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Structures of carborane cations derived from the reaction of 2-propyl cation with diborane: DFT/IGLO/GIAO-MP2/NMR investigations of alkylborane and alkylcarborane patterns

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Dedicated to Prof. Sheldon G. Shore on the occasion of his 70th birthday.

Abstract

Structures of carborane cations derived from the reaction of 2-propyl cation with diborane have been re-investigated by the DFT/IGLO/GIAO-MP2/NMR method. Based on the results the earlier proposed compound, *arachno*-$Me_2CBH_4^+$ (**4**) was not obtained. The carborane, *arachno*-$MeC_2BH_7^+$ (**5**) (3.4 kcal mol^{-1} more stable than **4**) is a better candidate for the second species observed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In search of carboranes incorporating CHB bridge hydrogens we attempted the preparation of carborane cations incorporating CHB bridge hydrogens from the fusion of carbocations and boron hydrides in superacids (see Fig. 1) [1]. Our initial objective was to prepare a carborane cation related to the simplest boron hydride, *nido*-B_2H_6 (**3**) (Fig. 1). A solution of 2-propyl cation (**2**) was prepared by dissolving 2-fluoropropane (**1**) in an excess of SbF_5–SO_2ClF at -78°C. The 75 MHz ^{13}C-NMR spectrum of the solution revealed a singlet at δ^{13}C 320.6 (C^+) and a quartet δ^{13}C 51.5 (CH_3) confirming the formation of 2-propyl cation, **2** under long lived, stable ion conditions [2]. Diborane **3** was passed through the solution containing isopropyl cation **2** at -78°C in an inert argon atmosphere. Most of the diborane **3** dissolved with no detectable gas evolution and a colorless solution was obtained.

The product from the reaction of **2** and **3** was considered to be the new carborane cation *nido*-C,C-$Me_2CBH_4^+$ (**4**) illustrated in Fig. 1. A triplet-of-triplets representing the $[(-H-)_2BH_2]$ moiety in **4** was expected to be observed in the ^{11}B-NMR spectrum of the clear solution. The boron in the $[(-H-)_2BH_2]$ moiety was anticipated to couple strongly ($J \cong 125 \pm 10$ Hz) with the two terminal hydrogens accounting for the major triplet and to couple weakly ($J \cong 49 \pm 10$ Hz) with the two bridge hydrogens. The estimated J- and δ^{11}B values for the $[(-H-)_2BH_2]$ moiety in cation **4**, which encompasses a ‘BC-skeleton’ were extrapolated from the known J- and δ^{11}B values of the $[(-H-)_2BH_2]$ portion of the isoelectronic and isostructural neutral compound bearing a ‘BB-skeleton’, *nido*-1,1-$Me_2B_2H_4$, see ^{me}**D** in Fig. 2. The expected ‘triplet-of-triplets’ observed in the ^{11}B-NMR spectrum at δ^{11}B -3 is only 6.6 ppm shielded from the expected value of $+3.6$ ppm

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in ^{me}**D**. A second smaller 'triplet-of-triplets' was also observed at considerably higher field, δ^{11}B −24. Related experiments with *nido*-B_5H_9 in SbF_5–SO_2ClF could not be carried out, as the sample became highly unstable. Further studies to obtain ^{13}C-NMR spectra of the 2-propyl cation adduct were also not pursued.

Forty years of accumulated ^{11}B chemical shift values of alkyl-substituted carborane clusters reveal many interesting patterns, two of which were thought to be useful for the identification of suggested structures **4** and **5**. The first pattern involves terminal group substitution: The replacement of an *exo*-terminal hydrogen on a carbon atom on all known carborane clusters by a (generic) alkyl group causes the ^{13}C resonance of that carbon atom to shift to lower field by about 15–25 ppm. A similar substitution on boron causes a shift of the ^{11}B resonance to lower field by 8–12 ppm (see Fig. 2). In contrast, interchanging 'generic' alkyl groups with each other (e.g. Me–, Et–, Pr–, Bu–, etc.) has virtually no influence upon the cluster ^{13}C and/or ^{11}B chemical shift values. For example, when ^{pr}**D** (with two Pr-groups) of Fig. 1 is compared with ^{me}**D** (with two Me-groups) in Fig. 2 the ^{11}B chemical shift values should be (and are) virtually identical. The experimentally observed two sets of 'triplets-of-triplets' (both with *J*-values of 138 and 44 Hz), were both assigned to compounds **4** and **5** in Fig. 1. They were felt to be acceptably similar to the anticipated values, 125 ± 10 and 49.7 ± 10 Hz, extrapolated from compound ^{me}**D** in Fig. 2. Both compounds **4** and **5** (with different structures) 'coincidentally' had the same *J*-values, 138 and 44 Hz, an unexpected and somewhat disturbing result.

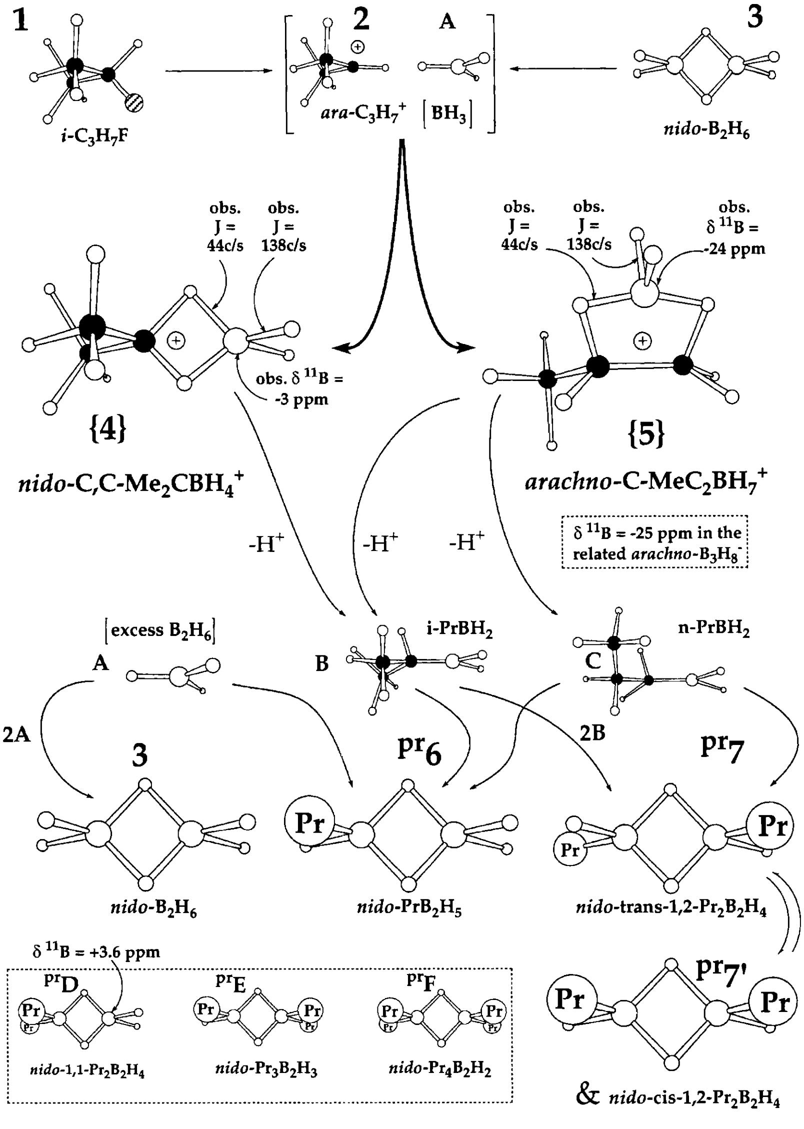


Fig. 1. Compounds labeled **2**, **3**, **6** and **7** represent species clearly observed in the ^{11}B-NMR spectrum. The anticipated compounds **4** and **5** were presumed to have being observed. **A**, **B** and **C** represent intermediates. **D**, **E** and **F** represent compounds that were definitely not observed.

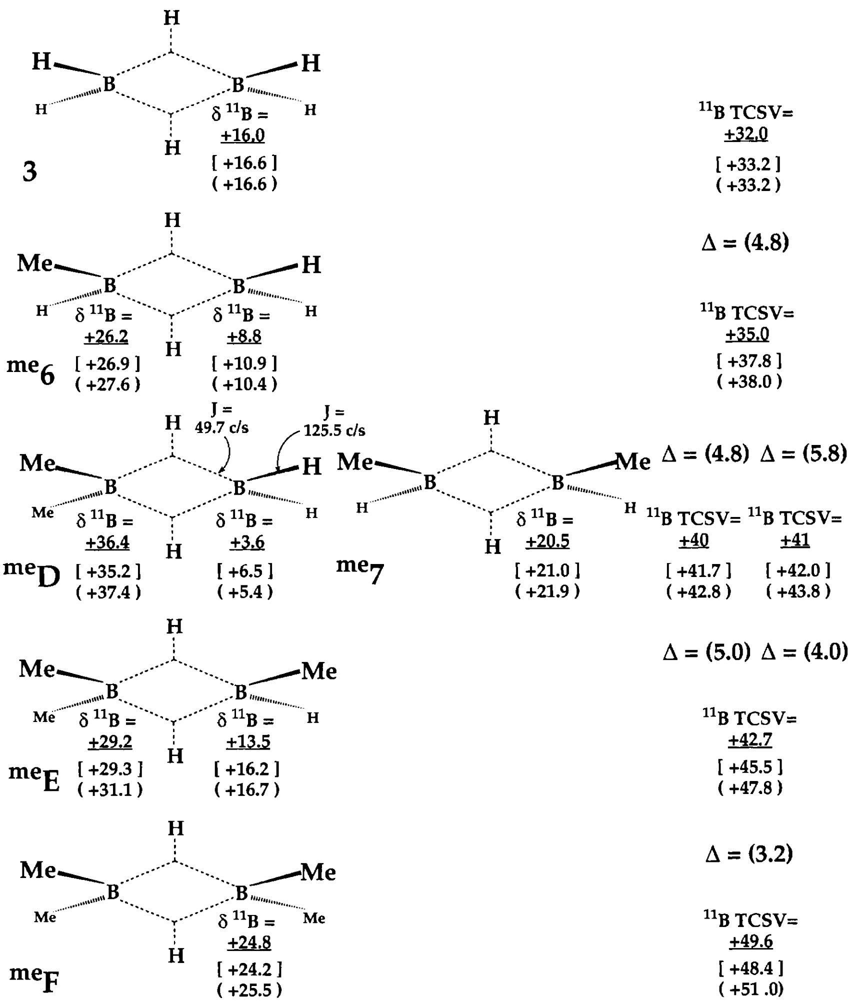


Fig. 2. The $\delta^{11}B$ chemical shift values (ppm) for *nido*-diborane and its various methyl and polymethyl derivatives. The experimental values are underlined, the IGLO values are in [brackets], while the GIAO values are in (parentheses).

The second pattern involves the effect of electronic charge on chemical shift values: It had long been noted that whether a boron atom in a given architectural environment is in a negatively, positively or neutrally charged 'atmosphere' makes little difference to the ^{11}B chemical shift value. As but one example, boron atoms neighboring two nitrogens and two hydrogens (i.e. N_2BH_2-moieties) *in electron precise environments* all have almost the same $\delta^{11}B$ chemical shift value. Thus, the ^{11}B chemical shift values of the anion, $(Me_2N)_2BH_2^-$; the cation, $(H_3N)_2BH_2^+$; and $(H_2NBH_2)_3$, a neutral analog of cyclohexane, are almost alike. Several other peaks at lower field in the experimental ^{11}B-NMR spectrum were easily identified as representing the ^{11}B resonances of **3**, **^{pr}6**, **^{pr}7** and **^{pr}7′** (see Fig. 1) as extrapolated (unchanged) from the known compounds **3**, **^{me}6** and **^{me}7** in Fig. 2. The intermediates **B** and **C** were presumed to arise from **4** and **5** by loss of a proton. Compounds **3**, **^{pr}6**, **^{pr}7** and **^{pr}7′** were produced by subsequent dimerization of fragments **A**, **B** and **C**. The intermediates **B** and **C** could not dimerize into **^{pr}D**, **^{pr}E** and **^{pr}F** and thus, no signals representing them (see **^{me}D**, **^{me}E** and **^{me}F** in Fig. 2) were present in the ^{11}B-NMR spectrum.

Previously, the larger 'triplet-of-triplets' signal, found at lower field and centered at − 3 ppm, was assigned to ion **4** illustrated in Fig. 1. It was felt that the boron atom in the $[(-H-)_2BH_2]$ portion of **4** should be very similar to the $[(-H-)_2BH_2]$ moiety in **^{me}D** in Fig. 2, given that both species are isoelectronic and isostructural. Both **^{me}D** and **4** incorporate Me-groups and the boron chemical shifts should not be much influenced by the positive charge. The $\delta^{11}B$ value of + 3.6 for in **^{me}D**, in Fig. 2, differs from the $\delta^{11}B$ value of − 3 for **4**, in Fig. 1, by only 6.6 ppm which was thought to be acceptably close, given that **4** was a cation and **^{me}D** a neutral species. The less abundant higher field 'triplet-of-triplets', centered at − 24 ppm, was assigned to ion **5** illustrated in Fig. 1. The closest analog for comparison with **5** was *arachno*-$B_3H_8^-$ which had one $[(-H-)_2BH_2]$ moiety and exhibited an 'averaged' $\delta^{11}B$ value of − 25 ppm which compares favorably with the observed shift at −24 ppm. Unfortunately, *arachno*-$B_3H_8^-$, is fluxional and has one $[(-H-)_2BH_2]$ group and two $[-H-BH_2-B]$ groups rather than one static $[(-H-)_2BH_2]$ group as in **5**, in Fig. 1. Since each boron atom in *arachno*-$B_3H_8^-$ spends only one third of its time in the $[(-H-)_2BH_2]$ group environment we did not particularly know how close the averaged $\delta^{11}B$ value of −24 ppm applied to the $[(-H-)_2BH_2]$ group in *arachno*-$B_3H_8^-$. At the end of a chapter reviewing carborane structures including **4** and **5** we stated [1], 'the ^{11}B data are impressive, if not conclusive ...we [do] not have ...the ^{13}C data to corroborate these conclusions'. However, due to experimental difficulties we could not obtain the ^{13}C-NMR data.

The number of published carborane structures is impressive and has grown vastly during these past 40 years. During the 1990s some of the proposed structures were corrected based on ab initio/IGLO/GIAO/NMR theoretical calculations (vide infra). We now wish to report reinvestigation of the structures of carborane cations derived from the reaction of 2-propyl cation with diborane by DFT/IGLO/GIAO-MP2/NMR calculations including previously considered cations **4** and **5** shown in Fig. 1.

2. Calculational methods

Calculations were carried out with the GAUSSIAN 98 program system [3]. The geometry optimizations were performed using the DFT [4] method at the B3LYP/6-31G** level [5,6]. Vibrational frequencies at the B3LYP/6-31G**//B3LYP/6-31G** level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG = 0) and to evaluate zero point vibrational energies (ZPE) which were scaled by a factor of 0.96. Final energies were calculated at the B3LYP/6-311G**//B3LYP/6-311G** + ZPE level. B3LYP/6-31G** geometrical parameters and final energies will be discussed throughout, unless stated otherwise. ^{11}B chemical shifts were calculated by the GIAO-MP2 [7,8] and IGLO [9] methods. GIAO-MP2 calculations using tzp/dz basis set [7,8] have been performed with the ACES II program [10]. The ^{11}B-NMR chemical shifts were first computed using B_2H_6 as reference (calculated absolute shift, i.e $\sigma(B) = 96.8$). IGLO calculations were performed according to the reported method [9] at IGLO II levels (B_2H_6; $\sigma(B) = 102.8$). Huzinaga [11] Gaussian lobes were used as follows; Basis II: B: 9s 5p 1d contracted to {51111, 2111, 1}, *d* exponent: 1.0; H: 5s 1p contracted to {311, 1}, *p* exponent: 0.70. The ^{11}B-NMR chemical shifts were finally referenced to BF_3:OEt_2 (δ (B_2H_6) 16.6 vs. BF_3:OEt_2).

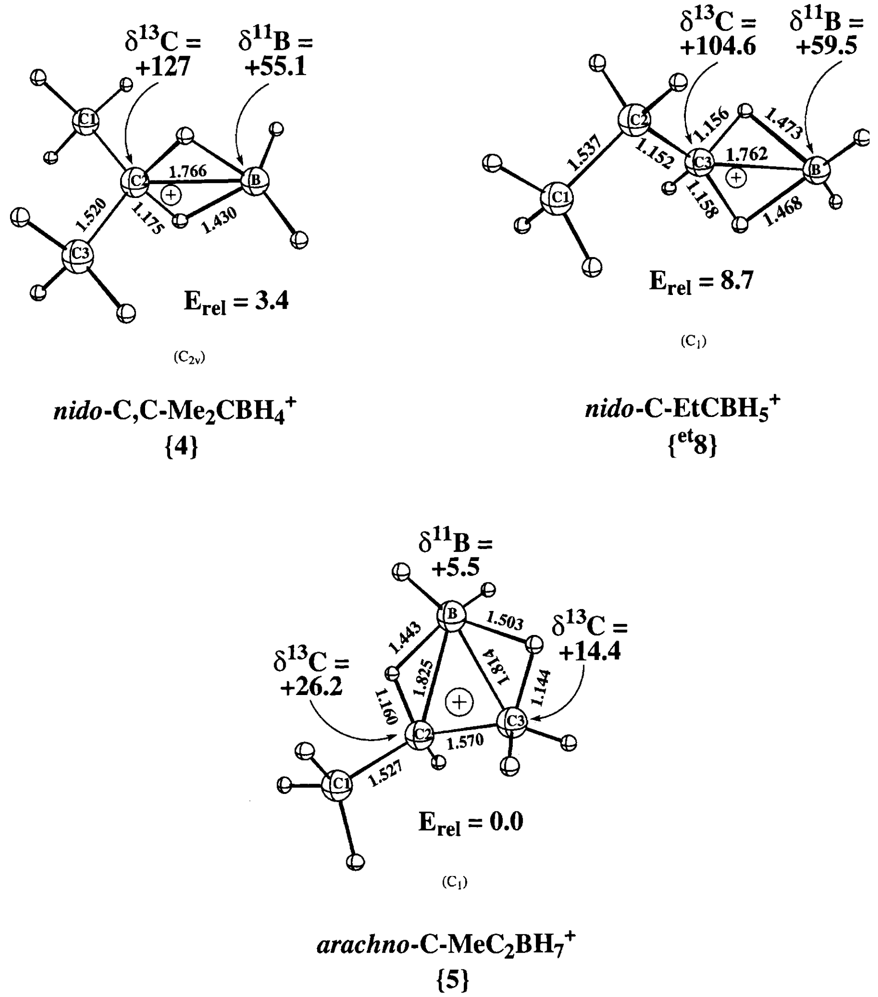
3. Results and discussion

The *nido*-C,C-$Me_2CBH_4^+$ (**4**) and *arachno*-C-$MeC_2BH_7^+$ (**5**) cations, suggested to be observed by NMR in the superacid media, were studied by the density functional theory (DFT)/IGLO/GIAO-MP2 procedure. The geometries were fully optimized at the B3LYP/6-31G** level. Both carborane cations **4** and **5** (Fig. 1) were found to be stable minima on the potential energy surface (see Fig. 3). The calculated $\delta^{11}B$ values were, however, totally unexpected!

The (calculated) $\delta^{11}B$ chemical shift value of +55.1 ppm for **4** (Fig. 3) differs from the assigned [1] (experimental) $\delta^{11}B$ value of −3 ppm for **4** (Fig. 1) by almost 60 ppm. A difference between experimental and calculated values of 6 ppm is acceptable, while a difference of much over 10 ppm is considered improbable. The difference of 58.1 ppm between experimental and calculated values is so large that it is not possible that the triplet-of-triplets at −3 ppm could possibly represent compound **4**. That the ^{11}B-NMR spectrum has no resonances at lower field than +40 ppm also excludes the presence of compound **4** in the mixture studied.

The elimination of structure **4** directs the focus to structure **5** (Fig. 1). The (calculated) $\delta^{11}B$ chemical shift value of +5.5 ppm for **5** (Fig. 3) differs from the assigned (experimental) $\delta^{11}B$ value of −24 ppm for **5** (Fig. 1) by about 30 ppm. The difference of 30 ppm between experimental and calculated values is again very large and makes it improbable that the triplet-of-triplets at −24 ppm could be due to cation **5**. On the other hand, the experimental value of −3 ppm is now compared to the (calculated) value of +5.5 ppm for ion **5**. The difference is somewhat acceptable, 8.5 ppm. Consequently the −3 ppm triplet-of-triplets can be assigned to the carborane cation **5**. Supporting this possibility is the fact that the ion **5** ($E_{rel} = 0.0$ kcal mol^{-1}) is calculated to be (Fig. 3) thermodynamically more stable than **4** ($E_{rel} = 3.4$ kcal mol^{-1}). Even if ion **4** was first formed in the reaction it could rapidly rearrange to **5**. These results support the formation of the cation **5** in the reaction of 2-propyl cation with diborane. However, this still leaves the question of the unassigned triplet-of-triplets at $\delta^{11}B$ −24.

In search for compatible alternate structures more alkylated derivatives of cation **5** were investigated. Any possible structure must incorporate a boron atom surrounded by two terminal hydrogens and two bridge hydrogens, i.e. a $(-H-)_2BH_2)$-moiety in order to give rise to a triplet-of-triplets centered at −24 ppm. Each of the bridge hydrogens must be attached to one boron and one other atom. From the data presented in Fig. 2 it is evident that as one end of the diborane molecule is substituted with alkyl groups (which shifts the 'alkylated end' to lower field) the unencumbered $(-H-)_2BH_2)$-moiety shifts to significantly higher field (see in Fig. 4).



nido-C,C-$Me_2CBH_4{}^+$ {4}

nido-C-$EtCBH_5{}^+$ {^{et}8}

arachno-C-$MeC_2BH_7{}^+$ {5}

Fig. 3. Calculated geometries and $\delta^{11}B$ chemical shifts, E_{rel} values and structures of compounds **4** and **5**. The E_{rel} values of compounds **4**, **5** and ^{et}**8** are compared.

In carborane cluster compounds, alkyl groups on boron stabilize the cluster; the nature of the alkyl group has a minimal effect. Thus, we calculated the stabilities of the variously alkylated derivatives of diborane (data in Fig. 5). The most stable is the most highly alkylated and alkylation of one end caused a sharp shift to higher field of the unencumbered $(-H-)_2BH_2)$-moiety in the ^{11}B-NMR spectra.

We also surmised that if the isopropyl cation **2** could form any propene then it could in turn react with a second isopropyl cation **2** to produce hexylcarbenium ions. Presumably such cations could produce several C,C′-polyalkylated derivatives of **5** in which the unencumbered $(-H-)_2BH_2)$-moiety would be forced to higher field, perhaps high enough to approach the experimental −24 ppm triplet-of-triplets. If the patterns illustrated in Figs. 1, 3–5 could apply to the C,C′-polyalkylated ‘relatives’ of ^{me}**5** (Fig. 3) then the monoalkylated derivative ^{bu}**5** in Fig. 6 should be least stable and have the lowest $\delta^{11}B$ value and the tetraalkylated derivative **13** should be the most stable and its

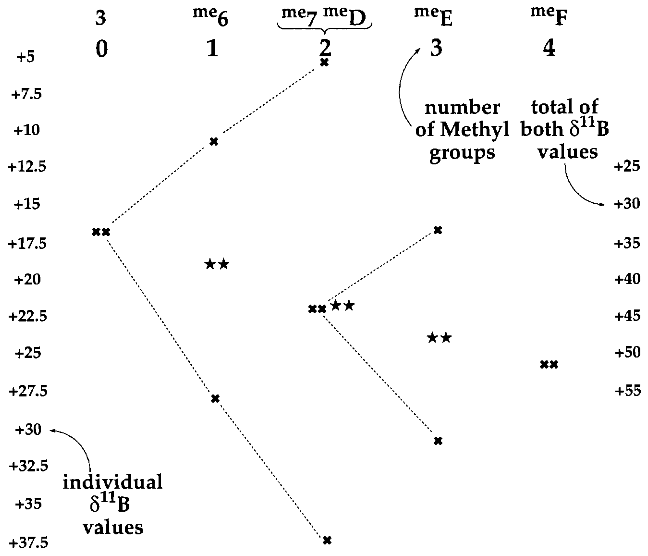


Fig. 4. (GIAO-MP2) $\delta^{11}B$ chemical shift values for *nido*-$Me_xB_2H_{6-x}$ compounds illustrated in Fig. 2.

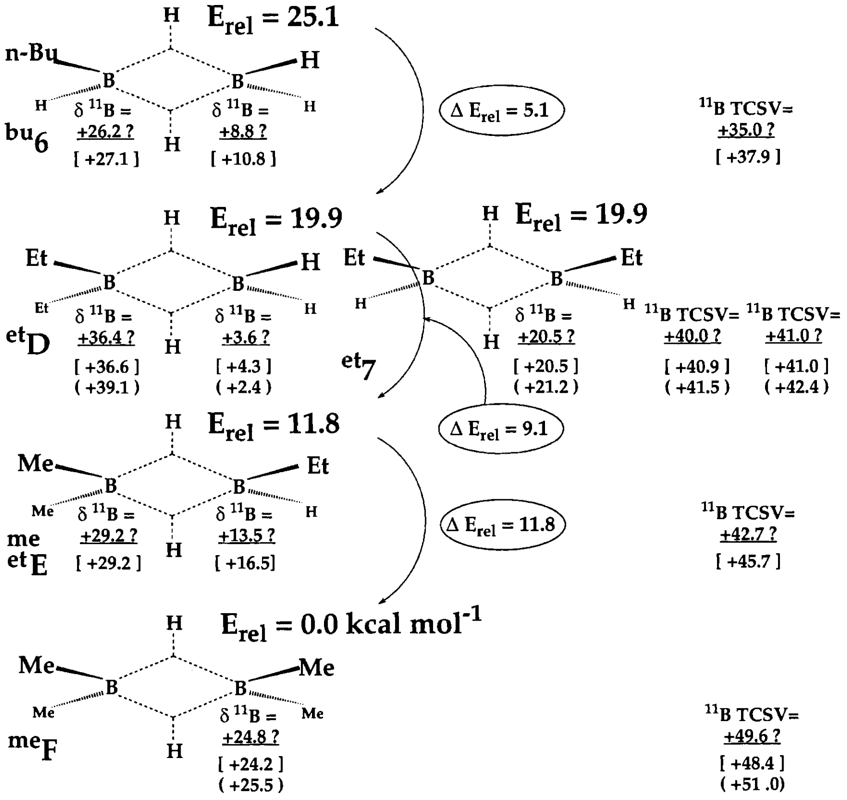


Fig. 5. Alkyl derivatives of *nido*-diborane; $C_4B_2H_{14}$ isomers.

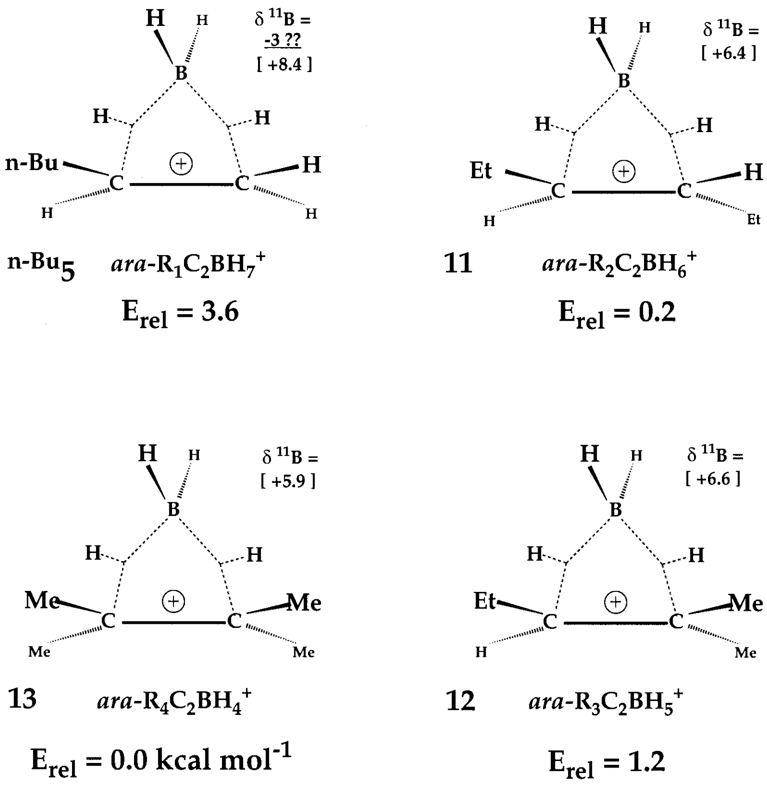


Fig. 6. Alkyl derivatives of *arachno*-$C_2BH_8^+$; $C_6B_1H_{16}^+$ isomers.

$(-H-)_2BH_2$)-moiety would be found at the highest field. IGLO calculations, however, do not confirm the $\delta^{11}B$ value projection. Moreover the differences between the four cations (**^{bu}5**, **11**, **12** and **13**) in Fig. 6 are too small to make any valid suggestions. The stabilities, E_{rel} values, are all between 0.0 and 3.6 kcal mol^{-1}. The $\delta^{11}B$ values are between $+5.9$ and $+8.4$ ppm. The stabilities were not predictable and there was no structure that showed ^{11}B-NMR data close to -24 ppm.

4. Conclusions

The previously suggested carborane cation structure, *arachno*-$Me_2CBH_4^+$ (**4**), for one of the species derived from the reaction of 2-propyl cation with diborane has been shown to be incorrect based on DFT/IGLO/GIAO-MP2/NMR calculations (Figs. 1 and 3). On the other hand, the carborane cation, *arachno*-$MeC_2BH_7^+$ (**5**) (3.4 kcal mol^{-1} more stable than **4**) is currently the best structural candidate for the observed ion (Figs. 1, 3 and 6) at -3 ppm. We are unable to suggest any other reasonable structure that could account for the triplet-of-triplets at -24 ppm observed experimentally in the original ^{11}B-NMR spectrum.

Acknowledgements

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References

[1] R.E. Williams, G.K.S. Prakash, L.D. Field, G.A. Olah, in: J.F. Liebman, A. Greenberg, R.E. Williams (Eds.), Advances in Boron and the Boranes, VCH, New York, 1988.

[2] (a) G.A. Olah, A.M. White, J. Am. Chem. Soc. 91 (1969) 5801. (b) G.A. Olah, D.J. Donovan, J. Am. Chem. Soc. 99 (1977) 5026.

[3] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, R.E. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, J.A. Pople, GAUSSIAN 98 (Revision A.5), Gaussian Inc, Pittsburgh PA, 1998.

[4] T. Ziegler, Chem. Rev. 91 (1991) 651.

[5] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[6] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley-Interscience, New York, 1986.

[7] J. Gauss, Chem. Phys. Lett. 191 (1992) 614.

[8] J. Gauss, J. Chem. Phys. 99 (1993) 3629.

[9] (a) W. Kutzelnigg, Isr. J. Chem. 19 (1980) 193. (b) W. Kutzelnigg, U. Fleischer, M. Schindler, NMR Basic Principles and Progress ,1991, 91, 651. (b) M. Schindler, W. Kutzelnigg, J. Chem. Phys. 76 (1982) 1919.

[10] (a) J.F. Stanton, J. Gauss, J.D. Watts, W.J. Lauderdale, R.J. Bartlett, ACES II, program. J.F. Stanton, J. Gauss, J.D. Watts, W.J. Lauderdale, R.J. Bartlett (Eds.), Quantum Theory Project, University of Florida, Gainesville, FL, 1991.

[11] S. Hazinaga, Approximate Atomic Wave Function, University of Alberta, Edmonton, Alberta, 1971.