Complex pairing of B_2H_4 with H_2O, CH_3OH, NH_3, NH_2CH_3, $NH(CH_3)_2$ and $N(CH_3)_3$

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Abstract

Ab initio calculations were carried out to analyze the interactions between a 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 through its bridged hydrogens (H_b) could act as a hydrogen bond donor while its B-B act as hydrogen bond acceptor. Thus, interaction of B_2H_4 with the mentioned molecules resulted in formation of H_b…X or B-B…H hydrogen bond complexes. In contrast, H_t atoms of B_2H_4 have not enogh strength to form H_t…H dihydrogen bond complexes with the above molecules. Results showed that the B-B...H interactions are stronger than its H_b...X counterpart. The obtained structures were analyzed by the natural bond orbital (NBO) and Atoms in Molecules (AIMs) methodologies.

Introduction

Borane complexes have been studied extensively and have even been the subject of Nobel Prize work by Brown [1,2]. It has been the subject of proton affinity experiments in chemical ionization mass spectrometers. Among non-covalent interactions which have been known in boron chemistry, both dihydrogen bonding and hydrogen bonding types are particularly significant [4-21].

B_2H_4, designated as diborane(4), probably is the best known electron-deficient analogue of ethylene [22-26]. The molecule 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 atoms 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 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 are participating in 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 [13,14,17-21,26]. On other hand, recent studies are showing that B-B bond also could act as HBA in the interactions of borane clusters with HBD species to form H…B-B hydrogen bonds [13,20,26].

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(4) as hydrogen bond acceptor or hydrogen bond donor towards other molecules. For this propose, we investigated interaction of B_2H_4 toward H_2O, CH_3OH and $NH_n(CH_3)_{3-n}$, n= 0-3 derivatives thorough theoretical calculation.

Computational methods

Calculations were performed using the Gaussian 03 system of codes [27]. The geometries of the isolated B_2H_4 and 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 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 [28]. The AIM package was used to obtain bond properties and molecular graphs [29,30]. The natural bond orbitals (NBO) method implemented within the Gaussian 03 set of codes was applied to perform NBO analysis [31].

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 demonstrting 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 1, stabilities of B_2H_4-$NH_n(CH_3)_{3-n}$ complexes 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 2 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.
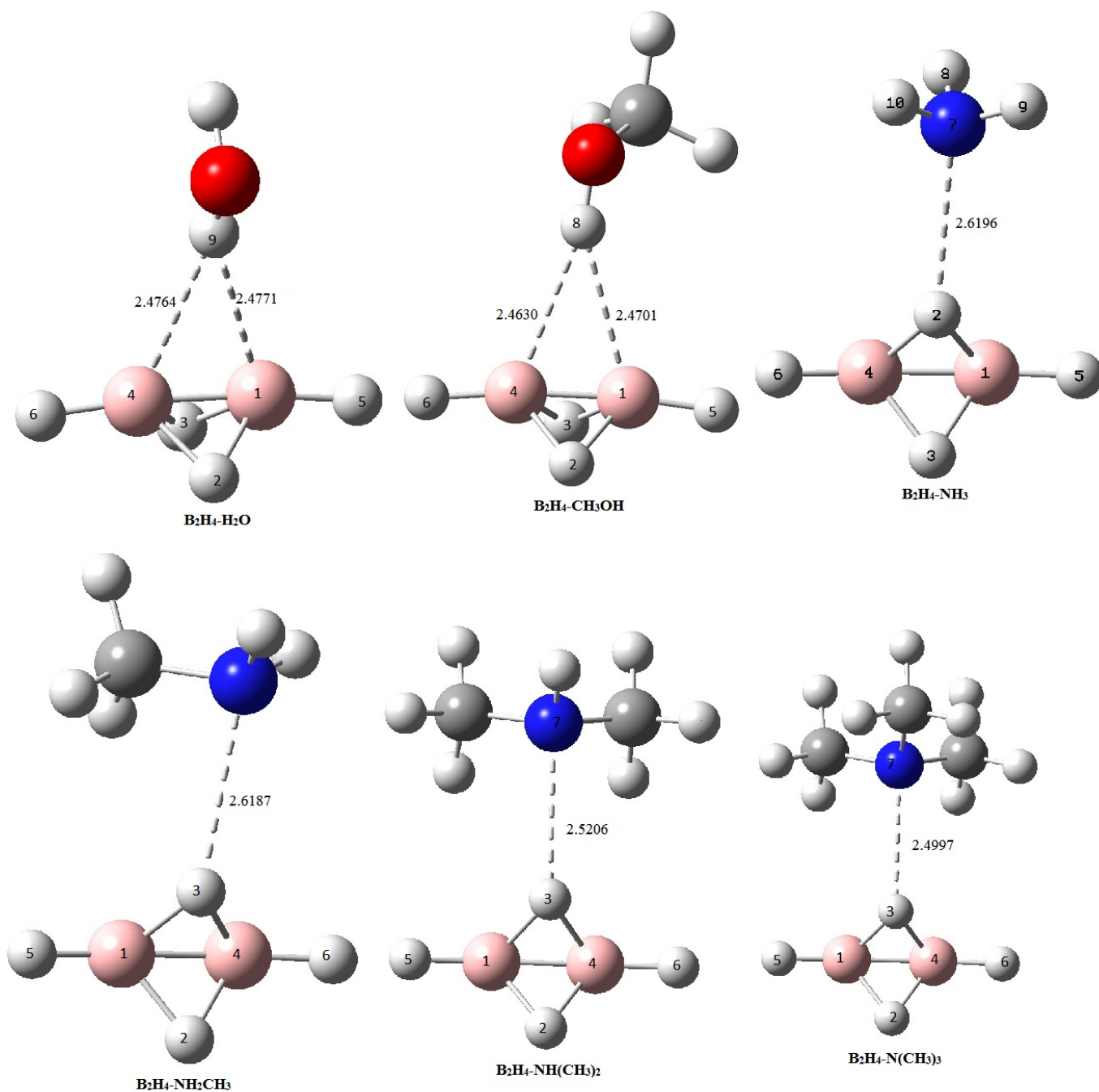
Figure 1. Schematic representation of optimized complexes at MP2/aug-cc-pVDZ computational level. Distances are in Å.

Table 1. 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-H_2O	-4.02	0.96	1.66	-1.40
B_2H_4-CH_3OH	-4.53	1.16	1.08	-2.29
B_2H_4-NH_3	-2.10	0.75	0.83	-0.52
B_2H_4-NH_2Me	-3.15	1.15	0.80	-1.20
B_2H_4-$NHMe_2$	-3.96	1.47	0.71	-1.78
B_2H_4-NMe_3	-4.32	1.73	0.61	-1.98

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: $SE^{corr} = SE^{uncorr} + \Delta ZPE + BSSE$

On the other hand, the $N \cdots H_b$ distances in the B_2H_4-$NHn(CH_3)_{3-n}$ 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 $H_b \cdots N$ distances showed that the obtaine trend was in agreement with the stability of these complexes.

In B_2H_4-NH_3, the NH_3 molecule interacts with H2 atom of B_2H_4. Data given in Table 2 showed that the bridging B-H-B bond, as well as B1-B4 bond, have contraction (-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, the terminal B1-H5 and B4H6 bonds showed small elongation upon complexation.

Table 2. Bonds length of free B2H4 and their variation during intermolecular interactions at MP2/aug-cc-pVDZ.

	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				

In B₂H₄-NH₂CH₃, interaction occured between NH₂CH₃ molecule and the bridging H3 atom of B₂H₄. 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, the terminal B1-H5 bond and the bridging B4-H2 bond revealed elongation after complexation.

In B₂H₄-NH(CH₃)₂ and B₂H₄-N(CH₃)₃, the interactions were occured between the bridging H3 atom of B₂H₄ and the amine molecules. In these complexes, B1-H2, B1-H3, B4-H2, B4-H3 and B1-B4 bonds showed contraction (from -0.0020 to -0.0044); while, the terminal B1-H5 and B4-H6 bonds showed small elongation after complexation.

The selected vibrational stretching frequencies (cm⁻¹) with the corresponding intensities (km mol⁻¹) for the studied complexes are listed in Table 3. The unsymetric stretching frequenciy of B1-H5 and B4-H6 showed a 5 cm⁻¹ blue shift in B₂H₄-H₂O and in B₂H₄-CH₃OH complexes, which is in line with the shortening of the related bonds. The sym-B1-H2-B4 band showed 7, 5, 15 and 15 cm⁻¹ blue shift in B₂H₄-NH₃, B₂H₄-NH₂CH₃, B₂H₄-H₂O and B₂H₄-CH₃OH complexes, respectively; while, it revealed -6 and -9 cm⁻¹ red shift in B₂H₄-NH(CH₃)₂ and B₂H₄-N(CH₃)₃ complexes.

Moreover, the unsym-B1-H2-B4 band showed 5 to 15 cm⁻¹ blue shift in these complexes. Also, the O-H band in B₂H₄-H₂O and B₂H₄-CH₃OH complexes showed -40 and -127 cm⁻¹ red shifts with respect to free H₂O and CH₃OH molecules, respectively. The B1-B4 vibrational absorbtion bands in B₂H₄-H₂O and in B₂H₄-CH₃OH complexes showed -8 cm⁻¹ red shift, which is in agreement with its lengthening due to the complex formation. In contrast, in B₂H₄-NH(CH₃)₃₋ₙ complexes, this bond was less affected by complex formation; thus, the observed shifts were negligible. In agreement with the lengthening of B1-H5 and B4-H6 bonds, their unsymetric stretching frequencies, which observed at 2811 cm⁻¹ in free B₂H₄, showed -6 to -9 cm⁻¹ red shift in the B₂H₄-NHₙ(CH₃)₃₋ₙ complexes.

Aim analysis

The atoms in molecules (AIM) theory is applied here to analyze the characteristics of the H…N and H…B-B interactions through the location of Bond Critical Points (BCP) with (3,-1) coordinates in the Hessian matrix fitted to the intermolecular contact area [29,30]. In Table 4, the results of the QTAIM topological parameters, namely as electronic density (ρ), Laplacian (∇²ρ) and the ratios between the kinetic (G) and potential (U) electron energy density are listed [32]. These last ones are embodied into the QTAIM formalism as follows:

$$H = G + U \tag{1}$$

$$(\hbar^2/4m)\nabla^2\rho = 2G + U \tag{2}$$

This equation indicates which type of interaction may exist between the two nuclei, wherein, the profile of ∇²ρ is embodied into the contribution of G and U. If the potential electron energy density is outweighed by the kinetic, the positive profile of ∇²ρ indicates a depletion of charge density along the inter-nuclear connecting Bond Path (BP) [33]. Furthermore, 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 π-staking [34-40]. Regarding the values gathered in Table 4, it should be highlighted that the positive values of ∇²ρ ensure that all H-bonds are closed-shell interactions due to the low charge density concentration. The inter-atomic and inter-molecular interactions are also studied in terms of local electron energy density (H) and its components, the local kinetic electron energy density (G), and local potential electron energy density (V) at the BCPs. The relation between these energetic parameters is given in Equation 1.

Also it has been suggested that both ∇²_BCP and the H should be used for characterizing hydrogen bond [41]. The weak hydrogen-bonds means that both ∇²_BCP and H are positive, medium hydrogen-bonds show that ∇²_BCP>0 and H<0; while, strong hydrogen-bonds bearing both ∇²_BCP and H<0. For the investigated complexes (Table 4), ∇²_BCP and H at BCP for H…N and H…B-B interactions are positive. This means that these interactions belong to close shell weak HB interactions.

The balance between G and V could be used to show the nature of interactions [42]. If $\frac{G}{V}$>1, then, the nature of the interaction is purely non-covalent. For all the examined complexes, this ratio was greater than 1, which confirmed the existence of weak interactions between the two systems and nature of the interaction was purely non-covalent.

Topological parameters ρ and ∇²_BCP, also describe the stability of complexes through the identification of charge density centres within the intermolecular bonds. Considering the results of the topological analysis presented in Table 4, good agreement could be found between the values of ∇²_BCP, ρ, and stabilization energies of complexes (Figures 2 and 3).

Natural bond orbital analysis

Natural bond orbital (NBO) analysis was performed for the minima found on the studied B₂H₄ 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 transferred from donor to the acceptor (ΔQ) due to the interaction of donor and acceptor orbitals were 0.0060, 0.0085, 0.0039, 0.0072, 0.0082 and 0.0085 for B₂H₄-H₂O, B₂H₄-CH₃OH, B₂H₄-NH₃, B₂H₄-NH₂CH₃, B₂H₄-NH(CH₃)₂, and B₂H₄-N(CH₃)₃ complexes, respectively. These charge transfers indicated that electron fraction is

Table 3. 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 Bond	B_2H_4	B_2H_4-H_2O		B_2H_4- MeOH		B_2H_4-NH_3		B_2H_4-NH_2Me		B_2H_4-HMe_2		B_2H_4-NMe_3	
	ν	ν	Δν	ν	Δν	ν	Δν	ν	Δν	ν	Δν	ν	Δν
B1 - B4	1343(3)	1335(2)	-8	1335(2)	-8	1345(2)	2	1342(2)	-1	1343(1)	0	1342(2)	-1
sym-B1-H2-B4	2129(18)	2144(15)	15	2144(15)	15	2136(27)	7	2134(34)	5	2123(13)	-6	2120(16)	-9
usy-B1-H2-B4	2136(44)	2151(33)	15	2149(29)	13	2147(13)	11	2147(21)	11	2141(40)	5	2141(40)	5
us-B1-H5,B4-H6	2811(36)	2816(25)	5	2816(23)	5	2805(42)	-6	2805(37)	-6	2803(35)	-8	2802(34)	-9
sym-B1-H5,B4-H6	2851(0.2)	2855(0)	4	2853(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		138(12)	93	126(0)									
symH-O-H		3711(247)	-40										
CH$_3$O-H	3804(4)[a]												
	3938(67)[b]	3898(141)		3714(358)	-127								
	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]	E (2)
B_2H_4-H_2O	bd(B1-B4)→σ*(O-H)	0.0060	3.85
B_2H_4-CH_3OH	bd(B1-B4)→σ*(O-H)	0.0085	5.54
B_2H_4-NH_3	lp(N)→σ*(B1-H2-B4)	0.0039	2.15
B_2H_4-NH_2Me	lp(N)→σ*(B1-H3-B4)	0.0072	1.27
B_2H_4-$NHMe_2$	lp(N)→σ*(B1-H3-B4)	0.0082	2.09
B_2H_4-NMe_3	lp(N)→σ*(B1-H3-B4)	0.0085	2.15

Table 4. Topological parameters for the fully optimized complexes at MP2/aug-cc-pVDZ.

Complex	H-bond	ρ_{BCP}	∇^2_{BCP}	-G/V	Hc
B_2H_4-H_2O	B5… H9	0.0153	0.0344	1.1122	0.0008
B_2H_4-CH_3OH	H8… B4	0.0164	0.0345	1.0735	0.0006
B_2H_4-NH_3	N7… H2	0.0094	0.0242	1.0629	0.0003
B_2H_4-NH_2Me	N7… H3	0.0097	0.0270	1.0931	0.0005
B_2H_4-$NHMe_2$	H3… N7	0.0118	0.0300	1.0257	0.0002
B_2H_4-NMe_3	H3… N7	0.0126	0.0308	0.9945	0.0001
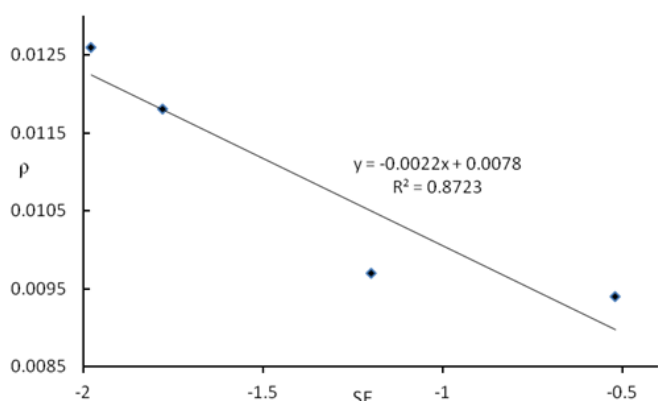
Figure 3. Relationship between the ρ_{BCP} (au) and SE(kcal mol^{-1}) for the B_2H_4-amine complexes.
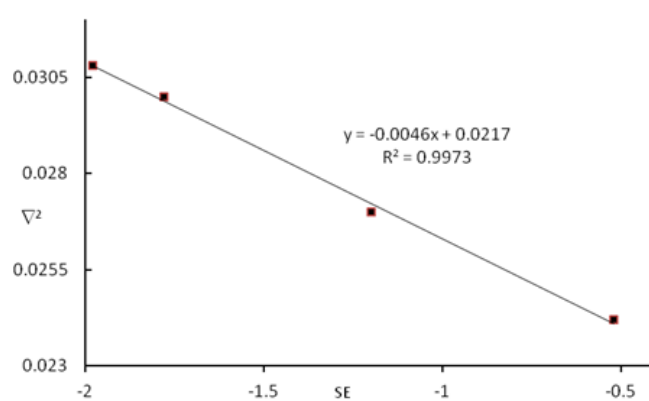
Figure 2. Relationship between the ∇^2_{BCP} (au) and SE(kcal mol^{-1}) for the B_2H_4-amine complexes.

transferred from HBA to HBD molecules. 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 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 (E^2). 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 transfer from the donor to the acceptor qCT and the second-order perturbation energy due to the interaction of donor and acceptor orbitals. E$^{(2)}$ allow us to quantitatively evaluate the charge transfer involving the formation of the B_2H_4 complexes. According to results, the E$^{(2)}$ value of B_2H_4-CH_3OH was greater than B_2H_4-H_2O, confirming the order obtained for the interaction energies of these complexes. Whereas, for the amine complexes some contraversies were seen between the order obtained for their E$^{(2)}$ and the interaction energies.

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