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Exotic Structures of $Si_2B_2H_4$

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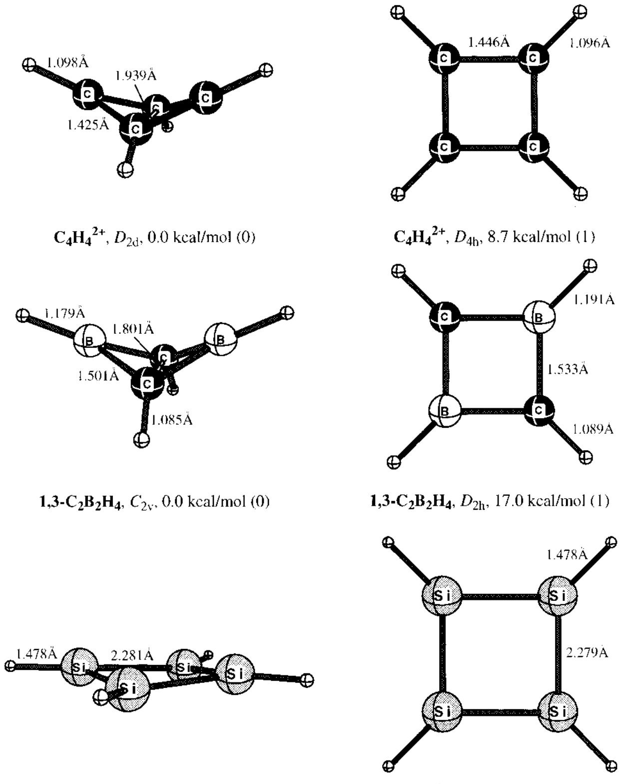
The potential energy surface of $Si_2B_2H_4$, explored *ab initio* at the MP2/6-31G* and density functional theory, Becke3LYP/6-311+G** levels, is rich in detail. Twelve minima were found out of the 39 stationary points located. 1,3-Disiladiboretene (**1a**), with a puckered four-membered ring, is predicted to be the global minimum. Its calculated inversion barrier (1.2 kcal/mol), however, is much lower than that of the analogous 1,3-diboretene (17.0 kcal/mol). The relative energies of two other $Si_2B_2H_4$ isomers (**5** and **7**) with B−H−Si bridges are only 2.0 kcal/mol above **1a**. The relative energies of **9** and **15a**, both with planar pentacoordinate borons, are 7.3 and 27.1 kcal/mol. The acyclic (**18**) and linear (**22a**,**b**) isomers are noncompetitive energetically. Many other $Si_2B_2H_4$ silaboranes, possessing similar structures and bonding as the corresponding carboranes, are calculated to be saddle points. In general, hydrogen bridging and cyclic π-delocalization stabilize $Si_2B_2H_4$ isomers, while structures with multiply bonded silicon are unfavorable.

Introduction

Theoretical calculations first revealed the cyclobutadiene dication ($C_4H_4^{2+}$)[1] to be nonplanar (Figure 1) despite being Hückel 2π electron aromatic.[2] Subsequently, the excellent agreement between the computed NMR-IGLO chemical shifts[3] and the experimental values[4] provided conclusive evidence for the nonplanarity of the tetramethyl derivative $C_4(CH_3)_4^{2+}$. The neutral isoelectronic 1,3-diboretene (1,3-$C_2B_2H_4$) and 1,3-$C_2B_2H_2(NH_2)_2$ also have nonplanar geometries and similar electronic structures.[5] Moreover, the theoretical predictions were verified subsequently by X-ray crystallography on 1,3-*t*-$Bu_2C_2(BNMe_2)_2$[6b] and on other derivatives.[6a,c−g] However, Korkin *et al.*'s[7a] recent computations found $Si_4H_4^{2+}$, the homologue of $C_4H_4^{2+}$, to be nearly planar.[7] What is the situation with 1,3-disiladiboretene (1,3-$Si_2B_2H_4$)?

While the potential energy surfaces (PES) of $C_4H_4^{2+}$ and $Si_4H_4^{2+}$ have not been explored fully,[1b,7] *ab initio* MO studies revealed remarkable structural variations for $C_2B_2H_4$ isomers.[8] The resulting fruitful interplay between theory and experiment guided the synthesis of many $C_2B_2R_4$ isomers by Berndt and co-workers.[9] Such successes serve as additional stimuli for the present exploration of the PES of $Si_2B_2H_4$.

The experimental literature on silaboranes is rather scarce.[10] The recent synthesis and X-ray structure determination of icosahedral mono- and disilaboranes by Seyferth, Wesemann, and their co-workers[10] mark the beginning of the combined boron−silicon chemistry. Smaller silaboranes like $SiBH_n$ ($n = 1-5$),[11] SiB_2H_4,[12a] and Si_2BH_3[12b] have been explored only computationally. These studies point to a structural correlation between boranes and silaboranes, i.e. the analogy between trivalent boron and divalent silicon moieties.[13] Thus, by equating a B−H bond pair to Si: (σ lone pair), the doubly bridged Si(μ-H)$_2$Si (C_{2v})[14] and silacyclopropenylidene (C_2H_2-Si)[15a,c] are related to the doubly bridged B_2H_4 (HB(μ-H)$_2$BH,C_{2v}) and to borirene (C_2H_2BH, C_{2v}).[16]



$C_4H_4^{2+}$, D_{2d}, 0.0 kcal/mol (0)

$C_4H_4^{2+}$, D_{4h}, 8.7 kcal/mol (1)

1,3-$C_2B_2H_4$, C_{2v}, 0.0 kcal/mol (0)

1,3-$C_2B_2H_4$, D_{2h}, 17.0 kcal/mol (1)

$Si_4H_4^{2+}$, D_2, 0.0 kcal/mol (0)

$Si_4H_4^{2+}$, D_{4h}, -0.5 kcal/mol (1)[7b]

Figure 1. Becke3LYP/6-311+G** optimized geometries of $C_4H_4^{2+}$, 1,3-$C_2B_2H_4$, and $Si_4H_4^{2+}$.

Further *ab initio* studies on small silicon compounds[17] have shown that the structural preferences can be quite different from those of the corresponding carbon compounds. For example, Si(μ-H)$_2$Si was predicted to be the global minimum on the PES of Si_2H_2[17c] rather than HSi≡SiH, and this was verified spectroscopically.[14] Similarly, silylsilylene (HSi−SiH_3) and HSi(μ-H)$_2$SiH were calculated to be energetically competitive alternatives to disilene ($H_2Si{=}SiH_2$).[17d] The spectroscopic identification of HSi(μ-H)Si[18a] (after its theoretical prediction)[17c] and the X-ray structure of a silylene chelate complex[18b] confirm the stability of molecules with divalent silicon. Systematic

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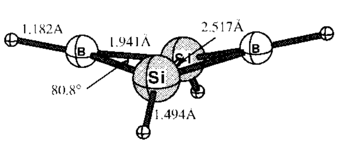
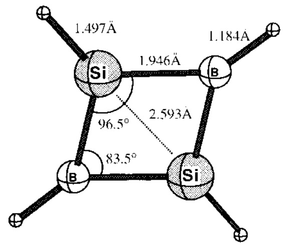
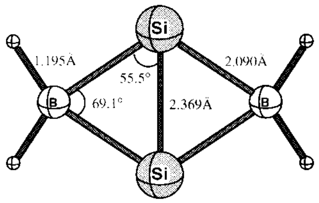


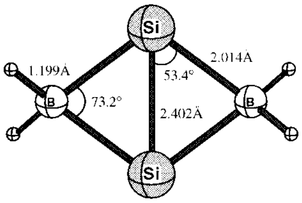
1a, C_{2v}, 0.0 kcal/mol (0)



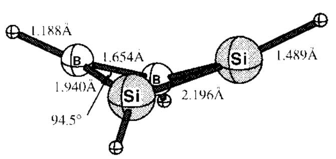
1b, D_{2h}, 1.2 kcal/mol (1)



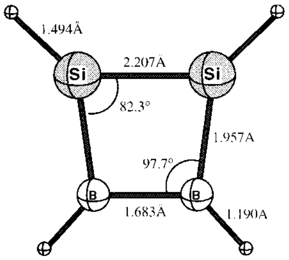
3b, D_{2h}, 23.6 kcal/mol (1)



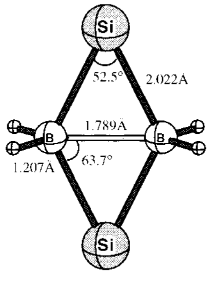
3c, D_2, 5.3 kcal/mol (1)



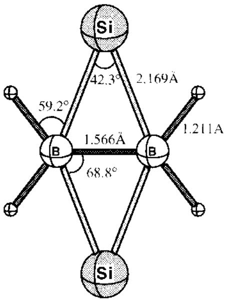
2a, C_2, 6.2 kcal/mol (0)



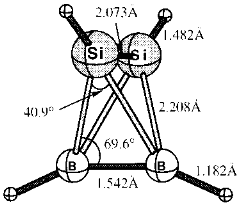
2b, C_{2v}, 8.7 kcal/mol (1)



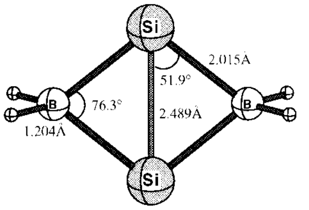
4a, D_{2h}, 15.4 kcal/mol (1)



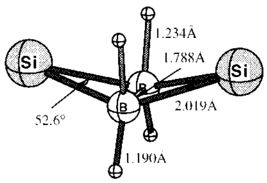
4b, D_{2h}, 71.0 kcal/mol (3)



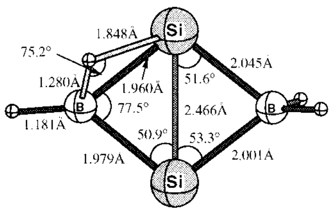
2c, C_{2v}, 28.8 kcal/mol (1)



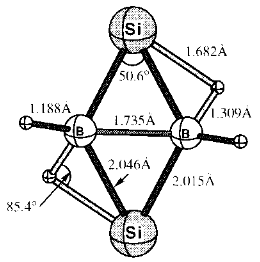
3a, D_{2h}, 7.4 kcal/mol (3)



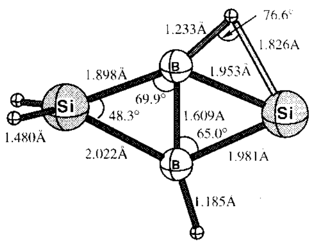
4c, C_{2v}, 8.2 kcal/mol (1)



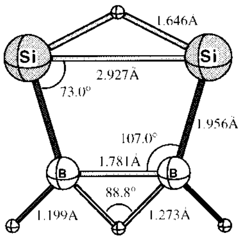
5, C_1, 2.0 kcal/mol (0)



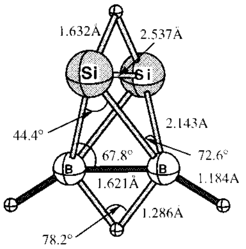
6, C_2, 10.9 kcal/mol (0)



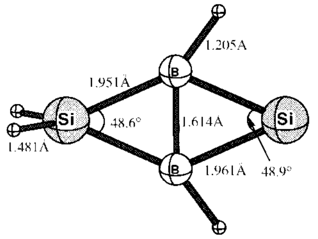
7, C_s, 2.0 kcal/mol (0)



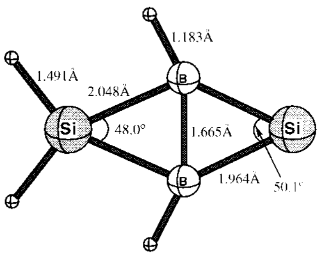
11a, C_{2v}, 53.6 kcal/mol (2)



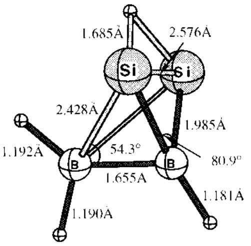
11b, C_{2v}, 16.2 kcal/mol (0)



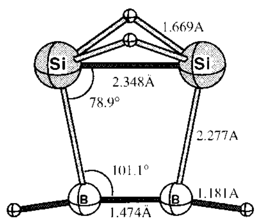
8a, C_{2v}, 1.9 kcal/mol (1)



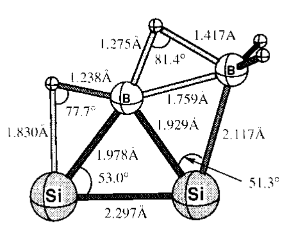
8b, C_{2v}, 31.9 kcal/mol (2)



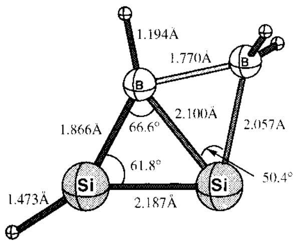
11c, C_s, 18.4 kcal/mol (1)



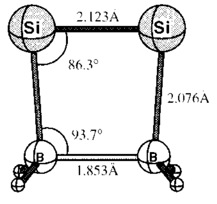
12, C_{2v}, 73.4 kcal/mol (3)



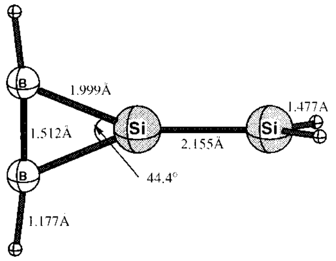
9, C_s, 7.3 kcal/mol (0)



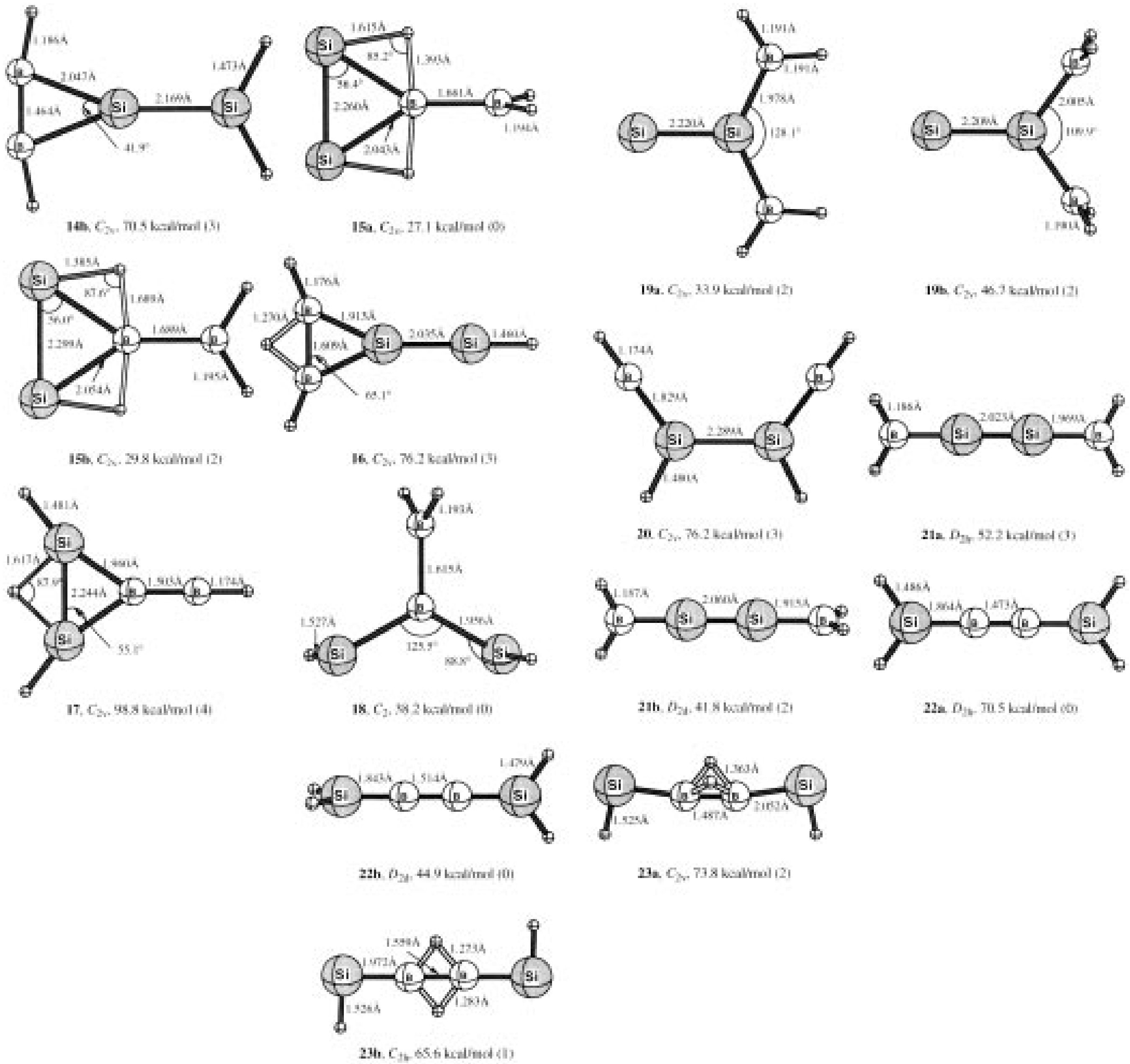
10, C_1, 11.3 kcal/mol (0)



13, C_{2v}, 61.2 kcal/mol (1)



14a, C_{2v}, 32.3 kcal/mol (1)



14b. C_{2v}, 70.5 kcal/mol (3)
15a. C_{2v}, 27.1 kcal/mol (0)
19a. C_{2v}, 33.9 kcal/mol (2)
19b. C_{2v}, 46.7 kcal/mol (2)
15b. C_{2v}, 29.8 kcal/mol (2)
16. C_{2v}, 76.2 kcal/mol (3)
20. C_{2v}, 76.2 kcal/mol (3)
21a. D_{2h}, 52.2 kcal/mol (3)
17. C_{2v}, 98.8 kcal/mol (4)
18. C_2, 58.2 kcal/mol (0)
21b. D_{2d}, 41.8 kcal/mol (2)
22a. D_{2h}, 70.5 kcal/mol (0)
22b. D_{2d}, 44.9 kcal/mol (0)
23a. C_{2v}, 73.8 kcal/mol (2)
23b. C_{2h}, 65.6 kcal/mol (1)

Figure 2. Becke3LYP/6-311+G** optimized geometries (distances in angstroms and angles in degrees) for **1**−**23**.

investigations of silicon−phosphorus compounds (SiH_mPH_n, $m + n = 0-5$) at the G2 level also indicate preference for structures with divalent silicon.[19] The multicenter bonded B−H−B and Si−H−Si moieties in boranes and silicon hydrides predicted theoretically[11−13] and observed experimentally[14,18] suggest similar bonding characteristics (B−H−Si) for the hybrid, silaboranes, in addition to structures with low-valent silicon.

Hence, unusual structures and energies of $Si_2B_2H_4$ isomers, compared with boranes, carboranes, and silicon hydrides, can be expected. The parent compounds might be observed in the gas phase or in matrix isolation. Hydrogen-bridged and other structures might be realized in condensed phases when bulky substituents are present. There are numerous precedents.[6,9,14,18] We have employed *ab initio* MO and DFT computations to explore the intriguing structural diversity of the $Si_2B_2H_4$ PES.

Computational Details

The geometries (Figure 2) were optimized at the electron-correlated MP2(fc)/6-31G* (MP2)[20a] and Becke3LYP/6-311+G** (B3LYP)[20c−e] levels using the Gaussian 92/DFT and Gaussian 94 program packages.[21] The nature of the stationary points were characterized by analytically computed frequencies both at MP2 and B3LYP. The total, relative, and zero-point energies are given in Table 1. Relative energies computed at MP2 include scaled (0.95) zero-point vibrational energy corrections.[20b] No scaling was used for the B3LYP zero-point vibrational energies.[22] The stability order of all the structures is comparable at both levels of theory. Hence, only the B3LYP geometries and energies are discussed.[23] Natural population analysis (NPA) charges[24a,b] and Wiberg bond indices (WBIs)[24c,d] for all minimum-energy structures are given in Figure 3.

Results and Discussion

Nonplanar 1,3-disiladiboretene (C_{2v}, **1a**), the most stable $Si_2B_2H_4$ isomer, is puckered[25] by 24.2° and has an inversion barrier of only 1.2 kcal/mol via the D_{2h} transition structure **1b**. The analogous 1,3-diboretene (C_{2v}) is low in energy, but is not the $C_2B_2H_4$ global minimum.[8] The isovalent and isoelectronic $C_4H_4^{2+}$ and $Si_4H_4^{2+}$ also prefer similar puckered structures

TABLE 1: Total (hartrees), Relative (kcal/mol), and Zero-Point Vibrational Energies (ZPE, kcal/mol) for 1−23 at the MP2-fc/6-31G* (MP2) and BECKE3LYP/6-311+G (B3LYP) Levels of Optimization (The Number of Imaginary Frequencies (NIM) Are Given in Parentheses)**

		total energy		relative energy		ZPE (NIM)	
no.	sym.	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
$C_4H_4^{2+}$	D_{4h}	−153.343 58	−153.886 52	10.9	8.7	39.0(1)	38.4(1)
$C_4H_4^{2+}$	D_{2d}	−153.360 80	−153.899 86	0.0	0.0	38.9(0)	38.1(0)
$C_2B_2H_4$	D_{2h}	−127.736 46	−128.264 99	20.7	17.0	35.3(1)	34.5(1)
$C_2B_2H_4$	C_{2v}	−127.769 89	−128.292 46	0.0	0.0	35.6(0)	34.7(0)
$Si_4H_4^{2+}$	D_{4h}	−1157.528 95	−1159.686 11	−0.2	−0.5	22.4(1)	21.4(1)
$Si_4H_4^{2+}$	D_2	−1157.529 04	−1159.686 70	0.0	0.0	22.7(0)	22.3(0)
1a	C_{2v}	−629.747 37	−631.073 66	0.0	0.0	27.0(0)	26.2(0)
1b	D_{2h}	−629.743 77	−631.071 38	2.1	1.2	26.8(1)	26.0(1)
2a	C_2	−629.735 24	−631.063 29	7.3	6.2	26.7(0)	25.9(0)
2b	C_{2v}	−629.727 56	−631.059 20	12.0	8.7	26.5(1)	25.8(1)
2c	C_{2v}	−629.700 49	−631.026 19	28.3	28.2	25.8(1)	25.2(1)
3a	D_{2h}	−629.730 83	−631.059 66	9.3	7.4	25.9(3)	24.8(3)
3b	D_{2h}	−629.708 14	−631.035 65	24.6	23.6	27.0(1)	25.9(1)
3c	D_2	−629.738 11	−631.064 24	5.7	5.3	26.9(1)	25.6(1)
4a	D_{2h}	−629.725 64	−631.048 81	13.9	15.4	27.3(1)	26.0(1)
4b	D_{2h}	−629.611 74	−630.958 06	82.9	71.0	24.7(3)	24.7(2)
4c	C_{2v}	−629.726 00	−631.059 20	13.1	8.2	26.7(1)	25.3(1)
5	C_1	−629.746 68	−631.070 74	1.3	2.0	27.9(0)	26.4(0)
6	C_2	−629.735 41	−631.058 10	9.5	10.9	29.1(0)	27.3(0)
7	C_s	−629.747 04	−631.070 28	0.1	2.0	26.9(0)	26.1(0)
8a	C_{2v}	−629.745 02	−631.069 59	0.7	1.9	26.2(1)	25.5(1)
8b	C_{2v}	−629.694 06	−631.021 29	32.3	31.9	25.8(2)	25.2(2)
9	C_s	−629.746 69	−631.064 18	2.0	7.3	28.7(0)	27.6(0)
10	C_1	−629.734 45	−631.055 08	8.7	11.3	27.6(0)	25.8(0)
11a	C_{2v}	−629.646 80	−630.988 23	63.4	53.6	27.3(2)	26.2(2)
11b	C_{2v}	−629.729 47	−631.050 61	13.4	16.2	29.3(0)	27.9(0)
11c	C_s	−629.715 32	−631.044 77	20.8	18.4	27.7(1)	26.5(1)
12	C_{2v}	−629.601 34	−630.952 02	90.9	73.4	26.2(3)	23.3(3)
13	C_{2v}	−629.657 40	−630.974 50	61.2	61.2	32.0(1)	25.2(1)
14a	C_{2v}	−629.686 26	−631.019 66	36.4	32.3	24.9(1)	24.6(1)
14b	C_{2v}	−629.615 73	−630.958 33	79.3	70.5	23.5(3)	24.3(2)
15a	C_{2v}	−629.701 03	−631.027 84	28.1	27.1	26.0(0)	24.5(0)
15b	C_{2v}	−629.697 28	−631.024 62	30.9	29.8	26.4(2)	25.2(2)
16	C_{2v}	−629.616 55	−630.951 51	81.2	76.2	26.1(3)	25.7(3)
17	C_{2v}	−629.556 81	−630.909 93	115.9	98.8	23.1(4)	22.3(4)
18	C_2	−629.658 51	−631.009 23	53.8	38.2	24.9(0)	24.0(0)
19a	C_{2v}	−629.682 02	−631.019 47	41.1	33.9	27.1(2)	26.1(1)
19b	C_{2v}	−629.660 45	−630.998 18	54.2	46.7	26.6(2)	25.5(2)
20	C_{2v}	−629.603 41	−630.947 84	87.5	76.2	24.0(3)	23.4(3)
21a	D_{2h}	−629.658 77	−630.989 79	55.8	52.2	27.2(2)	25.8(3)
21b	D_{2d}	−629.666 90	−631.006 71	50.6	41.8	27.1(2)	26.0(2)
22a	D_{2h}	−629.621 57	−630.958 76	79.0	70.5	27.1(0)	24.6(0)
22b	D_{2d}	−629.644 69	−630.998 45	62.0	44.9	24.4(0)	23.9(0)
23a	C_{2v}	−629.607 57	−630.950 37	85.2	73.8	24.4(2)	22.6(2)
23b	C_{2h}	−629.623 69	−630.967 01	77.0	65.6	26.3(1)	24.9(1)

(Figure 1).[1b,7] We have refined the calculations on these isoelectronic and isovalent systems at uniform levels of theory (MP2 and B3LYP) to enable direct comparisons. Table 2 reveals the excellent correlation between the relative energies (ΔE), the puckering angles ($\Delta\Theta$), and the shortening of the transannular distance (ΔD) upon folding. In addition, a comparison of the molecular orbitals (MOs) of the two forms (for example **1a**, **1b** in Scheme 1) shows that the 1,3-antibonding interaction (b_{2u}) of the σ orbitals in the planar structure diminishes on puckering (b_2).[5a] This stabilizing interaction ($\Delta\sigma = E_{b2} - E_{b2u}$) also follows the trends in relative energies (Table 2). Unlike the σ framework, the π orbital has positive 1,3 overlap (b_{3u}), which is destabilized marginally ($\Delta\pi = E_{a1} - E_{b3u}$) upon puckering (Scheme 1). However, the net effect of the σ and π MOs is stabilizing, except for $Si_4H_4^{2+}$. This qualitative interpretation is reflected in the increased transannular Wiberg bond indices (ΔWBI). The NPA charges in **1a** (Si = 0.607; B = −0.445) and in 1,3-diboretene (C = −0.593; B = 0.395) are opposite in sign due to the reversed electronegativity relationship (C = 2.5; B = 2.0; and Si = 1.8).[26]

1,2-Disiladiboretene favors a C_2 minimum **2a** akin to **1a** with a 142.8° $B^3Si^2B^4Si^1$ dihedral angle. Planar **2b** is the transition state for ring flipping; the calculated barrier of 2.5 kcal/mol is twice that for the 1,3-disiladiboretene ring inversion (**1a** vs **1b**). The B−B (1.654 Å), B−Si (1.940 Å), and Si−Si (2.196 Å) bonds in **2a** are comparable to the corresponding distances in the model species $H_2B{-}BH_2$ (D_{2d}, 1.629 Å), $H_2B{-}SiH_3$ (C_s, 2.017 Å), and $H_2Si{=}SiH_2$ (C_{2h}, 2.173 Å).[27] The WBIs for B−B, B−Si, and Si−Si in **2a** (1.132, 1.202, and 1.347, Figure 2) are greater than 1.0, reflecting the delocalized bonding of the puckered four-membered ring electronic structure. The NPA charges in **2a** (Si = 0.443; B = −0.300), however, are smaller than in **1a**. The 6.2 kcal/mol energy difference between **1a** and **2a** is attributed to the weak π-delocalization in **2a**. Structure **2c**, with short Si−Si and B−B bonds, is a transition state, 28.8 kcal/mol higher in energy than **1a**.

The tendency of silicon to favor divalent structures, e.g. in silicon hydrides and silaboranes,[11−15,17] prompted us to explore similar possibilities on the $Si_2B_2H_4$ PES. Although having short transannular Si−Si and B−B distances, structures **3a**−**3c** and **4a**−**4c** are not minima. The D_2 transition state, **3c**, collapses to the B−H−Si monobridged isomer, **5**, upon relaxation of symmetry constraints. Indeed, **5** is the second most stable $Si_2B_2H_4$ minimum. The B−H (1.280 Å) and H−Si (1.848 Å)

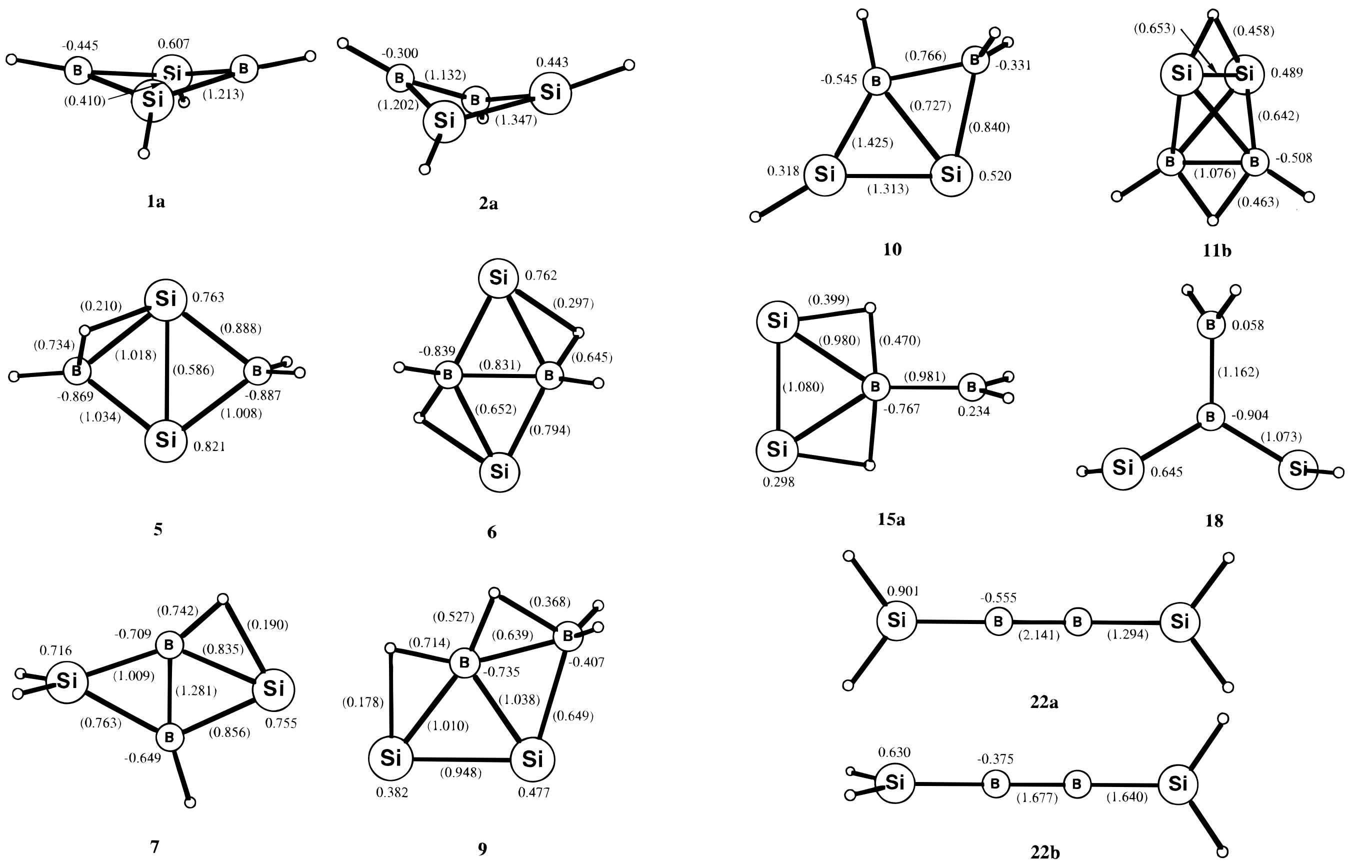


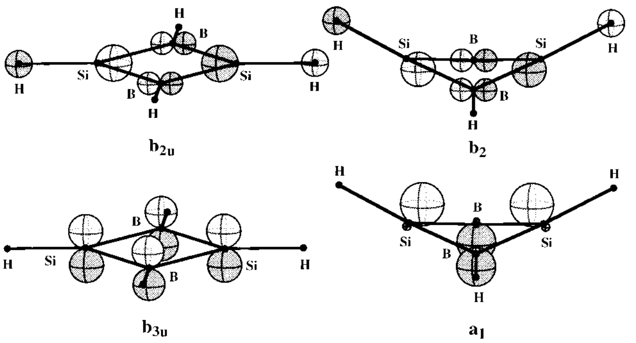
Figure 3. Natural population analysis charges and Wiberg bond indices (in parentheses) of $Si_2B_2H_4$ isomers at Becke3LYP/6-311+G** optimized geometries.

TABLE 2: Changes in Geometries, Energies, and Electronic Structures of 1,3-$C_2B_2H_4$, $C_4H_4^{2+}$, 1,3-$Si_2B_2H_4$, and $Si_4H_4^{2+}$ upon Puckering (at Becke3LYP/6-311+G)**

molecule	ΔE^a	$\Delta\Theta^b$	ΔD^c	$\Delta\sigma^d$	$\Delta\pi^e$	ΔWBI^f
1,3-$C_2B_2H_4$	−17.0	51.3	−0.369	−25.1	0.0	0.177
$C_4H_4^{2+}$	−8.7	43.7	−0.106	−15.7	0.6	0.037
1,3-$Si_2B_2H_4$	−1.2	24.2	−0.076	−5.0	3.8	0.016
$Si_4H_4^{2+}$	0.5	10.5	−0.005	0.6	3.8	−0.002

[a] $\Delta E = E_{\text{puckered}} - E_{\text{planar}}$ in kcal/mol. [b] $\Delta\Theta$ is the puckering angle in degrees (ref 25). [c] ΔD is the difference in the 1,3 transannular distance (puckered − planar) in Å. [d] $\Delta\sigma = [E(b_2) - E(b_{2u})]$ at B3LYP level in kcal/mol (refer to Scheme 1 for symmetry labels). [e] $\Delta\pi = [E(a_1) - E(b_{3u})]$ at B3LYP level in kcal/mol (refer to Scheme 1 for symmetry labels). [f] ΔWBI = 1,3-WBI$_{\text{puckered}}$ − 1,3-WBI$_{\text{planar}}$.

SCHEME 1



bridge bond lengths in **5** deviate significantly from the corresponding distances in B_2H_6 (1.316 Å) and in *cis*-HSi(μ-H)$_2$SiH (1.680 Å).[27] The B−H (0.733) and H−Si (0.201) WBIs quantify the B−H−Si bonding interaction (Figure 3). The B−H−Si bridge could be viewed either as a 2c−2e B−H bond hyperconjugating with the p orbital on silicon or, alternatively, as a 3c−2e bridge polarized toward B−H. Attempts to localize the MOs of **5** using the natural bond orbital (NBO) procedure[24a,b] result in poor descriptions, implying that the bonding is highly delocalized. Although the Si−Si distance in **5** (2.466 Å) is longer than in Si_2H_6 (2.355 Å),[27] the significant WBI (0.586) shows that **5** is bicyclic. Another bicyclic isomer, **6** (SiBBSi dihedral angle is 131.5°), is 10.9 kcal/mol higher in energy than **1a**. The strong B−B bonding in **6** is evident from the WBI of 0.831, with the B−B distance (1.735 Å) close to the calculated B−B bond length in B_2H_4 (1.744 Å, D_{2h}).[27] A σ lone pair orbital on each silicon and 3c−2e B−H−Si bonding describe part of the electronic structure of **6**. The extent of multicenter bonding is quantified by the WBI data (Figure 3).

The B−H−Si monobridged isomer **7** with planar tetracoordinate boron[28] is related via a B−H wagging motion to the nearly isoenergetic C_{2v} transition state **8a**.[7b] The all-planar alternative **8b** is a second-order saddle point. The molecular orbitals of **7** include a lone pair on Si and cyclic π-delocalization on the BSiB ring and fail to localize to a Lewis description in terms of NBOs due to the strongly delocalized electronic structure.

As is shown by the significant WBIs, isomer **9** possesses a covalently bound *planar pentacoordinate boron* with unsymmetrical and polarized B−H−Si and B−H−B bridges (Figure 3). The HOMO corresponds to an Si−B−Si π orbital. In addition, a σ lone pair orbital on each silicon and a 3c−2e BBSi bridge is included in the electronic structure description. No Lewis structure is appropriate. When both the bridging hydrogens in **9** become Si−H and B−H terminal bonds, as in **10**, the energy increases by 4.0 kcal/mol. This suggests that the B−H−Si and B−H−B bonds in **9** contribute to the stability of the molecule. The molecule orbitals of **10** feature a lone pair orbital on Si and SiBSi π-delocalization.

The symmetrically hydrogen bridged cyclic structure **11a** possesses two imaginary frequencies, while **11b**, with the Si−H−Si fragment perpendicular to HB−H−BH, is a minimum. Consequently, the B−B and Si−Si distances in **11b** are shortened, but the B−Si bonds are elongated relative to **11a**. The electronic structure of **11b** includes two lone pair MOs and triangulated multicenter bonding patterns. The transition structure **11c** corresponding to the rotation of the $-BH_2$ moiety is 2.2 kcal/mol above **11b**. Structure **12**, with a symmetrical $Si(\mu\text{-}H)_2Si$ bridge, is a higher order saddle point. In the transition structure **13**, only the bonding combination of the lone pair orbitals is occupied, while the antibonding combination is replaced by the Si−Si π orbital instead.

Interest in the B_2Si- and Si_2B- cyclic structures stem from the corresponding carboranes.[8] Krogh-Jesperson *et al.*[29] predicted that 2,3-diboramethylenecyclopropane (2,3-$C_2B_2H_4$) favors an anti-van't Hoff (perpendicular) over a planar stereochemistry (although neither was found to be a minimum).[8b] Likewise, **14a** and **14b** represent the anti-van't Hoff and van't Hoff stereochemistry among $Si_2B_2H_4$ structures. While **14a** is favored by 38.2 kcal/mol over **14b**, neither is a minimum (Table 1). However, **15a**, with an exocyclic $-BH_2$ substituent on the Si_2B ring and a planar pentacoordinate boron, is a minimum. This isomer can be related to the most stable isomer of B_3H_5[30] considering the isolobal analogy between $H-BH_2$ and $:SiH_2$.[13] The planar conformer, **15b**, is a higher order stationary point. In sharp contrast to the carboranes,[8,29] **15a** prefers bridged B−H−Si bonds over terminal Si−H bonds. The Si−H distance (1.615 Å) is shorter and the B−H (1.393 Å) longer compared to normal bridge bonds,[27] but the MO pattern accounts for the B−H−Si description supported further by the WBIs (Figure 3). The C_{2v} structures **16** and **17**, with symmetrical B−H−B and Si−H−Si bridges, are higher order stationary points and hence not discussed further. Thus, all the hydrogen-bridged isomers (Figure 3) exhibit three-center two-electron bonding involving boron and silicon. Such 3c−2e bonding involving three different elements is rare, since the necessary balance in the electronic structure is not often achievable.[31]

Of all the acyclic minima, **18**, with divalent silicons and similar to B_2H_4 (D_{2d}), has the lowest relative energy (38.2 kcal/mol, Table 1). The hyperconjugative interactions between the Si−B bonds and the boron p orbitals are reflected in the short B−B distance (1.615 Å compared to 1.744 Å in D_{2h} B_2H_4) and the WBI greater than 1.0 (Figure 3). Boryl-substituted disilavinylidene **19a** and **19b** are not minima. Similarly, **20**, analogous to a transition state for the interconversion of 1,2- to 1,3-diboretene on the $C_2B_2H_4$ PES,[8] is a higher order saddle point. The linear structures **21a** and **21b** also are not minima. The corresponding carboranes were predicted to be close in energy to 1,3-diboretene.[8] Substitution of the hydrogen by an $-SiH_2$ group in B_2H_2 leads to isomers **22a**,**b**. The B−B (1.473 Å) and B−Si (1.864 Å) bonds in planar **22a** are comparable to that in HB═BH (1.522 Å) and $H_2Si{=}BH$ (1.824 Å).[27] With orthogonal $-SiH_2$ groups, **22b** is favored by 25.6 kcal/mol over **22a**. The hydrogen-bridged quasi linear structures **23a** and **23b** are high-energy saddle points.

Conclusions

In contrast to the $C_2B_2H_4$ PES,[8,29] a much larger number of low-energy $Si_2B_2H_4$ minima (**1a**, **2a**, **5**−**7**, **9**, and **10** are within 12 kcal/mol) has been found. The most stable isomer is 1,3-disiladiboretene (**1a**); the puckered four-membered ring structure is similar to that of 1,3-diboretene.[5,8] However, the computed inversion barrier via the planar 2π aromatic transition state is only 1.2 kcal/mol for **1a**, much lower than the related carborane barrier (17.0 kcal/mol) at the B3LYP level. B−H−Si bridged isomers **5** and **7**, with divalent silicons, are close in energy to **1a**. Isomer **9**, with a planar pentacoordinate boron, is only 7.3 kcal/mol less stable than **1a**. Isostructural silaborane analogs, **2a**, **8a**,**b**, **14a**,**b**, **20**, **21a**,**b**, and **22a**,**b**, of the corresponding carboranes are high-energy structures and/or are characterized to be higher order stationary points.

The striking feature of the more stable isomers is their remarkable tendency to possess B−H−Si bridge bonds; C−H−B 3c−2e bonds do not exist among the corresponding carboranes ($C_2B_2H_4$). The PES of $Si_2B_2H_4$ further demonstrates that isomers with σ lone pairs on silicon and hydrogen bridging (**5**−**7**, **9**, **11b**, **15a**) are favorable. This contrasts with the preference for multiply bonded structures (cf. **13**, **21b**) exhibited by the analogous carboranes, $C_2B_2H_4$.[8] Both levels of theory (Becke3LYP/6-311+G** and MP2/6-31G*) employed here give similar results.

The synthesis of several $C_2B_2R_4$ compounds,[6,9] after their theoretical predictions,[5,29] suggests that experimental efforts toward preparing derivatives of $Si_2B_2H_4$ isomers or gas phase reactions involving silicon hydrides and boranes should be rewarding. Furthermore, examples of H-bridged carborane derivatives[9e] stimulate the search for derivatives of the low-energy H-bridged $Si_2B_2H_4$ isomers (for example **5**, **7**, and **9**), with only the terminal hydrogens replaced by bulky substituents.

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