

# Six-vertex *nido*-carborane structures with unusual CHB bridges or *endo*-CH hydrogens<sup>1</sup>

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## Abstract

The experimentally-observed C<sub>2</sub>B<sub>4</sub>Et<sub>6</sub>H<sub>2</sub> intermediate, claimed to be the first *nido*-2-carba-pentaborane(8) derivative, is shown by the ab initio/GIAO/NMR method actually to be a substituted *nido*-2,4-dicarba-hexaborane(8) (**10**). Both *nido*-2,4-dicarba-hexaboranes(8) and *nido*-2,3,5-tricarba-hexaboranes(7) have unsymmetrical *endo*-CH's which are strongly tilted towards one of the two neighbouring boron atoms to form partial CHB hydrogen bridges. The energies of *nido*-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>8</sub> (**10**) and *nido*-2,3,5-C<sub>3</sub>B<sub>3</sub>H<sub>7</sub> are 4.6 and 10.6 kcal mol<sup>-1</sup> higher than the most stable isomers, 2,3-C<sub>2</sub>B<sub>4</sub>H<sub>8</sub> and 2,3,4-C<sub>3</sub>B<sub>3</sub>H<sub>7</sub>, respectively. The ca. 10 kcal mol<sup>-1</sup> barriers for hydrogen migration in the anions, 1,2- and 2,3-C<sub>2</sub>B<sub>4</sub>H<sub>7</sub><sup>-</sup>, as well as in 1,2-C<sub>2</sub>B<sub>4</sub>H<sub>8</sub> involve *endo*-BH transition structures. A C<sub>2</sub>B<sub>4</sub>R<sub>6</sub>H<sub>2</sub> cluster derived from a pentagonal bipyramid by removing a basal vertex is proposed as another intermediate in the *arachno*-1-carba-pentaborane(10) to *closo*-1,5-dicarba-pentaborane(5) degradation. © 1998 Elsevier Science S.A.

**Keywords:** Boron; Carborane; Ab initio calculations

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## 1. Introduction

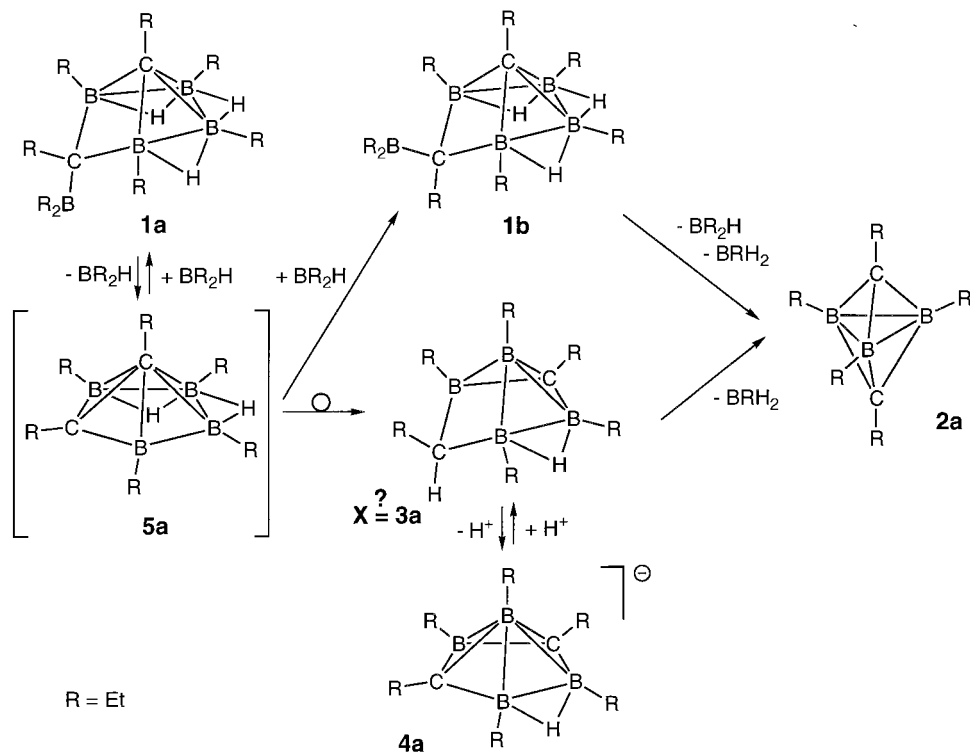
Structural and mechanistic complexities of carborane cluster formation and degradation can be unraveled with the aid of ab initio computations [1–17]. Recently, an intermediate 'X' was observed in the reaction leading from *arachno*-1-carba-pentaborane(10) derivatives [14–18] (e.g., **1a**) to *closo*-1,5-dicarba-pentaboranes(5) [15] (e.g., **2a**). On the basis of its NMR data, X was postulated to be the first *nido*-2-carba-pentaborane(8) derivative, **3a** (see Scheme 1) [16]. The claimed *nido*-2-carbapentaborane derivative would be unusual as it has a *nido* electron count [17,18] but an *arachno*-type structure [19–21]. Compound X was deprotonated to give the *nido*-2,4-dicarba-hexaborane anion derivative,

**4a**, structurally characterized by X-ray analysis [16]. As protonation of **4a** regenerates X, the process was claimed to be the first example of reversible carbon atom incorporation into a carborane cluster. Although no NMR signals were observed, the *nido*-1,2-dicarba-hexaborane(8) derivative **5a**, an isomer of **3a**, was suggested to be an additional intermediate in order to rationalize the observation both of X and of **1b**, the *exo*-isomer of **1a**.

We now report a computational investigation of the parent *nido*-C<sub>2</sub>B<sub>4</sub>H<sub>7</sub><sup>-</sup> and *nido*-C<sub>2</sub>B<sub>4</sub>H<sub>8</sub> isomers which clarifies the structures and relative energies of the species involved. Related compounds such as *nido*-C<sub>3</sub>B<sub>3</sub>H<sub>6</sub><sup>-</sup>, and *nido*-C<sub>3</sub>B<sub>3</sub>H<sub>7</sub> isomers, and hexamethyl derivatives of *nido*-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>7</sub><sup>-</sup>, *nido*-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>8</sub> and *nido*-2,3,5-C<sub>3</sub>B<sub>3</sub>H<sub>7</sub> also were studied. The ab initio/GIAO/NMR method [1–11] was applied to the <sup>11</sup>B NMR data for X; the results negate the validity of the structural proposal **3a** for X. The alternative we propose has an unusual structural feature: a CHB hydrogen bridge. Such *endo*-CH hydrogens are found in

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<sup>1</sup> Dedicated to Professor Ken Wade on the occasion of his 65th birthday in recognition of his outstanding contributions to organometallic and inorganic chemistry.



Scheme 1.

*nido*-2,4-dicarba and *nido*-2,3,5-tricarba-hexaboranes(8) and are also present in their peralkyl derivatives.

## 2. Computational details

All geometries were fully optimized within the given symmetry at the MP2(fc)/6-31G\* level of theory<sup>2</sup> using the Gaussian 94 program [24]. Only valence electrons were included in the electron correlation treatment (fc = frozen core approximation). Unless noted otherwise, the reported geometries and relative energies correspond to this level. Harmonic frequencies, computed from analytical second derivatives at HF/6-31G\*, establish the nature of stationary points as minima or transition structures. Chemical shifts were computed using the GIAO method [25–27] at SCF/6-31G\*. B<sub>2</sub>H<sub>6</sub> (computed absolute shielding constant,  $\sigma = 106.98$  ppm) served as a primary reference for computed <sup>11</sup>B chemical shifts and the experimental gas phase value,  $\delta = 16.6$  [28], was used to convert to the experimental standard, BF<sub>3</sub> · OEt<sub>2</sub> ( $\delta = 0.0$ ). <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced directly to tetramethyl silane ( $\sigma = 32.78$  ppm and  $\sigma = 201.09$  ppm, respectively).

<sup>2</sup> For an introduction to ab initio computations and methods employed, see Refs. [22,23].

## 3. Results and discussion

### 3.1. The *nido*-C<sub>2</sub>B<sub>4</sub>R<sub>6</sub>H<sup>-</sup> anion

Deprotonation of **X** gave the monoanion **4a**, the structure of which was solved by an X-ray structure analysis [16]. Geometrical parameters computed for the hexamethyl derivative 2,4-C<sub>2</sub>B<sub>4</sub>Me<sub>6</sub>H<sup>-</sup>, **4b**, are in close agreement with experimental data for **4a**. The parent *nido*-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>7</sub><sup>-</sup>, **4**, has long been known [29,30], and differences between theoretical structures of **4** and **4b** are insignificant (Fig. 1a).

According to empirical rules [31], the 2,4-dicarba isomer should be the lowest in energy, as both carbon atoms occupy non-adjacent, low coordination sites (C2, C4) and the extra hydrogen bridges two low coordinated boron atoms (B5/B6). This expectation is confirmed by computed relative energies of 15.4, 48.1 and 52.2 kcal mol<sup>-1</sup> for the 2,3- (**6**) as well as the C<sub>s</sub> (**7**) and the C<sub>1</sub> (**8**) 1,2-isomers vs. 2,4-C<sub>2</sub>B<sub>4</sub>H<sub>7</sub><sup>-</sup> (**4**, see Fig. 2). Isomer **6** [29,32] and derivatives [33–35] also are known experimentally; an X-ray structure and multinuclear NMR data were reported for *nido*-2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub><sup>-</sup>, **6a** [35]. The <sup>11</sup>B NMR chemical shifts computed for **4** fit the measured values reasonably well (see Table 1). Averaged theoretical values for C<sub>1</sub> symmetric **6**, but not the C<sub>s</sub> structure **TS-6/6**, give good agreement with experiment (Table 2). The hydrogen scrambling barrier

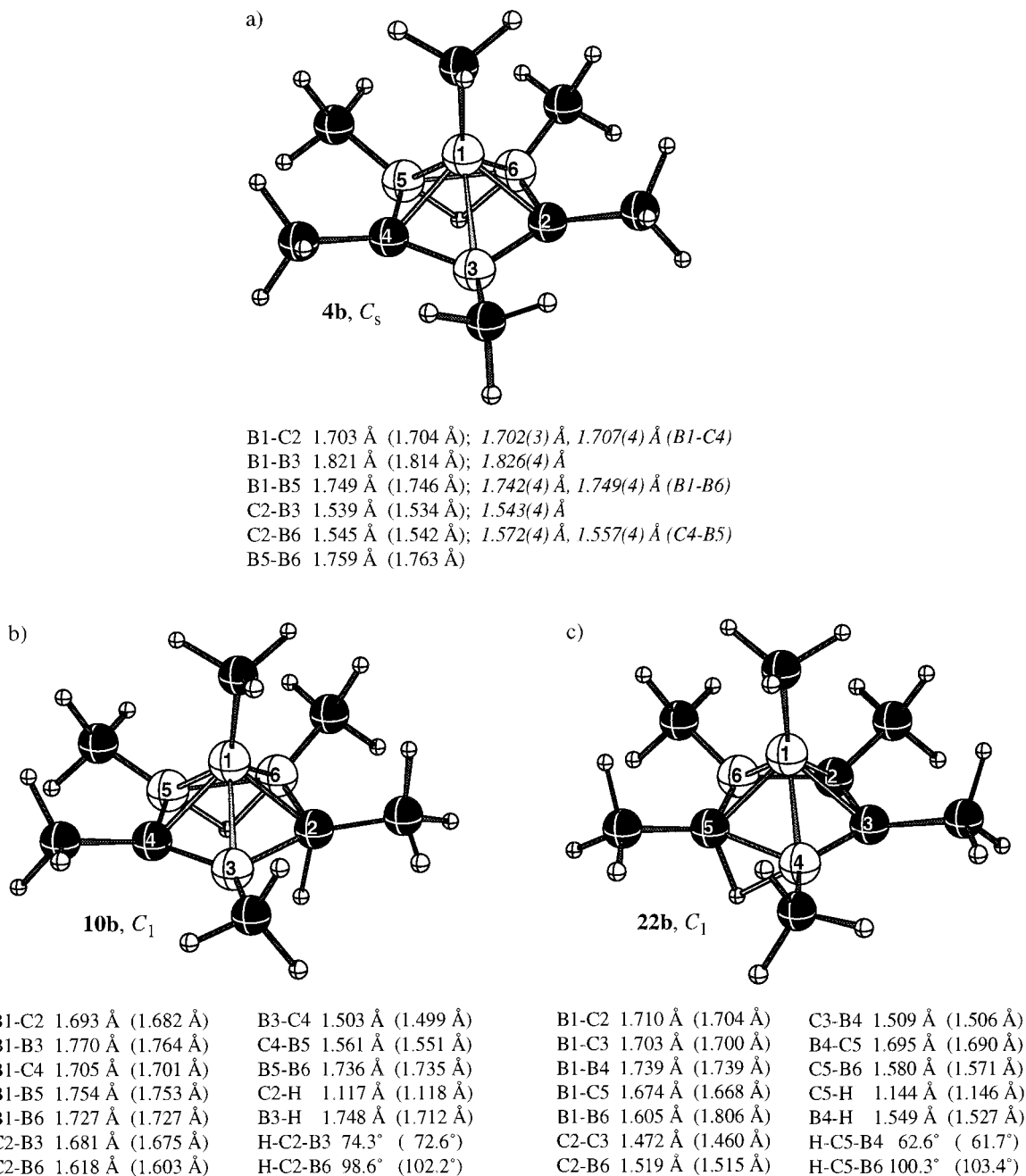


Fig. 1. Some parameters of optimized geometries (MP2(fc)/6-31G\*) for (a) *nido*-2,4- $C_2B_4Me_6H^-$ , **4b**, (italics: experimental X-ray values for *nido*-2,4- $C_2B_4Et_6H^-$ , **4a**, from Ref. [21,22]) (b) *nido*-2,4- $C_2B_4Me_6H_2$ , **10b**, and (c) *nido*-2,3,5- $C_3B_3Me_6H$ , **22b**. Values for the parent compounds, **4**, **10** and **22**, respectively, are given in parentheses.

in **6** is only 8.6 kcal mol<sup>-1</sup> via a transition structure **TS-6/6** (which has an *endo*-H at B5 rather than a BHB hydrogen bridge). The barrier for transforming **8** into **7** via **TS-7/8** (which also has an *endo*-BH (B4) between two boron atoms (B3,B5)) is about the same (10.3 kcal mol<sup>-1</sup>).<sup>3</sup>

<sup>3</sup>The transition state for bridge hydrogen scrambling for the neutral binary boron hydride,  $B_6H_{10}$ , also has an *endo*-H; the computed barrier is 10.7 kcal mol<sup>-1</sup>.

### 3.2. *nido*- $C_2B_4R_6H_2$

Protonation of **6** gives the well-known neutral *nido*-2,3- $C_2B_4H_8$ , **9**,<sup>4</sup> where the additional hydrogen is accommodated optimally as B5/B6 hydrogen bridge. The only (slightly) unfavourable structural feature [31] is the adjacent carbon placement. In contrast, there is no

<sup>4</sup>See for example, see Refs. [36–39].

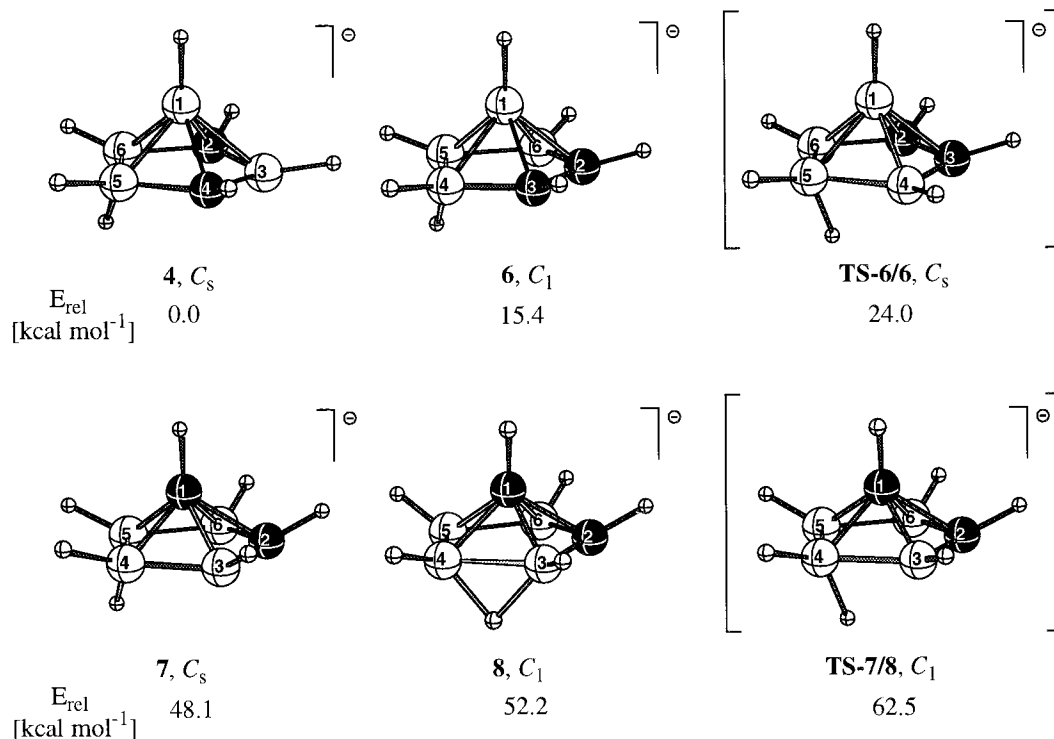


Fig. 2. Optimized geometries and relative energies of some *nido*-dicarbapentaborate(8) monoanion isomers. (Transition states for hydrogen rearrangement are shown in brackets.)

good position for an additional hydrogen in the 2,4-dicarba isomer, **4**, as unbridged B–B edges are not available.<sup>5</sup> The alternative *endo*-terminal BH or CH's are found only in *arachno*- and *hypho*- but not in *nido*-species. This may have been the basis for the proposed *nido* 2-carba-pentaborane(8) structure, **3a**, for the protonation product of **4a**. In **3a**, the protonated carbon is a methylene group, bound classically to B4 and B5 as an *endo* substituent, and is not a part of the electron deficient central cluster. Optimization of a  $C_2B_4H_8$  model geometry based on **3a** gave different results, depending on the theoretical level. No local minimum was found at HF/6-31G\*; optimization converged directly to **10**. The latter, unexpectedly was only 4.6 kcal mol<sup>-1</sup> higher in energy than **9** (at MP2(fc)/6-31G\*, Fig. 3). Optimizing the same  $C_2B_4H_8$  starting geometry (based on **3a**) at MP2, gave a minimum, **3**, the parent of **3a**. However, **3** was 39.0 kcal mol<sup>-1</sup> less stable than **10** and its computed boron chemical shifts (see below) did not agree with the experimental NMR data.

The CH<sub>2</sub> moiety in **10** is not an electron precise bridging substituent but is incorporated into the electron deficient central cluster. This is evident from the B1–C2

distance of 1.682 Å, even shorter than B1–C4 (1.701 Å). The C2–H<sup>endo</sup> distance (1.118 Å) is longer than the C2–H<sup>exo</sup> separation (1.084 Å). The *endo*-H is tilted considerably towards B3 (H<sup>endo</sup>–C2–B3: 72.6°, H<sup>endo</sup>–C2–B5: 102.2°); The B3 ··· H<sup>endo</sup> distance is 1.712 Å (see also Fig. 1). The H<sup>endo</sup> bonding can be regarded either as a C–H bond hyperconjugating with an electron deficient center (B3) or as a CHB hydrogen bridge polarized to the carbon atom. Note, however, that the C2–B3 separation (bridged, 1.675 Å) is 0.176 Å longer than the (unbridged) B3–C4 (1.499 Å). The difference is only 0.05 Å for C2–B6 and C4–B5 (both unbridged). Asymmetric CHB bridges were reported for related metalla carboranes [41]. For (toluene)Fe(2-Me-1,3,4,5-Et<sub>4</sub>-1,3-B<sub>2</sub>C<sub>3</sub>H, the asymmetry of the CH<sup>endo</sup> was confirmed by X-ray and neutron structural analyses with C–H<sup>endo</sup> and B–H<sup>endo</sup> distances of 1.13/1.14 Å and 1.51/1.53 Å, respectively.

When the extra hydrogen is attached to a boron (B3) instead of to a carbon atom (C2), a much higher energy species, **11** (25.3 kcal mol<sup>-1</sup> vs. **10**), results. The *endo*-BH moiety (B3) in **11** is adjacent to carbon (C2,4) rather than to boron atoms (as in **TS-6/6**, **TS-7/8**, **TS-5/13** and **TS20/20** whose stabilities are ca. 10 kcal mol<sup>-1</sup> less than those of the corresponding minima with BHB hydrogen bridges). Another 2,4-isomer with two CHB hydrogen bridges, **12**, also is a high energy minimum ( $E_{rel} = 29.9$  kcal mol<sup>-1</sup>). *Endo*-/bridge hy-

<sup>5</sup> Apart from Ref. [16], we are only aware of a very recent report in the literature of protonation of 2,4- $C_2B_4H_7^-$  derivatives, see Ref. [40].

Table 1

Computed<sup>a</sup> and measured <sup>11</sup>B and <sup>13</sup>C NMR chemical shifts for *nido*-2,4-dicarba-hexaborane(8), its monoanion and derivatives

Vertex	B1	B3	B5	B6	C2	C4
2,4-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> <sup>-</sup> , <b>4</b> , exp.	-51.9 <sup>b</sup>	21.2 <sup>b</sup>	0.8 <sup>b</sup>		75.2 <sup>c</sup>	
2,4-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> <sup>-</sup> , <b>4</b> , calc.	-50.3	18.9	0.6		60.4	
2,4-C <sub>2</sub> B <sub>4</sub> Et <sub>6</sub> H <sup>-</sup> , <b>4a</b> , exp. <sup>d</sup>	-39.1	28.9	10.3		86.5	
2,4-C <sub>2</sub> B <sub>4</sub> Me <sub>6</sub> H <sup>-</sup> , <b>4b</b> , calc.	-38.8	24.0	5.3		61.2	
C <sub>2</sub> B <sub>4</sub> Et <sub>6</sub> H <sub>2</sub> , <b>X</b> , exp. <sup>d</sup>	-27.8	39.6	17.8 <sup>e</sup>	12.3 <sup>e</sup>	91.5 <sup>f</sup>	41.3 <sup>f</sup>
C <sub>2</sub> B <sub>4</sub> H <sub>8</sub> , <b>3</b> , calc.	60.8	38.7	-16.2	19.8	134.1	129.2 (CH <sub>2</sub> )
2,4-C <sub>2</sub> B <sub>4</sub> H <sub>8</sub> , <b>10</b> , calc.	-36.8	34.2	12.5	4.3	21.0 <sup>f</sup>	67.8 <sup>f</sup>
2,4-C <sub>2</sub> B <sub>4</sub> Me <sub>6</sub> H <sub>2</sub> , <b>10b</b> , calc.	-23.8	39.3	16.9	10.3	24.1 <sup>f</sup>	72.4 <sup>f</sup>

<sup>a</sup>GIAO-SCF/6-31G\*//MP2(fc)/6-31G\*.<sup>b</sup>Ref. [30].<sup>c</sup>Ref. [8].<sup>d</sup>Ref. [16].<sup>e</sup>Experimentally, the values could not be assigned exactly, but comparison with the computed values suggests the given assignment 17.8 (B5) and 12.3 (B6).<sup>f</sup>Note that according to structure **3a**, proposed for **X**, C4 carries the *endo*-H but C2 in **10** and **10b**.

drogen exchange in **10** is inhibited since **11** and/or **12** should be involved as intermediates.

The 1,2-carba isomers **5** (C<sub>1</sub>), the parent of **5a**, and

**13** (C<sub>s</sub>) are also very unfavourable owing to the presence of carbon atoms in the apical position ( $E_{\text{rel}} = 34.6$  and 28.0 kcal mol<sup>-1</sup>, respectively). The rearrangement

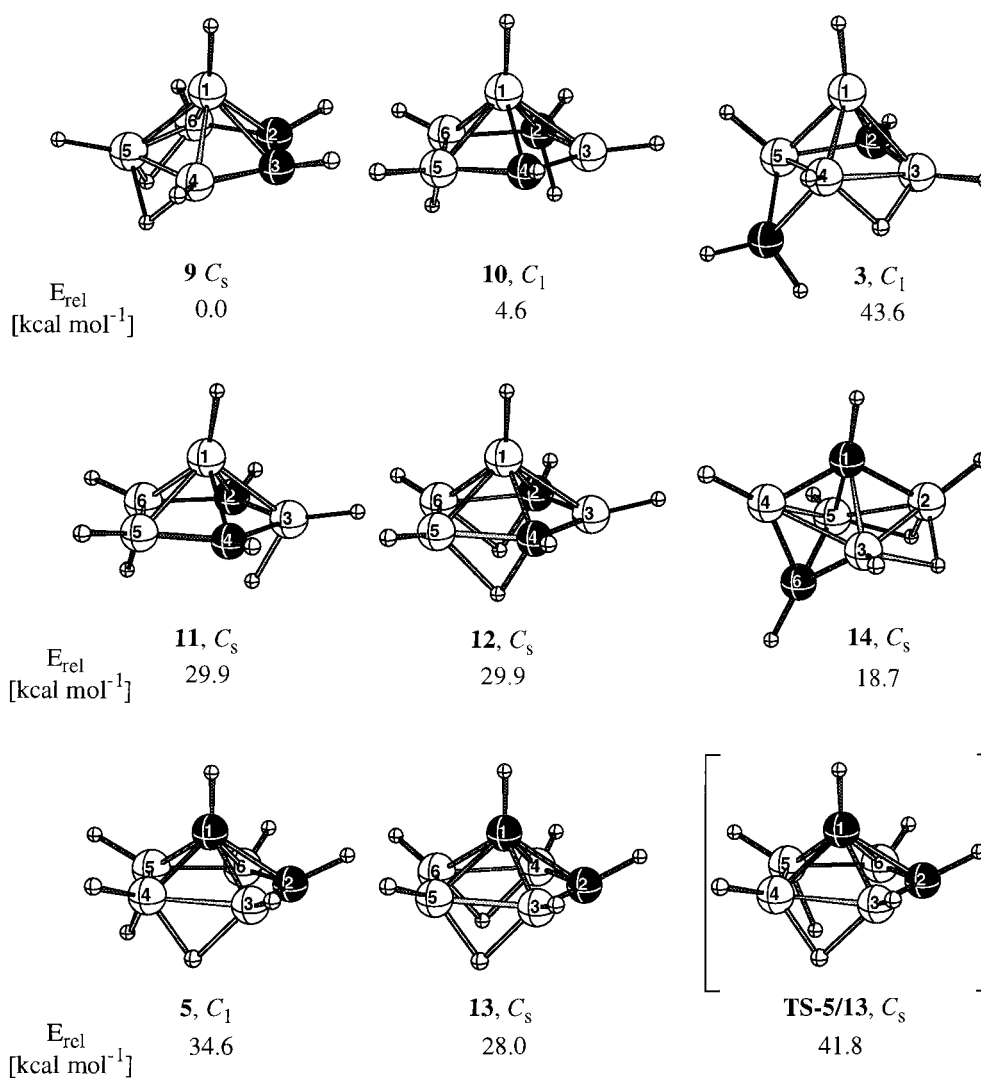
Fig. 3. Optimized geometries and relative energies of some *nido*-dicarbapentaborane(8) isomers.

Table 2

Comparison of computed<sup>a</sup> and measured <sup>11</sup>B NMR chemical shifts for *nido*-2,3-dicarba-hexaborane(8), the monoanion and derivatives

Vertex	B1	B4	B6	B5	C2	C3
2,3-(Me <sub>3</sub> Si) <sub>2</sub> -2,3-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> – , <b>6a</b> , exp. <sup>b</sup>	–50.76	14.08		–3.78	–	
2,3-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> <sup>–</sup> , <b>6</b> , exp. <sup>c</sup>	–55.0	7.1		–5.5	–	
2,3-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> <sup>–</sup> , <b>6</b> , calc.	–53.7	2.1	10.7	–5.3	99.4	77.0
2,3-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> <sup>–</sup> , <b>6</b> , calc., averaged	–53.7	6.4		–5.3	88.2	
2,3-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> <sup>–</sup> , <b>TS-6/6</b> , calc.	–47.3	19.6		–30.6	79.0	
2,3-C <sub>2</sub> B <sub>4</sub> H <sub>8</sub> , <b>9</b> , exp.	–52.9 <sup>d</sup>	–1.3 <sup>d</sup>		–0.3 <sup>d</sup>	123.7 <sup>e</sup>	
2,3-C <sub>2</sub> B <sub>4</sub> H <sub>8</sub> , <b>9</b> , calc.	–51.3 <sup>f</sup>	0.7 <sup>f</sup>		2.7 <sup>f</sup>	116.6	

<sup>a</sup>G1AO-SCF/6-31G\*//MP2(fc)/6-31G\*.<sup>b</sup>Ref. [35].<sup>c</sup>Ref. [29].<sup>d</sup>Ref. [5].<sup>e</sup>Ref. [8].<sup>f</sup>The IGLO/DZ values are –56.3 (B1), –0.5 (B4,6) and 0.2 B(5), see Ref. [1].

of the hydrogen bridge from **5** to **13** via **TS-5/13** has a barrier of 7.2 kcal mol<sup>–1</sup>. Isomer **14** ( $E_{\text{rel}} = 18.7$  kcal mol<sup>–1</sup>), considerably more stable than **5**, might be involved in the *arachno* to *closo* process (Scheme 2). Structure **14** was obtained directly by optimizing a starting geometry constructed by removing the carbon endo-substituent and one neighbouring bridging hydrogen atom from the parent compound of **1a**. The methylene carbon of **1a** is incorporated into the carborane cluster in **14**. This *nido*-structure (ni-6<IV>) <sup>6</sup> can be derived formally from a pentagonal bipyramid by removing a low coordinate basal rather than a high coordinate apical vertex (in contrast to ni-6<V> structure **5**). Both carbon atoms are basal, but only one is in the four-membered open face, and this allows two BB hydrogen bridges (B2/B3, B2/B5). Adding R<sub>2</sub>BH to the C6–B3 edge of a derivative of **14** would lead to **1a** or **1b**.<sup>7</sup> If B2 and the attached hydrogens (or substituents) are split off (e.g., as a BH<sub>2</sub>R fragment), a *closo*-1,5-C<sub>2</sub>B<sub>3</sub>R<sub>5</sub> structure would result. Isomerization of **5a** to **3a** (see Scheme 1) is very likely to be endothermic as found for the parent compounds (**3** is 9.0 and 15.6 kcal mol<sup>–1</sup> less stable than **5** and **13**, respectively). In contrast, **14** derivatives should rearrange exothermically to **10** derivatives. Thus, **14a** is an alternative intermediate <sup>8</sup> (instead of **5a**) in the reaction from carba-*arachno*-pentaboranes(10) to dicarba-*closo*-pentaboranes(5) (Scheme 2).

Based on these computational results, Wrackmeyer's C<sub>2</sub>B<sub>4</sub>Et<sub>6</sub>H<sub>2</sub>, **X**, should be a *nido*-2,4-dicarbahe-

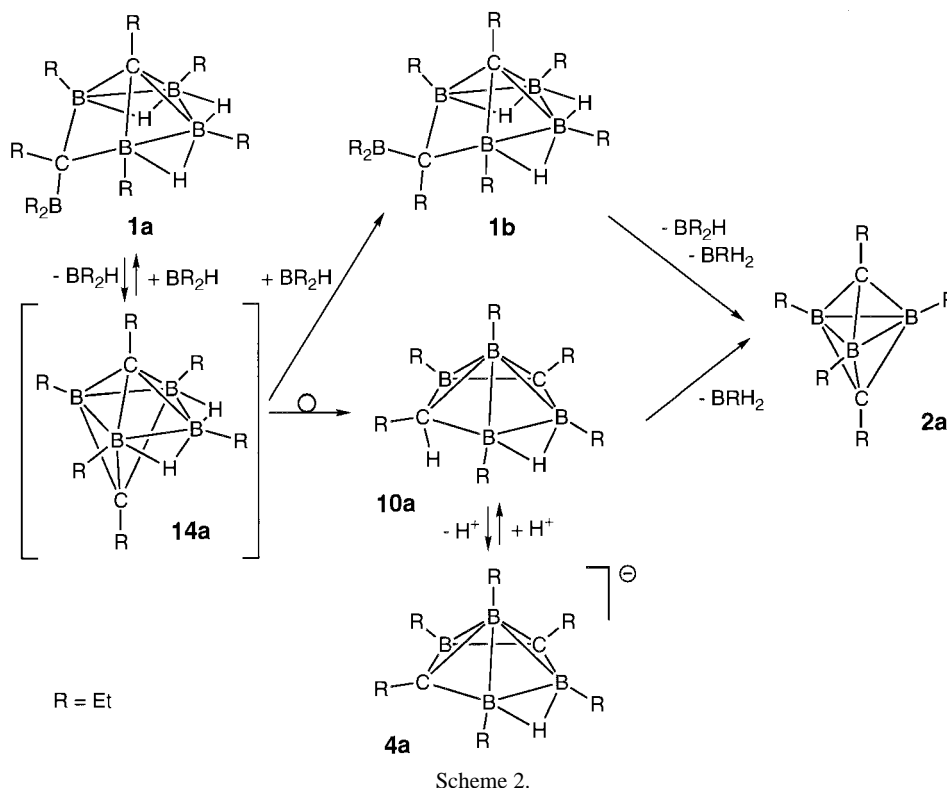
xaborane(8), **10a**, rather than a *nido*-2-carba-pentaborane(8) derivative **3a**. Further support comes from computed chemical shifts for **3** (the parent of **3a**) which are in gross disagreement with experimental values for **X**. Although <sup>11</sup>B NMR chemical shifts computed for **10** are at 4 to 13 ppm higher field compared to the values reported for **X** (Table 1) such differences are expected for ethyl substituent effects (compare, e.g., the chemical shifts of the anions **4a** and **4** in Table 1 or **22** and **22a** in Table 3). More convincing proof for the **10**-like solution structure of **X**, is given by chemical shifts computed for the hexamethyl derivative of **10**, *nido*-2,4-C<sub>2</sub>B<sub>4</sub>Me<sub>6</sub>H<sub>2</sub>, **10b** (a better model for the hexaethyl compound **X**). These data for **10b** (Table 1) are in excellent agreement with the experimental NMR data, confirming a *nido*-2,4-dicarba-hexaborane(8) structure **10a** for **X**. The *endo*-hydrogen in **10b** shows the same geometrical features (tilted towards B3) as in the parent **10** (Fig. 1b).

### 3.3. *nido*-C<sub>3</sub>B<sub>3</sub>R<sub>6</sub>H

Although unexpected, the partially bridging *endo*-CH in a *nido*-carborane cluster is not without precedent. Fessenbecker et al. [42] deduced the presence of a CHB hydrogen bridge from the <sup>1</sup>H chemical shift (of, e.g., –1.34 ppm) in peralkylated *nido*-2,3,5-tricarba hexaboranes(7). Considerations similar to dicarba hexaborane(8) apply to the tricarba-hexaborane(7) clusters.

When the extra hydrogen is absent, i.e., in the tricarborane anion C<sub>3</sub>B<sub>3</sub>H<sub>6</sub><sup>–</sup>, the 2,3,5-isomer **15** is the most stable (Fig. 4a).<sup>9</sup> This is in accord with empirical

<sup>6</sup> See Ref. [21], p. 190.<sup>7</sup> Computations on C<sub>2</sub>B<sub>5</sub>H<sub>11</sub> to model **1a** and **1b** favored the *endo*- over the *exo*-isomer by only 0.6 kcal mol<sup>–1</sup>. Rotation of the boryl group has a barrier of 9.2 (*endo*) and 10.3 kcal mol<sup>–1</sup> (*exo*).<sup>8</sup> The computed <sup>11</sup>B NMR chemical shifts of **14** might be helpful for identifying a derivative: –19.2 (B2), –8.8 (B3,5), 33.5 ppm (B4).<sup>9</sup> Computed chemical shifts for **15** are: –56.6 (B1), 9.1 (B4,6); 70.2 (C2,3), 61.7 ppm (C5). For peralkyl derivatives experimental <sup>11</sup>B shifts of around –40 (B1) and 18 ppm (B4,6) have been reported in Ref. [42].



rules [31], as all carbon atoms are located on low coordinated basal positions and are separated as far as possible. The second most stable isomer has three adjacent basal carbons (**16**,  $E_{\text{rel}} = 18.7 \text{ kcal mol}^{-1}$ ).<sup>10</sup> The presence of an apical carbon atom leads to a much higher energy (**17**,  $E_{\text{rel}} = 46.5 \text{ kcal mol}^{-1}$ ; **18**,  $E_{\text{rel}} = 64.3 \text{ kcal mol}^{-1}$ ).

The 1,2,4- (**19**) and 1,2,3-isomers (**20**) of the neutral compound, *nido*- $\text{C}_3\text{B}_3\text{H}_7$ , again are very high in energy ( $E_{\text{rel}} = 28.0$  and  $45.8 \text{ kcal mol}^{-1}$ ) owing to the unfavourable apical carbon placement C1 (Fig. 4b). On the other hand, *nido*-2,3,4- $\text{C}_3\text{B}_3\text{H}_7$ , **21** [43], is more stable than the 2,3,5-isomer **22** by  $10.6 \text{ kcal mol}^{-1}$  because of the more favourable BHB hydrogen bridge. Derivatives of **22** [42] and **21** [44] are known experimentally.<sup>11</sup> In **22**, the 'extra' hydrogen is an *endo*-terminal H at C5. Partial bridging of the *endo*-CH hydrogen to one neighbouring boron atom (B4) is more pronounced than in the dicarba analog **10**: the C–H<sup>*endo*</sup> distance is longer (1.146 Å), the H<sup>*endo*</sup>–B4 separation is shorter (1.527 Å), and the H<sup>*endo*</sup>–C5–B4 angle is smaller ( $61.7^\circ$ ) in **22** than corresponding values for **10**. Essentially the same is found for the hexamethyl derivatives **10b** and **22b** (see Fig. 1). The bridged C5–B4 edge

(1.690 Å) is considerably (by 0.12 Å) longer than the unbridged C5–B6 (1.571 Å).

A  $C_s$  *nido*-2,3,5- $\text{C}_3\text{B}_3\text{H}_7$  structure, **TS-22/22**, which does not allow the *endo*-H at C5 to bridge to B4 or to B6 (the H<sup>*endo*</sup>–B4 separation is 1.527 Å in **22** but 1.882 Å in **TS-22/22**), has intermediate C5–B4,6 distances of 1.641 Å and is a transition structure, 1.1 kcal mol<sup>-1</sup> higher in energy than  $C_1$  **22**. The barrier for hydrogen flipping is only  $0.7 \text{ kcal mol}^{-1}$  in the hexamethyl derivative **22b**. Thus, the *nido*-2,3,5-tricarba-hexaboranes(7) structures have apparent  $C_s$  symmetry in the NMR time scale. The two <sup>11</sup>B NMR signals reported, e.g., for 5-*i*Pr,5-H-2,3,5- $\text{C}_3\text{B}_3\text{Et}_6$ , **22a**, fit better to computed values averaged for **22b** ( $C_1$ ) than

Table 3  
Computed<sup>a</sup> and measured <sup>11</sup>B NMR chemical shifts for *nido*-2,3,5-tricarba-hexaborane(7) derivatives

Vertex	B1	B4	B6
5- <i>i</i> Pr,5-H-2,3,5- $\text{C}_3\text{B}_3\text{Et}_6^-$ , <b>22a</b> , exp. <sup>b</sup>	-36	23	
2,3,5- $\text{C}_3\text{B}_3\text{H}_7$ , <b>22</b> , $C_1$ , calc.	-49.6	11.9	14.3
2,3,5- $\text{C}_3\text{B}_3\text{H}_7$ , <b>22</b> , $C_1$ , calc., averaged	-49.6	13.1	
2,3,5- $\text{C}_3\text{B}_3\text{H}_7$ , <b>TS-22/22</b> , $C_s$ , calc.	-43.0	18.6	
2,3,5- $\text{C}_3\text{B}_3\text{Me}_6\text{H}$ , <b>22b</b> , $C_1$ , calc.	-35.6	19.6	21.4
2,3,5- $\text{C}_3\text{B}_3\text{Me}_6\text{H}$ , <b>22b</b> , $C_1$ , calc., averaged	-35.6	20.5	
2,3,5- $\text{C}_3\text{B}_3\text{Me}_6\text{H}$ , <b>TS-22b/22b</b> , $C_s$ , calc.	-31.0	24.1	

<sup>10</sup> The computed chemical shifts for **16** are: -59.8 (B1), 4.7 (B5,6); 86.6 (C2,4), 81.3 (C3).

<sup>11</sup> For additional computed  $\text{C}_3\text{B}_3\text{H}_7$  isomers, see Ref. [10].

<sup>a</sup> GIAO-SCF/6-31G\*//MP2(fc)/6-31G\*.

<sup>b</sup> Ref. [42].

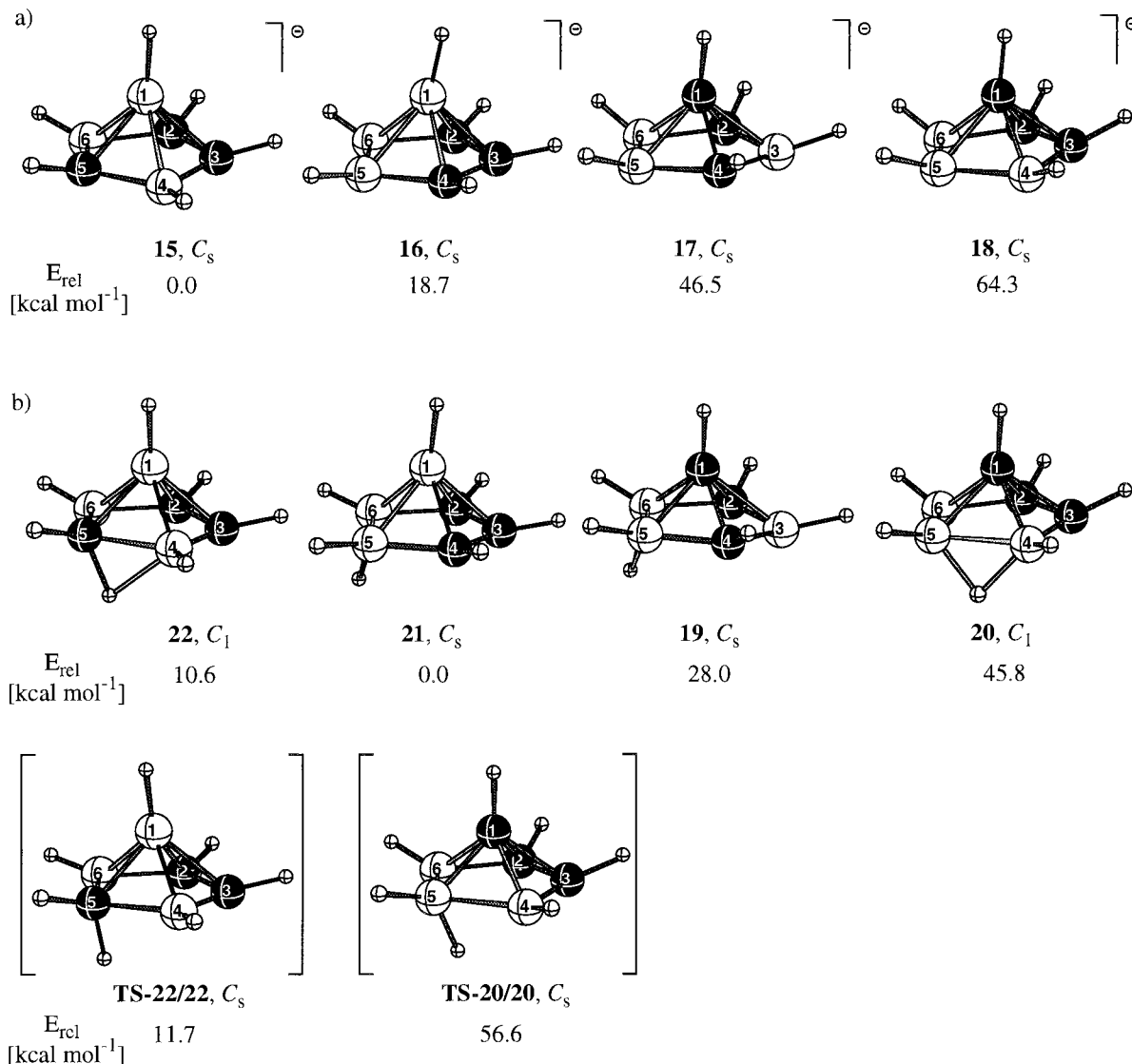


Fig. 4. Optimized geometries and relative energies of (a) some *nido*-tricarba-hexaborane(7) anions and (b) some *nido*-tricarba-hexaborane(7) isomers.

for the  $C_s$  symmetric transition structure **TS-22b/22b** (Table 3). This situation resembles that for  $B_5H_{11}$ : computed chemical shifts reproduce the experimental data for an averaged  $C_1$  but not for the  $C_s$  transition structure [3,45]. Although CHB hydrogen bridging results in an unsymmetrical cluster geometry (in **22**, C5–B4 becomes longer, C5–B6 becomes shorter compared to **TS-22/22**), B4 and B6 chemical shifts do not differ much and are both at lower field (in **22** and **22b**) compared to those in the  $C_s$  symmetric alternatives (**TS-22/22** and **TS-22b/22b**, Table 3). The computed  $^1H$  NMR chemical shift for the *endo*-H in **22b** (–2.6 ppm) is at only moderately higher field compared to **TS-22/22** (–1.5 ppm). Thus it is difficult to distin-

guish between *endo*-CH and CHB hydrogen bridging on the basis of  $^1H$  chemical shifts alone.

#### 4. Conclusions

The  $C_2B_4Et_6H_2$  compound **X**, claimed to be the first *nido*-2-carba-pentaborane(8), **3a** [16], is shown computationally actually to be a *nido*-2,3-dicarba-hexaborane(8) derivative, **10a**. Chemical shifts calculated for a hexamethyl model compound **10b**, but not for **3**, agree with the experimental NMR data [21,22]. Hence, deprotonation of **X** to give the corresponding 2,4-dicarba-hexaborane(8) anion, **4a**, (and re-protona-



tion to **X**) is not an example for a reversible incorporation of a carbon atom into a carborane cluster. *Nido*-2,4-dicarba hexaboranes(8) (e.g., **10**) and *nido*-2,3,5-tricarba hexaboranes(7) (e.g., **22**) have unsymmetrical *endo*-CH's which are strongly tilted towards one of the two neighbouring boron atoms to form partial CHB hydrogen bridges. The parent compounds, *nido*-2,4- $C_2B_4H_8$ , **10**, and *nido*-2,3,5- $C_3B_3H_7$ , **22**, have relative energies 4.6 and 10.6 kcal mol<sup>-1</sup> higher than those of the most stable isomers, *nido*-2,3- $C_2B_4H_8$ , **9**, and *nido*-2,3,4- $C_3B_3H_7$ , **21**, respectively.

Transforming a BHB hydrogen bridge into an *endo*-BH (embedded between boron atoms) results in transition structures for hydrogen migration (e.g., **TS-6/6**, **TS-7/8**, **TS-5/13**, **TS-20/20**) ca. 10 kcal mol<sup>-1</sup> higher in energy.

The *nido*- $C_2B_4H_8$  isomer **14**, with a cluster structure (ni-6<IV>) derived from a pentagonal bipyramid by removing a basal rather than an apical vertex, is 16 and 9 kcal mol<sup>-1</sup> more stable than the more conventional-appearing *nido*-1,2- $C_2B_4H_8$  structures (ni-6<V>) **5** and **13**, respectively. Compound **14** is proposed as an alternative to *nido*-1,2-dicarba-hexaborane(8) as a reasonable intermediate in the *arachno*-1-carba-pentaborane(10) to *closo*-1,5-dicarba-pentaborane(5) degradation.

Attention is called to the related study of Ezhova, Zhang, Maguire, and Hosmane on  $C_2B_4H_7^-$  derivatives<sup>12</sup>, which recently came to our attention. Attempted protonations failed to yield  $C_2B_4H_8$  derivatives.

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<sup>12</sup> Apart from Ref. [16] we are only aware of a very recent report in the literature of protonation of 2,4- $C_2B_4H_7^-$ , see Ref. [39].

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