International Journal of
Medical Nano Research

Tayebee and Zabardasti. Int J Med Nano Res 2016, 3:016
Volume 3 | Issue 1
ISSN: 2378-3664

Research Article: Open Access

Studying Complex Interaction of B_2H_4 with HOR(R = H, CH_3) and $Nh_n(CH_3)_{3-N}$ (N = 0-3) Molecules

Reza Tayebee[1]* and Abedien Zabardasti[2]

[1] *Department of Chemistry, School of Sciences, Hakim Sabzevari University, Sabzevar, Iran*

[2] *Department of Chemistry, Lorestan University, Khorramabad, Iran*

***Corresponding author:** *Reza Tayebee, Department of Chemistry, School of Sciences, Hakim Sabzevari University, Sabzevar, Iran, Tel: +98-571-4410310, Fax: +98-571-4410300, E-mail: Rtayebee@hsu.ac.ir*

Abstract

Ab initio calculations were carried out to analyze the interaction between one molecule of B_2H_4 with H_2O, CH_3OH, NH_3, NH_2CH_3, $NH(CH_3)_2$ and $N(CH_3)_3$ molecules at the MP2/aug-cc-pVDZ computational level. B_2H_4 could act as a hydrogen bond donor through its bridged hydrogens (H_b); while, the B-B can act as a hydrogen bond acceptor. Thus, the interaction of B_2H_4 with the mentioned molecules resulted in formation of H_b...X and/or B-B...H hydrogen bond complexes; whereas, H_t atoms of B_2H_4 were ineffective to form H_t...H dihydrogen bond complexes with the amine molecules. Results showed that the B-B...H interactions were stronger than H_b...X counterparts. The obtained structures were analyzed by the natural bond orbital (NBO) and Atoms in Molecules (AIMs) methodologies.

Keywords

Hydrogen bond complexes, Borane, Amine, B_2H_4, AIM, MP2

Introduction

Borane complexes are extensively studied and have even been the subject of Nobel Prize by Brown [1]. Many scientific data exist that have shown that boron is an essential microelement in animal cells. With the knowledge that borate linkages function in cell-to-cell adhesion, it has been hypothesised that boronates target structural glycoproteins located along the cytoskeletonplasma membrane-cell wall assembly. On the other hand, boron-carrier molecules can be used as a therapeutic mean to fight cancers [2,3]. Also, they have been the subject of proton affinity experiments in chemical ionization mass spectrometry. Among non-covalent interactions which have been known in boron chemistry, both dihydrogen and hydrogen bonding patterns are particularly significant [4-9].

B_2H_4, designated as diborane (4), is probably the best known electron-deficient analogue of ethylene [10-13]. B_2H_4 bears 10 valence electrons for chemical bonding. There are two standard two electron terminal B-H bonds, thus accounting for a total of four electrons. This leaves a total of six electrons to share between the two bridging H and the two B atoms. Consequently, there are two 3c-2e curved 'banana' B-H-B bridging bonds. According to the above illustrations, B_2H_4 has two types of hydrogen atoms: terminal (H_t-B) and bridging (B-H_b-B) ones, which differ in nature and characteristics. The bridging hydrogens of B_2H_4 participate in the electron deficient 'three-center, two-electron bonds'; thus, they bear enough partial positive charge to act as hydrogen bond donor (HBD) to form H_b…X (X = N, O) hydrogen bonds with electron donating molecules [6,7,13]. On the other hand, recent studies showed that the B-B bond also could act as HBA in the interactions of borane clusters with HBD species to form H…B-B hydrogen bonds [6,13].

From a fundamental point of view, the present work aims to extend the knowledge of the intrinsic activity of H_t, H_b and B-B bond of diborane as a hydrogen bond acceptor or hydrogen bond donor towards other molecules. For this purpose, we investigated the interaction of B_2H_4 with H_2O, CH_3OH and $NH_n(CH_3)_{3-n}$ (n = 0-3) derivatives through theoretical calculations.

Computational Methods

Calculations were performed using the Gaussian 03 system of codes [14]. The geometries of the isolated B_2H_4, H_2O, CH_3OH, and $NH_n(CH_3)_{3-n}$ molecules as well as their complexes were fully optimized at the MP2/aug-cc-pVDZ computational level. Harmonic vibrational frequency calculations 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 [15]. The AIMAll package was used to obtain bond properties and molecular graphs [16]. The natural bond orbitals (NBO) method was implemented within the Gaussian 03 set of codes and was applied to perform NBO analysis [17].

AIM analysis

The atoms in molecules (AIM) theory [16] is applied here to analyze the characteristics of the H…N and H…B-B interactions through studying the location of Bond Critical Points (BCP) with (3,-1) coordinates in the Hessian matrix fitted to the intermolecular contact area. In table 1, results of the QTAIM topological parameters, namely as electronic density (ρ), Laplacian ($\nabla^2\rho$) and the ratios between kinetic (G) and potential (U) electron energy density [18] are obtained. The last ones are embodied into the QTAIM formalism as follows:

$$H = G + U \qquad (1)$$

$$(\hbar^2/4m)\,\nabla^2\rho = 2G + U \qquad (2)$$

This equation indicates which type of interaction may exist

Citation: Tayebee R, Zabardasti A (2016) Studying Complex Interaction of B_2H_4 with HOR(R = H, CH_3) and $Nh_n(CH_3)_{3-N}$ (N = 0-3) Molecules. Int J Med Nano Res 3:016

Received: January 09, 2016: **Accepted:** January 30, 2016: **Published:** February 02, 2016

ClinMed
International Library

between the two nuclei, wherein, the profile of $\nabla^2\rho$ is embodied into the contribution of G and U. If the potential electron energy density is outweighed by the kinetic, the positive profile of $\nabla^2\rho$ indicates a depletion of charge density along the inter-nuclear connecting Bond Path (BP) [19]. Furthermore, the atomic connection is recognized as close-shell interaction, which is often designated to H-bonds or to other intermolecular weak bound contacts, such as halogen bonds [20], dihydrogen bonds [21-23], and π-staking [24]. Regarding the values gathered in table 1, first it should be highlighted that the positive values of $\nabla^2\rho$ ensure that all H-bonds are closed-shell interactions due to the low charge density concentration. The values of -G/U higher than 1, indicate that besides the non-covalent character, the N…H and H…B-B have no tend to be covalent [25].

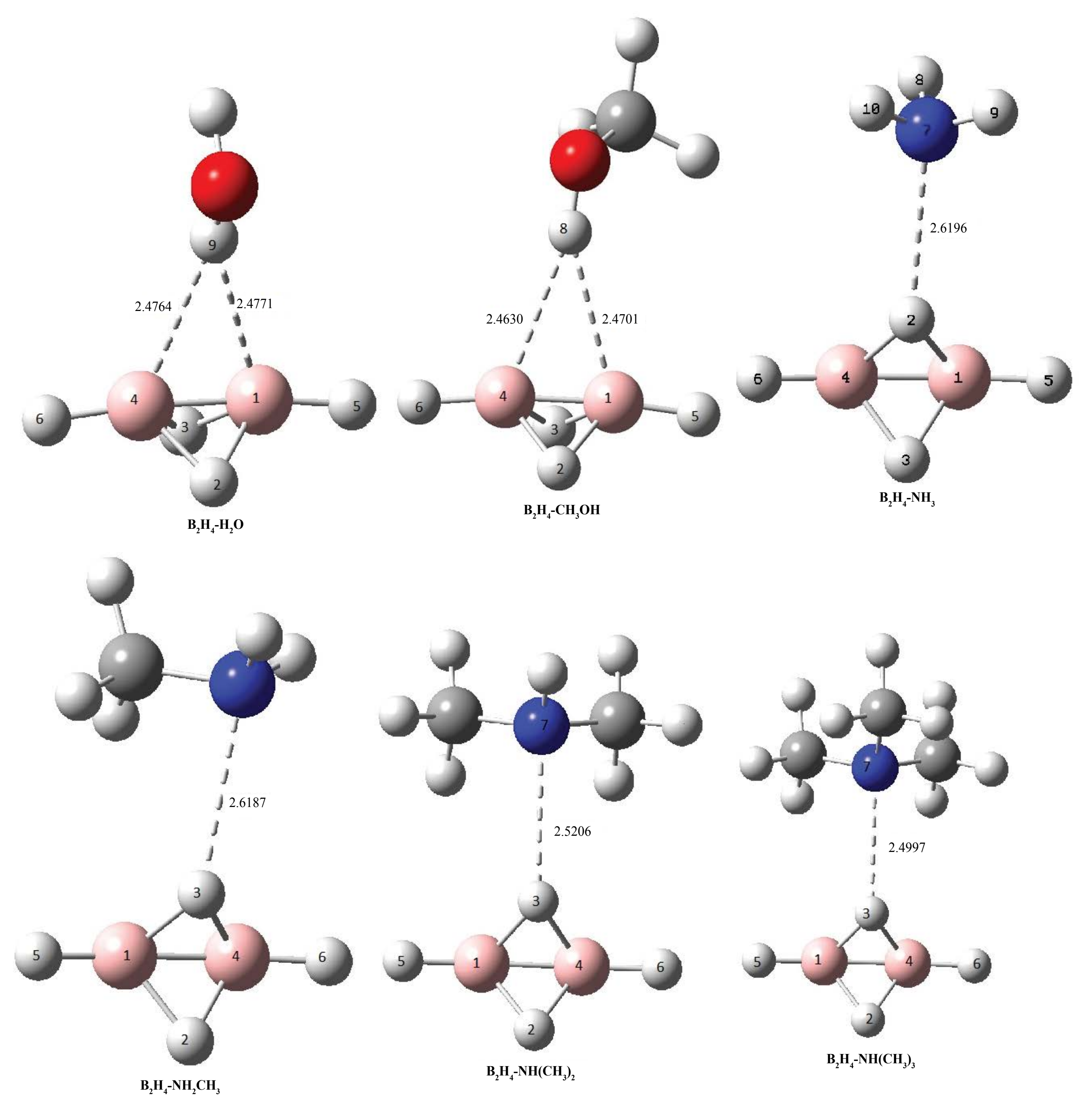
Table 1: Topological parameters for the fully optimized complexes at MP2/aug-cc-pVDZ.

Complex	H-bond	ρ_{BCP}	∇^2_{BCP}	-G/V
B_2H_4-NH_3-HB	N7… H2	0.0094	0.0242	1.0629
B_2H_4-NH_2Me-HB	N7… H3	0.0097	0.0270	1.0931
B_2H_4-NHMe$_2$-HB	H3… N7	0.0118	0.0300	1.0257
B_2H_4-NMe$_3$-HB	H3… N7	0.0126	0.0308	0.9945
B_2H_4-H_2O-HM	B5… H9	0.0153	0.0344	1.1122
B_2H_4-CH_3OH-HM	H8… B4	0.0164	0.0345	1.0735

Results and Discussion

Interaction of B_2H_4 with H_2O and CH_3OH molecules gave the B_2H_4-H_2O and B_2H_4-CH_3OH complexes which have hydrogen bond interactions between B-B bond as HBA and OH functions of H_2O and CH_3OH as HBD. Results are demonstrating that later complex has greater stability than the former one.

The association of B_2H_4 and $NH_n(CH_3)_{3-n}$ (n = 0-3) derivatives led to the formation of the 1:1 hydrogen bond complexes which has been denoted as B_2H_4-NH_3, B_2H_4-NH_2Me, B_2H_4-NHMe$_2$ and B_2H_4-NMe$_3$, figure 1. In these complexes hydrogen bond interactions has been found between a bridging proton of the B_2H_4 as a proton donor and nitrogen atom of amine as a proton acceptor (H_b…N). According to the data given in table 2, stabilities of B_2H_4-$NH_n(CH_3)_{3-n}$ complexes



B_2H_4-H_2O B_2H_4-CH_3OH B_2H_4-NH_3

B_2H_4-NH_2CH_3 B_2H_4-$NH(CH_3)_2$ B_2H_4-$NH(CH_3)_3$

Figure 1: Schematic representation of the optimized complexes at MP2/aug-cc-pVDZ computational level. Distances are in Å.

increased with enhancing basicity of amines in the following order: B_2H_4-NMe_3 >B_2H_4-$NHMe_2$ > B_2H_4-NH_2Me > B_2H_4-NH_3.

The results due to the intermolecular bond lengths are given in the table 3 and figure 1. In the B_2H_4-H_2O and B_2H_4-CH_3OH complexes, the B1-B4 bond has elongation (0.0015); but, other bonds of B_2H_4 are shortened (from -0.0009 to -0.0053) upon complex formation. Moreover, a 0.0061 lenthening was observed for O-H bond in these complexes.

On the other hand, the N…H_b distances in the B_2H_4-$NH_n(CH_3)_{3-n}$ complexes are in the range of 2.6196 to 2.4997 Å. These distances could be considered as weak bonding interactions between the two components. Comparison of the H_b…N distances showed that the obtaine trend was in agreement with the stability of these complexes.

In B_2H_4-NH_3-HB, the NH_3 molecule interacts with a bridging hydrogen atom of the B_2H_4 molecule. Data given in table 2 showed that bridging B-H-B bonds as well as B_1-B_4 bond were contracted (-0.0046, -0.0055, -0.0023,-0.0028 and -0.0024 for B1-H2, B4-H2, B1-H3, B4-H3 and B1-B4 bonds, respectively); while, terminal B1-H5 and B4H6 bonds designated a small elongation after complexation.

Table 2: The SE^{uncorr}, BSSE, ΔZPE, and SE^{corr} (corrected with BSSE and ΔZPE) in kcal. mol^{-1} calculated at MP2/aug-cc-pVDZ.

Complex	SE^{uncorr}	BSSE	ΔZPE	SE^{corr}
B_2H_4-NH_3-HB	-2.10	0.75	0.83	-0.52
B_2H_4-NH_2Me-HB	-3.15	1.15	0.80	-1.20
B_2H_4-$NHMe_2$-HB	-3.96	1.47	0.71	-1.78
B_2H_4-NMe_3-HB	-4.32	1.73	0.61	-1.98
B_2H_4-H_2O-HM	-4.02	0.96	1.66	-1.40
B_2H_4-CH_3OH-HM	-4.53	1.16	1.08	-2.29

Values of SE^{uncorr} were determined as follows: $SE^{uncorr} = E(B_2H_4\cdots Y) - [E(B_2H_4) + E(Y)]$ with Y = H_2O, CH_3OH, NH_3, NH_2CH_3, $NH(CH_3)_2$ and $N(CH_3)_3$; Values of SE^{corr} were determined as follows: $SE^{corr} = SE^{uncorr} + \Delta ZPE + BSSE$.

In the B_2H_4-NH_2CH_3-HB, an interaction occurs between the NH_2CH_3 molecule and the bridging H_3 atom of B_2H_4. In this complex, B1-H2, B1-H3, B4-H3 and B1-B4 bonds showed contraction (-0.0077, -0.0069, -0.0023, and -0.0015, respectively); while, terminal bond B1-H5 and the bridging bond B4-H2 were elongated after complex formation.

In B_2H_4-$NH(CH_3)_2$-HB and in B_2H_4-$N(CH_3)_3$-HB, interactions occured between the bridged H3 atom of B_2H_4 and the amine molecules. In these complexes, B1-H2, B1-H3, B4-H2, B4-H3 and B1-B4 bonds were contracted (-0.0020 to -0.0044); while, terminal bonds of B1-H5 and B4-H6 showed small elongation after complexation.

In B_2H_4-H_2O-HB and in B_2H_4-CH_3OH-HB complexes, the B1-B4 bond was elongated (0.0015); but, other bonds of B_2H_4 were shortenned (-0.0009 to -0.0053) upon complex formation. Also, a 0.0061 Å bond lengthening was observed for O-H bond in these complexes.

The selected vibrational stretching frequencies (cm^{-1}) with the corresponding intensities ($km.mol^{-1}$) for the studied complexes are listed in table 4. In the B_2H_4-$NH_n(CH_3)_{3-n}$ complexes, the B1-B4 vibrational absorption band is less affected by complex formation, thus their observed shifts are negligible. But, in B_2H_4-H_2O-HM and B_2H_4-CH_3OH-HM complexes this bond shows -8 cm^{-1} red shift which is in agreement with its lengthening due to complex formation. In agreement with lengthening of B1-H5 and B4-H6 bonds, their unsymmetric stretching frequencies, which appeared at 2811 cm^{-1} in free B_2H_4, are red shifted by 6 and 9 cm^{-1} in B_2H_4-$NH_n(CH_3)_{3-n}$ complexes. In contrast, unsymmetric stretching frequencies of B1-H5 and B4-H6 showed 5 cm^{-1} blue shift in B_2H_4-H_2O and B_2H_4-CH_3OH

Table 3: bonds length of free B_2H_4 and their variation during intermolecular interactions at MP2/aug-cc-pVDZ. Distances are in Å.

	B_2H_4	B_2H_4-H_2O	B_2H_4-CH_3OH	B_2H_4-NH_3	B_2H_4-NH_2Me	B_2H_4-$NHMe_2$	B_2H_4-NMe_3
Bond	d	Δd	Δd	Δd	Δd	Δd	Δd
B1-H5	1.1827	-0.0009	-0.0010	0.0004	0.0004	0.0004	0.0004
B4-H6	1.1828	-0.0009	-0.0009	0.0003	0.0000	0.0004	0.0004
B1-B4	1.4908	0.0015	0.0015	-0.0024	-0.0015	-0.0020	-0.0020
B1-H2	1.3586	-0.0033	-0.0024	-0.0046	-0.0077	-0.0029	-0.0028
B1-H3	1.3587	-0.0028	-0.0018	-0.0023	-0.0069	-0.0035	-0.0040
B4-H2	1.3593	-0.0039	-0.0041	-0.0055	+0.0024	-0.0036	-0.0035
B4-H3	1.3592	-0.0033	-0.0053	-0.0028	-0.0028	-0.0040	-0.0044
O-H	0.9658	0.0061	0.0061				
N….H		-	-	2.6196	2.6187	2.5206	2.4997
H…B1		2.4771	2.4701				
H…B4		2.4764	2.4630				

Table 4: Unscaled vibrational frequencies (cm^{-1}) with corresponding intensities (values given in parenthesis, km mol^{-1}) for B_2H_4 and its complexes at MP2/aug-cc-pVDZ.

Compound	B_2H_4	B_2H_4-NH_3		B_2H_4-NH_2Me		B_2H_4-$NHMe_2$		B_2H_4-NMe_3	
Bond	v	v	Δv	v	Δv	v	Δv	v	Δv
B_1 - B_4	1343(3)	1345(2)	2	1342(2)	-1	1343(1)	0	1342(2)	-1
sym-B_1-H_2-B_4	2129(18)	2136(27)	7	2134(34)	5	2123(13)	-6	2120(16)	-9
usy-B_1-H_2-B_4	2136(44)	2147(13)	11	2147(21)	11	2141(40)	5	2141(40)	5
us-B_1-H_5,B_4-H_6	2811(36)	2805(42)	-6	2805(37)	-6	2803(35)	-8	2802(34)	-9
sym-B_1-H_5,B_4-H_6	2851(0.2)	2847(0)	-4	2846(0.2)	-5	2844(0)	-7	2843(0)	-8
N…H		105(20)		110(11)		119(8)		94(1)	
H….B-B									
symH-O-H									
CH_3O-H	3804(4)[a] 3938(67)[b] 3841(34)								

[a] vsym O-H;[b] vunsym O-H

Table 5: The NBO analysis of studied complexes at MP2/aug-cc-pVDZ.

Complexes	donor→ acceptor	qCT^a (ΔQ)	E (2)
B_2H_4-NH_3-HB	lp(N)→σ^*(B1-H2-B4)	0.0039	2.15
B_2H_4-NH_2Me-HB	lp(N)→σ^*(B1-H3-B4)	0.0072	1.27
B_2H_4-NHMe$_2$-HB	lp(N)→σ^*(B1-H3-B4)	0.0082	2.09
B_2H_4-NMe$_3$-HB	lp(N)→σ^*(B1-H3-B4)	0.0085	2.15
B_2H_4-H_2O-HM	bd(B1-B4)→σ^*(O-H)	0.0060	3.85
B_2H_4-CH_3OH-HM	bd(B1-B4)→σ^*(O-H)	0.0085	5.54

E (2) in kcal.mol^{-1} and qCT in electron volt. ^{a}qCT refers to the charge transfer between H_2O, CH_3OH, NH_3, NH_2CH_3, $NH(CH_3)_2$ and $N(CH_3)_3$ molecules with B_2H_4.

complexes; which is in line with shortening of the related bonds. The sym-B1-H2-B4 band showed 7, 5, 15 and 15 cm^{-1} blue shifts in B_2H_4-NH_3, B_2H_4-NH_2CH_3, B_2H_4-H_2O and B_2H_4-CH_3OH complexes, respectively; while, -6 and -9 cm^{-1} red shifts were observed in B_2H_4-$NH(CH_3)_2$ and B_2H_4-$N(CH_3)_3$ additives. On the other hand, unsym-B1-H2-B4 band showed 5 to 15 cm^{-1} blue shifts in these complexes. Moreover, the O-H band in B_2H_4-H_2O and in B_2H_4-CH_3OH complexes showed -40 and -127 cm^{-1} red shifts with respect to free H_2O and CH_3OH molecules, respectively.

Natural bond orbital analysis

Natural bond orbital (NBO) analysis was performed for the minima found on the studied B_2H_4 complexes. These complex formations are associated with an orbital interaction between the bonding pairs in the electron donor and the antibonding orbital in the electron acceptor. The quantity of charge transfer from donor to the acceptor (ΔQ) due to the interaction of donor and acceptor orbitals were obtained as 0.0039, 0.0072, 0.0082, 0.0085, 0.0060 and 0.0085 for B_2H_4-NH_3, B_2H_4-NH_2CH_3, B_2H_4-$NH(CH_3)_2$, B_2H_4-$N(CH_3)_3$, B_2H_4-H_2O and B_2H_4-CH_3OH complexes, respectively. The charge transfers presented above indicated that electron fraction is transferred from HBA to HBD molecule, thus charge transfer is not concentrated on the interacting atoms; but, is mostly dispersed among the molecules. Therefore, interpretation of the bond variations and frequency shifts in the B_2H_4 could not be carried out simply.

A useful quantity which might be derived from the results of natural bond orbital analysis is NBO binding energy (E2). The second-order perturbation energy can be taken as an index to judge the strength of the intermolecular bonds. Table 5 lists the quantity of charge transfers from donor to the acceptor qCT and the second-order perturbation energy due to the interaction of donor and acceptor orbitals. E(2) allows quantitative evaluation of the charge transfer involving in the formation of B_2H_4 complexes. According to the results, the E(2) value for B_2H_4-CH_3OH was greater than for B_2H_4-H_2O, which confirmed the order obtained for the interaction energies of these complexes. But for amine complexes, some contraversies were seen between the order obtained for their E(2) and the interaction energies.

Conclusion

B_2H_4 has two types of terminal (H_t-B) and bridging (B-H_b-B) hydrogen atoms which differ in nature and characteristics. The bridging hydrogens of B_2H_4 participate in the electron deficient 'three-center, two-electron bonds'; thus, they bear enough partial positive charge to act as hydrogen bond donor (HBD) to form H_b…X (X = N, O) hydrogen bonds with electron donating molecules. The present work extended the knowledge of the intrinsic activity of H_t, H_b and B-B bond of diborane as a hydrogen bond acceptor or hydrogen bond donor towards other molecules. For this propose, the interaction of B_2H_4 with H_2O, CH_3OH and $NH_n(CH_3)_{3-n}$ (n = 0-3) derivatives thorough theoretical calculations are studied in detail.

References

1. Brown HC, Ramachandran V (1997) Advances in Boron Chemistry. Siebert W, The Royal Society of Chemistry. Cambridge, UK, 201-204.
2. Safronov AV (2014) Boron neutron capture therapy of cancer as a part of modern nanomedicine. Int J Med Nano Res 1: 001e.
3. Achilli C, Grandi S, Ciana A, Minetti G (2015) Bnct and Nanoparticles: A Long Way to a Routine Clinical Method. Int J Med Nano Res 2:007.
4. Morrison CA, Siddick MM (2004) Dihydrogen bonds in solid BH3NH3. Angew Chem Int Ed Engl 43: 4780-4782.
5. Meng Y, Zhou Z, Duan C, Wang B, Zhong Q (2005) Non-convertional Hydrogen Bonding Interaction of BH3NH3 Complexes: A Comparative Theoretical Study. J Mol Struct (Theochem) 713: 135-144.
6. Zabardasti A, Arabpour M (2012) Theoretical Study of Hydrogen and Dihydrogen Bond Interaction of B6H10 with the HF Molecule . Struct Chem 23: 473-477.
7. Zabardasti A, Arabpour M, Zare N (2013) Theoretical Studies of Intermolecular Interactions of Arachno-pentaborane (11) with HF and LiH. Comput Theor Chem 1008: 27-31.
8. Zabardasti A, Zare N, Arabpour M, Kakanejadifard A, Solimannejad M (2013) Theoretical Study of Mixed Hydrogen and Dihydrogen Bond Interactions in Clusters. J Chem: 1-7.
9. Zabardasti A, Kakanejadifard A, Moosavi S, Bigleri Z, Solimannejad M (2010) Anticooperativity in Dihydrogen Bonded Clusters of Ammonia and BeH4-2. J Mol Struc Theochem 945: 97-100.
10. Mohr RR, Lipscomb WN (1986) Structures and Energies of B2H4. Inorg Chem 25: 1053-1057.
11. Ruscik B, Schwarz M, Berkowitz J (1989) Molecular Structure and Thermal Stability of the B2H4 and B2H4+ Species. J Chem Phys 91: 4576-4581.
12. Shoji Y, Matsuo T, Hashizume D, Fueno H, Tanaka K, et al. (2010) A stable doubly hydrogen-bridged butterfly-shaped diborane(4) compound. J Am Chem Soc 132: 8258-8260.
13. Alkorta I, Soteras I, Elguero J, Del Bene JE (2011) The boron-boron single bond in diborane(4) as a non-classical electron donor for hydrogen bonding. Phys Chem Chem Phys 13: 14026-14032.
14. Popelier PLA (2000) Atoms in Molecules: An Introduction. Prentice Hall, Pearson Education Limited.
15. Bader RFW (1991) A Quantum Theory of Molecular Structure and its Applications. Chem Rev 91: 893-928.
16. Grabowski SJ, Ugalde JM (2010) Bond paths show preferable interactions: ab initio and QTAIM studies on the X-H...pi hydrogen bond. J Phys Chem A 114: 7223-7229.
17. Oliveira BG, Araújo RCMU, Leite ES, Ramos MN (2011) A Theoretical Analysis of Topography and Molecular Parameters of the CFCl3-O3 Complex: Linear and Bifurcate Halogen-Oxygen Bonding Interactions. Int J Quantum Chem 111: 111-116.
18. Oliveira BG, Araújo RCMU, Silva JJ, Ramos MN (2010) A Theoretical Study of Three and Four Proton Donors on Linear HX••• BeH2••• HX and Bifurcate BeH2••• 2HX Trimolecular Dihydrogen-bonded Complexes with X= CN and NC. Struct Chem 21: 221-228.
19. Oliveira BG, Araújo RCMU, Ramos MN (2008) Multiple Proton Donors on BeH2••• 2HCl Trimolecular Dihydrogen-bonded Complex: Some Theoretical Insights. Struct Chem 19: 665-670.
20. Oliveira BG, Araújo RCMU, Ramos MN (2008) The (H-d••• H+d) Charge Transfer and the Evaluation of the Harmonic Molecular Properties of Dihydrogen-bonded Complexes formed by BeH2••• HX with X= F, Cl, CN, and CCH. Struct Chem 19: 185-189.
21. Capim SL, Santana SR, Oliveira BG, Rocha GB, Vasconcellos MLAA (2010) Revisiting the Origin of the Preferential p-p Stacking Conformation of the (+)-8-phenylmenthyl Acrylate. J Braz Chem Soc 21: 1718-1726.
22. Oliveira BG (2012) Interplay Between Dihydrogen and Alkali–halogen Bonds: Is There Some Covalency Upon Complexation of Ternary Systems? Theor Comput Chem 998: 173-182.
23. Frisch M J (2013) GAUSSIAN 03, (Revision B.02), Gaussian, Inc, Pittsburgh, PA.
24. Boys SF, Bernardi F (1970) The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. Mol Phys 19: 553-566.
25. Weinhold F, Landis CR (2012) Discovering Chemistry With Natural Bond Orbitals, John Wiley & Sons, New Jersey, 132-133.