Insight into electronic and structural properties of $n\text{Li}@B_{20}$ ($n = 1-9$) nanotubules: a computational study

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MS received 16 April 2018; revised 23 June 2018; accepted 26 July 2018; published online 6 September 2018

Abstract. In this paper, we have theoretically focused on the doping of up to nine Li atoms to the double-ring B_{20} nanotubule to reveal the electronic and structural features of the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules. The most stable species for each of the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules has been reported on the singlet or doublet potential energy surfaces through density functional theory (DFT). The calculated results show that the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules have high thermodynamic and chemical stabilities due to high values of the adsorption energy, -2.51 eV to -3.57 eV, and the HOMO–LUMO energy gap, 1.32 eV to 2.34 eV. Additionally, the values reported for deformation of the double-ring B_{20} backbone, 0.10 eV to 4.29 eV, increase severely along with increasing number of the Li atoms in the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules. The NBO charges of positive values for the Li atoms along with those of negative values for the B atoms confirm the role of electron donor of the Li atom and electron acceptor of the B atom. Finally, we have not found any Li–Li interaction in the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules based on AIM analysis. Moreover, all reported Li–B interactions are weak and non-covalent.

Keywords. Boron-rich material; double-ring B_{20} ; Li atom doping; stability.

1. Introduction

Boron (B) is a unique element in the periodic table which includes only one electron in the p valence shell along with short covalent radius. The B atom is an electron-deficient material^{1,2} with semiconductor features.³ Therefore, it has a high tendency to form robust bonds^{4,5} with electron donor atoms and other B atoms.⁶ In the past years, the attention of both theoretical and experimental researchers have increased to boron-rich materials due to the singular properties of this element² resulting in the interesting applications⁷⁻¹¹ reported in the literature similar to the systems of hydrogen storage,⁷ fuels with high-energy density⁸ and so on. It is necessary to say that the boron-rich materials have high geometric diversity, from two-dimensional (2D) to three-dimensional (3D) structures such as planar, quasi-planar, convex, open-cage/cage, tubular, spherical, ring, dome-like, shell and capsule.^{6,12}

These structural geometries can be classified into three different categories as cluster,¹³⁻¹⁵ nanowire¹⁶ and nanotube.^{17,18}

Previous observations showed that the most stable structural geometries in boron-rich materials of the B_n ($n < 20$) should be incorporated in the cluster category, planar/quasi-planar structures of 2D.^{19,20} Additionally, the most stable geometry of the B_{20} species^{21,22} moves from 2D to 3D containing two ring- B_{10} subunits, shown as the double-ring B_{20} with a diameter of $5.5 \text{ \AA}$.^{21,22} Note that two B_{10} rings of the double-ring B_{20} species are connected through strong bonds of σ and delocalized bonds of π .²²

In recent years, the doping of the boron-rich materials has attracted much attention. Jian-Bing *et al.*,²³ studied the structural, the electronic, and the magnetic features for cluster anions of boron which doped with Al element. Romanescu *et al.*,²⁴ performed the experimental and the computational investigations on the octa- and

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Figure 1. The most stable geometry of the $nLi@B_{20}$ ($n = 1-9$) molecules.

Figure 1. continued

nona-coordinated planar iron-doped B_8 and B_9 clusters. Van Duong and Nguyen²⁵ have doped small boron clusters through silicon atoms to produce stable nanoribbon geometries for boron-rich materials.

On one hand, the boron-rich materials have high electron deficiency. Therefore, it should be interesting to add the species with high ability for electron donation to boron-rich materials. This strategy can result in species with unique properties. On the other hand, it is known that doping of Li atom to boron-rich materials can result in species with high potential abilities

to be used as anode material in the Li-based batteries. Therefore, we have chosen the Li atom to add to B_{20} species due to high ability of electron donation of the Li atom and the possibility of formation of materials for using as anode material in the Li-based batteries.

In the present study, we have systematically added up to nine Li atoms to the double-ring B_{20} molecule to report the most stable local minima for each $nLi@B_{20}$ ($n = 1-9$) molecules on the singlet or doublet potential energy surfaces (PESs) to understand the electronic and structural properties of the obtained local minima to

Table 1. The energies of E_1 , E_2 , E_3 , the adsorption energy (E_{ads}), the vertical ionization (VI) and deformation energies (E_d), at the PBE0-D3/cc-pVDZ level for all the $\text{Li}_n\text{@B}_{20}$ ($n = 1 - 9$) molecules.

Species	E_1 (Hartree)	E_2 (Hartree)	E_3 (Hartree)	E_{ads} per Li atom (eV)	VI (eV)	E_d (eV)
B_{20}Li_1	-503.76941	-503.53998	-496.16845	-3.57	6.24	0.10
B_{20}Li_2	-511.35101	-511.11923	-496.15620	-3.35	6.31	0.44
B_{20}Li_3	-518.92248	-518.70786	-496.14985	-3.19	5.84	0.61
B_{20}Li_4	-526.46841	-526.26244	-496.13084	-2.94	5.61	1.13
B_{20}Li_5	-534.02698	-533.82168	-496.11252	-2.85	5.59	1.62
B_{20}Li_6	-541.57889	-541.20384	-496.09449	-2.77	10.21	2.12
B_{20}Li_7	-549.13176	-548.94935	-496.02039	-2.71	4.96	4.13
B_{20}Li_8	-556.67506	-556.49677	-496.02463	-2.63	4.85	4.02
B_{20}Li_9	-564.19631	-564.03603	-496.01458	-2.51	4.36	4.29

Figure 2. The values of the adsorption, the vertical ionization and the deformation energies for all the reported $n\text{Li@B}_{20}$ ($n = 1-9$) molecules.

perform comparative study among the $n\text{Li@B}_{20}$ ($n = 1-9$) molecules in order to reveal the influence of increasing concentration of the Li atom on the double-ring B_{20} backbone. We hope that the results of the present study would help researchers in material design.

2. Computational methods

To the best of our knowledge, many researchers have used the PBE0 method to obtain possible local minima for the boron-rich materials.²⁶⁻³⁰ Therefore, we have used PBE0 method³¹⁻³³ conjugated to cc-pVDZ basis set³⁴ in the present paper to obtain optimized geometries of the $n\text{Li@B}_{20}$ ($n = 1-9$) molecules. Moreover, we have used the DFT-D3 method³⁵ for the correction of the dispersion energies in the $n\text{Li@B}_{20}$ ($n = 1-9$) molecules. Note that we have carried out the geometry optimizations of the $n\text{Li@B}_{20}$ molecules with $n=2, 4, 6$ and 8 and $n=1, 3, 5, 7$ and 9 on the singlet and

doublet PESs, respectively. In the next step, the calculations of adsorption energy per Li atom (E_{ads}), vertical ionization (VI) energy and deformation energy (E_d) in the most stable species for each $n\text{Li@B}_{20}$ ($n = 1-9$) molecules have been performed through Eqs. 1-3, respectively.

$$E_{\text{ads}} = [E_1 - nE(\text{Li}) - E(\text{B}_{20})]/n \quad (1)$$

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

$$E_d = E_3 - E(\text{B}_{20}) \quad (3)$$

Where, the E_1 , E_2 and the E_3 stand for the energy of optimized geometry of the $n\text{Li@B}_{20}$ ($n = 1-9$) molecule, single-point energy of the $[n\text{Li@B}_{20} (n = 1-9)]^+$ molecule and the energy of the $n\text{Li@B}_{20}$ ($n = 1-9$) molecule after the elimination of the all Li atoms by the calculation of single-point energy, respectively.

The lack of imaginary vibrational frequencies has been confirmed through the calculation of all vibrational frequencies of the $n\text{Li@B}_{20}$ ($n = 1-9$) molecules. Finally, the bond

Figure 3. The energy and energy gap of the HOMO and the LUMO orbitals for the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules.

Table 2. The HOMO and the LUMO energies and the HOMO–LUMO energy gaps (eV) for all reported molecules.

Species	Set α		Set β		HOMO–LUMO energy gap
	HOMO energy	LUMO energy	HOMO energy	LUMO energy	
B ₂₀ Li ₁	-4.92	-3.38	-6.18	-3.60	1.32
B ₂₀ Li ₂	-5.02	-3.07	-5.03	-2.99	1.95
B ₂₀ Li ₃	-4.60	-2.97	-5.03	-2.99	1.61
B ₂₀ Li ₄	-4.37	-2.95	-5.03	-2.99	1.42
B ₂₀ Li ₅	-4.37	-2.34	-4.39	-2.89	1.48
B ₂₀ Li ₆	-4.27	-1.93	-4.31	-2.23	2.34
B ₂₀ Li ₇	-3.82	-2.09	-4.31	-2.23	1.59
B ₂₀ Li ₈	-3.86	-1.70	-4.31	-2.23	2.16
B ₂₀ Li ₉	-3.29	-1.35	-3.45	-1.66	1.63

Italic values stand for the calculation of the HOMO–LUMO energy gap.

critical points (BCPs) and the geometric optimizations have been performed through the AIM2000³⁶ and Gaussian 09³⁷ software, respectively.

3. Results and Discussion

3.1 Stability

The double-ring B₂₀ species is created with 20 boron atoms that are located in two parallel rings. At first,

we have added one Li atom to different sites of the double-ring B₂₀ species on the double PES. In spite of numerous attempts, we have just found one optimized geometry for B₂₀Li₁ molecule as shown in Figure 1 through the face, side and top view. By starting from the B₂₀Li₁ molecule, the second Li atom has been added to different positions of the B₂₀Li₁ molecule on the singlet PES to obtain the possible optimized geometries of the B₂₀Li₂ molecule. The similar trend has been used to reveal the possible optimized geometries for each of the $n\text{Li}@B_{20}$ ($n = 3-9$) molecules

Figure 4. The position of the HOMO of the $nLi@B_{20}$ ($n = 1-9$) molecules.

through optimization process without constraint. Next, the obtained geometries in each $nLi@B_{20}$ ($n = 1-9$) molecules have categorized based on energy. It is necessary to say that we have found just one optimized geometry for the $Li_n@B_{20}$ ($n=1, 2$ and 9) systems. In contrast, several optimized geometries have been obtained in each of the $Li_n@B_{20}$ ($n=3-8$) systems. In the present work, we presented the most stable geometries for each $Li_n@B_{20}$ ($n = 1-9$) systems in Figure 1. Moreover, the obtained geometries for the second rank of stability in the $nLi@B_{20}$ ($n=3-8$) molecules have been shown in Figure S1 in Supporting Information.

The comparison of the most stable geometries of $nLi@B_{20}$ ($n = 1-9$) molecules through Figure 1 shows

that only one of the Li atoms locates interior of the double-ring of B_{20} species and other Li atoms locate external of the double-ring. Additionally, the existence of the Li atoms affects the geometry of the double-ring B_{20} species resulting into the distortion in the ring of the $nLi@B_{20}$ ($n = 1-9$) molecules. In Figure 1, we have shown atomic interactions through solid lines confirming B–B and Li–B interactions in the $nLi@B_{20}$ ($n = 1-9$) molecules. Note that Li–Li interaction has not been found in the $nLi@B_{20}$ ($n = 1-9$) molecules through AIM analysis.

To the best of our knowledge, the adsorption energies can provide obvious vision about the thermodynamic stability. Therefore, we have listed the adsorption energies per Li atom of the most stable geometries for each

Figure 5. The position of the LUMO of the $nLi@B_{20}$ ($n = 1-9$) molecules.

of the $nLi@B_{20}$ ($n = 1-9$) molecules in Table 1 and have shown them in Figure 2. The results show that the adsorption energies per Li atom are -2.51 eV to -3.57 eV. Firstly, these reported large values to reflect the high tendency of the double-ring B_{20} species for the adsorption of Li atoms. Secondly, the obtained values confirm that increasing the number of the Li atoms results in decreasing adsorption energy per Li atom in the $nLi@B_{20}$ ($n = 1-9$) molecules. Moreover, the $B_{20}Li_1$ species has the biggest (-3.57 eV) and the $B_{20}Li_9$ species has the smallest (-2.51 eV) adsorption energy among all molecules reported in the present paper. Therefore, the $B_{20}Li_1$ species has the highest thermodynamic stability in the $nLi@B_{20}$ ($n = 1-9$) molecules.

In addition to thermodynamic stability, we have obtained the vertical ionization (VI) energy in order to ability investigation of the $nLi@B_{20}$ ($n = 1-9$) molecules to use as the source of electron creation. The obtained values of VI energies for the $nLi@B_{20}$ ($n = 1-9$) molecules are given in Figure 2 and Table 1. The range of 4.36 eV to 10.21 eV has been obtained for the VI energies that the $B_{20}Li_6$ and the $B_{20}Li_9$ species have the biggest and the smallest VI energies, respectively. As shown in Figure 2, the values of VI energies are very big which show the $nLi@B_{20}$ ($n = 1-9$) molecules cannot be appropriate as a source for electron production in electron transfer reactions.

Due to doping of the Li atoms to the double-ring B_{20} species, the deformation occurs in double-ring of

Table 3. NBO charges of the atoms in the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules.

Atoms	Species								
	$B_{20}Li_1$	$B_{20}Li_2$	$B_{20}Li_3$	$B_{20}Li_4$	$B_{20}Li_5$	$B_{20}Li_6$	$B_{20}Li_7$	$B_{20}Li_8$	$B_{20}Li_9$
B1	-0.04	-0.05	-0.11	-0.17	-0.14	-0.14	-0.45	-0.42	-0.41
B2	-0.03	-0.06	-0.09	-0.12	-0.26	-0.28	-0.34	-0.44	-0.44
B3	-0.02	-0.03	-0.20	-0.15	-0.06	-0.10	-0.03	-0.06	-0.05
B4	-0.03	-0.02	-0.07	-0.18	-0.17	-0.55	-0.29	-0.54	-0.55
B5	-0.04	-0.04	-0.07	-0.18	-0.16	-0.14	-0.28	-0.15	-0.17
B6	-0.02	-0.05	-0.20	-0.15	-0.12	-0.13	-0.08	-0.40	-0.38
B7	-0.03	-0.04	-0.09	-0.12	-0.19	-0.17	-0.21	-0.40	-0.42
B8	-0.04	0.00	-0.11	-0.17	-0.08	-0.09	-0.12	-0.10	-0.08
B9	-0.03	0.00	0.01	-0.18	-0.21	-0.21	-0.15	-0.13	-0.51
B10	-0.02	-0.01	0.01	-0.18	-0.20	-0.22	-0.29	-0.23	-0.22
B11	-0.02	-0.14	-0.07	-0.09	-0.12	-0.13	-0.31	-0.39	-0.38
B12	-0.03	-0.06	0.00	-0.04	-0.19	-0.17	-0.40	-0.39	-0.42
B13	-0.04	-0.02	-0.10	0.00	-0.08	-0.09	-0.09	-0.10	-0.08
B14	-0.03	-0.02	0.00	-0.04	-0.21	-0.21	-0.14	-0.13	-0.51
B15	-0.03	-0.04	-0.07	-0.09	-0.20	-0.22	-0.17	-0.23	-0.22
B16	-0.04	-0.11	-0.19	-0.19	-0.14	-0.14	-0.14	-0.42	-0.41
B17	-0.03	-0.17	-0.10	-0.14	-0.26	-0.28	-0.38	-0.45	-0.44
B18	-0.02	-0.15	-0.15	-0.06	-0.06	-0.10	-0.42	-0.07	-0.05
B19	-0.04	-0.14	-0.10	-0.14	-0.17	-0.55	-0.29	-0.54	-0.55
B20	-0.04	-0.17	-0.19	-0.19	-0.16	-0.14	-0.26	-0.15	-0.17
Li1	0.61	0.45	0.20	0.16	0.03	0.06	0.14	0.20	0.20
Li2	—	0.83	0.85	0.84	0.78	0.78	0.74	0.76	0.75
Li3	—	—	0.84	0.79	0.78	0.78	0.72	0.76	0.75
Li4	—	—	—	0.78	0.81	0.79	0.78	0.77	0.76
Li5	—	—	—	—	0.81	0.79	0.78	0.77	0.76
Li6	—	—	—	—	—	0.85	0.76	0.82	0.8
Li7	—	—	—	—	—	—	0.85	0.84	0.83
Li8	—	—	—	—	—	—	—	0.84	0.82
Li9	—	—	—	—	—	—	—	—	0.83

the B_{20} molecule. We observed the range of 0.10 eV to 4.29 eV for the deformation energies. As shown in Figure 2, the deformation energies increase along with increasing number of the Li atoms. Namely, the $B_{20}Li_1$ and the $B_{20}Li_9$ species have the smallest (0.10 eV) and the biggest (4.29 eV) deformation energies of the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules. The values of deformation energies are very large which means that approaching Li atoms to the double-ring B_{20} backbone causes to severe distortion in the double-ring geometry of the B_{20} .

Chemical stability of molecules can be examined through HOMO–LUMO energy gaps (HLG) for α - and β -electrons (HOMO: highest occupied molecular orbital, LUMO: lowest unoccupied molecular orbital). The HOMO–LUMO energy gap and the HOMO and the LUMO orbitals energy have been given in Figure 3 and Table 2. Note that the molecules with $2n$ ($n = 1-4$) Li atoms have only α -set of electrons. In contrast, the molecules containing $2n-1$ ($n = 1-4$) Li atom(s) have both α -set and β -set of the electron. According to

Figure 3, the HOMO–LUMO energy gap of the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules changes from 1.32 eV to 2.34 eV, due to doping Li atoms to the double-ring B_{20} species. The results show that maximum HOMO–LUMO energy gap has been found for the $B_{20}Li_6$ (2.34 eV) species and the $B_{20}Li_1$ species has the smallest HOMO–LUMO energy gap, 1.32 eV. It is necessary to say that attacking the Li atoms to the double-ring B_{20} species affects both energies of the HOMO and the LUMO orbitals as shown in Figure 3. This means that both the HOMO and the LUMO orbitals contribute to the change of the HOMO–LUMO gap.

As we know, a larger value of the HOMO–LUMO energy gap relates to greater chemical hardness.³⁸ Therefore, the $B_{20}Li_6$ species has the greatest chemical hardness among the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules. The position pictures of the HOMO and the LUMO orbitals in the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules have been shown in Figures 4 and 5, respectively. As seen in these figures, the HOMO and the LUMO orbitals of the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules are located only on

Figure 6. The distribution of the spin density of the $nLi@B_{20}$ ($n = 1, 3, 5$ and 7) molecules.

the B atoms of the double ring B_{20} species. Indeed, the Li atoms do not contribute in the HOMO and the LUMO locations. Moreover, an increase in the number of Li atoms on the double-ring B_{20} species results in more localization of the HOMO and the LUMO orbitals, as shown in Figures 4 and 5.

3.2 NBO analysis

The charges of natural bond orbital (NBO)^{39–41} for atoms involved in the $nLi@B_{20}$ ($n = 1–9$) molecules have been listed in Table 3. The results show that all Li atoms have a positive charge, 0.03 e to 0.85 e. In other words, all Li atoms have the electron donor role in the $nLi@B_{20}$ ($n = 1–9$) molecules. It is interesting to say that the Li1 atoms of the $nLi@B_{20}$ ($n = 1–9$) molecules have the smallest NBO charges compared with other Li atoms, the Li2–Li9 atoms as shown in Table 3. Note that the Li1 atom of the $nLi@B_{20}$ ($n = 1–9$) molecules, different from other Li atoms, has located in the centre of the double-ring B_{20} species. Additionally, the NBO charges of all B atoms in the $nLi@B_{20}$ ($n = 1–9$) molecules are negative except for a few of the B atoms.

This means that the effective role of the B atoms is electron acceptor in the present paper.

3.3 AIM analysis

We have used the AIM theory^{42–48} in order to understand better about characteristics and strength of interactions. Based on the AIM theory, all possible BCPs of the $nLi@B_{20}$ ($n = 1–9$) molecules have been investigated. We have not observed any Li–Li interaction in the molecules reported in this paper. Moreover, we have only focused on the Li–B interactions of the $nLi@B_{20}$ ($n = 1–9$) molecules. Among all Li–B interactions reported in the $nLi@B_{20}$ ($n = 1–9$) molecules, the longest interaction belongs to the Li1–B14 interaction in the $B_{20}Li_1$ species (2.67 Å). In contrast, the shortest Li–B interaction has been found for $B_{20}Li_7$ species (Li2–B18 interaction, 2.05 Å). Subsequently, we have investigated the electron density, $\rho(r)$, and $\nabla^2\rho(r)$ for the $nLi@B_{20}$ ($n = 1–9$) molecules in their BCPs, only for the Li–B interactions. For the Li–B interactions, the ranges of 0.0099 a.u. to 0.0291 a.u. and 0.0488 a.u. to 0.1349 a.u. have been obtained for $\rho(r)$

and $\nabla^2\rho(r)$, respectively. The slight values of $\rho(r)$ and the positive values of $\nabla^2\rho(r)$ indicate that interactions between the Li and the B atoms in the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules have strength and characteristic of weak and non-covalent, respectively.

3.4 Spin density

The reported molecules in the present paper can be incorporated in two different categories based on the PES. The first category includes the $n\text{Li}@B_{20}$ ($n=2, 4, 6$, and 8) molecules at the singlet PES without odd electron. The $n\text{Li}@B_{20}$ ($n=1, 3, 5, 7$ and 9) molecules should incorporate in the second category which includes one odd electron at the doublet PES. It is very interesting to identify the distribution of an odd electron in the $n\text{Li}@B_{20}$ ($n=1, 3, 5, 7$ and 9) molecules. In this regard, we have presented spin density of the $n\text{Li}@B_{20}$ ($n=1, 3, 5, 7$ and 9) molecules in Figure 6. According to Figure 6, the odd electron of all the $n\text{Li}@B_{20}$ ($n=1, 3, 5, 7$ and 9) molecules have only localized on the B atoms. In other words, the Li atoms have no tendency for contribution in spin density. Moreover, we can observe an increase in the localization of odd electron along with increasing number of Li atoms in the $n\text{Li}@B_{20}$ ($n=1, 3, 5, 7$ and 9) molecules.

4. Conclusions

In the present study, we have systematically investigated doping of up to nine Li atoms to the double-ring nanotubule of the B_{20} . We have found the geometrical structures, the stabilities and the electronic properties of the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules. Our results on the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules can be summarized as follows: 1) The range of -2.51 eV to -3.57 eV was obtained for the adsorption energy per Li atom of the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules. Moreover, the $B_{20}\text{Li}_1$ and the $B_{20}\text{Li}_9$ species have the largest (-3.57 eV) and the smallest (-2.51 eV) adsorption energy. This result confirms the inverse relationship of the adsorption energy per Li atom and the number of the Li atoms. Namely, the $B_{20}\text{Li}_1$ species has high thermodynamic stability among the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules reported in the present paper. 2) We have obtained the wide range of 0.10 eV to 4.29 eV for the deformation energy. These values show that big geometric changes occur in the double-ring B_{20} species along with doping of the Li atoms. Additionally, the values reported for deformation energy increase severely along with increasing number of the Li atoms in the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules. 3) The evaluation of the

vertical ionization (VI) energies reflects that the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules have high VI energies, 4.36 eV (in the $B_{20}\text{Li}_9$ species) and 10.21 eV (in the $B_{20}\text{Li}_6$ species). The high values of the VI energies show that the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules cannot be appropriate as a source of electrons in electron transfer reactions. 4) The relatively narrow range of the HOMO–LUMO gap, 1.32 eV to 2.34 eV, compared to those of the deformation and the VI energies, shows the smaller fluctuation of the HOMO–LUMO gap due to the increasing number of Li atoms in the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules. Note that the $B_{20}\text{Li}_6$ species have the highest chemical stability among the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules. 5) According to the NBO charges, the Li atoms with positive charges, and the B atoms with negative charges play the role of electron donor and electron acceptor in the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules, respectively. 6) Based on the AIM analysis, the Li–Li interaction has been not observed in all the molecules reported in this paper. Also, the interactions between the Li and the B atoms in the $n\text{Li}@B_{20}$ ($n = 1-9$) molecules are weak and non-covalent. 7) The odd electron of all the $n\text{Li}@B_{20}$ ($n=1, 3, 5, 7$ and 9) molecules has localized only on the B atoms. In other words, the Li atoms have no tendency to contribute to spin density.

Supplementary Information (SI)

Supplementary Information is available at www.ias.ac.in/chemsci.

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