

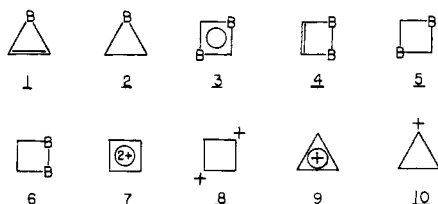
# Aromaticity in Small Rings Containing Boron and Carbon ((CH)<sub>2</sub>(BH)<sub>n</sub>, n = 1, 2). Comparisons with Isoelectronic Carbocations. The Decisive Roles of Orbital Mixing and Nonbonded 1,3-Interactions in the Structures of Four-Membered Rings

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**Abstract:** The small-ring Hückel 2π aromatic compounds (CH)<sub>2</sub>BH (1) and (CH)<sub>2</sub>(BH)<sub>2</sub> (3 and 4) are studied by ab initio molecular orbital theory. Comparisons are made with isoelectronic carbocations 7 and 9 and the related cyclic molecules (CH)<sub>2</sub>BH (2) and (CH)<sub>2</sub>(BH)<sub>2</sub> (5 and 6). Hartree-Fock geometries are determined with the STO-3G and 4-31G basis sets. Higher level calculations including the effects of polarization functions and of electron correlation are carried out on these geometries. The most stable isomer of (CH)<sub>2</sub>(BH)<sub>2</sub> is 1,3-diboretene (3) which is found to have a puckered skeleton of C<sub>2v</sub> symmetry like the isoelectronic cyclobutadiene dication 7. These puckering are due to 1,3-σ-type repulsive interactions in the planar skeleton forms. Similar puckering is found for 1,3-diboretane. With use of the 6-31G\* basis set at the STO-3G geometries, hydrogenation and resonance energies are estimated for borirene (21 and 47 kcal/mol, respectively) and the boretenes (31 and 14 kcal/mol for 3; 18 and 27 kcal/mol for 4). The resonance energies for 1 and 3 are almost 70% of the resonance energies similarly estimated for the isoelectronic cyclopropenium cation 9 and the cyclobutadiene dication 7.

The small-ring carbon-boron compounds, 1–6, have remained

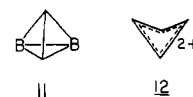


experimentally elusive despite their inherent chemical interest. 1, (CH)<sub>2</sub>BH, and 3 and 4, (CH)<sub>2</sub>(BH)<sub>2</sub>, represent the first members of the homologous series of carboranes, (CH)<sub>2</sub>(BH)<sub>n</sub>, which, with n = 3–10, are all known to have closo structures.<sup>2</sup> 1–6 are isoelectronic with carbocations 7–10 and thus bring to focus concerns traditionally associated with inorganic and with organic chemistry.

The cyclobutadiene dication 7<sup>3</sup> and the cyclopropenium ion 9<sup>4</sup> represent the smallest members of the Hückel 4n + 2 aromatic series; borirene 1<sup>5</sup> and the diboretanes 3 and 4 likewise would be expected to enjoy π-stabilization. The disrotatory ring opening of the cyclopropyl cation 10 to the allyl cation provided one of the earliest confirmations of the predictions of Woodward and

Hoffmann;<sup>6</sup> the boron analogue, borirane (2),<sup>7</sup> might open similarly.

What is the preferred structure of (CH)<sub>2</sub>(BH)<sub>2</sub>? Expectations differ depending on the line of reasoning. The organic chemist traditionally has expected 7 to be a planar aromatic; hence, 3 and 4 might also be predicted to be planar species. The inorganic chemist would note that (CH)<sub>2</sub>(BH)<sub>2</sub>, like the homologous carboranes,<sup>2</sup> should have a closo structure; diboratetrahedrane (11) seems likely on this basis. However, a pucker with 11 is apparent.



Tetrahedrane (*T<sub>d</sub>*) structures for (AH)<sub>4</sub> species should be possible only with 16 or with 20 valence electrons (illustrated by (BH)<sub>4</sub> and by (CH)<sub>4</sub>, respectively).<sup>8</sup> Jahn-Teller theory predicts that singlet 18 valence electron systems, e.g., (CH)<sub>4</sub><sup>2+</sup> or (BH)<sub>4</sub><sup>2-</sup>, will distort from *T<sub>d</sub>* symmetry. Strictly speaking, 11 (point group C<sub>2v</sub>) is not excluded on this basis, although the distortion might be greater than that implied by 11.

Theoretical calculations, excellently suited for the examination of such small molecules, can provide insight not currently available from other sources. A wealth of information concerning geometrical details, electronic structure, bonding, and energy is provided which may help guide the experimentalist in this search for such species. For example, our preliminary communication<sup>3a</sup> indicated that 7 (and 3) should possess neither planar nor tetrahedral structures; a puckered (*D<sub>2d</sub>*) form 12 was calculated to be significantly lower in energy. We suggested that the inversion barrier through the planar *D<sub>4h</sub>* form of 7 should be high enough to be experimentally detectable. A nonplanar structure for the isoelectronic (BH)<sub>4</sub><sup>2-</sup> molecule was indicated by MNDO calculations of Dewar and McKee.<sup>9</sup> We now present calculational

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results on 1–4 and a further examination of 7. For reference purposes, 5, 6, and 8 are included in this study.

### Methods

Ab initio molecular orbital calculations have been carried out on 1–8 by utilizing modified versions of the GAUSSIAN 70<sup>10a</sup> and GAUSSIAN 76<sup>10b</sup> series of programs. All molecular geometries were optimized completely, subject only to overall molecular symmetry constraints, by using restricted Hartree–Fock single determinant theory<sup>11a</sup> and the minimal STO-3G basis set (STO-3G//STO-3G).<sup>12a</sup> Energy refinements were obtained by single-point calculations at these optimal geometries with the more flexible split valence 4-31G basis<sup>12b</sup> (4-31G//STO-3G) and the 6-31G\* basis<sup>12c</sup> (6-31G\*//STO-3G), which also includes polarization functions of d-type symmetry on the boron and carbon atoms. Correlation energy estimates were obtained through the application of Møller–Plesset second-order perturbation theory at the 4-31G basis set level (MP2/4-31G//STO-3G).<sup>13</sup>

The importance of split valence basis sets for the geometries and molecular energies was assessed by using the 4-31G basis set to completely reoptimize 1, 2, and 7 as well as all independent parameters but the bond lengths to hydrogen for all the remaining molecules except 6. This was followed by single-point calculations on 1, 3, and 4 with the 6-31G\* basis set and correlation energy estimates. The changes in bond lengths upon reoptimization were generally small ( $\sim 0.015$  Å) with the largest changes occurring in the relatively weak carbon–boron ( $\sim 0.035$  Å) and boron–boron ( $\sim 0.07$  Å) bonds; all bonds except carbon–hydrogen bonds became longer. The energy lowerings are also small, ranging from a minimum value of 0.4 kcal/mol in 2 to 4.2 kcal/mol in 7 ( $D_{2d}$  symmetry); no dramatic energy changes occur at the higher calculational levels either. Hence, basically the same set of conclusions may be drawn from the STO-3G geometries provided the higher calculational levels are employed for the energy comparisons, a result which is in complete agreement with our previous investigation of carboranes.<sup>14</sup>

The geometry searches used gradient routines based on the Davidon–Fletcher–Powell steepest descent method;<sup>15</sup> the final values of the optimized parameters are listed in Table I. The total and relative molecular energies at the STO-3G geometries are shown in Table II, part A, and in Table II, part B, for the 4-31G geometries. The wave functions were subjected to electronic population analysis (charges  $q$ , overlap populations  $\rho$ ) through the conventional partitioning procedures due to Mulliken<sup>16</sup> (Table III). Unless otherwise noted, the geometrical parameters and overlap populations from the optimized STO-3G structures will be used in the subsequent discussion.

### Results and Discussion

**Borirene (1).** Attempts to synthesize derivatives of borirene have been reported,<sup>5</sup> but they have all met with limited success; dimeric compounds are often obtained instead.<sup>5a,b</sup> More recently, Eisch et al.<sup>5c</sup> have gained at least partial evidence for the formation

Table I. Molecular Equilibrium Geometries of Compounds 1–8<sup>a</sup>

molecule	symmetry constraint	parameter	optimization			
			STO-3G	4-31G		
borirene (1)	$C_{2v}$	$r(\text{B-C})$	1.440	1.476		
		$r(\text{C-C})$	1.340	1.347		
		$r(\text{B-H})$	1.146	1.168		
		$r(\text{C-H})$	1.079	1.065		
		$\angle(\text{HCC})$	140.1	139.5		
borirane (2)	$C_{2v}$	$r(\text{B-C})$	1.521	1.533		
		$r(\text{C-C})$	1.526	1.552		
		$r(\text{B-H})$	1.152	1.172		
		$r(\text{C-H})$	1.081	1.076		
		$\angle(\text{H}_2\text{CC})$	146.0	145.5		
		$\angle(\text{HCH})$	112.3	112.1		
		$r(\text{B-C})$	1.477	1.510		
1,3-diboretene (3)	$C_{2v}$	$r(\text{C-C})$	1.754	1.858		
		$r(\text{B-H})$	1.149	<i>b</i>		
		$r(\text{C-H})$	1.082	<i>b</i>		
		$\alpha^c$	54.9	48.2		
		$\tau_1^d$	6.2	5.2		
		$\tau_2^d$	7.4	11.4		
		$\angle(\text{CBC})^e$	72.9	75.9		
		$\angle(\text{HBCH})^e$	41.2	43.3		
		$\angle(\text{BCBC})^e$	41.2	36.0		
		$D_{2h}$	$r(\text{B-C})$	1.499	1.536	
			$r(\text{B-H})$	1.156	<i>b</i>	
			$r(\text{C-H})$	1.089	<i>b</i>	
			$\angle(\text{BCB})$	90.2	90.2	
$r(\text{B-C})$	1.652		1.722			
1,2-diboretene (4)	$C_{2v}$	$r(\text{B-C})$	1.536	1.565		
		$r(\text{C-C})$	1.359	1.367		
		$r(\text{B-H})$	1.158	<i>b</i>		
		$r(\text{C-H})$	1.088	<i>b</i>		
		$\angle(\text{HBB})$	143.8	144.5		
		$\angle(\text{HCC})$	127.5	126.9		
		$\angle(\text{BCC})^e$	95.5	96.5		
		1,3-diboretane (5)	$C_{2v}$	$r(\text{B-C})$	1.576	1.591
				$r(\text{B-H}_{\text{ax}})$	1.161	<i>b</i>
				$r(\text{C-H}_{\text{ax}})$	1.088	<i>b</i>
$r(\text{C-H}_{\text{eq}})$	1.081			<i>b</i>		
$\alpha^c$	35.8			36.2		
$\angle(\text{CBC})$	93.4			94.1		
$\tau_1^d$	9.7			10.4		
$\tau_2^d$	66.4			66.3		
$\tau_3^d$	42.6			41.9		
$D_{2h}$	$r(\text{B-C})$			1.587	1.600	
	$r(\text{B-H})$			1.163	<i>b</i>	
	$r(\text{C-H})$			1.086	<i>b</i>	
	$\angle(\text{BCB})$			85.8	85.8	
	$\angle(\text{HCH})$	107.0	104.7			
1,2-diboretane (6)	$C_{2v}$	$r(\text{B-B})$	1.703			
		$r(\text{B-C})$	1.589			
		$r(\text{C-C})$	1.566			
		$r(\text{B-H})$	1.161			
		$r(\text{C-H})$	1.087			
		$\angle(\text{HCC})$	113.2			
		$\angle(\text{HCH})$	107.5			
		$\angle(\text{BBC})^e$	87.5			
		$\angle(\text{HCBH})^e$	62.9			
		cyclobutadiene dication (7)	$D_{2d}$	$r(\text{C-C})$	1.457	1.431
$r(\text{C-H})$	1.120			1.077		
$\alpha^c$	33.2			35.8		
$\tau_1^d$	2.7			1.5		
$D_{4h}$	$r(\text{C-C})$			1.467	1.442	
	$r(\text{C-H})$			1.119	1.077	
	$r(\text{C-C}^*)$			1.538	1.499	
1,3-cyclobutanylidene dication (8)	$D_{2h}$			$r(\text{C}^*\text{-H})$	1.127	<i>b</i>
				$r(\text{C-H})$	1.112	<i>b</i>
				$\angle(\text{CC}^*\text{C})$	92.2	92.1
				$\angle(\text{HCH})$	107.0	103.7

<sup>a</sup> Distances in ångströms, and angles in degrees. <sup>b</sup> Parameter not reoptimized, kept fixed at STO-3G value. <sup>c</sup> Puckering angle, see Figure 1 for definition. <sup>d</sup> Tilt angle, see Figure 1 for definition. <sup>e</sup> Redundant parameter, not included in the optimization.

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Table II. Absolute and Relative Energies of Compounds 1-8<sup>a</sup>

molecule	symmetry	STO-3G energy	rel <i>E</i>	4-31G energy	rel <i>E</i>	6-31G* energy	rel <i>E</i>	MP2/4-31G energy	rel <i>E</i>
A. STO-3G Geometries									
borirene (1)	<i>C</i> <sub>2v</sub>	-100.84556		-101.94207		-102.10080		-102.16591	
borirane (2)	<i>C</i> <sub>2v</sub>	-102.01931		-103.11120		-103.26144		-103.34206	
1,3-diboretene (3)	<i>C</i> <sub>2v</sub>	-125.81417	0.0	-127.17023	0.0	-127.36523	0.0	-127.45135	0.0
	<i>D</i> <sub>2h</sub>	-125.78005	21.4	-127.15091	12.1	-127.33818	17.0	-127.42689	15.3
1,2-diboretene (4)	<i>C</i> <sub>2v</sub>	-125.78725	16.9	-127.15921	6.9	-127.34848	10.5	-127.42848	14.3
1,3-diboretane (5)	<i>C</i> <sub>2v</sub>	-127.01538	0.0	-128.36574	0.0	-128.55099	0.0	-128.64790	0.0
	<i>D</i> <sub>2h</sub>	-127.00776	4.8	-128.35838	4.6	-128.54070	6.5	-128.63525	7.9
1,2-diboretane (6)	<i>C</i> <sub>2v</sub>	-126.97104	27.8	-128.31800	30.0	-128.50347	29.8	-128.59419	33.7
cyclobutadiene dication (7)	<i>D</i> <sub>2d</sub>	-151.08576	0.0	-152.65837	0.0	-152.90692	0.0	-152.97915	0.0
	<i>D</i> <sub>4h</sub>	-151.08124	2.8	-152.65157	4.3	-152.89714	6.1	-152.96987	5.8
1,3-cyclobutanylidene dication (8)	<i>C</i> <sub>2v</sub>	-152.29532		-153.84379		-154.07467		-154.15491	
B. 4-31G Geometries									
borirene (1)	<i>C</i> <sub>2v</sub>			-101.94435		-102.10206		-102.16953	
borirane (2)	<i>C</i> <sub>2v</sub>			-103.11182					
1,3-diboretene (3)	<i>C</i> <sub>2v</sub>			-127.17476	0.0	-127.36616	0.0	-127.45840	0.0
	<i>D</i> <sub>2h</sub>			-127.15398	13.0	-127.34041	16.2	-127.43320	15.8
1,2-diboretene (4)	<i>C</i> <sub>2v</sub>			-127.16182	8.1	-127.35059	9.8	-127.43277	16.1
1,3-diboretane (5)	<i>C</i> <sub>2v</sub>			-128.36649	0.0				
	<i>D</i> <sub>2h</sub>			-128.35901	9.7				
cyclobutadiene dication (7)	<i>D</i> <sub>2d</sub>			-152.66498	0.0				
	<i>D</i> <sub>4h</sub>			-152.65773	4.5				

<sup>a</sup> Absolute energies in Hartrees (au) and relative energies in kcal/mol.

Table III. Selected 6-31G\* Mulliken Population Results<sup>a</sup>

molecule	symmetry	<i>q</i> <sub>C</sub> <sup>π</sup>	<i>q</i> <sub>B</sub> <sup>π</sup>	$\rho_{C_1-C_2}$	$\rho_{C_1-C_3}$	$\rho_{C-B}$	$\rho_{B_1-B_2}$	$\rho_{B_1-B_3}$	$\rho_{C_2^+-C_4^+}$
3 <sup>b</sup>	<i>C</i> <sub>2v</sub>				-0.036	0.858		0.001	
3 <sup>b</sup>	<i>D</i> <sub>2h</sub>	0.578	0.408		-0.227	0.940		0.003	
4 <sup>b</sup>	<i>C</i> <sub>2v</sub>	0.826	0.160	1.106		-0.187 <sup>d</sup>	0.962		
5 <sup>c</sup>	<i>C</i> <sub>2v</sub>				-0.344	0.817		-0.262	
5 <sup>c</sup>	<i>D</i> <sub>2h</sub>	1.118	0.056		-0.328	0.825		-0.229	
6 <sup>c</sup>	<i>C</i> <sub>2v</sub>	1.111	0.031	0.598		-0.281 <sup>e</sup>	0.988		
7 <sup>b</sup>	<i>D</i> <sub>2d</sub>			0.489	0.049				
7 <sup>b</sup>	<i>D</i> <sub>4h</sub>			0.905	-0.359				
8 <sup>c</sup>	<i>D</i> <sub>2h</sub>	0.091	1.365 <sup>f</sup>	0.606	-0.288				-0.377

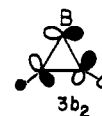
<sup>a</sup> *q*<sub>A</sub><sup>π</sup> is the gross minimal charge in the 2p orbital on A of π symmetry.  $\rho_{AB}$  is the total overlap population between atoms A and B. <sup>b</sup> 6-31G\*/4-31G. <sup>c</sup> 6-31G\*/STO-3G. <sup>d</sup> Refers to the nonbonded 1,3-interaction; the 1,2-overlap population is 0.846. <sup>e</sup> Refers to the nonbonded 1,3-interaction; the 1,2-overlap population is 0.776. <sup>f</sup> CH<sub>2</sub> group.

of the borirene nucleus as a diphenyl (diphenylvinylene)borate(III) salt. An early theoretical discussion of the possible aromatic character of **1** by Volpin et al.<sup>17</sup> stressed that trivalent B and trivalent C<sup>+</sup> possess the same electronic configurations. Replacement of C<sup>+</sup> by B in the then newly discovered cyclopropenium ion **9** might thus give rise to a stable molecule with significant aromatic character. Several years later, Pittman et al.<sup>18</sup> concluded on the basis of semiempirical INDO bond lengths and charge distributions that borirene was indeed an aromatic molecule, but no resonance energy estimate was provided. The electronic spectrum has been calculated by Allinger and Siefert.<sup>19</sup>

In borirene, the boron 2p(π) orbital acquires a gross orbital charge of 0.39 e and substantial π bonding develops between boron and carbon ( $\rho_{CB}^\pi = 0.17$ ), leading to a very reduced bond length of 1.44 Å, 0.1 Å shorter than the standard B-C value of 1.54 Å.<sup>20</sup> The calculated C-C bond length is 1.34 Å, 0.06 Å longer than the STO-3G value in cyclopropene (1.28 Å).<sup>21</sup> This lengthening arises mainly because of a large decrease in π<sub>CC</sub> bonding ( $\rho_{CC}^\pi = 0.28$  in **1**, 0.42 in cyclopropene). A net charge transfer of 0.13 e from the BH group is calculated in **1**; i.e., σ-donation from BH

actually amounts to more than 0.5 e. Boron is known to be a moderately strong π-acceptor but even stronger σ-donor when bonded to atoms of greater electronegativity.<sup>20</sup> All the boron compounds studied in this paper exhibit such charge reorganization.

The symmetrical π-electron delocalization in the cyclopropenium ion results in stronger C-C<sup>+</sup> bonds being formed ( $\rho_{CC}^\pi = 0.21$ ) relative to the C-B bonds in **1** and the optimal STO-3G carbon-carbon distance of 1.38 Å<sup>4</sup> is intermediate between the C-C and C-B distances calculated in **1**. The π orbital becomes the HOMO in **9**, whereas the C-B bonding but C-C antibonding antisymmetric Walsh orbital (3b<sub>2</sub>) is the HOMO in **1**.



**Borirane (2).** The second three-membered ring in our study, borirane (**2**) is isoelectronic with the cyclopropyl cation. There is some experimental evidence for derivatives of **2**.<sup>7</sup> The only orbital available for interaction with the B 2p(π) orbital in **2** is now a pseudo π orbital of the CH<sub>2</sub> groups (1b<sub>1</sub>) positioned far down in energy among the occupied orbitals. The hyperconjugative interaction leads to a population in the B π orbital of only 0.06 e. The gross charge transfer from the BH group is 0.24 e, i.e., in this structure a net of about 0.3 e is donated by B into the σ system. The optimized geometry for **2** is almost an equilateral triangle.

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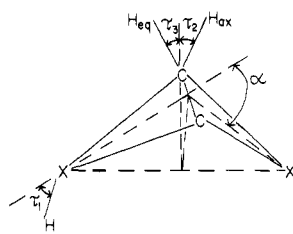
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Table IV. Valence Molecular Orbital Energies  $\epsilon$  (au) of Planar ( $D_{2h}$ ) and Puckered ( $C_{2v}$ ) 1,3-Diboretene (**3**) and 1,3-Diboretane (**5**) 6-31G\*\*/STO-3G

3, $D_{2h}$		3, $C_{2v}$		difference <sup>a</sup> ( $D_{2h} - C_{2v}$ )	5, $D_{2h}$		5, $C_{2v}$		difference <sup>a</sup> ( $D_{2h} - C_{2v}$ )
orbital	$\epsilon$	orbital	$\epsilon$		orbital	$\epsilon$	orbital	$\epsilon$	
2b <sub>1u</sub> ( $\pi^*$ )	0.265	4b <sub>2</sub>	0.200		1b <sub>2g</sub>	0.134	4b <sub>1</sub>	0.168	
1b <sub>2g</sub> ( $\pi^*$ )	0.126	7a <sub>1</sub>	0.172		2b <sub>1u</sub>	0.107	7a <sub>1</sub>	0.094	
1b <sub>3g</sub> ( $\pi^*$ )	0.047	4b <sub>1</sub>	0.164		3b <sub>3u</sub>	-0.389	3b <sub>1</sub>	-0.403	0.014
1b <sub>1u</sub> ( $\pi$ )	-0.379	6a <sub>1</sub>	-0.398	0.019	3b <sub>2u</sub>	-0.411	1a <sub>2</sub>	-0.422	-0.007
3b <sub>3u</sub>	-0.423	1a <sub>2</sub>	-0.421	-0.052	1b <sub>1g</sub>	-0.429	4b <sub>2</sub>	-0.433	0.022
3b <sub>2u</sub>	-0.473	3b <sub>2</sub>	-0.460	-0.013	1b <sub>3g</sub>	-0.529	3b <sub>2</sub>	-0.523	-0.006
1b <sub>1g</sub>	-0.473	3b <sub>1</sub>	-0.488	0.065	1b <sub>1u</sub>	-0.564	6a <sub>1</sub>	-0.535	-0.029
5a <sub>g</sub>	-0.559	5a <sub>1</sub>	-0.586	0.027	5a <sub>g</sub>	-0.567	5a <sub>1</sub>	-0.603	0.036
2b <sub>3u</sub>	-0.658	2b <sub>1</sub>	-0.671	0.013	4a <sub>g</sub>	-0.640	2b <sub>1</sub>	-0.642	-0.003
4a <sub>g</sub>	-0.678	4a <sub>1</sub>	-0.677	-0.001	2b <sub>3u</sub>	-0.645	4a <sub>1</sub>	-0.651	0.011
2b <sub>2u</sub>	-0.848	2b <sub>2</sub>	-0.812	-0.036	2b <sub>2u</sub>	-0.883	2b <sub>2</sub>	-0.883	0.000
3a <sub>g</sub>	-1.031	3a <sub>1</sub>	-1.091	0.060	3a <sub>g</sub>	-0.999	3a <sub>1</sub>	-1.017	0.018

<sup>a</sup> Differences between orbitals which correlate, as indicated by arrows when there is a change in the ordering. Positive values indicate stabilization of puckered forms.



**Figure 1.** Structural parameters of puckered 1,3-diboretene (**3**, X = B), 1,3-diboretane (**5**, X = B), and the cyclobutadiene dication (**7**, X = C<sup>+</sup>). In **3** and **7**, H<sub>eq</sub> is not present and  $\tau_3$  hence undefined.

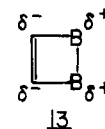
Since the interacting orbitals are considerably closer in energy, hyperconjugation is more effective in the isoelectronic cyclopropyl cation **10**. The C<sup>+</sup> p orbital population is 0.10 e, and the calculated C–C<sup>+</sup> and C–C distances are 1.49 and 1.52 Å,<sup>22</sup> respectively.

**Diboretanes 3 and 4.** 1,3-Diboretane (**3**) was optimized under two overall symmetry constraints,  $D_{2h}$  (planar) and  $C_{2v}$  (puckered). The two  $\pi$ -electrons are quite effectively delocalized in the planar form as evidenced by a charge in the B 2p( $\pi$ ) orbital of 0.43 e and a  $\pi$ -overlap population of 0.14 between boron and carbon. The optimized  $D_{2h}$  structure is essentially a square ( $\angle BCB = 90.2^\circ$ ) with B–C bond lengths (1.50 Å) reduced 0.04 Å below the standard single bond value.<sup>20</sup>

The geometry of the  $C_{2v}$  conformation is quite intriguing. The ring is strongly nonplanar with a puckering angle ( $\alpha$ , Figure 1) of  $54.9^\circ$ . This may be compared to calculated (STO-3G) puckering angles in bicyclo[1.1.0]butane, the cyclobutadiene dication, and cyclobutane of  $62.6^\circ$ ,<sup>23</sup>  $33.2^\circ$ <sup>3</sup> (Table I), and  $13.0^\circ$ ,<sup>23,24</sup> respectively. Upon reoptimization at the 4-31G level, the puckering angle decreases ( $\alpha = 48.2^\circ/4-31G$ ); this is opposite to the trends in cyclobutane<sup>24</sup> and the cyclobutadiene dication,<sup>3</sup> where  $\alpha$  increases consistently with increasing flexibility in the basis set employed. The B–C bond length of 1.48 Å is even shorter than that predicted for the  $D_{2h}$  form, but the most unusual feature is the C–C distance of 1.75 Å (1.86 Å at 4-31G), which is comparable to the longest C–C bond lengths determined experimentally. “Long” carbon–carbon bonds normally lie in the range of 1.60–1.65 Å<sup>25</sup> with a few exceptional cases up to 1.84 Å.<sup>26</sup> Wright and Salem<sup>27</sup> pointed out the importance of the methylene rocking motion accompanying the puckering of cyclobutane (tilt angle

=  $2.1^\circ$ /STO-3G).<sup>24</sup> The analogous tilt angles in **3**,  $\tau_1$  and  $\tau_2$  (Figure 1), are  $6.2^\circ$  and  $7.4^\circ$ .

One might expect the electronic delocalization in 1,2-diboretane (**4**) to result in a lengthened C=C bond but shortened C–B and B–B bonds (the standard bond lengths are C3=C3 = 1.34 Å, C4–B3 = 1.54 Å, B3–B3 = 1.64 Å),<sup>20,28</sup> in contrast, the B–B bond actually is lengthened (1.65 Å at STO-3G and 1.72 Å at 4-31G). The charge in the boron 2p( $\pi$ ) orbital is  $-0.17$ ; i.e., some delocalization does occur ( $\rho_{BB^\pi} = 0.04$ ,  $\rho_{CB^\pi} = 0.10$ ,  $\rho_{CC^\pi} = 0.28$ ), but the  $\sigma$  donation from boron to carbon leads to a net charge on boron of  $+0.16$ , and a net charge on carbon of  $-0.13$ . This coulombic charge repulsion is unfavorable energetically and forces the B atoms apart (see 13).



All calculational levels predict the puckered ( $C_{2v}$ ) form of **3** to be the most stable diboretene isomer; the planar  $D_{2h}$  structure of **3** is between 12 and 21 kcal/mol and the other isomer, **4**, is 7–17 kcal/mol higher in energy. Indeed, planar **3** is the transition state for ring inversion and not a local minimum on the potential energy surface. If the highest level Hartree–Fock  $C_{2v} - D_{2h}$  difference (16 kcal/mol, 6-31G\*\*//4-31G) is combined with the preferential lowering from correlation energy (3 kcal/mol, MP2/4-31G//4-31G vs. 4-31G//4-31G), a “best estimate” of 19 kcal/mol for the magnitude of the inversion barrier is obtained.

The role of 1,3-interactions in determining the geometry of four-membered rings<sup>29</sup> is also important here; relevant results from the Mulliken population analysis calculations with the 6-31G\* basis on **3** and **4** are listed in Table III. The absolute values from a Mulliken population analysis are strongly basis set dependent, but we prefer here to quote the 6-31G\* results, since they are the most accurate in terms of the underlying wave functions and in this case most clearly illustrate the significant points to be made. As mentioned earlier, an unfavorable charge distribution is created by the polarization in the  $\sigma$  and  $\pi$  frameworks of **4**. Furthermore, the 1,3-overlap population is  $-0.19$ , indicating considerable destabilizing interactions also diagonally across the ring. There are very strong destabilizing carbon–carbon interactions in the plane of the  $D_{2h}$  conformation of **3**. The overlap population between the two carbon 2p( $\pi$ ) orbitals is  $+0.08$  (stabilizing), but the total overlap population is  $-0.23$ . In the  $C_{2v}$  structure, however, the total carbon–carbon overlap population is only  $-0.04$ . Thus considerable relief of antibonding results from the puckering; the two extra valence electrons remain delocalized over the entire ring. Puckering results in  $\sigma$ - and  $\pi$ -orbital mixing; this is further en-

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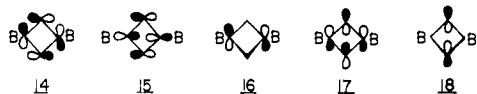
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hanced by the pyramidalization at the carbon and boron centers, all hydrogens moving toward axial positions.

An orbital energy diagram indicated by the correlations in Table IV shows which molecular orbitals are mostly responsible for the stabilization of the puckered structure (**3**,  $C_{2v}$ ). Through the decrease in symmetry from  $D_{2h}$  to  $C_{2v}$  the lowest virtual orbitals of the  $D_{2h}$  conformer,  $1b_{3g}(\pi^*)$  and  $1b_{2g}(\pi^*)$ , transform as  $b_2$  and  $b_1$ , respectively; since these symmetry representations are well represented among the occupied MO's strong orbital mixing results. All occupied  $a_1$  orbitals are stabilized in the puckered form, mostly due to the increased overlap in the more compact  $C_{2v}$  form; e.g.,  $R_{CC} = 1.75 \text{ \AA}$  vs.  $2.12 \text{ \AA}$  in the planar form (**3**,  $D_{2h}$ ) (STO-3G) and the corresponding B-B distances are  $2.11 \text{ \AA}$  vs.  $2.12 \text{ \AA}$ . The stabilization includes the HOMO ( $1b_{1u}(\pi)$ ,  $D_{2h}$ ;  $6a_1$ ,  $C_{2v}$ ), and there is thus no indication from the orbital eigenvalues of the expected decrease in  $\pi$ -delocalization upon puckering. The only occupied orbital of  $a_2$  ( $C_{2v}$ ) symmetry is the 1,2-bonding, 1,3-antibonding Walsh-type ring orbital of  $p_x$  and  $p_y$  character (**14**), which is destabilized upon puckering. All occupied valence



orbitals of  $b_1$  symmetry have been stabilized in the  $C_{2v}$  structure, particularly the  $3b_1$  ( $3b_{3u}$ ) orbital **15**. This orbital has back lobes of B-H bond orbitals pointing toward each other inside the ring in an antibonding fashion, but it is net C-C bonding. Through mixing with the second virtual MO, the B-B  $\pi^*$  combination **16** and from an increase in C-C overlap due to the large change in C-C distance, this orbital is stabilized tremendously on puckering. A large part of the increase in 1,3-C-C overlap population must be ascribed to this orbital. All  $b_2$  orbitals are destabilized in the puckered species, including the analogous  $3b_2$  ( $3b_{2u}$ ) C-H bond orbital **17**. Although considerable interaction with the LUMO (the C-C  $\pi^*$  orbital **18**) is indicated from the large change in LUMO orbital energy (the  $1b_{3g}$  LUMO transforms into the  $4b_2$  MO under  $C_{2v}$  symmetry, the third lowest unoccupied orbital), stabilization is counteracted by the reduced C-C distance and the enhanced C-H back lobe repulsion. No significant increase in B-B bonding occurs through this orbital, since the B-B distance remains almost constant in the two geometries.

Exploratory triplet state calculations<sup>11b</sup> using the optimized  $C_{2v}$  closed singlet geometry of **3** placed the lowest triplet ca. 200 kcal/mol above the singlet. Hence, biradical states do not appear to be competitive in energy.

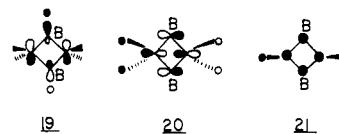
**Diboretanes 5 and 6.** 1,3-Diboretane (**5**) was also optimized within two overall symmetries, a  $D_{2h}$  form with a planar ring skeleton and a puckered  $C_{2v}$  form. As expected from the carbon  $sp^3$  hybridization, the BCB angle becomes smaller by about  $4^\circ$  ( $\angle BCB = 85.8^\circ$  in **5**,  $90.2^\circ$  in **3**). Hyperconjugation involving the  $CH_2$  group and the boron  $2p(\pi)$  orbital is weak ( $q = 0.07 e$ ), and the carbon-boron bond lengths remain fairly long ( $1.59 \text{ \AA}$ /STO-3G). The  $C_{2v}$  conformation is characterized by a puckering angle,  $\alpha$ , of  $32.3^\circ$ . Pyramidalization occurs at the boron centers, where the hydrogens tilt in an axial direction by  $9.7^\circ$ . The corresponding effect at the carbon centers is evidenced by rocking of the methylene group. The rocking angle, defined as the angle between the bisectors of the HCH and BCB angles, is  $11.8^\circ$ ; the motion of the hydrogen atoms is again toward axial positions.

In 1,2-diboretane (**6**) we also encounter (as in **4**) very long ring bond lengths. In particular, the boron-boron bond is  $0.06 \text{ \AA}$  longer than its standard value,  $1.70 \text{ \AA}$ . A highly unfavorable charge distribution is again partly responsible. Only weak hyperconjugative back-donation is possible as compensation for the strong  $\sigma$ -donation from boron; net charges of  $-0.23 e$  on carbon and  $0.20 e$  on boron result in two large bond dipoles which interact unfavorably.

The relative energies of **6** and the two conformations of **5** are parallel to the relative stabilities of the unsaturated rings **4** and **3**. The puckered  $C_{2v}$  structure of **5**, the best conformation, is more

stable than **6** by about 30 kcal/mol; if estimates of electron correlation are included, the "best estimate" of the barrier for planar inversion of **5** is about 10 kcal/mol (Table II).

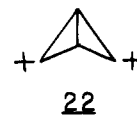
As emphasized by Bauld et al.,<sup>29</sup> pyramidalization and methylene rocking both relieve destabilizing  $\sigma$  overlap by forcing the back lobes of bond orbitals out of coplanarity, lending  $\pi$ -character to the interaction. Relief of nonbonded 1,3-interactions appear also to be decisive in determining the most stable diboretane structure. The preference for nonplanarity in **5** is reflected in the orbital energies of the  $D_{2h}$  and  $C_{2v}$  forms (Table IV). Mixing with the virtual orbitals leads to large stabilizations of the  $3b_{3u}$  (HOMO, **19**) and  $3b_{2u}$  (**20**) orbitals; both of these orbitals have out-of-phase



C-H and B-H back lobes pointing toward each other in the plane of the ring. The  $5a_g$  orbital **21**, which is the symmetric combination of  $\pi_{CH_2}$  and B  $2p(\pi)$  orbitals is stabilized the most upon puckering. The orbital energy decreases are generally smaller than those calculated for **3**, a result which is probably reflected in the smaller barrier to inversion in **5** than in **3**.

However, the nonplanarity of **5** cannot be rationalized on the basis of changes in the Mulliken overlap populations. The 1,3-populations are at all calculational levels more negative in the puckered structure than in the planar one, e.g.,  $\rho_{CC} = -0.344$  ( $-0.328$ ) and  $\rho_{BB} = -0.262$  ( $-0.229$ ) in the  $C_{2v}$  ( $D_{2h}$ ) conformations ( $6-31G^*/STO-3G$ ). A more detailed explanation of the causes of nonplanarity in four-membered rings in terms of MO theory will be presented separately.<sup>30</sup>

**Cyclobutadiene Dication 7.** Olah et al.<sup>31</sup> have succeeded in preparing substituted cyclobutadiene dications, but not the parent species, in superacid media.  $C_4H_4^{2+}$  ions have been reported in the gas phase, but their structures are unknown.<sup>32</sup> Previous theoretical treatments, semiempirical<sup>33</sup> as well as *ab initio*,<sup>34</sup> only have considered planar structures for **7**, whereas our results on isoelectronic **3** led us to expect a stable, puckered minimum energy conformation for **7** as well. As described more extensively elsewhere,<sup>3</sup> **7** is indeed puckered ( $D_{2d}$ ) with a barrier to inversion through the planar  $D_{4h}$  form of  $7.5 \text{ kcal/mol}$  at the Hartree-Fock level ( $6-31G^*/6-31G^*$ ); correlation energy estimates raise this best value to  $9.0 \text{ kcal/mol}$ . The puckering angle,  $\alpha$ , increases ( $33.2^\circ$  (STO-3G),  $35.8^\circ$  (4-31G),  $42.6^\circ$  ( $6-31G^*$ )) and the C-C bond lengths decrease ( $1.467 \text{ \AA}$  (STO-3G),  $1.442 \text{ \AA}$  (4-31G),  $1.432 \text{ \AA}$  ( $6-31G^*$ )) with increasing flexibility of the basis set employed. Puckering again is due to the relief of destabilizing in-plane 1,3-interactions. Whereas the 1,3-overlap populations of the  $D_{4h}$  configuration are very negative (Table III), they become slightly positive in the  $D_{2d}$  configuration; the orbital energy correlation diagram substantiates these conclusions.<sup>3</sup> A thorough search of the  $C_4H_4^{2+}$  potential surface shows that the bicyclobutane dication **22** opens to the puckered cyclobutadiene dication on optimization<sup>30</sup> and indicates **7** to be the most stable  $C_4H_4^{2+}$  isomer.<sup>3b</sup>



Despite the presence of two  $\pi$ -electrons, the 18 valence electron molecules,  $B_2C_2H_4$  and  $C_4H_4^{2+}$ , both favor puckered to planar

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Table V. Theoretical Hydrogenation Energies (kcal/mol) with Various Basis Sets at the STO-3G Geometries

rxn	reactant	product	STO-3G	4-31G	6-31G*
1	borirene	borirane	-35.3	-26.7	-21.3
2	cyclopropenyl cation <sup>a</sup>	cyclopropyl cation <sup>b</sup>	-17.2	-6.7	1.1
3	cyclopropene <sup>c</sup>	cyclopropane <sup>c</sup>	-92.5	-72.3	-68.4
4	1,3-diboretene	1,3-diboretane	-47.7	-38.6	-30.6
5	1,2-diboretene	1,2-diboretane	-41.6	-20.2	-17.7
6	cyclobutene <sup>d</sup>	cyclobutane <sup>d,e</sup>	-72.9	-45.3	-44.6
7	cyclobutadiene dication	cyclobutanylidene dication	-57.8	-36.9	-25.7

<sup>a</sup> Reference 4. <sup>b</sup> Reference 22. <sup>c</sup> Reference 21. <sup>d</sup> Reference 23. <sup>e</sup> Reference 24.

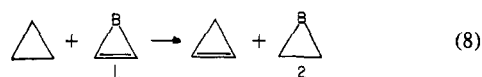
conformations. Similarly  $B_4H_4^{2-}$  prefers a puckered  $D_{2d}$  conformation<sup>9</sup> (MNDO; barrier = 3.4 kcal/mol), and  $B_2N_2H_4^{2+}$  prefers nonplanarity by 27 kcal/mol (STO-3G//STO-3G).<sup>35</sup>

**Cyclobutanylidene Dication 8.** Considering the obvious similarities between **3**, **5** and **7**, **8**, it is somewhat surprising that for **8** only an energy minimum with a planar ring could be located on the STO-3G hypersurface. The 1,3-overlap populations are substantial and negative ( $\rho_{C_1C_3} = -0.29$ ,  $\rho_{C_2C_4} = -0.38$ ), which would seem to warrant a puckered form. Charge repulsions may be responsible. The potential surface for out-of-plane distortion is extremely flat, but optimization leads back to a  $D_{2h}$  structure. This species is almost square with the smaller angle at the tetra-coordinate carbon ( $87.8^\circ$ ) and C-C<sup>+</sup> bond lengths longer than in **10** (1.54 Å vs. 1.49 Å).

### Hydrogenation and Resonance Energies

Table V gives the calculated heats of reaction for the most stable conformations of **1**, **3**, **4**, and **7** with 1 mol of hydrogen to form **2**, **5**, **6**, and **8**, respectively. Values for cyclopropene and cyclobutene are included for comparison. Hydrogenation energies calculated with the 6-31G\* basis set have been demonstrated to reproduce experimental trends quite well,<sup>12c</sup> smaller basis sets give less satisfactory results.<sup>36</sup> The negative values obtained illustrate that electron delocalization cannot overcome the preference for carbon to be singly bonded, but the hydrogenation energies for the carboranes are all considerably less than the corresponding values for the neutral hydrocarbons, viz., reaction 1 vs. 3 or 4 vs. 6.

Isodesmic reactions calculated from 6-31G\*//STO-3G data in Table V provide estimates of the resonance energies of **1**, **3**, **4**, and **7**. Combination of reactions 1 and 3 leads to eq 8 and a

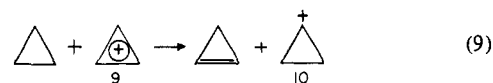


delocalization energy estimate for borirene of 47.1 kcal/mol. The

(35) Krogh-Jespersen, K., unpublished results.

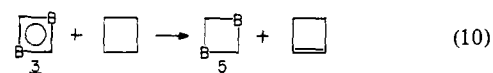
(36) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

corresponding value for the cyclopropenium ion (**9**) (eq 9) is 69.5

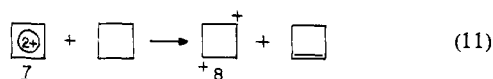


kcal/mol. The stabilization of borirene from delocalization of the  $2\pi$  electrons is thus quite considerable, amounting to about 70% of that calculated for the cyclopropenyl cation.

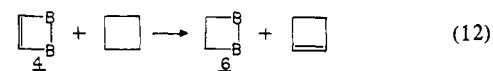
For 1,3-diboretene, eq 10 gives a resonance energy of 14.0



kcal/mol; the value for the cyclobutadiene dication (eq 11) is 18.6



kcal/mol. The resonance energy of the carborane is thus 75% of that in the isoelectronic carbocation. Actually, 1,2-diboretene (**4**) is calculated (eq 12) to possess a larger resonance energy than



either **3** or **7**, 26.9 kcal/mol, almost twice the value calculated for **3**. However, this energy reflects, in part, the unfavorable  $\sigma$  bonding in **6** (vide infra) which is ameliorated in **4**.

### Conclusions

The smallest carboranes  $(CH)_2(BH)_n$  ( $n = 1$  and  $2$ ) are Hückel  $2\pi$  aromatic molecules isoelectronic with the cyclopropenium ion (**9**) and the cyclobutadiene dication (**7**). As judged from the isodesmic reactions eq 8 vs. 9 and 10 vs. 11, borirene (**1**) and 1,3-diboretene (**3**) should have about 70–75% of the resonance energy of the carbocation analogues.

Like the cyclobutadiene dication (**7**), 1,3-diboretene (**3**) prefers a puckered rather than a planar structure. Relief of repulsive 1,3 cross-ring interactions are responsible for these violations of the general expectation that aromatic molecules will prefer planarity.

Due to the greater electronegativity of carbon than boron, the  $\sigma$ -electrons are distributed rather unevenly in 1,2-diboretene (**4**) and in 1,2-diboretane (**6**). Both these molecules are less stable than their 1,3-counterparts as a result.

Thermodynamically, at least **1–3** and **5** appear to be reasonably stable molecules. Derivatives with the proper substituents may be realizable experimentally. Chemical instability may be due to ring opening followed by further reaction or to addition of one carborane molecule to another. We plan to investigate such possibilities computationally.

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