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Blue-Green-Black phosphorene allotropes conversion: Energetically easy and potentially promising

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ABSTRACT

Three allotropic forms of phosphorene (Blue, Green and Black) are studied from both structural and electronic points of view. P–P bonds orientation change from vertical to lateral directions is behind the change from Blue to Black forms via Green one. The energetic profile shows that this conversion could take place easily. The rippling mode of the phosphorene sheet is rationalized using the naturel bond orbital (NBO) analysis. We present the landforms of these sheets as a result of MOs interaction depending on the kind (σ, σ^* and/or LP), on the mode (lateral or axial), and on the position (geminal, vicinal or remote) of these MOs leading to an electronic delocalization phenomenon called hyperconjugation. The conversion Blue-Green-Black phosphorenes is accompanied by a change of properties; for example, from natural band gap (Blue form) to a sizable and tunable one (Green and Black forms). This change would confer to the phosphorene the ability to be involved in the electronics and optoelectronics manufacturing. The geometrical optimization and the hyperconjugative rationalization were undertaken at B3LYP/6-311 + G(d,p) level of theory and NBO partitioning scheme respectively.

1. Introduction

The graphene-like materials based on main group elements constitute the subject of several groups' research activities all over the world. Since the preparation of the first graphene-like compound based on silicon called silicene [1,2], some intensive efforts have been made to develop other poste-graphene materials exhibiting properties which are not ensured by the graphene. Let's remind that this latter still has some deficiencies, in particular his gapless nature [3]. Hence, the graphene era seems to be outdated [4] although it was qualified as the magic compound of the beginning of the XXIst century. The eyes are directed, nowadays, towards the graphene congeners based on elements of the columns neighboring the carbon one.

However, it has been showed that the physico-chemical properties of such compounds depend, among others, on the geometrical structure of the graphenic sheet [5–8]. It's well known that the "honeycomb" structure of a layered compound is smooth only for the graphene where every C atom is sp^2 hybridized whereas this structure is rippled-shaped for the others like silicene, germanene, phosphorene, transition metal dichalcogenides (TMDs) [2,5,9–14]. The six membered cycles have D_{6h} (flat) as local symmetry for the graphene but they become D_{3d} (armchair) for the other congeners. Therefore, these give a smooth structure for the graphene sheet and a rippled one for the others. In two works we have previously published [15,16], we have showed that the rippling behavior of graphene-like compounds is a consequence of some interactions between occupied and virtual molecular orbitals (MOs) leading to a kind of electronic delocalization called hyperconjugation. Those MOs are oriented in a way to make vicinal bonds being lifted from either sides of their separating bond. The intensity of this interaction depends on how these MOs are energetically clause. In fact the rippling behavior increases, for example, when we descend down the 14th column of the periodic table of the basic atom from C to Pb because the energetic gap between interacting MOs decreases in this direction [15].

In this work, we try to explain the origin of the rippled structure of the mono layered (2D) phosphorus called phosphorene. This latter could exist in different allotropic forms (some are isolated and other are theoretically suggested) such as α-, β-, γ-, δ-, η-, θ-, ψ- [17–21] and the recently reported λ-phosphorene called Green Phosphorene [22]. We have been interested in three allotropic forms of the phosphorene namely Blue, Green and Black (noted Color-P) since they are clause of each other as well structurally as energetically but they are different in terms of properties. The Black-P, maybe also the Green one, are regarded as a promising material in the electronics industry since they could have a sizable and tunable band gap and also a significant carrier mobility [23–25]. The bulked Black phosphorus is already implied in the transistor devices thanks to his appealing properties [26–28]. It

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carries high interest in the applications of thermoelectric, fiber optics, thermal imaging, photovoltaics etc… Also the optical properties of phosphorene (optically anisotropic) are better than the graphene ones because of its zigzagging and rippling structure [29,30]. We will show that this converting behavior of the phosphorene between such three allotropes could occur energetically easily so that a change between three sets of properties could be ensured. However, this could have a manufacturing applicability like in the electronics and optoelectronics fields [31].

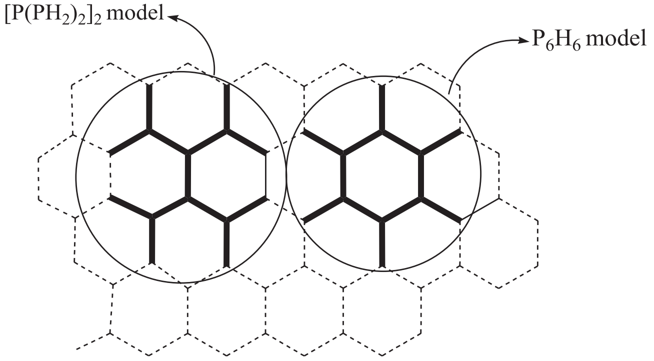
2. Computation details

All calculations have been performed using the Gaussian09 series of computer programs [32]. The geometrical optimizations were computed firstly for each system in its highest symmetry after that a stepwise geometrical parameters relaxation has been followed until the treatment without restrictions. The density functional theory (DFT) with B3LYP functional [33,34] has been adopted with the 6-311 + G(3df,2p) basis set [35,36]. Effects of hyperconjugative interactions were investigated using the natural bond orbitals (NBO) partitioning scheme [37]. The interacting orbitals responsible of this phenomenon were identified by the NBO treatment and the corresponding interactions were assessed by the freezing of the corresponding Fij elements of the corresponding non-diagonal elements of the Fock matrix.

3. Results and discussion

As it's mentioned in the Introduction section, the phosphorene could exist under different allotropic forms [17–22]. However, Blue and Black ones have been the focus of several researches as potential materials in electronic industries [38]. Like the black form, the green one which has been recently reported, could theoretically have some clause properties [22]. So, a structural analysis seems to be necessary to highlight about an eventual change of properties. In Fig. 1, are depicted three sheets of these three phosphorene forms.

As the honeycomb lattice is a juxtaposition of hexacycles, the difference between these allotropes structures depends on the way how such cycles stuck to each other. So, their sheets landforms depend on the geometrical structure of each cyclic unite (CU) A_6A_6 (A = basic atom of the monolayer material). Hence, the electronic and structural analysis of such layers is always reduced to the CU frameworks using A_6H_6 cycle as model where the H atoms are needed to give to heavy atoms a clause environment to honeycomb lattice one. In this work we have chosen also the $[P(PH_2)_2]_2$ entity as a model (Scheme 1) to deeply examine some electronic properties.



Scheme 1. Two models are used to analyze geometrical and electronic structures of the phosphorene.

We present in the following paragraph geometrical and electronic analyses using those models. P_6H_6 cycle serves to study the easy conversion between phosphorene allotropes and $[P(PH_2)_2]_2$ entity serves to identify the factors behind the rippled-shape of the phosphorus monolayers. This allows us to advance that the easy phosphorene conversion could be a seat of change of properties so that this material could have two (maybe three) sets of electronic properties reached by the geometrical change control.

3.1. P_6H_6 model: Blue-Green-Black-Ps structural conversion would lead to three sets of properties change

As it's expected, the armchair form is energetically favored for P_6H_6 model on the total potential energy surface (PES) supported by a vibrational treatment showing that all frequencies are positive. In reverse, the flat structure (benzene-like) exhibits a decade of negative force constants (imaginary frequencies) which qualify this structure without interest on the P_6H_6 PES. Nevertheless, there are three armchair conformers slightly different as well structurally as energetically (Fig. 2a, c, e).

The geometrical difference between these minima depends only on the P^4-H^7 and P^3-H^{10} bonds orientations. These orientations can be Cis or Trans in relation to the plan containing P^3, P^4 atoms and P^1–P^2 and P^5–P^6 bond middles. As we can see, the vertical Trans-orientation (VTO) of these bonds corresponds to the cycles' juxtaposition leading to Blue-P (Figs. 1a and 2a) [36] whereas the lateral Trans-orientation (LTO) corresponds to the Black-P lattice (Figs. 1c and 2e). Nevertheless, the Green-P is formed by the juxtaposition of two rows of cycles where the P-P bonds making the differences are Cis-oriented (CO) vis-à-vis to the same plan and one row of LTO (Figs. 1b and 2c) as it's showed by Chang et al. [22]. Hence Blue-P and Black-P are formed by VTOs and LTOs

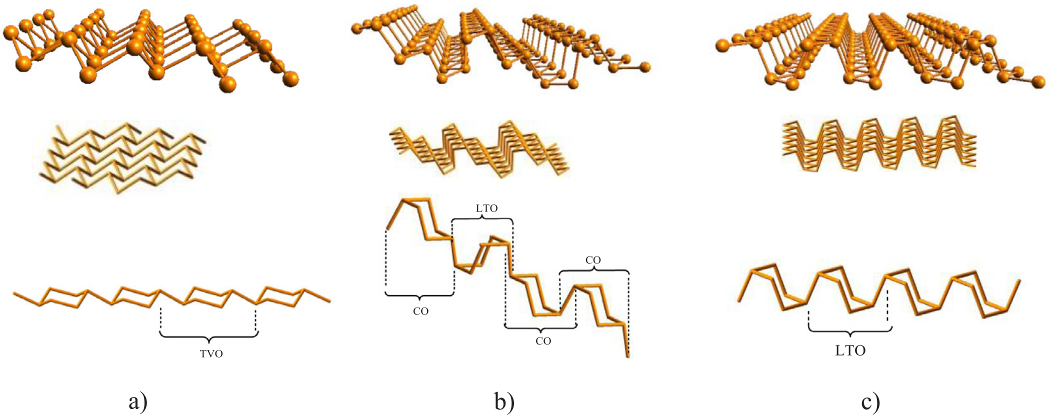


Fig. 1. Blue (a), Green (b) and Black (c) phosphorene sheets; ball & stick representation (top), tubes representation (middle) and P_6 frameworks junctions (bottom).