



Electronic properties of β -graphyne bilayers



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ARTICLE INFO

Article history:

Received 6 October 2014

In final form 16 December 2014

Available online 23 December 2014

ABSTRACT

The β -graphyne is a class of graphyne that presents an interesting difference from other graphynes shapes. The Dirac cone is not located in a point of high-symmetry in reciprocal space. In this work we perform a theoretical study of the electronic properties of bilayers of this material, for different stacking configurations. Our results show that the bilayer are metallic or semiconductor, depending on the staking. By incorporating an electric field to our study, we can see that the gap in semiconductors can be modulated.

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1. Introduction

In the last decades, new allotropic forms of carbon with extraordinary properties have appeared. To mention a few examples, the fullerene [1] was discovered in 1985, the carbon nanotubes [2] in 1991, and graphene [3] in 2004. These events were the beginning of a great activity in theoretical and experimental research on the properties of these nanostructures. In 1987, Baughman and colleagues theoretically predicted a bi-dimensional structure which they called graphyne (GY) [4]. They suggested various types of graphyne by inserting carbon triple bonds ($-C\equiv C-$) into ($C-C$) in graphene. In 1997 Haley et al postulated a material made of a two-dimensional layer of carbon atoms [5], they named this material as graphdiyne (GDY). Generally, these structures may be described as GY networks, where all acetylenic linkages are replaced by diacetylenic linkages ($-C\equiv C-C\equiv C-$). These predictions motivated simulations of materials like graphyne and graphdiyne [6–11]. At the same time, some experimental efforts were made to synthesize these structures [12,13]. Moreover, in recent years there have been significant advances in the synthesis of large areas GDYs semiconducting films on a copper surface [14], preparation of GDY nanowires with high conductivity [15], and attempts to utilize GDYs as components of polymer solar cells [16] or in nanocomposite photocatalysts [17]. In a recent publication, a group of researchers from China, reported the synthesis of graphdiyne nanotubes [18]. In an excellent review, A.L. Ivanovskii, said the theory has far surpassed the experiment of these materials [19]. This theoretical knowledge predicts exceptional properties of these

materials, such as electronic behavior that makes it more versatile than graphene [20], nonlinear mechanical behavior and other interesting mechanical properties [21,22]. Furthermore, these systems are proposed as candidates as materials for nanoelectronics, energy storage or as promising candidates for anode materials in batteries [23,24], for hydrogen storage [25] or as membranes for gases separation [26]. Magnetic properties of some metal atoms adsorbed on graphyne and graphdiyne surfaces were also studied [27], and some fluorographynes structures were recently proposed and examined [28]. According to the review on graphene-related materials [29], graphyne and graphdiyne will be intensively studied in the coming years.

In this article we present a theoretical study of β -graphyne bilayers for different Stacking. We also consider an electric field and its effects on the bilayer. Our results show that the bilayers have interesting properties intermediate between semiconductors and metallic.

2. Results and discussion

The electronic properties of the systems are obtained using the density functional theory (DFT) code OpenMX [30], which is based on localized pseudoatomic orbitals (PAOs) [31] and norm-conserving pseudopotentials [32]. The PAO of carbon atoms consists of two s -orbitals and two p -orbitals. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [33], which is derived within the generalized gradient approximation (GGA) is used, taking into account an energy cutoff equal to 150 Ry and a convergence criteria of 10^{-8} Hartree. All structures are relaxed using the Direct Inversion Iterative Subspace method [34] with a residual force criteria less than 10^{-4} Hartree/Bohr. For calculations of the electronic band structures, 50 k -points were

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Table 1
Separation distance between the layers and binding energy per atom of the β -graphyne and graphene bilayers, for different stacking positions.

Stacking	d (Å)	E_b (meV/atom)	E_b (meV/atom)
A-A	3.55	β -graphyne 17.1	Graphene 10.4–31.1
A-C	3.50	18.6	–
A-B	3.44	20.3	22–70

chosen along each high symmetry line (G-M, M-K and K-G lines) in the first Brillouin-zone. A $50 \times 50 \times 1$ Monkhorst-Pack k -space mesh is used to discretize the first Brillouin-zone for density of states (DOS) calculations [35]. The tetrahedron method is employed in the DOS calculations and the uniform electric field given by a sawtooth waveform is applied during the calculations [30].

First we calculate the electronic structure of one β -graphyne layer. Figure 1 shows the arrangement of carbon atoms and the unit cell employed. The band structure and density of states are also shown in Figure 1. These results (position of the Dirac cone in the band structure and density of states), agree with an investigation of one β -graphyne layer [20].

The separation distance between the layers is obtained by minimizing the total energy of the system. Table 1 shows the values obtained for the different stacking. The binding energy is calculated using the expression $E_b = 2E_{ML} - E_{BL}$, where E_{ML} and E_{BL} represent the total energy (per atom of the unit cell) of the monolayer and bilayer, respectively. The results of the bond energy per atom for different stacking considered are shown in Table 1. We can see that the most stable stacking corresponds to AB because the repulsion between the electron clouds of different layers is minimized in this configuration. In the same table, we incorporate the binding energy of graphene bilayers [36–40], for the purpose of making a qualitative comparison.

Figure 2 shows the results obtained for the bilayers for the different stacking considered. We can see that the system changes from a metal (A-A stacking) to a semiconductor with a small gap of ≈ 0.15 eV (A-B stacking). Our study of the total energy and stability, shows that the most stable configuration corresponds to the A-B stacking, followed by A-C stacking, and A-A stacking. Figure 2 (A-A stacking) shows that the bands of both layers are shifted relative to each other in the k -axis and one of them slightly crosses the Fermi level, giving the structure a metallic behavior. This shift in the bands is quite novel, and it is not produced in the alpha bilayers according to recent literature [41,42]. For the bilayers with the A-C and A-B stacking, a displacement and a non-symmetrical deformation of the bands are produced, ultimately resulting in structures with a small gap semiconductor.

We can distinguish two types of atoms in the structure of β -graphyne, the first one has a sp hybridization (atom B in Figure 1) and the other has a sp^2 hybridization (atom A in Figure 1). On the right side of Figure 2, we illustrate the local density of states for the atoms A and B in bilayers with AA, AB and AC stacking. We see that near the Fermi level, the local density of states of the A atom is higher than the one of the B atom, except for a resonant peak which locates near the Fermi level in the AB and AC stacking. This difference decreases gradually and disappears below the 1.5 eV energy. This behavior can be understood because the atoms A and B are not equivalent within the unit cell of the monolayer. This difference is accentuated in the bilayer and is reflected in the local density of state.

An electric field applied perpendicular to layers shows remarkable effects on the electronic properties of the bilayer β -graphyne. The main consequence of the electric field is that the gap of the A-C and A-B stacking becomes closed, which is interesting from the point of view of possible applications. Notice that in this situation the system behaves like a metal. The breakdown of this behavior is shown in Figures 3 and 4 respectively. In our study of the two semiconductor bilayers (A-C and A-B), the electric field causes

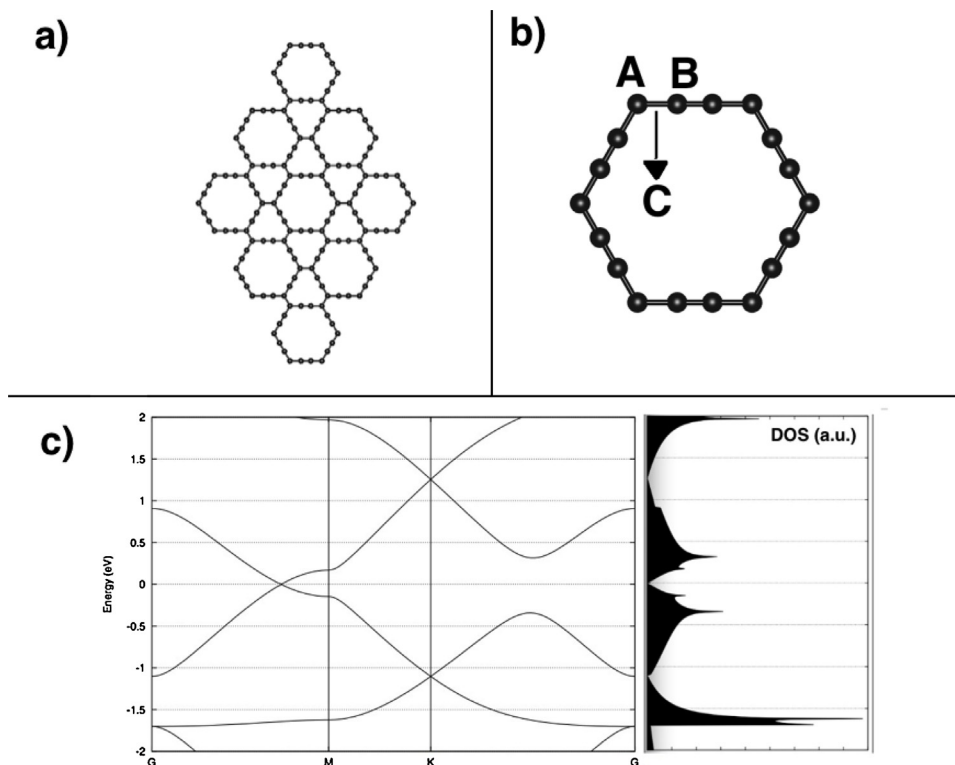


Figure 1. (a) Diagram of one β -graphyne layer and (b) unit cell with the stacking positions, used in this study. (c) Electronic structure of β -graphyne. Band structure and DOS.

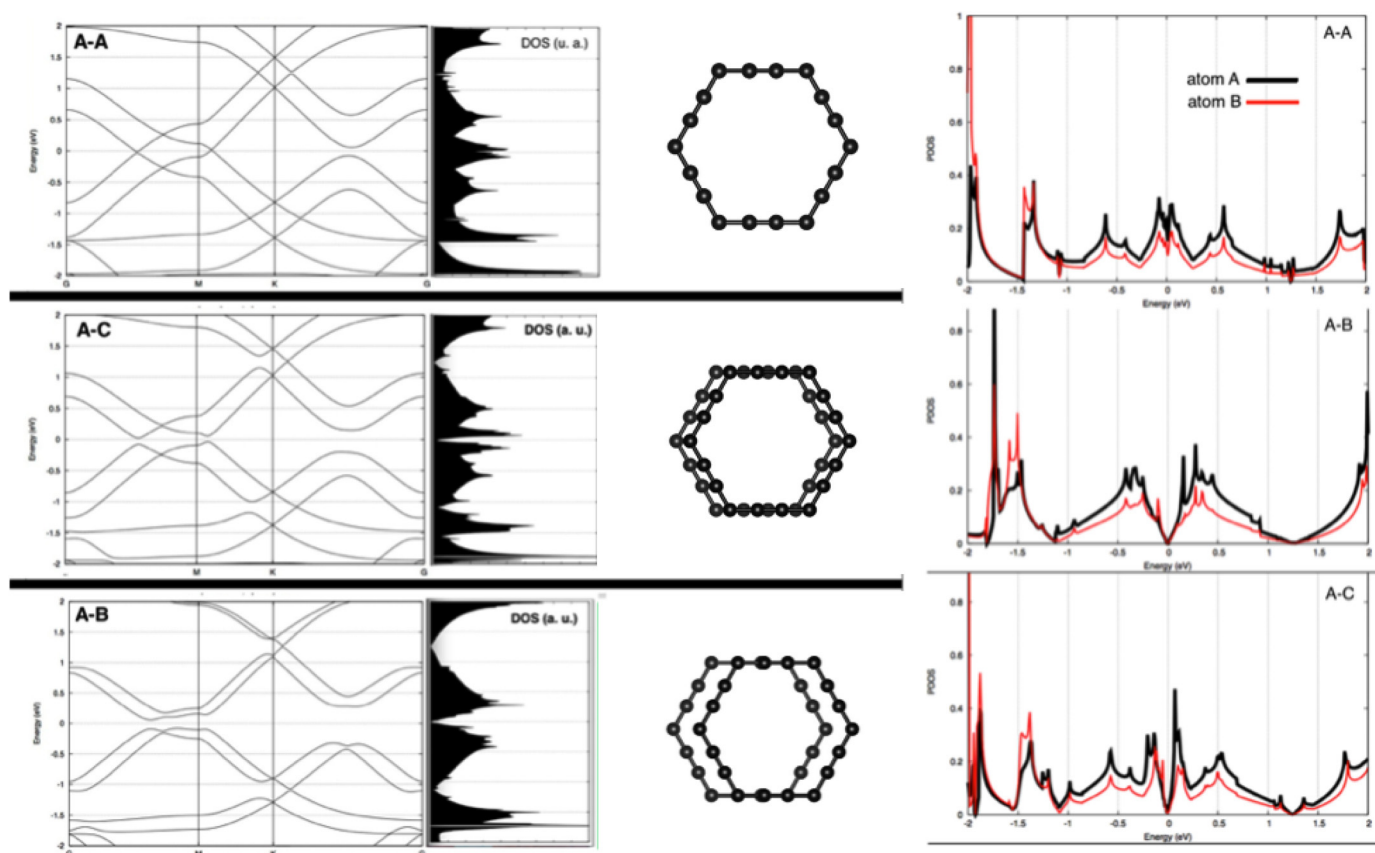


Figure 2. Electronic structure of the β -graphyne bilayer. Band structure, DOS and stacking diagram for AA (top), AC (center) and AB (below). Also, we incorporate the local density of states of the atom A (sp^2) and the atom B (sp), for the three types of stacking.

the gap closes and the system behaves like a metal. This behavior is contrary to what happens with alpha-graphyne [41,42]. For alpha bilayers, the semi-metallic systems become semiconductors when they are subjected to an electric field and the gap increases with the

intensity of the field. In our case, the electric field closes the gap by moving downward some bands which were above the Fermi level.

The opening of the gap in the stacking AB and AC is due to the mixture of the π orbitals of the monolayers. This

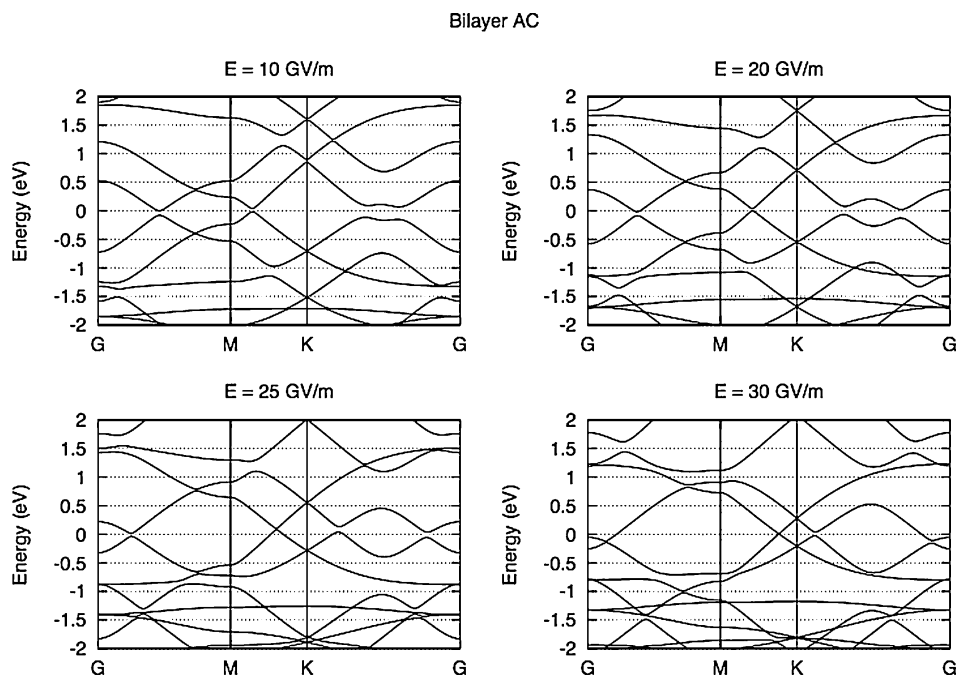


Figure 3. Bilayer with A-C stacking in presence of an electric field. The electric field is applied in the direction perpendicular to the plane of the bilayer.

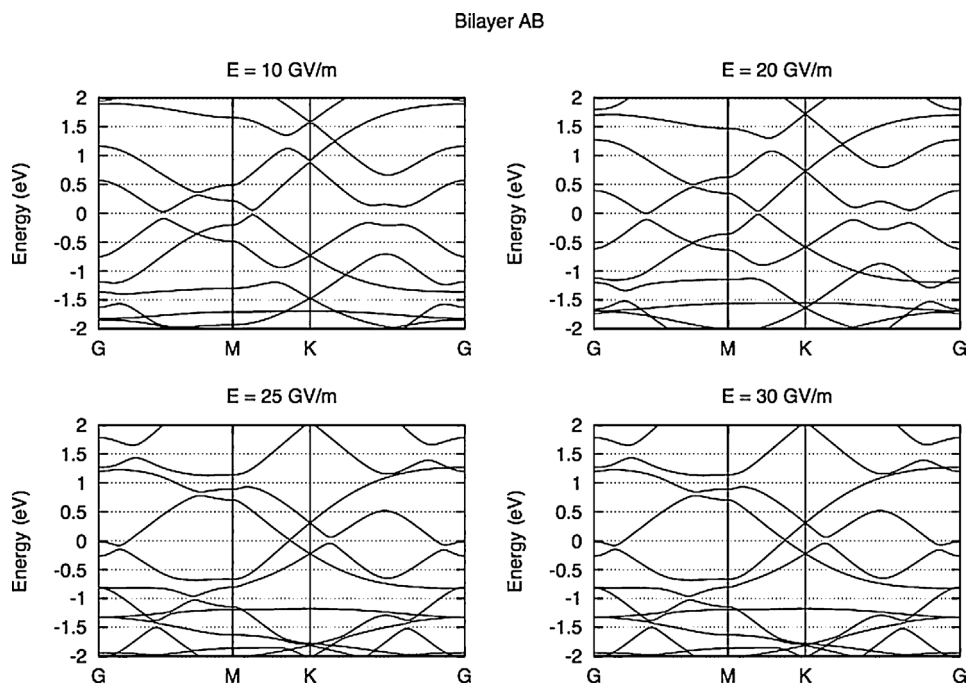


Figure 4. Bilayer with A-B stacking in presence of an electric field. The electric field is applied in the direction perpendicular to the plane of the bilayer.

mixture is different from those occurring in the α -graphyne, due to the difference in the geometry of both systems. The interaction between the π orbitals in the AA case, does not break the degeneracy in the Dirac cones present on the electronic structure. When an electric field is applied perpendicular to the layers, this field generates a distortion in the mixtures of the π orbitals.

This distortion favors the degeneration of states near the Fermi level for AB and AC stacks, by allowing the closure of the gap. This effect of the electric field on the β -graphyne bilayers, is different from the α -graphyne bilayers, due to the different geometry between the two systems and hence the different mix of π orbitals.

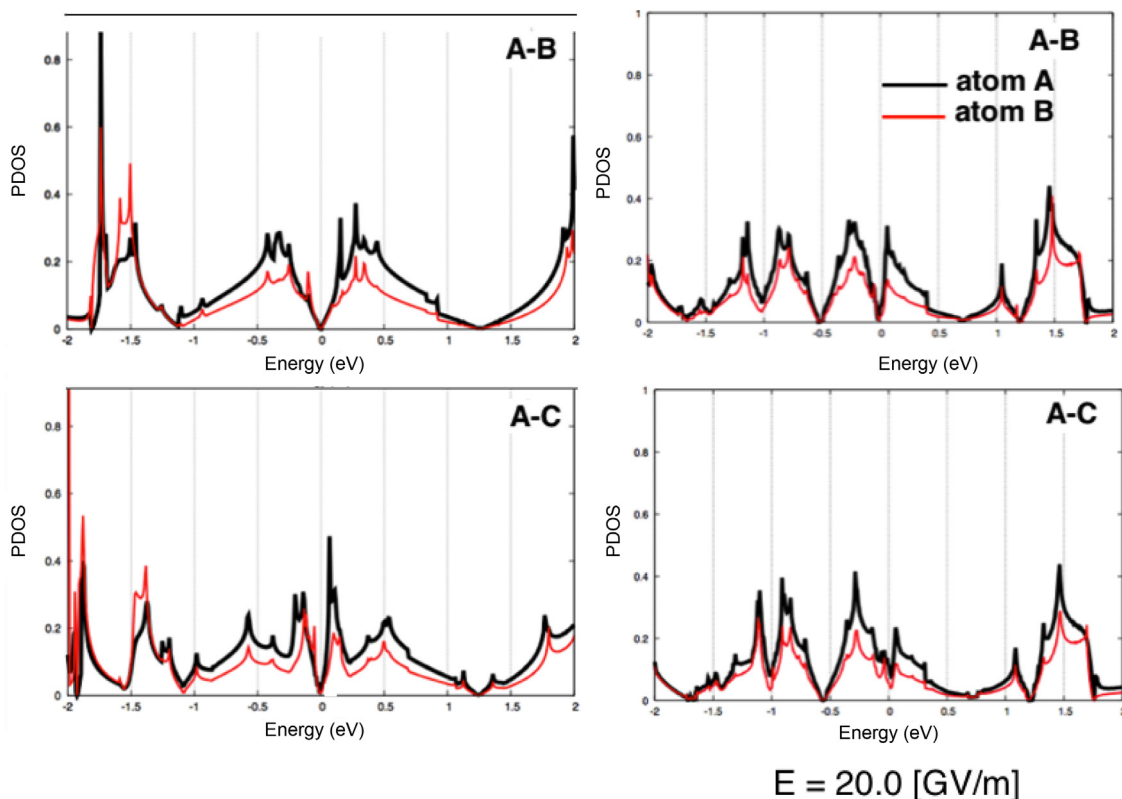


Figure 5. Electric field effect in the local density of states for the atoms A and B. The figures on the left correspond to the density of states with zero electric field. The figures on the right contain the same information but with electric field equal to 20 GV/m.



Figure 6. Isosurface of the real part of the wave function (HOMO), for the type AB stacking. (a) Situation with electric field. (b) Situation without electric field. (c) Position where the HOMO is calculated.

Table 2

Difference between the total energy of the unit cell with hydrogen atom bonded to A or B atom.

Stacking	ΔE (meV)
AA	19.7
AC	8.0
AB	33.3

The effect of electric field in the geometry of the bilayer is an increment in the separation between the layers. For the bilayer with AB stacking, the separation increased from 3.44Å to 3.45Å. In the case of AC stacking, the separation increased from 3.50Å to 3.51Å. The position of atoms did not change significantly in the *x* and *y* directions (monolayers). We tested the chemical reactivity of atoms with *sp* and *sp*² hybridization. The methodology consisted on adding a hydrogen atom on the respective atoms, relax the structure and calculate the total energy of the system. In the three studied cases (stacks AA, AB and AC), the total energy is lower when the hydrogen atom is bonded to atom B (*sp* hybridization). This suggests that the reactivity of the B atom, is greater than the reactivity of the A atom. Table 2 shows the energy difference of the unit cell, defined as $\Delta E = E(A) - E(B)$, where $E(A)$ is the energy of the unit cell with hydrogen atom bonded to A atom. Analogously we define $E(B)$.

In Figure 5, we see the effect of the electric field in the local density of states (PDOS) of atoms A and B. On the left side of the figure, we represent PDOS without electric field, and on the right side, the same information with the electric field. We can see that the resonant states of the atom B (near the Fermi level) disappear with the electric field. Notice that in the case of AC stacking, the gap disappears completely.

Finally, in Figure 6 we show the effect of the electric field in the real part of the wave function (HOMO). Part (a) shows the HOMO with an electric field of 20 GV/m, while the part (b) of the figure shows the HOMO without electric field. In part (c) we indicate the position where the wave function is calculated for HOMO. This figure illustrates the mixture produced by the electric field in the wave function of electrons near the Fermi energy level. This mixture would be responsible for closing the gap in the bilayer.

3. Conclusions

We have obtained electronic properties of β -graphyne bilayers with the use of DFT calculations. Our results show that the system

is semiconductor for a lower energy stacking configuration. In presence of an electric field perpendicular to the layers, the gap closes and the system presents a metallic behavior. This response to the electric field is contrary to the one reported for α -graphyne bilayers, and it is particularly interesting for potential applications in electronics.

Acknowledgements

This work was supported by Fondecyt program grant 11100045, Conicyt grant ACT 1204 and USM 11.14.68 internal grant.

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