ORGANOMETALLICS

Volume 4, Number 3, March 1985

Effects of Boron Substituents in Borirenes, Boriranes, and Boranes. The Energies of B–X Bonds

Peter H. M. Budzelaar, Alexander J. Kos, Timothy Clark, and Paul von Ragué Schleyer*

Institut für Organische Chemie der Universität Erlangen-Nürnberg,
D-8520 Erlangen, Federal Republic of Germany

Received July 17, 1984

The effects of first-row substituents Li, BeH, BH_2, CH_3, NH_2, OH, and F on the structures and stabilities of boranes, boriranes, and borirenes were investigated by ab initio methods. Due both to σ and to π effects, bonds of the electronegative groups CH_3, NH_2, OH, and F to boron are considerably stronger than the corresponding bonds to carbon. The borirane system has a high strain energy, ca. 16 kcal/mol higher than that of cyclopropane; this is probably a major contributor to the difficulties encountered in preparing compounds of this type. Borirene shows a large resonance energy of about 47 kcal/mol. This compensates for the strain of the small ring system, and substituted borirenes are expected to be chemically more stable than the corresponding boriranes. This is also indicated by the relative energies of the open-chain isomers; while borirane is less stable than vinylborane, borirene has a lower energy than ethynylborane. As with cyclopropanes, electropositive substituents stabilize the three-membered ring systems and lead to a characteristic shortening of the distal C–C bond and elongation of the vicinal B–C bonds. In the borirene series, π bonding with coplanar NH_2 and OH groups competes with the aromatic 2π delocalization; the resonance energies (37 and 40 kcal/mol, respectively) are reduced as a consequence.

Introduction

In 1962, Volpin et al. first suggested the possibility that borirene (1) might have Hückel 2π-aromatic character.[1] This was supported by subsequent INDO calculations[2] and by a more detailed ab initio study[3] which indicated 1 to have a large resonance energy (47 kcal/mol), 70% of that of the isoelectronic cyclopropenyl cation (2).

The first efforts to prepare small-ring organoboron compounds, derivatives of borirene (1) or of its saturated analogue borirane (3), were not successful; dimers or oligomers were obtained in most instances.[4,5] This situation has changed dramatically recently, and several representatives of both groups of compounds are now known.

Van der Kerk et al. prepared 4 in a mixture with other compounds by reaction of CH_3BBr_2, di-*tert*-butylacetylene, and C_8K,[6] Berndt reported the synthesis of two 1-*tert*-butyl-2-borylborirenes (5),[7] Meller isolated a number of quite stable [1-bis(trimethylsilyl)amino]borirenes (6), and West obtained 1-(triphenylsilyl)-2,3-bis(trimethylsilyl)borirene.[8b] Berndt also prepared the boriranes 7 and 8 by the addition of carbonyl compounds[9] or acetylenes[10] to "diboramethylenecyclopropane" derivatives.

These developments prompted us to extend our earlier investigation of the effect of substituents on simple boranes BH_2X[11] to the borirenes $(CH)_2BX$. In the earlier study,[11] only substituents with an electronegativity greater than or equal to that of boron were considered. We have now

---

(1) Volpin, M. E.; Koreshkov, Y. D.; Dulova, V. G.; Kursanov, D. N. *Tetrahedron* **1962**, *18*, 107.

(2) Pittman, C. U.; Kress, A.; Patterson, T. B.; Walton, P.; Kispert, L. D. *J. Org. Chem.* **1974**, *39*, 373. Also see: Allinger, N. L.; Siefert, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 752.

(3) Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 2589.

(4) The cyclohexanediol degradation product, attributed by: Ramsey, B. G.; Dennis, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 3182 to borirane could equally well have been derived from a diborinane. The reaction between olefins, CH_3BBR_2, and C_8K, originally reported to produce boriranes (Van der Kerk, S. M.; Boersma, G. J.; Van der Kerk, G. J. M. *Tetrahedron Lett.* **1976**, *51*, 4765) has been shown to produce borolanes: Van der Kerk, S. M.; Roos-Venekamp, J. C.; Van Beijnen, A. J. M.; Van der Kerk, G. J. M. *Polyhedron* **1983**, *2*, 1337.

(5) Van der Kerk, S. M.; Budzelaar, P. H. M.; Van Eekeren, A. H. M.; Van der Kerk, G. J. M. *Polyhedron* **1984**, *3*, 271 and references cited therein.

(6) Van der Kerk, S. M.; Budzelaar, P. H. M.; Van der Kert-von Hoof, A.; Van der Kerk, G. J. M.; Schleyer, P. v. R. *Angew Chem.* **1981**, *95*, 61. See also ref 5.

(7) Pues, C.; Berndt, A. *Angew. Chem.* **1984**, *96*, 306.

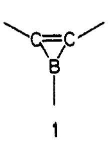
(8) (a) Habben, C.; Meller, A. IMEBORON V: 5th International Symposium on Boron Chemistry, *Chem. Abstr.* **1983**, *4*, 9. Meller, A., personal communication. (b) Pachaly, B.; West, R. *Angew. Chem.* **1984**, *96*, 444.

(9) Klusik, H.; Berndt, A. *Angew. Chem.* **1983**, *95*, 895.

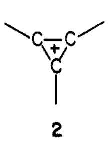
(10) Wehrmann, R.; Klusik, H.; Berndt, A. *Angew. Chem.* **1984**, *96*, 369.

(11) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3402.

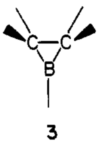
0276-7333/85/2304-0429$01.50/0



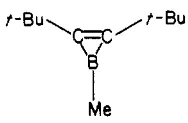
1



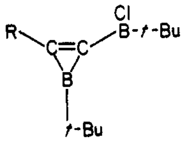
2



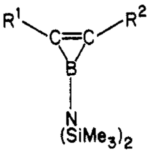
3



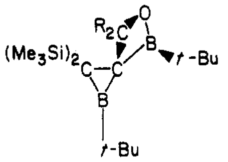
4



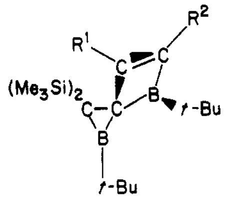
5, R=t-Bu, SnMe₃



6



7



8

extended the range of substituents to comprise the whole first row of the periodic table to provide a fuller assessment of the effects of such groups.

The substituents considered in this study are expected to interact both with the σ and with the 2π system of borirenes. To facilitate the interpretation of the results, the corresponding substituted boriranes $(H_2C)_2BX$ were also examined. The behavior of the analogous cyclopropane derivatives[12] provides further comparison.

Methods

Ab initio calculations on borirenes and boriranes with first-row substituents at B were carried out by using modified versions of the GAUSSIAN 76[13a] and 82[13b] programs. Geometries were optimized at the restricted Hartree-Fock level[14] using the small split-valence 3-21G basis,[15a] and energy refinements were obtained from single-point calculations with the 6-31G* polarization basis.[15b] All geometries were fully optimized in C_{2v} symmetry, except those of the methyl annd hydroxy compounds for which the geometry optimization was carried out in C_s symmetry. The most relevant geometrical data are listed in Table I; complete specifications of all molecular geometries (**Z** matrices and coordinates) are available as supplementary material. Table II lists the calculated total energies at the 3-21G geometries. Some energies for reference compounds are collected in Table III. Table IV contains π-orbital populations from the 3-21G calculations.

Energies for reactions 1–10 mentioned in the discussion are given in Table V. Some data for the reference compounds BH_2X, CH_3X, and CH_2X^+ [16] are reproduced here to facilitate comparison. 6-31G* data are better for this purpose, as polarized basis sets are essential for a quantitative description of strain energies.[17] Therefore, Table V contains both the 3-21G data and the more accurate 6-31G* data. Unless noted otherwise, reaction energies mentioned in the text are 6-31G* data; the level of optimization is given in Tables II and III.

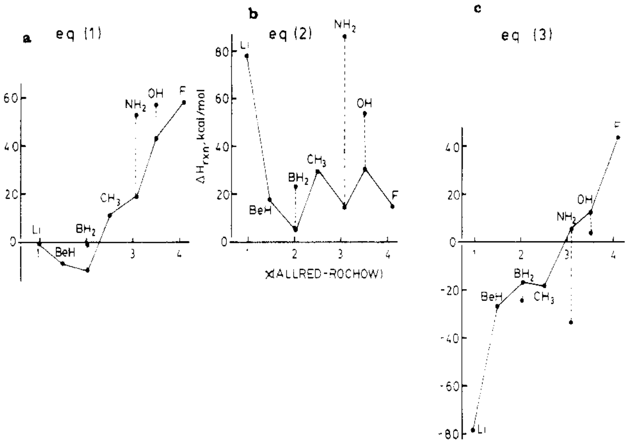


Figure 1. Electronegativity plots for the reactions 1–3. The solid lines connect the points corresponding to those conformations which have the *least* π-stabilization.

The earlier study on substituted cyclopropanes[12] employed the 4-31G basis,[15c] which is comparable in quality to the 3-21G basis;[15a] therefore, reactions 7 and 8 were evaluated by combining 3-21G data for reactions 1 and 4 with 4-31G data for reaction 6.

Results and Discussion

We first compare the substituted boranes BH_2X[11,18] with the methyl derivatives CH_3X and then with the isoelectric methyl cations CH_2X^+.[19,20] Accurate bond strengths cannot be calculated directly by using single-determinant Hartree–Fock theory.[21] However, B–X bond energies can be related to those of the more common C–X bonds, for which a far larger body of experimental data is available. This provides an indirect but reasonably accurate estimate of the strengths of B–X bonds and allows the σ and π contributions to be assessed.

We then evaluate the effects of substituents attached to boron in the three-membered ring system borirane. The results are compared with those recently reported for cyclopropanes.[12] Finally we use the behavior of the simple model systems to interpret the more complicated substituent effects encountered in the borirene series.

Comparison of B–X and C–X Bonds. The strengths of B–X and C–X bonds can be compared by means of the formal reaction

$$BH_2X + CH_4 \rightarrow BH_3 + CH_3X \qquad (1)$$

---

(12) Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412.

(13) (a) Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. "QCPE"; Indiana University: Bloomington, IN; No. 368. (b) Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, release A; Carnegie-Mellon University, 1983; the VAX-version, available from Prof. Pople, was adapted to a CDC computer by A. Sawaryn.

(14) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

(15) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acta* **1973**, *28*, 213. (c) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(16) Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 2nd ed., Pittsburgh, 1981.

(17) See, e.g.: Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 10. Wiberg, K. *J. Am. Chem. Soc.* **1983**, *105*, 1227.

(18) Substituent effects in BH_3X^- have been studied by: Pross, R. A.; Radom, L. *Tetrahedron* **1980**, *36*, 673. While π effects are not important in these species, the negative charge results in far larger polarization (σ) effects than are present in the neutral BH_2X molecules.

(19) Lathan, W. A.; Curtiss, L. A.; Hehre, W. J; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* **1974**, *11*, 175.

(20) (a) Chandrasekhar, J.; Pople, J. A.; Seeger, R.; Seeger, U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 3651. (b) Apeloig, Y.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291. Apeloig, Y.; Schleyer, P. v. R. *Tetrahedron Lett.* **1977**, 4667. Clark, T. T.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, 4661.

(21) Pople, J. A.; Frisch, M.; Luke, B. T.; Binkley, J. S. *Int. J. Quant. Chem. Symp.* **1983**, *17*, 307.

Table I. Geometrical Data for Borirenes, Boriranes, and Boranes[a]

	borirenes			boriranes			boranes[b]		
X	B-X	B-C	C-C	B-X	B-C	C-C	B-X	B-H	HBH
H	1.171	1.485	1.348[c]	1.175	1.545	1.559[d]	1.188	1.188	120.0
Li	2.188	1.525	1.334	2.202	1.592	1.530	2.261	1.208	110.9
BeH	1.854	1.503	1.338	1.862	1.571	1.530	1.896	1.197	114.0
BH_2(perp)	1.651	1.500	1.333	1.631	1.565	1.524	1.662	1.194	116.4
BH_2(copl)	1.697	1.490	1.350	1.722	1.550	1.550	1.748	1.192	116.4
CH_3	1.562	1.491	1.348	1.558	1.547	1.566	1.576	1.192	117.9
NH_2(perp)	1.440	1.492	1.361	1.447	1.547	1.588	1.471	1.199	116.5
NH_2(copl)	1.400	1.496	1.343	1.387	1.542	1.580	1.400	1.191	121.0
OH(perp)	1.375	1.483	1.359	1.362	1.534	1.602	1.374	1.192	120.4
OH(copl)	1.365	1.486, 1.480	1.352	1.357	1.536, 1.526	1.597	1.371	1.183, 1.192	122.3
F	1.337	1.470	1.360	1.333	1.519	1.611	1.347	1.182	124.4

[a] 3-21G optimized geometries; distances in Å and angles in degrees. [b] 3-21G optimized geometries from ref 16. [c] 6-31G* geometry: BH = 1.177, B–C = 1.465, and C–C = 1.340. [d] 6-31G* geometry: BH = 1.178, B–C = 1.534, and C–C = 1.544.

Table II. Total Energies (3-21G Geometries) (au)

	borirenes		boriranes		boranes[a]	
	HF/3-21G	HF/6-31G*	HF/3-21G	HF/6-31G*	HF/3-21G	HF/6-31G*
H	−101.522 67	−102.101 76[b]	−102.686 96	−103.261 84[c]	−26.237 30	−26.390 01
Li	−108.311 30	−108.933 34	−109.476 04	−110.094 82	−33.013 85	−33.209 94
BeH	−116.059 66	−116.720 89	−117.223 21	−117.880 43	−40.763 28	−40.997 68
BH_2(perp)	−126.629 53	−127.349 19	−127.798 55	−128.514 67	−51.339 74	−51.634 71
BH_2(copl)	−126.617 86	−127.338 80	−127.776 53	−128.494 95	−51.320 28	−51.618 01
CH_3	−140.364 22	−141.151 84	−141.530 55	−142.314 29	−65.078 09	−65.441 54
NH_2(perp)	−156.280 14	−157.148 90	−157.442 89	−158.306 74	−80.989 79	−81.435 18
NH_2(copl)	−156.307 79	−157.176 33	−157.490 96	−158.854 04	−81.043 44	−81.489 10
OH(perp)	−176.P21 13	−177.000 47	−177.192 68	−178.163 72	−100.742 88	−101.298 56
OH(copl)	−176.031 59	−177.012 42	−177.210 37	−178.184 52	−100.760 58	−101.321 40
F	−199.920 78	−201.095 72	−201.095 72	−202.185 08	−124.646 75	−125.322 13

[a] 3-21G//3-21G and 6-31G*//6-31G* data from ref 16. [b] −102.102 40, 6-31G*//6-31G*. [c] −103.262 06, 6-31G*//6-31G*.

Table III. 3-21G and 6-31G* Energies for Some Reference Compounds[a]

compound	3-21G	6-31G*
propane	−117.613 30	−118.263 65
cyclopropane	−116.401 21	−117.058 87
cyclopropene	−115.162.01	−115.823 05
2-propyl cation	−116.726 20	−117.380 75
allyl cation	−115.542 14	−116.193 21
dimethylborane[b]	−103.917 68	−104.491 34
vinylborane[b]	−102.714 57	−103.289 68
ethynylborane[c]		−102.093 90
vinylideneborane[c]		−102.052 63
11-H[b]	−102.644 69	−103.212 16
11-Li[b]	−109.410 34	−110.023 86
11-F[b]	−201.045 10	−202.128 06

[a] 3-21G/3-21G and 6-31G*//6-31G* data from ref 16, except where noted otherwise. [b] 3-21G//3-21G and 6-31G*//3-21G, this work. [c] 6-31G*//4-31G, this work.

in which BX and CX bonds are exchanged for their BH and CH counterparts. The "methyl stabilization energies" obtained from eq 1 are also influenced by the relative energies of CH vs. BH bonds, but this is a constant contribution and turns out to be small:

$$BH_2\cdot + CH_4 \rightarrow BH_3 + CH_3\cdot \qquad (1a)$$

−0.5 kcal/mol (3-21G//3-21G)
−2.6 kcal/mol (6-31G*//6-31G*)
+1.3 kcal/mol (best data)[21]

Alternatively, the relative bond dissociation energies of B–X and C–X bonds could be compared directly by means of eq 1b, which is the combination of eq 1 and 1a.

$$BH_2X + CH_3\cdot \rightarrow BH_2\cdot + CH_3X \qquad (1b)$$

The substituents chosen for examination comprise the entire "sweep" of first-row groups X = Li, BeH, BH_2, CH_3, NH_2, OH, and F; these allow the widest range of electronic effects to be examined.[12,18,20,22] Since practically no ex-

Table IV. π-Electron Densities from 3-21G Calculations

	borirenes			boriranes		boranes	
	q_X^π	q_B^π	q_C^π	q_X^π	q_B^π	q_X^π	q_B^π
H		0.330	0.835		0.045		0
Li	0.008	0.280	0.856	0.002	0.033		0
BeH	0.004	0.326	0.835	0.001	0.040		0
BH_2(perp)		0.328	0.847		0.059		0.025
BH_2(copl)	0.005	0.368	0.814	0.001	0.047		0
CH_3		0.347	0.841		0.083		0.044
NH_2(perp)		0.365	0.831		0.083		0.036
NH_2(copl)	1.781	0.449	0.885	1.718	0.314	1.708	0.292
OH(perp)		0.414	0.849		0.206		0.172
OH(copl)	1.822	0.437	0.883, 0.858	1.773	0.266	1.770	0.230
F	1.872	0.421	0.854	1.840	0.206	1.843	0.157

Table V. 6-31G* (3-21G) Reaction Energies for Reactions 1-10 (kcal/mol)

X	(1)	(2)	(3)	(4)	(5)
H	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Li	−0.3 (0.6)	78.1 (80.9)	−78.4 (−80.3)	7.9 (8.5)	8.2 (7.9)
BeH	−8.3 (−7.8)	18.0 (18.6)	−26.2 (−26.4)	−1.4 (−1.3)	6.9 (6.4)
BH_2(perp)	−1.0 (0.8)	23.1 (24.0)	−24.1 (−23.2)	4.1 (6.5)	5.1 (5.7)
BH_2(copl)	−11.5 (−11.4)	5.1 (3.9)	−16.7 (−15.3)	−8.3 (−7.3)	3.2 (4.1)
CH_3	11.3 (14.9)	29.5 (29.1)	−18.2 (−14.2)	11.8 (16.6)	0.6 (1.8)
NH_2(perp)	19.1 (29.9)	14.1 (19.2)	5.0 (10.8)	19.0 (32.1)	−0.2 (2.2)
NH_2(copl)	53.0 (63.6)	86.5 (93.4)	−33.5 (−29.8)	48.7 (62.3)	−4.3 (−1.3)
OH(perp)	42.9 (53.0)	30.3 (37.5)	12.6 (15.5)	38.7 (53.1)	−4.2 (0.1)
OH(copl)	57.2 (64.1)	53.7 (52.6)	3.5 (11.5)	51.7 (64.1)	−5.5 (0.1)
F	58.2 (65.5)	14.9 (8.7)	43.3 (56.8)	52.6 (65.1)	−5.6 (−0.4)

X	(6)[a]	(7)[b]	(8)[c]	(9)	(10)
H	(0.0)	(0.0)	(0.0)	47.5 (47.0)	0.0 (0.0)
Li	(2.1)	(6.4)	(5.8)	46.6 (46.7)	7.3 (7.6)
BeH	(0.1)	(−1.4)	(6.4)	47.9 (47.5)	7.2 (6.9)
BH_2(perp)	(0.8)	(5.7)	(4.9)	44.1 (44.0)	1.7 (2.8)
BH_2(copl)	(−6.5)	(−0.8)	(10.6)	50.0 (50.5)	5.7 (7.7)
CH_3	(−2.7)	(19.3)	(4.4)	46.0 (45.7)	−0.9 (0.5)
NH_2(perp)		(38.6)	(8.7)	48.9 (48.0)	1.2 (3.1)
NH_2(copl)	(−6.5)	(68.8)	(5.2)	36.5 (35.2)	−15.4 (−13.2)
OH(perp)		(58.9)	(5.9)	45.5 (42.4)	−6.2 (−4.5)
OH(copl)	(−5.8)	(69.9)	(5.8)	40.0 (37.9)	−13.0 (−9.0)
F	(−5.3)	(70.4)	(4.9)	43.1 (40.3)	−10.0 (−7.1)

[a] 4-31G data taken from ref 12; the designations perp and copl used here correspond to bisected and perpendicular, respectively, in ref 12. [b] By combination of reactions 4 (3-21G) and 6 (4-31G). [c] By combination of reactions 1 (3-21G) and 7.

Table VI. Relative Energies (kcal/mol) of C_2BH_3, C_2BH_5, C_3H_4, and C_3H_6 Isomers

C_2BH_3[a]		C_2BH_5[c]	
borirene (**1**)	0	borirane (**3**)	0
$HC{\equiv}CBH_2$, C_{2v}	+5.1	$CH_2{=}CH{-}BH_2$, C_s	−17.5
$CH_2{=}C{=}BH$, C_{2v}	+31.0	$CH_2{=}B{-}CH_3$, C_s	+7.6
$CH_2{=}BCH$, C_{2v}	+77.6	$CH_3{-}C{-}BH_2$, C_s	+27.9
$CH_3C{\equiv}B$, C_{3v}	+136.5	$CH_2{-}BH{-}CH_2$ (**11**)	+31.1
C_3H_4[b]		C_3H_6[b]	
cyclopropene	0	cyclopropane	0
$HC{\equiv}CCH_3$	−23.9	$CH_2{=}CHCH_2$	−7.9
$CH_2{=}C{=}CH_2$	−25.9	CH_3CCH_3	+54.6

[a] Compared at 6-31G*//4-31G; for geometrical details, see supplementary material. [b] 6-31G*//6-31G* from ref 16. [c] 6-31G*//3-21G; for geometrical details, see supplementary material.

perimental data exist for the boron compounds (and for some of the carbon compounds with electropositive substituents), theoretical data from Table II are used to evaluate eq 1. Reasonable accuracy can be expected, since in test cases the values do not change significantly when data obtained at higher levels of theory are employed.[16,21]

Such calculations have further advantages over experiment, since various conformations can be probed.[11,23] For example, H_2BNH_2 is a planar species due to the N→B π donation. This π interaction can be "turned off" (and thus evaluated) by examining the perpendicular conformation. Data for a number of conformations of BH_2, NH_2, and OH groups are included in this study.

σ-Effects. The resulting stabilization or relative bond dissociation energies are best interpreted by means of *electronegativity plots*[12,22,24] (e.g., Figure 1a for eq 1; points for different conformations are included). We have used the Allred–Rochow electronegativity scale for the first-row elements. Other scales are similar for these elements, and XH_n group electronegativities are not very different from those for the main atoms X.[25] The plot (solid line in Figure 1a) has a V shape. This shows that both strongly electropositive (lithium) and electronegative (NH_2, OH, F) substituents stabilize BH_2 (even when π effects are "turned off"). We have encountered such V-shaped curves commonly in similar studies of bond energies.[22] They are easily interpreted in terms of σ effects. Highly electropositive substitutents, e.g., lithium, donate electrons to the BH_2 and CH_3 groups; the bonds are largely ionic. Hence, the resulting situation can be appreciated quite well by comparing the anions BH_2^- and CH_3^-. Thus, electron affinities for the basic groups tell us what to expect. Since the EA of BH_2 is probably slightly larger than that of CH_3,[26] the B–Li bond should be about as strong as the C–Li bond. Equations 1c and 1d give comparable results.

$$\underset{\text{singlet}}{BH_2^-} + CH_4 \rightarrow CH_3^- + BH_3 \qquad (1c)$$

+5.9 kcal/mol

(+3.5 kcal/mol, MP2/6-311+G*//6-311+G*)[26]

$$BH_2Li + CH_4 \rightarrow CH_3Li + BH_3 \qquad (1d)$$

By analogy, the ionization potentials of BH_2 and CH_3 radicals can be used to predict the expected σ effects of highly electronegative substituents. In the extreme, such substituents would withdraw all the σ-bonding electrons and induce ionic character, e.g., $BH_2^+X^-$ and $CH_3^+X^-$. No reliable experimental value for IP(BH_2) appears to be available, but eq 1e can be used instead. As can be seen,

$$CH_4 + BH_2^+ \rightarrow CH_3^+ + BH_3 \qquad (1e)$$

+28.4 kcal/mol

---

(22) See: Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M. B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.*, submitted for publication, for an analysis of bonding involving silicon.

(23) Vincent, M. A.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1981**, *103*, 5677.

(24) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363.

(25) The electronegativities of substituent XH_n groups can be approximated by those of the heteroatom X; see, e.g.: Marriott, S.; Reynolds, W. F.; Taft, R. W.; Topsom, R. D. *J. Org. Chem.* **1984**, *49*, 959.

(26) No reliable experimental value is available. At MP2/6-311+G*//6-311+G*, the electron affinity of BH_2 (to singlet BH_2^-) is larger than that of CH_3 by 2.0 kcal/mol. Spitznagel, G. W., unpublished results.

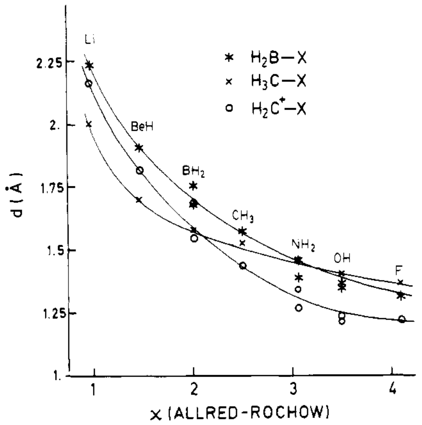


Figure 2. Electronegativity plot of B–X and C–X bond distances (6-31G* geometries).

boron stabilizes a positive charge better than carbon. Thus, B–X bonds are expected to be stronger than C–X bonds for electronegative groups X. The stabilization of BH_2F with respect to CH_3F (eq 1f) is, however, much larger than expected on the basis of the ionic model, which shows that π contributions are at least as important as σ effects in this case.

$$CH_4 + BH_2F \rightarrow CH_3F + BH_3 \qquad (1f)$$
$$+58.2 \text{ kcal/mol}$$

The B–B (in planar B_2H_4) and Be–B bonds are the weakest in Figure 1a. When the electronegativity differences between the elements are small and no strong π effects are present, bond energies are related to bond lengths since these influence orbital overlaps. For electropositive substituents, B–X bonds are 0.1–0.2 Å longer than the corresponding C–X bonds (Figure 2).

π-Effects. While the general V shape of Figure 1a is due to σ effects, π interactions contribute for the boron compounds. They are most important with good π donors involving lone pairs (NH_2 and OH groups in planar conformations) and those permitting hyperconjugation (BH_2 in the perpendicular conformation). The rotation barriers in these systems (Table VII) provide a *minimum* estimate of the π effects. In perpendicular H_2BOH the lower lying oxygen lone-pair orbital interacts with the "vacant" boron p_π orbital. This is shown by the boron populations (Table IV) and by the widening of the BOH angle (Table I).

In perpendicular BH_2NH_2, hyperconjugation can take place; the N–H bonds donate to the boron p_π orbital. While the hyperconjugative ability might be expected to follow the electronegativity, this is not confirmed by the boron populations of th perpendicular forms in Table IV. The observed order CH > NH > BH indicates that distance effects also are important.

The rotation barrier for B_2H_4 is calculated to be 10.5 kcal/mol, in good agreement with the value of 10.9 kcal/mol recently obtained by Vincent and Schaefer[23] using a double ζ + polarization basis; these authors found that correlation slightly raises the barrier (to 11.9 kcal/mol). After correcting for hydrogen–hydrogen repulsion in the planar conformer,[27] the rotation barrier can be interpreted as double the magnitude of a normal $BH_2 \rightarrow B$ hyperconjugative interaction, which is thus estimated to be about 5 kcal/mol. The hyperconjugative stabilization provided by the methyl group in CH_3BH_2 may be similar in magnitude.

This now emphasizes a major problem: the difficulties in a clean dissection of π from σ effects.[18] The solid line in Figure 1a is *not* the true σ line. While π effects may be small in the CH_3X compounds with the more electronegative substituents. π stabilization is absent in H_2BLi, H_2BBeH, and planar B_2H_4,[27] but is present in the points which were used to define the right-hand line of the "V": BH_2CH_3, perpendicular BH_2NH_2, and BH_2OH as well as BH_2F. As mentioned above, the π stabilization provided by fluorine is substantial and may be in the order of 25 kcal/mol.

Table VII. 6-31G* Rotation Barriers

compound	barrier, kcal/mol	Δ(B–X),[a] Å
H_2BBH_2	10.5	0.086
$(CH_2)_2BBH_2$	12.4	0.091
$(CH)_2BBH_2$	6.5	0.046
H_2BNH_2	33.8	0.071
$(CH_2)_2BNH_2$	29.7	0.060
$(CH)_2BNH_2$	17.2	0.040
H_2BOH	14.3	0.003
$(CH_2)_2BOH$	13.1	0.005
$(CH)_2BOH$	7.5	0.010

[a] Bond length increase on going from most stable to least stable conformation.

Thus, the "true" σ line in Figure 1a falls below the solid line on the right side of the "V", but we see no simple way of estimating the extra π contributions.[18,28] We thus will include the hyperconjugation and the residual π influences with the σ effects in most of the following discussion. In addition, by "π effects" we generally mean the lone pair–boron p_π orbital interactions.

π effects in these small systems were discussed in our earlier[11] and other papers and are manifested in B–X bond lengths (Table I; Figure 2), π populations (Table IV), and more subtle geometrical effects (e.g., in bond angles).

Comparison between B and C⁺. Parts 1b and c of Figure 1 show electronegativity plots for reactions 2 and 3. The energies of the first reaction (Figure 1b) show that

$$CH_2X^+ + CH_4 \rightarrow CH_3^+ + CH_3X \qquad (2)$$

$$BH_2X + CH_3^+ \rightarrow BH_3 + CH_2X^+ \qquad (3)$$

both σ and π effects can be large. The stabilization by lithium is remarkable,[20a] and BeH and coplanar BH_2 also stabilize by σ donation.[20b] Fluorine should be strongly destabilizing because of its σ effect, and the net stabilization observed indicates the even greater importance of the π contribution in this case. The other stabilization energies are also dominated by π effects; lone-pair donation by planar NH_2 and OH groups and hyperconjugation with perpendicular NH_2 and CH_3 and particularly in perpendicular BH_2. The large stabilization of the (classical) ethyl cation, relative to methyl, is well-known.[20b]

We have already noted the BOH angle widening in perpendicular H_2BOH; the corresponding carbenium ion H_2COH^+ is even more extreme. Optimization of this species in a perpendicular (C_s) conformation gives a COH angle of 159.2° (6-31G*; 180° at 3-21G).

Reaction 3, the difference between reactions 1 and 2, compares the substituent effects in boranes with those in

---

(27) Bond Opposition Effects. For such simple systems, other effects are relatively small, but some have not been fully appreciated. For example, the rotational barrier in B_2H_4 is not just due to hyperconjugative *stabilization* of the perpendicular form; *destabilization* of the planar form due to the eclipsing of the vicinal B–H bonds also contributes. Since the rotational barriers in CH_3CH_3, CH_3NH_2, and CH_3OH (3, 2, and 1 kcal/mol, respectively) mirror the number of bond oppositions in the eclipsed conformations, a destabilization of about 2 kcal/mol in planar B_2H_4 would be expected. The same effect should destabilize the planar forms of BH_2NH_2 and BH_2OH (as well as ethylene). In all conformations of CH_3BH_2, an average of one bond opposition is present.

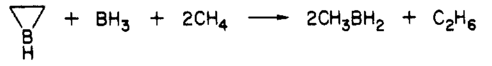
(28) The boron p_π orbital could in principle be left out of the basis set, but this is not easy to do with the GAUSSIAN 82 program we are using.

the isoelectronic carbenium ions. For the most electronegative substituents OH and F, the σ effect is most important with BH_2; conversely, Li strongly favors CH_2^+. Hence, the overall trend in Figure 1c is dominated by σ effects, but the π contributions also are apparent. Thus, in agreement with the earlier study[11] we conclude that boranes behave in some respects similarly to carbocations, but are weaker π acceptors and fairly strong σ donors.

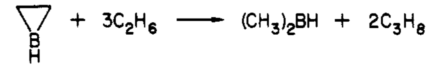
Borirane (3). The 3-21G optimized structure for 3 differs only insignificantly from the the 4-31G structure reported earlier[3] and is nearly an equilateral triangle. The B–C distance, 1.545 Å, is shorter than that calculated for methylborane (1.576 Å). Such a shortening would be expected for small rings containing "bent bonds". However, the C–C distance, 1.566 Å, is much longer than that in cyclopropane (1.513 Å)[16] and longer even than that calculated for ethane (1.543 Å)[16] (all at 3-21G). This lengthening is partly due to the transfer of electrons from the π-type C–C bonding MO of the CH_2CH_2 moiety into the vacant p_π occupancy of 0.045 e (Table IV).

We have also reoptimized the structure of 1 at 6-31G*. The B–C and C–C bond lengths decrease slightly (see Table I), and the lowering in absolute energy due to this change in geometry (0.1 kcal/mol) is negligible.

The strain energy of borirane can be estimated from the reactions:

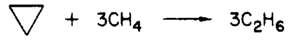


-43.7 kcal/mol

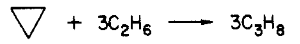


-44.3 kcal/mol

The resulting values are ca. 16 kcal/mol higher than the strain energy of cyclopropane calculated at the same level of theory:

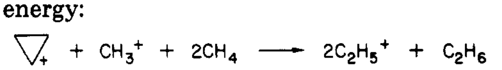


-26.3 kcal/mol



-28.8 kcal/mol

The higher strain energy of borirane is primarily due to the high-valence angle strain at boron. Boron normally is trigonal, and the reduction in borirane of the valence angle at boron from 120° to ca. 60° drastically reduces the boron 2s content of the ring B–C bonds and increases the bond energies. The same effect is observed in the isoelectronic cyclopropyl cation, which has an even larger strain energy:



-61.5 kcal/mol

-56.2 kcal/mol

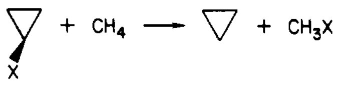
Substituent Effects in Boriranes. The energies calculated for reaction 4 (Table V) roughly parallel those for reaction 1, i.e., a stabilization of the boron compounds by electronegative substituents and π donors.

(4)

(5)

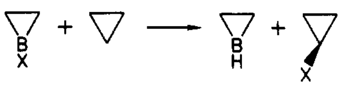
The effects particular to the three-membered ring system appear more clearly if we consider reaction 5, the difference between (4) and (1). The electronegativity plot of this reaction (Figure 3a) shows an approximately linear correlation with a surprisingly large slope. Some deviations of individual points are noted; the largest ones are found for BH_2(perp) and NH_2(copl). The "bent bonds" in three-membered rings are better hyperconjugative donors than the unperturbed B–H bonds in H_2B groups (Figure 4). The small relative destabilizations found for X = NH_2(copl) and OH(copl) groups are caused by a saturation effect; X→B π donation competes with the stabilization provided by hyperconjugation with the CH_2CH_2 moiety of the ring.

The slope in Figure 3a is due to σ effects and demonstrates the stabilization of the three-membered ring system by electropositive substituents (Li, BeH); a similar situation occurs in substituted cyclopropanes.[12,29] A direct comparison with the results of our recent study of substituent effects in cyclopropanes[12] is not possible because a different basis set (4-31G) was employed. However, the 4-31G and 3-21G basis are comparable so that subtraction of the 4-31G values for reaction 6 from the 3-21G values



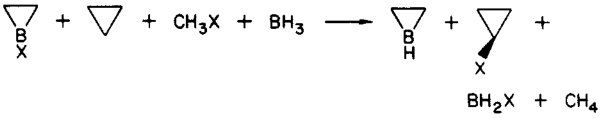
(6)

for (4) should give reasonable estimates for reaction 7.



(7)

The energies thus obtained show the usual behavior of B–X vs. C–X bonds, i.e., stabilization by π donors and electronegative groups. The effects of the differences in B–X and C–X bond strengths can be largely eliminated by subtracting reaction 1, producing eq 8. An electronegativity plot of this reaction (Figure 3b) shows a nearly



(8)

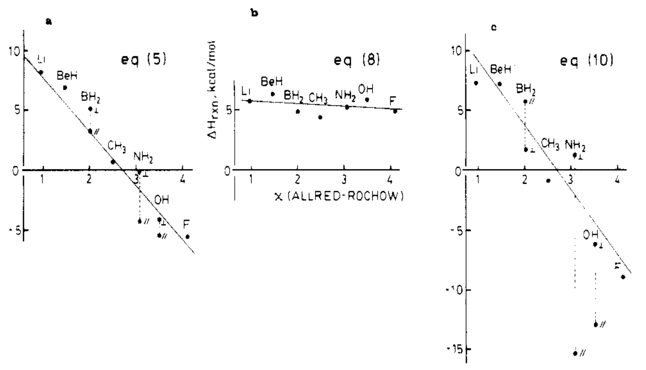


Figure 3. Electronegativity plots for reactions 5, 8, and 10. For definition of the solid (σ) line in a and c, see text. Only the points corresponding to the most stable conformations are shown in b.

Figure 4. Schematic representation of $BH_2 \rightarrow B$ and borirane → B hyperconjugation.

---

[29] Dill, J. D.; Greenberg, A.; Liebman, J. B. *J. Am. Chem. Soc.* **1979**, *101*, 6814.

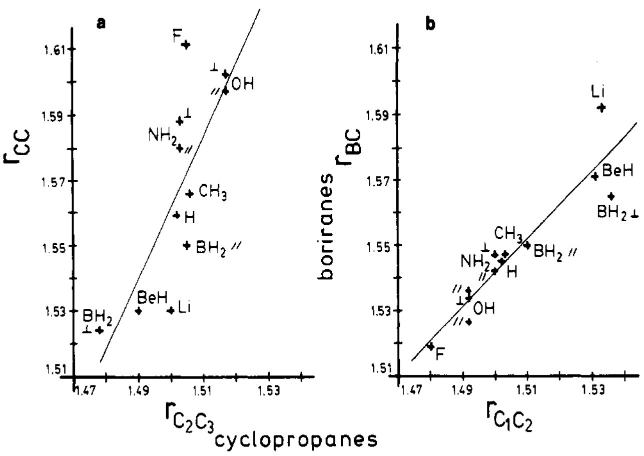
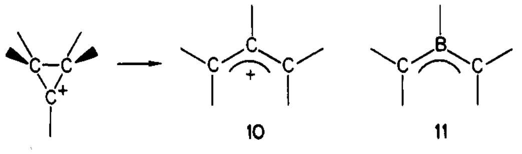


Figure 5. Comparison of bond lengths in substituted boriranes (3-21G) and cyclopropanes (4-31G).[12]

horizontal correlation line. The main conclusion to be drawn is that substituent effects in the two three-membered ring system are nearly equal.

Apart from energetic considerations, substituents also influence the geometry of the three-membered ring. In figure 5a,b the bond length changes induced by substituents in boriranes are compared with those in cyclopropanes. Although the correlation is not especially good, it is clear that the changes in the vicinal (1,2) bonds are roughly equal for the two systems (the least-squares line has a slope of 1.03). The distal (2,3) bond in boriranes is, however, much more sensitive to substituents than that in cyclopropanes (slope 2.18), and the C–C bond length in fluoroborirane is calculated to be as large as 1.611 Å!

A comparison of borirane with the isoelectronic cyclopropyl cation (**9**) is apt. The latter undergoes *exothermic* (−38.3 kcal/mol, 6-31G*) disrotatory ring opening to the allyl cation **10**. The corresponding opening of borirane



9 **10** **11**

to **11** is calculated to be *endothermic* by 31.1 kcal/mol (6-31G*//3-21G). While the long distal C–C bond in fluoroborirane (Figure 5a) suggests that ring opening to **11**-F would provide a low-energy pathway for oligomerization or polymerization, the actual calculated energy difference (35.8 kcal/mol, 6-31G*//3-21G) is not very favorable. The ring opening of the lithium compound is even more endothermic (44.5 kcal/mol). The high ring strain of the borirane system is reflected in the energy of its "dehydroboration" to the open-chain isomer vinylborane. This reaction is 10 kcal/mol more exothermic than the corresponding opening of cyclopropane to propene (Table VI).

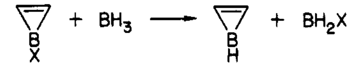
Borirene (1). The 3-21G structure of **1** is very similar to the 4-31G structure reported earlier.[3] Reoptimization at the 6-31G* level produces minor changes in the bond lengths (B–C = 1.465 Å; C–C = 1.340 Å) and only a small energy decrease (0.4 kcal/mol) with respect to the 6-31G*//3-21G value. Thus, the 3-21G basis seems to give satisfactory geometries for three-membered rings, although the use of a polarization basis is essential for quantitative energy comparisons of these highly strained systems with acyclic counterparts.

There is no simple way to obtain separate "strain energy" and "resonance energy" estimates for borirenes, as obviously any unstrained model system also lacks the 2π-aromatic stabilization. The resonance energy of borirene can be estimated from reaction 9 assuming the

(9)

difference in strain energy between borirenes and boriranes to be equal to that between cyclopropene and cyclopropane (24.8 kcal/mol).[30] For X = H, one thus obtains a strain energy of 68.8 kcal/mol and a resonance energy of 47.5 kcal/mol (6-31G*//6-31G*), in good agreement with the earlier estimate.[3] Thus, the aromatic stabilization of **1** is calculated to be quite large. This is illustrated dramatically be the fact that, in contrast to the corresponding reaction for borirane, ring opening to ethynylborane or to vinylideneborane is *endothermic*. Table VI compares the relative energies of some C_2BH_3 and C_2BH_5 isomers and those of the corresponding C_3H_4 and C_3H_6 species.

Substituent Effects in Borirenes. Figure 3c shows an electronegativity plot for the energies from reaction 10.



(10)

Comparing this with the borirane plot (Figure 3a), one sees that the substituent effects are roughly similar. Electropositive substituents stabilize the three-membered ring system; electronegative substituents produce a destabilization. In addition to this general σ effect, however, several substituents show a rather specific interaction with the 2π-aromatic system which causes large deviations from the σ line. π donation from NH_2(copl) and OH(copl) is relatively ineffective; the boron atom in C_2H_2BX is a poorer π acceptor than that in the reference compound BH_2X. Similar effects, though of much smaller magnitude, are found for X = BH_2(perp) and CH_3, where decreased X→B hyperconjugation with respect to BH_2X is found. The very electropositive Li substituent also appears to deviate; through its strong σ donation, the π-acceptor character of the boron atom is decreased. This polarizes the electron distribution in the 2π system and thus counteracts the normal stabilizing effect observed in lithioborirane and lithiocyclopropane. For similar reasons, electronegative substituents are expected to increase the delocalization, but this effect is masked in Figure 3c by the much larger direct π effects. Only for X = NH_2(perp) is a small stabilization observed.

It is interesting to attempt a separation of the σ and π effects. In view of the results obtained for boriranes, it seems reasonable to take the substituent electronegativity χ^{25} as a measure of the σ effect. An obvious choice for the π effect is the C→B π donation $q_{C\to B}^{\pi} = 2 - 2q_C^{\pi}$, calculated from Table IV. Linear regression then produces the relation

$$E(10) \approx \underset{\text{“}\sigma\text{ only”}}{5.4\,(2.7 - \chi)} + \underset{\text{“}\pi\text{ effect”}}{110(q_C^{\pi} - 0.33)}$$

to be compared with the corresponding expression for boriranes

$$E(5) \approx 4.5(2.7 - \chi)$$

χ = Allred–Rochow electronegativity; E in kcal/mol

The borirene electronegativity plot in Figure 3c shows the σ line, with the X axis intersection taken equal to that in Figure 3a. The ratio of the slopes of the σ lines in parts a and c of Figure 3, 5.4/4.5 = 1.2, indicates that the σ-

---

[30] Wiberg, K.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5679.

substituent effect is ca. 20% larger in borirenes than in boriranes. This seems reasonable in view of the 10% difference in CBC valence angle at boron. The π-donors NH_2(copl) and OH(copl) give large destabilizations, but the point for X = F is already quite close to the σ line.

The effects of substituents on the bond lengths in borirenes are much smaller than those in boriranes but in general show the same trend, i.e., a decrease of the vicinal B–C bonds and an increase of the distal bond lengths with increasing substituent electronegativity. Superimposed on this one finds a shortening of the C–C bond for π-donating substituents, corresponding to a decrease in delocalization, but the effect is rather small.

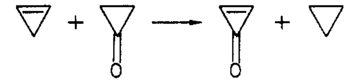
Aromaticity and B–X π Bonding. The resonance energy of unsubstituted borirene is ca. 47 kcal/mol, while B–N π bonding brings ca. 30 kcal/mol stabilization in aminoborirane. If the two interactions were independent, one would expect the energy change in reaction 10 to be small for X = NH_2(copl); if they were exclusive, one would expect a borirene destabilization of at least 30 kcal/mol. Actually (Table V) one finds this to about 15 kcal/mol, i.e., intermediate between the two extremes.

If the C→B and N→B π donations were small, their effects would be additive. Increasing π donation to boron leads, however, to a saturation effect, and planar aminoborirene has ca. 70% of the C→B π donation of borirene and nearly 80% of the N→B π donation in aminoborirane. Similarly, the destabilization of 15 kcal/mol calculated for planar aminoborirene indicates this compound to have ca. 80% of the sum of the normal B–N π-bond energy and the normal borirene resonance energy.

The saturation effect should be even stronger in methylenecyclopropene, the all-carbon analogue of aminoborirene, and Greenberg calculated a resonance energy of only 11 kcal/mol for this compound from reaction 11. However, cyclopropenone should be more aromatic, and the resonance energy calculated from the analogous reaction (12) is indeed seen to be substantially larger.


(11)

-11.3 kcal/mol[31]


(12)

-27.6 kcal/mol[31]

Rotation Barriers. Rotation barriers for boryl-, amino-, and hydroxy-substituted boranes, boriranes, and borirenes are collected in Table VII, together with the B–X bond length changes accompanying these rotations. The rotation barrier in borylborirane is larger than that in B_2H_4, indicating that the borirane→B hyperconjugative donation is stronger (by ca. 2 kcal/mol). In agreement with this, the B–B bond length increase associated with the rotation of the BH_2 group is slightly larger in borylborirane (0.091 Å) than in B_2H_4 (0.086 Å). A much lower barrier and bond length increase (0.046 Å) is calculated for borylborirene. It seems likely that the borirene→B hyperconjugative interaction will not be much smaller than the corresponding borirane value. However, the extensive π-electron delocalization in the borirene system effectively saturates the ring boron atom and thus largely eliminates the BH_2→B hyperconjugation.

Table VIII. MNDO Rotation Barriers for Aminoborirenes

compound	barrier, kcal/mol	Δ(B-N),[a] Å
$(CH)_2BNH_2$	16.0	0.042
$(CH)_2BN(CH_3)_2$	11.9	0.038
$(CH)_2BN(SiH_3)_2$	9.0	0.029
$(CH)_2BN(SiMe_3)_2$	6.1	0.028

[a] Bond length increase on going from planar to perpendicular conformation.

Table IX. Estimated B-X Bond Strengths in BH_2X Compounds[a]

X	ΔH(1b), 6-31G*	D_0(CH_3-X),[b] exptl	D_0(BH_2-X),[c] est
H	2.6	105.1	107.7
Li	2.3	45[d]	47
BeH	-5.7		
BH_2	1.6	(104.3)[e]	105.9
CH_3	13.6	90.4	104.3
NH_2	55.6	84.9	140.5
OH	59.8	92.3	152.1
F	60.8	109.9	170.7

[a] Values for most stable conformers of BH_2X. [b] From: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *11*, 493. [c] By addition of the first two columns. [d] See: Würthwein, E.-U.; Sen, K. D.; Pople, J. A.; Schleyer, P. v. R. *Inorg. Chem.* **1983**, *22*, 496. [e] Since no accurate experimental data are available, the estimated value for $D_0(CH_3-BH_2)$ from the next row was used.

The rotation barrier in aminoborane is calculated to be 33.8 kcal/mol. That in aminoborirane is somewhat smaller (29.7 kcal/mol) because the N→B π donation saturates the boron atom and reduces the hyperconjugation within the three-membered ring. The rotation barrier in aminoborirene is much smaller (17.2 kcal/mol) because of the competition of C→B and N→B π donation in the planar isomer, as discussed above. Meller has reported the synthesis of a number of [1-bis(trimethylsilyl)amino]borirenes,[8a] for which a perpendicular conformation was suggested. This prompted us to investigate the effect of substitution at N in aminoborirenes. Systems of this size cannot be treated by ab initio methods, so the semiempirical MNDO method[32] was employed for these calculations; the results should only be taken as indicative. MNDO reproduces the rotation barrier for the parent aminoborirene quite well (Table VIII). Increasing substitution at N, especially by the more electropositive silyl groups, decreases the rotation barrier and the degree of π bonding in the planar conformer. For trimethylsilyl substituents, the calculated energy difference of 6 kcal/mol is so small that minor steric or electronic effects of the substituents at carbon could be enough to reverse the stabilities of the two conformers. In view of the unusually small amount of π bonding in the planar (silylamino)borirenes the spectra of these compounds will probably resemble those of compounds without B–N π bonding, regardless of the actual conformation of the amino group.

The rotation barriers for hydroxy compounds are much smaller than those for the corresponding amino compounds (Table VII). This does not mean that B–O π bonding is much weaker than B–N π bonding. Rather, one must conclude that a large amount of O→B "π" donation is retained in the perpendicular conformer. This has already been mentioned for hydroxyborane, and is clear from the BOH bond angle and boron p_π population in perpendicular

---

(31) Greenberg, A.; Tomkins, R. P. T.; Dobrovolny, M.; Liebman, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 6855. For recent preparations of methylenecyclopropene, see: Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.*, **1984**, *106*, 3698. Staley, S. W.; Norden, T. D., *Ibid.* **1984**, *106*, 3699.

(32) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, *99*, 4899.

hydroxyborirane. Thus, it is clear that rotation barriers for OR groups give no reliable indication of B–O π bond strengths.

Chemical Implications. B–X bonds are stronger than C–X bonds for groups X with an electronegativity greater than or equal to that of carbon; an extra stabilization is observed (Table IX) with groups capable of B–X π bonding. In accord with this, many stable compounds containing B–C, B–N, B–O, and B–F bonds are known. The lowest energy B–X bonds (with respect to C–X bonds) are observed for X = BeH or BH_2, and indeed no B–Be single bonds are known while compounds containing single B–B bonds are notably labile and reactive. However, the B–Li bond is predicted to be as strong as the C–Li bond, and the existence of many organolithium compounds suggests that boron–lithium compounds might likewise be capable of existence. A more detailed study of the possible oligomers of simple boron-lithium compounds is currently in progress.[33] Table IX gives estimates for the various B–X bond energies, based on experimental C–X bond energies and our 6-31G* results for the B–X vs. C–X bond energy difference. These values are only rough estimates and have not been corrected for electron correlation effects and zero-point energy differences. Test calculations indicate, however, that the results are not likely to change much at higher levels of theory.

Strong B–X bonds are not a guarantee for the existence of stable derivatives. Unlike carbon compounds, most boron compounds are electron deficient and very susceptible to nucleophilic attack, resulting in a far higher reactivity than is usually observed for organic compounds. Thus, the chemical stability of boron compounds will be determined both by the thermodynamic stability and by the "protection" of the boron atom from nucleophilic attack, by, e.g., coordination saturation or steric hindrance.

Steric hindrance is obviously an important factor to enhance the persistence of alkyl borirenes, since the only examples reported to date contain *tert*-butyl groups;[6,7] synthetic attempts involving less bulky groups produced only dimers.[5] Similarly, the two known examples of boriranes carry *tert*-butyl and trimethylsilyl groups,[9,10] and even these are relatively unstable. Coordination saturation, through B$\rightarrow$X π bonding, is most effective in the amino and hydroxy series. Aminoborirenes have been prepared,[8a] and aminoboriranes and hydroxyborirenes would be possible synthetic goals.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. 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. $(CH)_2BH$, 16488-40-7; $(CH)_2BLi$, 93895-32-0; $(CH)_2BBeH$, 93895-33-1; $(CH)_2BBH_2$, 93895-34-2; $(CH)_2BCH_3$, 93895-35-3; $(CH)_2BNH_2$, 93895-36-4; $(CH)_2BOH$, 93895-37-5; $(CH)_2BF$, 93895-38-6; $(CH_2)_2BH$, 39517-80-1; $(CH_2)_2BLi$, 93895-39-7; $(CH_2)_2BBeH$, 93895-40-0; $(CH_2)_2BBH_2$, 93895-41-1; $(CH_2)_2BCH_3$, 93895-42-2; $(CH_2)_2BNH_2$, 93895-43-3; $(CH_2)_2BOH$, 93895-44-4; $(CH_2)_2BF$, 93895-45-5; BH_3, 13283-31-3; BH_2Li, 64360-74-3; BH_2BeH, 64360-78-7; BH_2BH_2, 18099-45-1; BH_2CH_3, 12538-96-4; BH_2NH_2, 14720-35-5; BH_2OH, 35825-58-2; BH_2F, 27944-03-2; $(CH)_2BN(CH_3)_2$, 93895-47-7; $(CH)_2BN(SiH_3)_2$, 93895-48-8; $(CH)_2BN(SiMe_3)_2$, 93895-49-9; dimethylborane, 7216-97-9; vinylborane, 5856-70-2; ethynylborane, 72507-59-6; vinylideneborane, 93895-46-6.

Supplementary Material Available: Complete specifications of the geometries of substituted borirenes and boriranes and of the reference compounds not available from ref 16 (**Z** matrices and coordinates) (23 pages). Ordering information is given on any current masthead page.

---

[33] Kaufmann, E.; Schleyer, P. v. R., to be submitted for publication.