Remarkable Structures of $C_2B_2H_4$ Isomers

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Abstract: A number of $C_2B_2H_4$ isomers were studied by ab initio MO methods. While many of these now have experimental analogies, no representatives of **13**, the global energy minimum, have been reported to date. Like **13**, a four-membered ring with the constitution $(CH_2)(BH)(CH)B$, most of the other relatively stable isomers show structural relationships to known carbocations. The most stable $(CH)_2(BH)_2$ constitution is the puckered 1,3-diboretene **1**; its 1,2-isomer **3** is predicted to isomerize to **1** with a low activation energy (ca. 8 kcal/mol). Neither the perpendicular ethylene **8** nor the "diboramethylenecyclopropane" **9** (members of the $CH_2C(BH)_2$ family) are local minima, and both rearrange without a barrier to the nonclassical four-membered ring **11**. The recently reported derivatives of **9** are suggested to be related to **11** instead, and the topomerization of these compounds is predicted to proceed via an intermediate, the 2π-carbene **10**. Of the remaining compounds, *C*-borylborirenes $(CH)(BH)CBH_2$ are more stable than their B-substituted isomers $(CH)_2BBH_2$, and perpendicular are preferred to planar conformations.

Small ring organoboron compounds represent one of the emerging fields of chemistry where theoretical calculations preceeded and helped to guide subsequent experimental investigations. Both interest in the lower members of the $(CH)_2(BH)_n$ ($n = 1$, 2) carborane series[2] and the formal relationship of boron compounds to carbocations[3] served as early stimuli. Thus, a theoretical study of the cyclobutadiene dication $(CH)_4^{2+}$ led to the surprising conclusion that this Hückel 2π aromatic system preferred a nonplanar over a planar geometry.[4] The isoelectronic 1,3-diboretene, $(CH)_2(BH)_2$, was also predicted to prefer a nonplanar geometry;[2,5] this has recently been verified experimentally for a derivative.[6] The cyclopropenium ion, $(CH)_3^+$, has the largest resonance energy of any monocyclic Hückel system; borirene $(CH)_2(BH)$, the neutral analogue, is indicated to be nearly as favorable in this respect.[2] Experimental searches for such molecules have now achieved success in several laboratories.[7-10]

An even earlier theoretical study predicted that the presence of two boron atoms in a three-membered ring might have remarkable geometrical consequences.[11] The substituents attached to the ring carbon should prefer "anti-van't Hoff" arrangements, i.e., planar tetracoordinate carbon, perpendicular ethylene retaining the double bond, etc. Again, the geometries preferred by the carbocations were similar.[4] Attempts to prepare such organoboron compounds have not succeeded; moreover, experimental[12] and theoretical[13,14] results indicate that the anti-van't Hoff structures are less favorable than even more exotic structures. Indeed, the last two years have seen a rapid development in the field of small-ring boron–carbon compounds, and several groups have succeeded in preparing four-membered rings with one[12,15] and two[6,7,16,17] boron atoms. Computational examinations have kept pace,[5,13,14,18,19] and the fruitful dialogue between theory and experiment in this area continues.

The present contribution reports a comprehensive study of $C_2B_2H_4$ isomers. These are intended to model experimental systems, where other substituents usually replace the hydrogens. The compounds we have examined are best categorized constitutionally by the hydrogen locations. There are six classes: $(CH)_2(BH)_2$ (**1–6**; this extends our earlier study[2]), $CH_2C(BH)_2$ (**7–12**; the "anti-van't Hoff" **7**[11] and its isomers), $CH_2(CH)(BH)B$ (**13–15**), *C*-borylborirenes $(CH)(BH)CBH_2$ (**16** and **17**), *B*-borylborirenes $(CH)_2BBH_2$ (**18** and **19**), and diborylacetylenes $C_2(BH_2)_2$ (**20** and **21**). These species include transition structures for the interconversion of isomers within each class. This should help the understanding of experimental results. As the substituents used experimentally generally remain fixed to a given boron or carbon atom, we have not considered processes involving hydrogen migration.

Methods

Ab initio molecular-orbital calculations were carried out on **1–21** with the GAUSSIAN 76[20a] and 82[20b] series of programs. The geometries of **1–3**, **5**, **7–11**, and **13–21** were optimized completely, subject only to overall molecular symmetry restrictions, with restricted Hartree–Fock (RHF) single-determinant theory[21] and the small split-valence 3-21G basis set.[22a] The transition structure **4** was optimized similarly, and the triplet **6** was optimized with the unrestricted Hartree–Fock (UHF) formalism of Pople and Nesbet.[23] Energy refinements were then obtained from single-point

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Table I. 3-21G (6-31G*) Optimized Geometries for **1–21**

	1	2	5	6		1	2	5	6
C–C	1.883 (1.787)	2.183	1.311	1.456	α[a]	47.6 (50.8)		126.4	104.3
B–C	1.521 (1.500)	1.543	1.818	1.618	τ_1[c]	5.1 (5.8)		48.9	21.7
B–B	2.187 (2.178)	2.183	1.529	1.722	τ_2[c]	11.5 (11.9)[d]		–26.9	–14.4
C–H	1.072 (1.077)	1.075	1.065	1.062	∠HCC	141.4 (138.1)		138.0	137.0
B–H	1.174 (1.180)	1.184	1.170	1.168	∠HBB	161.3 (160.4)		165.7	149.5

	3	4		3	4
C–C	1.370 (1.364)	1.597 (1.549)	∠HCC	126.9 (126.6)	129.7 (129.6)
C–B	1.571 (1.559)	1.405, 1.859 (1.392, 1.784)	∠HBB	144.4 (145.0)	135.2 (135.4)
B–B	1.725 (1.715)	2.012 (1.904)	∠HCCH		53.2 (55.3)
C–H	1.075 (1.081)	1.063 (1.071)	∠BCCB		81.7 (80.1)
B–H	1.185 (1.189)	1.167 (1.175)	∠HBBH		44.4 (39.4)

	7	8	9[j]	10	11	12[k]
C1–C2	1.331	1.309 (1.314)	1.558	1.820 (1.738)	1.468 (1.454)	(1.623)
C1–B1			1.539	1.716 (1.688)	1.590 (1.581)	(1.534)
C2–B1	1.529	1.562 (1.546)	1.506	1.420 (1.399)	1.564 (1.527)	(1.461)
C2–B2			1.356		1.348 (1.339)	(1.353)
B1–B2	1.684	1.516 (1.505)			1.884 (1.825)	
C1–H	1.077	1.078 (1.079)	1.079	1.078 (1.082)	1.077 (1.080)	(1.079)
B1–H	1.177	1.171 (1.177)	1.173	1.167 (1.172)	1.170 (1.175)	(1.178)
B2–H			1.166		1.162 (1.168)	(1.168)
∠HC1H	115.7	116.2 (116.1)	113.1	114.6 (113.6)	113.3 (113.1)	(113.3)
∠C2C1b[e]			142.3		147.2 (147.0)	(143.8)
∠C2B1H	143.6	125.1 (124.5)	146.7	153.1 (155.5)	160.1 (160.6)	(146.2)
∠C2B2H			177.4[f]		172.6 (172.3)[f]	(177.1)[g]
∠B1C2B2	66.8	58.1 (58.3)	146.4	125.1 (128.0)	80.3 (78.8)	(177.1)[g]

13		14		15		13		14		15	
C1–B1	1.744	C1–C2	1.647	C1–C2	1.640	C2–H	1.059	C2–H	1.069	C2–H	1.061
C1–B2	1.494	C1–B2	1.498	C1–B1	1.655	B1–H	1.174	B1–H	1.168	B1–H	1.173
C1–B1	1.517	C2–B1	1.490	C2–B1	2.437	∠HC1H	112.5	∠HC1H	113.5	∠HC1H	111.2
C2–B2	1.400	C2–B2	1.631	C2–B2	1.377	∠C1B1H	124.2	∠C1C2H	116.1	∠C1C2H	125.8
B1–B2	1.744	B1–B2	1.559	B1–B2	1.609	∠B1C2H	137.4	∠C2B1H	137.5	∠C1B1H	133.3
C1–H	1.078	C1–H	1.076	C1–H	1.082	∠B1C1b[e]	138.6	∠C2C1b[e]	136.9	∠C2C1b[e]	130.7

	16	17		18	19
C1–C2	1.356	1.361	C1–C2	1.350	1.333
C1–B1	1.492	1.522	C1–B1	1.490	1.500
C2–B1	1.492	1.452	B1–B2	1.697	1.651
C1–B2	1.559	1.509	C1–H	1.066	1.065
B1–H	1.172	1.170	B2–H	1.192	1.192
C2–H	1.066	1.064	∠C1C2H	139.1	140.9
B2–H	1.191[i], 1.187	1.188	∠HBH	116.5	116.7
∠C2C1B2	139.8	151.1			
∠C1B1H	153.6	148.9			
∠C1C2H	138.7	136.2			
∠C1B2b[e]	179.7[i]	177.2[h]			
∠HBH	119.0	119.5			

	20	21		20	21
C–C	1.203	1.214	B–H	1.185	1.185
C–B	1.529	1.499	∠HBH	119.5	120.2

[a] Distances in Å, angles in deg. [b] In most of the geometries redundant parameters are included to facilitate interpretation. [c] See Figure 1 for definition. [d] In the earlier paper,[2] the H(B) atoms in **1** were erroneously depicted as being tilted toward axial positions. They are, in fact, tilted toward equatorial positions, but the magnitudes of τ_2 given in ref 2 are correct. [e] *b* denotes the bisector of the HCH or HBH angle. [f] Trans to C1. [g] Cis to C1. [h] Trans to C2. [i] Cis to C2. [j] This structure does not correspond to a local minimum at the HF/6-31G* level. [k] Only exists (as a T.S.), at the least HF/6-31G* level.

calculations with extended basis sets (6-31G[22b] and 6-31G*[22c]) and inclusion of electron correlation corrections by Møller–Plesset second- and third- order perturbation theory[24] (with the 6-31G* and 6-31G basis sets, respectively). The final optimized geometries are summarized in Table I; total and relative energies are collected in Table II. The potential surface connecting the isomers **7–11** is rather flat at the 3-21G level and was found to be very sensitive to basis set extension effects. Therefore, **8**, **10**, **11**, and the transition state **12** were optimized at the 6-31G* level (**9** is no longer a minimum at this level of theory). **1**, **3**, and **4** were also reoptimized at HF/6-31G*. The 6-31G* geometrical data have been included in Table I; energies are given in Table III. Substituent effects in **8** and **10–12** were evaluated at the HF/6-31G level by freezing the molecular skeleton at its 6-31G* geometry and assuming standard geometries[25] for the CH_3 and SiH_3 substituents.

The wave functions were subjected to the usual Mulliken population analysis; values for charges and overlap populations quoted in the text represent 3-21G values.

Results

$(CH)_2(BH)_2$ Structures, 1–6. The structures of **1–3** have already been discussed in a previous paper,[2] although the calculations reported here are of a better quality. The nonplanar C_{2v} 1,3-diboretene **1** is the most stable structure within this group. The compound can be considered as the smallest possible nido-carborane; also, it is formally a 2π-aromatic system. Since the earlier study, three groups have reported the preparation of 1,3-diboretenes.[6,7,16] The compounds indeed show a considerable stability, in accord with their aromatic nature. Siebert has de-

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Table II. Total Energies at 3-21G Geometries[a]

	HF/3-21G	HF/6-31G	HF/6-31G*	MP2/6-31G	MP3/6-31G	MP2/6-31G*	MP3/6-31G*[a] (est)
1	−126.64963	−127.31158	−127.36623	−127.58768	−127.60946	−127.76730	−127.78908
2	−126.62994	−127.29250	−127.34138	−127.56330	−127.58699	−127.73587	−127.75956
3	−126.63364	−127.30089	−127.35139	−127.56338	−127.58877	−127.73729	−127.76268
4	−126.58989	−127.25056	−127.31310	−127.54071	−127.56173	−127.72818	−127.74920
5	−126.56960	−127.22921	−127.29199	−127.51804	−127.53907	−127.70482	−127.72585
6	−126.53006	−127.19327	−127.26449	−127.46453	−127.48925	−127.66429	−127.68901
7	−126.58224	−127.24789	−127.29461	−127.51220	−127.53736	−127.68308	−127.70824
8	−126.58604	−127.25031	−127.30116	−127.53934	−127.56128	−127.71452	−127.73646
9	−126.60445	−127.26605	−127.31259	−127.54244	−127.56316	−127.71446	−127.73518
10	−126.60641	−127.26699	−127.32334	−127.55015	−127.57075	−127.72907	−127.74967
11	−126.60565	−127.27213	−127.33988	−127.56535	−127.58412	−127.75529	−127.77406
13	−126.64502	−127.30762	−127.36360	−127.59562	−127.61639	−127.77635	−127.79712
14	−126.59298	−127.25671	−127.31663	−127.55284	−127.57313	−127.73649	−127.75678
15	−126.57213	−127.23435	−127.28496	−127.52088	−127.54421	−127.69405	−127.71738
16	−126.63081	−127.29610	−127.35470	−127.56031	−127.58319	−127.74030	−127.76318
17	−126.64419	−127.30927	−127.36770	−127.57674	−127.59924	−127.75755	−127.78005
18	−126.61786	−127.28194	−127.33880	−127.54580	−127.56999	−127.72375	−127.74794
19	−126.62953	−127.29328	−127.34919	−127.56064	−127.58449	−127.73775	−127.76160
20	−126.64549	−127.30873	−127.35535	−127.57943	−127.59536	−127.73895	−127.75488
21	−126.65780	−127.32117	−127.36604	−127.58789	−127.60544	−127.74796	−127.76551
			Relative Energies (kcal/mol)				
1	−2.9	−2.5	−1.6	5.0	4.3	5.7	5.0
2	9.5	9.5	13.9	20.3	18.4	25.4	23.6
3	7.1	4.2	7.7	20.2	17.3	24.5	21.6
4	34.6	35.8	31.7	34.4	34.3	30.2	30.0
5	47.3	49.2	44.9	48.6	48.5	44.8	44.7
6	72.1	71.7	62.1	82.2	79.7	70.3	67.8
7	39.4	37.5	43.3	52.3	49.6	52.2	55.7
8	37.0	35.9	39.1	35.3	34.6	38.8	38.0
9	25.4	26.1	32.0	33.3	33.4	38.8	38.8
10	24.2	25.5	25.2	28.5	28.6	29.6	29.8
11	24.7	22.3	14.9	19.0	20.2	13.2	14.5
13	0	0	0	0	0	0	0
14	32.6	31.9	29.5	26.8	27.1	25.0	25.3
15	45.7	45.9	49.3	46.9	45.3	51.6	50.0
16	8.9	7.2	5.6	22.1	20.8	22.6	21.3
17	0.5	−1.0	−2.6	11.8	10.8	11.8	10.7
18	17.0	16.1	15.5	31.2	29.1	33.0	30.8
19	9.7	9.0	9.0	21.9	20.0	24.2	22.3
20	−0.3	−0.7	5.2	10.2	13.2	23.4	26.5
21	−8.0	−8.5	−1.5	4.8	6.9	17.8	19.8

[a] MP3/6-31G* (est) = MP2/6-31G* + (MP3/6-31G − MP2/6-31G).

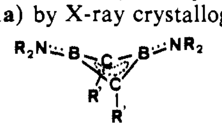
Table III. Total and Relative Energies (kcal/mol) at 6-31G* Geometries[a]

	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	HF/6-31G*	MP2/6-31G*	MP3/6-31G*
1	−127.36813	−127.76946	−127.79522	0	0	0
3	−127.35171	−127.73768	−127.76826	10.3	19.9	16.9
4	−127.31697	−127.73163	−127.75496	32.1	23.7	25.2
8	−127.30157	−127.71513	−127.74082	24.8	26.3	24.4
10	−127.32543	−127.73212	−127.75689	9.8	15.6	14.3
11	−127.34109	−127.75704	−127.77974	0	0	0
12	−127.31048	−127.71404	−127.73797	19.2	27.0	26.2

	HF/6-31G[b]		
	$CH_2C(BH)_2$	$CH_2C(BCH_3)_2$	$C(SiH_3)_2C(BH)_2$
8	−127.25009	−205.31958	−707.31388
10	−127.26587	−205.34725	−707.32340
11	−127.27124	−205.34377	−707.33101
12	−127.26117	−205.34541	−707.32673

[a] Energies of **1–4** relative to **1**; those of **8–12** relative to **11**. [b] The molecular skeleton was frozen at its 6-31G* geometry, and standard bond lengths and angles were assumed for the XH_3 substituents.

termined the structure of 1,3-bis(dimethylamino)-2,4-di-*tert*-butyl-1,3-diboretene (**1a**) by X-ray crystallography.[6]



1a, R = CH_3; R' = *t*-Bu
1b, R = R' = H

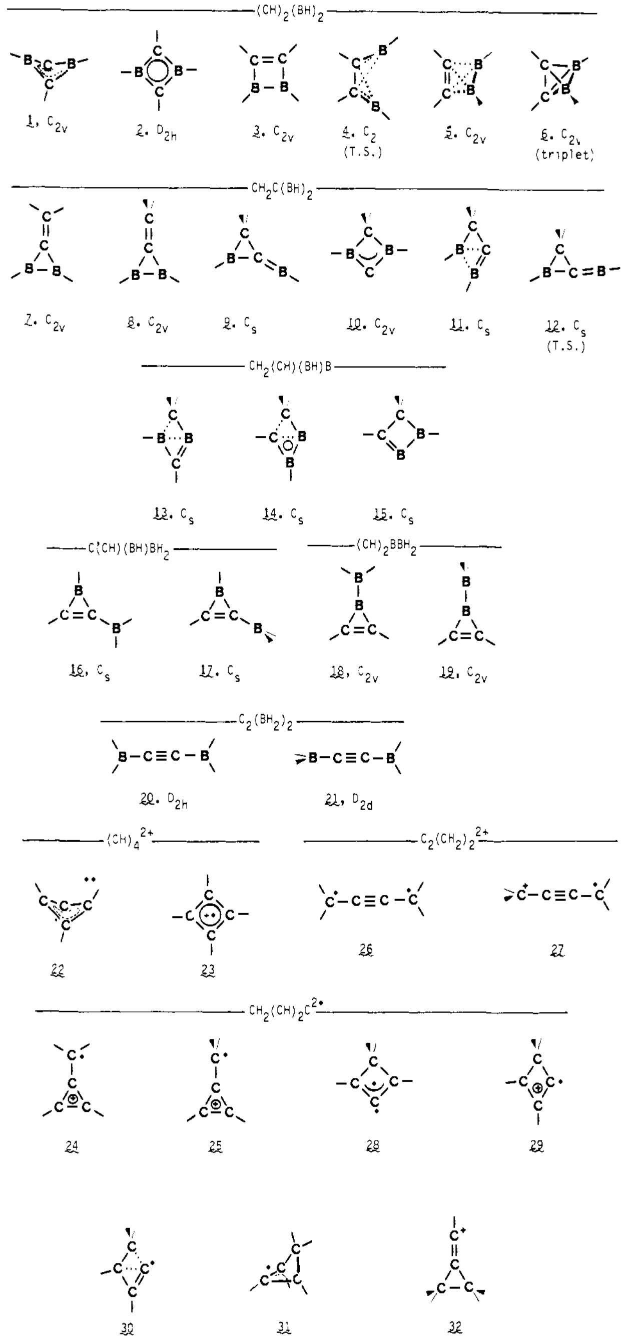
Even though the presence of amino groups might be expected to have a significant electronic influence, the agreement between the observed structural parameters for **1a** and those predicted for the parent **1** is surprisingly good. To study the effect of amino substituents in more detail, we also optimized the structure of 1,3-diamino-1,3-diboretene (**1b**) at the 3-21G level;[5] the results of the various calculations are compared with the experimental structure in Table IV. Inspection of the table confirms that the amino substituents hardly affect the geometry of the C_2B_2 skeleton, except for a shortening of the C–C distance. The situation is similar to that found in aminoborirene, in which we have also found that the amino group causes only a modest decrease in resonance energy and small changes in geometry.[19] In view of the bulky

Table IV. Comparison of Calculated and Experimental Geometries of 1,3-Diboretenes[a]

compd	method	C–C	C–B	B–N	∠RCC	α	τ_1	τ_2
1	STO-3G	1.754	1.477		140.6	54.9	6.2	7.4
	4-31G part. opt.	1.858	1.510		141.0	48.2	5.2	11.4
	3-21G	1.883	1.521		141.4	47.6	5.1	11.5
	6-31G*	1.787	1.500		138.1	50.8	5.8	11.9
1a	X-ray, av	1.814	1.504	1.410	133.9	52	2-3	12
1b	3-21G	1.794	1.528	1.403	139.4	48.4	6.4	16.7
2	STO-3G	2.116	1.499					
	4-31G part. opt.	2.168	1.536					
	3-21G	2.183	1.543					
2b	3-21G	2.174	1.546	1.421				

[a] Distances in Å, angles in deg. For definition of the angles α, τ_1, and τ_2, see Figure 1.

Chart I



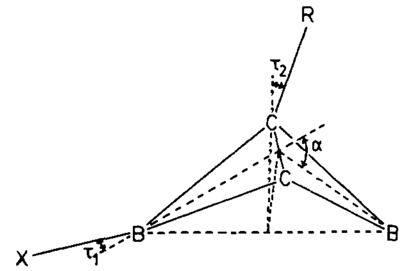


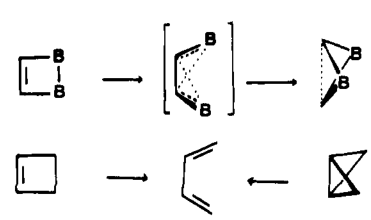
Figure 1. Definition of the geometrical parameters for **1**, **5**, and **6**.

substituents present in **1a**, better agreement between the experimental structure of **1a** and that calculated for **1b** could hardly be expected.

The planar D_{2h} form **2** of 1,3-diboretene is the transition state for the ring inversion of **1**.[2] Our best estimate for the inversion barrier (18.5 kcal/mol) is close to the older value. As expected, amino substituents increase this barrier, but the effect is modest (5.0 kcal/mol at HF/6-31G*//3-21G[5]).

The 1,2-diboretene **3** is considerably higher in energy than its 1,3-isomer, which we have attributed to the uneven σ-electron distribution and poor π-electron delocalization in **3**.[2] The long B–B bond and low boron π-electron density lead one to expect a high reactivity for this molecule. The conversion of **3** to **1** by rotation around the twofold axis of the BB and CC units with respect to each other is allowed in C_2 symmetry. We have located the transition state (**4**) for this reaction and found it to be only 8.4 kcal/mol above **3**. This suggests that 1,2-diboretenes will rearrange spontaneously to the more stable 1,3-isomers and thus are not likely to be observed experimentally.

It is interesting to compare the course of this isomerization reaction with that of the all-carbon analogue, cyclobutene ⇌ butadiene ⇌ bicyclobutane.



The transition structure **4** resembles a nonplanar form of 1,4-dibora-1,3-butadiene, and the first part of the reaction, **3** → **4**, is fully analogous to the conrotatory ring opening of cyclobutene to butadiene.[26] However, the boron atoms in **4** have empty acceptor orbitals which are oriented in the right way to interact with the adjacent π-bond (Figure 2), and even in this transition state there already exists a substantial 1,3 B–C bonding interaction. The carbon atoms in butadiene are coordinatively saturated and have no similar acceptor orbitals. This rationalizes why butadiene is a local minimum rather than a transition state and also why its formation from bicyclobutane has a rather high activation energy and proceeds via a biradicaloid intermediate.[27]

The last $(CH)_2(BH)_2$ singlet examined is **5**, which can best be regarded as a moderately strong complex between acetylene and

(26) For a recent ab initio study, see: Breulet, J.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1984**, *106*, 1221.
(27) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1975**, *97*, 2931.

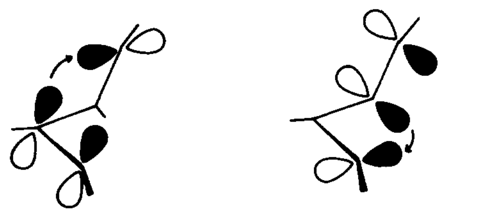


Figure 2. Interactions between B acceptor orbitals and adjacent B–C π-bonds in **4**.

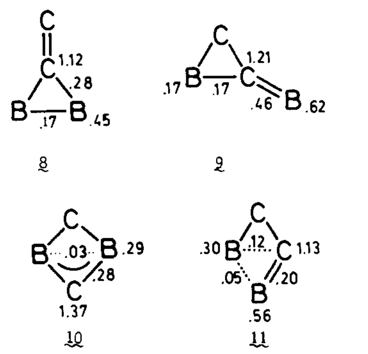


Figure 3. 3-21G π-electron densities and overlap populations in **8–11**.

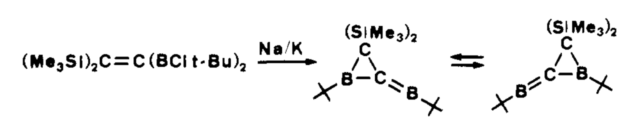
B_2H_2. The direct conversion of **5** to **1** is forbidden in C_{2v} symmetry. However, **5** is not a local minimum but is a transition state, unstable with respect to a deformation to C_2 symmetry. The rotation of the BB and CC units with respect to each other would eventually produce **3**, but it is more likely that **5** transforms to **4** and eventually into **1** without passing through **3**.

A closed-shell singlet diboratetrahedrane would be expected to undergo a pseudo-Jahn–Teller distortion.[2] The 1,3-diboretene **1** and the acetylene–B_2H_2 complex **5** both have C_{2v} symmetry and represent the two possible choices for occupation of the originally degenerate tetrahedrane orbitals. A triplet diboratetrahedrane would not be expected to undergo such a distortion, and indeed triplet **6** remains closed. Moreover, the structure of **6** is in many respects intermediate between those of **1** and **5** (see Table I). However, **6** is so much higher in energy than the closed-shell species **1** (ca. 60 kcal/mol) and **5** (ca. 20 kcal/mol) that it does not appear to be a likely candidate for experimental observation.

$(CH_2)C(BH)_2$ Structures, 7–12. The BBC ring compounds **7** and **8** have been discussed in an earlier paper; it was concluded that the carbon atom in diboriranes prefers an "anti-van't Hoff" stereochemistry.[11]

Although higher in energy than **8**, the planar ethylene **7** is a local minimum at the RHF/3-21G level. However, the barrier for conversion to **8** in C_2 symmetry is very small (ca. 4 kcal/mol) and is expected to disappear entirely at higher levels of theory.[11] Our best estimate for the energy difference between **7** and **8**, 17.6 kcal/mol, is close to the older value. The perpendicular ethylene **8**, however, is a transition structure at HF/3-21G; optimization in C_s symmetry leads to the unusual geometry **11** which will be discussed below.

Berndt has recently prepared compounds for which structures related to **9**, a "diboramethylenecyclopropane", were proposed.[12] These compounds were found to undergo a rapid topomerization reaction at room temperature, resulting in exchange of the boron atoms:



In view of our theoretical results, it seems more likely that these compounds are derivatives of **11**.[13,14] The structure **9** represents a local minimum at the RHF/3-21G level but not with larger basis sets (vide infra). The bonding in this molecule is adequately represented by its Lewis structure, i.e., a normal cyclopropane-like BCC ring and σ- and π-bonds to the exocyclic boron atom. The B–C bond is polarized in the sense $C^{\delta-}B^{\delta+}$, and some delocalization to the endocyclic boron atom is observed (Figure 3), but the structure clearly contains a localized BC double bond.

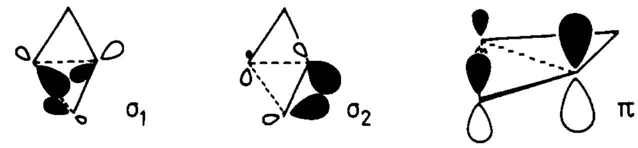


Figure 4. Schematic representation of the orbitals responsible for the bonding in the B(1)C(2)B(2) ring of **11**.

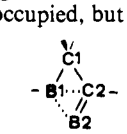
Table V. Substituents Effects in **8–12**[a]

compd	E_{rel}- $[CH_2C(BH)_2]$[b]	substituent effects[c] CH$_3$ at B	SiH$_3$ at C	E_{rel}- $[C(SiH_3)_2C(BCH_3)_2]$[d]
8	24.4	1.9	−2.5	23.8
10	14.3	−5.6	1.4	10.2
11	0	0	0	0
12	26.2	−7.3	−3.6	15.3

[a] Energies in kcal/mol, relative to **11**. [b] MP3/6-31G*//6-31G*, see Table III. [c] Single point HF/6-31G, see Table III. [d] Values estimated by assuming additivity of substituent effects.

The compound **10** is a π-carbene, which is stabilized very effectively by the boron atoms acting as σ-donors and π-acceptors to the carbene carbon. Boron–carbon π-bonding is evident from the short B–C bond lengths and from the π-orbital populations (Figure 3).

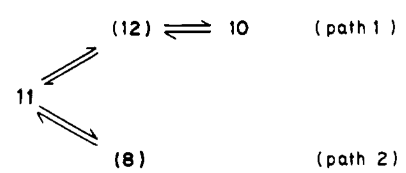
The species **11** is undoubtedly the most curious[13] in this class. It has normal B(1)C(1) and C(1)C(2) σ-bonds and a three-center C(2)B(2)C(1) π-bond (Figures 3 and 4). The C(2)B(2)-bonding Walsh-type orbital σ_2 is occupied, but its C(2)B(2)-antibonding



counterpart is empty (Figure 4). This results in weak B(1)C(2) and B(1)B(2) bonds and a strong B(2)C(2) double bond. This species has also been described by Frenking and Schaefer.[14]

At the 3-21G level, the potential energy surface connecting the isomers **8–11** is rather flat. Moreover, the data in Table II clearly show the large influence of polarization functions on the relative energies. Therefore, we decided to reoptimize the structures at the RHF/6-31G* level; the data obtained in this way are given in Tables I and III. Surprisingly, **9** no longer represents a local minimum but optimizes to **11** at this level of theory. The carbene **10** remains a local minimum; a structure **12** somewhat resembling **9** is now the transition state for the reaction **10** → **11**. Since **11** is by far the most stable of the $CH_2C(BH)_2$ isomers, we suggest that Berndt's "diboramethylenecyclopropane" is really a derivative of **11**.

We now turn to the mechanisms of the topomerization reaction mentioned above. There are two possibilities involving only the planar species **8–12**:



We have also searched for possible nonplanar intermediates but have not found any likely candidates. Thus, the barrier for the topomerization of **11** is either 26.2 (path 1) or 24.4 kcal/mol (path 2). Before comparing this with the experimental number of 11.4 kcal/mol for Berndt's compound, however, we have to take into account the electronic and steric effects of the substituents. The electronic effects were estimated at the 6-31G level by modeling $SiMe_3$ and t-Bu by SiH_3 and CH_3 groups, respectively.

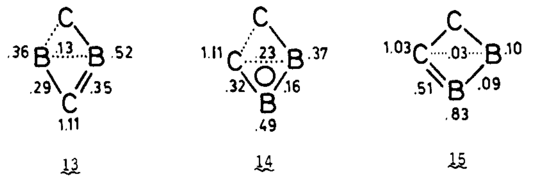
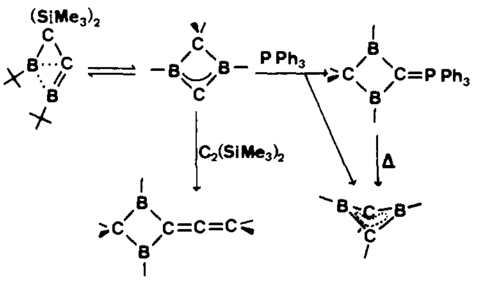


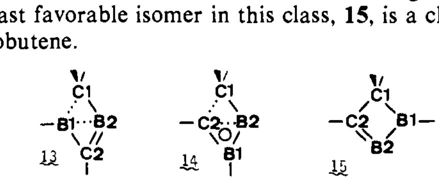
Figure 5. 3-21G π-electron densities and overlap populations in **13**–**15**.

The calculated substituent effects (Table V) result in a stabilization of **10** and **12** with respect to **8** and **11**, thus lowering the energy of path 1 but leaving that of path 2 virtually unchanged. For SiH_3 substituents at C and CH_3 substituents at B, path 2 can be ruled out. It is ca. 10 kcal/mol higher than path 1 for which our best estimate for the activation energy is 15.3 kcal/mol. Steric effects will be important for **11**, where the bulky *t*-Bu substituents on boron are forced closely together. This will destabilize **11** by an additional few kcal/mol relative to our methyl-substituted model and reduce the topomerization barrier further. It can be concluded that path 1 can account for the observed topomerization barrier of 11.4 kcal/mol. The intermediacy of **10** in the proposed mechanism can also explain some of the observed reactions of **11**,[12,17,28] e.g.

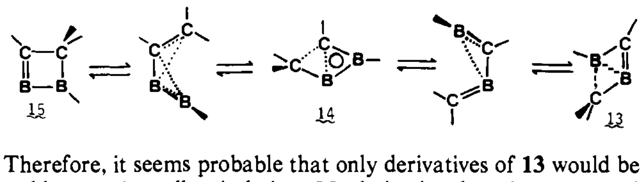


$CH_2(CH)(BH)B$ Structures, 13–15. The $CH_2(CH)(BH)B$ class of compounds contains the global minimum **13**. The bonding in **13** is in some respects similar to that in **11**. However, **11** contains a highly unsaturated carbene carbon atom (C(2)), so that **13**, in which boron assumes this role, is more favorable. This latter species has weak C(1)B(1) and B(1)B(2) bonds and a strong B(2)C(2) bond which is, however, appreciably longer than the C=B bond in **11**. The alternative structure **14** has a planar tetracoordinate carbon atom (C(2)) and is less favorable than **13**. The bonding in **14** closely resembles that in **13**, but the π-delocalization is extensive; the double bond is no longer localized.

The least favorable isomer in this class, **15**, is a classical diboracyclobutene.



One could envisage facile isomerization reactions among **13**–**15**, analogous to the isomerization of **3** to **1**:



Therefore, it seems probable that only derivatives of **13** would be stable enough to allow isolation. No derivatives have been reported to date, however, so we did not pursue these interconversions further.

(CH)(BH)CBH$_2$ (16, 17) and (CH)$_2$BBH$_2$ (18, 19) Structures. *C*-Borylborirenes (**16** and **17**) are found to be more stable than their B-substituted isomers (**18** and **19**). Perpendicular structures (**17** and **19**) are preferred over planar structures because of the favorable borirene → B hyperconjugation in the former conformers.[19] In view of the high reactivity of B–B compounds and of borirenes, *B*-borylborirenes do not seem to be attractive goals for synthesis. *C*-Borylborirenes are expected to be less reactive, and indeed Berndt has recently prepared two such compounds.[8]

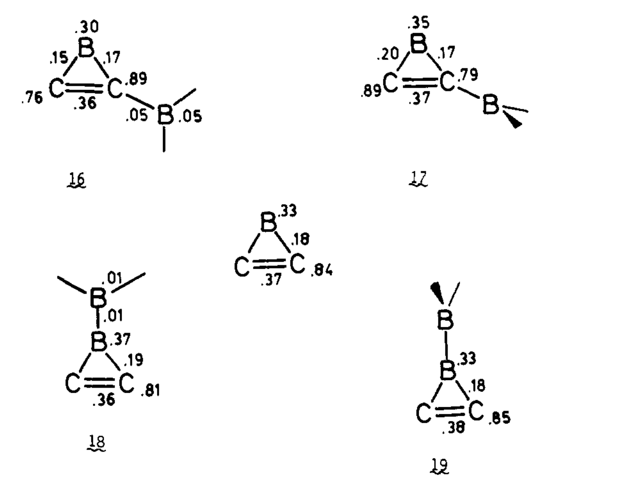


Figure 6. 3-21G π-electron densities and overlap population in **16**–**19** and borirene.[19]

It is interesting to consider the effect of the boryl group on the 2π-aromatic borirene system: π charges and overlap populations are shown in Figure 6, together with those for the parent borirene.[19] In the planar structures, the boryl group acts as a π-acceptor and draws π-density from the opposite ring atoms to the adjacent atom, although the amount of charge actually delocalized to the exocyclic boron atom remains small. In the perpendicular conformers, hyperconjugation of the BH_2 group causes the opposite effect, i.e., a shift of π-density away from the adjacent atom to the opposite atoms. Because of the uneven π-electron distribution in the parent borirene,[2] introduction of a perpendicular BH_2 group at carbon (**17**) results in an increase in delocalization, whereas in *B*-borylborirene (**19**) the delocalization is decreased. These effects are also reflected in the variation of the B–C and C–C bond lengths (Table I).

$C_2(BH_2)_2$ Structures, 20 and 21. At the 3-21G level, diborylacetylene **21** is calculated to be the lowest energy $C_2B_2H_4$ isomer. Inclusion of polarization functions and correlation corrections improves the description of small rings and nonclassical structures, to the effect that at the highest level of theory employed here the energy of **21** is well above that of the global minimum **13**.

The small structural changes between **20** and **21** may be readily rationalized on the basis of the more extensive π-delocalization present in **21**. Each of the two π-components of the acetylene triple bond delocalizes to an adjacent BH_2 group in **21** whereas only one π-component delocalizes to both BH_2 groups in **20**. Thus, the calculated C–C bond is longer in **21** (1.214 Å) than in **20** (1.203 Å), whereas the C–B bond is shorter (1.499 vs. 1.529 Å).

Alkynylboron compounds are notably scarce, and the compounds reported show a high susceptibility to nucleophilic attack at boron unless π-donating groups (OR, NR_2) are present,[29] demonstrating the high reactivity of alkynylboranes compared to alkenylboranes and alkylboranes. This can be ascribed to the fact that the alkynyl group is both a stronger σ-acceptor and a weaker π-donor than an alkenyl group.[29] Thus, the boron atom in alkynylboranes is more electron deficient and reactive than that in alkenyl- and alkylboranes.

The Relationship between Carbocations and Boron Compounds. $C_2B_2H_4$ isomers are isoelectronic with the carbodications, $C_4H_4^{2+}$.[4] Thus, structural analogies between the two groups of molecules would be expected. The $C_4H_4^{2+}$ structures corresponding to **1**–**21** are **22**–**29**; we will first consider some individual structures in detail.

(28) Klusik, H. Ph.D. Thesis, Marburg, 1983.

(29) Wrackmeyer, B.; Nöth, H. *Chem. Ber.* **1977**, *110*, 1086 and references cited therein.

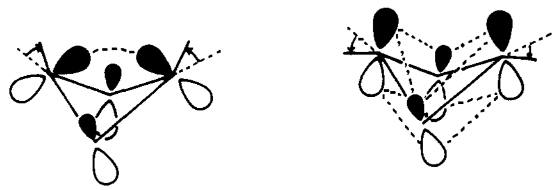


Figure 7. Tilting of hydrogens toward apical positions in $C_4H_4^{2+}$ produces increased 1,3 σ-overlap (a), whereas the tilting of H(B) toward equatorial positions in $C_2B_2H_4$ gives increased 1,2 π-overlap (b).

Cyclobutadiene Dication Analogues. 1,3-Diboretene **1** is the formal analogue of the puckered cyclobutadiene dication **22**. There are, however, characteristic differences between the structures of **1** and **22**. The puckering in both species is caused mainly by the large 1,3-repulsive interactions in the planar structures, **2** and **23**. Ring puckering not only relieves a large part of this ring strain but also gives the π-bonding HOMO a partially 1,3-σ-bonding character; this is reinforced by pyramidalization of the ring atoms (Figure 7). In **22**, where the π-density is evenly distributed, all hydrogen atoms move toward apical positions, and the ring puckering shortens both 1,3 C–C distances.[4] In **1**, however, the π-distribution is more uneven, and although the C–C distance is shortened on puckering, the B–B distance remains virtually unchanged. Also, the H(B) atoms move toward *equatorial* positions, which can be interpreted as an attempt to retain as much B–C π-bonding as possible, at the expense of possible weaker B–B σ-bonding (Figure 7; see also Table I, footnote *d*). The higher inversion barrier of **1** (18.5 kcal/mol) compared to **22** (7.5 kcal/mol) also reflects the less extensive delocalization in the boron compound.

Methylenecyclopropene Dication Analogues. The species **7**, **8**, and **16–19** are all related to the carbocations **24** and **25**. There are, however, large structural differences between the boron compounds and their carbocation model systems, which reflect the difference in acceptor strength between B and C^+. The cyclopropenium ring in **24** is a poor π-donor, and the exocyclic CC bond in this species is essentially a single bond.[4] Replacing two of the ring carbon atoms by boron (giving **7**) increases the donor strength of the ring to such an extent that most of the π-density is moved to the C–C bond, producing a C–C double bond with a small delocalization to the ring boron atoms.[11] A similar effect is seen in the perpendicular isomer **25**. Here, the hyperconjugation between the three-membered-ring σ-system and the empty methylene π-orbital already produces a considerable stabilization.[4] Replacing two ring carbon atoms by boron to give **8** so strongly increases this hyperconjugation that we are left with a C–C double bond and only 4 electrons in the σ-framework of the three-membered ring.[11] The structural changes observed in **16–19** are less extreme, but the difference in acceptor character of B and C^+ produces a characteristic localization of the π-system in each of these $C_2B_2H_4$ species. Also, the rotation barriers are smaller than those in the carbocation systems (**17**; 10.6 kcal/mol; **19**, 9.5 kcal/mol; **25**, 13.1 kcal/mol).

Butatriene Dication Analogues. The planar butatriene dication, **26**, has a normal C–C triple bond and shows little evidence of delocalization in the perpendicular π-system. The perpendicular conformer **27**, however, shows an extensive delocalization, involving both orthogonal π-systems, and has a significantly longer central C–C bond. The energy difference, in favor of **27**, is substantial (ca. 19 kcal/mol).[4] As expected, the delocalization in the diborylacetylenes **20** and **21** is much less extensive, and the rotation barrier is smaller (6.7 kcal/mol). The central C–C bond is a normal triple bond in both **20** and **21**.

Cyclobutenediyl Dications, 28 and 29. The analogy between carbocations and boron compounds suggested the structures of most of the $C_2B_2H_4$ isomers considered here. However, the computational "discovery" of some very unusual organoboron structures (**10**, **11**, **13–15**) now suggests that alternative, hitherto not considered $C_4H_4^{2+}$ structures could be competitive in energy with **22–27**. Therefore, we have also examined possible structures corresponding to **28** and **29**. The latter is not a local minimum (at the 4-31G level) and optimizes to **25**; **28** cannot rearrange within the C_{2v} symmetry imposed, but it is much higher in energy than the other isomers.

Thus, although analogies between $C_2B_2H_4$ and $C_4H_4^{2+}$ structures clearly exist, there are also some characteristic differences. These can be attributed to the fact that C^+ is a very strong acceptor, whereas boron is a weaker π-acceptor and moreover is a σ-donor. While the $C_2B_2H_4$ structures **11** and **13** are very favorable, the corresponding $C_4H_4^{2+}$ species **29** is unfavorable because it has a very high positive charge at the "naked" ring carbon atom, which cannot be compensated adequately by π-donation. Similarly, the boron atoms in **10** can function as σ-donors and π-acceptors toward the carbene carbon atom; the corresponding carbocation **28** cannot be stabilized in this way and is very high in energy.

Actually, some of the $C_2B_2H_4$ structures bear a closer resemblance to the 1-cyclobutenyl (**30**)[30] and 3-cyclobutenyl/3-bicyclobutyl (**31**)[31] $C_4H_5^+$ cations, in which one C^+ and one CH are replaced by two boron atoms. For example, in the 1-cyclobutenyl cation the electron deficiency of the "naked" carbon atom is relieved by the formation of a nonclassical structure (**30**) with a partial 1,3 σ-bond;[30] similar deformations are found in **11**, **13**, and **14**. The observed movement of the H(B) atoms in **1** toward equatorial positions corresponds to the pyramidalization at C(3) in **31**[31] and is opposite to that in **22**.[4] No $C_2B_2H_4$ structures corresponding to the cyclopropylidenemethyl cation **32** seem to exist. The diboramethylenecyclopropane **9** would be related to **32**, but **9** is not a local minimum at higher levels of theory. Our previous study of **30** and **32** indicated the latter species to be somewhat less stable than the former (by ca. 8 kcal/mol).[30] If, as seems likely, the flexibility of the boron compounds examined here carries over to the $C_4H_5^+$ species, **32** might very well be either an extremely shallow minimum or even a transition state for the topomerization of **30**.

Conclusions

The ease of isomerization of the $C_2B_2H_4$ species studied here is remarkable. Since the geometrical differences between **1** and **3** are quite large, a barrier as low as 8.3 kcal/mol for the reaction **1** → **3** certainly is surprising. The low or vanishingly small barriers for the rearrangements of **7–10** to **11** indicate a great flexibility of the molecular skeleton, and a similar lack of rigidity is expected for **13–15**. The facile rearrangements of these nonclassical, electron-deficient species differ sharply from the behavior of "classical" organic molecules.

In the absence of large substituent effects, it seems likely that only one structural type of each of the classes studied here will be stable enough to allow isolation. Representatives of $(CH)_2(BH)_2$ (**1**),[6,7,16] $CH_2C(BH)_2$ (**11**),[12] $C(CH)(BH)BH_2$ (**19**),[8] and $C_2(BH_2)_2$ (**21**)[29] are already known, and **13** offers an attractive goal for synthesis.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. Generous grants of computer time by the Rutgers Center for Computer and Information Services and an equipment grant from the National Science Foundation (PCM-8306023) are gratefully acknowledged. P.H.M.B. expresses his gratitude for a fellowship sponsored by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

Registry No. 1, 90171-84-9; **2**, 84304-27-8; **3**, 77385-68-3; **7**, 79535-06-1; **9**, 93368-41-3; **10**, 95250-91-2; **15**, 95250-92-3; **16**, 95250-93-4; **18**, 93895-34-2; **20**, 91260-25-2.

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(31) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1983**, *105*, 1118. Cremer, D.; Kraka, E.; Slee, T. S.; Bader, R. F. W.; Lau, C. D. H.; Nguyen-Dang, J. T.; MacDougall, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 5069.