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Ab initio and DFT Studies of $Be(BH_4)_2$

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ABSTRACT

In this study, the Ab initio and DFT calculations of optimized geometries, energy and vibrational spectra for the Beryllium borohydride $Be(BH_4)_2$ at different levels are achieved by Hartre – Fock (HF), perturbation theory (MP2) and density functional theory (B3LYP) methods. They utilize the 6-31G(d), 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p) basis sets. The theoretical results showed that Beryllium borohydride with the D_2d structure which contains two identical groups of double bridging hydrogen has the lowest energy at all levels. Consequently, this compound is considered as the most stable one and the results of IR and Raman Spectra at all levels support that. We found that both structures C_s, C_{3v} have the structure of D_{2d} kind at all levels. The values of bond lengths for these two structures are identical to the bond lengths to the structure D_{2d} kind which confirms this theory.

Key words: $Be(BH_4)_2$; FT-IR; FT-Raman; Ab initio; DFT.

INTRODUCTION

Metal borohydrides are fascinating compounds because they show a remarkable variety in bonding characteristics ranging from ionic salts of alkali metals (e.g., $LiBH_4$ and $NaBH_4$) to volatile covalent compounds; in these compounds, hydrogen bridge bonds link boron to the metal. Among the covalent compounds, $Al(BH_4)_3$ is believed to have a planar trigonal skeletal structure with double hydrogen bridges[1, 2], while $Zr(BH_4)_4$, $U(BH_4)_4$ are all thought to have tetrahedral T_d structures with triple bridges[3]. The borohydrides are among the most volatile compounds of the latter heavy metals; this characteristic is often used in their commercial purification.

They are observed in many shapes according to the bonding between borohydride groups with the central atom occurred as in Figure

1. To understand the bonding between the metal and the borohydride group BH_4, calculations of Molecular orbital (MO) are conducted to quantify that quantitative in formations including the interference energy and the exchange mechanism between bridge and terminal hydrogen atoms. This is very important for better understanding of bonding in those compounds[4]. To obtain these informations from the calculations of molecular orbital, Beryllium borohydride $Be(BH_4)_2$ was used as a typical compound to study similar transition elements compounds. This compound contains M-BH_4 bond which is not efficient as in the case of $NaBH_4$ and $LiBH_4$[5], while the vibrational spectra is the best way used for obtaining an important information that may determine the optimized geometries for many compounds of Tetrahydroborate Ion[6, 7].

In some cases, it was found that the vibrational spectra of the double bond or triple bond are very different in wide area of B-H, and this group can be determined in addition to the vibrational spectra. The determination of the kind of hydrogen bridge in these compounds essentially depends on the use of an experimental method such as X-ray diffraction and electron diffraction. Although it is easy to distinguish the hydrogen bonds in tetra borohydride group (double or triple bonds) in many compounds by X-ray diffraction, the determination is sometimes difficult in the presence of metals. This is because of the scattering force of hydrogen atoms to the x-ray and the electrons[7]. Several experiments were performed on Beryllium borohydride to conduce its composition in gas phase without any convenient results thus the molecular structure of Beryllium borohydride is one of the problems utnil now[8-11].

Computational details

The optimized geometries, energy and vibrational frequency of the fundamental modes for the Beryllium borohydride $Be(BH_4)_2$ were computed of four different structures of $Be(BH_4)_2$ as in Figure 2. Three methods were used to approximate the energy and its Hartre – Fock (HF), Moller-plesset perturbation theory (MP2) and Becke- style 3 Parameter Density functional theory (B3LYP) with 6-31G(d), 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p) basis sets using GAUSSIAN 03W program package[12].

RESULTS AND DISCUSSION

Potential Energy Calculations

The relative energies (kcal/mol) have been calculated for each of the four structures of Beryllium borohydride by using the three methods, for the basis sets 6-31G(d), 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p).Table 1 outlines the values of energy at these levels. In general, the structure of D_{2d} kind is more stable. The results of the relative values of energy assure that the structure D_{2d} is the most stable, while the the structure D_{3d} is less stable. This is consistent with the experimental result that was reached in a previous study[13]. It is clear that the

Table 1: Total relative energies (kcal/mol) for $Be(BH_4)_2$

Basis set	Method	C_{3V}	C_S	D_{2d}	D_{3d}
6-31G(d)	HF	5.5124	4.68209	0	5.512
	MP2	5.3342	5.1728	0	5.3336
	B3LYP	0.8186	1.3925	0	0.0003
6-311G(d,p)	HF	5.3243	4.634	0	5.3244
	MP2	5.1716	5.1688	0	5.1687
	B3LYP	0.8223	1.7895	0	0.8225
6-311+G(d,p)	HF	5.3348	4.6445	0	5.3348
	MP2	5.181	5.2787	0	5.178
	B3LYP	0.8579	1.8119	0	0.8582
6-311++G(d,p)	HF	5.3385	4.6498	0	5.3468
	MP2	5.1825	5.1756	0	5.1882
	B3LYP	0.85874	1.8557	0	0.8659

difference in energy between the structures D_{3d}, C_s, C_{3v} at all levels is very small. This means that both C_s, C_{3v} are in agreement with the structure D_{3d}.

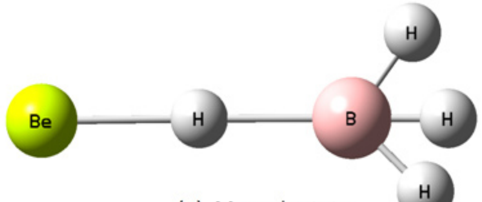
These results substantiated the values of bond lengths for both C_{3v}, C_s which are identical to that of the structure D_{3d}. The values of Torques for both structures are very close to zero and this assures that these two structures converge to the structure D_{3d} and this assure with old studies[14].

The studying of electron diffraction (ED) by Bauer for Beryllium borohydride assure the structure of D_{3d} while the previous diffraction proved that the structure D_{2d} is the stable shape for Berilium borohydride and thus the structure D_{2d} is the best[15].

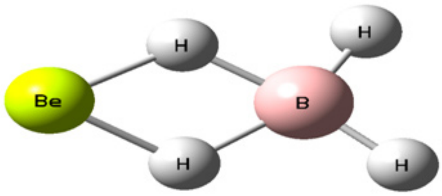
When we compared the calculated bonds for $Be(BH_4)_2$ that we obtained in table 2 with the bond lengths of identical borohydrides obtained from of studies[16-19], we find that these compounds tend to have ionic property more than covalent property because the lengths of bonds for these compounds is near to the values of length of ionic borohyarides bonds like $LiBH_4$, $NaBH_4$ Table 3.

Vibrational Spectra

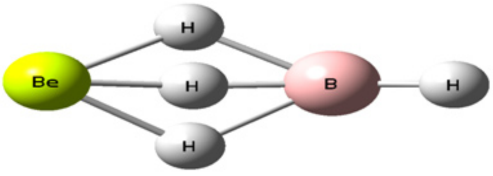
After calculating wave numbers, infrared intensities and Raman scattering activities for D_{2d}, D_{3d}, C_s and C_{3v} for the vibrational fundamentals of $Be(BH_4)_2$ at all levels were calculated by using



(a) Monodentate



(b) Bidentate



(c) Tridentate

Fig. 1: The modes of coordination of tetrahydroborate group to central metal

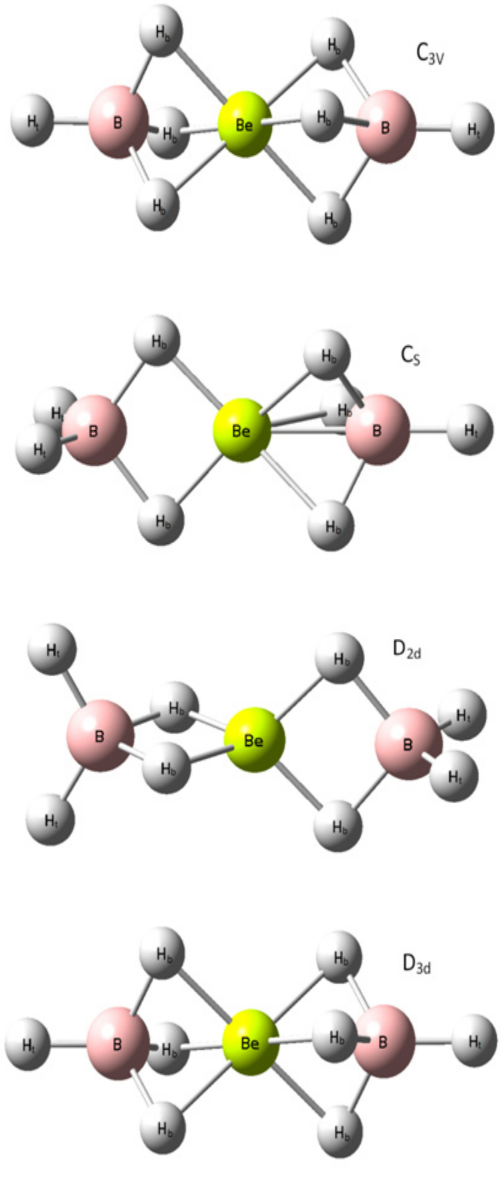


Fig. 2: Various possible structures of $Be(BH_4)_2$

the same basis sets. We obtained the best results at the B3LYP/6-311++G(d,p) level as explained in the Table 4. From these results, we observe that vibrations with high energy of Tetra borohydride are vibrational tensions to the bond between Boron atom and terminal hydrogen atom. This bundle appears in the IR spectra at (2647 cm^{-1}). While it appears in Raman spectra at (2605 cm^{-1}), these results agree with results of Nibler for Beryllium borohydrides. The tension band appeared in IR spectra at (2627 cm^{-1})[20, 21].

From Table 4, we observe that the position of band in IR and Raman spectra which we obtained by using Ab initio methods at B3LYP/6-311++G(d,p) level have very near values. This is primarily due to the nature of the structure of borohydrides which contain two identical BH_4 groups and this leads to the appearance of vibrational motion (op) in IR spectra and the vibrational motion (ip) in Raman spectra.

The vibrational bands which appear in the region (2100-1400 cm^{-1}) are due to the stretching of hydrogen tied bonds in ring shape (bridging hydrogen); it is found that if the compound is more ionic, the bands move gradually outside this region and some of them take higher values gradually outside this area and become (stretching vibration). Furthermore, the other take lower values and become deformation vibration[22] and this agrees with the results which are studied before these bands appear in IR spectra of B_2H_6 at (1990-1850 cm^{-1}) and (1600 cm^{-1}) and in case of $Be(BH_4)_2$ it will appear at (2165- 1985 cm^{-1}) and (1530 cm^{-1}) . As in the case of B_2H_6, the bands are clearer in spectrum with higher intensity. This is because of the bridging hydrogen considered as a base for the decrease of electrons and the shifted atoms in this region are able to make large dipole[22].

The theoretical results of vibrational motion are obtained in this study by using Ab initio methods and the two stretch bands which are the result of the vibrational bond B- H_b appeared in IR spectra at (2573 cm^{-1}) and (2574 cm^{-1}); the first is characterized by symmetric stretching and the second is characterized by the asymmetric stretching. In Raman spectra, the two bands appear at (2573 cm^{-1}) and (2575 cm^{-1}) in the symmetric stretching and asymmetric stretching consequently. This agrees with the results of previous studies[21]. The bending of B- H_b bond at

Table 2: Geometrical Parameters in Af of $Be(BH_4)_2$

Basis set	Method	r(B-H_t)	r(B-H_b)	r(Be-H_b)	r(Be-B)
6-31G(d)	HF	1.1900	1.2958	1.4669	1.8683
	MP2	1.1936	1.2834	1.4681	1.8404
	B3LYP	1.1949	1.2871	1.4687	1.8471
6-311G(d,p)	HF	1.1899	1.2979	1.468	1.8673
	MP2	1.1918	1.2829	1.4701	1.8506
	B3LYP	1.1908	1.2823	1.4652	1.8404
6-311+G(d,p)	HF	1.1899	1.2979	1.4679	1.8673
	MP2	1.1918	1.2829	1.4701	1.8505
	B3LYP	1.1909	1.2822	1.4652	1.8404
6-311++G(d,p)	HF	1.1899	1.2979	1.4679	1.8672
	MP2	1.1917	1.2828	1.4702	1.8504
	B3LYP	1.1909	1.2822	1.4652	1.8404

Table 3: Geometrical parameters in Af for $M(BH_4)_n$

	M-B	M-H_b	B-H_b	B-H_t
$NaBH_4$	2.2100	2.1600	1.2600	1.1600
$LiBH_4$	2.2230	2.1730	1.2560	1.1700
$Al(BH_4)_3$	2.1430	2.0100	1.2830	1.1960
$Zr(BH_4)_4$	2.1000	1.7400	1.9200	1.1950

Table 4: frequencies and Infrared Intensities Calculated for the Vibrational Fundamentals of $Be(BH_4)_2$ Using Gaussian at the B3LYP/6-311++G(d,p) level

Vibrational modes	frequencies (cm^{-1})	IR Intensities	Raman scattering activities	Approximate mode description
E				
v_1	421.1826	14.0137	0.0000	B-Be-B bend
v_2	351.5320	13.8284	0.0000	BH_b asym bend
v_3	1173.8077	3.4603	0.0000	BH_b sym deform (op)
v_4	1622.5912	0.8385	0.0000	BH wag (op)
v_5	2574.4237	3.4556	0.0000	BH_b asym str (op)
v_6	2573.0759	96.0812	0.0000	BH_b sym str (op)
v_7	2647.6727	75.2938	0.0000	BH_t str (op)
A_1				
v_8	550.3760	0.0000	16.9146	B-Be-B sym str
v_9	353.2426	0.0000	17.5656	BH_b sym bend
v_{10}	1169.2697	0.0000	14.4690	BH_b sym deform (ip)
v_{11}	2575.7881	0.0000	100.1102	BH_b asym str (ip)
v_{12}	2605.7573	0.0000	316.0911	BH_t str (ip)
B_1				
v_{13}	545.0395	0.6523	0.0000	B-Be-B asym str
v_{14}	1236.9411	34.3443	0.0000	BH_b asym deform (op)
B_2				
v_{15}	1666.0020	0.0000	0.1855	BH wag (ip)
v_{16}	1283.5967	0.0000	38.0773	BH_b asym deform (ip)
v_{17}	2573.6717	0.0000	72.0237	BH_b sym str (ip)
A_2				
v_{18}	1130.1214	0.0000	0.0000	BH_4 torsion

(351 cm^{-1}) in IR spectrum and (353 cm^{-1}) in Raman spectrum is identical to the experimental results which are obtained in previous studies for the same compound.

This band appears in IR spectra at (287 cm^{-1}) for $Be(BH_4)_2$[20] and in another study[21] and at (368 cm^{-1}) for the same compound. Two bands appear in the region B-M-B; the first is for the Stretching Vibration of B-M-B bond and appears at (600 cm^{-1}) and the other is a bending to this bond and appears at (400 cm^{-1}). In this study, we found that the band of Stretching Vibration of B-Be-B bond appears at (550 cm^{-1}) while the bending of the bond give a band at (421 cm^{-1}) and these values are in agreement with the experimental studies that made before[20].

The band of BH wag appears at (1622 cm^{-1}), (1666 cm^{-1}) in IR and Raman spectra consequently by using the basis set 6-311++G(d,p) at the level B3LYP from the theory.

Vibrational bond B- H_b deformation appear at (1169 cm^{-1}) and (1283 cm^{-1}). The first is vibration symmetric deformation and the second involves vibration form asymmetric deformation at in-plane (ip). This shows both bands at (1173 cm^{-1}) and (1236 cm^{-1}) to symmetric deformation and asymmetric deformation at out-of-plane (op) respectively using the basis set 6-31++G(d,p) at the level B3LYP from the theory.

CONCLUSION

From the theoretical result on beryllium borohydride $Be(BH_4)_2$ which are obtained, we can conclude that:

1. The structure D_{2d} which contains two identical groups of double bridging hydrogen has low energy at all levels of study so we consider it as the most stable structure for $Be(BH_4)_2$.
2. Both two structures C_S, C_{3V} have the structure of D_{3d} kind at all levels. The values of bond lengths for these two structures are identical for the bond lengths to the structure D_{3d} kind assure this theory.
3. The theoretical results of IR and Raman spectra which are obtained by using different methods to approach the energy of the system with basic different showed that the best results are groups obtained at the level B3LYP with using the basis set 6-311++G(d,p) and all these results prove that the structure D_{2d} is for $Be(BH_4)_2$.

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