P.H.M.B. expresses his gratitude for a fellowship sponsored by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.). We thank Prof. E. A. Halevi and Prof. G. E. Herberich for their interest.

Registry No. **1**, 16488-40-7; **2**, 77385-67-2; **3**, 13969-87-4; **4**, 101810-88-2; **5**, 28323-17-3; **6**, 101810-89-3; **7**, 101834-87-1; **8**, 68691-57-6.

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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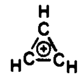
Received November 14, 1985

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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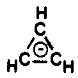

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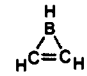

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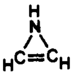

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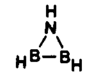

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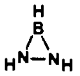

6

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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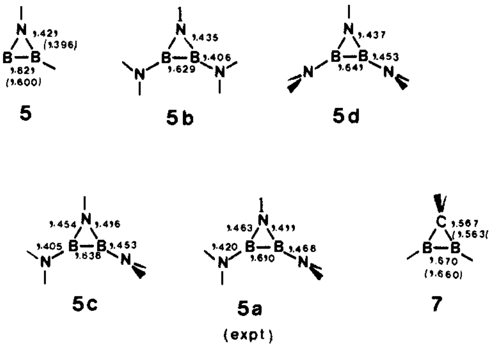

Figure 1. 3-21G(6-31G*) bond lengths (Å) for **5**, **5b–5d**, and **7** and experimental bond lengths for **5a**.

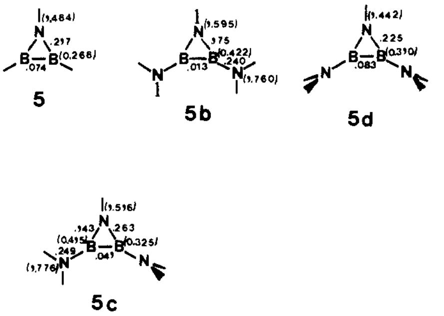

Figure 2. 3-21G π-overlap populations (π-electron densities) for **5** and **5b–5d**.

parison of theory with experiment in such an aromatic/antiaromatic pair for the first time. Since the perturbations introduced by the heteroatoms are by no means negligible, comparisons with a number of acyclic and cyclic reference molecules also are presented in this paper.

Methods

The geometries of **5**, **5b–5d**, **6a**, **6b**, **6d–6g**, **7**, and **8a–8c** were fully optimized,[12] subject only to overall molecular symmetry constraints, at the closed-shell restricted Hartree-Fock (RHF) level[13] using the small split-valence 3-21G basis set.[14a] The parent species **5**, **6a**, **6b**, **7**, and **8a–8c** were reoptimized at the split-valence plus polarization 6-31G* level,[14b] and the effects of electron correlation were included by second-order Møller-Plesset perturbation theory[15] (MP2/6-31G*) for **5**, **6a**, and **6b**. RHF/6-31G* energies for the substituted species **5b**, **5c**, and **6e–6g** were calculated at the 3-21G-optimized geometries.

Diagonalization of the force constant matrices[16] (at the 3-21G level) showed **5**, **6a**, **6e**, **6f**, **8a**, and **8b** to be local minima.[17] The two alternative diazaboridine structures **6b** and **6d** are not local minima, as their Hessian matrices have one and two negative eigenvalues, respectively. The C_s structure **6b** is the transition state for the inversion at nitrogen in **6a**, and **6d** is a higher-order saddle point. The C_1 structure **6g** is the transition state for the inversion at nitrogen in 3-aminodiazaboridine, and similarly the inversion in diaziridine **8** proceeds via the transition structure **8c**. Total energies are given in Table I; reaction energies quoted in the text are RHF/6-31G* values unless otherwise noted.

Table I. Total Energies for **5** and **6** and Reference Compounds

molecule			RHF/-3-21G	RHF/-6-31G*	MP2/-6-31G*
$HN(BH)_2$	C_{2v}	**5**	−104.964 48	−105.554 31	−105.864 54
$HN(BNH_2)_2$	C_{2v}	**5b**	−214.542 59	−215.710 53[c]	−216.347 61[c]
	C_s	**5c**	−214.513 76	−215.683 67[c]	−216.319 98[c]
	C_{2v}	**5d**	−214.483 34	−215.665 19[c]	
$HB(NH)_2$	C_2	**6a**	−134.499 87	−135.266 28	−135.665 89
	C_s	**6b**	−134.485 64	−135.255 17	−135.654 70
	C_{2v}	**6d**	−134.461 37		
$H_2NB(NH)_2$	C_2	**6e**	−189.297 76	−190.349 93[c]	
	C_s	**6f**	−189.283 39	−190.338 25[c]	
	C_1	**6g**	−189.280 38	−190.329 26[c]	
$CH_2(BH)_2$	C_{2v}	**7**	−88.947 40	−89.447 87	
$CH_2(NH)_2$	C_2	**8a**	−148.146 38	−149.004 03	
	C_s	**8b**	−148.132 65	−148.993 27	
	C_1	**8c**	−148.103 34	−148.951 67	
BH_2NH_2					
copl	C_{2v}	**9a**	−81.043 43[a]	−81.489 01[a]	
perp	C_s	**9b**	−80.990 27[a]	−81.442 19[a]	
perp	C_{2v}	**9c**	−80.989 79[a]	−81.435 18[b]	
$NH(BH_2)_2$	C_{2v}	**10**	−106.191 49	−106.781 37[a]	
$BH(NH_2)_2$	C_{2v}	**11**	−135.829 19[a]	−136.568 30[a]	
$B(NH_2)_3$	D_{3h}	**12**	−190.605 47	−191.637 84	
BH_3			−26.237 30[a]	−26.390 01[a]	
CH_3BH_2			−65.078 09[a]	−65.441 54[a]	
$(CH_3)_2BH$			−103.917 68[b]	−104.491 34[b,c]	
$(CH_2)_2BH$			−102.686 96[b]	−103.262 06[b]	
$(CH_2)_2BNH_2$					
copl			−157.490 96[b]	−158.354 04[b,c]	
perp			−157.442 89[b]	−158.306 74[b,c]	
$(CH)_2BNH_2$					
copl			−156.307 79[b]	−157.176 33[b,c]	
perp			−156.280 14[b]	−157.148 90[b,c]	
NH_3			−55.872 20[a]	−56.184 36[a]	
CH_3NH_2			−94.681 66[a]	−95.209 83[a]	
$(CH_3)_2NH$			−133.494 85[a]	−134.238 85[a]	
$(CH_2)_2NH$			−132.278 01[a]	−133.038 55[d]	
CH_3CH_3			−78.793 95[a]	−79.228 75[a]	
$(CH_2)_3$			−116.401 21[a]	−117.058 87[a]	

[a] From ref 18. [b] From ref 5. [c] 6-31G*//3-21G. [d] From ref 23.

Table II. B–N Bond Lengths (Å)[a] and π-Populations[b] for Some Reference Compounds

molecule		B–N	ρ_{BN}^{π}	q_B^{π}	q_N^{π}	ref
BH_2NH_2						
(C_{2v} copl)	**9a**	1.400 (1.389)	0.283	0.292	1.708	18
(C_s perp)	**9b**	1.478 (1.471)				18
$(BH_2)_2NH$	**10**	1.436 (1.419)	0.207	0.208	1.583	18
$BH(NH_2)_2$	**11**	1.422 (1.412)	0.209	0.404	1.798	18
$B(NH_2)_3$	**12**	1.438 (1.429)	0.166	0.463	1.846	this work
$(CH_2)_2BNH_2$		1.387	0.308	0.314	1.718	5
$(CH)_2BNH_2$		1.400	0.243	0.449	1.781	5

[a] 3-21G(6-31G*) values. [b] 3-21G//3-21G.

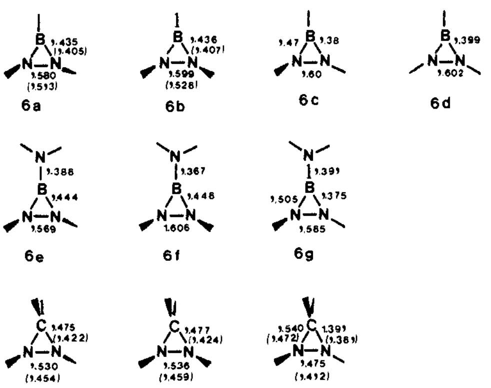

Figure 3. 3-21G(6-31G*) bond lengths (Å) for **6a–6g** and **8a–8c**. Note that **6c** is *not* a stationary point on the potential energy surface (see text).

Important geometrical parameters for azadiboridines and diazaboridines are presented in Figures 1 and 3, respectively (complete specifications of geometries are available as supplementary material). The π-overlap populations and electron densities in Figure 2 refer to the

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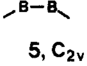
(17) Perpendicular C_{2v} diborirane **7** is less stable than its planar carbon isomer, and at high levels it probably does not even correspond to a local minimum. However, we feel that it is the most appropriate reference compound for a $(BH)_2$ incorporated in a three-membered ring system and therefore included it here.

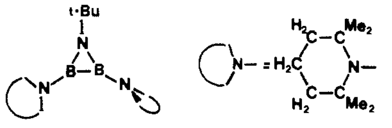
3-21G calculations. B–N bond lengths and 3-21G π-orbital and overlap populations for some reference compounds are collected in Table II.

Azadiboridine, 5

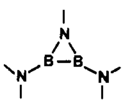
Let us first consider the structure of the 2π-electron molecule **5**. For the length of a "normal" B–B single bond, one can take the value calculated for the *planar* conformation of diborane (**4**), i.e., 1.76 Å,[18] which should correspond to the geometry of the diboron moiety in **5**. However, the B–B bond length is decreased by 0.10 to 1.66 Å upon incorporation of the B_2H_2 group into the three-membered ring of **7**.[17,19] Thus, the value of 1.60 Å in **5** certainly is shorter than expected for a normal B–B single bond, but ca. two-thirds of the shortening of 0.16 Å is due to the three-membered ring (3MR) contraction; the remaining 0.06 Å can be attributed to weak B–B π-bonding. In accord with this, the B–B π-overlap population is small (0.074; see Figure 2).



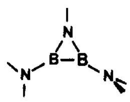
5, C_{2v}



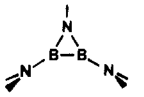
5a



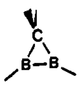
5b, C_{2v}



5c, C_s



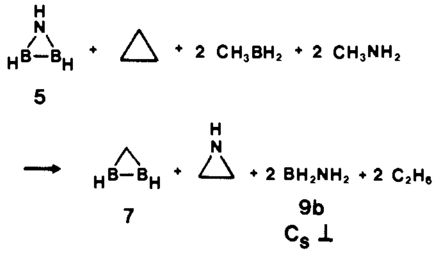
5d, C_{2v}



7, C_{2v}

The B–N bond (1.42 Å, Figure 1) is shorter than that in planar $HN(BH_2)_2$ **10** (1.44 Å; see Table II), but the modest difference can be attributed to the 3MR contraction.[20] The total N → B π-donation is larger in **5** than in **10** (by ca. 0.12 e), but apparently the small amount of "extra" delocalization contributes only to the B–B π-bond. This is also seen in the B–N π-overlap populations: 0.28 in **9a**, 0.21 in **10**, and 0.22 in **5**.

Thus, the calculations suggest that the amount of cyclic delocalization is rather small, and the bonding does not differ greatly from that in **10**. A similar conclusion can be reached from analysis of the energies. An estimate of the total delocalization energy of **5** can be obtained from eq 1, in which ring strain and bond energy effects are compensated as closely as possible.



(1)

+55.0 kcal/mol

The corresponding π-bond energy of **10** is obtained from eq 2. Subtraction gives an estimate of the "aromatic" cyclic delocalization energy, viz., 6.2 kcal/mol. Thus, the *extra* stabilization associated with the *closed* π-system in **5** (over the acyclic analogue **10**) is relatively small, but the *total* delocalization energy, over 50 kcal/mol, is even larger than that of borirene.[5]

$$\underset{\mathbf{10}}{(BH_2)_2NH} + 2\,CH_3NH_2 \longrightarrow (CH_3)_2NH + \underset{\mathbf{9b}}{2\,BH_2NH_2} \qquad (2)$$

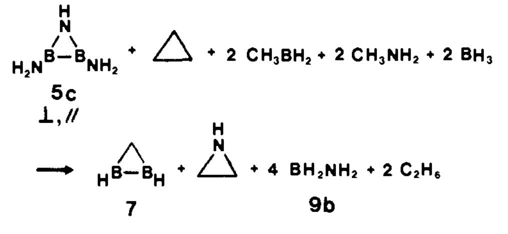
+48.8 kcal/mol

These thermochemical analyses (and those below) assume that many differences (e.g., in X–H bond or ring strain energies) cancel or are insignificant. However, the inversion barrier at nitrogen in a three-membered ring (aziridine = 19 kcal/mol) is much higher than that in acyclic amines (4–6 kcal/mol).[21] In planar molecules like **5** and its derivatives, π-delocalization must overcome this enhanced nitrogen pyramidalization energy. This has a large effect on the calculated resonance energy. For example, if eq 1 and 2 were evaluated by using the energies of aziridine and the methyl amines with *planar* arrangements at nitrogen, the estimated "aromatic" cyclic delocalization energy would be increased by about 15 kcal/mol.

2,3-Diaminoazadiboridine

The crystal structure of a derivative of **5**, 1-*tert*-butyl-2,3-bis(2,2,6,6-tetramethyl-1-piperidino)azadiboridine (**5a**), has been determined by X-ray diffraction.[10b] One of the piperidino groups is approximately coplanar with the BBN ring plane (dihedral angle 18°), while the other is nearly perpendicular (77°). As a simple model system, we investigated 2,3-diaminoazadiboridine in the three conformations **5b**–**5d**. The most stable conformation is the all-planar **5b**, and **5c** and **5d** are higher in energy by 17.3 and 34.7 kcal/mol, respectively (at MP2/6-31G* and 6-31G*, respectively). The B–N rotation barrier of 17 kcal/mol is much smaller than those of aminoborane (29 kcal/mol) and aminoborirane (30 kcal/mol) and close to that in the aromatic aminoborirene (17 kcal/mol).[5] As suggested by Nöth, the aromatic delocalization saturates the boron atoms and decreases π-bonding to the exocyclic amino groups.[10] Still, our calculations indicate a definite preference for the all-planar arrangement, and the observed[10b] coplanar/perpendicular arrangement in **5a** must be attributed to the crowding of the bulky tetramethylpiperidino groups.

The coplanar amino groups in **5b** and **5c** clearly reduce the delocalization in **5**, as shown by the changes in B–N bond lengths and overlap populations (Figures 1 and 2). In **5c**, the bond alternations indicate a tendency toward a structure with localized B–N π-bonds, analogous to methylenecyclopropene. However, the total delocalization energy of **5c**, calculated from eq 1a, is much larger than that of two isolated B–N π-bonds (ca. 59 kcal/mol) and indicates a considerable residual delocalization in **5b**.



(1a)

+84.5 kcal/mol (3-21G)

The geometry calculated for **5c** at the HF/3-21G level agrees nicely with the experimental structure of **5a** (see Figure 1), but this is partly fortuitous. Better basis sets are needed to obtain accurate bond lengths for such strained systems, and HF/6-31G* optimization results in a contraction of all bonds of **5**. However, the steric congestion in **5a** will lead to an elongation of most bonds, and apparently the two "errors" nearly cancel.

Diazaboridine, 6

The 4π-molecule **6** prefers a nonplanar C_2 geometry (**6a**). Because of greater lone pair–lone pair repulsion, the C_s structure **6b**, with both hydrogen atoms on the same side of the ring plane, is 7.0 kcal/mol higher in energy. Interestingly, this C_s structure is not a local minimum but a transition state. The Hessian matrix has one negative eigenvalue, and an analysis of the corresponding eigenvector shows that it corresponds to the asymmetric NH rock vibration; i.e., **6b** is the transition state for the inversion of **6a**. We have also followed the reaction path from **6a** to **6b**. In the

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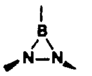
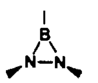
[18] Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Carnegie-Mellon: Pittsburgh, 1983.

[19] Krogh-Jespersen, K.; Cremer, D.; Poppinger, D.; Pople, J. A.; Schleyer, P. v. R.; Chandrasekhar, J. *J. Am. Chem. Soc.* **1979**, *101*, 4843.

[20] The 3MR contraction of a B–N bond, with its partial double-bond character, should be comparable to that of a C–C single bond (0.03 Å for ethane → cyclopropane) or double bond (0.041 Å for ethene → cyclopropene) calculated at the same level of theory (RHF/6-31G*).[18]

[21] See: Jennings, W. B.; Worley, S. D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1512.


6a, C_2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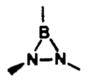
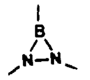
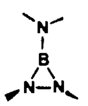
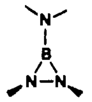
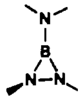
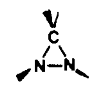

6c, C_1

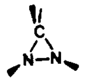

6d, C_{2v}

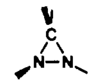

6e, C_2


6f, C_s


6g, C_1

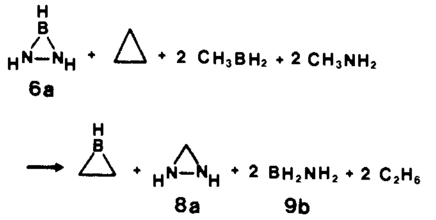

8a, C_2


8b, C_s


8c, C_1

intermediate stages, one of the B–N bonds (the one to the inverting nitrogen atom) shortens. Simultaneously, the other B–N bond elongates and the second nitrogen atom increases its pyramidalization. Apparently, the intermediate stage can be represented by a structure with one localized B–N π-bond; approximate geometrical details for the point of maximum localization (**6c**) are shown in Figure 3. Thus, the inversion at nitrogen is strongly assisted by B–N π-bond formation.[10] In diaziridine, where such assistance is lacking, the situation is more normal. There, we find two local minima (**8a** and **8b**) of C_2 and C_s symmetry, separated by a transition state **8c** of C_1 symmetry which is ca. 33 kcal/mol above **8a**.[22] The energy difference between **8a** and **8b**, 6.8 kcal/mol, is close to that between **6a** and **6b**; the lone pair–lone pair repulsions must be similar in the two molecules.

The N–N bond length of 1.51 Å in **6a** is 0.06 Å longer than that in diaziridine **8a**, indicating a strong N–N π-repulsions which is reflected in the negative N–N π-overlap population of −0.188 in planar **6d**. The B–N bonds in **6a** are only slightly longer than those in **5**, indicating a considerable $N_{\text{lone pair}} \rightarrow B$ π-donation, though less than in planar $HB(NH_2)_2$ **11**. The total delocalization energy can be estimated from eq 3.



(3)

+12.5 kcal/mol

This should be compared with the π-bond energy of **11**, evaluated from eq 4. The difference in energy between eq 3 and 4, 35 kcal/mol, can be attributed to the antiaromatic interactions in **6**; a similar destabilization is obtained for the isoelectronic azirine.[6] It should be emphasized that in **6**, the 4π-repulsive

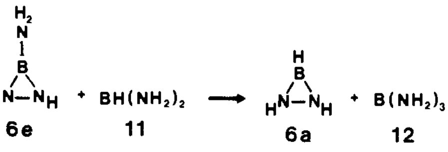
$$\underset{\mathbf{11}}{BH(NH_2)_2} + 2\,CH_3BH_2 \longrightarrow (CH_3)_2BH + 2\,\underset{\mathbf{9b}}{BH_2NH_2} \qquad (4)$$

+47.5 kcal/mol

interactions are partly avoided by a strong pyramidalization at the nitrogen atoms; if the planar structure **6d** is employed in evaluating eq 3, a much larger "pure" 4π-destabilization of over 60 kcal/mol results. Strong pyramidalization at nitrogen in azirine **4**[6] and at the carbanion center in the cyclopropenyl anion **2**[3] also reduces the unfavorable antiaromatic interactions in these 4π-electron systems.

3-Aminodiazaboridine

Since the two derivatives of **6** which have been reported[10,11] both bear nitrogen substituents at boron, we decided to include 3-aminodiazaboridine, **6e**, in our study. The short B–NH_2 bond (1.39 Å at 3-21G, equal to that calculated for 1-aminoborirane at the same level of theory[5]) indicates strong π-bonding to the exocyclic nitrogen atom; the ring B–N and N–N bonds in **6e** are ca 0.01 Å longer than in **6a**. The exocyclic B–N π-bond competes with the cyclic conjugation in **6** and thus *decreases* the 4π-antiaromatic *destabilization* of the BNN system, as illustrated by the energy change in eq 5. Although steric factors will certainly contribute,[10] our calculations indicate that the electronic effects of the amino substituent at boron also are important in stabilizing the 4π-diazaboridines.



(5)

+8.9 kcal/mol

The presence of an amino group also affects the inversion barriers of the ring nitrogen atoms. In contrast to the unsubstituted **6b**, the structure **6f**, though higher in energy than the C_2 minimum **6e**, also is a local minimum. The transition state **6g** for the inversion is 5.6 kcal/mol above the less-stable structure **6f**. The exocyclic amino substituent decreases the π-acceptor character of boron and thus reduces the degree to which π-effects influence the stereomutation of **6**. Our calculated inversion barrier of 13.0 kcal/mol for **6e** agrees nicely with the experimental estimate of 14 kcal/mol for 1,2-diisopropyl-3-(2,2,6,6-tetramethyl-1-piperidino)diazaboridine.[10a]

Conclusions

Azadiboridines are aromatic molecules with large resonance energies. However, the B–B π-bond in these molecules is rather weak, and amino substituents weaken it even further. Such substituents decrease the delocalization energy somewhat but do not destroy the aromaticity of the ring system; similar effects have been observed in aminoborirene.[5] Diazaboridines have large antiaromatic destabilization energies. The cyclic conjugation is partly interrupted, resulting in a decreased destabilization, by amino substituents at boron. If π-donor substituents can reduce the resonance energy of $(4n + 2)$ π-aromatic systems, it should not be surprising that they can also stabilize $(4n)\pi$-antiaromatic systems. Our results bring out this effect quite clearly.

Acknowledgment. We thank Prof. H. Nöth and Prof. U. Klingbiel results to us prior to publication.

Note Added in Proof. The X-ray structure of a diazaboridine derivative[11c] now confirms our structural predictions, except for the long N–N bond.

Registry No. 5, 85302-95-0; **5b/5c/5d**, 101199-27-3; **6a**, 101199-28-4; **6b**, 101199-29-5; **6d**, 85302-96-1; **6e**, 101199-30-8; **6f**, 101199-31-9; **6g**, 101199-32-0; **7**, 60720-12-9; **8a**, 41977-52-0; **8b**, 41977-53-1; **8c**, 463-64-9; **10**, 18447-54-6; **12**, 14939-14-1.

Supplementary Material Available: Complete geometry specifications (Z matrices and Cartesian coordinates) of the structures of **5**, **5b**–**5d**, **6a**, **6b**, **6d**–**6g**, **7**, and **8a**–**8c** (11 pages). Ordering information is given on any current masthead page.

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[22] No experimental data are available for inversion barriers in diaziridines. Mannschreck et al. (Mannschreck, A.; Radeglia, R.; Gründemann, R.; Ohne, R. *Chem. Ber.* **1967**, *100*, 1778) give a lower limit of 21 kcal/mol, but the actual value may well be as high as the 33 kcal/mol predicted by our calculations.

[23] Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800, 3811.