

# Stability and NMR correlations, experimental vs. calculational, among isoelectronic closo-hexaborane / carborane compounds<sup>1</sup>

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## Abstract

The results of IGLO/NMR and GIAO/NMR calculations on the known closo-hexaborate ions  $[R-XB_5H_5]^{2-}$  and their protonated counterparts  $[R-XB_5H_6]^-$  ( $R = H, CH_3, CN, Cl; X = B, R = H, CH_3; X = C$ ) are correlated with experimental data. A consideration of plausible transition states for  $[Me-B_6H_6]^-$  bridging hydrogen tautomerism leads to the conclusion that such tautomerism is expected to be more facile for the compound  $[R-XB_5H_6]^-$  where  $X = B$  than for the compounds where  $X = C$ . NICS calculations are performed on all compounds and compared to those reported earlier for 'aromatic' vs. 'non-aromatic' systems. © 1998 Elsevier Science S.A.

*Keywords:* Carborane; Boron hydride; IGLO/NMR; GIAO/NMR

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## 1. Introduction

The closo-monocarba-hexaborane,  $CB_5H_7$  [2,3], in which the lone carbon and the five boron atoms are arranged in a nearly octahedral fashion [2–6], Fig. 1, has been the subject of theoretical calculational examinations [7–11]. Methyl derivatives of this cluster compound system have undergone ab initio studies in which isomer stabilities [12] have been examined both experimentally and calculationally. Also, some NMR chemical shift comparisons, calculational vs. experimental, have been made on the parent  $CB_5H_7$  carborane [13,14]. Chemically, it should be pointed out that  $CB_5H_7$  can be converted to the conjugate ion,  $[CB_5H_6]^-$ , by reaction with NaH [15]. We have also effected this apparent bridging-hydrogen deprotonation step by interaction of closo- $CB_5H_7$  with trimethylamine.<sup>2</sup> With this in mind, it is to be noted that very much related to this monocar-

ba-hexaborane system is the isoelectronic [closo- $B_6H_6]^{2-}$  ion [17–21], Fig. 1, its protonated counterpart,  $[B_6H_7]^-$  ion [22,23], as well as their known derivatives [20,21,23]. In the present study we pursue a comparison of ab-initio-derived calculational results with structural and NMR data on these systems in a venture similar to, and an extension of, that carried out earlier on the  $CB_5H_7$  system [12].

## 2. Experimental

Energy-optimized calculated structures for all molecules (see Table 1; Figs. 1 and 2) in this study were obtained by application of the ab initio GAUSSIAN-94 codes [24] with split valence basis sets at the HF/3-21G level and with polarization functions at the HF/6-31G<sup>\*</sup> level of theory. For those fully optimized structures in which structural data are available the calculated structural parameters (Table 1) are very nearly those experimentally determined. Those full geometry optimizations resulting in a stable structures (e.g. those given in Tables 2 and 3) also gave no imaginary frequencies upon subjecting each compound to a vibrational frequency calculation at the respective levels of theory. Those transition state structures (vide infra) (Fig. 3) with a bridging hydrogen confined along a B–B edge

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<sup>1</sup> This study is dedicated to Professor Kenneth Wade on the occasion of his 65th birthday. His many contributions to cluster boron chemistry are legend. He developed what is now commonly called Wade's rules [1], paramount in the correlation of cluster, and ring, systems incorporating atoms all across the periodic table.

<sup>2</sup> We find that trimethylamine reacts with  $CB_5H_7$  to give the  $[CB_5H_6]^-$  ion [16].

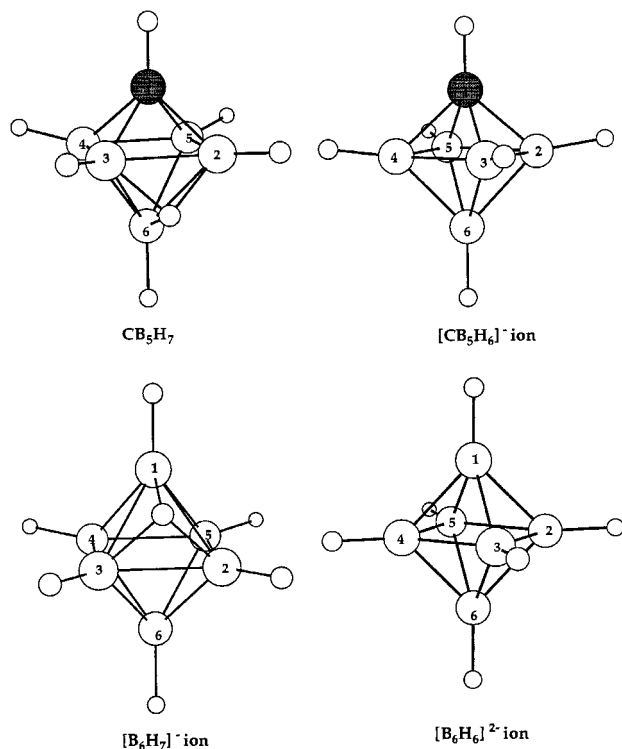


Fig. 1. 6-31G<sup>\*</sup>-optimized structures of CB<sub>5</sub>H<sub>7</sub>, the isoelectronic [CB<sub>5</sub>H<sub>7</sub>]<sup>−</sup> ion, and their corresponding deprotonated counterparts.

(rather than on a BBB face), and necessarily partially optimized within the constraints of the symmetry requirements, produced one negative frequency at the levels of theory used in the present calculations. MP2/6-31G<sup>\*</sup>//6-31G<sup>\*</sup> single point calculations, Table 2, were also carried out in those instances where relative stabilities of isomers were of interest. It should be noted that the molecular geometries that were optimized at the HF/6-31G<sup>\*</sup> level differ very little from the same molecules obtained from a geometry optimization at the HF/3-21G level of theory.

The total energies along with zero-point energies are given in Table 2 for the closo-hexaborane dianion and some derivatives, the parent closo-hexaborane monoanion, its methyl derivative (both isomers) and corresponding transition state structures. The relative energies for the same compounds are also tabulated in Table 3.

The energy-optimized structures were used to calculate the chemical shieldings using the IGLO<sup>3</sup> and GIAO [26] methods. The IGLO method makes use of Huzinaga Gaussian lobe functions [27]. All IGLO calculations were performed with a double- $\zeta$  (DZ) set in the contractions (21) for H, (4111/21) for first row ele-

ments, and (511111/3111) for the Cl atoms. The <sup>13</sup>C NMR chemical shifts are referenced to TMS and the <sup>11</sup>B chemical shifts are referenced to B<sub>2</sub>H<sub>6</sub> which are in turn experimentally referenced to Et<sub>2</sub>O · BF<sub>3</sub> [28]. GIAO calculations on geometry-optimized tetramethylsilane (at the 6-31G<sup>\*</sup> level of theory) give rise to a <sup>13</sup>C shielding  $\sigma$  of 201.7 ppm at the 6-31G<sup>\*</sup> level of theory. Thus, for the GIAO calculations of all other compounds in this study  $\delta(^{13}\text{C}) = 201.7 - \sigma(^{13}\text{C})$ .

The IGLO and GIAO results are summarized in Tables 4 and 5. The small geometry differences between structures optimized at the 3-21G and 6-31G<sup>\*</sup> levels did not generally cause significant changes in calculated chemical shifts.

Nucleus independent chemical shift (NICS) calcula-

Table 1  
Calculated and experimental bond distances for various hexaboranes

Compound		Experimental <sup>a</sup>	HF/3-21G	HF/6-31G <sup>*</sup>
[B <sub>6</sub> H <sub>7</sub> ] <sup>−</sup>	B1 – B2	—	1.940	1.888
	— B4	—	1.728	1.713
	B2 – B3	—	1.940	1.888
	— B5	—	1.728	1.713
	— B6	—	1.728	1.713
	B4 – B5	—	1.747	1.731
[B <sub>6</sub> H <sub>6</sub> ] <sup>2−</sup>	B4 – B6	—	1.747	1.731
	B1 – B2	1.69	1.759	1.739
[1-C1B <sub>6</sub> H <sub>5</sub> ] <sup>2−</sup>	Cl – B	—	1.985	1.932
	B1 – B2	—	1.730	1.715
	B2 – B3	—	1.770	1.748
	— B6	—	1.751	1.733
[B <sub>6</sub> H <sub>5</sub> (CN)] <sup>2−</sup>	C – N	1.164	1.152	1.148
	B1 – C	1.542	1.554	1.574
	B1 – B2	1.708	1.749	1.727
	— B3	1.727	1.749	1.727
	— B4	1.722	1.748	1.727
	— B5	1.720	1.748	1.727
	B2 – B3	1.762	1.762	1.744
	— B5	1.747	1.762	1.744
	— B6	1.724	1.755	1.735
	B3 – B4	1.733	1.762	1.744
[B <sub>6</sub> H <sub>6</sub> (CH <sub>3</sub> )] <sup>−</sup>	— B6	1.736	1.755	1.735
	B4 – B5	1.765	1.762	1.744
	— B6	1.750	1.755	1.735
	B5 – B6	1.709	1.755	1.735
	C – B1	1.578	1.595	1.606
	B1 – B2	1.842	1.973	1.904
	— B3	1.704	1.726	1.715
	— B4	1.743	1.725	1.715
	— B5	1.865	1.973	1.904
	B2 – B3	1.692	1.731	1.711
	— B5	1.823	1.920	1.887
	— B6	1.694	1.728	1.711
	B3 – B4	1.702	1.754	1.729
	— B6	1.698	1.742	1.728
	B4 – B5	1.718	1.731	1.711
— B6	1.697	1.742	1.728	
B5 – B6	1.688	1.728	1.711	

<sup>3</sup> The IGLO method employed here was designed by Kutzelnigg, Schindler and coworkers [25].

<sup>a</sup> For [B<sub>6</sub>H<sub>6</sub>]<sup>2−</sup> see Ref. [18]; for [B<sub>6</sub>H<sub>5</sub>(CN)]<sup>2−</sup> see Ref. [21]; for [B<sub>6</sub>H<sub>6</sub>(CH<sub>3</sub>)]<sup>−</sup> see Ref. [23].

Table 2

Total energies (in Hartrees) of  $[\text{B}_6\text{H}_6]^{2-}$  (and some derivatives),  $[\text{B}_6\text{H}_7]^-$ ,  $[\text{1-Me-B}_6\text{H}_6]^-$  and their corresponding transition state structures at different levels of optimization

Compound	3-21G//3-21G (ZPE) <sup>e</sup>	6-31G*//6-31G* (ZPE)	MP2/6-31G*//6-31G*	NF <sup>f</sup>
$[\text{B}_6\text{H}_7]^-$	-151.2734 (56.9936)	-152.1501 (57.7809)	-152.7118	(0)
$[\text{B}_6\text{H}_7]^-$ (ts)	-151.2553 (56.7153)	-152.1305 (57.2369)	-152.6912	(1)
$[\text{1-Me-B}_6\text{H}_6]^-$	-190.1060 (75.6270)	-191.1919 (76.6497)	-191.8859(8)	(0)
$[\text{1-Me-B}_6\text{H}_6]^-$ <sup>a</sup>	-190.1050 (75.8568)	-191.1917 (76.6206)	-191.8860(5)	(0)
$[\text{1-Me-B}_6\text{H}_6]^-$ (ts) <sup>b</sup>	-190.0865 (75.9534)	-191.1714 (76.3772)	-191.8645	(1)
$[\text{1-Me-B}_6\text{H}_6]^-$ (ts) <sup>c</sup>	-190.0891 (75.6011)	-191.1738 (76.0599)	-191.8671	(1)
$[\text{1-Me-B}_6\text{H}_6]^-$ (ts) <sup>d</sup>	-190.0873 (75.6916)	-191.1722 (76.1588)	-191.8654	(1)
$[\text{1-Cl-B}_6\text{H}_5]^{2-}$	-607.3807 (45.4470)	-610.4126 (45.3784)	-611.1006	(0)
$[\text{B}_6\text{H}_5(\text{CN})]^{2-}$	-241.8698 (51.0012)	-243.2439 (50.8915)	-244.0775	(0)
$[\text{B}_6\text{H}_6]^{2-}$	-150.5703 (49.8529)	-151.4276 (49.5552)	-151.9906	(0)
$[\text{1-Me-B}_6\text{H}_5]^{2-}$	-189.4022 (68.5530)	-190.4709 (68.2542)	-191.1662	(0)

<sup>a</sup> The other possible stable isomer of  $[\text{1-Me-B}_6\text{H}_6]^-$  in which the bridging hydrogen lies on one of the faces located on the lower part of the cage away from the carbon-attached boron atom.

<sup>b</sup> Transition state structure in which the bridging hydrogen is constrained along the B(1,2 or 1,3, etc.) edge.

<sup>c</sup> Transition state structure in which the bridging hydrogen is constrained along the B(2,6 or 3,6, etc.) edge.

<sup>d</sup> Transition state structure in which the bridging hydrogen is constrained along the B(2,3) edge but in the B(2,3,4,5) plane.

<sup>e</sup> The values in parentheses are zero-point energy corrections ( $\text{kcal mol}^{-1}$ ).

<sup>f</sup> The number of negative frequencies generated in the 3-21G and 6-31G\* frequency calculations.

tions were carried out as described by Schleyer et al. [29]. The GAUSSIAN-94 application allows for the use of 'ghost atoms' [30], at essentially any arbitrary point

relative to the spatial position of the molecule, to compute GIAO magnetic properties at that point. Placement of a ghost atom at the non-weighted mean of the heavy atom coordinates of a cage or ring molecule produced

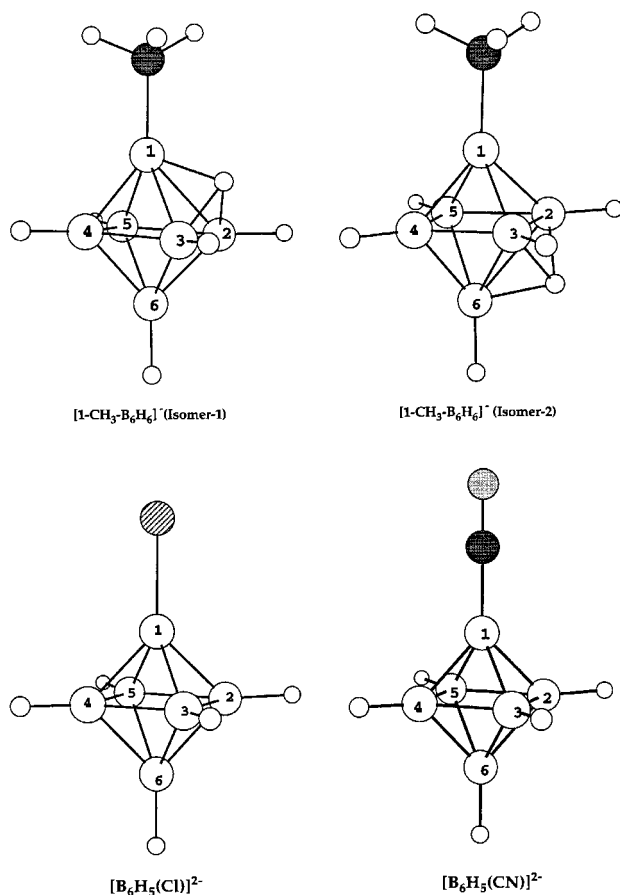


Fig. 2. 6-31G\*-optimized structures of the two isomers of the  $[\text{1-CH}_3\text{-B}_6\text{H}_6]^-$  ion and two derivatives of  $[\text{B}_6\text{H}_6]^{2-}$ , chloro and cyano.

Table 3

Relative energies ( $\text{kcal mol}^{-1}$ ) of  $[\text{B}_6\text{H}_7]^-$ ,  $[\text{1-Me-B}_6\text{H}_6]^-$  and their corresponding transition state structures at different levels of optimization

Compound	3-21G (+ ZPE) <sup>a</sup>	6-31G* (+ ZPE)
$[\text{B}_6\text{H}_7]^-$	0.0	0.0
$[\text{B}_6\text{H}_7]^-$ (ts)	11.4 (11.1)	12.3 (11.8)
$[\text{1-Me-B}_6\text{H}_6]^-$ (Isomer 1)	0.0	0.0
$[\text{1-Me-B}_6\text{H}_6]^-$ (ts) <sup>b</sup>	12.2 (12.5)	12.9 (12.6)
$[\text{1-Me-B}_6\text{H}_6]^-$ (Isomer 2) <sup>c</sup>	0.0	0.0
$[\text{1-Me-B}_6\text{H}_6]^-$ (ts) <sup>d</sup>	10.0 (9.7)	11.2 (10.7)
$[\text{1-Me-B}_6\text{H}_6]^-$ (ts) <sup>e</sup>	11.7 (11.8)	12.4 (11.9)
$[\text{1-Me-B}_6\text{H}_6]^-$ (ts) <sup>f</sup>	11.1 (10.9)	12.2 (11.8)

<sup>a</sup> The values in parentheses include the zero-point energy correction. The value of 0.0 is used as a standard relative to the value immediately below in the same column.

<sup>b</sup> Transition state structure in which the bridging hydrogen is constrained along the B(1,2) edge, keeping in mind that the B(1,2) position is degenerate with B(1,3), B(1,4) and B(1,5) positions in the non-protonated system.

<sup>c</sup> A stable form of  $[\text{1-Me-B}_6\text{H}_6]^-$  in which the bridging hydrogen is located on one of the triangular faces on the lower part (e.g. 2,3,6 or 3,4,6, etc.) of the cage.

<sup>d</sup> Transition state structure in which the bridging hydrogen is constrained along the B(2,6) edge, keeping in mind that the B(2,6) position is degenerate with B(3,6), B(4,6) and B(5,6) positions in the non-protonated system.

<sup>e</sup> Transition state structure in which the bridging hydrogen is constrained along the B(2,3) edge but in the equatorial B(2,3,4,5) plane of the molecule, keeping in mind that the B(2,3) position is degenerate with B(3,4), B(4,5) and B(5,2) positions in the non-protonated system. Energy is with respect to Isomer 1.

<sup>f</sup> As footnote e, except energy is with respect to Isomer 2.

the NICS values cited in Table 6 and discussed in the body of this study.

Calculations were carried out, variously, on SUN

4/280, and SUN SPARC station Model 10 computers.

The GAUSSIAN-94 code was also employed using the SDSC Cray C90 regional facility.

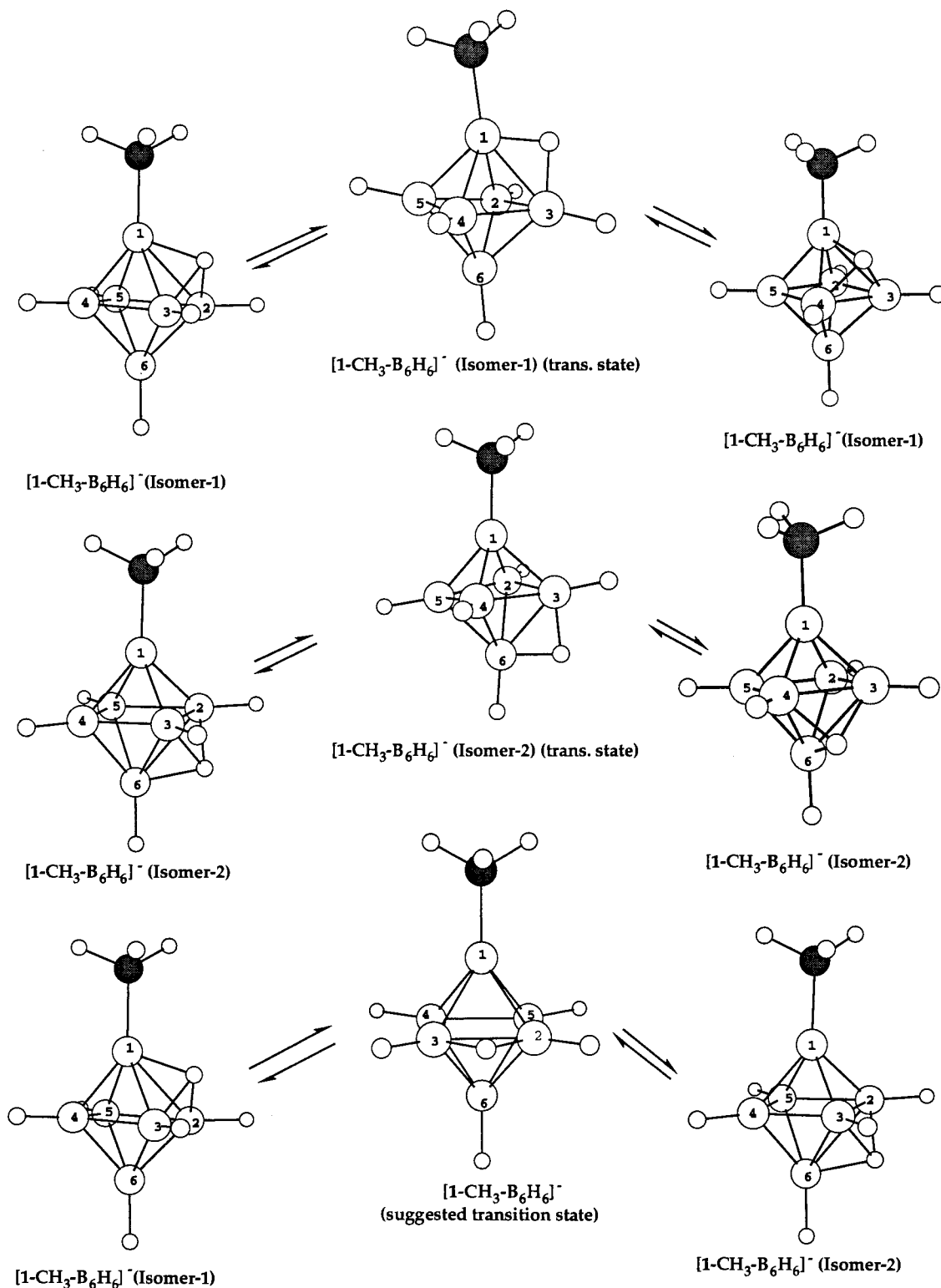


Fig. 3. Depiction of 6-31G\* -optimized structures of the two stable isomers of  $[1\text{-CH}_3\text{-B}_6\text{H}_6]^-$  ion and the considered transition states.

### 3. Results and discussion

#### 3.1. Structures and energies

Correlations of experimentally obtained bond distances (Table 1, Figs. 4 and 5), as well as other geometrical features, to ab-initio-derived parameters for those hexaborane compounds in which geometries have been determined, are generally excellent. In the case of the B-methyl derivative of  $[\text{B}_6\text{H}_7]^-$  there was some concern that, in solution (the phase in which NMR data was gathered), two possible isomers, Fig. 2, might well be in competition with one another. This led us to examine ab-initio-derived geometries, and relative stabilities, for both of these bridging hydrogen position isomers (tautomers), and to determine the barrier to tautomerism in a manner previously carried out for the isoelectronic 2-Me- $\text{CB}_5\text{H}_6/4\text{-Me-}\text{CB}_5\text{H}_6$  system [12]. The total energies (Table 2) of the two  $[\text{1-Me-}\text{B}_6\text{H}_6]^-$  isomers are found to be very similar to one another. At the 3-21G//3-21G and 6-31G\*/6-31G\* levels of theory, the total-energy differences between isomers are only  $0.63 \text{ kcal mol}^{-1}$  and  $0.13 \text{ kcal mol}^{-1}$  respectively in favor of the isomer reported in the literature [23], Fig. 2 (isomer 1), whereby the bridging hydrogen is located on one of the four symmetry-related triangular faces that contain the methyl-attached boron atom. The other

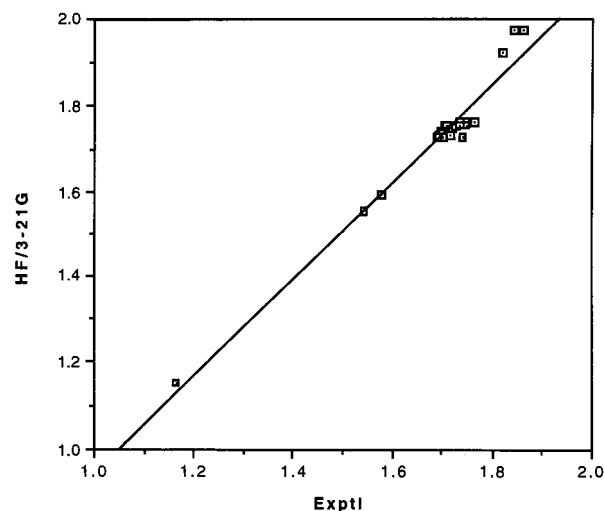


Fig. 4. HF/3-21G-optimized bond distances (Å) for  $[\text{B}_6\text{H}_5(\text{CN})]^{2-}$  and  $[\text{B}_6\text{H}_6(\text{CH}_3)]^-$  (combined) plotted against experimental values [21,23].  $\delta(\text{HF}/3\text{-}21\text{G}) = -0.1881 + 1.1297\delta$  (exptl.);  $r^2 = 0.958$ .

proposed isomer, Fig. 2 (isomer 2), is that in which the bridging hydrogen is located on one of the four symmetry-related triangular faces *not* containing the methyl-attached boron atom. Higher level calculations (at the MP2/6-31G\*/6-31G\* level of theory) carried out on the two isomers resulted in a  $0.04 \text{ kcal mol}^{-1}$  differ-

Table 4  
Experimental and calculated  $^{11}\text{B}$  NMR chemical shifts for various hexaboranes

Compound	Position	$\delta$ , exptl.	$\delta$ , IGLO		
			DZ//3-21G	DZ//6-31G*	6-31G*/6-31G*
$[\text{B}_6\text{H}_6]^{2-}$	B(1–6)	–13.50 <sup>d</sup>	–17.81	–16.84	–18.19
$[\text{B}_6\text{H}_7]^-$	B(1–6)	–13.51 <sup>e</sup>	–12.11	–13.64	–15.55
$[\text{1-Me-}\text{B}_6\text{H}_6]^-$ <sup>a</sup>	B(1)	–3.44 <sup>e</sup>	–1.23	–7.03	–10.40
	B(2,3,4,5)	–12.96	–11.79	–13.06	–14.56
	B(6)	–19.07	–16.56	–16.25	–16.00
$[\text{1-Me-}\text{B}_6\text{H}_6]^-$ <sup>b</sup>	B(1)	–3.44 <sup>e</sup>	–3.39	–4.03	–4.98
	B(2,3,4,5)	–12.96	–12.51	–13.93	–15.30
	B(6)	–19.07	–20.11	–22.56	–23.88
$[\text{1-Me-}\text{B}_6\text{H}_6]^-$ <sup>c</sup>	B(1)	–3.44 <sup>e</sup>	–2.31	–5.53	–7.69
	B(2,3,4,5)	–12.96	–12.15	–13.50	–14.93
	B(6)	–19.07	–18.33	–19.41	–19.94
$[\text{Cl-1-B}_6\text{H}_5]^{2-}$	B(1)	–1.00 <sup>d</sup>	0.16	–5.10	–2.49
	B(2,3,4,5)	–14.50	–18.56	–18.90	–19.16
	B(6)	–30.40	–29.44	–27.24	–27.60
$[\text{B}_6\text{H}_5(\text{CN})]^{2-}$	B(1)	–24.10 <sup>f</sup>	–23.84	–24.62	–25.43
	B(2,3,4,5)	–11.50	–15.01	–16.61	–16.36
	B(6)	–10.20	–12.77	–14.72	–13.71

<sup>a</sup> Bridging hydrogen is on the B(1,2,3) face, one that involves the carbon-attached boron atom.

<sup>b</sup> Bridging hydrogen is on the B(2,3,6) face, one in which none of these boron atoms are attached to the carbon.

<sup>c</sup> The calculated chemical shifts for the two above isomers were averaged together.

<sup>d</sup> See Ref. [20].

<sup>e</sup> See Ref. [22].

<sup>f</sup> See Ref. [21].

Table 5

Experimental and theoretical (IGLO/GIAO) chemical shifts of  $\text{CB}_5\text{H}_7$  and some of its methyl derivatives

Compound	Atom	Experimental <sup>a</sup>	IGLO	IGLO	GIAO
			DZ//3-21G	DZ//6-31G*	6-31G*//6-31G*
$\text{CB}_5\text{H}_7$	C(cage)	58.70	42.95	45.55	40.97
	B23 or 45	-7.21	0.90	-5.40	-8.88
	B45 or 23	-16.51	-16.63	-18.73	-20.05
	B6	5.17	24.90	12.39	8.38
1- $\text{CH}_3$ -1- $\text{CB}_5\text{H}_6$	C(cage)	—	49.80	52.44	53.74
	C(Me)	—	13.38	13.24	13.55
	B23 or 45	-7.90	-0.04	-4.76	-7.21
	B45 or 23	-17.60	-15.68	-19.20	-19.13
	B6	-4.60	19.78	5.85	1.78
2- $\text{CH}_3$ -1- $\text{CB}_5\text{H}_6$	C(cage)	58.00	44.60	46.85	42.48
	C(Me)	-5.50	-4.88	-5.34	-6.53
	B2	-5.27	-5.03	-6.97	-10.12
	B3	-17.60	-18.63	-18.60	-19.46
	B4	-15.20	-5.87	-12.32	-13.62
	B5	-8.20	-0.70	-6.64	-9.03
	B6	3.19	24.82	11.75	8.07
4- $\text{CH}_3$ -1- $\text{CB}_5\text{H}_6$	C(cage)	—	41.12	43.27	39.43
	C(Me)	—	-2.69	-3.60	-4.95
	B2	-24.10	-21.64	-23.96	-24.00
	B3	-18.40	-17.67	-19.51	-20.07
	B4	1.72	11.92	4.94	0.92
	B5	-7.20	1.75	-4.49	-6.34
	B6	3.00	24.13	14.78	11.29
6- $\text{CH}_3$ -1- $\text{CB}_5\text{H}_6$	C(cage)	—	33.78	34.13	30.05
	C(Me)	—	-1.21	-2.51	-2.86
	B23	-18.70	-15.65	-18.85	-19.04
	B45	-9.40	-1.26	-3.55	-6.21
	B6	17.20	38.06	29.24	24.96

<sup>a</sup> See Ref. [14] for experimental values associated with  $\text{CB}_5\text{H}_7$  and 2-Me- $\text{CB}_5\text{H}_6$ .

ence in total energies, but now favoring the 'other', Fig. 2 (isomer 2), isomer. These rather small energy differences, as well as the general trend, suggest that very close to a 50:50 mixture of the two tautomeric isomers could well exist at equilibrium. This is to be compared to the isoelectronic system, the 2- and 4- $\text{CH}_3$ -1- $\text{CB}_5\text{H}_7$  equilibrium [12], in which both experimental and calcu-

lational information lead to an approximately 3:1 equilibrium ratio of the two isomers respectively; in this carborane system the bridging hydrogen favors a posi-

Table 6

NICS [29] values for various closo-hexaboranes at the (6-31G\*//6-31G\* level of theory; geometric NICS center determined by averaging coordinates of all non-hydrogen cage atoms

Compound	NICS (ppm) <sup>b</sup>
$\text{CB}_5\text{H}_7$	-33.04
1-Me- $\text{CB}_5\text{H}_6$	-33.31
$[\text{B}_6\text{H}_6]^{2-}$	-33.79
$[\text{B}_6\text{H}_7]^-$	-33.21
$[\text{Cl-B}_6\text{H}_5]^{2-}$	-36.60
$[\text{B}_6\text{H}_5(\text{CN})]^{2-}$	-34.02
[1-Me- $\text{B}_6\text{H}_6]^-$ (isomer 1) <sup>a</sup>	-32.81
[1-Me- $\text{B}_6\text{H}_6]^-$ (isomer 2)	-33.04
1,2- $\text{C}_2\text{B}_4\text{H}_6$	-34.86
1,6- $\text{C}_2\text{B}_4\text{H}_6$	-35.89

<sup>a</sup> Isomer 1 has its bridging hydrogen closest to B-Me on the BBB face.

<sup>b</sup> Negative values are upfield.

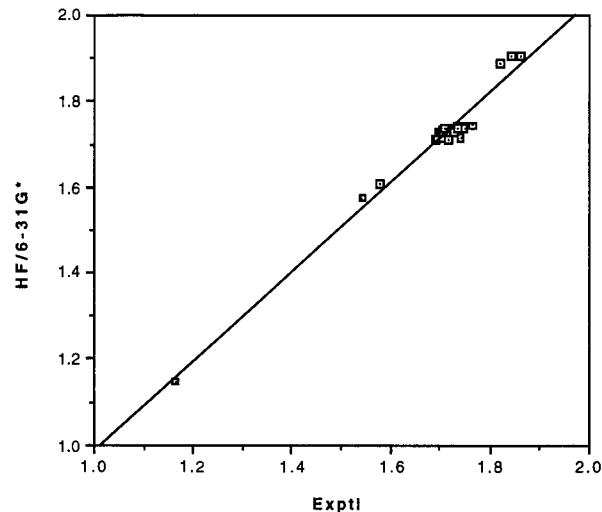


Fig. 5. HF/6-31G\*-optimized bond distances (Å) for  $[\text{B}_6\text{H}_6(\text{CN})]^{2-}$  and  $[\text{B}_6\text{H}_6(\text{CH}_3)]^-$  (combined) plotted against experimental values [21,23].  $\delta(\text{HF}/6-31\text{G}^*) = -0.063657 + 1.0451 \delta(\text{exptl.})$ ;  $r^2 = 0.971$ .

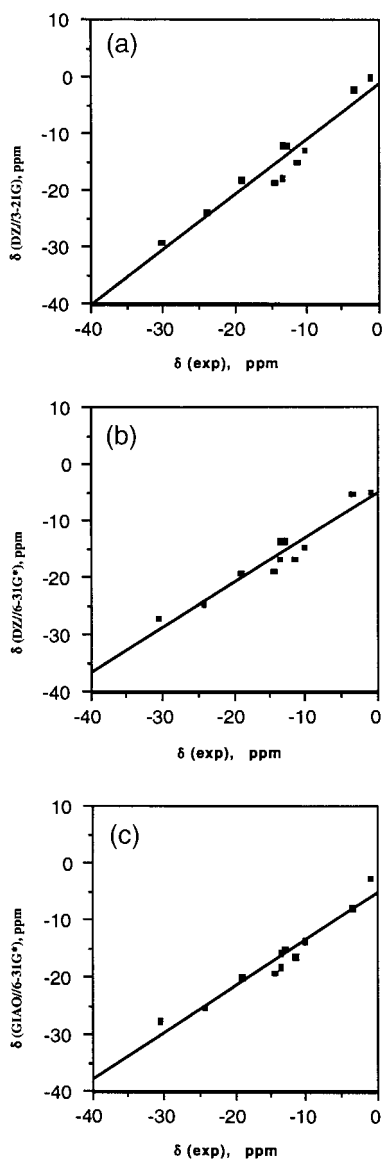


Fig. 6.  $^{11}\text{B}$  NMR chemical shift comparisons between experimental and: (a) IGLO (DZ//3-21G) calculated values for all the compounds in Table 4,  $\delta(\text{DZ//3-21G}) = 0.98238\delta_{(\text{exp})} - 0.974$  ( $r^2 = 0.925$ ); (b) IGLO (DZ//6-31G $^*$ ) calculated values for all the compounds in Table 4,  $y = 0.78474\delta_{(\text{exp})} - 5.0099$  ( $r^2 = 0.929$ ); (c) GIAO(6-31G $^{**}$ /6-31G $^*$ ) calculated values for all the compounds in Table 4,  $\delta(6-31\text{G}^*/6-31\text{G}^*) = 0.82661\delta_{(\text{exp})} - 4.8730$  ( $r^2 = 0.938$ ).

tion on a triangular BBB face in which one boron has the attached methyl group, much the same as suggested in the  $[\text{Me-B}_6\text{H}_7]^-$  ion system) [23].

Is it then plausible that tautomeric activity between the isomers in the  $[\text{1-Me-B}_6\text{H}_6]^-$  is potentially facile at room temperature and can thus lead to serious consideration of 'both' isomers for the purpose of ab initio NMR calculations and consequent comparisons with experimental data? The transition state structure to this type of tautomerism is considered to be that in which the bridging hydrogen is confined along an appropriate

B–B edge (Fig. 3). This portion of the study follows the same approach as previously cited in a closo- $\text{CB}_5\text{H}_7$  study [11,12], a compound in which significant intramolecular bridging hydrogen tautomerism is most likely occurring. The locations of the bridging hydrogen along two of the three non-equivalent edges (B1–B2 and B2–B6) of  $[\text{1-Me-B}_6\text{H}_6]^-$  are relatively easy to determine by a simple examination of the symmetry requirements. However, location of the bridging hydrogen along the third (B2–B3) edge of this ion would require a rather extensive ab initio examination of a series of structures to locate the saddle point. This was not considered necessary when one considers that the magnitude of other comparison tautomeric barriers fall between 10 and 14 kcal mol $^{-1}$ , an energy region that would lead to the prediction that at room temperature there would be, on the NMR time scale, reasonably facile interconversion of tautomeric isomers. Specifically, the energy barriers to bridging-hydrogen tautomerism, as calculated at the 6-31G $^*$  + ZPE level of theory, are found to be 11.8 kcal mol $^{-1}$  for  $[\text{B}_6\text{H}_7]^-$ , and 12.6 and 10.7 kcal mol $^{-1}$  for the two isomers of  $[\text{1-Me-B}_6\text{H}_6]^-$ , Tables 2 and 3. The magnitudes of these bridging hydrogen barriers are quite similar to, but slightly smaller than, those found for the isoelectronic  $\text{CB}_5\text{H}_7$  [11] and  $\text{CH}_3\text{-CB}_5\text{H}_6$  systems (13 to 16 kcal mol $^{-1}$ ) [12].

### 3.2. IGLO and GIAO chemical shifts

The IGLO and GIAO NMR chemical shift calculational results are tabulated in Table 4. For each compound the small differences between 3-21G-optimized and 6-31G $^*$ -optimized geometries did not cause significant changes in most of either the IGLO or GIAO calculated chemical shifts. Comparison of the experi-

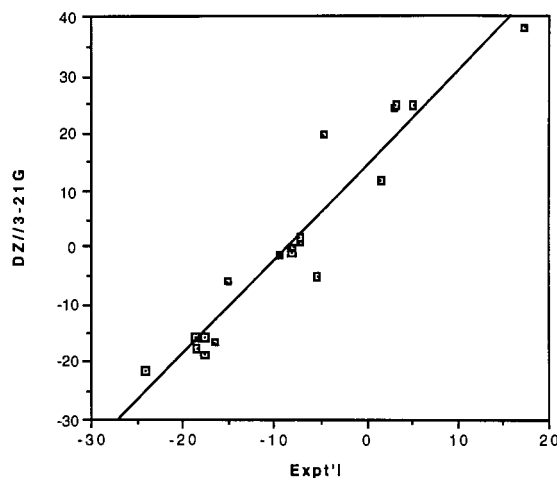


Fig. 7.  $^{11}\text{B}$  NMR chemical shift (ppm) comparisons between experimental and IGLO(DZ//3-21G) calculated values for all the compounds in Table 5;  $\delta(\text{DZ//3-21G}) = 0.919\delta_{(\text{exp})} + 14.2$  ( $r^2 = 0.919$ ).

mentally observed chemical shifts with those obtained computationally is shown graphically in Fig. 6. It should be noted that the average chemical shift values for the two isomers of  $[1\text{-Me-B}_6\text{H}_6]^-$  ion were used rather than the individual values for each isomer. This resulted in the best correlation, implying that fast bridging hydrogen tautomerism in this ion is most probably occurring. The effect of using calculated chemical shift values from only one isomer of  $[1\text{-Me-B}_6\text{H}_6]^-$ , compared to averaging chemical shifts from both isomers, is not very significant but does result in a less favorable correlation.

Correlations between IGLO-derived and experimental  $^{11}\text{B}$  NMR data, and between GIAO-derived and experimental NMR data, for various closo- $\text{CB}_5\text{H}_7$  systems are given in Table 5 and Figs. 7–9. The data for the parent  $\text{CB}_5\text{H}_7$  was reported previously [13,14], and in this present study the experimental and pertinent NMR information on the four methyl derivatives of this closo carborane are added. Expectedly, the IGLO correlation on the compounds that were geometry-optimized at the 3-21G level of theory is not nearly as good as that obtained at the 6-31G\* level. The GIAO correlation appears to be about the same as the IGLO correlation on the compounds that were geometry-optimized at the 6-31G\* level of theory, both with  $r^2$  values exceeding 0.95.

### 3.3. NICS calculations

The concept of NICS as an aromaticity probe has been outlined by Schleyer et al. [29]. Absolute magnetic shieldings computed at ring, or cage, centers (non-weighted mean of the heavy atom coordinates) have been suggested as indicators of aromaticity/anti-

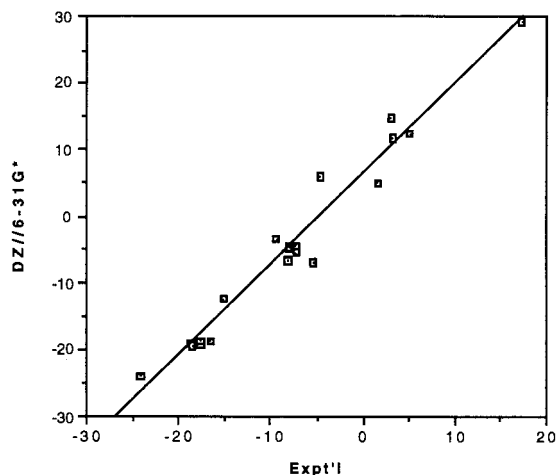


Fig. 8.  $^{11}\text{B}$  NMR chemical shift (ppm) comparisons between experimental and IGLO(DZ//6-31G\*) calculated values for all the compounds in Table 5;  $\delta(\text{DZ//6-31G}^*) = 1.36\delta_{(\text{exp})} + 6.12$  ( $r^2 = 0.962$ ).

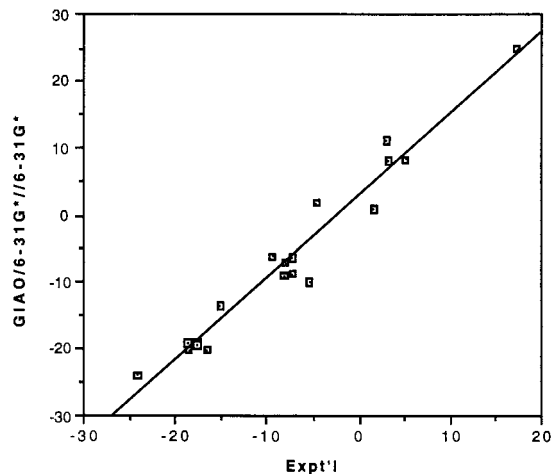


Fig. 9.  $^{11}\text{B}$  NMR chemical shift (ppm) comparisons between experimental and GIAO(6-31G\*//6-31G\*) calculated values for all the compounds in Table 5;  $\delta(6\text{-}31\text{G}^*//6\text{-}31\text{G}^*) = 1.23\delta_{(\text{exp})} + 2.81$  ( $r^2 = 0.953$ ).

aromaticity. Upfield shifts (negative values) indicate some degree of aromaticity whereas downfield shifts (positive values) are indicators of antiaromaticity; rings, or cages, with little upfield or downfield shift(s) are likely to be associated with saturated (non-aromatic), or nearly saturated, systems. For example, benzene gives a NICS value of  $-9.7$  ppm whereas cyclobutadiene gives a value of  $+27.6$  ppm and cyclohexane a value of  $-2.2$  ppm. Spherical aromaticity is suggested for the closo- $[\text{B}_{12}\text{H}_{12}]^{2-}$  ion (NICS of  $-34.4$  ppm), and it is mentioned that this NICS value is representative of the behavior of the entire closo-borane dianion family [29]. The NICS values for compounds mentioned in the present study at the 6-31G\* level of theory have been determined by us and are given in Table 6. These values certainly fall in the region close to that of the  $[\text{B}_{12}\text{H}_{12}]^{2-}$  ion. The problem with any simple interpretation of this as an indicator of aromaticity is that there are no 'saturated' (i.e. non-aromatic?) cage systems that can be used for comparison as there are with ring compounds such as the benzene/cyclohexane pair. It is important to note that the interpretation of three-membered ring NICSs is complicated by the local shielding of nearby  $\sigma$  bonds [29]. Could it be that small ring local  $\sigma$ -shielding contributions in the relatively small octahedral (or near-octahedral) cage systems just might, additively, give an NICS value that is unusually high (i.e. large upfield, negative, value)? It is exciting that the NICS concept [29] offers the prospect of assessing the degree of aromaticity in cage compounds; however, until some 'reference' cage compounds are found to illustrate downfield (antiaromatic) NICS value(s) or zero (or near-zero) non-aromatic systems, just as found in organic ring systems, the significance of NICS values as applied toward cage systems is momentarily elusive.



Nevertheless, the magnitude of the upfield NICS values for the closo-hexaborane compounds listed in Table 6 are impressive and very suggestive of a significant degree of aromatic character.

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