

# The B–C and C–C bonds as preferred electron source for H-bond and Li-bond interactions in complex pairing of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> with HF and LiH molecules

Abstract Ab initio calculations were used to analyze the interaction of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> with HF and LiH molecules at the mp2/6-311++g(2d,2p) computational level. Interaction of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> with HF results to H–F...H–C and C–B...H–F, C–C...H–F hydrogen bond as well as B–H...H–F dihydrogen bond complexes. Also interaction of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> with LiH results to B–C...LiH, C–C...LiH and B–H...LiH lithium bond as well as C–H...H–Li dihydrogen complexes. In the both cases, complexes involving interaction of HF or LiH with peripheral B–C and C–C bonds of the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> backbone have greater stabilities. The structures of complexes have been analyzed using AIM and NBO methodologies.

Keywords Hydrogen bonding \_ Dihydrogen bonding \_ Lithium bonding \_ Carborane \_ C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>

## Introduction

The unique properties of carboranes account for many application in materials science [1–4], nonlinear optics [2, 5, 6], and medicinal chemistry [1, 7–9], especially in boron neutron capture therapy (BNCT). Nido-2,3,4,5-tetracarbaheptaborane(6) (Scheme 1) is one of the most carbon-rich carborane systems known [1]. The pentagonal-pyramidal geometry of the nido-2,3,4,5-C<sub>4</sub>B<sub>2</sub> cage is supported by a microwave analysis of parent C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> [10], a gas-phase electron-diffraction study of Me<sub>4</sub>C<sub>4</sub>B<sub>2</sub>Me<sub>2</sub> [11], and X-ray crystallographic and multinuclear NMR investigations of several derivatives. C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> and its derivatives have been subject of theoretical studies, molecular and electronic structure calculations, dipole moment, and ionization potential [12–16]. Nido-2,3,4,5-tetracarbaheptaborane(6), C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>, exhibits four types of hydrogen atoms, Scheme 1. The H<sub>5</sub> and H<sub>12</sub> are two kinds of H atoms that they have been bonded to the B atoms (B<sup>δ-</sup>–d–H bonds), thus known as hydride. On the other hand, H<sub>6,9</sub> and H<sub>7,8</sub> are two other types of H atoms which because of their C–H bonds they act as protic hydrogens. An interesting overview of activities of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> could be pictured through its intermolecular interactions such as H-bonding, DHB-bonding and Li-bonding. The traditional idea that the hydrogen atoms involved in the HB should be electron-deficient has been overcome with those cases where both interacting atoms were hydrogen, one positively charged and another negatively charged, and this special kind of hydrogen bond has designated as dihydrogen bond [17–29]. For C–H bonds in the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>, H-bonding with HX (H<sup>δ+</sup>–X<sup>δ-</sup>...H<sup>δ+</sup>–C<sup>δ-</sup>) or DHB-bonding with metal hydrides (M<sup>δ+</sup>–H<sup>δ-</sup>...H<sup>δ+</sup>–C<sup>δ-</sup>) is expected. In contrast, for B–H bonds due to bearing negative charge on H atom DHB-bonding with HX (B<sup>δ-</sup>–H<sup>δ-</sup>...H<sup>δ-</sup>–X<sup>δ-</sup>) and M-bonding with metal hydrides (B<sup>δ-</sup>–H<sup>δ-</sup>...M<sup>δ+</sup>–H<sup>δ-</sup>) are expected. Considering extent of applications and importance of carboranes clusters systematic studies on their structures, energies, bonding and other properties is on demand. Here certifying types and relative strength of interactions which could be occurred between C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> with HF and LiH is aim of this investigation.

## Computational methods

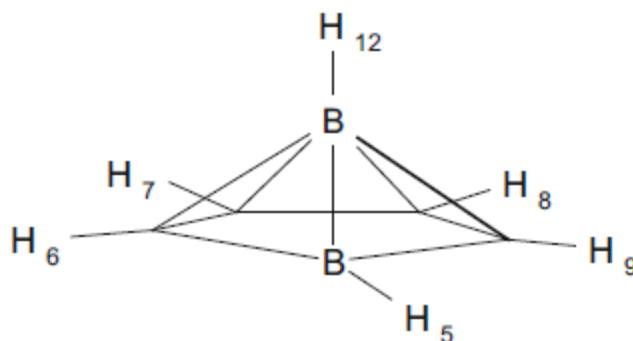
Calculations were performed using the Gaussian 03 system of codes [30]. The geometries of the isolated C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>, HF and LiH molecules as well as C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-HF and C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-LiH complexes were fully optimized at the mp2/6-311++g(2d,2p) computational level [31, 32]. Harmonic vibrational frequency calculation confirmed the structures as minimal and enabled the evaluation of zero-point energy (ZPE). The counterpoise procedure was used to correct the interaction energy for basis set superposition error [33]. The AIMAll [34] package was used to obtain bond properties and molecular graphs. The natural bond orbitals (NBO) method implemented within the Gaussian 03 set of codes was applied to perform NBO analysis.

## Result and discussion

### C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-LiH complexes

Association of LiH with C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> led to lithium bond complexes LiB-bc, LiB-5 and LiB-12 as well as DHB-bond complexes DHB-Li-7 and DHB-Li-78, Fig. 1. The LiB and DHB abbreviations were used for showing the Li-bond and DHB-bond interactions, respectively. In the LiB-bc, lithium bond interaction was carried out between the Li atom and peripheral B-C and C-C bonds of the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> molecule. In this complex, the Li atom has the role of electron acceptor while the peripheral B-C and C-C bonds of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> simultaneously play as electron donor. In the LiB-5 and LiB-12 complexes, the LiH molecule has lithium bonding with H5 and H12 atoms (Li-H5 and Li-H12) of the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>, in which the B-H bonds of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> roles as electron donor and Li-H acts as electron acceptor. On the other hand, DHB-Li-7 is a DHB-bond complex which obtained from interaction of LiH with H7 atom (H-H7) of the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>. In this complex, H atom of LiH plays as electron donor and C-H7 bond of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> acts as electron acceptor. Eventually, in the DHB-Li-78, a bifurcate dihydrogen bond interaction was appeared between H atom of LiH as electron donor and H7 and H8 atoms of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> as electron acceptor (H7d<sup>+</sup>-Hd<sup>-</sup>-H8d<sup>+</sup>). Table 1 gives the stabilization energies (SE<sub>corr</sub>, corrected with zero-point energies and BSSE) of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-HF complexes. Stabilities of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-LiH complexes are in the following order, Table 1: LiB-bc>LiB-5>LiB-12>DHB-Li-7 > DHB-Li-78. Results are showing that Li-bonding between these molecules is stronger than their DHB-bond interactions. Results are showing different tendencies for B-H and C-H bonds in the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> for intermolecular interactions. Stabilities of studied complexes are indicating that B10-H5 roles out as a better electron donor than B11-H12 for intermolecular interactions. Apparently, conjugations to peripheral B-C bonds make help it in the complex formation with LiH molecule. Thus, LiB-5 is a more stable complex than LiB-12. On the other hand, for the C-H bonds labeled as C1-H6 (or C4-H9) and C2-H7 (or C3-H8), due to greater hydrogen bond donor ability of C2-H7 (C3-H8), we could only assigned the Li<sup>+</sup>-H<sup>-</sup>-d<sup>+</sup>-dH7-C2 (or Li<sup>+</sup>-H<sup>-</sup>-d<sup>+</sup>-dH8-C3) interactions. Initial geometries proposed for Li<sup>+</sup>-H<sup>-</sup>-d<sup>+</sup>-dH6-C1 (or Li<sup>+</sup>-H<sup>-</sup>-d<sup>+</sup>-dH9-C4) interactions went to Li<sup>+</sup>-H<sup>-</sup>-d<sup>+</sup>-dH7-C2 (or Li<sup>+</sup>-H<sup>-</sup>-d<sup>+</sup>-dH8-C3) structures during optimization. The Li-H bond in the free LiH molecule is 1.604 Å which show 0.026, 0.021, 0.017, 0.001 and 0.002 Å ° elongations in the LiB-bc, LiB-5, LiB-12, DHB-Li-7 and DHB-Li-78 complexes, respectively, Fig. 1 and Table 2. These variations are showing that more engthening of Li-H correspond to complexes with greater stabilities. Also, for Li-bond complexes, a good relationship was seen between interaction energy and elongation of Li-H bond. In the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> part of these complexes, different but smaller bond variations (comparing to the LiH molecule) could be observed, Table 2. In the LiB-bc, the Li atom interacts with peripheral B-C and C-C bonds in the backbone of the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>. Data given in Table 2 are showing that B-B bond has the

most contraction (-0.019) while C1–B10 and C4–B10 have considerable lengthening (0.006) with complex formation. In the LiB-5, the B–B bond has the greatest shortening (-0.022) while C4–B11, B10–H5 and C3–B11 have the most lengthening (0.011, 0.009, 0.008) with complex formation. Similarly in the LiB-12, greater changes were seen for bonds joined to the B11 atom. So that B11–H12 has the most lengthening in contrast C1–B11 and C2–B11 have the greatest shortening with complex formation. Eventually in the DHB-bond complexes, the C4B2H6 bonds less have been affected by intermolecular



Scheme 1 Schematic representation of C4B2H6 structure

interactions, and thus, their changes are smaller than previously mentioned systems. The selected vibrational stretching frequencies (cm<sup>-1</sup>) with corresponding intensities (km mol<sup>-1</sup>) for complexes are detailed in Table 3. The Li–H bond shows -73, -58 and -49 cm<sup>-1</sup> red shift in Li-bond complexes (LiB-bc, LiB-5 and LiB-12), but it shows 24 and 21 cm<sup>-1</sup> blue shift in DHB-bond systems DHB–Li-7 and DHB–Li-78, respectively. These shifts are in agreement with order found for stabilities of complexes. In Li-bond complexes, an efficient agreement was observed between red shift of Li–H bond and its bond length variation. For LiB-bc complex, the C1–H6 stretching frequency shows -10 cm<sup>-1</sup> red shift but remaining C–H and B–H bonds have 11–34 cm<sup>-1</sup> blue shift with complex formation. In LiB-5, the B10–H5 and C1–H6 bonds show -67 and -33 cm<sup>-1</sup> red shift while B11–H12 shows 17 cm<sup>-1</sup> blue shift and other C–H bonds show 4–14 cm<sup>-1</sup> blue shift with complex formation.

In LiB-12, the C3–H8 and B11–H12 show -30 and -88 cm<sup>-1</sup> red shift but B10–H5 stretching frequency shows 10 cm<sup>-1</sup> blue shift with respect to their original bands. For remaining C–H bonds, small red shift was observed. Considering the shifts given for Li-bond complexes (LiB-5 and LiB-12), it might be concluded that the B–H bond involved in the interaction shows red shift while other one shows blue shift with complexation. Also greater shifts were seen for

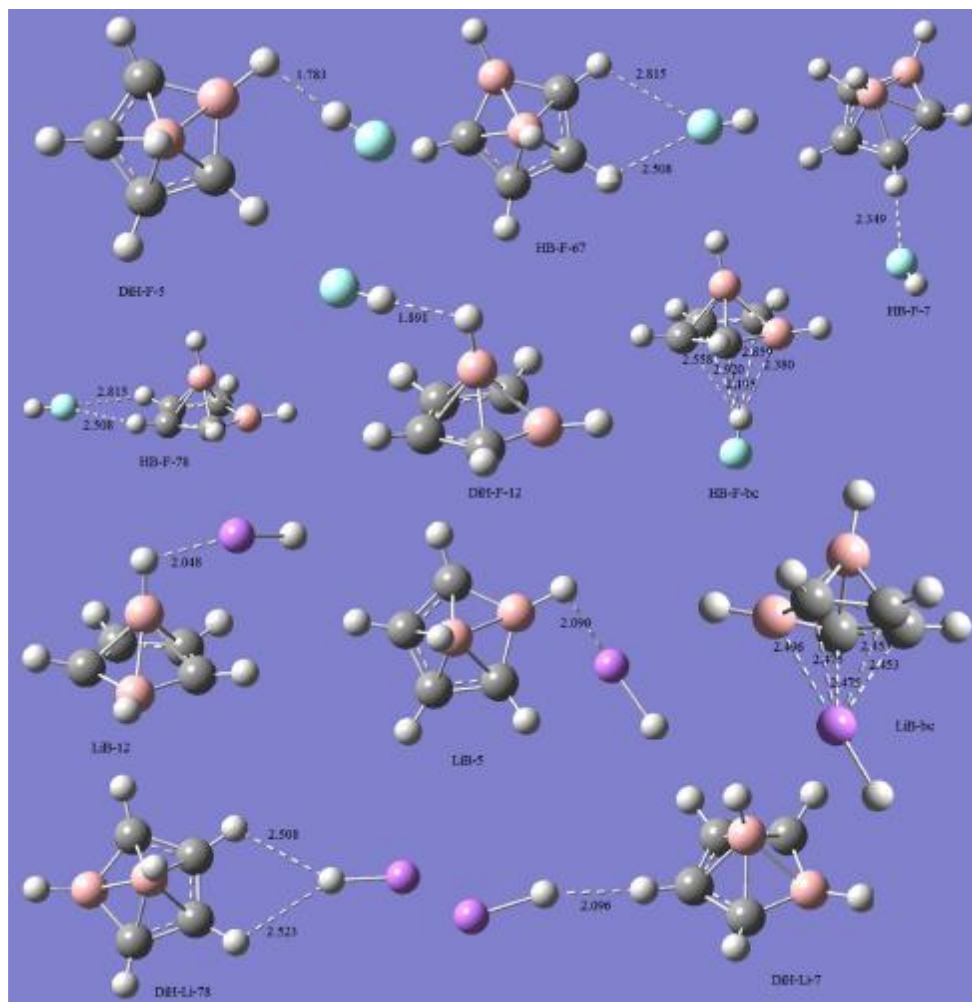


Fig. 1 Schematic representation of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> complexes with HF and LiH optimized at MP2/6-311++G(2d,2p) computational level

bonds that have more contributions in intermolecular interactions. In the DHB–Li-7 complex, the C<sub>2</sub>–H<sub>7</sub> and B<sub>10</sub>–H<sub>5</sub> show -70 and -13 red shift, and also for remaining C–H bonds smaller amount of red shift (-2 to -5 cm<sup>-1</sup>) was observed. In the DHB–Li-78, the C<sub>1</sub>–H<sub>6</sub>, C<sub>2</sub>–H<sub>7</sub> and B<sub>10</sub>–H<sub>5</sub> show -25, -25 and -13 red shift, and also for remaining C–H bonds smaller amount of red shift (-4 to -5 cm<sup>-1</sup>) was observed. Similar to Li-bond complexes in DHB-bond types, greater shifts belong to bonds which are close to interaction position. C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>–HF complexes The 1:1 association of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> with HF leads to the formation of DHB–F-5, DHB–F-12, HB–F-7, HB–F-78, HB–F-67, and HB–F-bc complexes, Fig. 1.

The DHB–F-5 and DHB–F-12 are two complexes in which DHB-bond interactions have been found between HF and B–H<sub>5</sub> and B–H<sub>12</sub> of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>, respectively. In these complexes, the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> behave as HBA and HF as HBD in (B–H<sub>d</sub>–\_\_\_d+H–F) DHB-bonding. The HB–F-7, HB–F-78, and HB–F-67 are H-bond complexes having H-bond interactions between the C–H<sub>7</sub>, H<sub>7,8</sub>, and the C–H<sub>6,7</sub> (bifurcated H-bonds) of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> as HBD with F atom of HF as HBA. Finally, in HB–F-bc, the HF molecule has H-bond interaction with peripheral B–C and C–C bonds of carborane. According to data given in Table 1, stabilities of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>–HF complexes are in the order:

HB-F-bc[DHB-F-5[DHB-F-12[HB-F-78[ HB-F-7[HB-F-67

Table 1 The SE<sup>uncorr</sup> (uncorrected stabilization energies), BSSE, DZPE, and SE<sup>corr</sup> (corrected with BSSE and DZPE) in kcal mol<sup>-1</sup> calculated at MP2/6-311++G(2d,2p)

Complex	SE <sup>uncorr</sup>	BSSE	$\Delta$ ZPE	SE <sup>corr</sup>
HB-F-67	-1.75	0.57	0.47	-0.71
HB-F-7	-1.74	0.53	0.42	-0.79
HB-F-78	-2.03	0.63	0.55	-0.84
DHB-F-12	-3.29	1.00	1.23	-1.06
DHB-F-5	-4.41	1.01	1.30	-2.10
HB-F-bc	-6.23	1.63	1.43	-3.17
LiB-bc	-14.73	1.83	1.47	-11.43
LiB-5	-10.45	0.97	1.26	-8.22
LiB-12	-7.46	0.91	1.13	-5.42
DHB-Li-7	-4.30	0.39	0.74	-3.17
DHB-Li-78	-4.30	0.38	0.73	-3.19

Values of SE<sup>uncorr</sup> were determined as follows: SE<sup>uncorr</sup> = E(C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>\_\_\_Y) - [E(C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>) + E(Y)] with Y = HF or LiH Values of SE<sup>corr</sup> were determined as follows: SE<sup>corr</sup> = SE<sup>uncorr</sup> + DZPE + BSSE Table 2 Bond length (in Å ) of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-LiH complexes at MP2/6-311++(2d, 2p)

The HF bond is 0.918 Å in the free HF molecule which shows 0.010, 0.005, 0.004 Å elongations in the HB-F-bc, DHB-F-12, DHB-F-5 and 0.001 Å in HB-F-78, HB-F-7 and HB-F-67 complexes, respectively, Table 2. These variations are showing that HB-F-bc with greatest stabilization energies between C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-HF complexes has more lengthening for HF bond. In rest of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-HF complexes, elongation of HF in DHB-bond complexes is greater than simple H-bond ones. Some considerable bond variations could be observed in the carborane part of the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-HF complexes, Table 2.

Table 2 Bond length (in Å) of C4B2H6–LiH complexes at MP2/6-311++(2d, 2p)

Bond	C <sub>4</sub> B <sub>2</sub> H <sub>6</sub>	LiB-bc	LiB-5	LiB-12	DHB- Li-7	DHB- Li-78	HB- F-67	HB- F-78	HB- F-7	DHB- F-12	DHB- F-12	HB- F-bc
	<i>r</i>	$\Delta r$										
C1–H6	1.078	0	0.004	0.001	0.001	0.001	0	0.001	0.001	0	-0.001	0
C2–H7	1.077	-0.001	0	0.001	0.005	0	0	0	0	0.001	-0.001	0
C3–H8	1.077	-0.001	0.001	0.003	0	0	0	0	0	0.001	-0.001	0
C4–H9	1.078	0	0	0.002	0.001	0.001	0.002	0.002	0.001	0	-0.001	0
B10–H5	1.183	-0.004	0.009	-0.001	0.002	0.002	0.001	0.001	0.001	-0.001	0.006	-0.002
B11–H12	1.173	-0.001	-0.001	0.011	0.002	0.002	0.001	0.001	0.001	0.006	-0.001	0
B10–B11	1.839	-0.019	-0.022	-0.007	-0.003	-0.003	-0.001	-0.001	0	-0.004	-0.002	-0.01
C1–B10	1.533	0.006	0.004	0.002	0	0	0	0	-0.001	0.001	-0.005	0.006
C1–B11	1.717	-0.001	-0.002	-0.016	-0.003	-0.002	-0.001	-0.001	-0.002	-0.006	0.004	-0.005
C1–C2	1.442	0.004	-0.001	0.005	0.001	0.001	0	0.001	0.001	0.001	-0.001	0.004
C2–C3	1.426	0.001	-0.001	0	0	-0.002	0	-0.001	0	0.002	-0.002	-0.001
C2–B11	1.718	0.001	0.006	-0.012	0.001	-0.002	-0.001	-0.001	0	-0.004	0.002	-0.002
C3–C4	1.442	0.004	-0.003	0.004	0.002	0.002	0.001	0.001	0.001	0.001	-0.001	-0.001
C3–B11	1.718	-0.002	0.008	-0.002	-0.004	-0.002	-0.001	-0.001	-0.002	-0.003	0.002	0.004
C4–B10	1.533	0.006	-0.01	0.003	-0.001	0	0	0	0	0.001	-0.003	-0.001
C4–B11	1.717	-0.001	0.011	-0.009	-0.001	-0.002	0	-0.001	-0.001	-0.006	0.004	0.002
Li–H	1.604	0.026	0.021	0.017	0.001	0.002	0.001	0.001	0.001	0.005	0.004	0.01

For HB–F-bc, data given in Table 2 are showing that B–B bond has the most contraction (-0.010) while C1–B10 has considerable elongations (0.006) with complex formation. These variations are implying that those parts of C4B2H6 which have smaller intermolecular distances (2.195 and 2.380 for H13\_\_\_C1 and H13\_\_\_B10) have greater changes. In the DHB–F-5, the C1–B10 bond has the greatest shortening (-0.005) while B10–H5 has the most lengthening (0.006) with complex formation. Similarly in the DHB–F-12, greater changes were seen for bonds joined to the B11 atom. So that B11–H12 has the most lengthening, in contrast C1–B11 and C4–B11 have the greatest shortening among its bonds. Eventually in the H-bond complexes HB–F-78, HB–F-7 and HB–F-67, the C4B2H6 bonds less have been affected by intermolecular interactions; thus, their changes are smaller than previously mentioned systems (0.001–0.002). These results are showing that bond variations are in line with relative stabilities of complexes. The selected vibrational stretching frequencies (cm<sup>-1</sup>) with corresponding intensities (km mol<sup>-1</sup>) for HF and C4B2H6 free molecule as well as their complexes are listed in Table 4.

In the C4B2H6–HF complexes, the H–F bands show red shift upon complex formation. These red shifts are -219, -127, -108, -18, -17, and -15 for HB–F-bc, DHB–F-12, DHB–F-5, HB–F-7, HB–F-78, and HB–F-67, respectively.

These results are showing that red shift of HF band in the DHB-bond complexes is greater than simple H-bond complexes (HB–F-7, HB–F-78, and HB–F-67). Apparently, due to rB–H to r\*H–F charge transfer, interactions in which HF acts as HBD have greater red shift than interaction with HF as HBA. For the B10–H5 bond we have -5 cm<sup>-1</sup> red shift in HB–F-7 and HB–F-67 complexes; also this bond has -49 cm<sup>-1</sup> red shift in DHB–F-5. But in HB–F-78, DHB–F-12 and HB–F-bc it show 4, 8 and 15 cm<sup>-1</sup> blue shift, respectively. Similarly for B11–H12 stretching frequencies -43 red shift in DHB–F-12, 14 and 9 cm<sup>-1</sup> blue shift in DHB–F-5 and HB–F-bc were seen. Results of this study is dialing with the presence of multisites on the C4B2H6 backbone which could act as Lewis acid or Lewis base for intermolecular interactions. According to above

discussions for both C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-HF and C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-LiH systems, the peripheral B-C and C-C bonds as electron donor have strongest interaction with target molecules as electron acceptors. Therefore, from different models which have been considered for interaction of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> with HF and LiH molecules, complexes involving peripheral B-C and C-C bonds as electron donor have the greatest stabilities. Comparing results of current study with our last work [27] (CB<sub>4</sub>H<sub>8</sub>-HF complexes) is showing that interaction of HF with B-B bond in the CB<sub>4</sub>H<sub>8</sub> is stronger than its interactions with B-C bonds in the C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> molecule. Also HB (H-F...H-C) and DHB (B-H...H-F) interactions of HF with CB<sub>4</sub>H<sub>8</sub> are close to similar interactions between HF and C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>. Both studies are dealing with stronger interactions for HF with B-B and B-C bonds relative to H-F...H-C and B-H...H-F interactions in both carborane molecules.

Table 3 Unscaled vibrational frequencies (cm<sup>-1</sup>) with corresponding intensities (values given in parenthesis, km mol<sup>-1</sup>) for C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>-Hli Complexes

	C <sub>4</sub> B <sub>2</sub> H <sub>6</sub>		LiB-5		LiB-12		DHB-Li-7		DHB-Li-78		LiB-bc	
	$\nu$		$\nu$	$\Delta\nu$	$\nu$	$\Delta\nu$	$\nu$	$\Delta\nu$			$\nu$	$\Delta\nu$
C1-H6	3246 (0)		3213 (6)	-33	3247 (0)	1	3244 (3)	-2	3242	-25	3257 (0)	-10
C2-H7	3267 (0)		3271 (1)	4	3263 (1)	-4	3197 (110)	-70	3242	-25	3283 (5) <sup>a</sup>	16
C3-H8	3267 (0)		3261 (1)	4	3237 (7)	-30	3260 (1)	-7	3242	-4	3274 (6) <sup>b</sup>	28
C4-H9	3246 (0)		3251 (1)	14	3237 (7)	-9	3242 (1)	-4	2781	-5	3257 (0)	22
B10-H5	2712 (105)		2645 (100)	-67	2722 (87)	10	2699 (126)	-13	2699	-13	2746 (66)	34
B11-H12	2786 (45)		2803 (30)	17	2698 (104)	-88	2781 (50)	-5	3242	-4	2808 (31)	11
X...Y	-		247 (37)	-	209 (165)	-	101 (78)	-	1439	21	267 (18)	-
H-Li	1418 (229)		1361 (389)	-58	1370 (318)	-49	1442 (349)	24			1343 (440)	-75

### AIM analysis

The atoms in molecules (AIM) theory [34] are applied here to analyze the characteristics of the H...H, F...H, H...B-C, Li...B-C and Li...H interactions through the location of bond critical points (BCP) with (3, -1) coordinates in the Hessian matrix fitted to the intermolecular contact area. The parameters electronic density ( $\rho$ ), Laplacian ( $\nabla^2\rho$ ), and the ratios between the kinetic (G) and potential (U) electron energy density [35] derived from the Bader theory could indicate the type of interaction. The atomic connection is recognized as close-shell interaction, which is often designated to H-bonds or other intermolecular weakly bound contacts, such as halogen bonds, dihydrogen bonds, and p-stacking [36-42]. The analysis of the electron density within the AIM methodology shows the presence of bond critical points (Table 5) between the atoms involved in the interactions. All kinds of H...H, H...F, H...B-C, Li...B-C, and Li...H interactions have  $\rho_{BCP} > 0$  and  $-\nabla^2\rho/2\rho < 1$  which might consider as interactions with noncovalent character.

Table 5 Topological parameters for the fully optimized complexes

Complex	H-bond	$\rho_{\text{BCP}}$	$\nabla^2_{\rho_{\text{BCP}}}$	$-G_c/V_c$
LiB-5	Li...H5	0.0122	0.0649	1.2177
LiB-12	Li...H12	0.0108	0.0587	1.2641
DHB-Li-7	H14...H7	0.0113	0.0246	1.06
DHB-Li-78	H14...H7	0.0062	0.0158	1.2115
	H14...H8	0.006	0.0156	1.2168
LiB-bc	Li...B-C	0.0125	0.0665	1.218
HB-F-67	F13...H6	0.0039	0.018	1.3066
	F13...H7	0.0064	0.0284	1.2116
HB-F-7	F14...H7	0.0082	0.0343	1.1605
HB-F-78	F13...H7	0.0054	0.0241	1.2401
	F13...H8	0.0056	0.0246	1.2349
DHB-F-12	H13...H12	0.0144	0.0399	1.0536
DHB-F-5	H13...H5	0.0165	0.0453	1.0217
HB-F-bc	H...B-C	0.0184	0.049	1.0236

Natural bond orbital analysis Natural bond orbital (NBO) analysis [43] was performed for the minima found on the studied LiH-C4B2H6 and HF-C4B2H6 complexes. These complex formations are associated with orbital interactions between the bonding pairs in the electron donor and the antibonding orbital in the electron acceptor. The quantity of charge transferred from donor to the acceptor (DQ) due to the interaction of donor and acceptor orbitals is 0.0762, 0.0366, 0.0256, 0.0092, and 0.0032 for LiB-bc, LiB-5, LiB-12, DHB-Li-7, and DHB-78 as well as 0.0019, 0.0019, 0.0020, 0.0022, 0.0024, and 0.0045 for HB-F-7, HB-F-67, HB-F-78, DHB-F-5, DHB-F-12, and HB-F-bc, respectively. Data given in Table 6 are illustrating sets of charge transfers between HF and LiH with C4B2H6 in each of the studied complexes. From these sets, charge transfers having greater binding energies might be considered as preferred part of interaction during complex formation. For example in LiB-bc complex, the  $rC1-B10 + r^*Li13-H14$ , and  $rC4-B10 + r^*Li13-H14$  acts as stronger parts of interactions. Also in DHB-F-12, the  $rB11-H12 + r^*H13-F14$  is more important than other charge transfers. Conclusions C4B2H6 could have intermolecular interactions with HF and LiH molecules. For interaction of C4B2H6 with HF, H-bond, and DHB-bond and for LiH, Li-bond, and DHB-bond, complexes have been obtained. According to our results, C4B2H6-LiH dimers are more stable than C4B2H6-HF, and this returns to the greater dipole moment of LiH with respect to HF. Also from different models of interactions, complexes involving peripheral B-C and C-C bonds as electron donor have greatest stabilities in both systems.



Table 6 NBO parameters for the optimized complexes

Complex	QCT	Charge transfer		$E^{(2)}$
DHB-F-5	0.00224	$\sigma C1-B11$	*H13-F14	0.15
		$\sigma C4-B11$	*H13-F14	0.26
		$\sigma H5-B10$	*H13-F14	4.20
HB-F-7	0.00193	LP F14	*C2-H7	1.49
HB-F-bc	0.00446	$\sigma C1-B10$	*H13-F14	1.92
		$\sigma C1-B11$	*H13-F14	2.54
		$\sigma B11-H12$	*H13-F14	0.22
DHB-F-12	0.00235	$\sigma C1-B10$	*H13-F14	0.19
		$\sigma C1-B11$	*H13-F14	0.58
		$\sigma C2-C3$	*H13-F14	0.49
		$\sigma C4-B10$	*H13-F14	0.18
		$\sigma C4-B11$	*H13-F14	0.50
		$\sigma B11-H12$	*H13-F14	2.00
HB-F-67	0.00186	lp F13	*C2-H7	0.30
HB-F-78	0.00200	lp F13	*C2-H7	0.12
		lp F13	*C3-H8	0.13
		$\sigma C1-C2$	*Li13-H14	0.64
Li B-12	0.02556	$\sigma C1-B10$	*Li13-H14	0.78
		$\sigma C2-C3$	*Li13-H14	0.73
		$\sigma C3-C4$	*Li13-H14	0.20
		$\sigma C3-H8$	*Li13-H14	0.68
		$\sigma C4-H9$	*Li13-H14	1.16
		$\sigma C4-B10$	*Li13-H14	0.79
		$\sigma C1-C2$	*Li13-H14	2.81
LiB-5	0.03664	$\sigma C1-H6$	*Li13-H14	3.27
		$\sigma C1-B10$	*Li13-H14	9.68
		$\sigma C1-B11$	*Li13-H14	1.56
		$\sigma C2-C3$	*Li13-H14	0.45
		$\sigma C3-C4$	*Li13-H14	0.11
		$\sigma C4-B10$	*Li13-H14	3.36
		$\sigma C4-B11$	*Li13-H14	2.50
		$\sigma H5-B10$	*Li13-H14	13.18
		$\sigma B11-H12$	*Li13-H14	0.19
		LiB-bc	0.07547	$\sigma C1-C2$
$\sigma C1-H6$	*Li13-H14			1.87
$\sigma C1-B10$	*Li13-H14			16.12
$\sigma C1-B11$	*Li13-H14			3.22
$\sigma C2-C3$	*Li13-H14			11.06
$\sigma C2-H7$	*Li13-H14			2.78
$\sigma C3-C4$	*Li13-H14			9.01
$\sigma C3-H8$	*Li13-H14			2.78
$\sigma C4-H9$	*Li13-H14			1.87
$\sigma C4-B10$	*Li13-H14			16.09
$\sigma C4-B11$	*Li13-H14			3.23
$\sigma H5-B10$	*Li13-H14			4.18
$\sigma B11-H12$	*Li13-H14			1.72
DHB-Li-7	0.00915			$\sigma Li13-H14$

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