

# Articles

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## Nonempirical Study of the Structure and Stability of Beryllium, Magnesium, and Calcium Borohydrides

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This paper reports and analyzes the results of ab initio calculations on the complex metal borohydrides  $M(\text{BH}_4)_2$  ( $M = \text{Be, Mg, Ca}$ ). Attention is drawn to the comparisons of geometrical structures (at the SCF level) and relative energies (at the SCF, MP2, MP3, and SDQMP4 levels) of the several local minima on the potential surface. Reasonable trends in the geometrical and energetic parameters, due to the change of the metal atom, are placed in evidence. It is shown that the effect of electronic correlation, of some importance in assessing the relative energy of the various geometrical forms, is reproduced by a simple electron pair contribution model. This study is complemented by information about the energetics of possible decomposition reactions, including other species, such as  $\text{HMBH}_4$ ,  $\text{MBH}_4^+$ ,  $\text{HMBH}^+$ , etc.

### Introduction

Systematic nonempirical calculations on borohydrides of general formula  $M(\text{BH}_4)_2$ ,  $\text{HMBH}_4$ , and  $\text{MBH}_4^+$  ( $M = \text{Be, Mg, Ca}$ ) are employed in this paper to get a coherent picture of the salient features of these compounds. The large class of complex metal hydrides is characterized by the occurrence for each chemical formula of different geometrical structures corresponding to local minima in the potential energy surface. A considerable part of the chemical properties of the different compounds within the class may be rationalized by considering the relative energies and the geometrical parameters of the singular points (local minima, saddle points). To do so, a systematic investigation considering all the compounds at the same level of approximation is necessary. On the other hand, the approximation used in the calculation must be of a high level, because in many cases the difference in energy among the different structures is small and sensitive to electronic correlation effects as well as to the quality of the basis set. These general considerations hold also for the specific case of the metal borohydrides considered here.

This paper may be considered part of a larger systematic investigation into the whole set of metal hydrides, but it is complete in itself, as far as the borohydrides of the metals belonging to the upper portion of the second group are concerned.

Previous calculations on the related light metal beryllohydrides<sup>1</sup> using a CIPSI<sup>2</sup> multideterminant wave function have shown that in the hydrides under examination the coefficient of the leading Hartree-Fock configuration is larger than 0.97-0.98. One may therefore be justified in supposing that our compounds are eligible for the use of Møller-Plesset perturbation theory, which works quite well when there is a leading configuration with a large coefficient. We have considered important, in view of the extension of the study to larger molecular systems, a comparison of the results obtained by the MP theory at different levels of approximation. To this end, we have repeated our calculations at the MP2, MP3, and MP4 levels (the last including single, double, and quadruple excitations). The basis set adopted for the energy calculations includes polarization functions for all the atoms, and the geometry optimizations have first been performed with basis sets of somewhat lower quality and then refined with the larger basis set, without finding appreciable deviations. So, we are confident that the description of structures and energies given in

the following pages are of homogeneous and reliable quality.

The examination of the borohydrides is accompanied by calculations at the same level on the various possible products of unimolecular decomposition reactions,  $\text{HMBH}_4$  and  $\text{MBH}_4^+$  in particular. From these data it is possible to get information on the thermal stability of the metal borohydrides. A systematic evaluation of the barriers for the unimolecular dissociation processes has not been attempted, however. The considerable computational effort necessary to define all the parameters for an accurate study of the decomposition channels lies beyond the scope of this investigation. In some cases, additional calculations have been made in order to have a better semiquantitative appraisal of the kinetic stability of the molecule.

Beryllium borohydrides have been the object of a number of theoretical and experimental investigations. A critical survey of the experimental studies has recently been made by Stanton et al.<sup>3</sup> Reference 3 reports geometry optimizations of three structures of  $\text{Be}(\text{BH}_4)_2$  at the MP2 level with a (321/21) basis set, followed by MP4-SDQ calculations of the energy.  $\text{Be}(\text{BH}_4)_2$  has been the object of other ab initio calculations: IEPA calculations with a DZ+P basis sets by Ahlrichs<sup>4</sup> and MP2/6-311G\* energy calculations on geometries optimized at the SCF level with a limited basis set by Ortiz and Lipscomb.<sup>5</sup> A recent paper by Hori et al.<sup>6</sup> reports geometry optimizations at the SCF level with the 3-21G and 3-21G\* basis sets. Older calculations at a lower level of accuracy are summarized in ref 3.

The geometries of  $\text{HBeBH}_4$ ,  $\text{BeBH}_4^+$ , and  $\text{HBeBH}^+$  have been optimized at the H-F/6-31G\* level, with final energies computed with the SCEP/6-31G\* approximation.<sup>7-10</sup> Calculations on the

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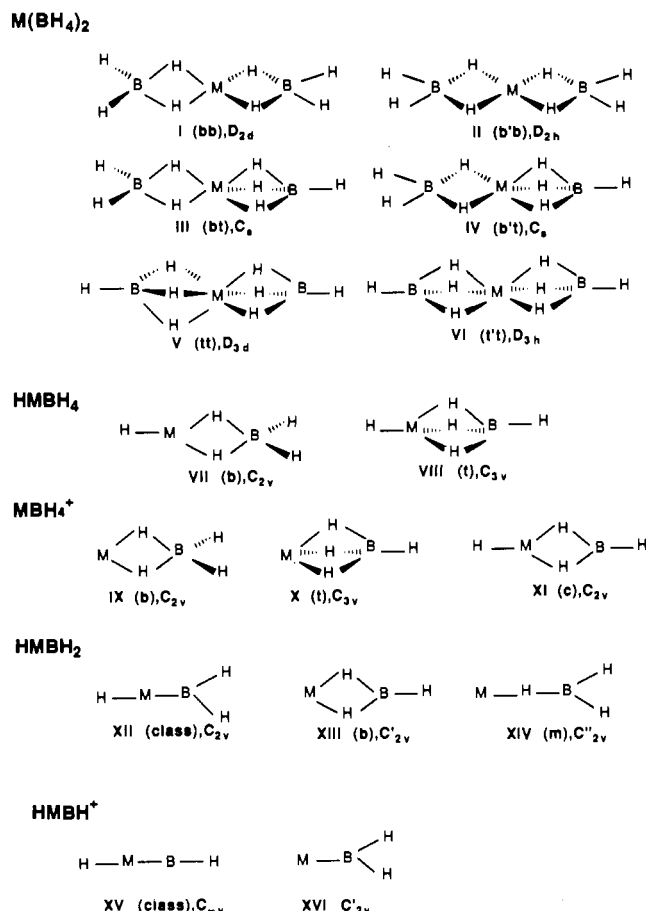


Figure 1. Schematic drawings of the geometries considered in this paper.

HBeBH<sub>4</sub> system are also reported in ref 4. Recently, three isomers of this system have been reconsidered by De Frees et al.<sup>11</sup> at the MP4/6-31G\*\*//H-F/6-31G\* level.

Magnesium borohydrides have been investigated less in detail. In ref 10 the geometries of HMgBH<sub>4</sub>, MgBH<sub>4</sub><sup>+</sup>, HMgBH<sub>2</sub>, and MgBH<sub>2</sub><sup>+</sup> have been optimized within the SCF/3-21G\* approximation, and the study also includes single point calculations at the SCEP/DZ+P level (Huzinaga–Dunning–Hay basis set<sup>12</sup> plus polarization functions). Preliminary results on magnesium borohydrides, related to the present investigation, have been published in ref 13.

Calcium borohydrides have previously been studied only at the SCF level<sup>10</sup> by using the following basis sets of moderate size: the Roos–Veillard–Vinot basis set<sup>14</sup> for Ca and the Roos–Siegbahn basis set<sup>15</sup> for B and H. Some preliminary results at the SCF level of our study have been published in ref 16.

### Computational Details

The calculations have been performed by using the 6-31G\*\* basis set<sup>17</sup> for all atoms, with the exception of Ca for which the comparable basis set of Golc et al.,<sup>18</sup> (15s,12p,4d/5s,4p,2d) with contraction (633111/5322/22), has been employed.

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The GAUSSIAN-82 program, running on the CRAY-MP serial 305/54 computer at the CINECA Centre (Bologna, Italy), has been used for geometry optimizations at the SCF level, using the analytical gradient technique, with checks at the MP2 level and energy calculations performed at the SCF, MP2, MP3, and MP4(SDQ) levels on the valence orbital spaces. The geometry optimizations have been performed by keeping some geometry constraints; the six structures of M(BH<sub>4</sub>)<sub>2</sub> reported in Figure 1 have led to a critical point. The nature and the characteristics of these critical points (symmetry-constrained minima) have been checked by diagonalization of the Hessian matrix. Supplementary calculations, including localization of the SCF molecular wave functions and general surface scan and geometry optimizations with a smaller basis set (the 3-21G\* one<sup>19</sup> have been performed on the GOULD-SEL 32/8705 computer at the ICQEM (Pisa, Italy).

### Results and Discussion

The alternative structures of the molecules and ions considered in this paper are plotted in Figure 1. The optimized geometry parameters are reported in Table Ia–c.

In Table IIa–c we report a selection of total energies, and in Table IIIa–c the relative energies of the structures are taken into consideration, as well as the energies of the possible products of decomposition reactions. We shall first examine the structural and conformational aspects of the complex molecules, leaving the consideration of their decomposition to the following section.

**Structure and Conformation.** Table I shows that the structures of the M–BH<sub>4</sub> fragments, for a given M, are not very sensitive to the position of the second borohydride group (compare the geometries of the (bb), (b'b), (bt) and of the (tt), (t't), (bt), (b't) structures of the M(BH<sub>4</sub>)<sub>2</sub> molecules). The internal geometry of the M–BH<sub>4</sub> fragments is also relatively insensitive to the replacement of the second BH<sub>4</sub> group with a simpler ligand, such as the H atom: compare e.g. the *R*<sub>Be–B</sub> values in (b)–HBeBH<sub>4</sub> with those in (bb)–, (b'b)–, (bt)–, and (b't)–Be(BH<sub>4</sub>)<sub>2</sub> and the same distance in (t)–HBeBH<sub>4</sub> with those in the (bt), (b't), (tt), and (t't) conformations of Be(BH<sub>4</sub>)<sub>2</sub>. Similar considerations hold for the M–B distances in HMgBH<sub>4</sub> and Mg(BH<sub>4</sub>)<sub>2</sub> as well as in the HCaBH<sub>4</sub> and Ca(BH<sub>4</sub>)<sub>2</sub> compounds at the corresponding conformations. An increase of the coordination at the M atom, i.e. the passage from (b) to (t), leads to a coherent decrease of the M–B distance of the order of 0.18–0.20 Å in the neutral compounds. Small changes in the M–B distance in compounds having the same coordination pattern are present only when M is equal to Be; in this case we have found a change in *R*<sub>Be–B</sub> of 0.03 Å in passing from the (bb) to the (b'b) conformation and of 0.01 Å in passing from the (tt) to the (t't) conformation of the borohydride dimer.

The deformation of M–BH<sub>4</sub> is larger in passing from neutral molecules to positive ions of the MBH<sub>4</sub><sup>+</sup> type. The deformations due to the positive charge decrease when M goes down along the periodic table (Be > Mg > Ca).

The internuclear distance *R*<sub>M–B</sub> in structures with bridged bonds M–H<sub>b</sub>–B has the characteristics of a nonrigid parameter: changes of 0.05–0.10 Å have a very small effect on the total energy. The use of different numerical codes to get this distance gives value varying within several hundredths of an angstrom. The flatness of this section of the potential energy surface prompted us to recalculate the M–B distance in a couple of representative conformations of M(BH<sub>4</sub>)<sub>2</sub> for each M (the (bb) and the (t't) conformations) at the MP2 level: we found a constant shortening of the distance of 0.06–0.08 Å. For structures containing a direct M–B bond, HMBH<sub>2</sub> and HMBH<sup>+</sup>, geometry optimization at the MP2 and MP3 levels gives slightly shorter M–B distances as compared to the SCF ones, while the use of a multireference approximation (NRD-CI and CIPSI) gives slightly higher values.<sup>1,20</sup>

The analysis of the regular trends found for the M–B distances could be repeated for the M–H ones as well as for the MBH angles reported in Table I. The reader is referred to a simple inspection of the values in the table.

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**Table I.** Optimized Geometry of Alternative Configurations of Borohydrides<sup>a</sup>

molecule struct, sym	<i>R</i> (M–B)	<i>R</i> (M–H <sub>t</sub> )	<i>R</i> (B–H <sub>b</sub> )	<i>R</i> (B–H <sub>t</sub> )	∠MBH <sub>b</sub>	∠MBH <sub>t</sub>
(a) M = Be						
Be(BH <sub>4</sub> ) <sub>2</sub>						
I (bb), <i>D</i> <sub>2d</sub>	1.89		1.32	1.19	51	120
II (b'b), <i>D</i> <sub>2h</sub>	1.92		1.32	1.19	52	120
III (bt), <i>C</i> <sub>s</sub>	1.92/1.74		1.32/1.26	1.19	52/64	120/180
IV (b't), <i>C</i> <sub>s</sub>	1.92/1.74		1.32/1.26	1.19	52/64	120/180
V (tt), <i>D</i> <sub>3d</sub>	1.73		1.26	1.19	64	180
VI (t't), <i>D</i> <sub>3h</sub>	1.74		1.26	1.19	64	180
HBeBH <sub>4</sub>						
VII (b), <i>C</i> <sub>2v</sub>	1.87	1.33	1.29	1.19	52	120
VIII (t), <i>C</i> <sub>3v</sub>	1.70	1.33	1.25	1.18	63	180
BeBH <sub>4</sub> <sup>+</sup>						
IX (b), <i>C</i> <sub>2v</sub>	1.83		1.40	1.18	48	118
X (t), <i>C</i> <sub>3v</sub>	1.61		1.30	1.17	62	180
XI (c), <i>C</i> <sub>2v</sub>	2.04	1.33	1.22	1.19	57	180
HBeBH <sub>2</sub>						
XII (class), <i>C</i> <sub>2v</sub>	1.90	1.34		1.19		123
HBeBH <sup>+</sup>						
XV (class), <i>C</i> <sub>∞v</sub>	1.97	1.29		1.17		180
XVI, <i>C</i> <sub>2v</sub>	1.97			1.18		113
(b) M = Mg						
Mg(BH <sub>4</sub> ) <sub>2</sub>						
I (bb), <i>D</i> <sub>2d</sub>	2.29		1.29	1.19	55	121
II (b'b), <i>D</i> <sub>2h</sub>	2.30		1.29	1.19	55	121
III (bt), <i>C</i> <sub>s</sub>	2.30/2.10		1.29/1.25	1.19	55/68	121/180
IV (b't), <i>C</i> <sub>s</sub>	2.30/2.10		1.29/1.25	1.19	55/68	121/180
V (tt), <i>D</i> <sub>3d</sub>	2.10		1.25	1.19	68	180
VI (t't), <i>D</i> <sub>3h</sub>	2.10		1.25	1.19	68	180
HMgBH <sub>4</sub>						
VII (b), <i>C</i> <sub>2v</sub>	2.33	1.71	1.29	1.19	54	121
VIII (t), <i>C</i> <sub>3v</sub>	2.13	1.72	1.25	1.19	67	180
MgBH <sub>4</sub> <sup>+</sup>						
IX (b), <i>C</i> <sub>2v</sub>	2.25		1.34	1.19	53	117
X (t), <i>C</i> <sub>3v</sub>	2.03		1.27	1.18	67	180
XI (c), <i>C</i> <sub>2v</sub>	2.58	1.68	1.21	1.17	59	180
HMgBH <sub>2</sub>						
XII (class), <i>C</i> <sub>2v</sub>	2.31	1.72		1.19		123
XIII (b), <i>C</i> <sub>2v</sub>	>5.5		1.18	1.18	60	180
HMgBH <sup>+</sup>						
XV (class), <i>C</i> <sub>∞v</sub>	2.43	1.67		1.18		180
XVI, <i>C</i> <sub>2v</sub>	2.29			1.19		114
(c) M = Ca						
Ca(BH <sub>4</sub> ) <sub>2</sub>						
I (bb), <i>D</i> <sub>2d</sub>	2.69		1.29	1.19	54	123
II (bb'), <i>D</i> <sub>2h</sub>	2.69		1.29	1.19	54	123
III (bt), <i>C</i> <sub>s</sub>	2.69/2.49		1.29/1.25	1.19/1.18	55/69	123/180
V (tt), <i>D</i> <sub>3d</sub>	2.49		1.25	1.18	69	180
HCaBH <sub>4</sub>						
VII (b), <i>C</i> <sub>2v</sub>	2.71	2.11	1.29	1.19	55	123
VIII (t), <i>C</i> <sub>3v</sub>	2.51	2.11	1.25	1.18	69	180
CaBH <sub>4</sub> <sup>+</sup>						
IX (b), <i>C</i> <sub>2v</sub>	2.60		1.30	1.19	52	120
X (t), <i>C</i> <sub>3v</sub>	2.40		1.26	1.18	66	180
XI (c), <i>C</i> <sub>2v</sub>	3.19	2.11	1.20	1.18	59	180
HCaBH <sub>2</sub>						
XII (class), <i>C</i> <sub>2v</sub>	2.77	2.11		1.19		125
HCaBH <sup>+</sup>						
XV (class), <i>C</i> <sub>∞v</sub>	2.96	2.11		1.18		180
XVI, <i>C</i> <sub>2v</sub>	2.67			1.19		122

<sup>a</sup> Distances in angstroms, angles in degrees. The terminal and bridging hydrogen atoms are indicated by H<sub>t</sub> and H<sub>b</sub>, respectively. For the (bt) and (b't) configurations of the M(BH<sub>4</sub>)<sub>2</sub> molecules, the values preceding the slash refer to the bidentate groups and those following it refer to the tridentate groups.

Passing now to the energy values, the data collected in Table III show that the increase of the level in the MP perturbation theory has little effect on the relative energies of the alternative structures of the metal borohydrides: the differences between MP3 and MP4 results never exceed 0.4–0.6 kcal/mol. The most economical MP2 approximation gives results close enough to the MP4 one; the differences in the estimate of the relative energies of different conformations never exceed 1–1.5 kcal/mol. The difference is larger, especially for the Be compounds, between SCF and MP results.

The (tt) conformation of M(BH<sub>4</sub>)<sub>2</sub> is preferred in all cases, with the exception of Be(BH<sub>4</sub>)<sub>2</sub> at the SCF level. For this last molecule MP calculations give (bb) and (tt) structures quasi-degenerate in energy. Both structures correspond to a well-defined minimum, according to the results of the diagonalization of the pertinent Hessian matrices. According to previous CEPA/DZ+P calculations<sup>4</sup> the (tt) structure of Be(BH<sub>4</sub>)<sub>2</sub> appears to be sensibly more stable (5–6 kcal/mol) than the (bb) one. We suspect that the CEPA/DZ+P computational scheme tends to overestimate the correlation energy increment of the three-center bridged fragments

**Table II.** Selection of Total Energies (in au) of Alkali-Earth-Metal Borohydrides Calculated in Several Approximations

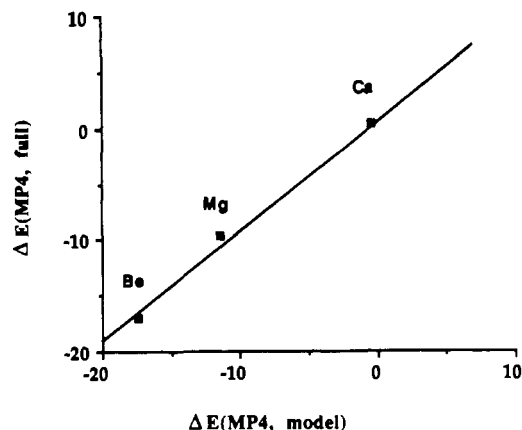
molecule struct, sym	SCF	MP2	MP3	MP4
(a) M = Be				
Be(BH <sub>4</sub> ) <sub>2</sub>				
I (bb), D <sub>2d</sub>	-68.6449	-68.9288	-68.9722	-68.9791
HBeBH <sub>4</sub>				
VIII (t), C <sub>3v</sub>	-42.2100	-42.3815	-42.4083	-42.4126
BeBH <sub>4</sub> <sup>+</sup>				
X (t), C <sub>3v</sub>	-41.3140	-41.4584	-41.4802	-41.4837
HBeBH <sub>2</sub>				
XII (class), C <sub>2v</sub>	-41.0000	-41.1215	-41.1448	-41.1494
HBeBH <sup>+</sup>				
XV (class), C <sub>∞v</sub>	-40.1188	-40.2035	-40.2227	-40.2275
BeH <sub>2</sub>	-15.7669	-15.8157	-15.8263	-15.8289
BeH <sup>+</sup>	-14.8502	-14.8752	-14.8811	-14.8827
Be	-14.5669	-14.5933	-14.6038	-14.6089
BH <sub>3</sub>	-26.3929	-26.4861	-26.5033	-26.5064
BH <sub>2</sub> <sup>+</sup>	-25.4734	-25.5312	-25.5435	
H <sub>2</sub>	-1.1313	-1.1577	-1.1631	-1.1645
(b) M = Mg				
Mg(BH <sub>4</sub> ) <sub>2</sub>				
V (tt), D <sub>3d</sub>	-253.6099	-253.8894	-253.9314	-253.9381
HMgBH <sub>4</sub>				
VIII (t), C <sub>3v</sub>	-227.1646	-227.3261	-227.3520	-227.3568
MgBH <sub>4</sub> <sup>+</sup>				
X (t), C <sub>3v</sub>	-226.3182	-226.4582	-226.4791	-226.4825
HMgBH <sub>2</sub>				
XII (class), C <sub>2v</sub>	-225.9492	-226.0673	-226.0899	-226.0945
HMgBH <sup>+</sup>				
XV (class), C <sub>∞v</sub>	-225.0949	-225.1766	-225.1959	-225.2013
MgH <sub>2</sub>	-200.7168	-200.7607	-200.7706	-200.7733
MgH <sup>+</sup>	-199.8859	-199.9098	-199.9156	-199.9176
Mg	-199.5956	-199.6176	-199.6248	-199.6274
(c) M = Ca				
Ca(BH <sub>4</sub> ) <sub>2</sub>				
V (tt), D <sub>3d</sub>	-730.0885	-730.3574	-730.3979	-730.4046
HCaBH <sub>4</sub>				
VIII (t), C <sub>3v</sub>	-703.6204	-703.7724	-703.7965	-703.8011
CaBH <sub>4</sub> <sup>+</sup>				
X (t), C <sub>3v</sub>	-702.8438	-702.9777	-702.9978	-703.0012
HCaBH <sub>2</sub>				
XII (class), C <sub>2v</sub>	-702.3776	-702.4873	-702.5080	-702.5125
HCaBH <sup>+</sup>				
XV (class), C <sub>∞v</sub>	-701.5586	-701.6343	-701.6524	-701.6577
CaH <sub>2</sub>	-677.1509	-677.1864	-677.1939	-677.1962
CaH <sup>+</sup>	-676.3830	-676.4016	-676.4056	-676.4069
Ca	-676.0338	-676.0513	-676.0579	-676.0602

Be-H<sub>b</sub>-B with respect to those of the Be-H and B-H groups. The increasing preference of the central metal atom for a larger coordination number as the atomic number increases, put in evidence by the present calculations, seems to us a real feature of the systems and not an artifact of the computation.

The (tt) structure is a minimum for all systems at all the levels of calculation. The energy difference between the (tt) and the (t't) structures is small and decreases when the atomic number increases: the (t't) conformation in the beryllium and magnesium borohydrides is a saddle point with one very small imaginary frequency, while in the Ca system there is in fact an almost free rotation connecting two equivalent (tt) conformations.

Conformations (bt) and (b't) have practically the same energy and there are good indications that the rotation connecting these two conformations is without barrier.

The conformations (bb) and (b'b) correspond to tetrahedral and square-planar conformations for the central atom; the difference between these two molecular arrangements sharply decreases, at all the levels of approximation, in passing from Be to Mg and to Ca. The (b'b) conformation is for all metals a saddle point: the negative Hessian eigenvalue corresponds to an evolution of the molecule toward the (bb) structure. Actually (b'b) for the Mg and Ca borohydrides is a super saddle point with a second negative eigenvalue in the Hessian matrix corresponding to an evolution of the system toward a (bt) structure.



**Figure 2.** Comparison of the difference in energy between the (tt) and (bb) structures of the three M(BH<sub>4</sub>)<sub>2</sub> compounds computed at the MP4 level via full calculations [ $\Delta E(\text{MP4,full})$ ] and model electron pair contributions [ $\Delta E(\text{MP4,model})$ ]. Values are in kcal/mol; Be = Be(BH<sub>4</sub>)<sub>2</sub>, Mg = Mg(BH<sub>4</sub>)<sub>2</sub>, and Ca = Ca(BH<sub>4</sub>)<sub>2</sub>.

The description of the conformational preferences of the HMBH<sub>4</sub> systems is simpler. The (t) structure, where the central atom has a coordination number equal to 4, is always preferred. There is a small increase of the (b)-(t) energy difference in passing from Be to Ca.

The MBH<sub>4</sub><sup>+</sup> systems have two different types of structure. In the (b) and (t) structures the BH<sub>4</sub> group maintains its identity; in the (c) structure there are M-H<sub>b</sub>-B bonds as in the complex borohydrides (see Figure 1). The (t) structure is preferred in all cases, but it is worth remarking that in the Be compounds there is a small difference between the (t) and the (c) structure, while this difference remarkably increases, at the MP level, in passing to Mg and especially to Ca.

The fast convergence of the Møller-Plesset series we have found in our calculations is probably due to the fact that the three- and two-center bonds of the metal borohydrides are well localized and slightly dependent on the molecular environment. We are not reporting here the details of the results of the Boys localization<sup>21</sup> we have performed for all the compounds. It is sufficient to indicate that the transferability of the main components of the localized orbitals, computed with the usual criteria,<sup>22</sup> is considerably larger than in normal organic compounds and a little larger than in complex beryllhydrides. The good localization and the small intragroup couplings made these compounds eligible for description of the correlation energy through additive schemes as already made for metal beryllhydrides.<sup>1a</sup>

We have used an empirical procedure, based on the identification of a set of typical situations in which an electron pair of the valence shell may be found in the set of compounds under consideration: B-H, M-H, M-B, and B-HM, where M represents Be, Mg, and Ca according to the case. The mean contributions to the correlation energy of these fragments have been determined by a linear least-squares procedure. We have considered it of some interest to report the values obtained for separate M atoms as well as those obtained without introducing differences due to the metal atom. The results are reported in Table IV. The results indicate again that correlation corrections at the MP3 and MP4 level slightly modify the picture given by the MP2 approximation. In passage from Be to Ca there is a decrease in the correlation of the B-H-M and M-B electron pairs. The changes are modest, however, and the set of global values for the three metal atoms is still significant. The interested reader may check that the use of these averaged values in the analyses made in the present and in the following section do not change the conclusions we have drawn. As an example, we compare in Figure 2 the prediction of the difference in energy between the (tt) and (bb) conformations

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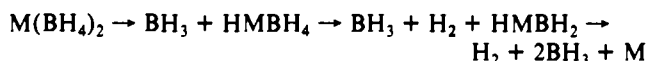
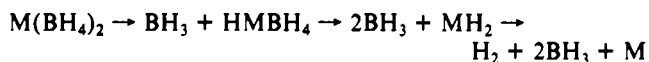
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**Table III.** Relative Energies of Alternative Configurations and Energies of Unimolecular Decay (from the Most Stable Configurations) of Alkali-Earth-Metal Borohydrides Calculated According to Several Approximations (in kcal/mol)

molecule struct, sym	SCF	MP2	MP3	MP4	molecule struct, sym	SCF	MP2	MP3	MP4
(a) M = Be									
Be(BH <sub>4</sub> ) <sub>2</sub>					BeBH <sub>4</sub> <sup>+</sup>				
I (bb), D <sub>2d</sub>	0	0.8	0	0	IX (b), C <sub>2v</sub>	7.5	12.1	11.7	11.3
II (b'b), D <sub>2h</sub>	11.3	11.7	11.0	11.1	X (t), C <sub>3v</sub>	0	0	0	0
III (bt), C <sub>s</sub>	5.5	3.0	2.6	2.9	XI (c), C <sub>2v</sub>	2.2	14.8	13.8	13.2
IV (b't), C <sub>s</sub>	5.5	3.0	2.6	2.9	(t) → BH <sub>3</sub> + BeH <sup>+</sup>	44.5	60.5	60.1	59.4
V (tt), D <sub>3d</sub>	5.5	0	0.0	0.4	(t) → H <sub>2</sub> + HBeBH <sup>+</sup>	40.1	61.0	59.2	57.5
VI (t't), D <sub>3h</sub>	7.7	2.2	2.2	2.6	HBeBH <sup>+</sup>				
(bb) → BH <sub>3</sub> + HBeBH <sub>4</sub>	26.4	39.2	38.0	37.7	XV (class), C <sub>∞v</sub>	0	5.1	5.0	3.5
HBeBH <sub>4</sub>					XVI, C <sub>2v</sub>	3.3	0	0	0
VII (b), C <sub>2v</sub>	2.7	5.6	5.4	5.1	(C <sub>∞v</sub> ) → Be + BH <sub>2</sub> <sup>+</sup>	49.3	54.7	52.3	44.9
VIII (t), C <sub>3v</sub>	0	0	0	0	BeH <sub>2</sub> → Be + H <sub>2</sub>	43.1	40.6	37.3	34.9
(t) → BH <sub>3</sub> + BeH <sub>2</sub>	31.5	50.0	49.4	48.5	HBeBH <sub>2</sub> → Be + BH <sub>3</sub>	25.2	26.4	23.7	21.4
(t) → H <sub>2</sub> + HBeBH <sub>2</sub>	49.4	64.2	63.0	61.9	BeH <sup>+</sup> → Be + H <sup>+</sup>	177.8	176.9	174.0	171.8
					BeH <sup>+</sup> → Be <sup>+</sup> + H	46.9	62.6	66.3	67.3
(b) M = Mg									
Mg(BH <sub>4</sub> ) <sub>2</sub>					MgBH <sub>4</sub> <sup>+</sup>				
I (bb), D <sub>2d</sub>	7.6	10.2	9.9	9.7	IX (b), C <sub>2v</sub>	5.8	7.5	7.4	7.2
II (b'b), D <sub>2h</sub>	8.8	11.3	11.0	10.8	X (t), C <sub>3v</sub>	0	0	0	0
III (bt), C <sub>s</sub>	4.1	5.3	5.1	5.1	XI (c), C <sub>2v</sub>	7.1	20.2	18.9	18.1
IV (b't), C <sub>s</sub>	4.1	5.3	5.1	5.1	(t) → BH <sub>3</sub> + MgH <sup>+</sup>	24.7	39.1	37.8	36.7
V (tt), D <sub>3d</sub>	0	0	0	0	(t) → H <sub>2</sub> + HMgBH <sup>+</sup>	26.4	36.3	34.6	
VI (t't), D <sub>3h</sub>	0.4	0.3	0.3	0.3	HMgBH <sub>2</sub> → Mg + BH <sub>3</sub>	-24.7	-22.8	-24.0	
(tt) → BH <sub>3</sub> + HMgBH <sub>4</sub>	32.9	48.7	47.8	47.0	MgBH <sub>2</sub> <sup>+</sup>				
HMgBH <sub>4</sub>					XV (class), C <sub>∞v</sub>	31.4	41.4	40.8	
VII (b), C <sub>2v</sub>	4.6	5.8	5.6	5.5	XVI, C <sub>2v</sub>	0	0	0	
VIII (t), C <sub>3v</sub>	0	0	0	0	(C <sub>2v</sub> ) → Mg + BH <sub>2</sub> <sup>+</sup>	47.6	58.8	58.1	(57.7)
(t) → BH <sub>3</sub> + MgH <sub>2</sub>	34.4	49.8	49.0	48.4	MgH <sub>2</sub> → Mg + H <sub>2</sub>	-6.3	-9.2	-10.9	-11.7
(t) → H <sub>2</sub> + HMgBH <sub>2</sub>	52.8	63.4	62.1	61.4					
(c) M = Ca									
Ca(BH <sub>4</sub> ) <sub>2</sub>					CaBH <sub>4</sub> <sup>+</sup>				
I (bb), D <sub>2d</sub>	15.3	17.5	17.3	17.0	IX (b), C <sub>2v</sub>	10.8	11.7	11.6	11.6
II (b'b), D <sub>2h</sub>	15.7	17.8	17.6	17.4	X (t), C <sub>3v</sub>	0	0	0	0
III (bt), C <sub>s</sub>	7.7	8.7	8.5	8.4	XI (c), C <sub>2v</sub>	34.0	47.8	47.0	46.4
V (tt), D <sub>3d</sub>	0	0	0	0	(t) → BH <sub>3</sub> + CaH <sup>+</sup>	42.6	56.5	55.8	55.2
(tt) → BH <sub>3</sub> + HCaBH <sub>4</sub>	47.2	62.1	61.6	61.0	(t) → H <sub>2</sub> + CaBH <sub>2</sub> <sup>+</sup>	57.4	67.6	66.4	
HCaBH <sub>4</sub>					CaBH <sub>2</sub> <sup>+</sup>				
VII (b), C <sub>2v</sub>	7.7	8.5	8.3	8.3	XV (class), C <sub>∞v</sub>	39.2	48.9	48.0	
VIII (t), C <sub>3v</sub>	0	0	0	0	XVI, C <sub>2v</sub>	0	0	0	
(t) → BH <sub>3</sub> + CaH <sub>2</sub>	48.1	62.7	62.3	61.8	(C <sub>2v</sub> ) → Ca + BH <sub>2</sub> <sup>+</sup>	71.4	81.4	80.0	
(t) → H <sub>2</sub> + HCaBH <sub>2</sub>	70.0	80.0	78.7	77.9	CaH <sub>2</sub> → Ca + H <sub>2</sub>	-8.9	-14.2	-17.0	-18.5
					HCaBH <sub>2</sub> → Ca + BH <sub>3</sub>	-30.8	-31.4	-33.4	-33.9

of the M(BH<sub>4</sub>)<sub>2</sub> compound calculated at the MP4 level with the data of Tables II and III (full calculation) and with electron pair contributions of Table IV. The regression line is  $y = 1.122 + 1.012x$  ( $R = 1.00$ ).

**Unimolecular Decompositions.** The introduction of the electron correlation has a not negligible effect on the evaluation of the energetics of unimolecular decomposition reactions. There are two main unimolecular decomposition patterns, reported as follows:



The SCF picture underestimates the energy necessary for the decomposition of the complex metal borohydrides M(BH<sub>4</sub>)<sub>2</sub> giving origin to BH<sub>3</sub> and HMBH<sub>4</sub>; the relatively important corrections obtained at the MP2 level (12 kcal/mol for Be, 15.8 kcal/mol for Mg, and 14.9 kcal/mol for Ca) are slightly modified by MP corrections of higher order, and the relative stability of the complex borohydride with respect to these decomposition products remains considerably high at all the levels of approximation. The same holds for the decomposition of the HMBH<sub>4</sub> molecules into BH<sub>3</sub> and MH<sub>2</sub> as well as into H<sub>2</sub> and HMBH<sub>2</sub>; the relatively high difference in energy between the undecomposed molecule and the decomposition products obtained at the SCF level is still increased by the MP2 corrections and slightly modified by MP corrections of higher order. For all the metals the decomposition pathway

**Table IV.** Electron Pair Contribution to the Correlation Energy at the Various Levels of MP Perturbation Theory (Values in kcal/mol)

group	no. of cases	MP2	MP3	MP4
Be Compounds				
BH	35	-20.13	-23.72	-24.63
BHBe	42	-24.07	-27.30	-27.60
BeH	8	-14.66	-18.21	-19.24
BeB	3	-20.30	-24.82	-24.80
std devn		4.40	5.64	6.59
Mg Compounds				
BH	35	-20.09	-23.61	-24.47
BHMg	42	-22.84	-26.05	-26.41
MgH	8	-15.45	-19.18	-20.63
MgB	3	-18.45	-22.68	-21.65
std devn		6.10	7.10	7.72
Ca Compounds				
BH	35	-19.75	-23.18	-24.01
BHCa	42	-21.63	-24.69	-25.06
CaH	8	-10.76	-13.39	-14.12
CaB	3	-17.79	-21.91	-23.28
std devn		3.01	3.80	4.34
M Compounds (M = Be, Mg, Ca)				
BH	105	-20.32	-23.63	-24.32
BHM	126	-22.88	-26.13	-26.57
MH	24	-13.50	-16.78	-17.83
MB	9	-18.53	-23.03	-23.49
std devn		6.19	7.38	8.00

of  $M(\text{BH}_4)_2$  giving origin to  $2\text{BH}_3 + \text{MH}_2$  is less unfavorable, on the basis of the values of Table III, with respect to the alternative one giving origin to  $\text{BH}_3 + \text{H}_2 + \text{HMBH}_2$ . This last molecule corresponds in all cases to a relative minimum on the energy hypersurface. In the Be case the decomposition into  $M + \text{BH}_3$  is endothermic, while for the two heavier atoms it is exothermic. The correlation corrections to these energy differences modify the numerical values without altering the conclusions.

### Conclusions

In the present paper we have examined the structures and the energetic properties of three metal borohydrides,  $\text{Be}(\text{BH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2$ , and  $\text{Ca}(\text{BH}_4)_2$ , at a comparable and fairly good degree of precision. Several conclusions may be drawn from these calculations.

The metal borohydride  $M(\text{BH}_4)_2$  is in all the three case a stable compound, with a remarkable character of internal flexibility (politopy). There are many similarities among the three hydrides, as the similarity of the structures corresponding to the critical points indicate, but also noticeable differences. The beryllium borohydride exhibits a larger propensity for a smaller coordination number, while the Mg and Ca compounds have, under this viewpoint, a similar behavior. In passage from Be to Mg and Ca there is a progressive flattening of the portion of the potential

energy hypersurface corresponding to stable structures of  $M(\text{BH}_4)_2$ .

Comparisons of the energetic results at the SCF and at the correlated levels show that correlation effects are important in each compound in assessing the general shape of the potential energy surface, as represented by the relative energies of the critical points under examination. These energetic effects are fairly well represented by the lowest level of the correlation theory, i.e. by MP2 calculations; the higher levels of the perturbation theory introduce only minor corrections. Electron correlation has less important effects on the geometrical parameters; we have performed checks only at the MP2 level, but what was said here above about the  $\text{MP}_n$  ( $n = 2-4$ ) energies at fixed geometry supports a generalization of this statement to the MP3 and MP4 levels. The correlation energy contribution, which, as we have said, depends on the geometry, may be easily modeled in terms of additive group contributions, with good precision, at every level of the Møller-Plesset theory. In addition these group contributions are relatively insensitive to the chemical nature of the metal atom. These characteristics confirm what was observed in a preceding occasion for other metal hydrides<sup>1</sup> and make it possible to utilize for future calculations on similar compounds a simpler computational procedure: a SCF calculation with a good basis set, followed by the use of correlation group contributions.

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## Multiple Bonding in Perfluorodiphosphene (FPPF) and Perfluorodiphosphenylidene (PPF<sub>2</sub>)

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Seven energy minima for the  $\text{P}_2\text{F}_2$  system have been determined by means of ab initio self-consistent-field (SCF) and single- and double-excitation configuration interaction (CISD) analytic gradient methods using basis sets as large as triple- $\zeta$  plus double polarization (TZ2P). Detailed analyses of the bonding nature of these structures have been carried out, with an emphasis on the P-P bond. In particular, we find one structure corresponding to a planar PPF<sub>2</sub> configuration that contains a P-P triple bond, yielding a central phosphorus atom with a formal valence of 5. Our results indicate that this hypervalence is primarily the result of the ionic character of the P-F bonds, and the triple bond is comprised mainly of phosphorus s and p orbitals.

### 1. Introduction

Interest in polyphosphorus chemistry has risen steadily since 1950.<sup>1</sup> In particular, a large number of diphosphenes<sup>2-4</sup> have been synthesized since Yoshifuji and co-workers synthesized a true "phosphabenzene" in 1981.<sup>5</sup> Experimentally only diphosphenes with large substituent groups have been isolated, and most of these assume a planar trans configuration in the crystalline state with a PPX (X = C, N) angle of 102-109°. The parent diphosphene,  $\text{P}_2\text{H}_2$ , has been observed experimentally via its mass spectrum in the pyrolysis of diphosphene,  $\text{P}_2\text{H}_4$ .<sup>6-8</sup> Both the singlet and triplet potential energy surfaces of  $\text{P}_2\text{H}_2$  have been carefully studied by

theoretical methods.<sup>9-18</sup>  $\text{P}_2\text{H}_2$  is found to have a singlet trans bent ground state with a cis isomer only slightly higher in energy (3-4 kcal/mol) and a planar structure with  $\text{H}_2\text{PP}$  linkage about 25-30 kcal/mol higher than the trans isomer. On the triplet potential energy hypersurface, a skewed HPPH and a pyramidal  $\text{H}_2\text{PP}$  appear approximately 17 and 25 kcal/mol, respectively, above the singlet, *trans*-HPPH isomer. Although the effect of amino substituents was studied by Schoeller and Staemmler,<sup>19</sup> no one has yet considered the fluorine-substituted species  $\text{P}_2\text{F}_2$ . Experimentally, only its "parent" radicals  $\text{PF}_2$ <sup>20-22</sup> and  $\text{PF}_2$ <sup>23,24</sup> are

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