Synthesis, Structure and Reactivity of 3,4-Dihydro-2*H*-1,2,4,3-triazaboroles

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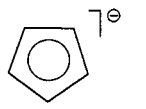
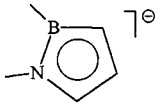
3,4-Dihydro-2,4-diphenyl-2*H*-1,2,4,3-triazaboroles **3a**, **3b**, and **4** were synthesized by cyclocondensation of N^1,N^3-diphenylformamidrazone (**1**) with dibromophenylborane, dibromomethylborane, and boron trichloride. 3-Chloro-3,4-dihydro-2,4-diphenyl-2*H*-1,2,4,3-triazaborole (**4**) was converted into 3,4-dihydro-2,4-diphenyl-2*H*-1,2,4,3-triazaborole (**5**) by treatment with $LiAlH_4$. The corresponding 3-cyanato and 3-cyano derivatives **6** and **7** resulted from the reaction of **4** with AgOCN and AgCN, respectively. Compound **7** was transformed into the bis(1,2,4,3-triazaborolyl)oxane **8** by silver oxide. Compounds **1–8** were characterized by elemental analyses and spectroscopic methods (^{1}H, ^{11}B, and ^{13}C NMR; IR; MS). The molecular structure of **8** was established by single-crystal X-ray diffraction analysis.

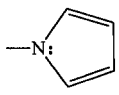
Replacing a pair of adjacent carbon atoms in the cyclopentadienide anion **I** by the isoelectronic B−N combination affords the dihydro-1,2-azaborolyl anion **II**. With pyrrol **III** and imidazole **V** the same formalism leads to 2,3-dihydro-1*H*-1,3,2-diazaboroles **IV** and 3,4-dihydro-2*H*-1,2,4,3-triazaboroles **VI**, respectively.



I



II



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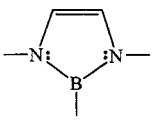
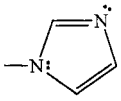


IV



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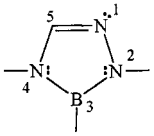
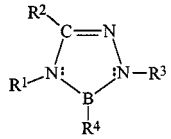
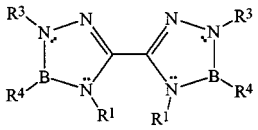


VI

Whereas the chemistry of 1,2-azaborolyl anions **II** has been thoroughly studied, especially with respect to its ligating properties,[1][2] and a series of papers has dealt with 1,3,2-diazaboroles **IV**,[3][4] information on 3,4-dihydro-2*H*-1,2,4,3-triazaboroles is scarce. 3,4-Dihydro-2,3,4,5-tetraphenyl-2*H*-1,2,4,3-triazaborole was formed in 5% yield during the cothermolysis of the pyridine adduct of diphenylboron azide and 2,5-diphenyltetrazole at 210°C.[5] In a brief communication the preparation of eight 1,2,4,3-triazaboroles **VI** by cyclocondensation of amidrazones $R^2C(NHR^1)=NNHR^3$ with boronic acid derivatives R^4BX_2 (X = Cl, OMe, OEt, OH, NMe_2) was reported.[6] Similarly, four bis(1,2,4,3-triazaborole)s **VII** were obtained from $PhB(OH)_2$ or $BuB(OH)_2$ and oxamidrazones.[7] No spectroscopic details were given for **VI** and **VII**.



VI a: $R^1 = R^3 = H$; $R^2 = Me$, $R^4 = Ph$
b: $R^1 = H$; $R^2 = R^3 = Me$; $R^4 = Ph$
c: $R^1 = R^4 = Ph$; $R^2 = R^3 = H$
d: $R^1 = R^3 = H$; $R^3 = 2$-py; $R^4 = Ph$
e: $R^1 = R^3 = R^4 = Ph$; $R^2 = H$
f: $R^1 = R^2 = R^4 = Ph$; $R^3 = H$
g: $R^1 = R^2 = R^3 = R^4 = Ph$
h: $R^1 = R^2 = Ph$; $R^3 = H$; $R^4 = n$-Bu



VII a: $R^1 = R^3 = H$; $R^4 = Ph$
b: $R^1 = R^3 = H$; $R^4 = n$-Bu
c: $R^1 = H$; $R^3 = R^4 = Ph$
d: $R^1 = R^4 = Ph$; $R^3 = H$

Bezuglaya et al. were concerned with IR,[8] mass[9], electronic absorption,[10] and X-ray photoelectron spectra,[11] as well as electrochemical studies,[12] acylation[13] and protonation reactions on 2,3,5-triaryl-1,2,4,3-triazaboroles[14] in which the aryl rings were *para*-substituted phenyl groups. Theoretical studies on the 2,3,5-triphenyl derivative as well as the UV spectra are not in accordance with heteroaromaticity.[10] Interestingly, in all the described 1,2,4,3-triazaboroles no other substitutents than phenyl (or *para*-substituted phenyl) rings and the *n*-butyl group are ligated to the boron atom.

We decided to investigate the chemistry of this ring system in more detail and from our experience with 2-halo-1,3,2-diazaboroles first envisaged the synthesis of 3-halo-1,2,4,3-triazaboroles. For synthetic and spectroscopic reasons the carbon atom of the ring should bear a hydrogen atom.

Results and Discussions

For the preparation of 3-halo-1,2,4,3-triazaboroles and derivatives thereof it was necessary to explore the experimental conditions in more detail and, moreover, provide

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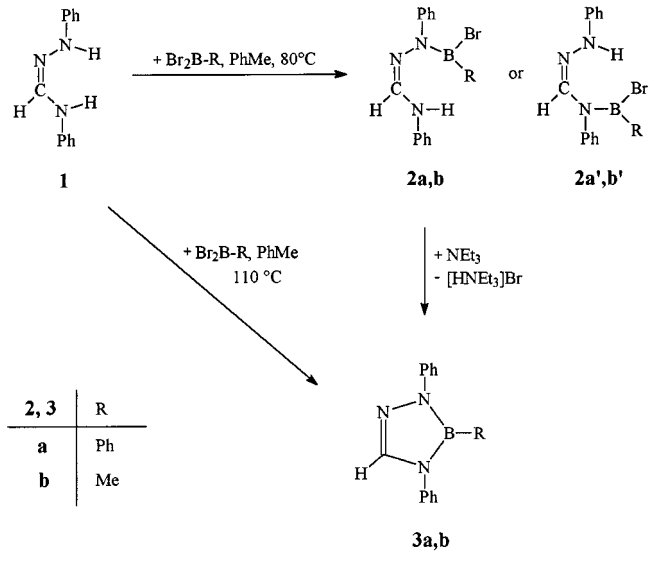
the NMR data that was lacking for some of the known species.

Combination of equimolar amounts of $PhBBr_2$ with formamidrazone **1** in toluene at 80°C for 1 h did not lead to the ring system **3a** as indicated in ref.[6] Instead the acyclic bromo(hydrazino)phenylborane derivative **2a/2a′** was obtained as a colorless crystalline solid (62% yield). Similarly, the bromo(hydrazino)methylborane derivative **2b/2b′** resulted from the reaction of **1** with $MeBBr_2$ in toluene at 80°C (52%). The air- and moisture-sensitive compounds display singlets at δ = 28.9 and 29.1 in the $^{11}B\{^1H\}$-NMR spectra. The amidine hydrogen atoms in the ^1H-NMR spectra of **2a/2a′** and **2b/2b′** give rise to singlets at δ = 8.93 and 9.03. In the $^{13}C\{^1H\}$-NMR spectrum the corresponding carbon atoms of **2a/2a′** and **2b/2b′** were observed as singlets at δ = 141.3 and 140.8. Basicly, the boryl group can be attached to the hydrazino group as indicated in **2a** and **2b** or alternatively to the anilino function as shown in **2a′** and **2b′**. No unambigious differentation between the two isomers was possible only by means of the spectroscopic data. Unfortunately, crystals of **2a/2a′** or **2b/2b′** suitable for an X-ray analysis were not available.

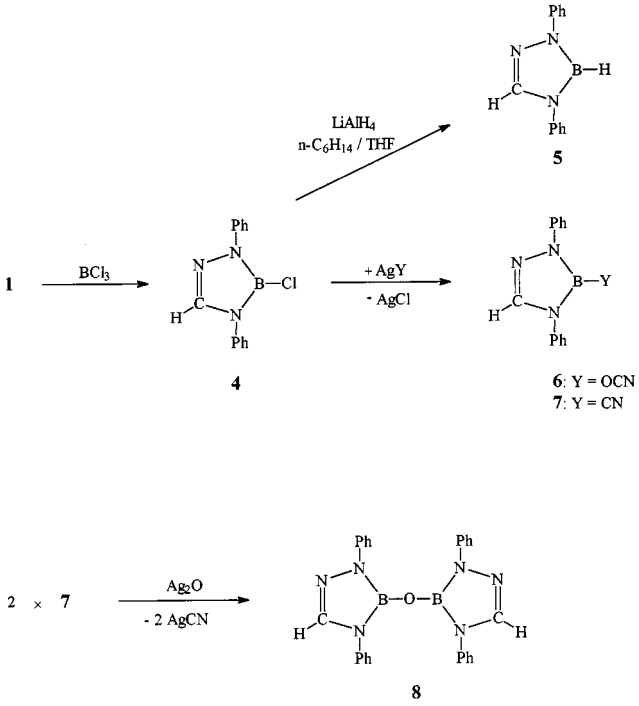
Cyclization of **2a/2a′** and **2b/2b′** to **3a** and **3b**, respectively, was effected by dehydrobromination with triethylamine. Alternatively the heterocycles were directly obtained by cyclocondensation of **1** with equimolar amounts of $PhBBr_2$ or $MeBBr_2$ in boiling toluene. By this method improved yields (74 and 69%) were achieved. In a control experiment the cyclization also occurred by heating a toluene solution of **2a/2a′** to 110°C.



Scheme 1

Heating a toluene solution of boron trichloride with a threefold excess of **1** at 90°C for 2.5 h led to the formation of the 3-chloro-1,2,4,3-triazaborole **4**, which was isolated as a colorless, extremely moisture-sensitive solid in 63% yield. This compound proved to be a valuable starting material for a series of other 1,2,4,3-triazaborole derivatives. Thus, formation of **3b** from **4** and an equimolar amount of methyllithium cleanly occurred in 83% yield.

Lithium aluminium hydride reduction of **4** in an *n*-hexane/THF mixture afforded the colorless crystalline 3-hydro-substituted 1,2,4,3-triazaborole **5** (84%). Treatment of **4** with equimolar amounts of silver cyanate or silver cyanide in acetonitrile in the absence of light smoothly generated the compounds **6** and **7** in 68% and 63% yield. Like **4** both products are extremely moisture-sensitive colorless solids. Their great propensity for hydrolysis is evident from impurities, revealed as bis(1,2,4,3-triazaborolyl)oxane (**8**) (δ ^{11}B = 20.5). A clean high-yield synthesis of **8** made use of the reaction of 3-cyano derivative **7** with silver oxide in acetonitrile (Scheme 2).



Scheme 2

The $^{11}B\{^1H\}$-NMR spectra of the triazaboroles described here display an increased shielding as follows: **3b** (δ = 27.8) > **3a** (26.4) > **4** (22.8) > **5** (21.5) > **8** (20.5) > **6** (17.1) > **7** (13.9). A comparable order was observed with the corresponding *N*-arylated 1,3-diazaboroles. Thus, in $PhN^a-C(Me)=C(Me)N^b(Ph)B-Me(N^a-B)$,[15] $XylN^aC(H)=C(H)-N^b(Xyl)BCl(N^a-B)$,[4a] $XylN^a-C(H)=C(H)-N^b(Xyl)BH(N^a-B)$, and $XylN^aC(H)=C(H)-N^b(Xyl)BCN(N^a-B)$ (Xyl = 2,6-$Me_2C_6H_3$) ^{11}B-NMR signals were recorded at δ = 28.0,[15] 21.1,[4a] 21.9,[4c] and 13.5[4a]. In the proton-coupled ^{11}B-NMR spectrum of **5** a doublet ($^1J_{B-H}$ = 162.5 Hz) was observed. The corresponding doublet in the diazaborole $tBuN^a-CH=CH-N^b(tBu)BH(N^a-B)$ at δ = 21.9 showed a coupling constant $^1J_{B-H}$ = 158 Hz.[4c] In the ^1H-NMR spectra of **3a,b–8** the CH protons of the heterocycle were observed as singlets at δ = 7.33–7.87. In the $^{13}C\{^1H\}$-NMR spectra the corresponding ^{13}C atoms gave rise to singlets at δ = 138.39–141.03. Interestingly, in the ^1H-NMR spectrum of **5** a broad 1:1:1:1 quadruplet at δ = 5.39 ($^1J_{B-H}$ = 158 Hz) appeared for the proton at the boron atom. In *t*BuN-

$^{a}C(H)=C(H)N^{b}(tBu)BH(N^{a}-B)$ a quadruplet at $\delta = 4.78$ ($^{1}J_{B-H} = 150$ Hz) was attributed to this proton.[4c]

The IR spectrum of **5** displayed a week, sharp band at $\tilde{\nu} = 2645$ cm^{-1} for the BH stretching vibration. A weak band at $\tilde{\nu} = 2224$ cm^{-1} in the IR spectrum of **7** was assigned to the stretching mode of the cyano group. The antisymmetric NCO vibration gave rise to a strong band at $\tilde{\nu} = 2309$ cm^{-1} in the IR spectrum of **6**. In isocyanato boranes of the type $(R_2N)_2BNCO$ intense bands for ν_{as}(NCO) were measured in the range $\tilde{\nu} = 2290 \pm 15$ cm^{-1}.[16]

X-ray Structural Analysis of 8

In the crystal, molecule **8** (Figure 1) has an overall similarity to the bent twisted structures of the bis(1,2,3-diazaborolyl)oxane **9**[4b] and tetramesityldiboroxane,[17] which display B−O−B angles of 157.1(3)° and 165.5(12)°, respectively. In **8**, however, the valence angle at the oxygen atom is more compressed [133.6(3)°]. Both BCN_3 rings in **8** are planar, enclosing an interplanar angle $\Psi = 66.0°$. Due to the bulky *tert*-butyl group in **9** the diazaborole rings in **9** are mutually orthogonal.

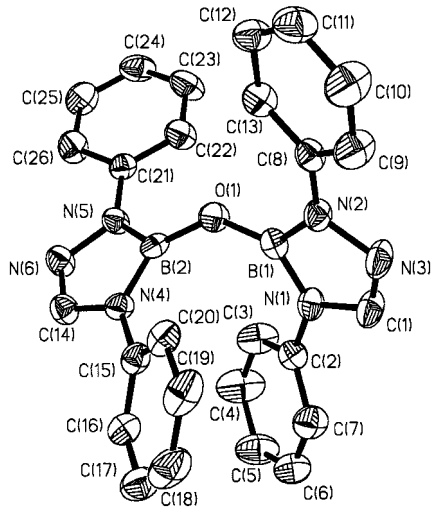
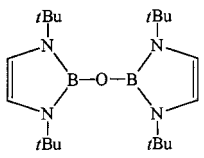


Figure 1. Crystal molecular structure of **8**; selected bond lengths [Å] and angles [°]: O(1)−B(1) 1.365(4), O(1)−B(2) 1.370(4), B(1)−N(1) 1.434(5), B(1)−N(2) 1.427(4), B(2)−N(4) 1.429(5), B(2)−N(5) 1.426(4), N(2)−N(3) 1.409(4), N(5)−N(6) 1.406(4), N(3)−C(1) 1.283(4), N(1)−C(1) 1.377(4), N(1)−C(2) 1.425(4), N(2)−C(8) 1.414(4), N(4)−C(14) 1.379(4), N(6)−C(14) 1.294(4), N(4)−C(15) 1.425(4), N(5)−C(21) 1.417(4); B(1)−O(1)−B(2) 133.6(3), O(1)−B(1)−N(2) 126.6(3), O(1)−B(1)−N(1) 129.3(3), O(1)−B(2)−N(4) 128.8(3), O(1)−B(2)−N(5) 127.0(3), N(1)−B(1)−N(2) 104.1(3), N(4)−B(2)−N(5) 104.2(3), B(1)−N(2)−N(3) 109.8(3), B(1)−N(1)−C(1) 105.1(3), N(2)−N(3)−C(1) 105.2(3), N(1)−C(1)−N(3) 115.8(3), B(2)−N(5)−N(6) 110.0(3), B(2)−N(4)−C(14) 105.3(3), N(4)−C(14)−N(6) 115.4(3), N(5)−N(6)−C(14) 105.1(3), B(1)−N(1)−C(2) 132.1(3), B(1)−N(2)−C(8) 134.1(3), C(1)−N(1)−C(2) 122.3(3), N(3)−N(2)−C(8) 115.8(3), B(2)−N(4)−C(15) 130.2(3), B(2)−N(5)−C(21) 132.5(3), C(14)−N(4)−C(15) 124.5(3), N(6)−N(5)−C(21) 117.4(3)



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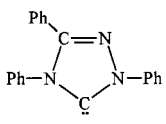

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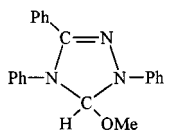

11

The respective bond lengths and bond angles within both 1,2,4,3-triazaborole units of **8** are identical within experimental error. The B−N distances [av. 1.429(5) Å] fall in the range of 1.407(3) to 1.450(7) Å measured for B−N bond lengths in a series of 1,3,2-diazaboroles and indicate multiple bond character. The endocyclic bond lengths N(1)−C(1) [1.377(4) Å] and N(4)−C(14) [1.379(4) Å] are significantly shorter than the exocyclic N−C (sp^2) bonds [av. 1.421(4) Å]. Within experimental error they are comparable to the N(Ph)−C(Ph) distances in 4,5-dihydro-1,3,4-triphenyl-1*H*-1,2,4-triazole-5-ylidene (**10**) [1.391(2) Å] and 4,5-dihydro-5-methoxy-1,3,4-triphenyl-1*H*-1,2,4-triazole (**11**) [1.391(6) Å].[18] The endocyclic bonds N(3)−C(1) [1.283(4) Å] and N(6)−C(14) [1.294(4) Å] are also close to those in **10** [1.304(3) Å] and **11** [1.296(6) Å], and are thus not significantly elongated relative to the calculated C=N bond length in formaldehyde imine [1.283 Å][18] or the experimentally determined C=N bond length in formaldehyde oxime [1.276 Å].[19] The interatomic distance N(2)−N(3) in **8** [1.409(4) C] is similar to the N−N bond length in **11** [1.394(6)] C,[18] and has to be regarded as a localized single bond.

The endocyclic angles B(1)−N(2)−N(3) [109.8(3)°] and B(2)−N(5)−N(6) [110.0(3)°] in **8** are more obtuse than the endocyclic angles B(1)−N(1)−C(1) [105.1(3)°] and B(2)−N(4)−C(14) [105.1(3)°]. The latter values compare well with the corresponding angles B−N−C in **9** [105.7(3)−106.5(2)°]. The angles at the endocyclic carbon atoms in **9** [110.3(3)−110.5(3)°] are markedly compressed relative to the endocyclic angles at C(1) [115.8(3)°] and C(14) [115.8(3)°] in **8**. The angles at the dicoordinate ring nitrogen atoms N(3) and N(6) are 105.2(3) and 105.1(3)°. In conclusion, the structural parameters of **8** provided by the X-ray analysis give no support for a 6π-electron delocalization within the 1,2,4,3-triazaborole ring as claimed in ref.[6]

In order to analyze this aspect in more detail we performed quantum-chemical ab initio calculations[20] at RHF/6-31g* and density functional level (B3LYP/6-31g*)[21] on **8** and its parent compound without the phenyl groups. Corresponding Molden plots[22] of the computed equilibrium geometries are given in Figure 2.

In the parent compound the two five-membered ring units are twisted (torsion angle N−B−O−B 23.2°). The RHF and density functional calculations yield almost similar bond lengths within the ring geometries. The structure of the diborolyloxane changes markedly on the introduction of the four phenyl substituents. It adopts an equilibrium structure which is in perfect agreement with the results of the X-ray investigations (torsion angle N−B−O−B 45.0°). Consequently, the actual structure of **8** is largely determined by the steric demand of the phenyl groups. Since from the computed structure it is not clear how the π bonds are delocalized in the heterocyclic units, we performed population analyses at the given equilibrium geometries, utilizing the natural bond orbital scheme.[23] The results of these investigations will not be recorded here in detail. However, an inspection of the corresponding Wiberg bond

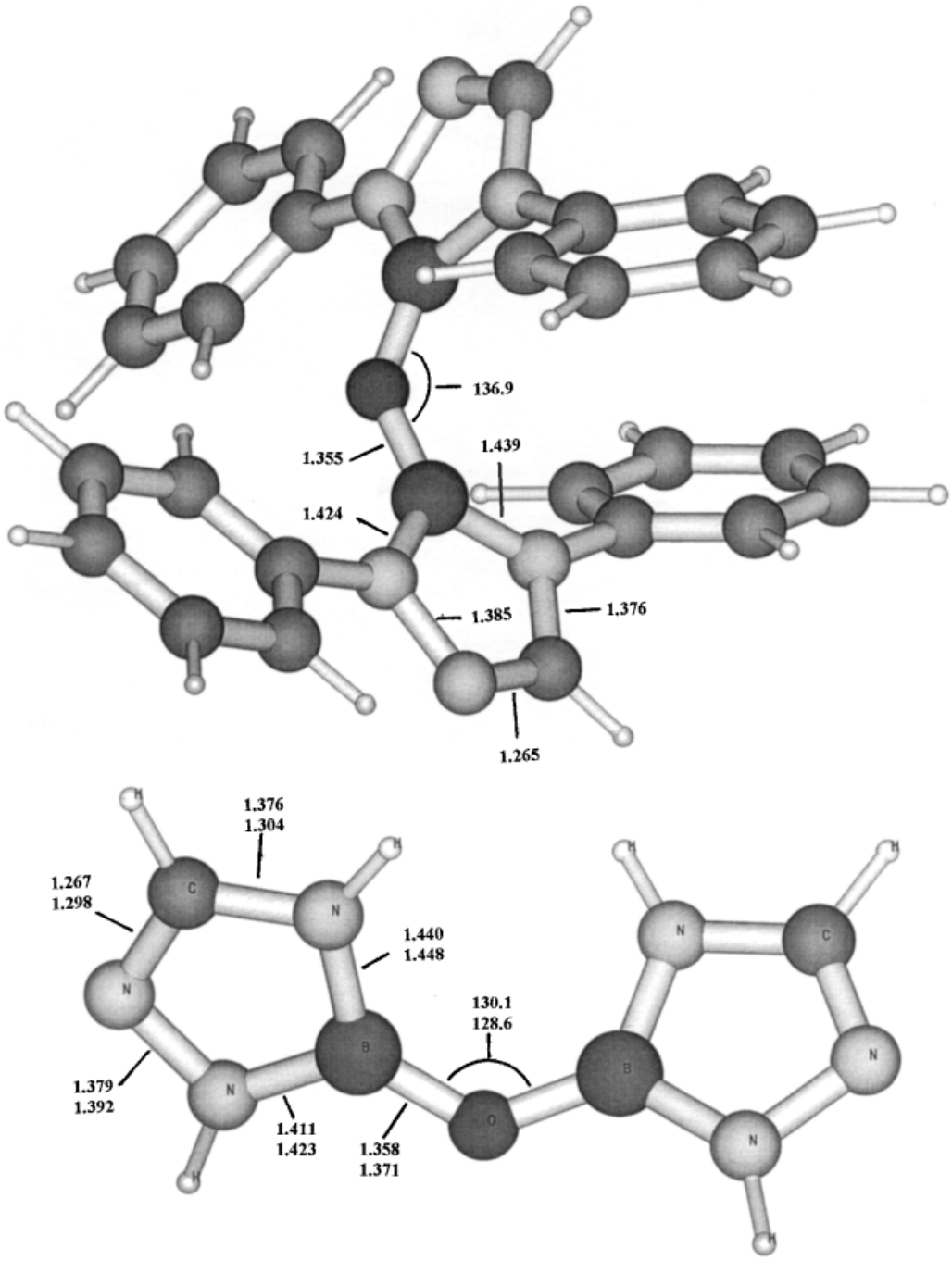

Figure 2. Computed equilibrium structures of 8 (A) and parent compound (B) (bond lengths in Å) at RHF/6-31g* (top) and B3LYP/6-31g* (bottom) level.

indices[23] indicates that the π bonds in the five-membered rings are essentially localized. In other words these results do not indicate significant π delocalization in **8**. These considerations are equally true for all computed structures and agree with the results reported in ref.[10]

Experimental Section

General: All manipulations were performed under dry argon. Solvents were rigorously dried with an appropriate drying agent and distilled before use. The following compounds were prepared as described in the literature: ethyl *N*-phenylformimidate,[24] dibromophenylborane,[25] dibromomethylborane.[25] Boron trichloride, boron tribromide, tetraphenylstannane, tetramethylstannane, lithium aluminium hydride, phenylhydrazine, silver cyanide, silver cyanate, and silver oxide were purchased commercially. − IR spectra: Bruker FT IR IFS66. − ^{1}H-, ^{11}B-, and ^{13}C-NMR spectra: Bruker AC 100 (^{1}H, 100.13 MHz) and Bruker Avance DRX 500 (^{1}H, 500.13 MHz; ^{11}B, 160.46 MHz; ^{13}C, 125.75 MHz); references: $SiMe_4$ (^{1}H, ^{13}C), $BF_3 \cdot OEt_2$ (^{11}B). − Mass spectra (EI): VG Autospec sector-field mass spectrometer (Micromass) 70 eV.

***N*^{1},*N*^{3}-Diphenylformamidrazone (1):** A mixture of ethyl *N*-phenylformimidate (10.0 g, 67.0 mmol) and phenylhydrazine (7.24 g,

67.0 mmol) in ethanol (20 mL) was stirred at 20°C for 16 h. The resulting viscous red solution was layered with *n*-pentane (50 mL) and stored overnight at −18°C. Orange crystals were collected by filtration and washed with *n*-pentane (2 × 50 mL) to afford 12.81 g (90%) of **1**. − ^{1}H NMR (CD_3OD): δ = 6.74 (t, J_{H-H} = 7.3 Hz, 1 H, C_6H_5), 6.96 (m, 3 H, C_6H_5), 7.05 (d, J_{H-H} = 8.0 Hz, 2 H, C_6H_5), 7.17 (t, J_{H-H} = 7.32 Hz, 2 H, C_6H_5), 7.28 (t, J_{H-H} = 7.6 Hz, 3 H, C_6H_5 and HC=N). − $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 114.24, 116.42, 120.15, 122.95, 129.91, 130.60, 136.71, 142.17 (C-phenyl), 148.76 (HC=N). − MS/EI (70 eV); *m/z* (%): 212 (65) [M^+ + H], 119 (10) [M^+ − HNPh], 91 (100) [PhN]. − $C_{13}H_{13}N_3$ (211.24): calcd: C 73.98, H 6.18, N 19.83; found C 73.60, H 6.14, N 19.98.

PhN(H)C(H)=N−N(Ph)B(Br)Ph (2a) or PhN(BBrPh)C(H)=N−N-(H)Ph (2a′): A solution of dibromophenylborane (5.21 g, 21.0 mmol) in 30 mL of toluene was added dropwise to a chilled toluene solution (100 mL, 0°C) of **1** (4.44 g, 21.0 mmol). After warming to room temp., the mixture was heated at 80°C for 1 h. Cooling to 20°C led to the separation of an ocher precipitate. Volatile compounds were removed in vacuo, and the tan solid residue was dissolved in 200 mL of CH_2Cl_2. It was filtered and the filtrate was concentrated to 50 mL. Storing at 4°C for 16 h afforded 4.92 g (62%) of colorless crystalline **2a**. − ^{1}H NMR (CD_2Cl_2): δ = 7.26−7.51 (m, 15 H, Ph), 8.93 (s, 1 H, HC=N). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 124.87, 125.23, 128.56, 128.83, 129.13, 129.82, 130.16, 130.99, 134.44, 136.45, 136.61 (C-phenyl), 141.28 (HC=N). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 28.9.

PhN(H)C(H)=NN(Ph)B(Br)(Me) (2b) or PhN(BBrMe)C(H)=N−N-(H)Ph (2b′): Analogously, the combination of dibromomethylborane (3.34 g, 18.0 mmol) and 3.80 g (18.0 mmol) of **1** in 130 mL of toluene gave 4.32 g (52%) of colorless crystalline **2b**. − ^{1}H NMR (CD_2Cl_2): δ = 0.85 (s, 3 H, CH_3), 7.10−7.52 (m, 10 H, C_6H_5), 9.03 (s, 1 H, HC=N). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 123.28, 124.35, 127.91, 128.61, 129.67, 130.04, 136.42, 136.74 (C-phenyl), 140.77 (HC=N). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 29.1. − $C_{14}H_{15}BBrN_5$ (316.01): calcd: C 53.21, H 4.78, N 13.30; found C 53.14, H 4.89, N 13.38.

PhN^a−N=C(H)−N(Ph)BPh(*N*^{a}−*B*) (3a): A solution of 4.13 g (16.6 mmol) of dibromophenylborane in toluene (30 mL) was added dropwise at 0°C to a stirred solution of 3.52 g (16.6 mmol) of **1** in toluene (100 mL). After warming to room temp., the mixture was refluxed for 3 h. Cooling to ambient temp. was accompanied by the formation of an ocher precipitate. Solvent and all volatile components were removed at 10^{-2} Torr. The red-brown residue was dissolved in CH_2Cl_2 (100 mL) and filtered. The ocher filtrate was concentrated to 50 mL and stored for 16 h at −18°C to afford 3.65 g (74%) of colorless crystals. − ^{1}H NMR (CD_2Cl_2): δ = 7.13−7.40 (m, 15 H, C_6H_5), 7.74 (s, 1 H, HC=N). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 121.83, 124.63, 124.85, 126.56, 128.63, 129.01, 129.28, 129.58, 134.17, 139.69 (C-phenyl), 141.03 (HC=N), 143.76 (C-phenyl). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 26.4. − MS/EI; *m/z*: 297 (100) [M^+]. − $C_{19}H_{16}BN_3$(297.15): calcd. C 76.79, H 5.42, N 14.14; found C 74.83, H 5.35, N 12.40.

PhN^{a}N=C(H)−N(Ph)BMe(*N*^{a}−*B*) (3b). − Path 1: A solution of 2.49 g (13.4 mmol) of dibromomethylborane in 30 mL of toluene was added dropwise at 0°C to a solution of 2.83 g (13.4 mmol) of **1** in 50 mL of toluene and allowed to warm to 20°C with stirring. Then the mixture was heated at reflux for 2 h. Solvent and volatiles were removed in vacuo to yield a red-brown residue. The residue was dissolved in 20 mL of CH_2Cl_2 and filtered. The violet filtrate was stored overnight at −18°C to afford 2.16 g (69%) of colorless crystalline **3b**. − **Path 2:** A solution of triethylamine (0.55 g, 5.43 mmol) in 10 mL of toluene was added dropwise to the solution of **2b/2b′** (2.50 g, 5.43 mmol) in 30 mL of toluene at room temp. After 1 h of stirring, the mixture was concentrated to dryness and the light brown residue was extracted with 50 mL of *n*-pentane and filtered. The filtrate was concentrated to dryness to afford 0.83 g of **3b**. − **Path 3:** An *n*-hexane solution made of 0.75 mL of 1.6 M ethereal methyllithium solution (1.20 mmol) in 30 mL of *n*-hexane was added dropwise to a chilled solution (−20°C) of **4** (0.30 g, 1.17 mmol) in 150 mL of *n*-hexane. It was slowly warmed to room temp. Precipitated LiCl was removed by filtration. The filtrate was concentrated to 50 mL and stored overnight at −18°C to give 0.23 g (83%) of **3b**. − ^{1}H NMR (CD_2Cl_2): δ = 0.87 (s, 3 H, CH_3), 7.16 (t, J_{H-H} = 7.5 Hz, 1 H, *p*-C_6H_5), 7.29 (m, 2 H, C_6H_5), 7.31 (t, J_{H-H} = 7.6 Hz, 1 H, *p*-C_6H_5), 7.39 (t, J_{H-H} = 7.8 Hz, 2 H, C_6H_5), 7.46 (t, J_{H-H} = 7.8 Hz, 2 H, C_6H_5), 7.50 (d, J_{H-H} = 7.5 Hz, 2 H, C_6H_5), 7.63 (s, 1 H, CH=N). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 120.69, 123.95, 124.29, 126.33, 129.24, 129.81, 140.05 (C-phenyl), 140.46 (CH=N), 144.28 (C-phenyl). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 27.8. − MS/EI; *m/z* (%): 235 (100) [M^+]. − $C_{14}H_{14}BN_3$ (235.13): calcd. C 71.45, H 6.00, N 17.87; found C 71.11, H 6.01, N 17.55.

PhN^a−N=C(H)−N(Ph)BCl(*N*^{a}−*B*) (4): A chilled solution (−30°C) of boron trichloride (1.76 g, 15.0 mmol) in toluene (30 mL) was added dropwise within 2 h to a chilled suspension (−35°C) of **1** (5.44 g, 40 mL) in toluene (160 mL). The mixture was allowed to warm to room temp., and then was stirred for 2.5 h at 90°C. The resulting suspension was cooled to 20°C and filtered. The filtrate was concentrated to dryness. The residue was extracted with *n*-hexane (100 mL) during the course of 4 h. Removal of solvent from the extract yielded 2.15 g (63%) of **4** as a colorless solid. − ^{1}H NMR (CD_2Cl_2): δ = 7.22 (t, J_{H-H} = 7.5 Hz, 1 H, *p*-C_6H_5), 7.36−7.49 (m, 7 H, C_6H_5), 7.71 (d, J_{H-H} = 7.3 Hz, 2 H, *o*-C_6H_5), 7.72 (s, 1 H, HC=N). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 120.74, 123.89, 125.28, 127.15, 129.29, 129.89, 138.08 (C-phenyl), 140.53 (HC=N), 142.31 (C-phenyl). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 22.8. − MS/EI; *m/z* (%): 255 (100) [M^+]. − $C_{13}H_{11}BClN_3$ (255.07): calcd. C 61.16, H 4.35, N 16.47; found C 61.32, H 4.42, N 16.56.

PhN^a−N=C(H)N(Ph)BH(*N*^{a}−*B*) (5): A sample of solid $LiAlH_4$ (0.23 g, 6.0 mmol) was added to a solution of 1.53 g (6.0 mmol) of **4** in a mixture of *n*-hexane (80 mL) and THF (20 mL). The slurry was stirred for 30 min at room temp., then filtered and the filtrate was concentrated to dryness. The residue was dissolved in *n*-hexane (100 mL) and stored overnight at −18°C to yield 1.11 g (84%) of colorless crystalline **5**. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2645 w−m [ν(B−H)]. − ^{1}H NMR (CD_2Cl_2): δ = 5.39 (q, J_{B-H} = 158.3 Hz, 1 H, BH), 7.15 (t, J_{H-H} = 7.3 Hz, 1 H, *p*-C_6H_5), 7.28 (t, J_{H-H} = 7.2 Hz, 1 H, *p*-C_6H_5), 7.37−7.47(m, 6 H, C_6H_5), 7.66 (d, J_{H-H} = 7.1 Hz, 2 H, *o*-C_6H_5), 7.87 (s, 1 H, HC=N). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 118.10, 121.30, 124.45, 126.16, 129.47, 130.01 (C-phenyl), 139.54 (HC=N), 143.38 (C-phenyl). − ^{11}B NMR (CD_2Cl_2): δ = 21.5 (d, J_{B-H} = 162.5 Hz). − MS/EI; *m/z* (%): 221 (100) [M^+]. − $C_{13}H_{12}BN_3$ (221.11): calcd. C 70.55, H 5.47, N 19.00; found: C 70.58, H 5.59, N 18.65.

PhN^a−N=CHN(Ph)BNCO(*N*^{a}−*B*) (6): A mixture of **4** (2.10 g, 8.24 mmol) and silver cyanate (1.23 g, 8.24 mmol) in acetonitrile (50 mL) was stirred at room temp. in the dark for 3 h. The slurry was then concentrated to dryness, and the residue was extracted with *n*-hexane (3 × 50 mL). The combined filtered extracts were liberated from solvent to afford 1.68 g (68%) of **6** as a colorless solid. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2309 s [ν_{as}(NCO)]. − ^{1}H NMR (CD_2Cl_2): δ = 7.18 (m, 1 H, *p*-C_6H_5), 7.42−7.55 (m, 7 H, C_6H_5), 7.61 (d, J_{H-H} = 7.5 Hz, 2 H, *o*-C_6H_5), 7.65 (s, 1 H, HC=N). −

$^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 119.45 (C-phenyl), 121.44 (NCO), 122.93, 124.87, 126.95, 129.51, 130.18, 138.16 (C-phenyl), 139.55 (HC=N), 142.46 (C-phenyl). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 17.1. − MS/EI; *m/z* (%): 262 (4) [M^+]. − $C_{14}H_{11}BN_4$ (262.10): calcd. C 64.10, H 4.23, N 21.37; found: C 64 17, H 4.46, N 20.65.

$PhN^a-N=CHN(Ph)BCN$*(N^a-B) **(7):** Analogously, **4** (3.06 g, 12.0 mmol) and 1.61 g (12.0 mmol) of silver cyanide were allowed to react in acetonitrile (50 mL). The mixture was filtered, and the filtrate was concentrated to 20 mL. Storage overnight at −18°C afforded 1.86 g (63%) of **7** as colorless needles. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2224 w [ν(CN)]. − ^1H NMR (CD_2Cl_2): δ = 7.42−7.55 (m, 8 H, C_6H_5), 7.75 (d, J_{H-H} = 7.5 Hz, 2 H, *o*-C_6H_5), 7.85 (s, 1 H, HC=N). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 120.17, 123.05, 126.50, 127.88, 129.69, 130.33, 137.55 (C-phenyl), 140.90 (HC=N), 141.73 (C-phenyl). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 13.9 . − MS/EI; *m/z* (%): 246 (4) [M^+]. − $C_{14}H_{11}BN_4$ (246.11): calcd. C 68.26, H 4.50, N 22.76; found: C 68.02, H 4.61, N 22.35.

$[PhN^a-CH=NN(Ph)B]_2O$*(N^a-B) **(8):** A sample of silver oxide (2.07 g, 9.00 mmol) was added to a solution of **7** (2.13 g, 8.66 mmol) in a mixture of acetonitrile (50 mL) and THF (10 mL), and stirred for 24 h at room temp. Solvent and volatile components were removed in vacuo. The residue was extracted with *n*-hexane (3 × 50 mL). After filtration, the combined extracts were freed from solvent to give 1.64 g (83%) of **8** as colorless solid. − ^1H NMR (CD_2Cl_2): δ = 6.87 (m, 2 H, *o*-C_6H_5), 7.09 (m, 1 H, *p*-C_6H_5), 7.18 (m, 1 H, *p*-C_6H_5), 7.24 (m, 2 H, *m*-C_6H_5), 7.33 (m, 3 H, *m*-C_6H_5 and HC=N). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 118.40, 122.34, 123.69, 126.15, 129.35, 129.67, 137.74 (C-phenyl), 138.39 (HC=N), 142.85 (C-phenyl). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 20.5. − MS/EI; *m/z* (%): 456 (100) [M^+], 211 (80) [1^+]. − $C_{26}H_{22}B_2N_6O$ (456.20): calcd. C 68.39, H 4.86, N 18.42; found C 68.04, H 4.97, N 18.36.

X ray Structural Analysis of 8:[26] Colorless single crystals from *n*-pentane. A crystal of appoximate dimensions 0.08 × 0.1 × 0.3 mm was examined with a Siemens SMART CCD area detector system with three-axis geometry using Mo-K_α radiation (λ = 0.71073 Å) at 173 K. Crystal data and refinement details: Crystal system triclinic, cell dimensions *a* = 10.6800(13), *b* = 10.8811(14), *c* = 12.0371(15) Å, α = 70.006(2), β = 68.868(2), γ = 66.777(2)°, *V* = 1166.0(3) $Å^3$ (refined from 1396 reflections) *Z* = 2, $d_{calcd.}$ = 1.299 g cm^{-3}, μ = 0.082 mm^{-1}, space group $P\bar{1}$, hemisphere data collections in ω at 0.3° scan width in three runs with 606, 435, and 230 frames (φ = 0.88 and 180°) at a detector distance of 5 cm (2 Θ_{max} = 54°), data reduction with the SAINT programm (V 4.028 Siemens) by which more than 95.3% of the data are converted, empirical absorption correction with redundant data (SADABS programm, Siemens) max/min transmission 1.000/0.768; 6811 intensities collected, 4870 unique (R_{int} = 0.0438); structure solution and refinement on F^2 with SHELX 97, 317 parameters, hydrogen atoms treated as riding groups with a 1.5-fold isotropic *U* value of the equivalent *U* value of the corresponding C atom. *R*1 = 0.0777; *wR*2 = 0.1761 for all data, $w^{-1} = \sigma(F_o^2) + (0.0580P)^2$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$, maximum/minimum residual electron densities 0.271 and −0.250 $eÅ^{-3}$.

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