

Ab Initio Calculations of Equilibrium Geometries and Vibrational Frequencies of Alkali Metal Tetrahydroborates MBH_4 ($\text{M}=\text{Li}, \text{Na}$ and K) and some Boron Hydrides (BH_3 , B_2H_6 and BH_4^-)

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Abstract

Alkali metal tetrahydroborates (MBH_4 , $\text{M}=\text{Li}, \text{Na}$ and K) and boron hydrides (BH_3 , B_2H_6 and BH_4^-) have been studied by ab initio MO calculations. Geometry optimizations and frequency calculations have been performed at HF/3-21G** level for MBH_4 in monodentate, bidentate and tridentate configurations. Calculated dipole moments in the tridentate configuration indicate that B-M bonds in MBH_4 are highly ionic, and the ionicity of B-M bond is related to the variation of geometrical parameters during the alkali metal substitution. Experimental B-M bond lengths and ν_4 (B-M stretching) frequencies for LiBH_4 and NaBH_4 are well reproduced by MP2/6-31G** calculation. Differences of B-H bond distances, B-H stretching and H-B-H bending force constants in each MBH_4 are discussed in relation to the difference of bonding environment between bridging and terminal hydrogen atoms.

Introduction

Alkali metal tetrahydroborate complexes have attracted much attention to the nature of bonds between boron and alkali metals.¹⁻⁹⁾ For these complexes, three different types of coordination are expected through bridging hydrogen (s) as shown in Fig. 1; tridentate, bidentate and monodentate configurations; (t-, b- and m-configurations). Earlier ab initio calculations have shown that t-configuration is most stable for LiBH_4 , NaBH_4 , and KBH_4 in gaseous state.^{1,2)} Very recently, Francisco and Williams studied the relative stability and frequencies of LiBH_4 and NaBH_4 in the three configurations.⁹⁾ Here, we extended this series of alkali metal tetrahydroborates to include KBH_4 and some

boron hydrides (BH_3 , B_2H_6 and BH_4^-) for a survey of the geometries and the electron densities of these complexes and molecules, with a special reference to the change of B-M bond during the substitution of alkali metal. The spectroscopic data to be compared with these calculations have not been available because of experimental difficulty. Recently, Kawashima

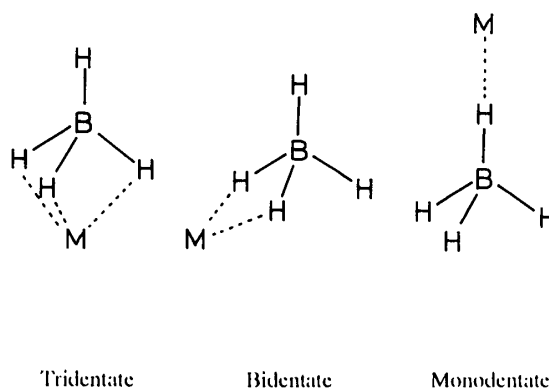


Fig. 1 Three different types of coordination in MBH_4 .

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Received Sep. 5, 1994

et al. succeeded in observing the microwave spectra of LiBH_4 , NaBH_4 and KBH_4 in the gas phase.¹⁰⁻¹²⁾ The observed microwave spectra indicated that for these complexes, the tridentate configuration is most stable. In addition, the observed spectral patterns of vibrational satellites were found to be quite different among these three complexes. This anomaly was accounted for by an accidental degeneracy of the two vibrational states which are strongly coupled by Coriolis interaction.¹²⁾

In the present study, the energy and equilibrium geometries of t-, b-, and m-configurations in LiBH_4 , NaBH_4 and KBH_4 were obtained, and the differences among them were derived. Then, the vibrational force fields were calculated in the most stable t-configuration. To evaluate the errors of the present calculations, the vibrational frequencies of BH_3 , B_2H_6 , and BH_4^- were calculated in the same time, and compared with the experimental values.¹³⁻¹⁶⁾ Variations of the geometrical parameters and vibrational frequencies of MBH_4 during the substitution of alkali metal will be discussed in relation to the change of the ionicity in B-M bond and the difference of bonding character between those in the terminal and bridging hydrogen atoms.

Methods

Ab initio calculations were carried out at three levels; HF/3-21G**¹⁷⁾ for LiBH_4 , NaBH_4 and KBH_4 ; HF/6-31G**¹⁸⁾ and MP2/6-31G**¹⁹⁾ for LiBH_4 and NaBH_4 . In 6-31G** basis set, the polarization functions were assumed as shown in Ref. 18. HF/3-21G** calculation was carried out to make a systematic survey of three complexes on the basis of uniform approximation, because large basis sets like 6-31G and 6-311G do not cover the third-row atoms. 3-21G** basis set used here includes polarization func-

tions on boron and hydrogen, where Gaussian exponents ($\alpha=0.68$ for H and $\alpha=0.388$ for B) were taken from Ref. 17d. Polarization functions were not assumed on alkali-metal atom, because in the complexes studied here, SCF calculations sometimes failed to converge when the basis set for alkali metals was augmented by p functions.²⁰⁾ An examination of the population analysis in preliminary calculations shows that electron populations are considerably large on B and H, and correspondingly small on alkali metal atom (especially on K); these complexes are best described as M^+BH_4^- . Therefore, polarization functions on alkali metal atoms are not so important as those on H and B. Electron correlated MP2/6-31G** calculations were carried out to predict geometrical parameters, energy differences, and vibrational force fields in LiBH_4 and NaBH_4 , then the systematic errors in the present ab initio calculations were estimated.

The geometries of three (t-, b- and m-) configurations were optimized by gradient minimization, then the energy differences were derived from the optimized energies. The vibrational force fields were calculated for the most stable t-configuration. Calculations were performed on Vax 8350 and Vax Station 3100 using Gaussian-90.²¹⁾

Results and Discussion

a) Stable structure and relative energies

Relative energies among three configurations are shown in Table 1. The magnitudes of the energies depend, to some extent, on the level of calculation; the order of energy of three configurations is, however, independent of the level of calculation; the tridentate is the most stable and the monodentate is the least stable as shown previously.^{1,2)} The HF/3-21G** results show that as the atomic number of

alkali-metal atom increases, the energy differences between tridentate and bidentate and those between tridentate and monodentate

Table 1 Energy Differences ($\Delta E/10^3 \text{cm}^{-1}$) among Tridentate, Bidentate and Monodentate Configurations

Level of calc.	Molecule	$\Delta E(\text{b-t})^{\text{a)}}$	$\Delta E(\text{m-t})^{\text{b)}}$
HF/3-21G**	LiBH ₄	1.63	8.99
	NaBH ₄	2.31	7.25
	KBH ₄	1.97	5.71
HF/6-31G**	LiBH ₄	1.71	9.05
	NaBH ₄	1.53	7.09
HF/6-311G**	LiBH ₄	1.77 ^{c)}	8.88 ^{c)}
	NaBH ₄	1.51 ^{c)}	6.90 ^{c)}
MP2/6-31G**	LiBH ₄	2.49	10.27
	NaBH ₄	1.86	7.89
MP2/6-311G**	LiBH ₄	2.02 ^{c)}	10.04 ^{c)}
	NaBH ₄	1.50 ^{c)}	7.19 ^{d)}

a) $\Delta E(\text{b-t}) = E_{\text{b}} - E_{\text{t}}$ b) $\Delta E(\text{m-t}) = E_{\text{m}} - E_{\text{t}}$

c) Ref. 9.

d) Present work.

decrease, respectively.

The energy differences between t- and b -configurations, and those between t- and m -configurations are quite large that a tunneling effect would not perturb the vibrational energy levels appreciably in these complexes. Therefore, the vibrational frequencies in t -configuration were calculated on the basis of a harmonic approximation.

Optimized geometries of MBH₄ in t -configuration are shown in Table 2. It is evident from HF/3-21G** calculations that the distances between boron and alkali metals are considerably shorter than the sum of atomic radii as shown in Table 3. It is also evident in every complexes that the calculated values of $r(\text{B-H}_{\text{b}})$ are larger than $r(\text{B-H}_{\text{t}})$, and the differences between them are almost independent of the level of approximation, where H_b

Table 2 Geometrical Parameters of MBH₄ in Tridentate Configuration

Molecule	Level of Calc.	$r(\text{B-H}_{\text{t}})$	$r(\text{B-H}_{\text{b}})$	$r(\text{B-M})$	$\theta(\text{H}_{\text{t}}-\text{B}-\text{H}_{\text{b}})$
LiBH ₄	HF/3-21G**	1.199	1.257	1.968	113.1
	HF/6-31G**	1.194	1.251	1.964	112.9
	HF/6-311G**	1.193 ^{a)}	1.253 ^{a)}	1.929 ^{a)}	113.4 ^{a)}
	MP2/6-31G**	1.188	1.237	1.935	112.6
	MP2/6-311G**	1.193 ^{a)}	1.244 ^{a)}	1.923 ^{a)}	113.2 ^{a)}
	exp	1.216 ^{b)}	1.256 ^{b)}	1.9394	(113.0) ^{b)}
NaBH ₄	HF/3-21G**	1.206	1.252	2.267	111.2
	HF/6-31G**	1.201	1.250	2.313	111.3
	HF/6-311G**	1.202 ^{a)}	1.251 ^{a)}	2.316 ^{a)}	111.3 ^{a)}
	MP2/6-31G**	1.195	1.236	2.280	110.8
	MP2/6-311G**	1.200 ^{a)}	1.241 ^{a)}	2.303 ^{a)}	111.0 ^{a)}
	exp	1.24 ^{c)}	1.28 ^{c)}	2.308	(111.0) ^{c)}
KBH ₄	HF/3-21G**	1.214	1.251	2.728	110.9
	exp	1.233 ^{d)}	1.272 ^{d)}	2.656	(110.8) ^{d)}
unit		A	A	A	deg.

a) Ref. 9

b) $\theta(\text{H}_{\text{t}}-\text{B}-\text{H}_{\text{b}})$ was assumed to be 113.0 deg. from ab initio calculation. (Ref. 11.)

c) $\theta(\text{H}_{\text{t}}-\text{B}-\text{H}_{\text{b}})$ and $r(\text{B-H}_{\text{b}})-r(\text{B-H}_{\text{t}})$ were assumed to be 111.0 deg. and 0.04A respectively from ab initio calculations. (Ref. 10)

d) $\theta(\text{H}_{\text{t}}-\text{B}-\text{H}_{\text{b}})$ was assumed to be 110.8 deg. from ab initio calculation. (Ref. 27)

Table 3 Atomic Distances (A) between Boron and Alkali-metal in Tridentate Configuration

Molecule (Sum of atomic radii) ^{a)}	Rsum	Rcalc (HF/3-21G** value)	Rsum-Rcalc
LiBH ₄	2.24	1.97	0.27
NaBH ₄	2.44	2.27	0.17
KBH ₄	2.86	2.73	0.13

a) Assumed covalent radii (B: 0.90, Li: 1.34, Na: 1.54, K: 1.96A) were taken from L. Sutton ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions". The Chemical Society, London, Special Publication, No. 11 and 18, 1958, and 1965.

stands for a bridging hydrogen, and H_t stands for a terminal one. The average of these differences ranges from 0.055A (in LiBH₄) to 0.036A (in KBH₄); these are very close to 0.046A, which is the difference of B-H bond distances between those obtained in BH₃ (1.184 A) and BH₄⁻ (1.230A) at MP2/6-31G** level. This seems to suggest that elongations of B-H_b bonds in these complexes may be caused by increments of electron population on bridging hydrogen atoms due to complex formation.

b) B-M bonding character

The nature of bonding between boron and alkali-metal atoms is one of our major interest. Dipole-moments in these complexes may be mostly dominated by the bonding character between BH₄ and alkali-metal atoms, and there may be a small contribution from the distortion of BH₄. The structures of BH₄ in three complexes are very close to a tetrahedron as shown in Table 2. Therefore, the contribution of distortion to the dipole moments was assumed to be negligible in the present case. A parameter δ was defined in the following equation, to represent the extent of ionicity of B-M bond and the resultant values are shown in

Table 4 Dipole Moments (D)^{a)} and δ of MBH₄ at HF/3-21G** Level

Molecule	Dipole moment	$\delta^{(b)}$
LiBH ₄	6.29	0.666
NaBH ₄	8.63	0.793
KBH ₄	11.47	0.875

a) 1D=3.336×10⁻³⁰ C • m.

b) For the definition of δ , see text.

Table 4.

$$\mu = r(\text{B-M}) \cdot \delta e \quad (1)$$

On the basis of δ , the B-M bond is most ionic in KBH₄, and least ionic in LiBH₄. This trend is consistent with that expected from the electronegativity difference between B and M; the differences between B and M atoms are 1.06 (LiBH₄), 1.11 (NaBH₄) and 1.22 (KBH₄), respectively.²²⁾

c) Geometrical parameters

HF/3-21G** calculations demonstrate that, as alkali-metal atom varies from Li to K, $\theta(\text{H}_t\text{-B-H}_b)$ decreases from 113.11 to 110.9 degrees, and the difference between $r(\text{B-H}_b)$ and $r(\text{B-H}_t)$ decreases from 0.0583 A to 0.036 A. If B-M bond in these complexes is completely ionic, $\theta(\text{H}_t\text{-B-H}_b)$ will be 109.47 degrees (tetrahedral angle), and the difference between $r(\text{B-H}_b)$ and $r(\text{B-H}_t)$ will be zero. $\Delta\theta$ and Δr defined by eq.2 stand for the deviations of geometry from tetrahedral symmetry, and these were plotted against δ . (Fig. 2)

$$\Delta\theta = \theta(\text{H}_b\text{-B-H}_t) - 109.47 \quad (2a)$$

$$\Delta r = r(\text{B-H}_b) - r(\text{B-H}_t) \quad (2b)$$

As δ increases from 0.666 (LiBH₄) to 0.875 (KBH₄), $\Delta\theta$ and Δr decrease and the plots are extrapolated to be nearly zero at $\delta=1$. This results suggest that the structural changes of BH₄ in these complexes reflect the change of ionicity in B-M bond and electron population on BH₄.

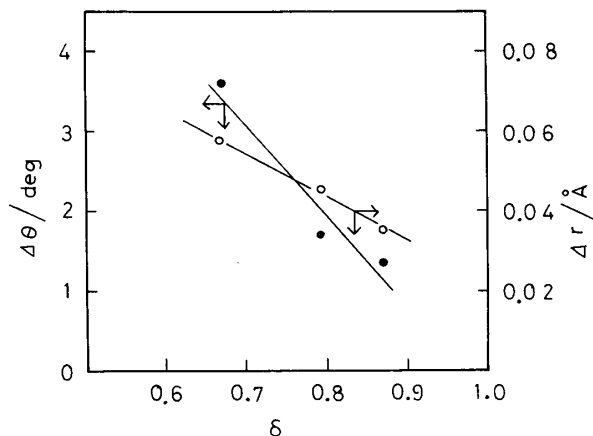


Fig. 2 Relation between Δr and δ (○); and that between $\Delta\theta$ and δ (●).

d) Comparison with experimental geometries

The substitution structures $r_s(\text{Li-B})$, $r_s(\text{Na-B})$, and $r_s(\text{K-B})$ were obtained in LiBH_4 , NaBH_4 , and KBH_4 ; these are 1.9394Å, 2.308Å, and 2.656Å respectively.^{10,11,26)} Table 2 shows that the bond lengths $r(\text{Li-B})$ and $r(\text{Na-B})$ calculated at MP2/6-31G** level are in a fairly excellent agreement with the experimental.^{10,11)} In the case of KBH_4 , HF/3-21G** value is slightly larger than the experimental. This may be partly due to the quality of a. o. on boron and potassium in this small 3-21G** basis set. As for the structure of BH_4 , the number of available rotational constants is insufficient to determine the structure of BH_4 completely. Ab initio calculations predicts, however, that bridging hydrogen atoms tend to form longer bonds with boron atoms than the terminal ones do, and $\theta(\text{H}_t\text{-B-H}_b)$ in BH_4 deviates a few degree from the tetrahedral angle in these complexes.

e) Vibrational force fields and fundamental frequencies

Vibrational force fields were calculated for LiBH_4 , NaBH_4 , and KBH_4 in tridentate configuration, and also for three boron hydrides (BH_3 , B_2H_6 and BH_4^-). HF/3-21G** and MP2/

6-31G** frequencies of MBH_4 and BH_3 , B_2H_6 and BH_4^- are shown in Table 5 and 6, together with the experimental values. Fundamental frequencies of BH_3 , B_2H_6 and BH_4^- were predicted by MP2/6-31G** with average deviations of 6.3%, 7.7% and 6.1% respectively.¹³⁻¹⁶⁾ Some comments are necessary for the in-plane vibration ν_4 of BH_3 . There have been much arguments on the location of this mode; the largest value is 1765 cm^{-1} by Shepp and Bauer²³⁾ and the smallest one is 1134 cm^{-1} by Garnett²⁴⁾. If we adopt 1604 cm^{-1} by Kaldor and Porter,¹³⁾ the calc./obs. ratio for MP2/6-31G** frequency amounts to 0.794 and this is too small to be acceptable. Recently, Kawaguchi succeeded in the direct observation of ν_4 .^{14c)} MP2/6-31G** value of ν_4 is 6.4% larger than their observed frequency 1196.6 cm^{-1} , and this deviation is very close to the average of overall deviation (6.0% for MP2/6-31G**).

Vibrational frequencies of B_2H_6 were calculated by Hout et al. using numerical second differentiation of energies at MP2/6-31G* level.²⁵⁾ The vibrational frequencies were calculated at the same level, but we could not reproduced their results; the ratio of their frequency to ours ranges from 1.22 (in ν_{15}) to 0.738 (in ν_{18}). Therefore, there may be some problems in their numerical calculations. On the basis of the above results, the MP/6-31G** frequencies obtained for LiBH_4 and NaBH_4 may be regarded to contain error of the same magnitude, and the fundamental frequencies of these alkali metal tetrahydroborates are expected to be reproduced with an average error of about 7%.

The frequencies of ν_4 (B-M stretching vibration) could be estimated from the rotational constant (B_0) and centrifugal distortion constant (D_0) by the following equation.

Table 5 Comparison of Calculated and Experimental Frequencies (ν/cm^{-1})
of $^{11}\text{BH}_3$, $^{11}\text{B}_2\text{H}_6$ and $^{11}\text{BH}_4^-$

(1) $^{11}\text{BH}_3$

Mode	MP2/6-31G**	Exp	Calc/Exp	Assignment
$A_1' \nu_1$	2671.2	(2623.) ^{a)}	1.018	B-H sym str
$A_2'' \nu_2$	1207.4	1147.5 ^{b)}	1.052	out of plane def
$E' \nu_3$	2816.8	2601.6 ^{c)}	1.082	B-H deg str
ν_4	1273.5	1196.6 ^{b)}	1.064	in plane def
Average of Calc/Exp 1.060				

a) Ref. 13. b) Ref. 14c. c) Ref. 14b.

(2) $^{11}\text{B}_2\text{H}_6$

Mode	MP2/6-31G**	Exp ^{a)}	Calc/Exp	Assignment
$A_{1g} \nu_1$	2730.1	2530.2	1.079	BH_2 sym str
ν_2	2279.9	2112.2	1.080	ring str
ν_3	1260.9	1184.	1.065	BH_2 s bend
ν_4	844.2	790.	1.069	ring def
$A_u \nu_5$	878.7	833.1	1.055	BH_2 twist
$B_{2g} \nu_6$	1973.9	1755.	1.125	ring str
ν_7	901.5	(796.3)	-	BH_2 wag
$B_{2u} \nu_8$	2828.4	2608.9	1.084	BH_2 a str
ν_9	1008.6	948.	1.064	BH_2 rock
ν_{10}	375.8	369.3	1.018	ring puck
$B_{1g} \nu_{11}$	2817.0	2597.	1.085	BH_2 a str
ν_{12}	973.0	914.	1.065	BH_2 rock
$B_{1u} \nu_{13}$	2101.3	1858.6	1.130	ring str
ν_{14}	1023.3	972.1	1.052	BH_2 wag
$B_{3g} \nu_{15}$	1086.7	1025.	1.062	BH_2 twist
$B_{3u} \nu_{16}$	2714.7	2519.6	1.077	BH_2 s str
ν_{17}	1819.2	1600.8	1.136	ring str
ν_{18}	1252.6	1174.	1.067	BH_2 s bend
Average of Calc/Exp 1.077				

a) Ref. 16.

(3) $^{11}\text{BH}_4^-$

Mode	MP2/6-31G**	Exp ^{a)}	Calc/Exp	Assignment
$A_1 \nu_1$	2375.1	2274.6	1.044	B-H sym str
$E \nu_2$	1283.5	1224.8	1.048	deg def
$F_2 \nu_3$	2401.9	2250.5	1.067	B-H deg str
ν_4	1180.8	1103.7	1.070	deg def
Average of Calc/Exp 1.061				

a) Ref. 15.

Table 6 Vibrational Frequencies (ν/cm^{-1}) and Infrared Intensities ($\text{A/Km} \cdot \text{mol}^{-1}$) of $\text{Li}^{11}\text{BH}_4$, $\text{Na}^{11}\text{BH}_4$ and K^{11}BH_4 in Tridentate Configuration

Molecules (Level)	$\text{Li}^{11}\text{BH}_4$ (MP2/6-31G**)	$\text{Na}^{11}\text{BH}_4$ (MP2/6-31G**)	K^{11}BH_4 (HF/3-21G**)		
Mode	ν	A	ν	ν	Assignment
ν_1	2720.7	129.	2661.6	2592.	B-H _t str
ν_2	2345.6	161.	2340.2	2330.	B-H _b sym-str
A ₁ ν_3	1296.4	110.	1266.2	1280.	H _t BH _b sym-def
ν_4	707.9	153.	449.1	347.	B-M str
	(727.) ^{a),b)}		(435.) ^{a),c)}	(358.) ^{a)}	
ν_5	2335.0	716.	2332.0	2280.	B-H _b deg-str
ν_6	1341.3	6.	1329.8	1337.	H _t BH _b deg-def
E ν_7	1184.9	71.	1180.0	1216.	H _t BH _b deg-def
ν_8	538.1	4.	448.0	446.	H _t BM bend

a) Values in parentheses are experimental frequencies of ν_4 estimated from equation

$$\nu_4 = (4B_0^3/D_0)^{1/2}.$$

b) Ref. 11. c) Ref. 10.

$$\nu_4 = (4B_0^3/D_0)^{1/2} \quad (3)$$

Frequencies of ν_4 estimated from the above equation are 727 cm^{-1} (LiBH_4)¹²⁾, 435 cm^{-1} (NaBH_4)¹¹⁾, and 358 cm^{-1} (KBH_4)²⁶⁾, respectively; excellent agreements were observed between the MP2/6-31G** and the experimental values in LiBH_4 and NaBH_4 . The spectral anomaly found in NaBH_4 suggests that the energy difference between $\nu_4=1$ and $\nu_8=1$ states is very small; the energy separation was estimated to be approximately 30 cm^{-1} by Kawashima et. al.¹²⁾ MP2/6-31G** frequencies of these vibrations are 449.1 and 448.0 cm^{-1} , respectively and this result supports their interpretation.

f) Force constants

Force constants of MBH_4 and boron hydrides (B_2H_6 and BH_4^-) are shown in Table 7. The diagonal force constants of B-H stretching seem to be divided into two groups, i. e., boron-terminal hydrogen (B-H_t) stretching and boron-bridging hydrogen (B-H_b) stretching. The B-H_t stretching force constants in LiBH_4 and NaBH_4 are close to that for boron terminal

Table 7 Force Constants (10^2N/m) Calculated at MP2/6-31G**

(1) B-H stretching

Molecule	$f(\Delta r_a, \Delta r_a)^a)$	$f(\Delta r_b, \Delta r_b)^b)$
LiBH_4	4.02	3.03
NaBH_4	3.86	3.02
B_2H_6	4.20	-
BH_4^-	-	3.16

a) $r_a = r(\text{B-H}_t)$ b) $r_b = r(\text{B-H}_b)$

(2) H-B-H deformation

Molecule	$f(\Delta \alpha, \Delta \alpha)^c)$	$f(\Delta \beta, \Delta \beta)^d)$
LiBH_4	0.707	0.502
NaBH_4	0.675	0.469
B_2H_6	0.767	-
BH_4^-	-	0.423

c) $\alpha = \theta(\text{H}_t\text{-B-H}_b)$ d) $\beta = \theta(\text{H}_b\text{-B-H}_b)$

hydrogen stretching in B_2H_6 , and the B-H_b stretching force constants in LiBH_4 and NaBH_4 are close to the corresponding one in BH_4^- . As for the diagonal term of bending force constants, the calculated values for $\theta(\text{H}_t\text{-B-H}_b)$ deformation and $\theta(\text{H}_b\text{-B-H}_b)$ deformation in MBH_4 are very close to the corresponding ones in B_2H_6 and BH_4^- . This seems to suggest that the bonding character of the termi-

nal hydrogens in LiBH_4 and NaBH_4 is close to that in B_2H_6 , and the bonding character in boron-bridging hydrogens in LiBH_4 and NaBH_4 are close to that in BH_4^- .

The author wishes to express his thanks to Prof. Y. Kawashima of Kanagawa Institute of Technology for his kind cooperation. Ab initio calculations were carried out at Research and Education Center of Software Engineering, Tokyo Institute of Polytechnics.

References

- 1) J. D. Drill, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **99**, 6159 (1977).
- 2) J. D. DeFrees, K. Raghavachari, H. B. Schlegel, J. A. Pople, and P. v. R. Schleyer, *J. Phys. Chem.*, **91**, 1857 (1987).
- 3) V. Kelloe, M. Urban and A. I. Boldyrev, *Chem. Phys. Lett.*, **106**, 455 (1984).
- 4) A. I. Boldyrev, O. P. Charkin, N. G. Rambidi and V. I. Avdeev, *Chem. Phys. Lett.*, **44**, 20 (1976).
- 5) R. Bonaccorsi, E. Scrocco, and J. Tomasi, *Theoret. Chim. Acta (Berl.)* **52**, 113 (1979).
- 6) V. Barone, G. Dolcetti, F. Lelj, and N. Russo, *Inorg. Chem.*, **20**, 1687 (1981).
- 7) O. P. Carkin, D. G. Musaev, and N. M. Klimenko, *Kood. Khim.*, **11**, 728, (1985).
- 8) A. S. Zyukin, D. G. Musaev, and O. P. Charkin, *Kood. Khim.*, **13**, 1329 (1987).
- 9) J. S. Francisco and I. H. Williams, *J. Phys. Chem.*, **96**, 7567 (1992).
- 10) Y. Kawashima, C. Yamada and E. Hirota, *J. Chem. Phys.*, **94**, 7707 (1991).
- 11) Y. Kawashima and E. Hirota, *J. Chem. Phys.*, **96**, 2460 (1992).
- 12) Y. Kawashima, and E. Hirota, *J. Mol. Spectrosc.*, **153**, 466 (1992).
- 13) A. Kaldor and R. F. Porter, *J. Am. Chem. Soc.*, **93**, 2140 (1971).
- 14) a) K. Kawaguchi, J. E. Butler, C. Yamada, S. H. Bauer, T. Minowa, H. Kanamori, and E. Hirota, *J. Chem. Phys.*, **87**, 2438 (1987).
- b) K. Kawaguchi, *J. Chem. Phys.*, **96**, 3411 (1992).
- c) K. Kawaguchi, Symposium on Molecular Science (Kyoto), 2A03 (1992).
- 15) M. I. Memon, W. F. Sherman and G. R. Wilkinson, *Spectrochim. Acta*, **37A**, 461 (1981).
- 16) C. E. Blom and A. Mueller, *J. Chem. Phys.*, **69**, 3397 (1978).
- 17) a) J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980).
- b) M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and J. W. Hehre, *ibid*, **104**, 2797 (1982).
- c) K. D. Dobbs and W. J. Hehre, *J. Comput. Chem.*, **7**, 359, (1986).
- d) S. Huzinaga (Editor), "Gaussian Basis Sets for Molecular Calculations", Elsevier, Amsterdam, 1984.
- 18) a) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).
- b) J. D. Drill and J. A. Pople, *ibid*, **62**, 2921 (1975).
- c) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, *ibid*, **77**, 3654 (1982).
- d) P. C. Hariharan, and J. A. Pople, *Theoret. Chem. Acta*, **28**, 213 (1973).
- 19) a) J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem. Symp.*, **10**, 1 (1976).
- b) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem. Symp.*, **13**, 225 (1979).
- 20) Exponents α for p functions (Li 0.076, Na 0.061, K 0.039) were taken from Ref. 17d.
- 21) M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1990.
- 22) Electronegativities were taken from A. L. Alred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).
- 23) A. Schepp and S. H. Bauer, *J. Am. Chem. Soc.* **76**, 265 (1954).
- 24) S. H. Garnett, PhD. Thesis, Princeton University, Princeton, N. J., 1968.
- 25) R. F. Huout, Jr., B. A. Levi, and W. J. Hehre, *J. Comput. Chem.*, **3**, 234 (1982).
- 26) Y. Kawashima, private communication.