavrinskii V V 2018 *Letters on Materials* **8** 169-173
[13] Belenkov E A, Mavrinskii V V, Greshnyakov V A and Brzhezinskaya M M 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **537** 022070
[14] Belenkov E, Brzhezinskaya M and Mavrinskii V 2019 Graphynes: advanced carbon materials with layered structure *Handbook of Graphene, Volume 3: Graphene-like 2D Materials* ed M Zhang (Hoboken: John Wiley & Sons) chapter 4 pp 113–150
[15] Koch W A, Holthausen M C 2001 *Chemist’s guide to density functional theory. 2nd edition.* (Weinheim: Wiley-VCH) 293 p
[16] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[17] Giannozzi P, Baroni S, Bonini N et al. 2009 *J. Phys.: Condens. Matter.* **21** 395502