interest. This work was supported by the Fonds der Chemischen Industrie.

Note Added in Proof. R. Alder has called attention to this study,[32] both calculational and experimental, of double bridgehead dienes in bicyclo[4.4.4]tetradecane systems. That some of the energies do not always agree perfectly with those we have calculated independently for the same molecules emphasizes the difficulty in ensuring that the most stable conformation was found in each case.

Registry No. 3, 36532-38-4; **3a**, 79312-79-1; **4**, 284-51-5; **4a**, 89507-04-0; **21**, 279-23-2; **21a**, 21810-44-6; **22**, 280-33-1; **22a**, 3618-06-2; **23**, 283-19-2; **23a**, 25048-48-0; **24**, 284-26-4; **24a**, 67152-31-2; **25**, 53974-82-6; **25a**, 79312-78-0; **26**, 24504-36-7; **26a**, 101999-73-9; **27**, 284-53-7; **27a**, 101999-74-0; **28**, 284-67-3; **28a**, 101999-75-1; **29**, 101999-76-2; **30**, 102046-62-8; (*E*)-**32**, 101999-77-3; (*Z*)-**32**, 101999-78-4; (*E*)-**34**, 101999-79-5; (*Z*)-**34**, 101999-80-8; (*E*)-**36**, 101999-81-9; (*Z*)-**36**, 101999-82-0; (*EE*)-**38**, 101999-83-1; (*ZE*)-**38**, 101999-84-2; (*ZZ*)-**38**, 101999-85-3; (*EE*)-**39**, 101999-86-4; (*ZZ*)-**39**, 101999-87-5; (*EE*)-**40**, 101999-88-6; (*ZZ*)-**40**, 101999-89-7; (*EE*)-**41**, 101999-90-0; (*EZ*)-**41**, 102046-63-9; (*ZZ*)-**41**, 101999-91-1; **42**, 54101-79-0; **45**, 77159-19-4; (*Z*)-**46**, 102046-64-0; (*EZ*)-**47**, 101999-92-2; (*ZZ*)-**47**, 102046-65-1; **48**, 88671-93-6; (*E*)-**50**, 101999-93-3; (*Z*)-**50**, 101999-94-4; **52**, 101999-95-5; (*EE*)-**54**, 102046-66-2; (*ZZ*)-**54**, 101999-96-6; (*EE*)-**55**, 101999-97-7; (*ZE*)-**55**, 101999-98-8; (*ZZ*)-**55**, 101999-99-9; **56**, 102000-00-0; **57**, 7490-33-7; (*E*)-**59**, 102000-01-1; (*Z*)-**59**, 102000-02-2; (*EE*)-**61**, 88816-29-9; (*ZZ*)-**61**, 102000-03-3; (*EE*)-**62**, 102000-04-4; (*EZ*)-**62**, 102000-05-5; (*ZZ*)-**62**, 102000-06-6; **63**, 34401-00-8; (*E*)-**65**, 102000-07-7; (*Z*)-**65**, 102000-08-8; (*EE*)-**67**, 102000-09-9; (*ZZ*)-**67**, 102000-10-2; **69**, 88656-03-5; *cis*-**69a**, 102000-11-3; *trans*-**69a**, 102000-12-4; **70**, 102000-13-5; *cis*-**70a**, 102000-14-6; *trans*-**70a**, 102000-15-7; **71**, 102000-18-0; *cis*-**71a**, 102000-19-1; *trans*-**71a**, 102000-20-4; **72**, 102000-21-5; *cis*-**72a**, 102000-22-6; *trans*-**72a**, 102129-59-9; **73**, 102000-23-7; *cis*-**73a**, 102000-24-8; *trans*-**73a**, 102130-34-7; **74**, 30614-34-7; *cis*-**74a**, 102000-16-8; *trans*-**74a**, 102000-17-9; cyclopentene, 142-29-0; cyclohexene, 110-83-8; *cis*-cycloheptene, 628-92-2; *cis*-cyclooctene, 931-87-3; *trans*-cyclooctene, 931-89-5; *cis*-cyclononene, 933-21-1; *trans*-cyclononene, 3958-38-1; *cis*-cyclodecene, 935-31-9; *trans*-cyclodecene, 2198-20-1; *cis*-cyclododecene, 1129-89-1; *trans*-cyclododecene, 1486-75-5; benzene, 71-43-2; 1,3,5-cycloheptatriene, 544-25-2; 1,3,5,7-cyclooctatetraene, 629-20-9.

Supplementary Material Available: Geometries of minimum energy conformations (111 pages). Ordering information is given on any current masthead page.

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Dimerization of Borirene to 1,4-Diboracyclohexadiene. Structures and Stabilities of $(CH)_4(BH)_2$ Molecules

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Abstract: Possible pathways for the dimerization of borirene (**1**) to 1,4-diboracyclohexa-2,5-diene (**3**) (DBCH) and to the more stable isomer 2,3,4,5-tetracarba-*nido*-hexaborane(6) (**5**) were studied by semiempirical and ab initio MO theory. Two possible paths of C_2 and C_i symmetry, respectively, were found for the dimerization of **1** to **3**; both involve highly nonplanar four-center transition states in which the boron acceptor orbitals play a crucial role. The low activation energy, ca. 11 kcal/mol for the C_2 path, indicates that borirenes will easily dimerize to DBCH's unless π-donor groups at boron or bulky substituents are present. Despite extensive searches, no low-energy pathway was found for the dimerization of **1** to **5**. Two paths were found for the "disproportionation" of two borirene molecules into 1,3-diboretene (**2**) and acetylene. This disproportionation reaction is nearly thermoneutral, and the activation energy (ca. 15 kcal/mol) is so low that we expect this reaction to occur for borirenes without π-donor substituents attached to boron. Several additional $(CH)_4(BH)_2$ isomers were also examined. The energies increase in the order carborane **5** < 1,4-diboracyclohexadiene (**3**) < 2,6-diborabicyclo[3.1.0]hexene (**7**) ~ 1,2,3,5-tetracarba-*nido*-hexaborane(6) (**6**) ~ 1,2-diboracyclohexa-3,5-diene (**4**) < 5,6-diborabicyclo[2.1.1]hexene (**8**).

The aromaticity of borirene (**1**) was first predicted by Volpin[2] and later discussed more extensively and quantified by Schleyer et al.[3,4] Several groups have recently reported the synthesis of borirene derivatives;[5-8] all of these have bulky substituents or a π-donor group at boron (Chart I). It has been suggested that borirenes carrying small substituents could readily dimerize to 1,4-diboracyclohexa-2,5-dienes (DBCH's, **3**).[5,9] Such facile dimerization could explain the formation of DBCH's from the reactions of acetylenes with $MeBBr_2$ and C_8K.[9-11] Derivatives of 2,3,4,5-tetracarba-*nido*-hexaborane(6) (**5**), a valence isomer of DBCH, were also obtained from these reactions,[9,12] and their formation could conceivably also involve the dimerization of borirenes.

We have now investigated computationally several possible reactions of two borirene molecules, viz., the dimerization to **3**

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Table I. Total and Relative Energies of $(CH)_4(BH)_2$ Isomers[a,b]

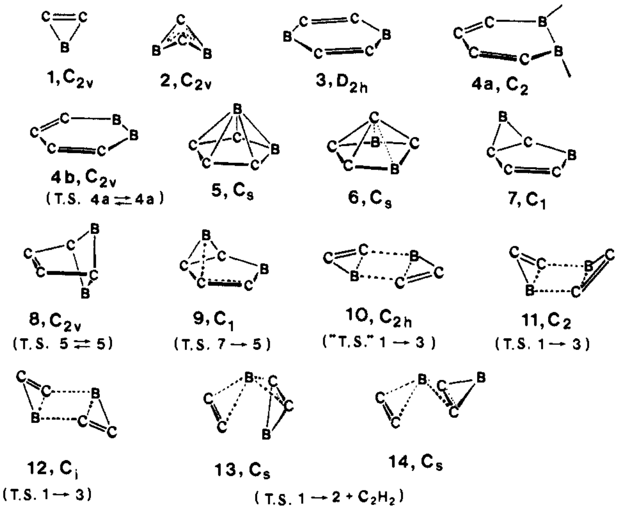
		E_{tot}, au			
molecule	MNDO	HF/3-21G// 3-21G	HF/6-31G// 3-21G	MP3/6-31G// 3-21G	HF/6-31G*// 3-21G
3	19.4	−203.164 66	−204.225 96	−204.691 83	−204.297 36
4a	38.7	−203.124 99	−204.192 29	−204.660 69	−204.264 48
4b	42.9	−203.124 96	−204.192 07	−204.659 38	−204.264 21
5	56.3	−203.144 41	−204.204 29	−204.699 22	−204.306 37[f]
6	67.6	−203.090 16	−204.147 54	−204.637 03	−204.247 70
7	46.9	−203.125 25	−204.184 15	−204.661 28	−204.264 40
8	58.3	−203.097 18	−204.149 78	−204.631 61	−204.234 13
10	219.3	−202.875 24	−203.930 71	−204.403 04	−204.013 83
11	131.2[c]	−203.000 90	−204.057 84	−204.558 77	−204.155 76
12	137.9[d]	−202.984 34	−204.041 95	−204.545 40	−204.140 75
13	137.9	−202.973 57	−204.030 72	−204.540 05	−204.130 79
14	137.5	−202.976 35	−204.032 58	−204.541 81	−204.133 10
1 + 1	103.0	−203.045 34	−204.106 36	−204.577 34	−204.203 52
2 + C_2H_2	90.0	−203.045 59	−204.104 23	−204.587 03	−204.183 98

	E_{rel}, kcal/mol					
molecule	MNDO	HF/3-21G// 3-21G	HF/6-31G// 3-21G	MP3/6-31G// 3-21G	HF/6-31G*// 3-21G	ΔE[e]
3	−36.9	−12.7	−13.6	4.6	5.7	23.9
4a	−17.6	12.2	7.5	24.2	26.3	43.0
4b	−13.4	12.2	7.7	25.0	26.5	43.8
5	0.	0.	0.	0.	0.	0.
6	11.3	34.1	35.6	39.0	36.8	40.2
7	−9.4	12.0	12.6	23.8	26.3	37.5
8	2.0	29.6	34.2	42.4	45.3	53.5
10	163.0	168.7	171.7	185.9	183.6	197.8
11	74.9[c]	90.1	91.9	88.1	94.5	90.7
12	81.6[d]	100.4	101.9	96.5	103.9	98.5
13	81.6	107.2	108.9	99.9	110.2	101.2
14	81.2	105.5	107.7	98.8	103.1	94.2
1 + 1	46.7	62.2	61.5	76.5	64.5	79.6
2 + C_2H_2	33.7	62.0	62.8	70.4	76.8	84.4

[a] Energies with 6-31G and 6-31G* basis sets at HF/3-21G geometries. [b] The barrier for the reaction **7** → **5** is less than 0.2 kcal/mol at HF/3-21G, which is too small to allow a satisfactory optimization of the transition state **9**. [c] Transition-state optimization in C_1 symmetry produces an unsymmetrical transition state with $\Delta H_f° = 129.4$ kcal/mol, $E_{rel} = 73.1$ kcal/mol. [d] Transition-state optimization in C_1 symmetry produces an unsymmetrical transition state with $\Delta H_f° = 131.2$ kcal/mol, $E_{rel} = 74.9$ kcal/mol. [e] Estimated as ΔE(HF/6-31G*//3-21G + MP3/6-31G//3-21G − HF/6-31G//3-21G). This applies the MP3/6-31G correlation corrections to the HF/6-31G* relative energies. [f] At 6-31G*//6-31G*, the energy (−204.310 04) is lowered by only 2.3 kcal/mol.

and to **5** as well as the disproportionation to acetylene and 1,3-diboretene (**2**).[2,5,13-16] In addition, we have studied the two $(CH)_4(BH)_2$ molecules **3** and **5** and some of their isomers (**4** and **6**–**8**) in detail. Several DBCH derivatives, both free[9,10,17-19] and complexed to transition metals,[1,8,20-23] have been reported.

Chart I



Carborane **5** has been prepared by pyrolysis of 1,2-tetramethylenediborane(6)[24] or from acetylene and 1,2-$C_2B_3H_7$,[25] and its structure has been determined.[26] Alkylated derivatives of **5** have also been reported[9,12,25,27,28] and structurally characterized;[29] they are gen-

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(11) The formation of DBCH's in this reaction[9,10] has recently been questioned by Schlögl and Wrackmeyer.[12] Careful reexamination of the earlier results[5,9,10] supports the formation of DBCH products, as originally reported. However, in this paper we do not make any attempt to interpret the earlier experimental data; we only delineate the theoretical possibilities for borirene dimerization. Experimental aspects of this problem will be discussed elsewhere (Van der Kerk, S. M.; Budzelaar, P. H. M.; Van der Kerk-van Hoof, A., unpublished results).

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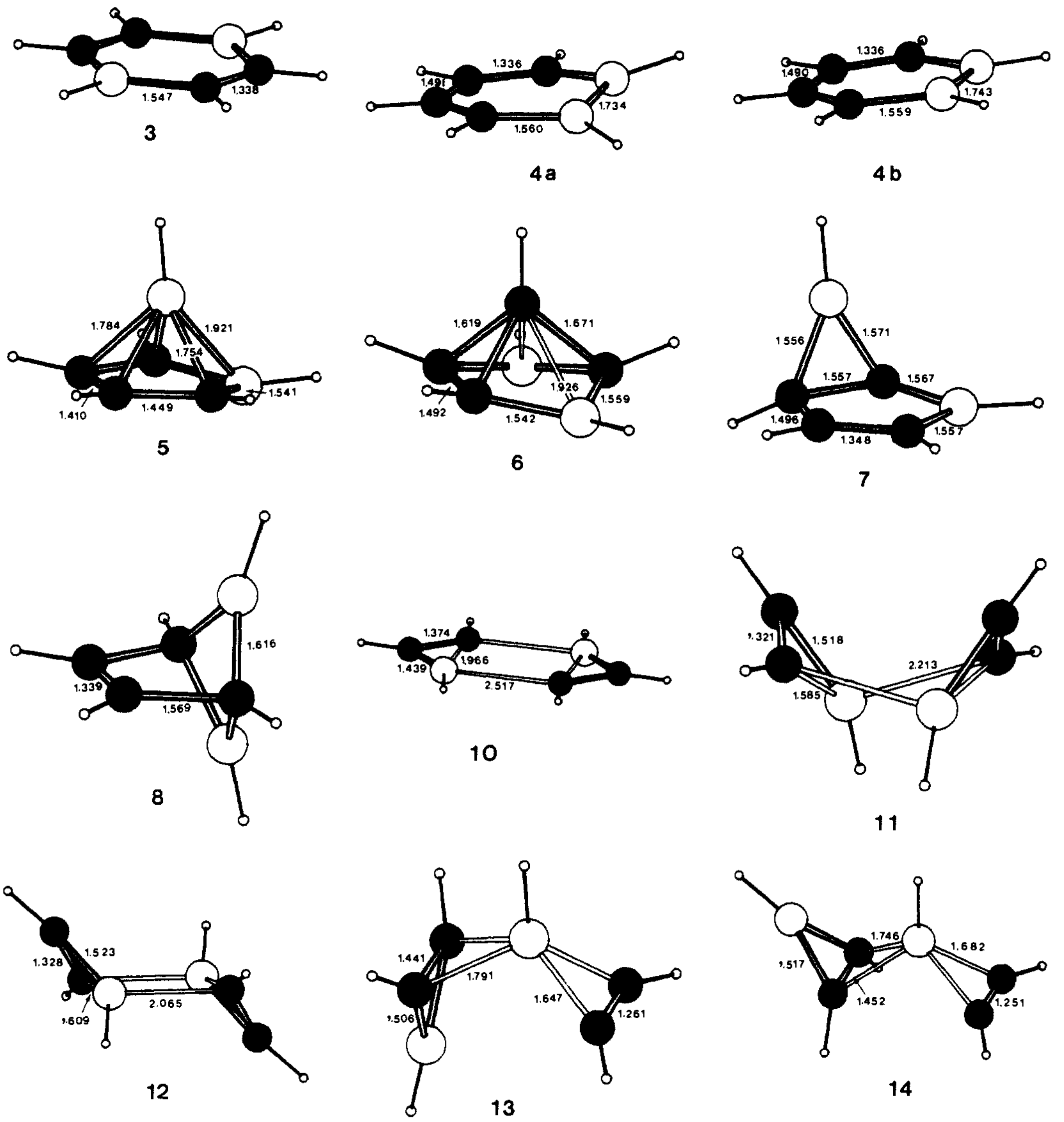

Figure 1. Ball-and-stick drawings and selected HF/3-21G bond lengths for **3**–**14**. See Table III for 6-31G* bond lengths for **5**.

erally more stable and inert than the DBCH's. The two types of molecules have never been observed to interconvert. A derivative of the bicyclic structure **7** has recently been reported by Herberich to have a fluxional structure.[30]

Wade's rules[31] and the six-interstitial-electron rule[32] predict that the *nido*-carborane **5** will be the most stable $(CH)_4(BH)_2$ structure. However, PRDDO calculations by Lipscomb suggested that **3** is not much higher in energy than **5** and might be an intermediate in transformations of the carborane.[33] Our calculations are intended to provide more accurate data concerning the relative stabilities of classical (**3**, **4**, **7**, and **8**) and nonclassical (**5** and **6**) isomers.

Theoretical Procedures

The geometries of structures **3**–**14** were optimized completely, subject only to overall molecular symmetry constraints, with MNDO[34] and ab initio methods using the restricted Hartree–Fock (RHF) formalism.[35] A modified version of the MOPAC package,[36] supplemented with a separate routine for optimizing transition states,[37] was employed for the MNDO calculations. The ab initio calculations were carried out with the GAUSSIAN-82[38a] and GAMESS[38b] programs, using first the minimal STO-3G basis[39a] (HF/STO-3G//STO-3G) and then the small split-valence 3-21G basis[39b] (HF/3-21G//3-21G) for the geometry optimizations. HF/3-21G geometries for **1**[4] and **2**[15] were taken from earlier work. Energy refinements were obtained from single-point calculations at the 3-21G-optimized geometries using the 6-31G* split-valence + polarization basis[39c] (HF/6-31G*//3-21G), and correlation corrections were estimated by using Møller–Plesset third-order perturbation theory[40] with the 6-31G

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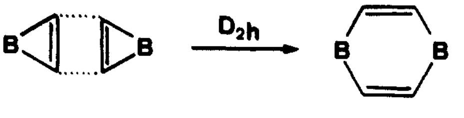
basis[39d] (MP3/6-31G//3-21G). Total and relative energies are given in Table I. Unless specified otherwise, the relative energies quoted in the text are "best" ab initio values estimated as ΔE[HF/6-31G*//3-21G + MP3/6-31G//3-21G − HF/6-31G//3-21G], i.e., by applying the correlation corrections calculated with a split-valence basis set to the relative Hartree–Fock energies obtained with a polarized basis set. The most important geometrical details (3-21G optimization results) of **3**–**14** are shown in Figure 1. The most stable isomer, **5**, was reoptimized at 6-31G*; details are given in Table III. Complete specifications of the geometries (Z matrices and Cartesian coordinates) are available as supplementary material.

Dimerization of Borirene to 1,4-Diboracyclohexadiene (3)

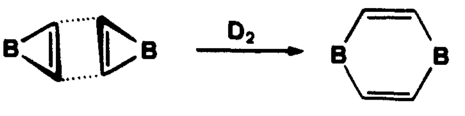
The highest symmetry in which a borirene could dimerize to a DBCH derivative is D_{2h} (eq 1). However, this mode of dimerization is forbidden both thermally and photochemically. The



(1)

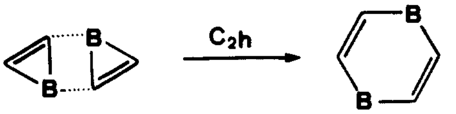
situation is entirely comparable to that of the dimerization of silirene, and OCAMS[41] gives the two possible symmetry lowerings that will make the reaction allowed (eq 2 and 3). The first

a_u distortion



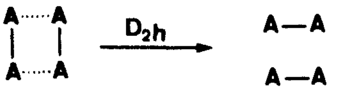
(2)

b_{1g} distortion



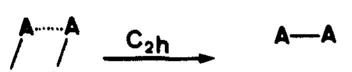
(3)

possibility is analogous to an uncatalyzed olefin metathesis and is expected to be very unfavorable. The second possibility was investigated further and the C_{2h} "transition state" **10**[42] was located. The activation energy for this pathway is, however, prohibitively high (118 kcal/mol, see Table I). This could have been anticipated. The metathesis reaction (4) involving only σ-orbitals is symmetry-forbidden; the "offending" symmetry elements are the mirror planes bisecting the A–A bonds.

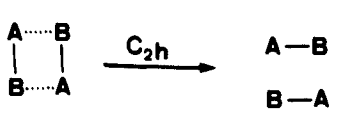


(4)

Lowering the symmetry of the system to C_{2h} destroys these symmetry elements and the reaction is now formally allowed (eq 5). A similar result is obtained when two diametrically opposed A atoms are replaced by B atoms (eq 6). As long as the degree



(5)



(6)

of asymmetry is not very large, however, one would not expect the activation energy to become much smaller than that of the "forbidden" reaction. The boron–carbon bond is not very polar, and the major difference between boron and carbon, namely the presence of an empty acceptor orbital on B, cannot affect the C_{2h} mechanism. Thus, although the C_{2h} mechanism is formally allowed, it is clearly not realistic. A more favorable dimerization pathway would utilize the boron acceptor orbitals. There are two possible distortions from C_{2h} symmetry which enable these orbitals to participate, eq 7 and 8.

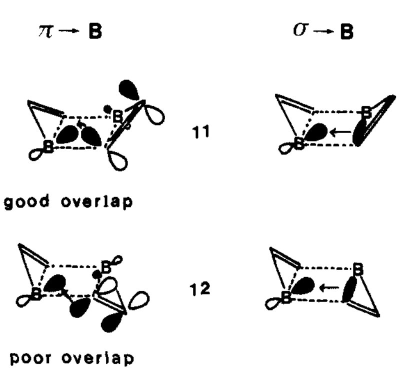
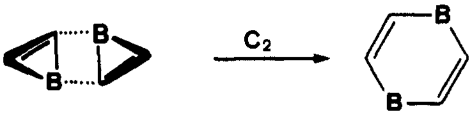


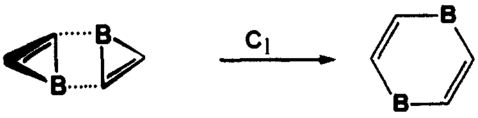
Figure 2. Important orbital overlaps in the transition states **11** and **12** for borirene dimerization.

a_u distortion



(7)

b_g distortion



(8)

The first of these possibilities is actually a combination of the a_u and b_{1g} distortions of the initial D_{2h} mechanism. The two transition states **11** and **12**[44] were located and are indeed found to be much lower in energy than the C_{2h} structure **10** (Table I): the activation energy calculated for the C_2 path is only 11 kcal/mol! Both **11** and **12** are highly nonplanar structures. Involvement of the boron acceptor orbitals, resulting in decreased delocalization in the borirene ring systems, is indicated by the geometries (Figure 1).

The C_2 transition state **11** is somewhat more favorable than the C_i transition state **12** (by 8 kcal/mol) which may be explained as follows. In the initial stages of the C_2 mechanism, each boron atom acts as an acceptor for the C–C π-bonding orbital of the other borirene molecule. In **11** the boron acceptor orbital overlaps with both the C–C π-bond and the B–C σ-bonding orbital (see Figure 2). In the C_i mechanism, the relative orientations of the B acceptor orbitals and the C–C π-bonds are unfavorable, so that **12** is not stabilized by olefin π-complexation to boron (Figure 2).

Actually, it would not have been necessary to arrive at these transition states by such a circuitous reasoning. The C_2 and C_i mechanisms are simply the two possibilities derived from the normal four-center exchange mechanism of trialkylboron compounds[46] (eq 9) by choosing either $R^1R^2 = R^{1\prime}R^4 =$ —CH=CH—,

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[41] Katriel, J.; Halevi, E. A. *Theor. Chim. Acta* **1975**, *40*, 1. Halevi, E. A. *Helv. Chim. Acta* **1975**, *588* 2136. Halevi, E. A. *Angew. Chem.* **1976**, *88*, 664. Halevi, E. A.; West, R. *J. Organomet. Chem.* **1982**, *240*, 129.

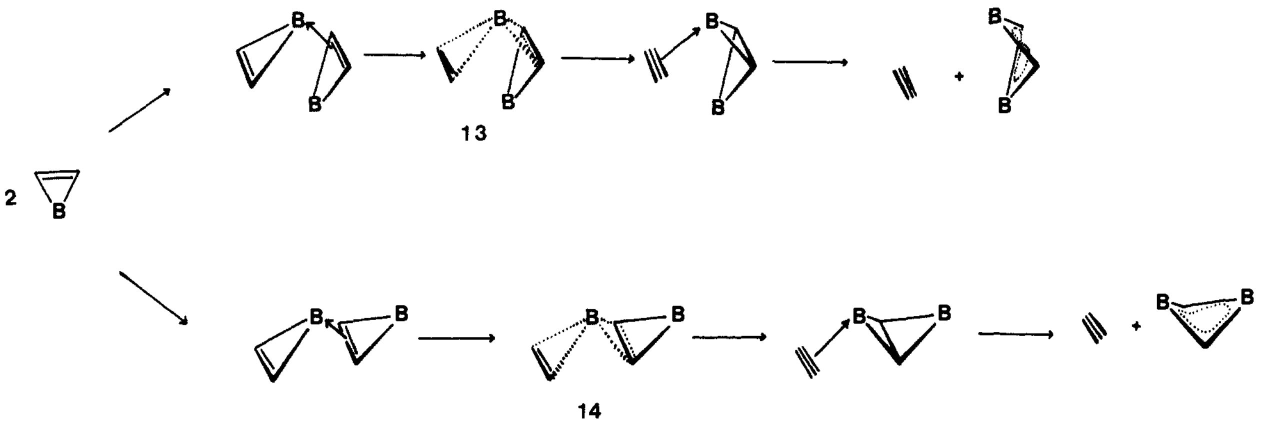
[42] This is not a real transition state, as diagonalization of the Hessian matrix[43] gives not one but five negative eigenvalues (at the MNDO level). The most negative of these corresponds to the dimerization reaction, the other four to distortions toward the nonplanar structures discussed in the text.

[43] Murrell, J. N.; Laidler, K. J. *Trans. Faraday Soc.* **1968**, *64*, 371. Stanton, R. E.; McIver, J. W. Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3632.

[44] At the MNDO level, the Hessian matrices[43] of both **11** and **12** have two negative eigenvalues, and further optimizations lead to two different transition structures of C_1 symmetry (see footnotes to Table I). This is, however, an artifact of MNDO, and a frequency analysis at the ab initio RHF/STO-3G level showed **11** (C_2 symmetry) to have only one imaginary frequency. It has been noted before that MNDO tends to make transition states too unsymmetrical.[45]

[45] Caramella, P.; Houk, K. N.; Domelsmith, L. N. *J. Am. Chem. Soc.* **1977**, *99*, 4514. Bernardi, F.; Bottoni, A.; Robb, M. A.; Field, M. J.; Hillier, I. H.; Guest, M. F. *Chem. Commun.* **1985**, 1051. Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554.

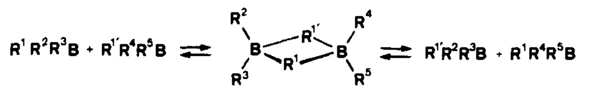
Chart II



(13)

(14)

$R^3 = R^5 = H$ (**11**), or $R^1R^2 = R^{1'}R^5 = —CH{=}CH—$, $R^3 = R^4 = H$ (**12**).



(9)

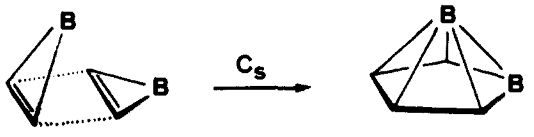
11

12

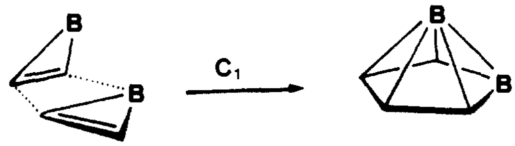
The considerations given above do, however, illustrate the symmetry aspects of the dimerization and also emphasize the orbital interactions which are necessary. This background is particularly useful when considering the dimerization to the alternative product, the carborane **5**.

Dimerization of Borirene to Carborane 5

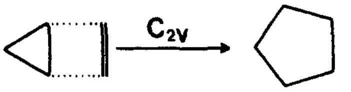
There are two simple ways in which **1** could be visualized dimerizing to **5** (eq 10 and 11). The first mechanism is forbidden in C_s symmetry, so we attempted at first to find a pathway for the second, allowed C_1 mechanism. However, extensive potential-surface scans at both the MNDO and ab initio levels failed to reveal a path leading from two molecules of **1** to **5**. As in the formally allowed C_{2h} mechanism (3), the C_1 mechanism (11) *does not* utilize the boron acceptor orbitals, and thus the "allowedness" is again only formal. The addition of ethene to cyclopropane to give cyclopentane is forbidden in C_{2v} symmetry (eq 12). Although the asymmetry introduced by the boron atoms and the extra C–C π-bond is considerable, the reaction still occurs primarily at the three carbon atoms and in the σ-system of one boron atom, so there is really no reason to expect a low activation energy for (11).



(10)



(11)



(12)

Having obtained these negative results, we considered the "forbidden" C_s path (10). This reaction cannot be described properly at the closed-shell restricted Hartree–Fock level, so a two-configuration wave function was used in attempts to locate a reasonable reaction path. However, despite many extensive and time-consuming searches, the only reaction found was the transfer of a borylene unit from one borirene molecule to another (vide infra). So, we conclude that there is no low-energy pathway for the dimerization of **1** to **5**.

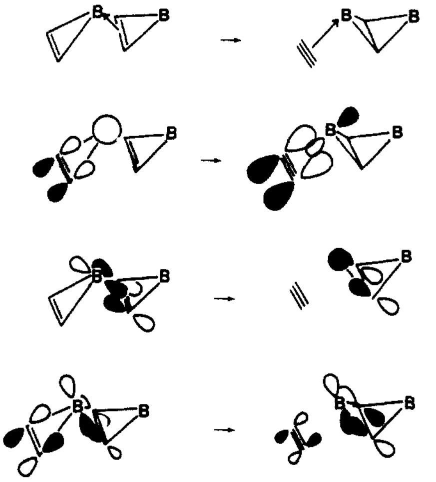


Figure 3. Orbital changes in the disproportionation of borirene to diboretene and acetylene via **14**.

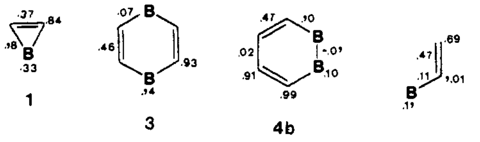


Figure 4. HF/3-21G π-orbital and overlap populations in **1**,[4] **3**, **4a**, and vinylborane.[4]

Disproportionation of Borirene to Diboretene (2) and Acetylene

The disproportionation of two borirenes, which results in the transfer of a BH group, can proceed via two paths, both of C_s symmetry. They differ in the relative orientation of the borirene rings. The anti path (14) via **14** is lower in energy (by 7 kcal/mol) than the syn path (13) via **13**, probably for steric reasons (Chart II).

In both cases, the first stage of the reaction is complexation of one C–C π-bonding orbital with the boron p_π acceptor orbital of another borirene molecule. The changes in the orbitals are illustrated in Figure 3 for the anti path. The initial result of the BH transfer is a complex of a diborabicyclobutane with acetylene. In the last stage of the reaction, the C–C σ-bond opens to form the delocalized π-orbital of 1,3-diboretene.[3,15,16] This decreases the acceptor character of the boron atoms and the acetylene molecule is expelled.

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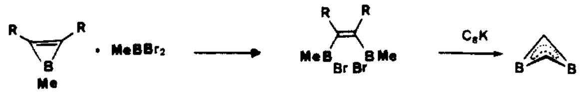
[46] Parsons, T. D.; Ritter, D. M. *J. Am. Chem. Soc.* **1954**, *76*, 1710. Hennion, G. F.; McCusker, P. A.; Ashby, E. C.; Rutkowski, A. J. *J. Am. Chem. Soc.* **1957**, *79*, 5190.

Table II. Bond Lengths (Å) in 1,4-Diboracyclohexadienes

compound	method	ref	C–C	B–C	B–X[c]
$(CH)_4(BH)_2$	MNDO	*a*	1.357	1.538	1.161
	HF/STO-3G	*a*	1.328	1.561	1.162
	HF/3-21G	*a*	1.338	1.574	1.192
$(CH)_4(BF)_2$	MNDO	*a*	1.352	1.558	1.310
$(CMe)_4(BF)_2$	X-ray	18[b]	1.329	1.577	1.306
			1.350	1.558	1.303
$[(CMe)_4(BF)_2]_2Ni$	X-ray	21	1.392	1.531	1.359
$[(CMe)_4(BF)_2]Ni(CO)_2$	X-ray	18	1.395	1.527	1.386
$[(CH)_4(BMe)_2]CoC_5H_5$	X-ray	20	1.423	1.514	1.593
$[(CH)_4(BMe)_2]$-$[RhC_5H_5]_2^{2+}$	X-ray	22	1.44	1.54	

[a] This work. [b] The unit cell contains two crystallographically independent DBCH molecules. [c] X refers to the exocyclic atom or group attached to B.

According to our calculations, this BH transfer is slightly endothermic (by ca. 5 kcal/mol). However, substituents at boron and carbon might easily change this value. In particular, alkyl substituents are better at stabilizing triple bonds than double bonds[47] so that alkyl groups at carbon could make the reaction exothermic. Combined with the low activation energy (ca. 15 kcal/mol via **14**), this suggests that a borylene-transfer reaction could be responsible for the formation of the diboretene in the t-$Bu_2C_2/MeBBr_2/C_8K$ reaction,[5] although other routes cannot be excluded, e.g., (15).[12]



(15)

1,4- and 1,2-Diboracyclohexadienes, 3 and 4

The DBCH's **3** and **4** are isoelectronic with the 4π-electron benzene dication.[48,49] The degeneracy of the original e_{1g}-type HOMO's of $C_6H_6^{2+}$ has been removed by the substitution of B for C^+, and both **3** and **4** contain largely localized C=C double bonds. The modest delocalization of π-electron density from C to B is comparable to that in vinylborane[4,50] but much smaller than that in the aromatic borirene **1**[3,4] (Figure 4).

Interestingly, 1,2-DBCH prefers a nonplanar geometry **4a** of C_2 symmetry to the planar C_{2v} structure **4b**. The ring carbon and boron atoms in **4a** are nearly coplanar, but the H(B) atoms are bent significantly out of the ring plane (see Figure 1; the HBBH dihedral angle is 67° at MNDO, 46° at HF/STO-3G, and 22° at HF/3-21G but will probably increase again with polarized basis sets). This bending has the effect of reorienting the boron 2p orbitals so that the B–B π-interaction is much reduced while the B–C conjugation remains largely intact. The deformation is a consequence of the Hückel 4π-electron antiaromaticity of the 1,2-DBCH system: interrupting the cyclic conjugation actually lowers the total energy.

The DBCH's have two occupied π-orbitals and a low-lying empty π-acceptor orbital, which could be used in the formation of transition-metal complexes. Several such derivatives of **3** are known.[18,20–23] The crystals of $[(CMe)_4(BF)_2]Ni(CO)_2$ contain both complexed and uncomplexed ligands, and the X-ray structure determination[18] thus allows a comparison of the calculated geometries of **3** with those of $(CMe)_4(BF)_2$ and an assessment[18] of the structural changes accompanying complexation. Relevant details are given in Table II; both MNDO and ab initio calculations satisfactorily reproduce the geometry of **3**. On complexation of the 1,4-F_2DBCH to nickel, the B–C bonds are shortened and the C–C bonds are lengthened as expected. The largest change, however, occurs in the B–F bonds, which indicates that the B–F π*-orbitals are the main ligand acceptor orbitals in these complexes. In the complexes of 1,4-Me_2DBCH, where such orbitals are absent, the bond length changes within the ring are more pronounced because the C–C-antibonding, B–C-bonding π*-LUMO is now the main acceptor.

Derivatives of 1,4-DBCH with and without π-donor groups attached to boron are known.[9,10,17,19] Although all derivatives are sensitive to hydrolysis and oxidation, they are reasonably stable thermally. In contrast, no 1,2-DBCH (**4**) derivatives have been reported. This is probably due to the high reactivity of the B–B single bond; bulky substituents or π-donor groups on boron might confer enough stability to allow isolation.

2,3,4,5-Tetracarba-*nido*-hexaborane(6), 5

According to Wade's rules,[31] a carborane having the composition $(CH)_4(BH)_2$ should prefer a nido structure like **5**, a pentagonal pyramid. This possesses six interstitial electrons and can be considered to be a three-dimensional aromatic system.[32] The structures of $C_4B_2H_6$[26] and its hexamethyl derivative[29] have been determined and confirm these expectations. While it would seem that these structure determinations provide adequate reference data for comparison with our calculational results, this turns out not to be the case.

The structure of the hexamethylcarborane was determined by electron diffraction (ED),[29] which is not a very suitable technique for molecules containing so many similar bond lengths. The reported B–methyl distances (1.264 (15) and 1.472 (30) Å) are much too small, and the C–methyl bonds (1.592 Å) are somewhat too long. More importantly, the basal boron atom was reported to be bent out of the plane of the four carbon atoms *toward* the apical boron atom, whereas both experimental data[26] and our theoretical results for $C_4B_2H_6$ insist on a sizable tilting *away* from the apex. Finally, all methyl groups were reported to be tilted out of the basal plane away from the apical boron (by 40° for the Me(B) group!), whereas the hydrogens in **5** were calculated to be tilted toward apical positions. It seems that only very few features of this structure determination can be relied upon.

The microwave (MW) study of $C_4B_2H_6$[26] is probably more accurate. Unfortunately, the sign of one of the carbon coordinates could not be determined, leaving two possible solutions, one of which was thought to have more realistic bond lengths than the other. The hydrogen atomic positions were not determined. Table III compares the MNDO and ab initio fully optimized HF/STO-3G, HF/3-21G, and HF/6-31G* geometries of **5** with the two MW structures (I and II) and with the ED structure of the hexamethyl derivative. All the ab initio geometries show nice agreement with the most likely MW structure I of **5**, whereas the MNDO geometry is closer to the alternative MW structure II. However, the MNDO structure is almost certainly incorrect, as discussed below. Thus, our results do support the preference of Pasinski and Baudet[26] for MW structure I.

Pyramidal **5** can be formally constructed from an aromatic $C_4BH_5^{2-}$ ring and a BH^{2+} cap.[32] The isoelectronic $C_6H_6^{2+}$, which can be built similarly from $C_5H_5^-$ and CH^{3+}, has a regular pentagonal pyramidal shape.[48,49] The perturbing influence of the ring boron atom results in a shift of π-density toward the more electronegative carbon atoms. Therefore, the capping BH^{2+} group will bond most strongly to the carbon atoms and much less to the ring boron atom. This is reflected in the overlap populations (Figure 5) and in the bending away of the basal boron atom. The calculations show the hydrogen atoms to be tilted toward the apical boron atom. Such a bending improves the overlap between the basal ring π-orbitals and the p orbitals of the capping atom[51] and has also been predicted for *nido*-$C_6H_6^{2+}$.[48]

Although MNDO generally produces reliable geometries and energies for organic compounds having classical structures,[34] its performance for nonclassical boranes and carboranes is much less

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[47] C.f., the energy change of +4.2 kcal/mol in the reaction $CH_3C{\equiv}CH + CH_2{=}CH_2 \rightarrow HC{\equiv}CH + CH_3CH{=}CH_2$ (RHF/6-31G*//6-31G* data from: Whiteside, R. A.; Frisch, M.; Pople, J. A. *Carnegie*-Mellon Quantum Chemistry Archive, 3rd ed.; Carnegie-Mellon: Pittsburgh, 1983).

[48] Lammertsma, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 1049 and references cited.

[49] Dewar, M. J. S.; Holloway, M. K. *J. Am. Chem. Soc.* **1984**, *106*, 6619.

[50] Allinger, N. L.; Siefert, J. H. *J. A. Chem. Soc.* **1975**, *97*, 752. Williams, J. E., Jr.; Streitwieser, A., Jr. *Tetrahedron Lett.* **1973**, 5041.

[51] Alexandratos, S.; Streitwieser, A., Jr.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1976**, *98*, 7959.

Table III. Structural Data for **5** and Me_6-**5**[a]

molecule	method[d]	ref	B1C2	B1C3	B1B6	C2C3	C3C4	C2B6	τ[b]
$C_4B_2H_6$	MW I	26	1.709	1.697	1.886	1.436	1.424	1.541	10
	HF/STO-3G	*c*	1.702	1.720	1.863	1.447	1.417	1.506	9
	HF/3-21G	*c*	1.753	1.783	1.921	1.449	1.410	1.541	10
	HF/6-31G*	*c*	1.714	1.729	1.859	1.437	1.401	1.529	8
	MW II	26	1.531	1.697	1.886	1.486	1.424	1.585	38
	MNDO	*c*	1.623	2.009	1.977	1.518	1.392	1.568	40
$C_4B_2Me_6$	ED	29	1.447	1.534	1.719	1.436	1.452	1.755	−10

[a] Distances in Å, angles in deg. [b] Angle between C2C3C4C5 and C2C5B6 planes; a positive (negative) value denotes tilting of B6 away from (toward)B1. [c] This work. [d] MW = Microwave (possible solutions I and II[26]); ED = electron diffraction.

5 **6**

Figure 5. HF/STO-3G total overlap populations in **5** and **6**.

satisfactory.[52] Particularly large errors have been found for molecules having five- and six-coordinate boron or carbon atoms: in such cases, MNDO erroneously predicts distortions which lower the coordination numbers of these atoms.[52] The failure of MNDO to account for the stability of $C_6H_6^{2+}$ has been noted before;[48,49] a similar failure occurs in this case and results in a large deformation of **5** toward the classical isomer **8**.[52] Since **8** is a transition state for the topomerization of **5** and no exchange between boron atoms has ever been observed in NMR spectra of **5** and its alkyl derivatives,[24,25,28] the topomerization barrier must be at least 20 kcal/mol and the MNDO value of 2 kcal/mol is much too low. Thus, MNDO cannot properly account for the multicenter bonding in **5** and produces unrealistic energies and geometries. MINDO/3 has been found to give better results for some nonclassical carbocations, including pyramidal $C_6H_6^{2+}$.[49] However, MINDO/3 results for boron compounds are generally too poor to make the method useful here.

We have also studied an isomer of **5**, namely 1,2,3,5-tetracarba-*nido*-hexaborane(6) (**6**), briefly. However, this molecule is 40 kcal/mol higher in energy than **5** and is predicted to have a nearly classical tricyclohexane-like geometry. The large distances between the borons and the capping carbon atom clearly show the strong reluctance of more electronegative and contracted atoms to occupy highly coordinated sites in carboranes.[32] The localized character of the bonds is also indicated by the overlap populations (Figure 5). The final pyramidal structure, 1,2,3,4-tetracarba-*nido*-hexaborane(6), with an apical carbon and two adjacent borons in the basal ring, was not expected to be favorable and was studied at the MNDO level only. (Isomers with separated boron atoms are generally much lower in energy than those with adjacent borons, e.g., **3** vs. **4** (see Table I), 1,2- vs. 1,3-diboracyclobutane, and 1,2- vs. 1,3-dihydrodiboretе).[3] MNDO optimization gave a completely classical 2,3-diboratricyclo[2.1.1.0^{5,6}]hexane geometry of C_{2v} symmetry; the heat of formation of 95.7 kcal/mol makes it the least stable $(CH)_4(BH)_2$ isomer by far, and we decided not to pursue this species further.

Classical Structures 7 and 8: Alternatives for Carborane 5

The C_{2v} diboracyclohexene **8** was considered by Lipscomb to be a possible intermediate in reactions of **5**.[33] Actually, **8** is not a local minimum but a transition state for the topomerization of **5**; the absence of NMR evidence for such a topomerization[24,25,28] indicates that **8** is at least 20 kcal/mol higher in energy than **5**, in agreement with our ab initio results (54 kcal/mol). The alternative classical structure **7** not considered by Lipscomb is lower in energy than **8** (by 16 kcal/mol). A rapid equilibrium between **5** and **7** cannot be detected by NMR techniques, but we can exclude such an equilibrium on the basis of the ab initio results, which place **7** 38 kcal/mol above **5**. The activation energy for the isomerization **7** → **5** is very low, 1.3 kcal/mol at HF/STO-3G and <0.2 kcal/mol at HF/3-21G; at higher levels of theory, where the energy difference between **5** and **7** is larger, **7** probably no longer is a local minimum.

π-Donor substituents could be expected to alter the relative energies of **5**, **7**, and **8**;[33] this has been confirmed by recent experiments of Herberich.[30] The introduction of a π-donor group at the basal boron atom in **5** would further decrease the already weak B–B bonding. A significant destabilization of the cage structure should result. Such a derivative (with $N(i\text{-Pr})_2$ at B6 and CH_3 at B1) has been prepared and is found to be extremely reactive.[30] In contrast, peralkylated derivatives of **5** show an extraordinary chemical and thermal stability.[27] The introduction of a π-donor group at the *second* boron atom would destroy the carborane structure altogether, as the capping atom can no longer interact effectively with all of the ring π-orbitals. Indeed, NMR investigations have indicated $(CH)_4[BN(i\text{-Pr})_2]_2$ to prefer the classical structure **7**;[30] at room temperature a rapid topomerization via **8** or less probably via **5** takes place, but at low temperatures four different signals were observed for the ring carbons.

MNDO seriously underestimates the stability of the carborane **5** (Table I), and even RHF/3-21G makes **5** much too unstable. Polarization functions are needed for a good description of the highly strained **7**, and both polarization functions and electron correlation corrections are seen to favor the nonclassical **5**. The final ordering of stabilities, **5** < **3** < **7** ~ **6** ~ **4** < **8**, seems reasonably certain, and this makes **5** the global $(CH)_4(BH)_2$ minimum. DBCH **3** is not much higher in energy, but the interconversion between **3** and **5**, as postulated by Binger,[27] is in fact forbidden in C_s symmetry. Indeed, hexaalkyl derivatives of both **3**[9,10] and **5**[9,27,28] have been reported and show no evidence of isomerization reactions.

Conclusions

DBCH derivatives can be readily formed by dimerization of borirenes. The reaction has a very low activation energy (11 kcal/mol) and proceeds via a highly nonplanar four-center transition state. The boron acceptor orbitals are very important in this reaction, and π-donor groups at boron will hinder the dimerization. Because of the close approach of two boron and two carbon atoms in the transition state, bulky groups could also inhibit this dimerization.

The other possible reaction of two borirenes, disproportionation into 1,3-diboretene and acetylene, has an activation energy of 15 kcal/mol. Our calculations predict this BH exchange to be nearly thermoneutral. Like the dimerization, it will be hindered by π-donor groups at boron, but the influence of bulky substituents should not be as large since the transition state is less crowded. Dimerization to a carborane, although energetically the most favorable reaction, does not occur because no low-energy pathway is available.

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[52] Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231.

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Supplementary Material Available: HF/STO-3G//STO-3G and MP2/6-31G//3-21G energies and complete specifications (Z matrices and Cartesian coordinates) of the MNDO, HF/STO-3G, and HF/3-21G geometries of **3–14** (41 pages). Ordering information is given on any current masthead page.

Azadiboridine and Diazaboridine: Aromatic and Antiaromatic Three-Membered-Ring Prototypes

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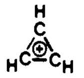
Abstract: The heterocycles azadiboridine (**5**) and diazaboridine (**6**) were studied by using ab initio MO methods. The 2π-species **5** (C_{2v}) has a large resonance energy of ca. 55 kcal/mol, but only a small part of this (ca. 6 kcal/mol) is due to the cyclic delocalization, and the B–B π-bond is weak. The 2,3-diamino derivative also prefers an all-planar geometry (**5b**), and the observed coplanar/perpendicular conformation of 1-*tert*-butyl-2,3-bis(2,2,6,6-tetramethyl-1-piperidino)azadiboridine (**5a**) must be due to steric effects. The 4π-species **6** prefers a strongly nonplanar geometry and has a small delocalization energy resulting from opposing B–N π-bonding (ca. 48 kcal/mol) and antiaromatic destabilization (ca. 35 kcal/mol). The derivatives of **6** isolated to date bear amino substituents at boron, and our calculations indicate that the amino group in **6e** helps to relieve the antiaromatic destabilization by reducing the unfavorable cyclic 4e π-conjugation.

While benzene and cyclobutadiene are the smallest neutral carbocycles with $4n + 2$ and $4n^1$ π-electrons, the energetic effects of aromaticity and antiaromaticity are expected to be much larger in three-membered ring systems. Thus, the cyclopropenium ion (**1**) has more than twice the resonance energy of benzene,[2] and the cyclopropenyl anion (**2**) is indicated not to be a bound species as an isolated entity.[3]



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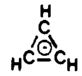

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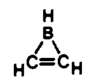

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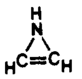

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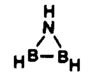

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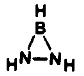

6

Many features of the charged systems are not readily measurable. Only energies are available in the gas phase, and strong ion–solvent or ion–gegenion interactions influence the behavior in the condensed phases.[4] Hence, the neutral isoelectronic heterocyclic analogues, e.g., borirene (**3**)[2a,5] and azirine (**4**),[6] have long been of interest. Only recently have derivatives of **3** been prepared,[7] but **4** remains unknown experimentally.[6]

Theoretical calculations are ideally suited to provide geometries, energies, electronic structures, and indeed deeper insights into the causes and effects of π-electron interactions. Small-ring systems are particularly attractive for fundamental studies, and **1–4** have been thoroughly investigated computationally.[2–6,8,9]

The recent syntheses[10,11] of derivatives of the neutral heterocycles, azadiboridine (**5**) and diazaboridine (**6**), allow the com-

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(4) C.f., the behavior of 3-cyclopropenyllithium (Schleyer, P. v. R.; Kaufmann, E.; Spitznagel, G. W.; Janoschek, R.; Winkelhofer, G. *Organometallics* **1986**, *5*, 79.

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