Inorg. Chem. **2004**, *43*, 8176–8184

Inorganic Chemistry

Article

Can the Bis(diboranyl) Structure of B_4H_{10} Be Observed? The Story Continues

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Received April 4, 2004

Pathways for the conversion of the unknown bis(diboranyl) isomer of tetraborane(10) (B_4H_{10}) to the known arachno isomer have been determined for the first time with the use of an electron correlation ab initio quantum chemical method and without the use of constraints in determination of the transition structures. Two isomers of tetraborane(10), one new, with a pentacoordinated boron atom have been found on the theoretical potential energy surface. Several other pathways for molecular rearrangement of tetraborane(10) have also been characterized. The theoretical method was MP2 theory with the 6-31G(d,p) basis set. The most likely pathway for the conversion of the bis(diboranyl) isomer of tetraborane(10) to the arachno isomer is a concerted pathway with two pentacoordinated intermediates. The highest energy transition state for this pathway lies 27.7 kcal/mol above the bis(diboranyl) isomer. At the same level of the theory, the bis(diboranyl) isomer lies 9.2 kcal/mol above the known arachno isomer. The two isomers with a pentacoordinated boron atom lie 12.5 and 13.1 kcal/mol above the arachno isomer.

Introduction

It has been a puzzle for some years that the bis(diboranyl) isomer of tetraborane(10) (Figure 1a) has not been found even though its energy is very close to that of the known *arachno*-tetraborane(10) (Figure 1b). The two methods of synthesis of tetraborane, one by the mercury-sensitized photolysis of diborane,[1] and the other by the Wurtz-type coupling of B_2H_5I in the presence of sodium amalgam,[2] indicate the possibility of the initial production of the bis(diboranyl) isomer. In 1991, experimental evidence was found by Binder et al.[3] that when B_4H_{10} is reacted with bifunctional thiols, transannularly bridged $H_2(\mu_2)_2S_2RBH(B_2H_5)$ (Figure 2a) similar to the bis(diboranyl) isomer is formed, which on cooling rearranges to $H_2B(\mu_2)_2S_2RB_3H_6$ (Figure 2 b) analogous to the *arachno*-isomer.

Possible pathways for interconversion of the two isomers were studied by McKee,[4] but this early study was restricted by the need to use correlated methods only at Hartree–Fock (HF) optimized geometries and the use of constrained optimizations. This study uses higher levels of theories with no restrictions on the optimization of the geometries of isomers, intermediates, and transition structures.

Earlier theoretical investigations have shown that the HF level of theory has serious disadvantages in predicting the energies of these isomers effectively. The bis(diboranyl) structure is found to have a lower energy than the *arachno*-tetraborane isomer at the HF level, and only when correlation is added does the bis(diboranyl) structure rise above the *arachno*-tetraborane structure in energy. For example, at the HF level of theory the energy of the bis(diboranyl) isomer is lower than the arachno tetraborane isomer by 6.9 kcal with the 6-31G basis set and raises 5.8 kcal above the arachno tetraborane at the Møller–Plesset perturbation theory to second order (MP2) level of theory. Very similar results are obtained with other basis sets. In particular, at the HF level, the bis(diboranyl) isomer is always lower in energy than the *arachno*-tetraborane, and at all correlated levels the *arachno*-tetraborane structure is lowest.

In 1986, M. L. McKee[4] proposed three possible paths for the conversion of bis(diboranyl) to the *arachno*-tetraborane.

Path A, which preserves the C_2 symmetry common to both bis(diboranyl) and *arachno*-tetraborane structures, was found

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[1] Plotkin, J. S.; Astheimer, R. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1979**, *101*, 4155–4163.

[2] Garst, J. F. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley & Sons: New York, 1973; Vol. 1, pp 539–541.

[3] Binder, H.; Melidis, P.; Söylemez, S.; Heckmann, G. *J. Chem. Soc., Chem. Commun.* **1991**, *1091*.

[4] McKee, M. L. *Inorg. Chem* **1986**, *25*, 3545–3547.

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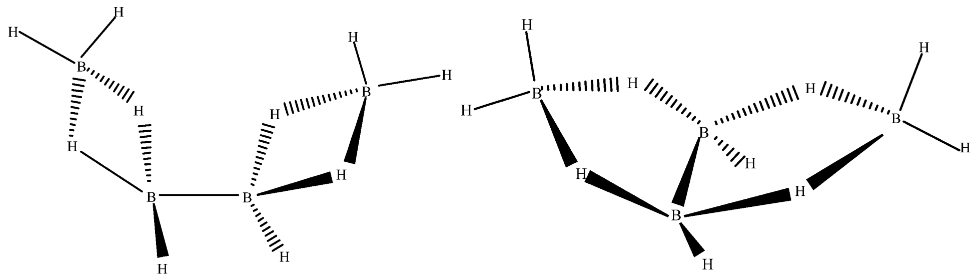
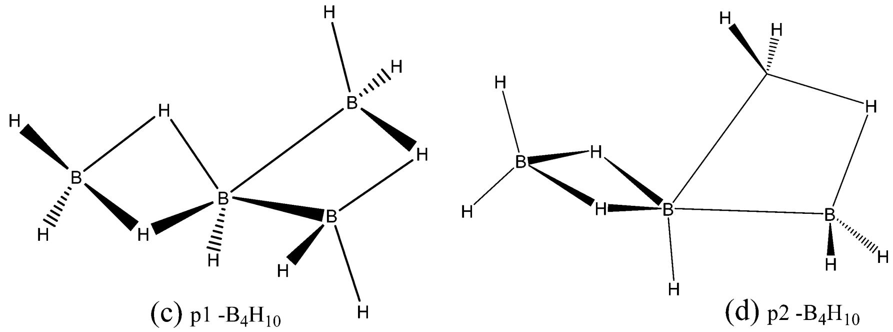


(a) bis-B_4H10 (b) arachno-B_4H10



(c) p1 -B_4H_{10} (d) p2 -B_4H_{10}

Figure 1. Structures of B_4H_{10} isomers.

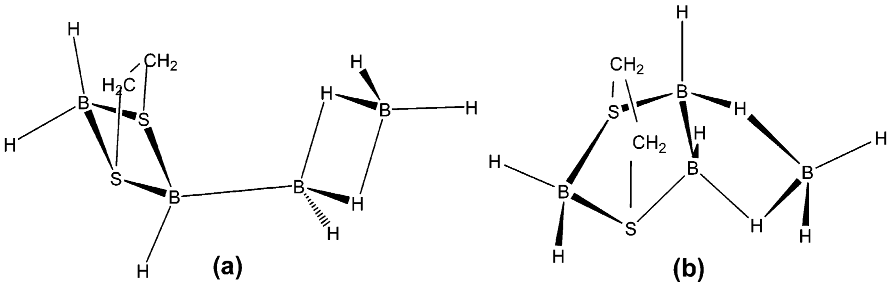


Figure 2. Structures of transannularly bridged di-μ_2-thiotetraborane (10) isomers.[3]

unfavorable since the stationary structure had 4 imaginary frequencies and was not a true transition structure.

Path B was eliminated by McKee, because the geometry of the transition structure in this path was constrained and the energy of the transition structure along this path was very high.

Path C involved a donation-back-donation step where the bis(diboranyl) structure first dissociates to B_3H_7 and BH_3 with the back-donation of the BH_3 moiety to a different B_3H_7 isomer as a second step. The path for the interconversion of the B_3H_7 isomers[5] was not found.

The geometries were optimized only at the HF level of theory with the 3-21G basis set, with polarization and correlation effects applied as additivity approximations from single point energies.

Computational Details

The three major factors that have to be considered in the selection of the level of theory and basis sets are listed in the following paragraphs.

1. The bridging hydrogen atoms in boranes, involved in the three-center two-electron bonding, are different from the hydrogen atoms in two-center two-electron bonding in terminal B−H bonds and in C−H bonds in organic compounds. A number of previous calculations on these electron deficient boranes have shown that electron correlations methods are essential to predict energies[6−8] and geometries[9,10] in close agreement with the experimental values.

2. Although it has been shown[10,11] that polarization functions on the hydrogen atoms provide an improved description of bridging hydrogen atoms in carboranes, it does not have much effect on the energy or geometry of boranes. Nevertheless, we have included the p-type polarization functions on hydrogen atoms as well as the d-type polarization functions on boron atoms, because some of the transition structures that have very close energies, but different geometries on the potential energy surface (PES), could not be distinguished without them.

3. Due to the large number of calculations that need to be done to scan the potential energy surface for all the transition structures

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(5) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem* **1982**, *21*, 2846−2850.

(6) Lipscomb, W. N. *Pure Appl. Chem.* **1983**, *55*, 1431−1438.

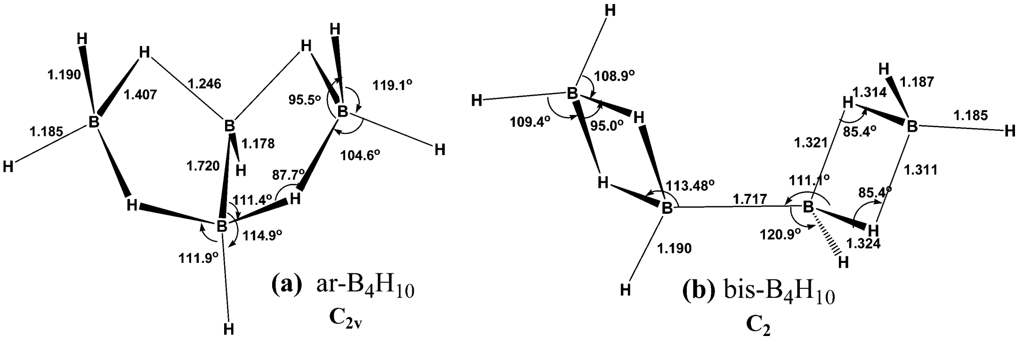
(7) Page, M.; Adams, G. F.; Binkley, J. S.; Melius, C. F. *J.Phys. Chem.* **1987**, *91*, 2675−2678.

(8) Horn, H.; Ahlrichs, R.; Kölmel, C. *Chem. Phys. Lett.* **1988**, *150*, 263−268.

(9) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(10) Buehl, M.; Schleyer, P. v. R. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Ed.; John Wiley & Sons: New York, 1991; pp 113−142.

(11) Stanton, J. F.; Lipscomb, W. N.; Bartlett, R. J.; McKee, M. L. *Inorg. Chem* **1989**, *28*, 109−111.



(a) ar-B_4H_{10} C_{2v} **(b)** bis-B_4H_{10} C_2

Figure 3. *arachno*-Tetraborane and bis(diboranyl) isomers: optimized geometries at MP2/6-31G(d,p) in ångstroms and degrees.

Table 1. Total Energies, ZPE Correction, and Relative Energies of Stable Isomers and Transition Structures

molecule	symmetry	MP2/6-31G(d,p) (E_h)	ZPE corr (E_h)	total E (E_h)	ΔE (E_h)	ΔE (kcal/mol)
arachno-B_4H_{10}	C_{2v}	−104.9197037	0.115277	−104.80443	0.0	0.0
bis-B_4H_{10}	C_2	−104.9045460	0.114854	−104.78969	0.01473	9.2
I-B_4H_{10}	C_1	−104.8520966	0.110903	−104.74119	0.06323	39.7
a-B_3H_7 +BH_3	C_1	−104.8388251	0.105185	−104.73364	0.07079	44.4
TS1 + BH_3	C_1	−104.8339851	0.103926	−104.73006	0.07437	46.7
b-B_3H_7 +BH_3	C_1	−104.8539452	0.106203	−104.74774	0.05668	35.6
TS2	C_1	−104.8479199	0.109151	−104.73877	0.06566	41.2
TS3	C_1	−104.8484620	0.111487	−104.73698	0.06745	42.3
TS4	C_1	−104.8514915	0.110049	−104.74144	0.06298	39.5
TS5	D_2	−104.8575327	0.110719	−104.74681	0.05761	36.2
TS6	C_1	−104.8540918	0.111432	−104.74266	0.06177	38.8
TS7	C_1	−104.8453793	0.111616	−104.73376	0.07066	44.3
TS8	C_1	−104.8575533	0.111970	−104.74558	0.05884	36.9
TS9	C_s	−104.8984713	0.114242	−104.78423	0.02020	12.7
TS10	C_1	−104.8961903	0.114354	−104.78184	0.02259	14.2
TS11	C_1	−104.8601747	0.111595	−104.74858	0.05585	35.0
p1-B_4H_{10}	C_s	−104.8979557	0.114461	−104.78350	0.02093	13.1
p2-B_4H_{10}	C_1	−104.8992090	0.114723	−104.78449	0.01994	12.5

and isomers, a reasonably good but economical method and basis set needs to be chosen.

The geometry optimization and molecular energy calculations of all the species have been carried out using second-order Møller−Plesset perturbation theory with the 6-31G(d,p) basis set. Analytic normal-mode harmonic frequencies were also obtained at the same level of theory to characterize the stationary points. The energies are then corrected by including the zero-point correction at the same MP2/6-31G(d,p) level. Intrinsic reaction coordinate (IRC) calculations have been performed on all the reported transition states to verify the minima connecting the transition states.

This basis set is large enough to give reasonably accurate results while being sufficiently economical to allow a large number of calculations. In certain cases, geometry optimizations and frequency calculations have been performed at MP2/6-311G(2d,p) and B3LYP/6-311G(2d,p) levels of theory to assess the validity of the MP2/6-31G(d,p) level. Also, single point CCSD(T) energies have been calculated to give better estimates of energies. The ab initio molecular orbital calculations have been performed using the GAUSSIAN 98[12] program.

Results and Discussions

A number of different transition structures have been found in an effort to elucidate the mechanism of conversion of the bis(diboranyl) isomer of tetraborane(10) to the *arachno*-tetraborane isomer. The potential energy surface for the system is very complicated with numerous transition structures. Some of the transition structures found are involved in the conversion of the bis-B_4H_{10} structure to the *arachno*-B_4H_{10} structure, while a large number of them are for the interchange of the terminal hydrogens with bridged hydrogens.

Two local minima with a pentacoordinated central boron (p1-B_4H_{10}, Figure 1c and p2-B_4H_{10}, Figure 1d) are predicted to have energies close to 13 kcal/mol above the *arachno*-B_4H_{10} isomer. p2-B_4H_{10} was earlier characterized by Bühl and McKee[13] at the MP2/6-31G(d) level of theory. p1-B_4H_{10} has not previously been characterized and is slightly higher in energy. Bühl and McKee also characterized the transition structure for conversion of p2-B_4H_{10} to *arachno*-B_4H_{10}. The paths for the conversion of p1-B_4H_{10} and p2-B_4H_{10} to bis-(diboranyl) and *arachno*-tetraborane(10) are also examined.

The structures and geometric parameters (in ångstroms and degrees) of *arachno*-tetraborane and bis(diboronyl), computed at MP2/6-31G(d,p) level of theory, are shown in Figure 3. Table 1 gives total energies, along with relative zero-point

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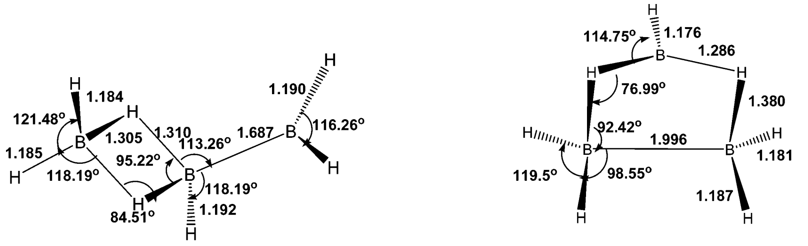
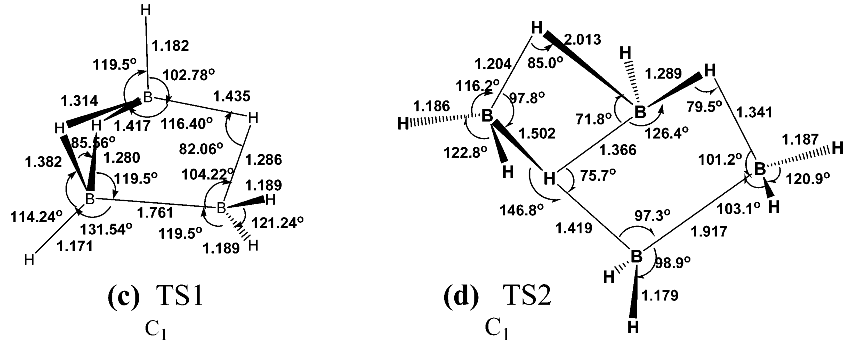
(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(13) Bühl, M.; McKee, M. L. *Inorg. Chem* **1998**, *37*, 4953−4958.



(a) a-B_3H_7
C_s

(b) b-B_3H_7
C_s



(c) TS1
C_1

(d) TS2
C_1

Figure 4. Optimized geometry of stable and transition structures involved in path 1 at MP2/6-31G(d,p) in ångstroms and degrees.

corrected energies, of all the isomers, intermediates, and transition structures of tetraborane(10) characterized in this study.

Three pathways between bis(diboranyl) and the arachno structure have been found. The first (path 1) is similar to the dissociative pathway to B_3H_7 and BH_3 proposed by McKee. The second (path 2) is a concerted pathway over two transition states separated by a local minimum and is different from the pathways suggested by McKee. The third (path 3) involves the pentacoordinated isomers, p1-B_4H_{10} and p2-B_4H_{10}, as intermediates and is also a concerted pathway.

Path 1. The structures and geometric parameters (in ångstroms and degrees) of stable isomers and transition structures involved in the stepwise pathway for the interconversion are shown in Figure 4. A schematic representation of this path (path 1) is shown in Figure 5.

The first step along the pathway is the dissociation of the bis(diboranyl) isomer into B_3H_7 and BH_3. The product of the dissociation is a-B_3H_7 (Figure 4a), which then converts to b-B_3H_7 (Figure 4b), via transition structure TS1 (Figure 4c), for the B_3H_7 system. One of the hydrogens in the terminal BH_2 moiety of a-B_3H_7 forms a bridge with the boron in the other end resulting in the transition structure TS1, with three bridged hydrogens. Simultaneously, one of the bridged hydrogens moves away from the boron atom and turns into a terminal hydrogen forming b-B_3H_7. The reaction coordinate has a barrier height of 2.2 kcal/mol for the forward reaction from isomer a-B_3H_7 and a barrier height of 11.0 kcal for the reverse reaction from isomer b-B_3H_7.

The BH_3 moiety, then inserts back to b-B_3H_7 via the transition structure TS2 (Figure 4d). The boron of the BH_3 attaches to one of the bridged hydrogens, and a hydrogen atom attaches to the apex boron forming the transition structure TS2. This insertion transition state has a barrier of 32.0 kcal/mol relative to the bis(diboranyl) isomer going to *arachno*-B_4H_{10}.

The dissociation of B_4H_{10} to B_3H_7 and BH_3 involves the breaking of one B_2H_5 unit and is thus similar to the breaking of B_2H_6 to give two BH_3 molecules. The recombination of two BH_3 molecules to form B_2H_6 appears to occur without a barrier[14] or with a barrier no higher than 1 kcal/mol.[7] It is difficult to identify the transition structure. The dissociation of B_4H_{10} is similar; no transition structure has been identified. The dissociation energy of B_4H_{10} is 35.2 kcal/mol, very close to the dissociation energy of diborane, which is 34.9 kcal/mol at the same level of theory. Both these energies are close to the experimental dissociation energy of B_2H_6 to two BH_3 moieties, which is 36 ± 3 kcal/mol.[15] The highest point on the path is 37.4 kcal/mol above the energy of bis(diboranyl). While this pathway is a possible path for the interconversion of bis(diboranyl) to *arachno*-tetraborane, it is unlikely. The recombination of B_3H_7 with BH_3 will be slow due to the low concentration of these intermediates. Also, the possibility for alternative paths is high as both B_3H_7 and BH_3 are intermediates in the general pyrolysis reactions of diborane, which lead to many different products.

Path 2. The structures and geometric parameters (in ångstroms and degrees) of stable isomers and transition structures involved in the first concerted pathway for the interconversion are shown in Figure 6. A schematic representation of this path (path 2) is given in Figure 7.

The concerted pathway involves the breaking of a hydrogen bridge in one of the boranyl ends of the bis(diboranyl) isomer (Figure 3b) and the formation of a third hydrogen bridge at the other boranyl end. This results in the reaction

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(14) DeFrees, D. J.; Raghavachari, K.; Schlegel, H. B.; Pople, J. A.; Schleyer, P. v. R. *J. Phys. Chem.* **1987**, *91*, 1857−1864.

(15) Redman, L. T.; Purvis, G. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 2856.

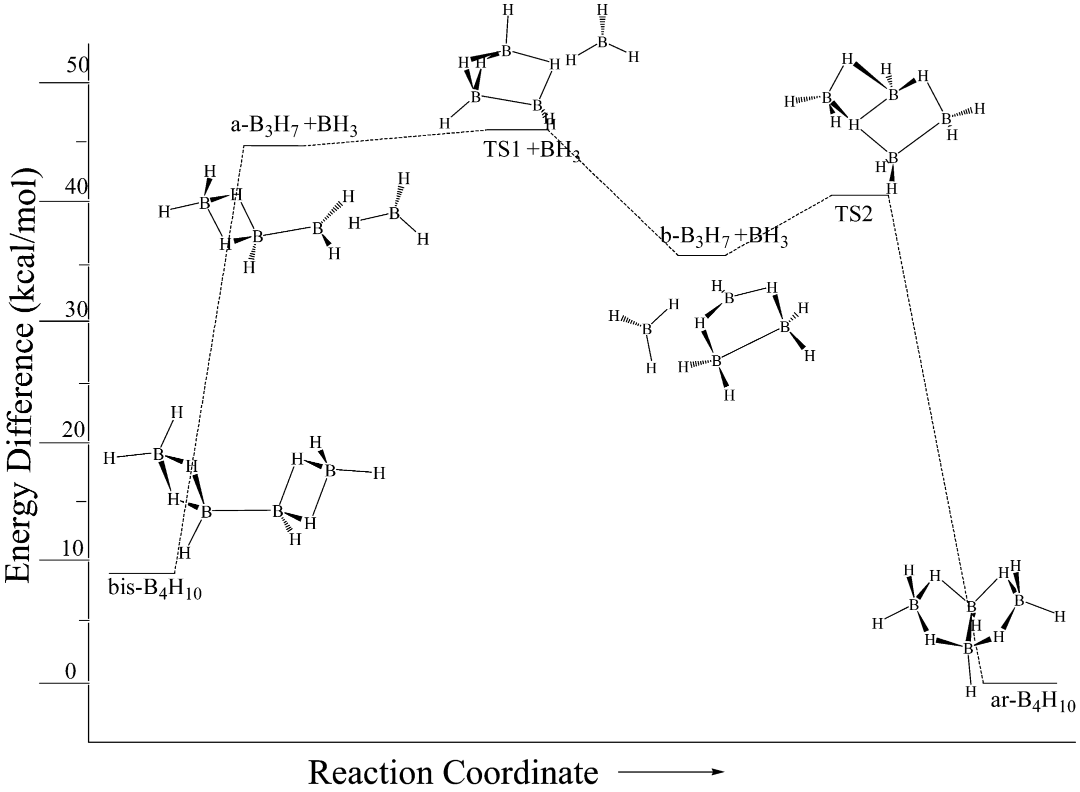
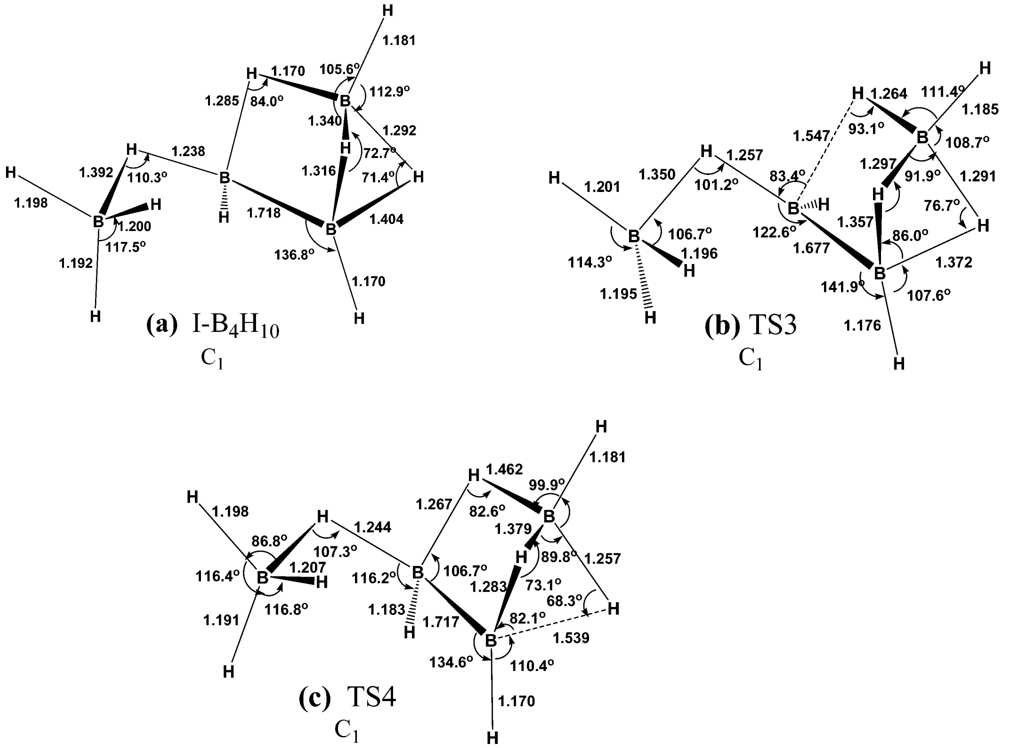


Figure 5. Schematic representation of path 1 pathway of interconversion of isomers of B_4H_{10}.



(a) I-B_4H_{10}
C_1

(b) TS3
C_1

(c) TS4
C_1

Figure 6. Optimized geometry of transition structures and intermediate involved in path 2 at MP2/6-31G(d,p) in ångstroms and degrees.

intermediate I-B_4H_{10} (Figure 6a), through the transition structure TS3 (Figure 6b). The barrier height for the forward reaction is 33.1 kcal/mol at MP2/6-31G(d,p) level and that for the reverse reaction is 2.6 kcal/mol. A second transition state TS4 (Figure 6c) connects I-B_4H_{10} to the *arachno*-tetraborane isomer (Figure 3a), with an energy barrier of −0.2 kcal/mol, for the forward reaction, and 39.5 kcal/mol for the reverse reaction. (The barrier height for the forward reaction is positive on the PES and becomes negative only on the inclusion of the zero point energy correction.) Here the terminal boron with a single hydrogen bridge moves closer to the other central boron forming a new hydrogen bridge, with, simultaneously, one of the two original hydrogen bridges breaking.

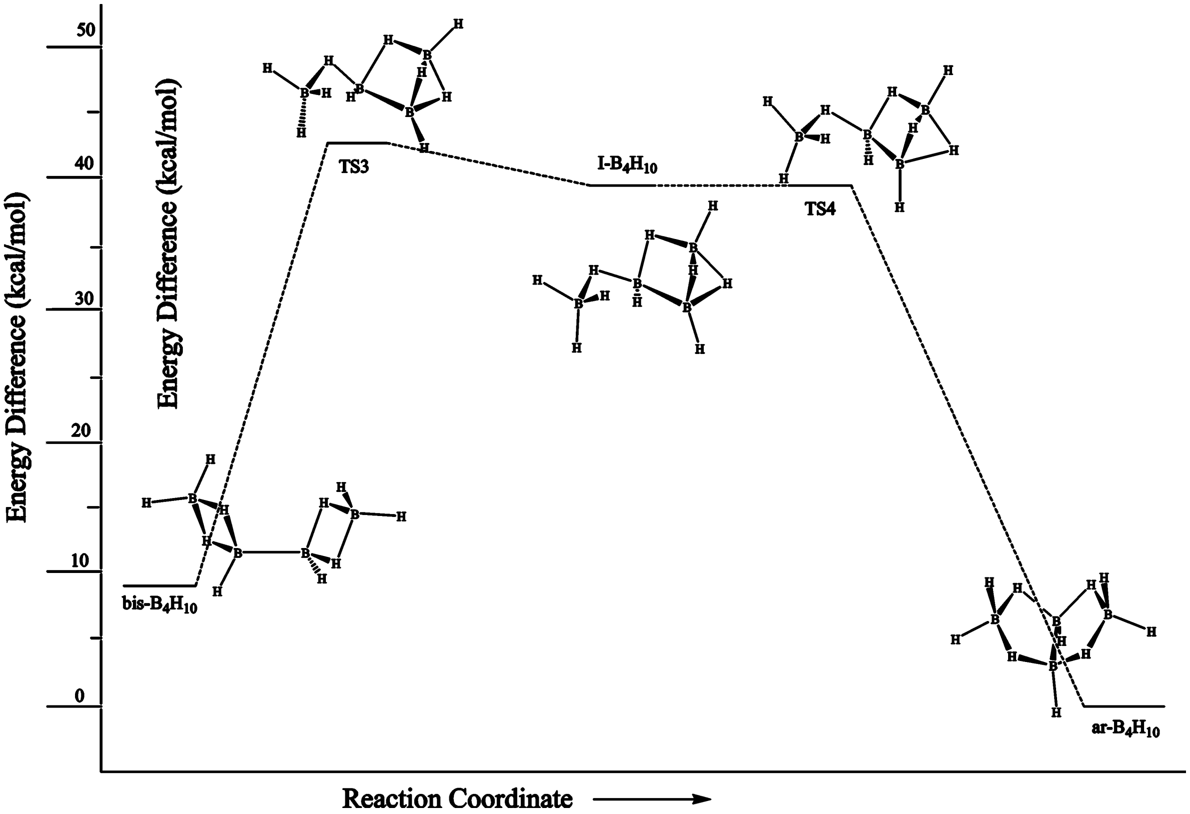


Figure 7. Schematic representation of path 2, pathway of interconversion of isomers of B_4H_{10}.

Table 2. Energies of the Transition Structures Relative to I-B_4H_{10} (in kcal/mol) at Different Levels of Theory

level of theory	TS3	TS4
MP2/6-31G(d,p)	2.65	−0.16
CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p)	1.46	−0.22
MP2/6-311G(2d,p)	3.04	0.18
CCSD(T)/6-311G(2d,p)//MP2/6-311G(2d,p)	1.64	−0.01
B3LYP/6-311G(2d,p)	1.75	−0.33
CCSD(T)/6-311G(2d,p)//B3LYP/6-311G(2d,p)	1.68	−0.08

The geometries of these three structures (TS3, I-B_4H_{10}, and TS4), even though they look similar, are significantly different at the bridge breaking and forming positions. To confirm the existence of these three structures, which are almost isoenergetic, optimizations with different basis sets and theory were carried out. Relative energies of the two transition structures (TS3 and TS4) with respect to I-B_4H_{10} are given in Table 2.

The geometries of TS3, I-B_4H_{10}, and TS4 are almost identical at MP2/6-31G(d,p), MP2/6-311G(2d,p), and B3LYP/6-311G(2d,p) levels of theory. For example, the distance between the boron and the hydrogen in TS3, represented by a dotted line in Figure 6b, where the new bridge is forming, is 1.547, 1.547, and 1,543 Å at MP2/6-31G(d,p), MP2/6-311G(2d,p), and B3LYP/6-311G(2d,p) levels, respectively. Similarly, the bond distance between the boron and the hydrogen in TS4, represented by a dotted line in Figure 6c, where the existing bridge is breaking, is 1.539, 1.544, and 1.521 Å, at MP2/6-31G(d,p), MP2/6-311G(2d,p), and B3LYP/6-311G(2d,p) levels, respectively.

The intermediate I-B_4H_{10} has no imaginary frequencies at all the above-mentioned levels of theory, suggesting that it is not an artifact of theory or basis set. The almost nonexistent barrier of −0.2 kcal/mol (adding the ZPE correction makes it negative) for this intermediate to TS4, at MP2/6-31G(d,p) level, continues to be flat at other levels of theory as can be seen in Table 2. Path 2 has a slightly lower barrier than path 1, and as a concerted reaction it is a much more likely path.

Path 3. The structures and geometric parameters (in ångstroms and degrees) of stable isomers and transition structures involved in the concerted pathway for the interconversion via the pentacoordinated tetraborane(10) structures are given in Figure 8. A schematic representation of this path (path 3) is shown in Figure 9.

Two structures, with a central pentacoordinated boron atom, are found in the tetraborane system (Figure 8a,b). These are analogous to the two pentacoordinated structures also identified for the gallatetraborane systems.[16] The isomer p1-B_4H_{10} (Figure 8a) is a local minimum where the two hydrogens and the two borons attached to the central pentacoordinated boron are positioned at the base of a rectangular pyramid and the terminal hydrogen attached to the central boron in at the apex of the pyramid. It has C_s symmetry, with the plane consisting of the terminal boron, central boron, and the bridged hydrogen.

The second structure, p2-B_4H_{10} (Figure 8b), has no element of symmetry. It is a local minimum and differs from p1-B_4H_{10} by the orientation of the two rings to each other, and also by the way the five bonds around the central boron are oriented. Unlike p1-B_4H_{10}, in p2-B_4H_{10}, two hydrogens and a boron occupy the triangular equatorial positions of a

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(16) Ramakrishna, V.; Duke, B. J. *Inorg. Chem.* , in press.

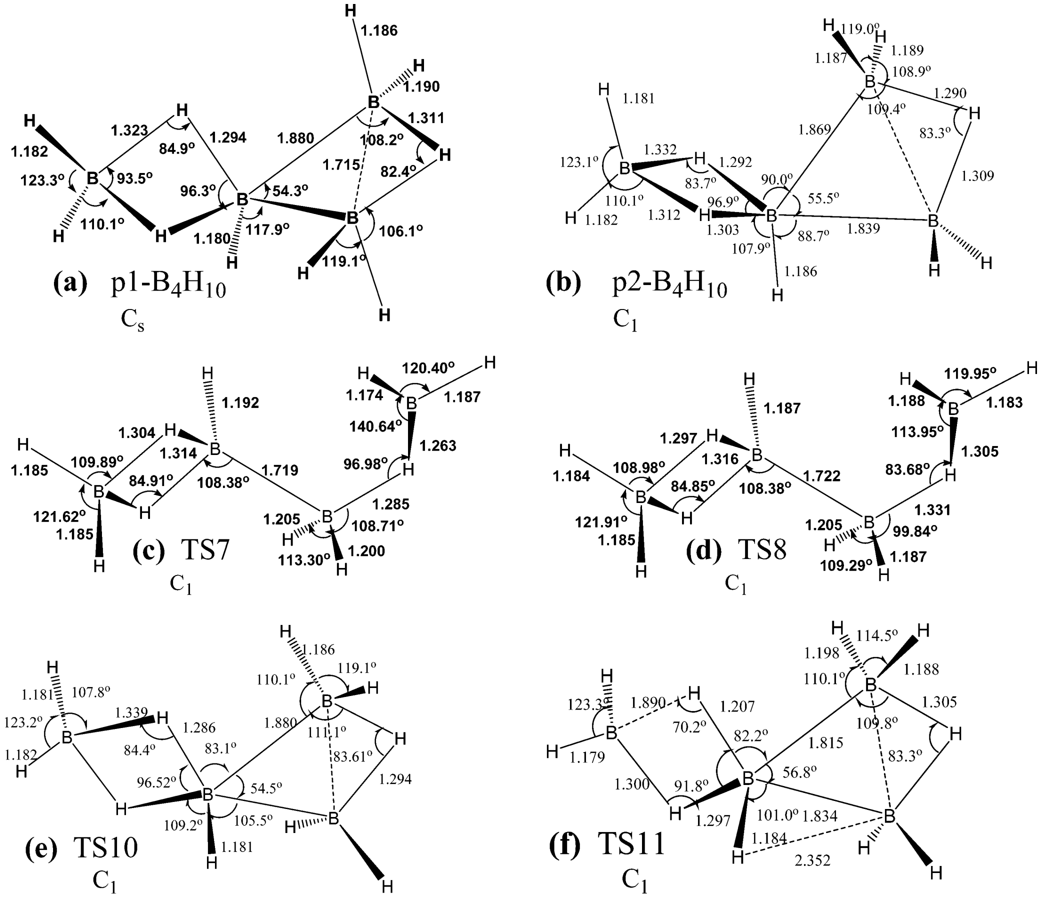

Figure 8. Optimized geometry of isomers and transition structures of path 3 at MP2/6-31G(d,p) in ångstroms and degrees.

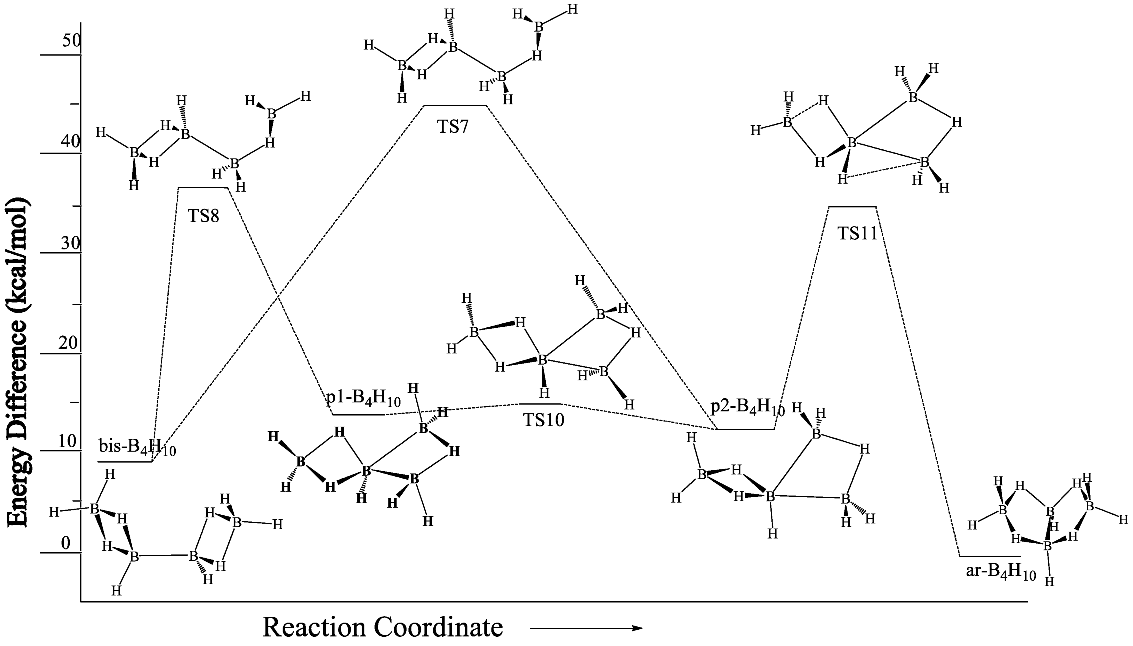

Figure 9. Schematic representation of path 3, pathway of interconversion of isomers of B_4H_{10}.

distorted trigonal pyramid. The terminal hydrogen attached to the central boron occupies one of the apex positions, and a boron atom occupies the other apex position.

TS8 (Figure 8d) is the transition structure for the interconversion of the bis(diboranyl) isomer, to the pentacoordinate isomer p1-B_4H_{10}. A bond between the central boron and one of the borons on the single bridge side of p1-B_4H_{10} breaks and a terminal hydrogen moves in, to form a hydrogen bridge between the two borons forming the bis(diboranyl) structure. The barrier for the forward reaction is 27.7 kcal/mol and for the backward reaction is 23.8 kcal/mol. TS7 (Figure 8c) is a transition structure between the bis(diboranyl)

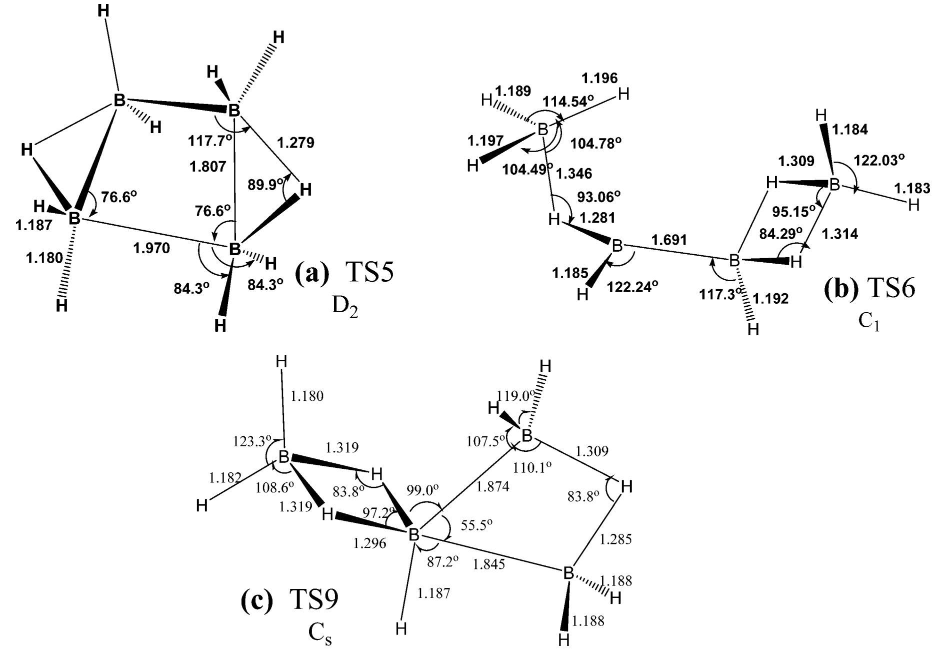

Figure 10. Optimized geometry of other transition structures of path 3 at MP2/6-31G(d,p) in ångstroms and degrees.

isomer and the p2-B_4H_{10} isomer, with a mechanism similar to that described above, with a forward activation of 35.1 kcal/mol and backward activation of 31.8 kcal/mol.

The lowest energy pathway via the pentacoordinated structures is through transition structure TS8 to p1-B_4H_{10} (Figure 9). p1-B_4H_{10} converts to p2-B_4H_{10} via TS10 (Figure 8e) and a small barrier of 1.1 kcal/mol. The direct route from bis(diboranyl) to p2-B_4H_{10} is via a higher energy transition structure TS7, which is 35.1 kcal/mol higher than bis(diboranyl). p2-B_4H_{10} converts to *arachno*-tetraborane(10) via transition structure TS11 (Figure 8f) and a barrier of 22.5 kcal/com. TS11 was previously characterized by Bühl and McKee[13] at the MP2/6-31G(d) level of theory. The optimized structure at the MP2/6-31G(d,p) level of theory in this study is similar to that found by Bühl and McKee, but the outer BH_3 group has moved significantly closer to the central pentacoordinated boron atom. This is a good example of the changes to transition structures when polarization p functions are added to the hydrogens in the basis set. The highest point on this pathway is TS8 which is 27.7 kcal/mol above bis(diboranyl).

Other Transition Structures on the PES. Among the numerous transition structures found on the PES of B_4H_{10}, the geometry and structural parameters of some important ones are shown in Figure 10. Transition structure TS5 (Figure 10a) of B_4H_{10} is a transition structure for the conversion of the two central borons to terminal borons in the arachno isomer. The two wing tip borons come closer to form a bond, and simultaneously the bond length between the two central borons increases, forming the transition structure TS5. This transition structure has energy 36.2 kcal/mol above *arachno*-B_4H_{10}. A similar transition structure would convert the known 2-GaB_3H_{10} to the unknown 1-GaB_3H_{10}.[17,18] TS6 (Figure 10b) is a transition structure for the conversion of a bridged hydrogen to a terminal hydrogen in the bis(diboranyl) isomer, with a barrier height of 35.51 kcal/mol.

TS9 (Figure 10c) is a transition structure, geometrically very similar to p2-B_4H_{10}, but the plane of the two rings are exactly at right angles to each other, whereas in p2-B_4H_{10} the rings are in a "gauche" position, neither flat nor at right angles to each other. TS9 has a C_s plane of symmetry consisting of the three-membered ring (B−B−B) and the two terminal hydrogens in the diborane end. TS9 is in fact the transition structure where the rings flip to the gauche form (p2-B_4H_{10}) on either side over a barrier of 0.2 kcal/mol.

The possibility of finding experimental evidence for a pentacoordinate boron atom is intriguing. These tetraborane structures may be more likely candidates for experimental verification than the pentacoordinated boron isomer of triborane(9) predicted by Duke et al.[19] However, the pathway for these structures isomerizing to the most stable *arachno*-tetraborane(10) isomer is lower than the lowest pathway for conversion of bis-B_4H_{10} to *arachno*-B_4H_{10}.

Conclusion

For the conversion of the bis(diboranyl) isomer to the *arachno*-tetraborane isomer, the concerted pathways (paths 2 and 3) seem more likely compared to the stepwise pathway (path 1). The presence of the dissociated intermediates in path 1 in low concentration will inevitably reduce the rate of this reaction, and they also open up the possibility of a range of alternative pathways. For example, the BH_3 and

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(17) Pulham, C. R.; Downs, A. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1990**, 1520−1521.

(18) Ramakrishna, V.; Duke, B. J.; McKee, M. L. *Mol. Phys.* **2000**, *98*, 745−750.

(19) Duke, B. J.; Gauld, J. W.; Schaefer, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 7753−7755.

B_3H_7 formed in path 1 may combine with B_4H_{10}, giving rise to many other boranes similar to the pyrolysis of diborane.[20]

Both paths 2 and 3 are energetically favorable compared to path 1, with path 3 at 27.7 kcal/mol activation energy, lower than path 2 at 33.1 kcal/mol. Path 3, via the pentacoordinated isomers, appears to be the most favorable pathway. A barrier of 27.7 kcal/mol does not completely rule out the possibility that the bis(diboranyl) structure could be found.

The experiment by Binder et al.[3] with B_4H_{10} and bifunctional thiols forming transannularly bridged $H_2(\mu_2)_2S_2RBH(B_2H_5)$ similar to the bis-isomer (Figure 2a) and its rearrangement into $H_2B(\mu_2)_2S_2RB_3H_6$ analogous to the *arachno*-isomer (Figure 2b) on cooling indicate that the bis-isomer of tetraborane(10) might be found if experiments were conducted at suitable conditions. Bis(diboranyl) remains a challenge to experimentalists.

Acknowledgment. We thank one of the referees for drawing our attention to the work by Bühl and McKee.[13]

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(20) Stanton, J. F.; Lipscomb, W. N.; Bartlett, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 5165−5173.