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The Structures of the hypho-Compounds $B_5H_{12}^-$ and B_6H_{14}: Application of the Combined Ab Initio/IGLO/NMR Method[†]

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ABSTRACT

Ab initio and NMR chemical shift (IGLO) calculations on the TZP//MP2/6-31G level suggest a* C_s (**1c**)*, or the closely related* C_1 (**1d**) *structure, rather than the proposed* C_{2v} (**1a**) *geometry for hypho-*$B_5H_{12}^-$*. The two equivalent* C_s *forms interconvert rapidly with a barrier of ca 5 kcal/mol. For hypho-*B_6H_{14} (**2**)*, at least six isomers examined lie within ca 7 kcal/mol in energy suggesting fluxional behavior, but none of the geometries (including the current proposals in the literature) reproduces the experimental chemical shifts.*

INTRODUCTION

Ab initio molecular orbital theory is increasingly successful in predicting molecular structures and establishing their accuracy [1–3]. We have been using the combined ab initio/IGLO/NMR method to distinguish among structural alternatives for numerous carbocations [2] and boron hydrides [3]. A systematic study of boron hydrides and carboranes showed that experimental ^{11}B chemical shifts can be reproduced computationally with remarkable accuracy (ca 2 ppm) provided accurate structures are employed. Geometries optimized ab initio at a correlated level (MP2/6-31G*) generally give significantly better results than the best available experimental structures [3c,d].

We have now applied the ab initio/IGLO/NMR method to the binary hypho-boranes $B_5H_{12}^-$ (**1**) and B_6H_{14} (**2**). According to Wade's rules [4], polyhedral compounds may be classified as closo, nido, arachno, and hypho with respect to the number of skeletal electrons. For hypho-species ($2n + 8$ framework electrons), open, flexible structures are to be expected. In the case of polyhedral boron compounds, this has been confirmed for various Lewis-base adducts, e.g. $B_6H_{10}L_2$ ($L = PR_3$) [5], but no structural information is available for any binary hypho-boron hydride.

$B_5H_{12}^-$ was the first hypho-borane to be synthesized (in 1975) [6]. Its ^{11}B NMR spectrum, which displays two signals in a 1 : 4 ratio, was interpreted in terms of a pyramidal structure with four basal boron atoms. Fluxional behavior is shown by the observation of but a single proton resonance at higher temperatures. For the static, low-temperature form, structure **1a** (C_{2v} symmetry, cf. Figure 1) was proposed [7].

More recently (1988), a species assigned the B_6H_{14} composition was synthesized via dimerization of in situ generated B_3H_7 [8]. The compound exhibits chemical reactions expected for B_3H_7 (e.g., formation of B_3H_7L Lewis base adducts), but the observed ^{11}B NMR spectrum (2 signals in a 2 : 1 ratio) together with the dynamic behavior (only one proton resonance) are not consistent with monomeric B_3H_7.

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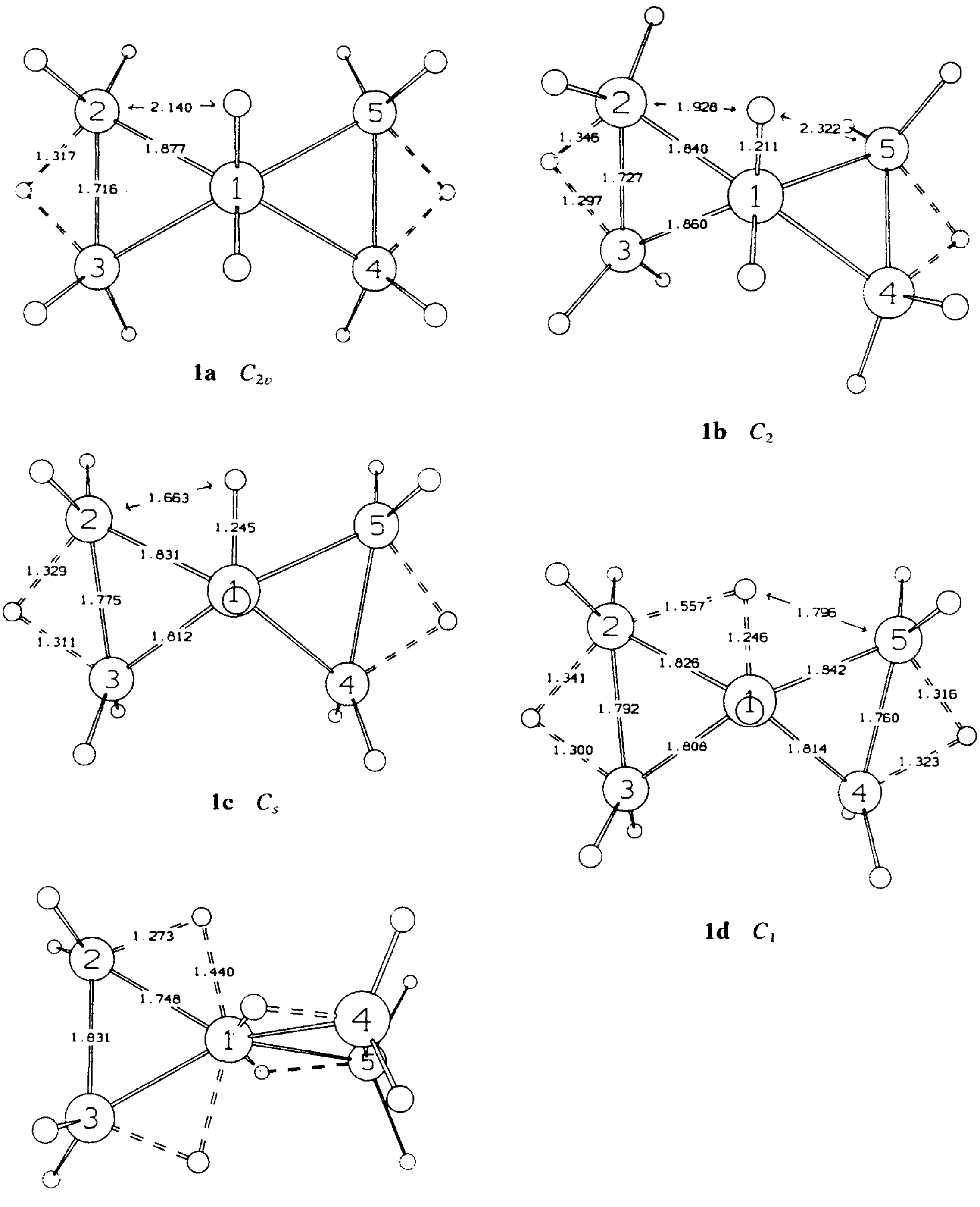


1a C_{2v}

1b C_2

1c C_s

1d C_1

1e D_{2d}

FIGURE 1 MP2/6-31G* Optimized Structures of $B_5H_{12}^-$ (bond distances in Å)

Two prior ab initio studies of B_6H_{14} [9, 10] located at least three isomers (cf. **2a–c** in Figure 2) rather close in energy (within ca 6 kcal/mol). While calculations at the CPF//DZP level (including electron correlation) favored the tris-diborane structure **2a** [9], inclusion of zero-point corrections results in nearly equal energies for **2a** and the C_{2h} "trans dimer" **2b** (MP2/6-31G*//3-21G + ZPE (3-21G) level) [10]. No comparison of these theoretical results with experimental data was possible, and the structure could not be established definitely. Hence, the combined ab initio/IGLO/NMR method seemed particularly suited to provide more information about these B_6H_{14} alternatives.

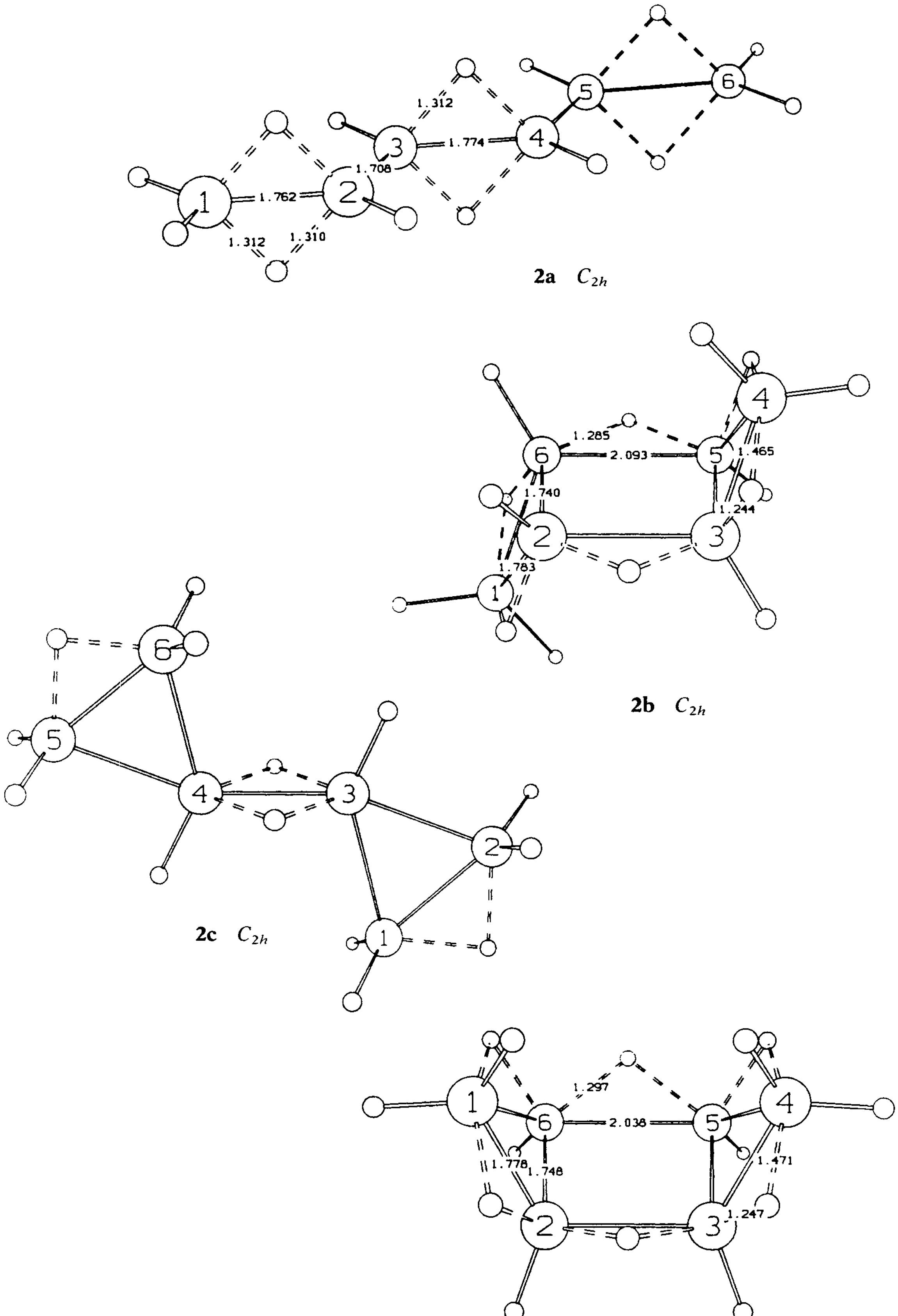
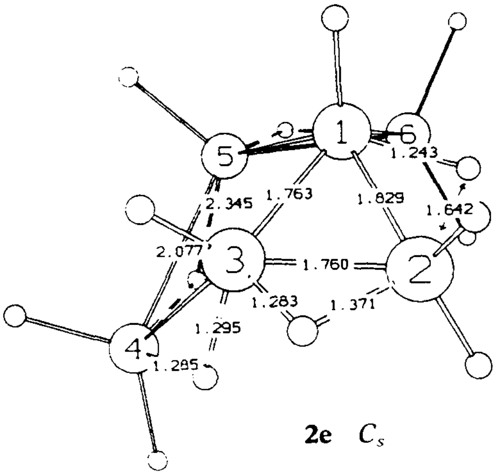
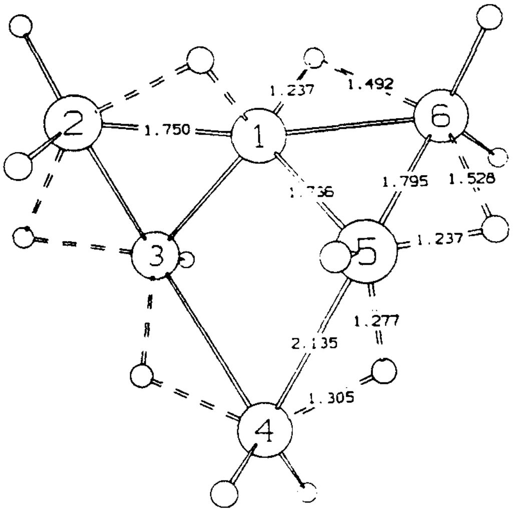


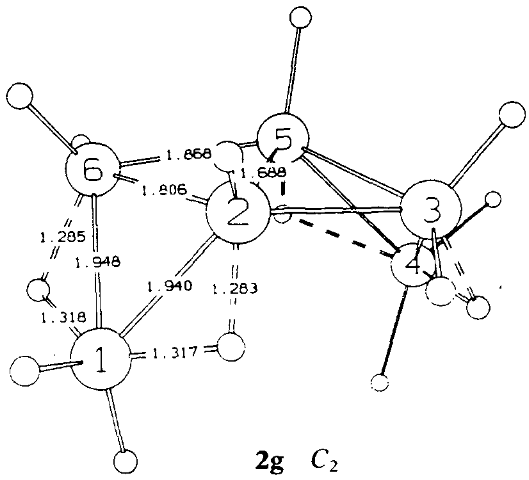
FIGURE 2 MP2/6-31G* Optimized B_6H_{14} Isomers (bond distances in Å). **2c**: 3-21G from [10]



2e C_s



2f C_2



2g C_2

FIGURE 2 (*continued*)

METHODS

Geometries were fully optimized in the given symmetry at the HF/6-31G* and at the correlated MP2(Full)/6-31G* levels [11] employing the Gaussian 88 and CADPAC program packages [12]. The nature of each stationary point was probed by frequency calculations at the HF/6-31G* level. For the isomers of **1**, single point calculations at MP4sdtq/6-31G* (frozen core approximation) were performed with the MP2/6-31G* geometries. Chemical shifts were calculated using the IGLO (Individual Gauge for Localized Orbitals) method [13] employing the MP2/6-31G* geometries and a Huzinaga basis of Triple Zeta + Polarization quality (notation II'//MP2/6-31G*) contracted as follows: B 9s5p1d {51111,2111,1} (d-exponent 0.5), H 3s {21} [13b].

The MP2/6-31G* optimized structures of the various $B_5H_{12}^-$ (**1a–1e**) and B_6H_{12} (**2a–2g**) isomers are presented in Figures 1 and 2. The numbering system and key geometric parameters are included. Absolute and relative energies are given in Tables 1 and 2, IGLO ^{11}B chemical shifts are summarized in Tables 3 and 4.

TABLE 1 Absolute (−a.u.) and Relative (kcal/mol) Energies of $B_5H_{12}^-$ Structures **1a–1e**

Compd.	*Symmetry*	*ZPE*[a]	*MP2/6-31G* //MP2/6-31G**	*MP4sdtq/6-31G* //MP2/6-31G**	E_{rel}[b]
1a	C_{2v}	86.08 (2)	130.83107	130.89154	7.6
1b	C_2	86.29 (1)	130.83609	130.89611	5.0
1c	C_s	86.42 (1)	130.84627[c]	130.90427	−0.1
1d	C_1	86.54 (0)	130.84626[c]	130.90436	0.0
1e	D_{2d}	85.33 (0)	130.82997	130.88872	8.7

[a] Zero point energy at the 6-31G* level; in parentheses: number of imaginary frequencies.

[b] Relative energy at the MP4sdtq/6-31G*//MP2/6-31G* + ZPE (6-31G*) level; the zero point energies have been scaled by 0.89 as recommended in [11].

[c] Despite large geometric differences (Figure 1), **1c** and **1d** have essentially the same energy at the MP2 level (the transition state **1c** even seems to be slightly more stable than the minimum **1d**, but this may be due to the termination criteria of the optimization algorithm).

TABLE 2 Absolute (−a.u.) and Relative (kcal/mol) Energies for B_6H_{14} Isomers **2a–2g**[a]

Compd.	*Symmetry*	*ZPE*[b]	*MP2/6-31G* //MP2/6-31G**	E_{rel}[c]
2a	C_{2h}	104.32 (0)	156.68735	7.7
2b	C_{2h}	102.78 (0)	156.69307	2.8
2d	C_{2v}	103.50 (0)	156.69850	0.0
2e	C_s	103.72 (0)	156.69556	2.0
2f	C_2	102.93 (0)	156.68750	6.4
2g	C_2	103.81 (0)	156.69218	4.2

[a] The geometry of isomer **2c** was not refined at higher levels, for energies see [9, 10].

[b] Zero point energy at the 6-31G* level; in parentheses; number of imaginary frequencies.

[c] Relative energy at the MP2/6-31G*//MP2/6-31G* + ZPE (6-31G*) level; the zero point energies have been scaled by 0.89 as recommended in [11].

RESULTS AND DISCUSSION

$B_5H_{12}^-$

The proposed C_{2v} form **1a** [7] is not a minimum on the potential energy surface (PES) but has two imaginary frequencies denoting a "hilltop." Reduction of the symmetry leads to **1b** and **1c** with C_2 and C_s point groups, respectively. Both turn out to be transition states (1 imaginary frequency each). The minimum, **1d**, lacks all symmetry (C_1 point group). Isomer **1c** is the transition state for the degenerate rearrangement of the apical bridging hydrogen H12, which interconverts the **1d** enantiomers. The situation resembles that in B_5H_{11} (see below) [3a], however, the barrier is much smaller in **1**: **1c** is only 0.1 kcal/mol less stable than **1d** at the MP4sdtq/6-31G*//MP2/6-31G* level. Inclusion of the 6-31G* zero point energy favors the transition

TABLE 4 Averaged[a] IGLO ^{11}B Chemical Shifts (II′//MP2/6-31G* level) for B_6H_{14} Isomers[b]

Compd.	*Symmetry*	*IGLO* δ ^{11}B[a] *(4B)*	*(2B)*
2a	C_{2h}	20.4	25.5[c]
2b	C_{2h}	−38.7	−5.6
2d	C_{2v}	−40.8	−7.8
2e	C_s	−11.4	−40.3[d]
2f	C_2	−11.9	−10.6[e]
2g	C_2	−27.2	−18.5[f]
Experiment [8]		*−10.7*	*−30.4*

[a] Averaged values assuming fluxional motion resulting in a 2:1 signal ratio.

[b] The chemical shifts of isomer **2c** were not calculated at the same high level, see text.

[c] Scrambling of the terminal B_2H_5 groups assumed, cf [9].

[d] Scrambling via **2e** ⇌ **2b** ⇌ **2e′** assumed (see text).

[e] Rapid equilibrium with the related **2e** assumed.

[f] Scrambling via **2g** ⇌ **2d** ⇌ **2g′** assumed.

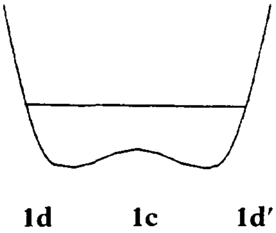
TABLE 3 IGLO ^{11}B Chemical Shifts (II′//MP2/6-31G* level) for $B_5H_{12}^-$ Structures[a]

Compd.	*Symmetry*	*B1*	*B2*	*B3*	*B4*	*B5*	ϕ*B(2–5)*[b]
1a	C_{2v}	−57.1					−2.9
1b	C_2	−56.6	−9.2	1.3	−9.2	1.3	−4.0
1c	C_s	−59.6	−7.3	−19.2	−19.2	−7.3	−13.3
1d	C_1	−58.9	−6.8	−13.2	−25.0	−8.4	−13.4
Experiment [6]		*−57.6*					*−15.9*

[a] Isomer **1e** is not a "structural candidate" (see text); δ = 10.1 (B1), −34.7 (B2–5).

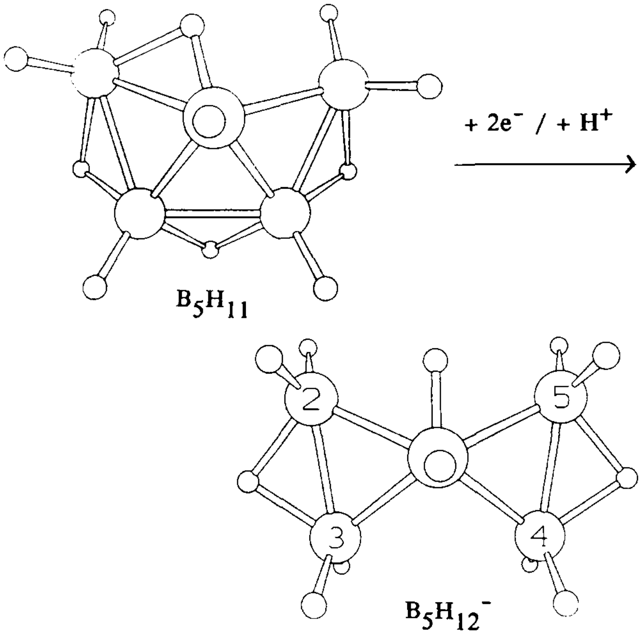
[b] Averaged values (except **1a**) assuming fluxional motion (see text).

state with respect to the minimum and even reverses the relative order of **1c** and **1d**! Hence, the following shallow double-minimum potential is suggested, which results in an overall (averaged) C_S symmetry for the vibrational ground state of **1**:



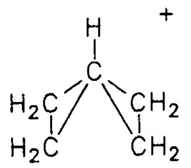
Transition state **1b** is involved in the interchange of the bridging and the terminal apical hydrogens. The H-bridge between B1 and B2 in **1d** is transformed into an H-bridge between B1 and B4. Due to the shallow PES (see above), **1b** represents the barrier between two equivalent C_S forms. Since the barrier is only ca 5 kcal/mol (MP4/6-31G* level), these interconvert rapidly on the NMR time scale. This explains the single signal for the four basal boron atoms, observed experimentally.

The IGLO ^{11}B chemical shift data in Table 3 underscore these conclusions: Only **1c** and **1d** give IGLO values in accord with experiment. In contrast, the proposed C_{2v} form **1a** can be excluded ($\Delta\delta$ = 13 deviation for B(2–5)). Hypho-$B_5H_{12}^-$ is structurally related to arachno-B_5H_{11}. Formal reduction by two electrons results in cleavage of the B3B4 bond (see Reaction 1).



REACTION 1

$B_5H_{12}^-$ **1** is isoelectronic with the intermediate **3** involved in the carbon scrambling of the cyclopentyl cation [14]:



3

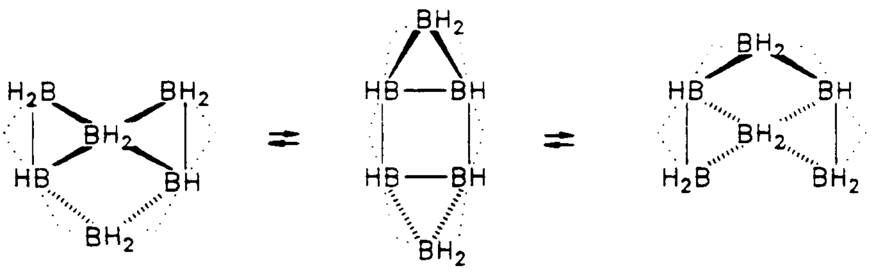
Due to the lack of bridging hydrogens, the carbon analogue (**3**) is symmetrical; the C_{2v} form is a minimum [14b].

We investigated another isomer of $B_5H_{12}^-$, **1e**, in D_{2d} symmetry (Figure 1). This is isoelectronic with spiropentane and contains a boron atom without terminal hydrogens. Since the presence of terminal hydrogens for both kinds of boron atoms is shown by decoupling experiments [6], **1e** is not a $B_5H_{12}^-$ "structural candidate." But interestingly, it is a minimum only 9 kcal/mol above **1d**. The IGLO δ ^{11}B values for B1 and B(2–5) are 10.1 and −37.4, respectively.

B_6H_{14}

Our first orientating IGLO calculations (DZ basis) employed the 3-21G geometries of **2a–2c**, the three lowest energy candidates from previous theoretical calculations [10]. The "corner-corner dimer" **2c**, which is the least stable of these isomers (ca 6 kcal/mol higher in energy), gave positive IGLO δ ^{11}B values (14.4, 13.2, 3.4), whereas the experimental ^{11}B chemical shifts have a *negative* sign (−10.7, −30.4 [8]). The tris-diborane structure **2a** (IGLO DZ//3-21G: δ = 19.4, 19.9, 23.6), which has δ ^{11}B values similar to that of diborane (16.6 [15]), can be excluded similarly. The "edge-edge dimer" **2b**, on the other hand, gives IGLO values closer to the region observed experimentally (DZ//3-21G: δ = 2.3, −27.8). Refinement at the higher II'//MP2/6-31G*), level affords IGLO chemical shifts of −5.6 and −38.7 for B(1, 4) and B(2, 3, 5, 6), respectively (see Table 4). While these numerical values are in moderate agreement with experiment, the "intensity ratio" of the two signals is reversed! The theoretical values −5.6 (2B) and −38.7 (4B) compare to the experimental ones, −10.7 (4B) and −30.4 (2B), resulting in deviations of $\Delta\delta$ = 25 and 28. Hence, none of the structures proposed in the literature reproduces the experimental chemical shifts.

Our search for other possible B_6H_{14} isomers located several new minima. The four most favorable (**2d–2g**, see Figure 2) are rather close in energy (within ca 7 kcal/mol, see Table 2). Another edge-edge dimer, **2d**, with syn-oriented B_3-moieties (C_{2v} symmetry), is the most stable of all isomers considered so far (ca 3 kcal/mol lower in energy than **2b**). As with **2b**, the computed chemical shifts for **2d** have the wrong intensity ratio: δ = −7.8 (2B) and −40.8 (4B).



2e **2b** **2e'**

REACTION 2

Isomer **2e** (C_s symmetry) can arise from **2b** by the movement of one BH_2 group over the central four-membered ring. Since we calculate **2b** to be only ca 0.8 kcal/mol higher in energy than **2e**, a rapid equilibrium affords a plausible scrambling mechanism averaging B1 and B4 [16] (see Reaction 2). The IGLO ^{11}B chemical shifts, averaged accordingly, do have the correct intensity ratio, $\delta = -11.4$ (4B) and -40.3 (2B), and show the best agreement of all B_6H_{14} isomers of this study with the experimental values. However, two problems remain: first, the maximum deviation from experiment, $\Delta\delta$ ca 10, is considerably larger than we have found for any other borane at the same level ($\Delta\delta$ ca 2) [3c,d]. Second, **2e** is not the lowest-energy form; **2d** is more stable by ca 2 kcal/mol. Hence, we are not convinced that **2e** represents the actual structure of B_6H_{14}.

The structure of **2f** is rather similar to that of **2e**, but is more than 4 kcal/mol higher in energy. Isomer **2g** (C_2 symmetry) represents the 4204 structure (styx formulation) proposed by Lipscomb in 1963 [16], but is ca 4 kcal/mol less stable than the C_{2v} form **2d**.

In summary, none of the B_6H_{14} isomers included in this study reproduces the experimental ^{11}B chemical shifts with the usual accuracy [3]. The size of the molecule (20 atoms!) complicates the search for further structural candidates. It may well be that the global minimum has not yet been found. A promising approach might be a molecular dynamics simulation (e.g. employing the density functional method [17]).

Several questions remain unsolved: Can B_6H_{14} be described by a single static structure (which may undergo degenerate tautomerization) or are two or more rapidly equilibrating isomers involved? Is it possible that even higher B_3H_7 aggregates, e.g., trimers or polymers, are actually present in solution [18]? More experimental and theoretical work would be helpful to establish the detailed nature of this compound.

CONCLUSION

The hypho-boranes $B_5H_{12}^-$ and B_6H_{14} are indicated to be highly fluxional molecules. $B_5H_{12}^-$ has an open structure related closely to B_5H_{11}, but with a triply bridging apical hydrogen. Two equivalent C_s structures interconvert rapidly with a very low activation barrier (5 kcal/mol) resulting in effective C_{2v} symmetry on the NMR time scale. The potential energy surface of B_6H_{14} is characterized by numerous minima with similar energy. Since none of the isomers considered reproduces the experimental chemical shifts, the actual nature of this compound is still in doubt.

ACKNOWLEDGMENTS

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[16] A referee noted that this simple way of averaging the chemical shifts of equilibrium geometries might not be applicable here. On a flat PES, the vibrationally averaged structures may not be near the minima, and one should average over the whole zero-point motion. We did not locate the transition states connecting the various B_6H_{14} isomers. However, the geometrical changes along the possible reaction pathways are considerable (e.g. going from **2e** to **2b** requires the cleavage of the B1B3 and B1B5 contacts as well as the formation of a contact between B3 and B5). Hence, we would expect the barriers to be sufficiently high (i.e. higher than the vibrational ground state levels) to permit the "classical" treatment we have applied.

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