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On lithium doping in two stable nano-flakes of the B_{24}: The double-ring versus the quasiplanar configuration

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ABSTRACT

The stable local minima due to the addition of the Li atom to the double-ring and the quasiplanar configurations of the B_{24} molecule have been searched on the doublet potential energy surface to reveal the structural and electronic features of the Li@B_{24} system. We report two and seven stable local minima without imaginary vibrational frequency for the Li@B_{24}(double-ring) and the Li@B_{24}(quasiplanar) systems, respectively. The criteria of the adsorption energy, the vertical ionization (VI) energy, the deformation energy, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy gap, the atomic charges, the spin density distribution, the electron transfer (ET), atoms in molecules (AIM) analysis and the nonlinear optical (NLO) properties have been investigated for all the reported molecules of the Li@B_{24} system in the present paper. Our results present that both thermodynamic and chemical stability of the Li atom doping to the quasiplanar configuration of the B_{24} molecule are more than those of the double-ring configuration. Additionally, both the double-ring and the quasiplanar configurations can produce the Li@B_{24} system with values of high first hyperpolarizability (β_{total}) due to the Li atom doping. In all the reported molecules of the Li@B_{24} system, electron density of the Li atom decreases due to the existence of the double-ring and the quasiplanar configurations confirming the role of the electron donor for the Li atom. In contrast, both decreasing and increasing electron density have been observed in the B atoms of the Li@B_{24} system. However, the role of electron acceptor (increasing electron density) for the B atoms is more dominant than the role of electron donor (decreasing electron density). This result highlights chemical flexibility of the B atoms.

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1. Introduction

One of the unique electronic advantages of the B atom compared to other atoms of the periodic Table is chemical flexibility. Indeed, the B atom can play both roles of electron donor and electron acceptor in the chemical reactions. This unique feature of the B atom causes to the different behaver of boron rich molecules when they confront with the atoms of either more electronegative or more electropositive than the B atom [1–3]. Therefore, boron rich molecules have obtained much attentions in both theoretical and experimental fields due to their unique properties [4–13].

In 2003, Boustani et al. [14] focused on the investigation of the possible equilibrium structures of the B_{24} molecule. They optimized the different geometries for the B_{24} molecule such as the quasiplanar, the ring, the convex, the tube and the closed molecules. Their calculated results show that the double−ring B_{24} molecule is the most stable geometry for the connection of the twenty four B−atoms compared to other geometries. It is necessary to say that both the quasiplanar and the convex configurations reported by Boustani et al. [14] include the subunits of hexagonal pyramid B_7 [14] confirming lack of hole in the structural geometries.

In 2007, Tang and Ismail-Beigi [15] proposed the new quasiplanar B_{24} molecule containing a hexagon hole at the center of molecule. The stability comparison of new quasiplanar B_{24} molecule with that of the double−ring B_{24} molecule reported by Boustani et al. [14] shows that this new quasiplanar B_{24} molecule can be serious opponent of the double−ring B_{24} molecule. This means that the three-dimensional (3D) structure of the double ring B_{24} is slightly more stable than the two-dimensional (2D) structure of the new quasiplanar B_{24} [14,15].

Note that the search of the most stable structures among the different sizes of the B_n molecules displays that in the size range

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of $3 \leq n \leq 19$ [16–24], the 2D structures are much more stable than those of 3D. According to experimental [21] and theoretical studies [10,25], the B_{20} molecule is transitional bridge from 2D to 3D structures. Note that the 3D structure of the double-ring B_{20} molecule is much more stable than its 2D structures (such as planar and quasiplanar). The close stability between the 3D and 2D structures of the B_{24} molecule motived us to carry out more theoretical investigations in order to selecting of more suitable backbone for the Li atom doping.

To the best of our knowledge, atomic doping influences the electronic and structural properties. In the present paper, the Li atom (as good electron donor) has been added to both the double−ring and quasiplanar configurations on the doublet potential energy surface (PES). Our main objectives are to report the most stable local minima of the Li@B_{24}(double−ring) and the Li@B_{24}(quasiplanar with hexagonal hole) systems to reveal the electronic and structural properties of the Li@B_{24} system to perform the comparative investigation between Li@B_{24}(double−ring) and the Li@B_{24}(quasiplanar with hexagonal hole) systems.

2. Computational details

In the first step, we have optimized two the molecules of the double-ring B_{24}, denoted as the BR backbone, and the quasiplanar B_{24}, denoted as the BQ backbone, on the singlet PES at the UPBE0-D3/6–311 + G(d) level [26–31]. In the second step, we have placed one the Li atom in the different locations of the BR and the BQ backbones to provide all possible structures of the Li@B_{24} system on the doublet PES at the UPBE0-D3/6–311 + G(d) level. In the third step, the vibrational frequencies of the optimized structures have been calculated at the UPBE0-D3/6–311 + G(d) level to avoid the structures with imaginary vibrational frequency. All these calculations have been carried out by the Gaussian 09 software [32].

After identification of the most stable structures, we have calculated the adsorption (denoted as E_{ads}), vertical ionization (denoted as VI) and deformation (denoted as E_D) energies using the Eqs. (1)–(3), respectively.

$$E_{ads} = E_1 - E(Li) - E(B_{24}) \tag{1}$$

$$VI = E_2 - E_1 \tag{2}$$

$$E_D = E_3 - E(B_{24}) \tag{3}$$

Where, the values of the E_1 (by geometry optimization) and the E_2 (by the calculation of single-point energy on the optimized geometry) stand for the energy of the Li@B_{24} and $[Li@B_{24}]^+$ systems, respectively. Additionally, the value of the E_3 (by the calculation of single-point energy on the optimized geometry) presents the energy of the Li@B_{24} system after the elimination of the Li atom.

In the present paper, we have used the AIM2000 [33] and the multiwfn [34] softwares to extract the data on the bond crucial points (BCPs) of the Li—B interactions such as electron density ($\rho(r)$) and $\nabla^2\rho(r)$ and the difference map of electron density.

As known, the obtained values for the first hyperpolarizability, β_{total}, are sensitive to spin contamination. To overcome the negative influence of spin contamination, we have carried out the calculations of single–point energy in the restricted-open shell (RO) situation on all optimized geometries at the BHandHLYP-D3/6–311 + G(d)//UPBE0-D3/6–311 + G(d) level. Note that the BHandHLYP method [35] with high percentage of HF exchange calculates the reliable values for β_{total} confirming by researchers [36–38]. Finally, the β_{total} values and its corresponding components have been extracted through the homemade code

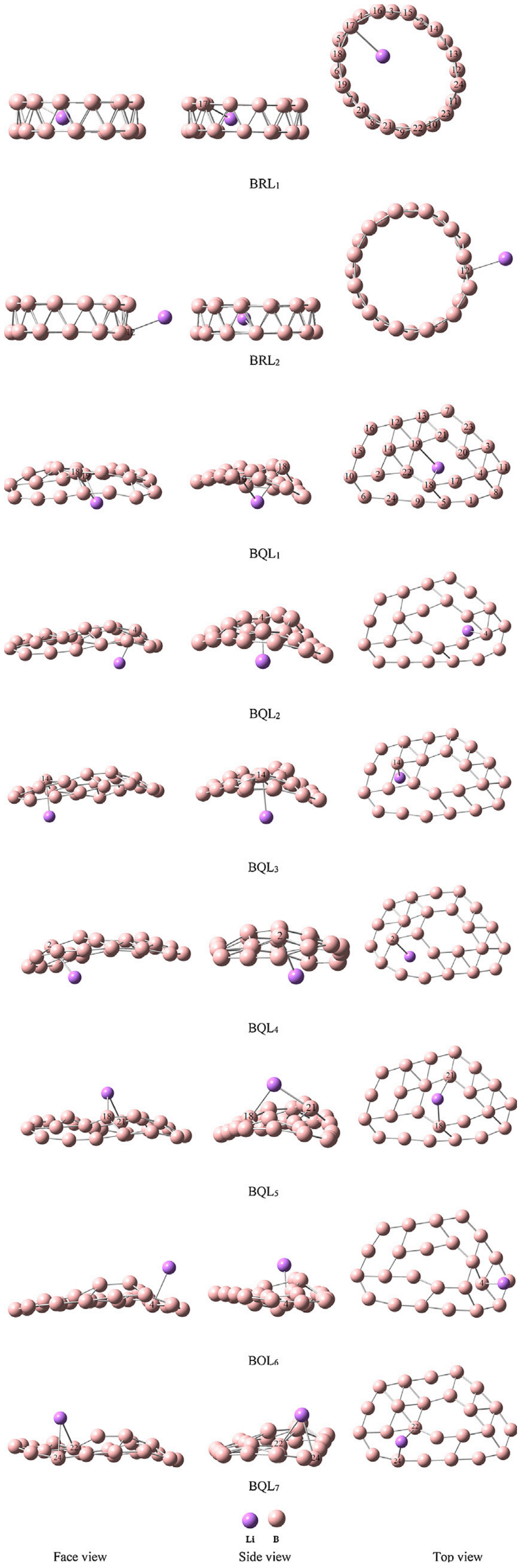

Fig. 1. The optimized geometries for the Li@B_{24} systems.

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