

Insight into $Y@X_2B_8$ ($Y = Li, CO_2$ and $Li-CO_2$, $X = Be, B$ and C) nanostructures: A computational study

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ABSTRACT

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The doping of the Li atom and CO_2 molecule to the X_2B_8 ($X = Be, B$ and C) backbones have been carried out on the potential energy surface to provide clear vision on the structural and electronic features of the $Y@X_2B_8$ ($Y = Li, CO_2$ and $Li\&CO_2$, $X = Be, B$ and C) systems. Our results show that the adsorption energies of the Li atom in the $Li@X_2B_8$ systems (-1.52 eV \sim -3.05 eV) are much bigger than those of the CO_2 molecule in the $CO_2@X_2B_8$ systems (-0.10 eV \sim -0.89 eV). Moreover, the B_2B_8 and the Be_2B_8 can be selected as prefer backbones for the adsorption of Li atom and the CO_2 molecule, respectively. Finally, bigger adsorption energy of the $Li\&CO_2@Be_2B_8$ system (-1.06 eV) compared with that of the $CO_2@Be_2B_8$ system (-0.89 eV) presents that the Li atom doping in the Be_2B_8 backbone increases adsorption energy of the CO_2 molecule. Similar result has been not found for the B_2B_8 and the C_2B_8 backbones.

1. Introduction

Boron is one of the very interesting elements in the periodic Table. Pure boron molecules are intermediate compounds between the materials with purely nonmetallic and metallic characteristics. This feature results into high chemical flexibility of boron rich molecules and it motives many researchers to search the ground-state geometries of boron rich molecules and reveal their unique characteristics [1-8].

The organized investigation has been carried out by Boustani [9] on possible structural geometries of the B_n ($n = 2-14$) molecules. The results show that the B_{10} molecule can have three different configurations of the convex B_{10} (C_{2v}), the quasiplanar B_{10} (C_{2h}) and the nonplanar B_{10} (C_s) on the singlet potential energy surface (PES). Moreover, the quasiplanar B_{10} (C_{2h}) molecule contains two different fragments in its structural geometry and is more stable than two other configurations. The quasiplanar B_{10} (C_{2h}) molecule has the planar ring with eight B-atoms along with two central B atoms which locate up and under planar ring. Note that the central B atoms of the B_{10} (C_{2h}) molecule have strong chemical bonds with those of planar ring.⁹

It is necessary to say that the replacement of two central B atoms of the quasiplanar B_{10} (C_{2h}) molecule with either two more electropositive atoms of the Be, denoted as the nonplanar Be_2B_8 (D_{8h}) molecule, or two more electronegative atoms of the C, denoted as the planar C_2B_8 (D_{2h}) molecule, has been carried out by Frenking et al. [10-11] The C_2B_8 (D_{2h}) molecule has been found to be the planar molecule [10]. This means that the replacement of two central B atoms of the quasiplanar B_{10} (C_{2h}) molecule with those of C atoms causes to incorporation of the central C_2 unit in the sheet of the planar C_2B_8 (D_{2h}) molecule. In the planar C_2B_8 (D_{2h}) molecule, the strong chemical bonds can be observed between the central C_2 unit and the peripheral B atoms. [10] Different from the planar C_2B_8 (D_{2h}) molecule, the replacement of the central B_2 unit of the quasiplanar B_{10} (C_{2h}) molecule with two Be atoms causes to form the nonplanar Be_2B_8 (D_{8h}) molecule [11] which contains the symmetric ring through eight B atoms in which two Be atoms are vertical to the B atoms ring. The stability factor of the nonplanar Be_2B_8 (D_{8h}) molecule is the strong chemical bonds between Be and B atoms. These B-Be bonds act such as the wheel spokes and cause to unusual short Be-Be distance. In spite of very short

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Be–Be distance, no bond critical point (BCP) has been observed between the two Be atoms of the nonplanar Be_2B_8 (D_{8h}) molecule. [11]

In the present paper, our main objective is to increase adsorption energy of the CO_2 molecule in X_2B_8 ($\text{X} = \text{Be}, \text{B}$ and C) species. In this regard, high electron deficiency of X_2B_8 ($\text{X} = \text{Be}, \text{B}$ and C) molecules motivated us to use the Li atom as good electron donor in the X_2B_8 ($\text{X} = \text{Be}, \text{B}$ and C) species. Therefore, in first step, we have doped the Li atom to the X_2B_8 ($\text{X} = \text{Be}, \text{B}$ and C) species to report the possible local minima to reveal the electronic and structural features of the $\text{Li}@\text{X}_2\text{B}_8$ ($\text{X} = \text{Be}, \text{B}$ and C) species. In second step, we have revealed geometry and adsorption energy of $\text{CO}_2@X_2B_8$ and $\text{Li}\&\text{CO}_2@X_2B_8$ ($\text{X} = \text{Be}, \text{B}$ and C) species to carry out the comparative study on adsorption energy of the $\text{Y}@X_2B_8$ ($\text{Y}=\text{Li}, \text{CO}_2$ and Li-CO_2 , $\text{X} = \text{Be}, \text{B}$ and C) molecules to find the influence of Li-atom in the adsorption energy of CO_2 molecule.

2. Computational details

At first, we have carried out re-optimization for the most stable structures of the Be_2B_8 (D_{8h}), the B_2B_8 (C_{2h}) and the C_2B_8 (D_{2h}) molecules at the RMP2/6-311+G(d) level. Subsequently, the Li and CO_2 have been added to the optimized geometries of the Be_2B_8 (D_{8h}), the B_2B_8 (C_{2h}) and the C_2B_8 (D_{2h}) molecules in the different positions to obtain all possible local minima of the $\text{Y}@X_2B_8$ ($\text{Y}=\text{Li}, \text{CO}_2$ and Li-CO_2 , $\text{X} = \text{Be}, \text{B}$ and C) molecules on the singlet or doublet PESs at the R(U)MP2/6-311+G(d) level. In the next step, we have carried out the calculations of single-point energy on the optimized geometries at the R(U)MP2/aug-cc-pVDZ level to provide more reliable energies. Additionally, all vibrational frequencies of the reported local minima have been checked at the R(U)MP2/6-311+G(d) level to confirm the optimized geometries as valid local minima. Subsequently, information on the bond critical points (BCPs) and the difference map of electron density have been obtained through the AIM2000 [12] and the multiwfn [13] softwares, respectively. Finally, we have calculated the values of β_{total} at the R(M)P2/aug-cc-pVDZ//UMP2/6-311+G(d) level through the code developed by Kurtz et al. [14] in which the magnitude of the electric field is 0.0010 a.u. Note that we have used the GAMESS [15] in the present paper.

3. Results and discussions

3.1. The addition of Li atom to X_2B_8 ($\text{X} = \text{Be}, \text{B}$ and C) species

The doping of Li atom, a well-known electron donor to molecules can lead to significant changes in their electronic and structural properties. In the present paper, we have added Li atom to the X_2B_8 ($\text{X} = \text{Be}, \text{B}$ and C)

molecules to investigate electronic and structural features of the $\text{Li}@X_2B_8$ ($\text{X} = \text{Be}, \text{B}$ and C) molecules on the doublet PES. As shown in Figure 1, we have only found two (the $\text{Be}_2\text{B}_8\text{-Li-}\alpha$ and the $\text{Be}_2\text{B}_8\text{-Li-}\beta$ molecules), three (the $\text{B}_2\text{B}_8\text{-Li-}\alpha$, the $\text{B}_2\text{B}_8\text{-Li-}\beta$ and the $\text{Be}_2\text{B}_8\text{-Li-}\gamma$ molecules) and one (the $\text{C}_2\text{B}_8\text{-Li}$ molecule) structures due to the doping of the Li atom to the Be_2B_8 (D_{8h}), the B_2B_8 (C_{2h}) and the C_2B_8 (D_{2h}) molecules, respectively.

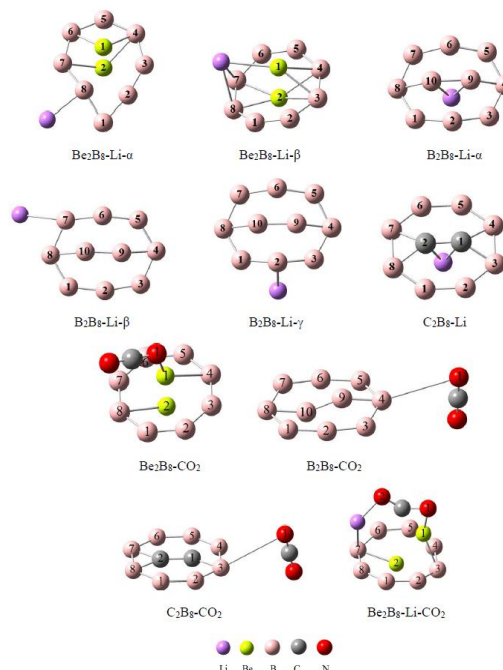


Fig. 1 The obtained structures for the $\text{Y}@X_2B_8$ ($\text{Y}=\text{Li}, \text{CO}_2$ and Li-CO_2 , $\text{X} = \text{Be}, \text{B}$ and C) molecules.

3.2. AIM analysis

The atoms in molecules (AIM) theory has been used¹⁶ to search possible BCPs in the $\text{Li}@X_2B_8$ ($\text{X} = \text{Be}, \text{B}$ and C) molecules. Based on the AIM analysis, we have displayed atomic connections through solid lines in all molecules in Figure 1. The comparative investigation of the atomic connections in Figure 1 reveals two significant points. Firstly, there is no interaction (through the BCPs) between two Be atoms in the $\text{Be}_2\text{B}_8\text{-Li-}\alpha$ and the $\text{Be}_2\text{B}_8\text{-Li-}\beta$ molecules. This result is in agreement with lack of the Be-Be interaction in the Be_2B_8 (D_{8h}) molecule reported by Frenking et al. [11] This means that the addition of the Li atom to the Be_2B_8 (D_{8h}) molecule, denoted as the $\text{Be}_2\text{B}_8\text{-Li-}\alpha$ and the $\text{Be}_2\text{B}_8\text{-Li-}\beta$ molecules, results into no interaction between Be atoms. Secondly, all $\text{Li}@X_2B_8$ ($\text{X} = \text{Be}, \text{B}$ and C) molecules include the Li-B interaction except for the $\text{C}_2\text{B}_8\text{-Li}$ molecule. In the $\text{C}_2\text{B}_8\text{-Li}$ molecule, the Li atom has no interaction with the B atoms as shown in Figure 1. Subsequently, we have listed the values of the electron density ($\rho(r)$) and $\nabla^2\rho(r)$ in the BCPs of Li-Be, Li-B and Li-C interactions in Table S1 in electronic supporting information (ESI). From Table S1, the ranges 0.0141 a.u. ~ 0.0270 a.u and 0.0406 a.u ~ 0.1419 a.u

have been found for the $p(r)$ and $\nabla^2\rho(r)$, respectively. The small values reported of $p(r)$ and the positive values of $\nabla^2\rho(r)$ confirm that the interaction between the Li atom and other atoms (Be, B and C) in the $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules are weak and non-covalent. Note that the strongest interaction of the Li atom among all reported interactions of the Li atom in the $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules belongs to the Li-B interaction in the $\text{Be}_2B_8\text{-Li-}\alpha$ molecule with the bond length of 2.07 Å which is the shortest bond length (2.07 Å) for the interaction of the Li in the $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules.

3.3. Stability

The adsorption and vertical ionization (VI) energies for all local minima of the $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules have been presented in Figure 2 and listed in Table S2 of the ESI. According to Figure 2, the range of the adsorption energies for the six local minima is -1.52 eV ~ -3.05 eV due to doping of Li atom. Moreover, the ranking of the reported adsorption energies is $\text{B}_2B_8\text{-Li-}\alpha > \text{Be}_2B_8\text{-Li-}\gamma > \text{B}_2B_8\text{-Li-}\beta > \text{Be}_2B_8\text{-Li-}\beta > \text{C}_2B_8\text{-Li} > \text{Be}_2B_8\text{-Li-}\alpha$. Note that three bigger adsorption energies among all reported adsorption energies belong to the $\text{B}_2B_8\text{-Li-}\alpha$, the $\text{B}_2B_8\text{-Li-}\beta$ and the $\text{Be}_2B_8\text{-Li-}\gamma$ molecules, the $\text{Li}@B_2B_8$ system. This means that the doping of the Li atom to the B_2B_8 (C_{2h}) causes the molecules with bigger adsorption energies (higher thermodynamic stability) compared to that of the Be_2B_8 (D_{8h}) and the C_2B_8 (D_{2h}) molecules. Additionally, the calculated results show that the values of the VI energy for the $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules are in narrow range 6.89 eV ~ 7.19 eV. These big values show that the $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules are not appropriate electron donor in the electron transfer reactions. Additionally, the fluctuation of the reported VI energies is very small as shown in Figure 2.

As known, the HOMO and the LUMO energy and their corresponding gaps provide more clear vision on the ability of an electron transfer from the HOMO to the LUMO. In Table S3 of the ESI, we have listed the HOMO and the LUMO energies for both sets α and β of the $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules on the doublet PES and set α of the Be_2B_8 (D_{8h}), the B_2B_8 (C_{2h}) and the C_2B_8 (D_{2h}) molecules on the singlet PES and their corresponding energy gaps. According to Figure 3, the doping of Li atom to all the Be_2B_8 (D_{8h}), the B_2B_8 (C_{2h}) and the C_2B_8 (D_{2h}) molecules causes to decrease energy gap of HOMO-LUMO. The biggest and smallest energy gaps due to doping of the Li atom belong to the $B_2B_8\text{-Li-}\alpha$ (7.49 eV) and the $B_2B_8\text{-Li-}\beta$ (6.08 eV) molecules, respectively. As known, the HOMO-LUMO energy gap reflects the chemical stability of the molecules. This means that the $B_2B_8\text{-Li-}\alpha$ molecule has the highest chemical stability among all the reported $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules. As shown in

Figures 4 and 5, the HOMOs locate on the Be_2B_8 , the B_2B_8 and the C_2B_8 backbones in the $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules. In contrast, the distribution of the LUMOs is mainly on the Li atom except for the $C_2B_8\text{-Li}$ molecule. In the $C_2B_8\text{-Li}$ molecule, the LUMO locates mainly on both the Li and the C atoms.

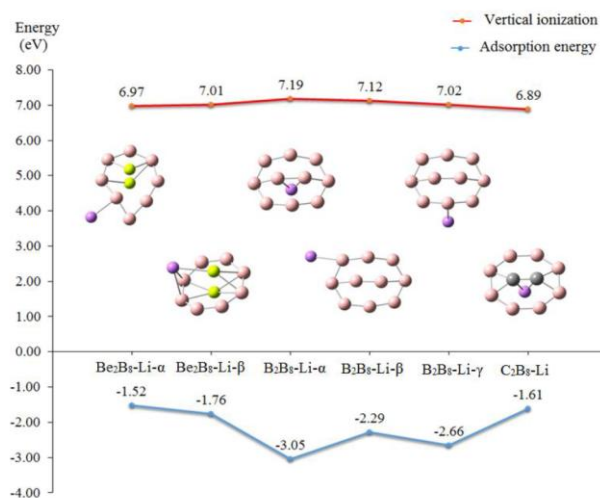


Fig. 2 The adsorption and the vertical ionization energies of all the obtained molecules for the $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules.

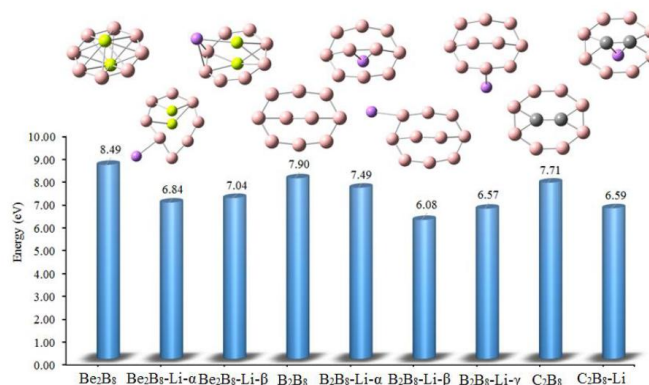


Fig. 3 The HOMO-LUMO energy gap of the obtained structures for the $\text{Li}@X_2B_8$ ($X = \text{Be, B and C}$) molecules along with the Be_2B_8 (D_{8h}), the B_2B_8 (C_{2h}) and the C_2B_8 (D_{2h}) species.

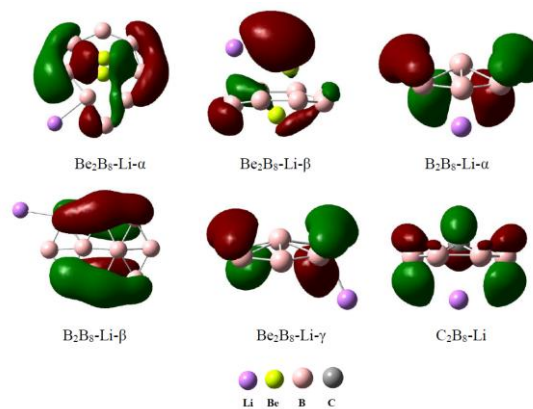


Fig. 4 The distribution of the HOMO in the $\text{Li}@Be_2B_8$, the $\text{Li}@B_2B_8$ and the $\text{Li}@C_2B_8$ molecules (isosurface = 0.04).

3.4. NBO charges

The natural bond orbital (NBO) charges as alternative factor can provide clear insight into the atomic electron donor or electron acceptor of the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules. In this regard, we have listed the NBO charges of all atoms in Table S4 of the ESI. The precise investigation of the NBO charges reveals three significant points. Firstly, the positive range $0.76 e \sim 0.91 e$ has been found for the NBO charges of the Li atom in the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules. The Li atom of the $\text{C}_2\text{B}_8\text{-Li}$ molecule has the smallest NBO charge ($0.76 e$) compared to the Li atom of other molecules. Secondly, the Be atoms of the $\text{Be}_2\text{B}_8\text{-Li-}\alpha$ and the $\text{Be}_2\text{B}_8\text{-Li-}\beta$ molecules and the C atoms of the $\text{C}_2\text{B}_8\text{-Li}$ molecule have positive and negative NBO charges, respectively. These results show that the Li (and the Be) and the C atoms have the role of electron donor and electron acceptor, respectively in the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules. Thirdly, in the $\text{Be}_2\text{B}_8\text{-Li-}\alpha$, the $\text{Be}_2\text{B}_8\text{-Li-}\beta$ and the $\text{B}_2\text{B}_8\text{-Li-}\alpha$ molecules, all B atoms have the negative NBO charges except for the B1 atom of the $\text{Be}_2\text{B}_8\text{-Li-}\alpha$ molecule. In contrast, all the B atoms of the $\text{C}_2\text{B}_8\text{-Li}$ molecule have the positive NBO charges as shown in Table S4 of the ESI. It is very interesting to say that the B atoms of the B_2B_8 backbone in the $\text{B}_2\text{B}_8\text{-Li-}\beta$ and the $\text{Be}_2\text{B}_8\text{-Li-}\gamma$ molecules can have both positive and negative NBO charges. On the other words, the B atoms of the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules can play both roles of electron donor and electron acceptor confirming their high chemical flexibility.

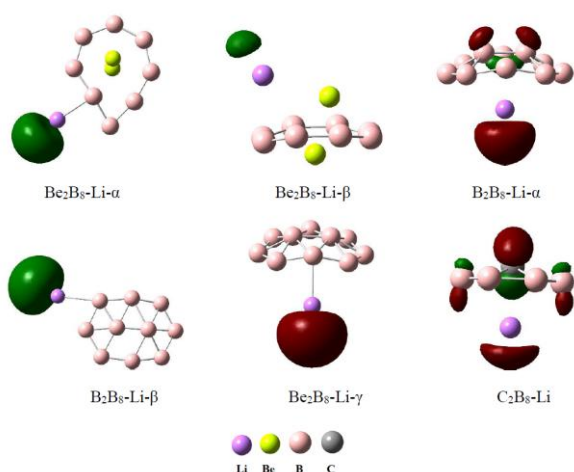


Fig. 5 The distribution of the LUMO in the $\text{Li@Be}_2\text{B}_8$, the $\text{Li@B}_2\text{B}_8$ and the $\text{Li@C}_2\text{B}_8$ molecules (isosurface = 0.04).

3.5. Spin density

All the reported molecules in the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) system are the local minima on the doublet PES containing one odd electron. Therefore, the identification of the odd electron distribution in the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules can help to provide more clear vision about the electronic features of the reported molecules. Figure 6 presents that in the $\text{Be}_2\text{B}_8\text{-Li-}\alpha$ and the $\text{Be}_2\text{B}_8\text{-Li-}\beta$ molecules, the odd

electron locates on either the B or the Be atom. In contrast, the delocalization of the odd electron has been observed on some B atoms of the B_2B_8 backbone in the $\text{B}_2\text{B}_8\text{-Li-}\alpha$, the $\text{B}_2\text{B}_8\text{-Li-}\beta$ and the $\text{Be}_2\text{B}_8\text{-Li-}\gamma$ molecules. In the $\text{C}_2\text{B}_8\text{-Li}$ molecule, the odd electron distributes only on two central C atoms. This means that none of the B atoms in the C_2B_8 backbone collaborate in the distribution of the odd electron.

3.6. Electron transfer (ET)

The addition of the Li atom to the X_2B_8 ($X = \text{Be, B and C}$) molecules changes electron density in both Li atom and the X_2B_8 ($X = \text{Be, B and C}$) molecules. The source of these electron density changes is the electron transfer (ET). In the present paper, we have given a picture of the difference map of electron density between the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules and two fragments of the Li atom and the X_2B_8 ($X = \text{Be, B and C}$) molecules in Figure 7 to provide the appropriate vision on the regions with the increasing or decreasing electron density due to the Li atom doping. It is necessary to say that the regions with the increasing (decreasing) electron density in Figure 7 have been presented through the green (red) regions. Figure 7 shows that electron density of the Li atom decreases in all $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules. This means that the Li atom plays the role of the electron donor in all reported molecules. In the $\text{Be}_2\text{B}_8\text{-Li-}\alpha$ and the $\text{Be}_2\text{B}_8\text{-Li-}\beta$ molecules, the electron density changes of the Be_2B_8 backbone due to doping of the Li atom have been observed mainly in the Be and the B atoms close to the Li atom which reflects these atoms are the main responsible for the ET. Additionally, the difference map of electron density in the $\text{B}_2\text{B}_8\text{-Li-}\alpha$, the $\text{B}_2\text{B}_8\text{-Li-}\beta$ and the $\text{Be}_2\text{B}_8\text{-Li-}\gamma$ molecules is much more different than that of the $\text{Be}_2\text{B}_8\text{-Li-}\alpha$ and the $\text{Be}_2\text{B}_8\text{-Li-}\beta$ molecules as shown in Figure 7. In three molecules of the $\text{B}_2\text{B}_8\text{-Li-}\alpha$, the $\text{B}_2\text{B}_8\text{-Li-}\beta$ and the $\text{Be}_2\text{B}_8\text{-Li-}\gamma$, all B atoms of the B_2B_8 backbone include the changes of electron density due to the Li atom doping. On the other words, all atoms of the $\text{Li@B}_2\text{B}_8$ molecules have the significant collaboration in the ET. Different from the $\text{Be}_2\text{B}_8\text{-Li-}\alpha$, the $\text{Be}_2\text{B}_8\text{-Li-}\beta$, the $\text{B}_2\text{B}_8\text{-Li-}\alpha$, the $\text{B}_2\text{B}_8\text{-Li-}\beta$ and the $\text{Be}_2\text{B}_8\text{-Li-}\gamma$ molecules, the changes of the electron density have been observed mainly in two central C atoms of the $\text{C}_2\text{B}_8\text{-Li}$ molecule as shown in Figure 7. Indeed, the B atoms of the C_2B_8 backbone have the minor role in the ET.

3.7. The first hyperpolarizability

Nowadays, the materials with the nonlinear optical (NLO) properties obtain the great attentions by researchers [17-23].

The first hyperpolarizability (β_{total}) is the significant criterion to identify materials with the NLO properties.

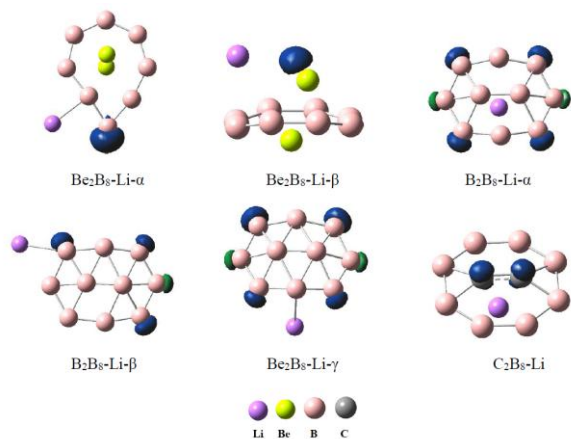


Fig. 6 The distribution of spin density in the Li@Be₂B₈, the Li@B₂B₈ and the Li@C₂B₈ molecules (isosurface = 0.02).

To achieve this purpose, we have listed the values of β_{total} and their components in Table S5 of the ESI and displayed in Figure 8. The calculated results show that β_{total} values of the Li@X₂B₈ (X = Be, B and C) molecules are in the range 50 a.u. ~ 2200 a.u. at the ROMP2 level. The smallest and the biggest β_{total} values have been observed for the B₂B₈-Li- α (50 a.u.) and the B₂B₈-Li- β (2200 a.u.) molecules. Additionally, the obtained β_{total} values for B₂B₈-Li- α (50 a.u.), B₂B₈-Li- β (2200 a.u.) and Be₂B₈-Li- γ (457 a.u.) molecules reflect severe dependence between the β_{total} value and the Li atom position on the B₂B₈ backbone. Finally, the β_{total} value of the Li@Be₂B₈ molecules, 1085 a.u. and 1257 a.u., are bigger than that of the Li@C₂B₈ molecule, 1079 a.u.

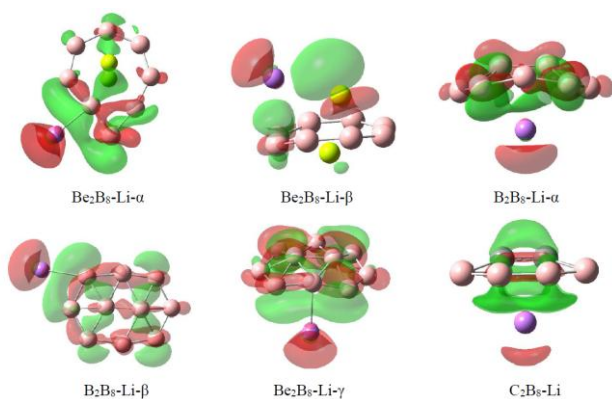


Fig. 7 The difference map of electron density in the Li@X₂B₈ (X = Be, B and C) molecules (The green (+0.003 a.u.) and red (-0.003 a.u.) regions show the increasing and decreasing electron density, respectively).

Our results in the previous part show that the adsorption energy in the Li@X₂B₈ (X = Be, B and C) species is bigger than that of CO₂@X₂B₈ (X = Be, B and C) species. This means that we can obtain the most stable geometries of the Li&CO₂@X₂B₈ (X = Be, B and C) species through addition of the CO₂ molecule to the Li@X₂B₈ (X = Be, B and C) species.

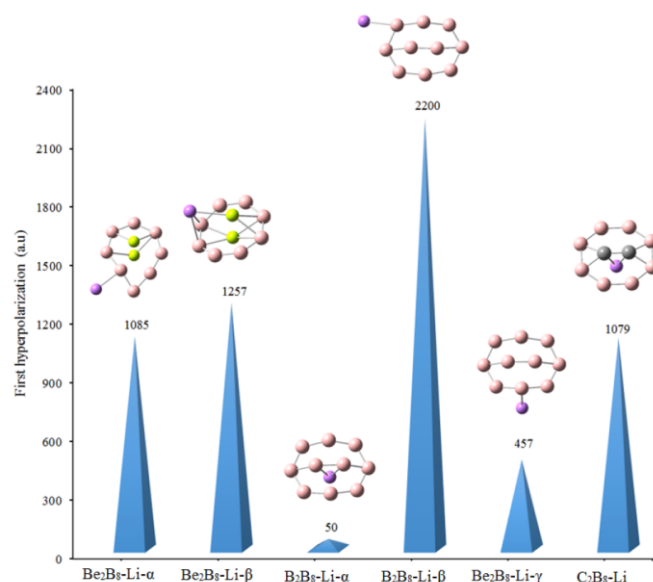


Fig. 8 The values of the first hyperpolarizability for the Li@X₂B₈ (X = Be, B and C) molecules.

3.8. The addition of both Li atom and CO₂ molecule to X₂B₈ (X = Be, B and C) species

In this regard, we have added the CO₂ molecule to different positions of Be₂B₈-Li- β , B₂B₈-Li- α and C₂B₈-Li species. In spite of numerous attempts, we have found no suitable local minima for CO₂@B₂B₈-Li- α and CO₂@C₂B₈-Li species. Indeed, all optimized geometries for the CO₂@B₂B₈-Li- α and the CO₂@C₂B₈-Li species in the present paper include either imaginary frequency or positive adsorption energy. In contrast, one local minimum has been found through the addition of the CO₂ molecule to the Be₂B₈-Li- β species, shown as the Be₂B₈-Li-CO₂ species in Figure 1. The interaction of the Li and Be atoms with O atoms of the bent CO₂ molecule can be considered in the Be₂B₈-Li-CO₂ species. Our results show that the adsorption energy of the CO₂ molecule on the Be₂B₈-Li- β in the Be₂B₈-Li-CO₂ species is -1.06 eV. The comparison of the adsorption energy of the CO₂ molecule in the Be₂B₈-Li-CO₂ species (-1.06 eV) with that of the Be₂B₈-CO₂ species (-0.89 eV) confirms that the doping of the Li atom in the Be₂B₈ causes to increase adsorption energy of the CO₂ molecule. Similar result has been not found for the B₂B₈ and the C₂B₈ species.

4. Conclusions

In the present paper, we have carried the addition of the Li atom and CO₂ molecule to the nonplanar Be₂B₈ (D_{8h}), the quasiplanar B₂B₈ (C_{2h}) and the planar C₂B₈ (D_{2h}) molecules on the singlet or doublet PESs. The obtained results can be listed as follows:

a) Two, three, and one structures have been found for the doping of Li atom to the Be₂B₈ (D_{8h}), the B₂B₈ (C_{2h}) and the C₂B₈ (D_{2h}) molecules, respectively. The AIM

analysis of the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules shows that the interactions between the Li atom and the backbones of the Be_2B_8 , the B_2B_8 and the C_2B_8 are weak and non-covalent. Additionally, no bond path has been found between two the Be atoms of the $\text{Li@Be}_2\text{B}_8$ molecules.

b) According to the adsorption energies of the Li atom, $-1.52 \text{ eV} \sim -3.05 \text{ eV}$, the thermodynamic stability of the $\text{Li@B}_2\text{B}_8$ molecules are much bigger than that of the $\text{Li@Be}_2\text{B}_8$ and the $\text{Li@C}_2\text{B}_8$ molecules. Therefore, the B_2B_8 species is more suitable for doping of the Li atom.

c) No significant difference exists among the VI energies of the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules. Additionally, big values of VI show that the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules are not appropriate electron donor in the electron transfer reactions.

d) The energy gap of the HOMO-LUMO in all the Be_2B_8 (D_{8h}), the B_2B_8 (C_{2h}) and the C_2B_8 (D_{2h}) molecules decreases due to doping of Li atom. The biggest energy gap among the reported $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules belongs to the $\text{B}_2\text{B}_8\text{-Li-}\alpha$ molecule of the $\text{Li@B}_2\text{B}_8$ system.

e) The positive NBO charges of the Li and the Be atoms and that of negative in the C atoms reflect the roles of electron donor and electron acceptor for the Li (and the Be) and the C atoms in the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules, respectively. In contrast, the B atoms have dual role. Indeed, they can accept both roles of electron donor and electron acceptor in the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules which confirms high chemical flexibility of the B atoms.

f) The investigation of the spin density distribution reveals that the odd electron of the $\text{Li@B}_2\text{B}_8$ molecules is much less localized than that of the $\text{Li@Be}_2\text{B}_8$ and the $\text{Li@C}_2\text{B}_8$ molecules.

g) Although, the different atoms involve in the electron transfer, the overall tendency of the electron transfer is from the Li atom to the Be_2B_8 , the B_2B_8 and the C_2B_8 backbones in all $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules.

h) The β_{total} values of the $\text{Li@X}_2\text{B}_8$ ($X = \text{Be, B and C}$) molecules are in the range $50 \text{ a.u.} \sim 2200 \text{ a.u.}$ Moreover, the calculated results reveals that the β_{total} value of the $\text{Li@B}_2\text{B}_8$ molecules has severe dependence to the Li atom position on the B_2B_8 backbone.

i) That the adsorption energy of the CO_2 molecule on the Be_2B_8 species (-0.89 eV) is much bigger than that of the B_2B_8 (-0.10 eV) and C_2B_8 (-0.11 eV) species. Therefore, the Be_2B_8 species is more prefer than the B_2B_8 and the C_2B_8 species in order to adsorb the CO_2 molecule.

k) The results show that the values of the adsorption energy of the Li atom ($-1.52 \text{ eV} \sim -3.05 \text{ eV}$) are much bigger than those of the CO_2 molecule ($-0.10 \text{ eV} \sim -0.89 \text{ eV}$). Therefore, the adsorption of the Li atom in the

X_2B_8 ($X = \text{Be, B and C}$) species is more prefer than that of the CO_2 molecule.

m) The doping of the Li atom in the Be_2B_8 species causes to increase adsorption energy of the CO_2 molecule. Similar result has been not found for B_2B_8 and C_2B_8 species. Therefore, the Be_2B_8 species is more prefer than the B_2B_8 and the C_2B_8 species in order to adsorb both Li atom and CO_2 molecule.

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