

$B_{11}H_{14}^-$ : A Nido Cage with No H...H InteractionPhillipe Maitre,<sup>†</sup> Odile Eisenstein,<sup>\*†</sup> Demetrius Michos,<sup>‡</sup> Xiao-Liang Luo,<sup>‡</sup> Allen R. Siedle,<sup>§</sup> Linda Wisnieski,<sup>‡</sup> Kurt W. Zilm,<sup>‡</sup> and Robert H. Crabtree<sup>\*‡</sup>*Contribution from the Laboratoire de Chimie Théorique, Bâtiment 490, Université de Paris-Sud, F-91405 Orsay, France, 3M Corporate Research Laboratory, St. Paul, Minnesota 55144, and Chemistry Department, Yale University, New Haven, Connecticut 06511*

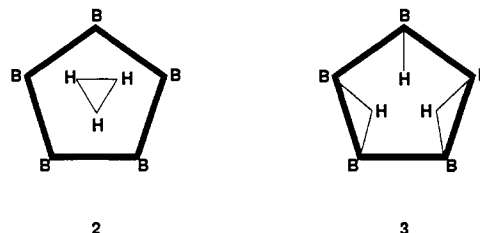
Received March 1, 1993

**Abstract:** The structural and dynamic properties of the  $B_{11}H_{14}^-$  anion has been investigated by solution and solid-state NMR methods and by HF *ab initio* calculations, focusing on the interaction between the three endo hydrogens ( $H_{endo}$ ).  $T_1$  and isotope perturbation of resonance studies do not support the nonclassical structure that has been considered for the  $H_{endo}$ , in which a triangular ( $H_{endo}$ )<sub>3</sub> caps the pentagonal face of the nido  $B_{11}H_{11}$  cage. The experimental and theoretical results are in agreement with a classical ground-state structure with no H...H interactions. Full gradient optimization of 1-CB<sub>10</sub>H<sub>14</sub> and  $B_{11}H_{14}^-$  shows that the structure is similar to that suggested by Shore *et al.* with one terminal and two edge-bridging  $H_{endo}$ . The transition state for the hydrogen exchange has been identified and shown to lie only 1.4 kcal/mol higher than the ground state; it too lacks H...H interactions. The reason for the low barrier is that the  $H_{endo}$  centers remain equally bonded to the boron atoms during the rearrangement.

## Introduction

In this paper we attempt to resolve a long-standing puzzle over the structure of the  $B_{11}H_{14}^-$  anion (1) which has taken on a new importance recently with the discovery of  $H_2$  complexes<sup>1</sup> and the suggestion<sup>2</sup> that  $H_3$  complexes might be stable. In 1961, Lipscomb<sup>3a</sup> suggested that 1 might be considered as being derived, at least in a formal sense, from the  $H_3^+$  ion and  $B_{11}H_{11}^{2-}$  (2). Parshall, Muetterties, *et al.*<sup>3b</sup> then studied 1 by NMR and noted certain anomalies consistent with the trihydrogen structure 2. In particular they found an abnormally low  $J(B,H)$  coupling between the endo hydrogens ( $H_{endo}$ ) and boron. In addition, the 2:1 ratio of terminal to bridging endo hydrogens expected for 3 was not seen; instead a single, somewhat broad resonance was seen at all accessible temperatures. Fritchie<sup>3c</sup> determined the X-ray crystal structure of the  $B_{11}H_{14}^{2-}$  anion and found that the two hydrogens bridge in an entirely conventional way. He proposed that 1 might have the conventional structure 3, containing terminal and bridging endo hydrogens. In 1988, Shore *et al.*<sup>4</sup> carried out an X-ray crystallographic study on the  $[PMe_3H]^+$  salt of 1 which showed the conventional structure 3.<sup>5</sup> Because X-ray diffraction detects electron density and not nuclear positions, it remained possible that the protons were closer together than suggested by the separation of the electron density maxima reported by Shore *et al.*

In 1984, Kubas<sup>1a</sup> reported the first  $H_2$  complex, of which there are now hundreds of examples.<sup>1b</sup> Burdett<sup>2</sup> suggested that an  $H_3$  complex might be isolable, and we have attempted to prepare transition metal examples. So far all candidate structures have proved to be dihydrogen hydrides. In one case,  $Re(CO)_2(H_2)(H_2)L_3^+$  ( $L = PMe_2Ph$ ), we were able to present evidence<sup>6</sup>



that an  $H_3$  structure, probably of the "open", or H-H-H, type, is an intermediate or transition state in the fluxional exchange between classical and nonclassical sites.

In this work we have used NMR spectroscopy and HF *ab initio* calculations to obtain further insight into the structure and dynamic behavior of  $B_{11}H_{14}^-$ .

## NMR Data

The  $^1H$  NMR of 1 at 298 K and 250 MHz displays two broad overlapping signals: the first, resonance A, at  $\delta$  0.42–2.62 with intensity 11, is assigned to the exo hydrogens of the nido cluster. The second, resonance B, at  $\delta$  -3.67 and with intensity 3 and half-width of 100 Hz, is assigned to the endo hydrogens.

$T_1$  data have sometimes proved useful in assigning structures of nonclassical hydrides, because closely spaced ( $<1 \text{ \AA}$ ) protons relax each other very effectively.<sup>7</sup> We have therefore measured the  $T_1$  values for A and B in the range 188–298 K (Table I and Figure 1). Unfortunately, two problems prevented a useful interpretation of the data. First, the moment of inertia of 1 is so small that the  $T_1$  minimum was not attained, so detailed quantitative interpretation by our usual method<sup>7</sup> is not possible. The data show only that the relaxation rates of both signals are very similar and that the endo hydrogens relax less rapidly than the exo ones. The second problem is that B has a large boron-hydrogen dipole-dipole contribution<sup>8</sup> to the relaxation of B-H protons, so any H...H interactions would not be dominant. The lower  $T_1$  value for the endo protons is thus most simply interpreted as a result of the longer B-H distances expected for bridging

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<sup>†</sup> Université de Paris-Sud.

<sup>‡</sup> 3M Corporate Research Laboratory.

<sup>§</sup> Yale University.

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(5) For simplicity, in 2 and 3 we show only the  $B_5$  ring which adjoins the missing vertex.

(6) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912.

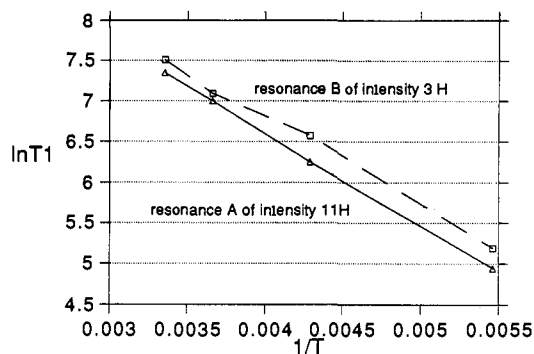


Figure 1. Plot of  $\ln T_1$  vs  $1/T$  for  $[\text{Ph}_4\text{P}][\text{B}_{11}\text{H}_{14}]$ .

Table I. The  $T_1$  Data for **1** in  $\text{CD}_2\text{Cl}_2$  at 250 MHz

temp, K	$T_1(\text{A})$ , ms	$T_1(\text{B})$ , ms
298	1552	1823
273	1097	1203
233	518	716
183	140	179

Table II. The IPR Data for **1** in  $\text{CD}_2\text{Cl}_2$  at 250 MHz Showing the Large Temperature-Dependent Isotope Shifts Consistent with Structure **3**

temp, K	$\delta(\text{HD}_2)$ , ppm	$\Delta\delta(\text{HD}_2)$ , ppm	$\delta(\text{H}_2\text{D})$ , ppm	$\Delta\delta(\text{H}_2\text{D})$ , ppm	$\delta(\text{H}_3)$ , ppm
298	-3.520	0.146	-3.600	0.066	-3.666
242	-3.528	0.215	-3.648	0.095	-3.743

rather than terminal B-H groups. The minimum  $T_1$  value expected from B-H DD relaxation in a normal terminal B-H group ( $r = 1.08 \text{ \AA}$ ) is ca. 30 ms at 250 MHz. Extrapolating Figure 1, implies that the minimum should be reached at about 140 K, below our accessible range of temperatures. Again by extrapolation, a  $T_1(\text{min})$  for the B resonance of ca. 50 ms would be a reasonable estimate. If so, very short ( $<1 \text{ \AA}$ ) H-H distances can clearly be excluded; longer, but still partially bonding, H...H distances are still possible, however.

Another method that has proved useful in distinguishing symmetrical structures such as **2** from unsymmetrical ones such as **3** is isotopic perturbation of resonance (IPR).<sup>9</sup> This operates in the high-temperature limit of fluxionality on the partially deuterated sample and relies on isotopic fractionation between sites having different vibrational frequencies leading to a temperature-dependent shift of the averaged resonances for the different isotopomers. In this case, partial deuteration of the endo hydrogens is easily affected by treatment with MeOD, a process which leaves the exo hydrogens unaffected. The B resonance of each isotopomer was readily distinguished once the  $^{11}\text{B}$  nuclei were decoupled. Table II shows how the temperature dependence of the chemical shift even of the  $\text{d}^0$  resonance is unexpectedly large. This may result from a relatively flat potential energy surface (see Theoretical Study), leading to a variety of closely related structures being differentially populated at different temperatures. Taking the  $\text{d}^0$  resonance as the reference point, the  $\text{d}^1$  and  $\text{d}^2$  resonances do indeed show substantial temperature-dependent shifts. This is much more consistent with the conventional structure **3** than with the symmetrical structure **2**.

Solid-state NMR studies of **1** by the methods described by Zilm *et al.*<sup>10</sup> show no sign of any short  $\text{H}_{\text{endo}}\cdots\text{H}_{\text{endo}}$  distance, but distances greater than  $1.2 \text{ \AA}$  might not be detected. These observations are consistent with structure **3**.

Attempts to grow crystals of a size suitable for neutron diffraction studies were only successful for the  $\text{PPh}_4^+$  salt. Unfortunately, preliminary analysis of the X-ray data on this derivative by Professor J. A. K. Howard showed that the boron cages were highly disordered, and although neutron data were collected, no useful analysis in terms of the location of  $\text{H}_{\text{endo}}$  has yet proved possible.

### Theoretical Study

The spectroscopic analysis gave reasonable but only circumstantial evidence that structure **3** was more probable. It did not explain the very rapid fluxionality, however, which was one of the properties that led Parshall *et al.* to postulate a trihydrogen structure.<sup>3b</sup> Furthermore, even if the ground-state structure were classical, a trihydrogen transition state of type **2** might explain the rapid fluxionality. For these reasons we have undertaken a theoretical study of the structure and dynamics of this cage, focusing especially on the bonding properties of the  $\text{H}_{\text{endo}}$  centers.

Apart from limited examples mentioned below, previous calculations on borane clusters have mostly involved semiempirical methods,<sup>11</sup> which did not permit an accurate determination of the geometry of the cage. In particular, no theoretical studies which predict the preferred location and exchange mechanism of  $\text{H}_{\text{endo}}$  are available.

(a) **Method and Model of Calculations.** It is well-known that *ab initio* descriptions of an anion involve complications which are not encountered in the studies of the isoelectronic neutral species.<sup>12</sup> A neutral cluster  $1\text{-CB}_{10}\text{H}_{14}$  (**4**) isoelectronic with the target anion  $\text{B}_{11}\text{H}_{14}^-$  (**5**) has therefore been chosen for the exploration of the potential energy surface (PES). The salient results on the neutral species were then confirmed by selected additional calculations on  $\text{B}_{11}\text{H}_{14}^-$ .

Previous studies on anionic boranes and neutral isoelectronic carborane cages led us to assume that the location of the three  $\text{H}_{\text{endo}}$  on the pentagonal open face of the nido cluster would not be significantly affected by the nature of the net ionic charge on the cage. For example, the geometries of the two species, the closo neutral  $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$  and the anionic  $\text{B}_{12}\text{H}_{12}^{2-}$  icosahedral clusters, closely related to our neutral model  $1\text{-CB}_{10}\text{H}_{14}$  (**4**) and to the target compound  $\text{B}_{11}\text{H}_{14}^-$  (**5**), respectively, have been optimized by Green *et al.*,<sup>13</sup> at the RHF level with a double- $\zeta$  3-21G basis set, who found that the B-B and B-H distances are similar. We can therefore expect that the B-B and B- $\text{H}_{\text{exo}}$  distances may also be similar in the two nido clusters **4** and **5**. Moreover, changing the nature of the atom at the apex opposite to the open pentagonal face should not affect the symmetry of the cage and should have no appreciable effect on the position of the remote  $\text{H}_{\text{endo}}$  centers. We thus believe that the nature of the extrema (minimum and transition state)<sup>14</sup> should be similar in the neutral  $1\text{-CB}_{10}\text{H}_{14}$  (**4**) and the anionic  $\text{B}_{11}\text{H}_{14}^-$  (**5**) nido cages.

All *ab initio* calculations were done with the GAMESS<sup>15a</sup> or HONDO-7<sup>15b</sup> program packages. Because of the size of the systems, we used an RHF wavefunction with a double- $\zeta$  3-21G

(11) See, for instance: O'Neill, M. E.; Wade, K. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 1, p 1. Lipscomb, W. N. *Acc. Chem. Res.* **1973**, *6*, 8 and references therein. Dixon, D. A.; Kleier, D. A.; Halgren, T. A.; Hall, J. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226.

(12) Simons, J.; Jordan, K. D. *Chem. Rev.* **1987**, *87*, 535.

(13) Green, T. A.; Switendick, A. C.; Emin, D. *J. Chem. Phys.* **1988**, *89*, 6815.

(14) However, it should be remembered that, in carboranes, the carbon atom should be located at the site of lowest connectivity. Consequently, structure **4** is not necessarily the absolute minimum for  $\text{CB}_{11}\text{H}_{14}$  and could be only a local minimum. See, for instance: Williams, R. E. *Chem. Rev.* **1992**, *92*, 177.

(15) (a) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*. (b) Dupuis, M.; Watts, J. D.; Villar, H. O.; Hurst, G. J. B. HONDO-7. IBM Corporation, Scientific and Engineering Computations, Department 48B/MS 428.

(9) (a) Saunders, M.; Telkovski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(10) Zilm, K. W.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837.

**Table III.** RHF/3-21G Absolute (au) and Relative Energies (kcal/mol, in Parentheses) for the Two Optimized Extrema of 1-CB<sub>10</sub>H<sub>14</sub><sup>a</sup>

structure	4a	4b
energies	-291.124 75 (0.0)	-291.122 54 (1.4)
type	minimum	transition state

<sup>a</sup> The geometries are shown in Figure 2.**Table IV.** Selected Bond Lengths (Å) for B<sub>11</sub>H<sub>14</sub><sup>-</sup> (4a) and 1-CB<sub>10</sub>H<sub>14</sub> (5a)<sup>a</sup>

	exptl	B <sub>11</sub> H <sub>14</sub> <sup>-</sup> (5a)		1-CB <sub>10</sub> H <sub>14</sub> (4a)
		(3-21G*)	(3-21G)	(3-21G)
B8-H23	1.13	1.199	1.202	1.202
B9-H25	1.19-1.38	1.343	1.352	1.351
B11-H25	1.19-1.38	1.278	1.281	1.280
B8-B9	1.747-1.775	2.046	2.055	2.045
B9-B11	(1.762) <sub>av</sub>	1.845	1.861	1.877
B11-B12	(1.762) <sub>av</sub>	2.015	2.005	2.006
B8-H18	0.99-1.16	1.198	1.193	1.185
B9-H19	0.99-1.16	1.188	1.183	1.175
B11-H21	0.99-1.16	1.189	1.185	1.178

<sup>a</sup> Experimental values are given in column 2.<sup>4</sup>

basis set.<sup>16a</sup> This level of theory has given reasonable results on other borane clusters. Despite the presence of a negative charge on **5**, there is no need for diffuse orbitals because of the large size of the system.<sup>17a</sup> Nevertheless, it has been recently shown that the structural parameters are better reproduced when a set of polarization functions is added on the heavy atoms.<sup>17</sup> This has been tested by **5** by adding polarization functions ( $\zeta = 0.8$ )<sup>16b</sup> on boron. Geometric optimizations of **4** and **5** have been performed with an analytical gradient technique, and the nature of all the extrema on the PES of **4** has been established by a fully frequency calculation.

**(b) Results. The Neutral 1-CB<sub>10</sub>H<sub>14</sub> Nido Cluster (4).** To locate the extrema, we have explored a part of the PES. The geometry of the 1-CB<sub>10</sub>H<sub>11</sub> fragment was taken from the optimized RHF/3-21G structure of 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>. A triangular (H<sub>endo</sub>)<sub>3</sub> was then added on top of the pentagonal open face of the cluster within the constraint of C<sub>s</sub> symmetry. The distances between the H<sub>endo</sub> centers and between (H<sub>endo</sub>)<sub>3</sub> and the cage were varied from 0.9 to 1.2 Å and from 0.815 to 0.969 Å, respectively, in order not to miss a minimum with a short H<sub>endo</sub>-H<sub>endo</sub> distance; but none was found. A calculation of the forces acting on the atoms was carried out for each geometry. Two extrema (**4a** and **4b**), very close in energy (Table III), have been located on the PES, and their structures are shown in Figure 2 with selected structural parameters given in Table IV. Frequency calculation shows that **4a** is a real minimum and **4b** a transition state. Structure **4b** is calculated to be only 1.4 kcal/mol above **4a**.

Structures **4a** and **4b** differ essentially in the position of the three H<sub>endo</sub> protons. In **4a**, two H<sub>endo</sub> are edge-bridging (H24 and H25) while the third one (H23) is at an endo terminal site. The edge-bridging H24 is bonded to B10 and B12 with B10-H24 being slightly longer (1.352 Å) than B12-H24 (1.280 Å). As expected, the terminal B8-H23 is shorter (1.208 Å) than the bonds to the edge-bridging hydrogen. This is the type of structure reported by Shore *et al.* In **4b**, the three H<sub>endo</sub> are edge-bridging the B-B bonds. The bond distances increase in the order B9-H25 (1.243 Å) < B11-H23 (1.315 Å) < B8-H25 (1.491 Å). Thus B8, which bonds to H24 and H25, can only make weak bonds to both of them. In structures **4a** and **4b**, the distance

between two H<sub>endo</sub> protons is larger than 2 Å, showing the absence of any H...H interaction.

**The Target Anion B<sub>11</sub>H<sub>14</sub><sup>-</sup> (5).** The target compound B<sub>11</sub>H<sub>14</sub><sup>-</sup> was optimized at the RHF/3-21G level in conformation **5a**, and the resulting structure was compared to the experimental one. Calculated and experimental values of selected structural parameters involving atoms close to the open face of the cage are given in Table IV. From a comparison of columns 3 and 4 it appears that the calculated (HF/3-21G) structures of the neutral and anionic cages are very similar. This shows that it is possible to use the neutral carboranes as a model for anionic boranes not only in the case of the closo cages<sup>13</sup> but also in the case of more open clusters. Greater differences appear between the calculated and experimental bond lengths. As expected, the experimental B-H bond lengths are shorter than the calculated ones. More surprisingly, experimental B-B bond lengths are also significantly shorter (by around 0.2 Å) than the calculated ones. The addition of polarization functions shortens some of the B-B bond lengths,<sup>17b</sup> but it is clear that the experimental cage is still more compact than the calculated one. Since a good agreement<sup>13</sup> between theory and experiment in the case of the parent closo cages 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> and B<sub>12</sub>H<sub>12</sub><sup>2-</sup> was found at a comparable level of theory (3-21G and 4-31G\*) and since the same type of basis set can account for the structure of several nido systems,<sup>17</sup> we needed better structural data for B<sub>11</sub>H<sub>14</sub><sup>-</sup>. Unfortunately, as mentioned earlier, disorder in the crystal prevented accurate determination of the structure (average B-B distance of the disordered structure = 1.824 Å compared with average B-B of the calculated structure = 1.829 Å)<sup>18</sup> of the cage by neutron diffraction.

Since the bonding of H<sub>endo</sub> to the pentagonal face of the nido cage is similar in **4a** and **5a**, it is reasonable to assume that transition **5b** would be similar to **4b** and would also lie at a low energy above **5a**.

**(c) Discussion.** Two general classes of models can be considered: a classical one like **3** (more precisely represented by **4a-5a** or **4b-5b**) without significant H...H interactions and a nonclassical one (**2**) with such interactions. A classical structure like **3** was proposed by Shore *et al.*<sup>4</sup> on the basis of an X-ray crystal structure and **2** by Lipscomb<sup>3a</sup> but in the latter case without any structural data to support it. If the classical model is adopted, rapid fluxionality, as evidenced by the very low and experimentally inaccessible decoalescence temperature for the H<sub>endo</sub> atoms, remains a puzzle. A high activation energy could have been associated with the necessary cleavage of B-H bonds during the exchange mechanism. In contrast, facile rotation with respect to the nido cage could be expected in a nonclassical complex of the triangular molecule (H<sub>endo</sub>)<sub>3</sub><sup>+</sup> like **2**.

Our theoretical calculations clearly establish<sup>19</sup> that **2** should be definitely discarded: in both extrema, all the H<sub>endo</sub>-H<sub>endo</sub> are greater than 2 Å.<sup>20</sup> H<sub>endo</sub> are well bonded to the borons with B-H<sub>endo</sub> distances that are within the expected range for bridged and terminal bonds. The Mulliken overlap population, which is 0 between the H<sub>endo</sub> protons and significantly positive (see below) between the B and H<sub>endo</sub> centers, confirms this bonding pattern.

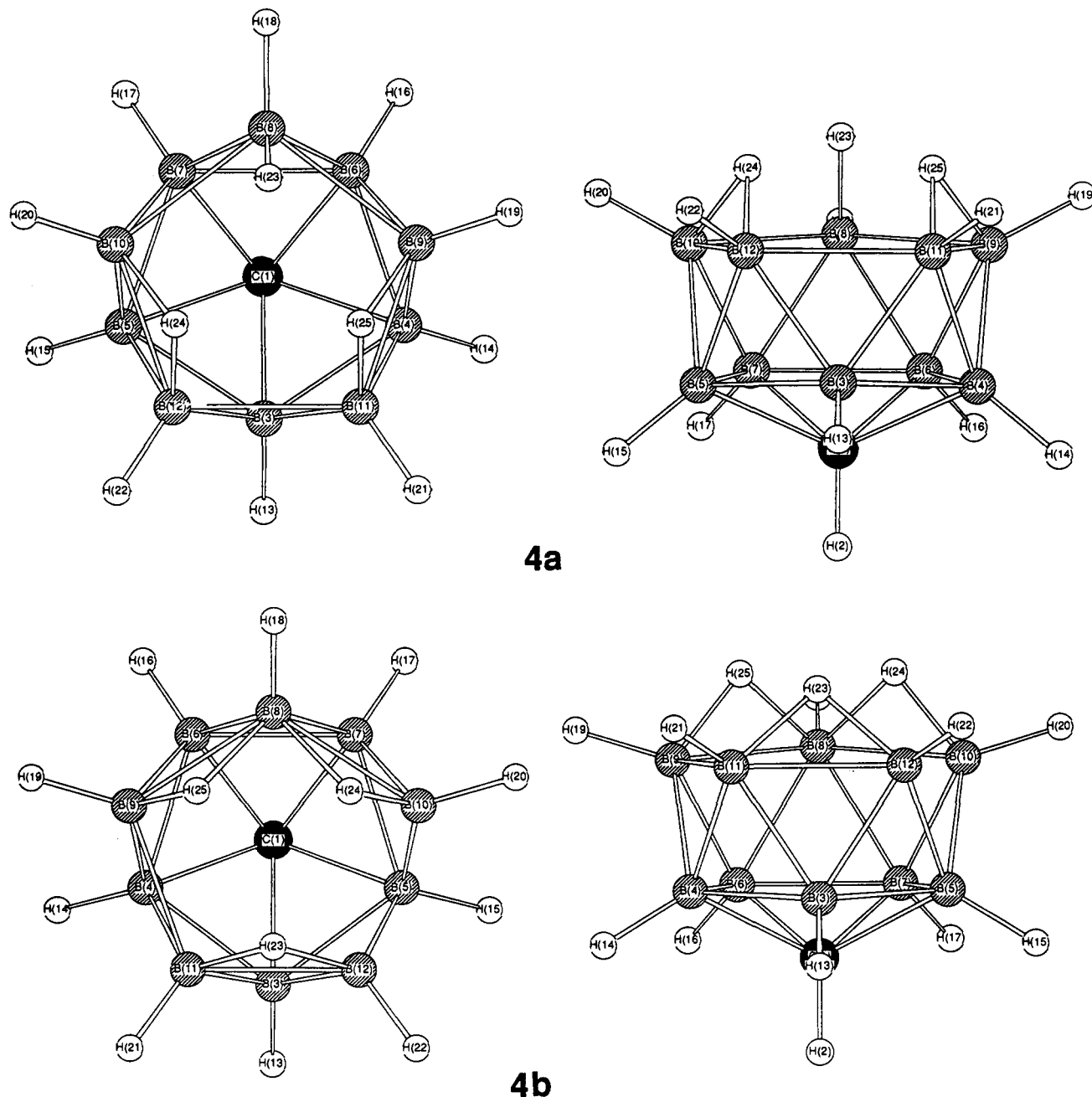
(17) (a) It is well-known that the lack of diffuse Gaussian in the basis set is no longer a problem when the size of the system increases. For example, in the case of (Li<sub>n</sub>)<sup>-</sup> clusters (n = 1-7), recent calculations show that the results are affected by the lack of diffuse functions only for n = 1, 3 (Bauschlicher, C. R., Jr. Private communication). See also ref 17b. (b) Zahradnik, R.; Balaji, V.; Michl, J. *J. Comput. Chem.* **1991**, *12*, 1147. (c) Recent studies show that similar basis sets can also account for the structure and NMR chemical shift of boranes and carboranes of moderate size: Buhl, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 477.

(18) Howard, J. A. K. Private communication.

(19) These conclusions are valid at the HF level. However, other studies on borane clusters have shown that the inclusion of correlation energy (MP2) does not modify significantly the results (ref 17).

(20) This distance is shorter than the van der Waals contact (2.4 Å). The other distances between the hydrogen centers are longer (H<sub>endo</sub>...H<sub>endo</sub> is around 1.9-2 Å; H<sub>endo</sub>...H<sub>endo</sub> is around 3 Å). The Mulliken overlap populations are equal to 0 within each pair, indicating the absence of any bonding situation.

(16) 3-21G basis set: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. d orbital for first-row elements in GAUSSIAN80: Binkley, J. S.; Whiteside, R.; Krishnan, R.; Seeger, R.; Schlegel, H. B.; DeFrees, D. J.; Pople, J. A. *QCPE* **1981**, *13*, 406.

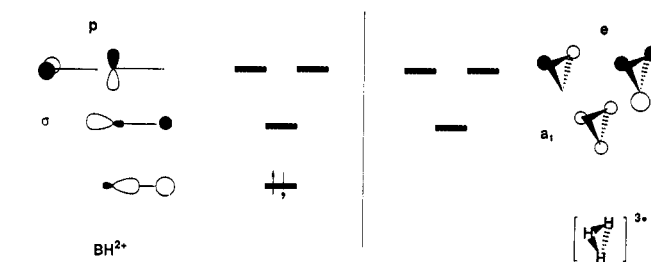


**Figure 2.** **4a** RHF/3-21G optimized structure of the equilibrium geometry of 1-CB<sub>10</sub>H<sub>14</sub>. Selected bond lengths are given in Table IV and in the text. **4b** RHF/3-21G optimized structure of the transition-state geometry of 1-CB<sub>10</sub>H<sub>14</sub>. BH bond lengths are given in the text. Full structural details for **4a** and **4b** are given in the supplementary material.

We will now discuss why **2** is disfavored and why the hydrogen exchange is so rapid.

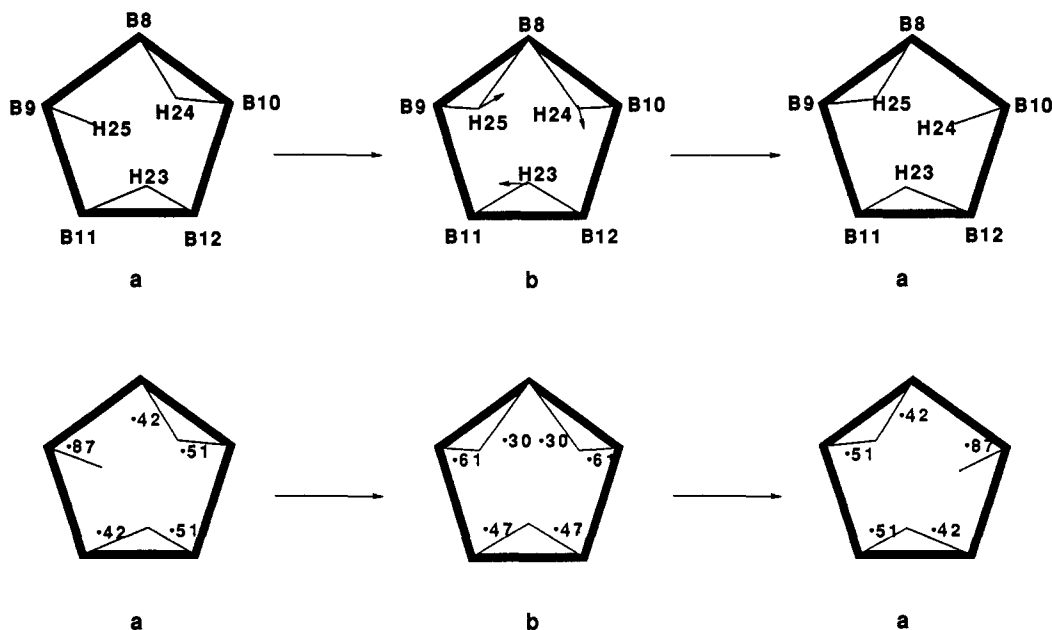
**Why Is the Nonclassical Structure 2 Disfavored?** While model **2** does not seem appropriate, it does provide a good starting point to understand the interesting geometric features of B<sub>11</sub>H<sub>14</sub><sup>-</sup>, i.e. the arrangement of the three H<sub>endo</sub> on the open pentagonal face of B<sub>11</sub>H<sub>11</sub><sup>2-</sup>.

The parent closo cluster B<sub>12</sub>H<sub>12</sub><sup>2-</sup> is made of 12 BH groups sharing 26 skeletal electrons. These 26 skeletal electrons are distributed among *one* radial MO, built from the  $\sigma$  orbital of BH groups and 12 tangential orbitals built from the two p orbitals of each BH group (Figure 3).<sup>11</sup> Therefore, the electron occupancy is 1/6 and 1 for each  $\sigma$  and p orbital of each BH vertex, respectively. If one replaces one BH<sup>2+</sup> vertex by the isolobal (H<sub>endo</sub>)<sub>3</sub><sup>3+</sup> group and supposes that this replacement does not perturb the electron distribution inside the boron cage, the a<sub>1</sub> and e orbitals of the (H<sub>endo</sub>)<sub>3</sub> fragment (which have the same nodal properties as the  $\sigma$  and p orbitals of BH as shown in Figure 3) should be also



**Figure 3.** Molecular orbitals of the two isolobal fragments BH<sup>2+</sup> and equilateral H<sub>3</sub><sup>3+</sup>.

occupied by 1/6 and 1 electron, respectively. Electron density is thus put into (H<sub>endo</sub>)<sub>3</sub><sup>3+</sup> with a smaller amount in the bonding a<sub>1</sub> than in the antibonding e orbitals. This favors an increase of the H...H distances, and this is confirmed by the *ab initio* calculations. Thus, starting from the optimized geometry of 1,2-



**Figure 4.** Mechanism for the H<sub>endo</sub> exchange. **b** is the transition state between two **a** type minima. The upper part of the figure gives the atom numbering and direction of the transition vector (**b**). The lower part of the figure gives the Mulliken overlap populations between H<sub>endo</sub> and the closest boron atoms.

C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> and replacing a CH<sup>3+</sup> vertex by (H<sub>endo</sub>)<sub>3</sub><sup>3+</sup>, the calculations show that the gross populations in the a<sub>1</sub> and e orbitals of the triangle of hydrogens are in agreement with the qualitative discussion. Moreover, these electron occupancies do not strongly depend on either the H<sub>endo</sub>...H<sub>endo</sub> distance or the distance of the (H<sub>endo</sub>)<sub>3</sub> plane from the cage. The gradient of the energy relative to the nuclear displacements also clearly shows that the (H<sub>endo</sub>)<sub>3</sub> triangle tends to expand. For an equilateral geometry of (H<sub>endo</sub>)<sub>3</sub> with an H<sub>endo</sub>...H<sub>endo</sub> distance ranging from 0.9 to 1.2 Å, the energy gradient indicates a displacement of the three H<sub>endo</sub> in the direction of increased H<sub>endo</sub>...H<sub>endo</sub> distances. We thus have established that no minimum with a short H<sub>endo</sub>...H<sub>endo</sub> distance has been missed on the PES for **4** and **5**.

**Exchange Mechanism.** Finally, from the above discussion, the exchange of the three H<sub>endo</sub> proceeds via a concerted motion of the three H<sub>endo</sub>, but at no stage during the motion are significant H...H interactions present. The five identical minima of type **a** interconvert via five identical transition structures of type **b** (Figure 4). The direction of the transition vector associated with the imaginary frequency of **b** illustrates the nuclear motion happening at the transition structure (Figure 4). The evolution of the B-H<sub>endo</sub> bond orders from those of **a** to those of **b** also confirms that **b** is a transition state connecting two **a** type minima. On going from **b** to **a** the B<sub>9</sub>-H<sub>25</sub> bond weakens while B<sub>8</sub>-H<sub>25</sub> is strengthened. The already weak B<sub>8</sub>-H<sub>24</sub> bond fully cleaves, while H<sub>24</sub> bonds only to B<sub>10</sub>. The H<sub>23</sub> center hardly moves from a symmetrical bonding situation to B<sub>11</sub> and B<sub>12</sub> to an unsymmetrical one. It should be noted that the transformation **a**-**b**-**a** involves very small displacements of the H<sub>endo</sub> atoms. In addition each H<sub>endo</sub> remains well bonded to the face of the cage as shown by the B-H<sub>endo</sub> bond orders (summed over B atoms), which are almost equal in **a** and **b**. This explains the very small activation energy for the H<sub>endo</sub> exchange process.<sup>21</sup>

Although experimental and theoretical studies independently suggest the nonexistence of the nonclassical structure, we should be aware of one of the limitations of our theoretical study. We have not been able to explore the whole PES and have limited ourselves to systems of C<sub>s</sub> symmetry for practical reasons. However, we do not believe that any other extrema should exist at low energy since the 10 extrema which have been located are very close in energy and are also closely related structurally.

## Conclusion

In conclusion, this work suggests that the H<sub>endo</sub> protons in B<sub>11</sub>H<sub>14</sub><sup>-</sup> are classically bonded to the cage as terminal and edge-bridging atoms as suggested by Shore *et al.* The fast exchange process between the three H<sub>endo</sub> does not involve the formation of any H-H bonds. The extremely low activation energy is due to the fact that only small nuclear motions of H<sub>endo</sub> are required to reach the transition state and that strong bonding interactions between H<sub>endo</sub> and the boron atoms of the pentagonal face of the cage are maintained during the exchange process.

**Acknowledgment.** R.H.C. thanks the CNRS for financing his stay in Orsay. We would like to thank Professor J. A. K. Howard for preliminary communication of her results on the structure of [PPh<sub>4</sub><sup>+</sup>][B<sub>11</sub>H<sub>14</sub><sup>-</sup>] and Eric Clot (Orsay) for useful discussions. The Laboratoire de Chimie Théorique is associated with the CNRS (URA 506) and is a member of ICMO and IPCM.

**Supplementary Material Available:** List of Cartesian coordinates (in atomic units) for **4a**, **4b**, and **5a** (3 pages). Ordering information is given on any current masthead page.

(21) Tunneling may occur in the rearrangement process. However, the very low activation energy calculated in this work indicates that fluxionality is extremely facile in all respects.