



The Be atom doping: An effective way to improve the Li-atom adsorption in boron rich nanoflake of B₂₄

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ARTICLE INFO

ABSTRACT

Article history:

Received 15 July 2018

Received in revised form 25 August 2018

Accepted 30 August 2018

Available online 1 September 2018

Keywords:

B₂₄

doping

First hyperpolarizability

NCI

Based on the density functional techniques, we have carried out the doping Be atom to the B₂₄ molecule, nBe@B₂₄ (n = 1 and 2), which follows through addition of the Li atom to the most stable nBe@B₂₄ (n = 1 and 2) molecules. The calculated results show that the doping Be atom causes to the severe deformation of the B₂₄ molecule along with big values of vertical ionization energy for the nBe@B₂₄ (n = 1 and 2) molecules. Moreover, the range -2.65 eV ~ -4.49 eV for the adsorption energy per Be atom confirms unique thermodynamic stability of the nBe@B₂₄ (n = 1 and 2) molecules. Note that the dominant thermodynamic and chemical stability among all the nBe@B₂₄ (n = 1 and 2) molecules belongs to the cage configuration of the B₂₄ molecule. The positive charges of the Be atoms, 0.60 e ~ 0.97 e, the lack of the Be-Be interaction and high chemical flexibility of the B atoms have been observed in the nBe@B₂₄ (n = 1 and 2) molecules based on the natural bond orbital (NBO) and the atoms in molecules (AIM) analysis. The value of first hyperpolarizability, β_{total}, in the nBe@B₂₄ (n = 1 and 2) molecules depends severely on both the number of the Be atoms and the backbone configuration. Moreover, addition of Li atom presents the existence of the Be atom(s) increases the adsorption energy of the Li atom in the B₂₄ molecule.

1. Introduction

The boron atom (B) has high chemical flexibility compared with another atoms. This means that the B atoms can be used as electron donor or electron acceptor. In atomic doping the boron rich materials, the role of the B atoms (electron donor or electron acceptor) depends on the kind of dopant. Indeed, this exclusive feature has motivated researchers to carry out many theoretical and experimental studies on the boron rich materials [1-13].

The calculated results on the B_n (n=3-19) materials [14-22] reflect that the two-dimensional configurations of the boron rich materials are superior geometries compared with those of three-dimensional based on energy. Additionally, the three-dimensional configuration of the B₂₀ molecule, known as double-ring molecule, is more stable than the configurations of its

two-dimensional [23, 24]. On the other words, the B₂₀ molecule can be introduced as transition state from two-dimensional configurations to ones of three-dimensional in the B_n materials [23, 24]. Boustani et al. [25] searched the possible configurations of the B₂₄ molecule. According to the obtained results, the most possible configurations can be incorporated in four different categories of the ring, tube, convex (and quasiplanar) and cage. The ring category includes two different configurations of the monocyclic-ring and the double-ring. Note that double-ring B₂₄ molecule is much more stable than the monocyclic-ring of the B₂₄ molecule. In the tube category, Boustani et al. [25] reported three tubes with the different number of the B atoms in each ring of tube. The results present that the tube geometry with the three planar rings containing eight B atoms in each ring is dominant configuration for the tube category. In the cage category, Boustani et al.

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introduced the cage-II which contains the fusion of two icosahedra B_{12} molecules as the most stable configuration among other configurations. Two configurations of the convex and the quasiplanar have been incorporated in the convex (and quasiplanar) category. Common aspect of these two configurations is the components of the hexagonal pyramid B_7 . This means that the convex and the quasiplanar configurations include no hole in their molecular structure. Note that the convex configuration is more stable than the quasiplanar. It is necessary to say that double-ring configuration of the ring category has been known as the most stable configuration of the B_{24} molecule among all the reported configurations by Boustani et al [25]. Subsequently, Tang and Ismail-Beigi [26] introduced new configuration for the B_{24} molecule due to the appearance of hexagonal hole in the molecule geometry, shown as quasiplanar configuration. It is interesting to say that new quasiplanar configuration is comparable with the most stable configuration reported for the B_{24} molecule, the double-ring configuration, by Boustani et al. [25].

In the present paper, we have selected the most stable configurations reported by Boustani et al. for each category of the B_{24} molecule and Tang and Ismail-Beige's new quasiplanar configuration as backbones to carry out the doping one and two Be atoms to the B_{24} molecule, the $nBe@B_{24}$ ($n = 1$ and 2) molecules. In next step, we add the Li atom to the most stable the $nBe@B_{24}$ ($n = 1$ and 2) molecules. To the best of our knowledge, the doping can be appropriate strategy to provide new materials with the electronic and structural properties different from backbones. Our main objectives in the present paper are to search the most stable configurations for both the $Be@B_{24}$ and the $2Be@B_{24}$ molecules to present the structural and electronic features of the $nBe@B_{24}$ ($n = 1$ and 2) molecules to reveal the role of the Be atom(s) doping in the adsorption energy of the Li atom in the B_{24} molecule. We hope that our results in the present paper open new way for improving Li-atom adsorption which is significant criterion in many systems such as Li based batteries.

2. Computational details

In the first step, we have provided many inputs through the addition of one Be atom to different positions of each the ring, the tube, the convex, the quasiplanar and the cage configurations of the B_{24} molecule. The resulted structures have been listed based on energy to select the most stable geometry for each the ring, the tube, the convex, the quasiplanar and the cage configurations of the B_{24} molecule, denoted as $Be@B_{24}$ system. In the second step, similar trend has been repeated through addition of second Be atom to different positions of the most stable geometry in each

category of the $Be@B_{24}$ molecules, denoted as $2Be@B_{24}$ system. In the third step, Li atom has been incorporated in the B_{24} and the most stable geometry of each the $Be@B_{24}$ and $2Be@B_{24}$ molecules. We confirm the all three steps include optimization process without constraint.

Note that the PBE0 [27-29] method conjugated with cc-pVDZ [30] basis set has been used for the geometry optimization on the PES [31-36]. Additionally, we have performed the correct of the dispersion energy through the DFT-D3 method of Grimme et al. [37] shown as the PBE0-D3/cc-pVDZ level of theory. To access reliable energies, the calculations of single point energy have been carried out at the PBE0-D3/cc-pVTZ level of theory on the optimized geometries of the PBE0-D3/cc-pVDZ level of theory. The calculated vibrational frequencies for all molecules at the PBE0-D3/cc-pVDZ level of theory confirm that all reported molecules in the present paper are valid local minima which contain no vibrational frequencies of imaginary. Subsequently, the energies of adsorption per Be atom, vertical ionization (VI) and deformation for the most stable configuration of each category have been calculated through equations (1)-(3).

$$E_{\text{adsorption}} = [E_1 - nE(\text{Be}) - E(B_{24})]/n \quad (1)$$

$$E_{\text{VI}} = E_2 - E_1 \quad (2)$$

$$E_{\text{deformation}} = E_3 - E(B_{24}) \quad (3)$$

Where, the E_1 and the E_2 have been obtained through the geometry optimization and the calculation of single-point energy in the $nBe@B_{24}$ ($n=1$ and 2) and the $[nBe@B_{24} (n=1 \text{ and } 2)]^+$ molecules, respectively. Additionally, the E_3 is the energy of the $nBe@B_{24}$ ($n=1$ and 2) molecules after the removal of the Be atoms through the calculation of single-point energy.

In the present paper, the interactions confirmation due to the bond critical points (BCPs), the calculation of electron density ($\rho(r)$) and their corresponding $\nabla^2\rho(r)$ in the BCPs and providing of non-covalent interaction (NCI) map have been performed by the multiwfn software [38]. Finally, we have calculated the hyperpolarizability (β_{total}) and its corresponding components at the BHandHLYP-D3/cc-pVTZ//PBE0-D3/cc-pVDZ level of theory through the electric field magnitude of 0.001 a.u. by using equations (4) and (5). It is necessary to say that the BHandHLYP method [39] can calculate the reliable β_{total} due to high percentage of HF exchange [40-42].

$$\beta_i = \frac{3}{5} (\beta_{\text{iii}} + \beta_{\text{ijj}} + \beta_{\text{ikk}}) \quad (4)$$

$$\beta_{\text{total}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}} \quad (5)$$

Note that the subscripts i, j and k ($= x, y$ and z) stand for the directions of the β components. Finally, the

Gaussian 09 software [43] has been used in the present work.

3. Results and discussions

It is well-known that atomic doping can cause to significant changes in both geometric and electronic properties of molecules. Therefore, we have carried out doping of one and two Be atoms to the ring, the tube, the convex, the quasiplanar and the cage configurations of the B_{24} molecule which follows through addition of Li atom. Note that the $nBe@B_{24}$ ($n = 1$ and 2) molecules without and with Li atom have investigated on the singlet and doublet PESs, respectively. Finally, we have used the nomenclature of X, Be-X, 2Be-X, Be-X-Li and 2Be-X-Li ($X =$ ring, tube, convex, quasiplanar and cage) to show backbones and the doping of Be and Li atoms to backbones.

3.1. The doping Be atom in the B_{24} molecule, $nBe@B_{24}$ ($n = 1$ and 2) system

3.1.1 Thermodynamic stability

Figure S1 of supporting information (SI) shows the most stable geometry of the $nBe@B_{24}$ ($n = 1$ and 2) molecules on the singlet PES. Note that possible atomic connections for each the $nBe@B_{24}$ ($n = 1$ and 2) molecules based on the atoms in molecules (AIM) analysis [44] have been presented through the solid lines.

As known, the adsorption energy provides good vision about thermodynamic stability of molecules. In this regard, we have calculated the adsorption energies per Be atom of the $nBe@B_{24}$ ($n = 1$ and 2) molecules on the singlet PES. From Figure 1 and Table S1 of SI, the calculated adsorption energies per Be atom for the $nBe@B_{24}$ ($n = 1$ and 2) molecules can incorporate in range -2.65 eV (in the Be-ring) ~ -4.49 eV (in the Be-cage). More precise investigation of Figure 1 reveals significant points. Firstly, the addition of the second Be atom to the $Be@B_{24}$ molecules causes to the decreasing adsorption energy per Be atom except for the ring backbone. This means that the adsorption energies per Be atom for the 2Be-ring molecule (-3.03 eV) is bigger than that of the Be-ring (-2.65 eV) molecule. Secondly, the ranking of the adsorption energies per Be atom for the $Be@B_{24}$ and the $2Be@B_{24}$ molecules is the Be-cage $>$ the Be-tube $>$ the Be-convex $>$ the Be-quasiplanar $>$ Be-ring and, the 2Be-cage $>$ the 2Be-tube $>$ the 2Be-convex \sim 2Be-quasiplanar $>$ 2Be-ring, respectively. Therefore, we can introduce the cage configuration of the B_{24} molecule as superior backbone due to the doping the Be atoms. Thirdly, the biggest difference of the adsorption energy per Be atom between the $Be@B_{24}$ and the $2Be@B_{24}$ molecules for each ring, the tube, the convex, the quasiplanar and the cage configurations

belongs to the ring configuration of the B_{24} molecule. Indeed, the 2Be-ring molecule is more stable than Be-ring molecule by 0.38 eV.

To identify additional aspects of the electronic features of the $nBe@B_{24}$ ($n = 1$ and 2) molecules, the energies of deformation and vertical ionization (IV) have been presented in Figure 1 and Table S1 in the ESI. According to Figure 1, the range of the deformation energies is 1.23 eV ~ 3.20 eV which confirms severe changes of the backbone geometry due to the addition of the Be atoms. Additionally, the biggest and the smallest deformation energy belong to the 2Be-cage (3.20 eV) and the Be-quasiplanar (1.23 eV), respectively. It is interesting to say that the deformation energies of the $2Be@B_{24}$ molecules are bigger than those of the $Be@B_{24}$ molecules except for the tube backbone. As shown in Figure 1, the deformation energy of the 2Be-tube molecule, 1.33 eV, is smaller than that of the Be-tube molecule, 1.47 eV. Moreover, the VI energies of the $nBe@B_{24}$ ($n = 1$ and 2) molecules are in range 6.56 eV ~ 7.48 eV. This means that the $nBe@B_{24}$ ($n = 1$ and 2) molecules are not the appropriate candidates to include the role of electron donor in the ET reactions. Additionally, the doping of the second Be atom to the $Be@B_{24}$ molecules causes to decreasing the VI energies as shown in Figure 1. Note that the biggest decreasing of the VI energy due to the doping the second Be atom has been observed in the Be-tube molecule.

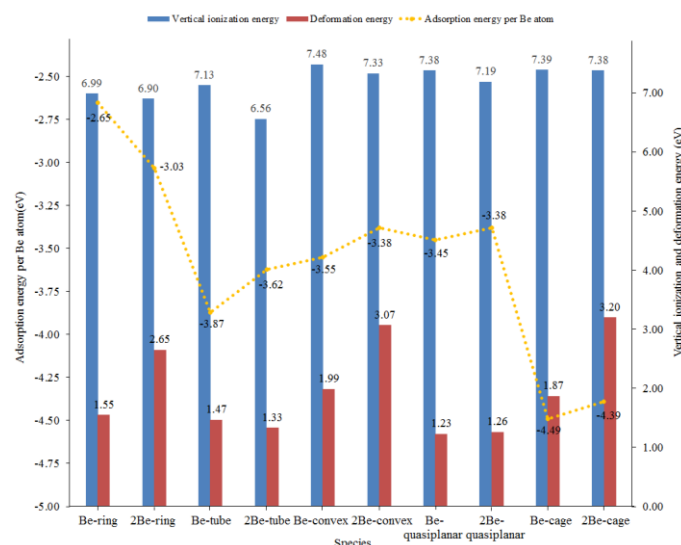


Fig. 1 The values of the adsorption, the vertical ionization and the deformation energies for all the reported molecules.

3.1.2. Chemical stability

Figure 2 and Table S2 in the ESI show the obtained energies for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the HOMO-LUMO gaps of the $nBe@B_{24}$ ($n = 1$ and 2) molecules in the present paper. These energies can help us to compare the HOMO and the LUMO stabilities and the ability of electron transfer from the HOMO to the LUMO. According to Figure 2,

we have found the narrow ranges -5.30 eV ~ -6.28 eV, -3.28 eV ~ -4.36 eV and 1.79 eV ~ 2.81 eV in the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules for the energies of the HOMO, the LUMO and the HOMO-LUMO gap, respectively. Note that the biggest and the smallest energy gaps belong to the Be-ring (1.79 eV) and the Be-cage (2.81 eV) molecules among all reported energy gaps due to the addition of the Be atoms to the B_{24} molecule, respectively. It is necessary to say that the doping the Be atoms to the cage and the convex backbones of the B_{24} molecule results into increasing the HOMO-LUMO gap. In contrast, the decreasing HOMO-LUMO gap has been considered for the addition of the Be atoms to the quasiplanar backbone in the B_{24} molecule. Note that in the ring and the tube backbones, the fluctuation of the HOMO-LUMO gap due to doping the Be atoms is sensitive to the number of the Be atoms. This means that doping the Be atoms to the ring and the tube backbones can cause to both the increasing and the decreasing HOMO-LUMO gap. Finally, the HOMO-LUMO energy gap stands for the chemical stability of molecules. Therefore, the bigger HOMO-LUMO gap of the Be-cage (2.81 eV) and the 2Be-cage (2.79 eV) shows that the addition of the Be atoms to the cage backbone can produce the molecules with bigger chemical stability compared with the other backbone of the B_{24} molecule.

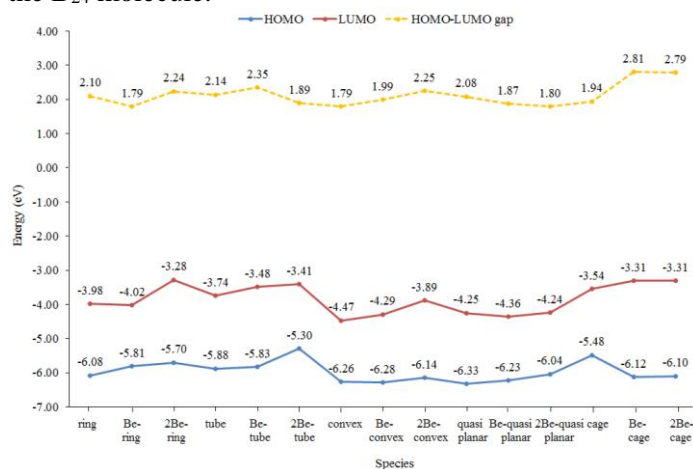


Fig. 2 The HOMO-LUMO energy gap and the HOMO and the LUMO energies and for the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules.

3.1.3. NBO charges

It should be interesting to determine the atoms of electron donor and electron acceptor in the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules. To achieve this goal, we have listed the natural bond orbital (NBO) [45-47] charges of all atoms in Table S3 in the ESI. According to Table S3 in the ESI, all the Be atoms of the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules have positive charges which are in range 0.60 e ~ 0.97 e. Additionally, the biggest positive charges for the Be atoms have been found in the 2Be-ring (0.97 e) and Be-ring (0.96 e) molecules. Based on the reported NBO charges, the role of the Be atoms in

the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules is electron donor. From Table S3 in the ESI, we can incorporate the B atoms of the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules in two different categories based on NBO charges of positive or negative. This means that the B atoms can act as either electron donor or electron acceptor which confirms high chemical flexibility for the B atoms.

3.1.4. AIM analysis

The atoms in molecules (AIM) theory [44] opens suitable way to access the valuable information about strength and characteristic of chemical bonds. These information originate from the magnitude of electron density, $\rho(r)$, and $\nabla^2\rho(r)$ sign in the bond critical points (BCPs). In the non-covalent interactions, the $\nabla^2\rho(r)$ sign is positive which confirms depletion of the $\rho(r)$ in the BCPs. However, negative sign of $\nabla^2\rho(r)$ reflects the $\rho(r)$ concentration [48-50]. We have listed only $\rho(r)$ and $\nabla^2\rho(r)$ for Be-B interactions in Table S4 in the ESI to provide clear vision about kind of the interactions. From Table S4 in the ESI, the calculated results for $\rho(r)$ and $\nabla^2\rho(r)$ present that they should be in ranges 0.06 a.u. ~ 0.08 a.u. and 0.11 a.u. ~ 0.18 a.u., respectively. These results confirm the characteristic of non-covalent in all Be-B interactions. For more confirmation, the non-covalent interaction (NCI) maps of the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules have been presented in Figure 3. Similar to the final result of $\rho(r)$ and $\nabla^2\rho(r)$ for the bond characteristic of the Be-B, the NCIs present that interaction characteristic of the Be and the B atoms is the non-covalent. Finally, there is no Be-Be connection in the reported $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules in the present paper.

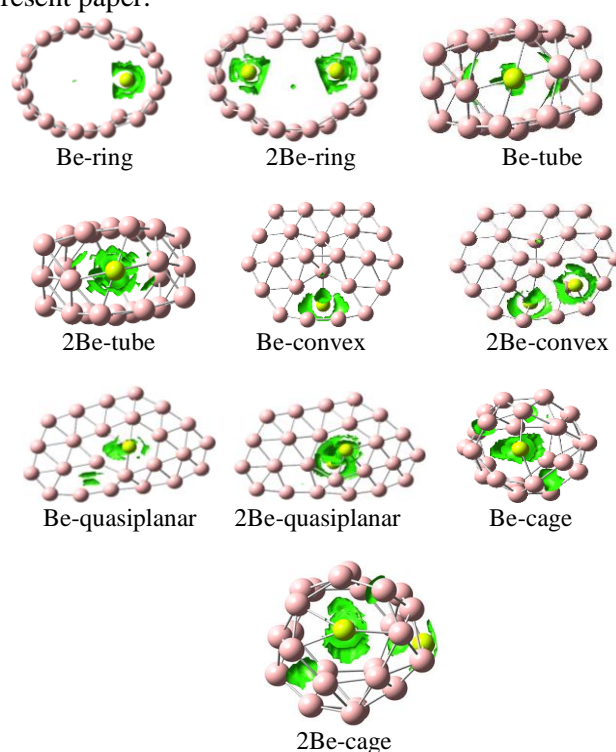


Fig. 3 The non-covalent interaction (NCI) for the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules, in isosurface 0.40 .

3.1.5. The first hyperpolarizability

To access clear understanding about the nonlinear optical (NLO) features of the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules, the first hyperpolarizability (denoted as β_{total}) and β components have been presented in Figure 4 and listed in Table S5 in the ESI at the BHandHLYP-D3/cc-pVTZ//PBE0-D3/cc-pVDZ level. The calculated results reflect that the β_{total} of the reported $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules in the present paper are in the range 44 a.u. (2Be-tube) \sim 810 a.u. (Be-quasiplanar).

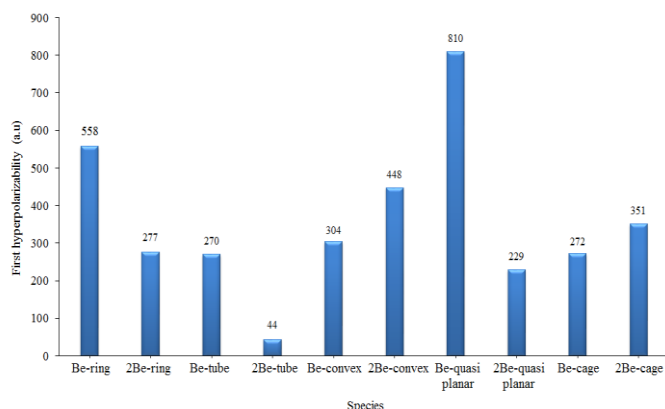


Fig. 4 The values of the first hyperpolarizability, β_{total} , for all the reported $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules.

It is very interesting to say that in the ring, the tube and the quasiplanar backbones, the addition of the second Be atom to the $\text{Be}@B_{24}$ molecules results into severe decreasing β_{total} as shown in Figure 4. However, the values of β_{total} in the $2\text{Be}@B_{24}$ molecules with the convex and the cage backbones, the 2Be-convex and the 2Be-cage molecules, are bigger than those of the $\text{Be}@B_{24}$ molecules, the Be-convex and the Be-cage molecules. This means that the values of β_{total} in the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules can be adjusted through both the number of the Be atoms and backbone configuration.

3.2. The doping Li atom in the Be-cage and 2Be-cage molecules

Our results show that the Be-cage and the 2Be-cage molecules have the highest thermodynamic stability among all the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules. In the present section, we investigate the doping Li atom in the Cage, the Be-cage and the 2Be-cage molecules to reveal the role of the Be atom(s) in the adsorption energy of the Li atom. To achieve this goal, we have added the Li atom to different positions of the cage, the Be-cage and the 2Be-cage molecules which follows through full optimization process. The most stable geometry for each the Cage-Li, the Be-cage-Li and the 2Be-cage-Li molecules has been present in Figure S1 of SI. The adsorption energy of the Li atom on the Cage, the Be-cage and the 2Be-cage molecules is -2.95 eV (the Cage-Li molecule), -3.28 eV (the Be-cage-Li molecule) and $-$

-2.98 eV (the 2Be-cage molecule), respectively. The comparison of these adsorption energies includes two significant points. Firstly, the adsorption energy of the Li atom in the Be-cage-Li (-3.28 eV) and 2Be-cage-Li (-2.98 eV) molecules is bigger than one of the Cage-Li (-2.95 eV) molecule. This means that doping the Be atom(s) in the Cage molecule increases the adsorption energy of the Li atom. Secondly, the calculated adsorption energy for the Li atom in the Be-cage-Li molecule (-3.28 eV) is 0.30 eV bigger than one of the 2Be-cage-Li molecule (-2.98 eV). This result reflects that complex 1:1 of the Be and the Cage (the Be-cage molecule) is superior to complex 2:1 of the Be and the Cage (the 2Be-cage-Li molecule) in order to adsorption of the Li atom.

Acknowledgments

We gratefully acknowledged from Dr. M. Goodarzi for his useful comments to this research work.

4. Conclusions

In the present paper, the computational investigation of the Be atoms doping to the most stable configuration of the ring, the tube, the convex and the cage categories in the B_{24} molecule have been carried out on the singlet PES which follows through addition of Li atom. The obtained outcomes can be listed as follows:

1) The adsorption energies per Be atom for the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules are in range -2.65 eV (in the Be-ring) \sim -4.49 eV (in the Be-cage) which confirms unique thermodynamic stability of the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules. The cage configuration of the B_{24} molecule has the biggest thermodynamic stability in the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules.

2) The range of the deformation energies, 1.23 eV \sim 3.20 eV, and the VI energies, 6.56 eV \sim 7.48 eV, of the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules reflect severe changes of the backbone geometries due to the addition of the Be atoms and the slight ability of the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules to use as source of electron donor in the electron transfer reactions.

3) The range of HOMO-LUMO gap is from 1.79 eV (in the Be-ring) to 2.81 eV (in the Be-cage) the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecule. Additionally, the Be-cage and the 2Be-cage have the biggest chemical stability based on the HOMO-LUMO gap.

4) Based on the reported NBO charges for the Be atoms, 0.60 e \sim 0.97 e, the role of the Be atoms in the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules is electron donor. However, the B atoms can act as either electron donor or electron acceptor.

5) Based on the values of $\rho(r)$ and $\nabla^2\rho(r)$ in the BCP of the Be-B interactions through AIM analysis and the NCIs, all Be-B interaction in the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules are weak and non-covalent. Moreover, no Be-

Be interaction has been found in the reported $2\text{Be}@B_{24}$ molecules in the present paper.

6) The obtained β_{total} values for the $n\text{Be}@B_{24}$ ($n = 1$ and 2) molecules can incorporate in the range 44 a.u. (2Be -tube) \sim 810 a.u. (Be -quasiplanar). These values have high sensitivity to both the number of the Be atoms and backbone configuration.

7) The comparison of the Li adsorption energies in the Cage-Li (-2.95 eV), Be-cage-Li (-3.28 eV) and 2Be -cage-Li (-2.98 eV) molecules presents that the doping the Be atom(s) in the cage configuration of the B_{24} molecule increases the adsorption energy of the Li atom.

8) The complex 1:1 of the Be and the cage (the $\text{Be}@B_{24}$ system) is superior to complex 2:1 of the Be and the cage (the $2\text{Be}@B_{24}$ system) in order to adsorption of the Li atom.

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How to Cite This Article

Fatemeh Gharibzadeh; Samira Gohari; Kamellia Nejati; Bahlol Hashemzadeh; Soheila Mohammadiyan. "The Be atom doping: An effective way to improve the Li-atom adsorption in boron rich nanoflake of B₂₄". *Chemical Review and Letters*, 1, 1, 2018, 16-22. doi: 10.22034/crl.2018.85213