Macropolyhedral thiaboranes with unusual *arachno* subclusters—a computational investigation

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Abstract

The cluster structures of experimentally characterized macropolyhedral thiaboranes $[S_2B_{17}H_{17} \cdot SMe_2]$ (**1**) and $[S_2B_{18}H_{19}]^-$ (**2**) were investigated at the B3LYP/6-311 + G**//B3LYP/6-31G* density functional theory level. Their conjuncto structures combine a usual *nido*-$\{SB_{10}\}$ subcluster and *iso arachno* 10 and 11 vertex subclusters, respectively. The latter are exceptional in having a sixfold coordinated vertex, not known in *arachno* borane chemistry. While for isolated $[SB_9H_{12}]^-$ and $[SB_{10}H_{13}]^-$ the expected structures are more stable by 31.2 and 17.2 kcal mol^{-1} than the structures realized in the conjuncto compounds, the stability order is reversed in the conjuncto structures: the unexpected clusters are preferred by 4.2 and 14.0 kcal mol^{-1} over alternatives incorporating regular *arachno* subclusters. Compounds **1** and **2** do not form for kinetic reasons only. Large geometrical distortions of the *nido* subcluster occur, when it is attached to regular *arachno* subclusters but not with the *iso* subclusters. *Nido* subcluster opening may be due to transfer of electron density from the *arachno* to the *nido* part, which is prevented in the presence of the more electron deficient sixfold coordinated vertex of the *iso* subclusters. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Structural systematics of (hetero) boron hydrides with up to ca. 12 vertices are well understood. Corresponding cluster structures can be predicted qualitatively on the basis of Wade's electron counting rules [1] and Williams' geometrical systematics [2]. Larger compounds with 16 or more cluster atoms adopt conjuncto structures which are also called macropolyhedra. They can be viewed as fused deltahedra sharing a common atom, edge, or face as the connecting unit. Recently, Jemmis et al. [3,4] extended Wade's rules of electron counting to conjuncto clusters, but the geometrical shape of a large conjuncto (hetero)borane is still not predictable on the basis of the molecular formula. A number of macropolyhedral boron hydrides and heteroboranes with 18 or more vertices was characterized experimentally [5]. In general, the building blocks, so-called subclusters, show regular structures as antici-

pated for the corresponding free clusters on the basis of the Wade–Williams rules [1,2].

However, two exceptional conjuncto thiaboranes have been reported, i.e. $[S_2B_{17}H_{17} \cdot SMe_2]$ (**1**) [6] and $[S_2B_{18}H_{19}]^-$ (**2**) [7]. In these compounds, a regular *nido*-$\{SB_{10}\}$ subcluster, **A**, is fused to an *arachno*-$\{SB_9\}$, **B'** and to an *arachno*-$\{SB_{10}\}$ thiaborane subcluster, respectively (Scheme 1) [8]. Both subclusters **C'** share a B–B edge, bare of terminal substituents. While the *nido* part has the expected structure, the *arachno* subclusters are special in having one six-coordinate vertex ($6k_C$) with respect to cluster connections (i.e. the total num-
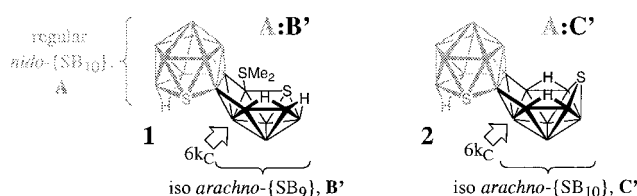
Scheme 1. Cluster structures of macropolyhedral thiaboranes $[S_2B_{17}H_{17} \cdot SMe_2]$, **1**, [6] and $[S_2B_{18}H_{19}]^-$, **2** [7]. The unusual six-coordinate $6k_C$ vertices of *iso arachno*-$\{SB_9\}$ and -$\{SB_{10}\}$ subclusters **B'** and **C'** are marked by arrows.

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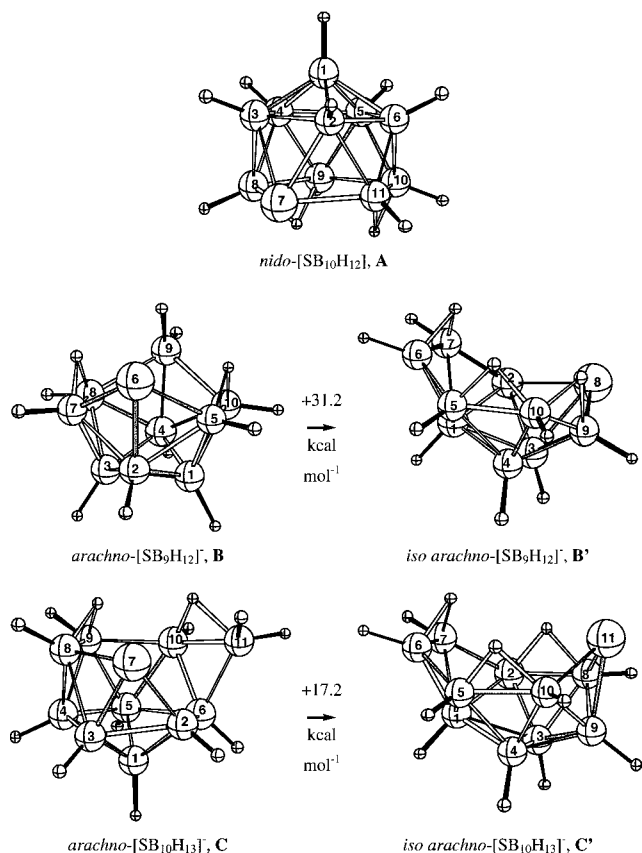*E-mail address:* matthias.hofmann@urz.uni-heidelberg.de (M. Hofmann).

Fig. 1. Optimized structures of the free *nido*-{SB$_{10}$} cluster, **A**, as well as *arachno*-{SB$_9$} and *arachno*-{SB$_{10}$} thiaboranes with regular (**B** and **C**, respectively) and with *iso* cluster structures incorporating a 6k$_C$ vertex at position 1 (**B'** and **C'**, respectively). Sulfur atoms are shown as grey balls.

ber of next neighbors is seven including the exo-terminal ligand). This feature is unknown for free *arachno* boranes.

It is not clear whether the *arachno* 10 and 11 vertex clusters, **B** and **C**, conforming to the rules, are thermodynamically more stable or less stable than the *arachno iso*-clusters, **B'** and **C'**, which are realized in **1** and **2**, respectively. Possibly, the *iso*-clusters are energetically competitive, but so far have just not been isolated experimentally. Whether or not the relative stability order of structures with and without 6k$_C$ vertices is maintained or reversed for the conjuncto polyhedra is not known, either. Formation of **1** and **2** could occur for thermodynamic or for kinetic reasons. This computational investigation was undertaken to provide answers to these questions.

2. Results and discussion

2.1. Energetic considerations

For isolated [SB$_9$H$_{11}$·SMe$_2$] the regular cluster structure **B** is more stable than *iso*-cluster **B'** with a 6k$_C$

vertex at position 1 by 33.7 kcal mol^{-1}. Replacing the *exo* S(CH$_3$)$_2$ ligand at B2 by a hydride gives an essentially identical energy difference of 31.2 kcal mol^{-1} between [SB$_9$H$_{12}$]$^-$ isomers with **B** and **B'** cluster structures (see Fig. 1). Hence, further computational investigations rely on structures modeling the dimethylsulfido ligand by a hydride. Among the eleven vertex [SB$_{10}$H$_{13}$] isomers the regular structure **C** is preferred over the unusual alternative **C'** by 17.2 kcal mol^{-1}.

Conjuncto structures incorporating the *iso arachno* clusters **B'** and **C'** together with the *nido*-{SB$_{10}$} subcluster **A**, i.e. **A:B'** and **A:C'**, see Fig. 2, are computed to be *more* stable than isomers with regular *arachno* subclusters **A:B** and **A:C** by 4.2 and 14.0 kcal mol^{-1}, respectively [9]. The *nido*:*arachno* subcluster fusion reverses the stability order of regular and *iso arachno* clusters, favoring the 10 and 11 vertex *iso* forms by 35.4 and 31.2 kcal mol^{-1}, respectively. Compounds **1** and **2** form not just because of kinetic reasons, but their unexpected structures are really thermodynamically preferred over the anticipated alternatives. The preference of *iso arachno* subclusters in conjuncto clusters is also reflected by condensation energies ΔE_{cond} according to the following formal reaction (1).

$$A + X \rightarrow A{:}X + B_2H_6 \quad \Delta E_{cond} \quad (1)$$

Formation of the conjuncto structure is computed to be *endo*thermic for regular *arachno*-{SB$_9$} and-{SB$_{10}$} clusters, i.e. $X = B$, C ($\Delta E_{cond} = +17.5$ and $+15.9$ kcal mol^{-1}, respectively), but *exo*thermic for the isomeric *arachno* clusters with a 6k$_C$ vertex, i.e. $X = B'$, C' ($\Delta E_{cond} = -18.0$ and -15.4 kcal mol^{-1}, respectively).

The reversal of preferred cluster structures upon macropolyhedra incorporation is not limited to thiaboranes, as is shown by results for *iso* electronic carborane and borane anions (Table 1). When the sulfur atoms are replaced by CH$_2$ groups, the macropolyhedron stabilizes the *iso arachno* structure over the regular one by 25.5 and 22.9 kcal mol^{-1} in the 10 and 11 vertex case, respectively. For the corresponding boron hydrides, the values are even closer to those found for the thiaboranes: 36.4 and 33.9 kcal mol^{-1}, respectively.

2.2. Comparison of free subclusters to conjuncto structures

In order to elucidate the origin of the strong preference of the 6k$_C$ *iso arachno* clusters **B'** and **C'** over the expected clusters **B** and **C** in the conjuncto structures, we compared subclusters from macropolyhedra to the free cluster equivalents. Large changes for the boron atoms of the shared edge can be expected as the chemical nature is very different: A (HB-μH-BH) moiety of the free subclusters corresponds to a (B–B) unit without any terminal exo ligand in the conjuncto structures. The question is how much the rest of one subcluster

'senses' the presence of a second subcluster fragment. As the same *nido* subcluster is present in all conjuncto structures considered, but the *arachno* subcluster part varies, one might anticipate that big differences will be identified for the *arachno* part and that much less changes occur for the *nido* part.

First, we considered geometries by comparing next neighbor differences and used an arbitrary threshold of 18:00 h to identify large differences. The result of this analysis is graphically displayed in Fig. 3. Geometrical changes within both the *nido* as well as the *arachno* subclusters are mostly small for **A:B′** and **A:C′**. Not

many large changes are found for the regular *arachno* subclusters of **A:B** and **A:C**. However, major rearrangements are identified in the *nido* subcluster **A** in the presence of regular *arachno* subclusters, i.e. in **A:B** and **A:C** (see Fig. 3). This is in contrast to naive expectations outlined above. The geometrical changes observed in **A** of **A:B** and in **A** of **A:C** are qualitatively the same, i.e. the same bonds are shortened or enlarged.

A similar conclusion can be drawn from an analysis of computed ^{11}B-NMR chemical shifts: in **A:B′** and **A:C′** there is only one significant (i.e. larger than 6 ppm) change, which corresponds to the $6k_C$ vertex, but
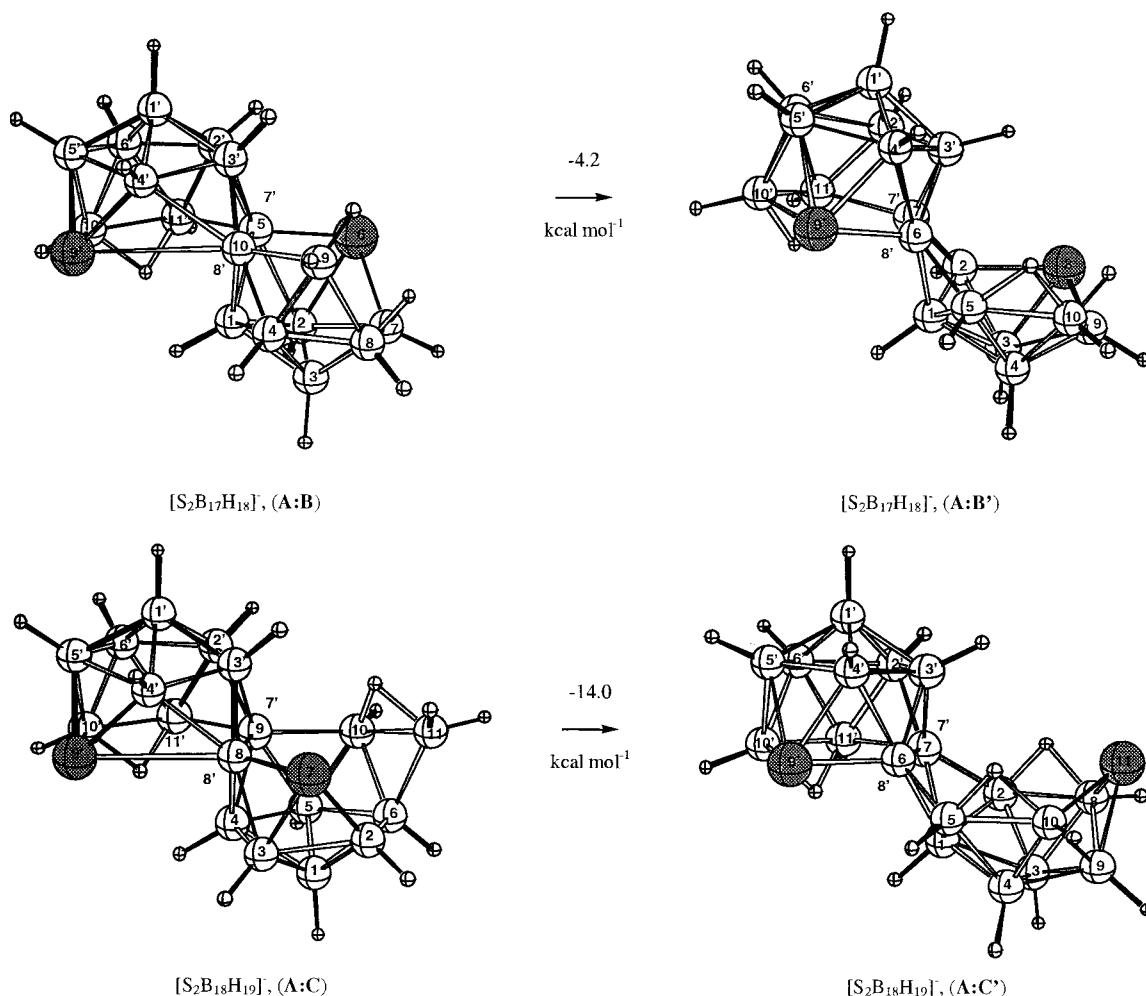

Fig. 2. Optimatized structures of conjuncto clusters built from *nido*-{SB$_{10}$} cluster, **A**, (labeled with primed numbers) and regular or isomerics *arachno*-{SB$_9$} (**A:B** and **A:B′**) as well as *arachno*-{SB$_{10}$} thiaboranes (**A:C** and **A:C′**). Sulfur atoms are shown as grey balls.

Table 1
Relative energies of regular *arachno* structures vs. isomers with $6k_C$ vertices (labeled with a prime) for conjuncto clusters and corresponding subclusters including boranes, carboranes and thiaboranes

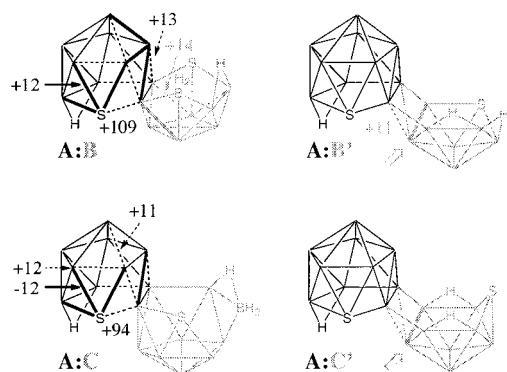| X	**B** → **B′** [XB$_9$H$_{12}$]$^-$	(**A:B**) → (**A:B′**) [X$_2$B$_{17}$H$_{18}$]$^-$	**C** → **C′** [XB$_{10}$H$_{13}$]$^-$	(**A:C**) → (**A:C′**) [X$_2$B$_{18}$H$_{19}$]$^-$
X = S	+31.2	−4.2	+17.2	−14.0
X = CH$_2$	+29.3	+3.8	+15.3	−7.6
X = BH$_2^-$	+33.4	−3.0	+6.9	−27.0

Fig. 3. Differences in computed next neighbor separations (pm) when free subclusters are compared with conjuncto structures. Distances which are computed to widen or shorten by more than 18:00 h are drawn with broken and bold lines, respectively. For changes larger than 22:00 h values are given. The common B_2 edge is not considered.
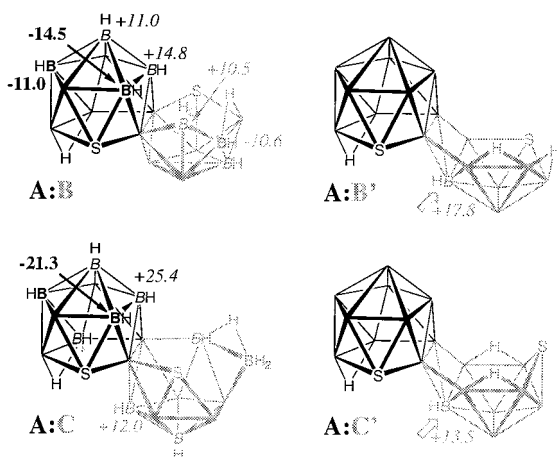

Fig. 4. Differences in computed ^{11}B-NMR chemical shifts [ppm] when free subclusters are compared with conjuncto structures. Boron atoms which are computed to show a change of more than 6 ppm are typeset in bold face and italics to indicate high and low field shifts, respectively. Changes larger than 10 ppm are listed by value. The common B2 edge is not considered.

Table 2
Distortion energies (kcal mol^{-1}) computed for subclusters in $[S_2B_{17}H_{18}]^-$ and $[S_2B_{18}H_{19}]^-$ conjuncto thiaboranes

Formula	Iso arachno subclusters		Regular arachno subclusters	
$[S_2B_{17}H_{18}]^-$	**A:B'**		**A:B**	
	A:3.9	**B'**:3.3	A:17.9	**B**:2.0
$[S_2B_{18}H_{19}]^-$	**A:C'**		**A:C**	
	A:4.9	**C'**:2.8	A:17.9	**C**:2.0

many big changes are found for subcluster **A** in both **A:B** and **A:C**. Macrocluster incorporation of **B** and **C** into **A:B** and **A:C**, respectively, has only a moderate effect while combining **A** with **B'** or **C'** to give **A:B'** and **A:C'**, has a minor effect on the ^{11}B-NMR chemical shifts (see Fig. 4).

The perturbation of subcluster geometries which is due to conjuncto cluster incorporation was also quantified energetically. We computed energies for fixed subcluster geometries from macropolyhedra optimizations and compared them to those obtained from full geometry optimizations of free subclusters. Of course, the macropolyhedral fragments have to be supplied with additional three hydrogen atoms at the site of the shared edge. The positions of the latter were freely optimized while all other coordinates were kept fixed. Relative energies obtained by this procedure are given in Table 2. Small values are obtained (2–3 kcal mol^{-1}) for the arachno subclusters—for regular (**B** and **C**) as well as iso arachno clusters (**B'** and **C'**). However, distortion energies for the nido subcluster are only small (4–5 kcal mol^{-1}) in macropolyhedra which are based on iso arachno subclusters (**A:B'** and **A:C'**), but are considerably larger (17.9 kcal mol^{-1}) in isomers with regular arachno subclusters (**A:B** and **A:C**).

2.3. The electronic structure of different conjuncto structures

These observations suggest that both regular and iso arachno-{SB$_9$} and -{SB$_{20}$} are equally well accommodated in a conjuncto polyhedron, but that only the iso subclusters leave the attached nido-{SB$_{10}$} subcluster undistorted. Nido-clusters, which have $(n + 2)$ skeletal electron pairs, where n is the number of cluster atoms, are more electron deficient than arachno clusters with $(n + 3)$ skeletal electron pairs. Combination of nido and arachno clusters in a conjuncto structure might thus lead to transfer of electron density from the arachno to the nido subcluster. Increased electron density in the nido part then could lead to partial opening of the cluster towards an arachno structure (as observed for **A** in **A:B** and **A:C**). On the other hand, the loss of electron density from the arachno subcluster does not need to have a similar structural effect—at least not in case of the ten vertex arachno subcluster **B**, whose cluster atom arrangement is very similar to that of a ten vertex nido cluster (compare parent boron hydrides in Scheme 2).
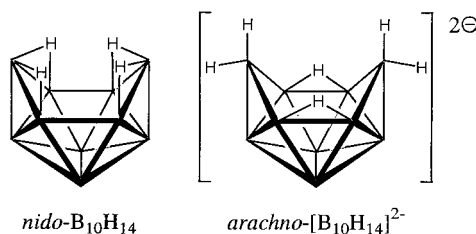
Scheme 2. Regular cluster structures for parent nido and arachno ten vertex clusters, nido-$B_{10}H_{14}$ and arachno-$[B_{10}H_{14}]^{2-}$.
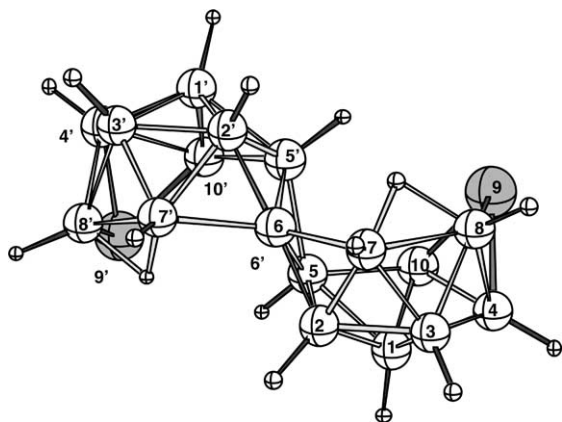
Fig. 5. Optimized structure of the C_2 symmetric conjuncto-$[S_2B_{17}H_{18}]^-$ isomer **3** [11a,11b], which is 11.3 kcal mol^{-1} more stable than the **A:B′** isomer.

Partial charges, computed according to a Natural Population Analysis [10], are in line with these speculations: for the *nido* subcluster **A** minus the common edge a partial charge of -0.03 is found when the free subcluster is considered. The charge computed for the corresponding macropolyhedral fragment is very similar in clusters **A:B′** (-0.09) and **A:C′** (-0.07). However, it is much more negative in **A:B** and **A:C** (-0.33 each).

Due to its higher coordination number, the $6k_C$ vertex 1 in **B′** and **C′** next to the shared B_2 edge is more electron deficient than regular vertices. Therefore, it might prevent relocation of electron density from the *arachno* subclusters of **A:B′** and **A:C′** to the *nido* subcluster.

A $[S_2B_{17}H_{18}]^-$ anion **3** was reported [11a,b], which is an isomer to **A:B′** and **A:B**. Its C_2 symmetric structure was described as two *arachno*-$\{SB_9\}$ subclusters sharing one vertex (B6) and being linked by an additional B5–B5′ bond (Fig. 5). Alternatively, it can be regarded as two *arachno*-$\{SB_{10}\}$ subclusters which share one face (B5, B5′, B6). Due to the molecular symmetry the electrons are necessarily equally distributed between the two subcluster fragments. Isomer **3** is 11.3 kcal mol^{-1} more stable than the **A:B′** structure. One might conclude that *nido*:*nido* and *arachno*:*arachno* combinations might result in more stable conjuncto structures than the *nido*:*arachno* hybrids. If this is true in general or not has to be shown by a more systematic study which is undertaken at present.

3. Summary

Conjuncto thiaborane structures reported for $[S_2B_{17}H_{17}\cdot SMe_2$ (**1**) and $[S_2B_{18}H_{19}]^-$] (**2**) which have usual *nido* but unexpected *arachno* subclusters, are com-

puted to be thermodynamically more stable than alternatives with regular *arachno* subclusters. Hence, compounds **1** and **2** were not just kinetically trapped. However, for the free *arachno* ten and eleven vertex compounds the regular structures are preferred over alternatives with an unusual sixfold coordinated vertex. Conjuncto structures of thia- and carborates as well as borates favor these unusual clusters by ca. 25–35 kcal mol^{-1}. Hypothetical macropolyhedra which incorporate regular *arachno* subclusters would suffer considerable geometrical distortion in their *nido* part. Transfer of electron density from the *arachno* to the *nido* subcluster is put forward as a possible explanation.

4. Computational details

Structures were fully optimized at the B3LYP/6-31G* density functional theory level. The combination of Becke's three-parameter exchange functional (B3) [12] together with the correlation functional due to Lee, Young and Parr (LYP) [13] as implemented in GAUSSIAN 98 was employed [14]. The latter program package was used throughout. Geometries and vibrational frequencies were computed using Pople's polarized valence double-zeta quality 6-31G* basis set while energies and GIAO-NMR chemical shifts [15,16] were obtained employing the larger polarized valence triple-zeta quality 6-311 + G** basis set which includes polarization functions on both heavy (d type for C, B, and S) and hydrogen atoms (p type) and also additional diffuse functions (sp set) on heavy atoms. Relative energies reported in the text are corrected for (unscaled) differences in zero point vibrational energies and correspond to the B3LYP/6-311 + G**//B3LYP/6-31G* + ZPE (B3LYP/6-31G*) level of theory, unless specified otherwise. Test calculations showed a basis set including diffuse functions not to be necessary for geometry optimizations: relative energies obtained from B3LYP/6 - 311 + G**//B3LYP/6 - 31 + G* + ZPE(B3LYP/6-31 + G*) computations are 32.2 kcal mol^{-1} for **B′** versus **B** and 17.3 kcal mol^{-1} for **C′** versus **C**. These values are basically identical to those corresponding to our standard level (32.2 and 17.2 kcal mol^{-1}, respectively).

5. Supplementary material

Cartesian coordinates of optimized geometries (//B3LYP/6-31G*) and computed electronic energies (B3LYP/6-311 + G**) of thiaborane structures discussed in the text (eight pages).

Acknowledgements

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