SHORT COMMUNICATION

Cyclic Ketiminoboranes

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Dedicated to Prof. M. F. Hawthorne on the occasion of his 70th birthday

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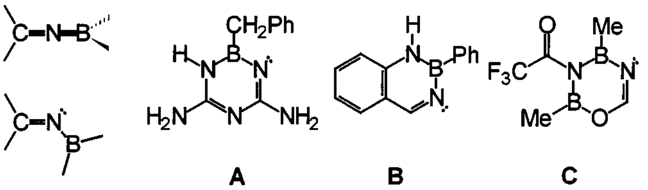
The cyclocondensation reaction of benzil-bis(trimethylsilylimin) (**3**) and Cl_2B–N*i*Pr_2 via silicon-boron exchange results in the solvent-dependent formation of the 1,3,2-diazaborole **1a** or the 1,3,6,8,2,7-tetraazadiborecin **2a**. Using the more rigid 9,10-bis(trimethylsilylimino)phenanthrene instead of **3** only the five-membered heterocycle 4,5-biphenylene-2-diisopropylamino-1,3,2-diazaborole (**1b**) is formed. The cyclic ketiminoboranes are characterized by NMR and X-ray diffraction data. The 1,3,2-diazaborole ring is almost planar, while the conformation of the 1,3,6,8,2,7-tetraazadiborecin has the shape of a figure-eight loop.

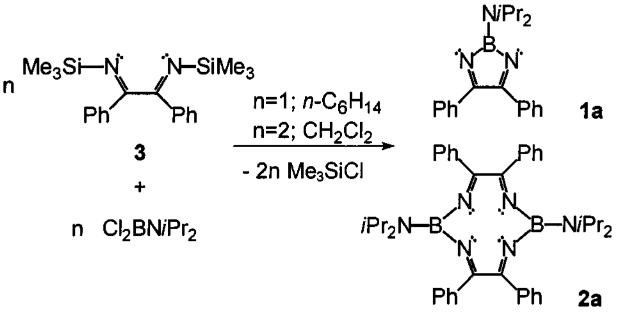
More than 35 years ago Hawthorne[1] synthesized the first examples of alkylideneaminoboranes. Information about their geometry and BNC bond order were obtained from IR data and X-ray structure analyses[2]. The results were complemented by theoretical studies[3], which postulate a cumulene-like arrangement for the $>C=N=B<$ group. Geometry-optimized calculations on 6-31G niveau resulted for $HB(N=CH_2)_2$[4] and $B(N=CH_2)_3$[5] energetic differences of 74 and 12 KJ/mol, respectively, between the linear and bent CNB structure.



Scheme 1

A cumulene-like arrangement is difficult to verify in small cyclic molecules, in which the $C=N-B$ unit may be compared with an allyl cation. To our knowledge only a few six-membered heterocycles such as **A−C**[6,7,8] with an incorporated $C=N-B$ unit have been described. A dithiatetraazadiborocin[9] is an example of an eight-membered ring with $B-N=S$ units.

Here we present the five- and ten-membered boron-nitrogen heterocycles 4,5-diphenyl-2-diisopropylamino-1,3,2-diazaborole (**1a**), 4,5-biphenylene-2-diisopropylamino-1,3,2-diazaborole (**1b**) and 2,7-bis(diisopropylamino)-4,5,9,10-tetraphenyl-1,3,6,8,2,7-tetraazadiborecin (**2a**), obtained via silicon-boron exchange reactions and characterized by X-ray structure analyses.



Scheme 2

The reaction of benzil-bis(trimethylsilylimin) (**3**)[10] with (diisopropylamino)dichloroborane in *n*-hexane leads to the formation of **1a** in 71% yield. Its composition follows from NMR and MS data. The ^{11}B-NMR signal is shifted 7 ppm to lower field ($\delta = 37$) relative to comparable non-cyclic ketiminoboranes $R_2N-B(N=CPh_2)_2$ (R = Me, Et)[11][12]. This shift is a consequence of the orbital symmetry, which does not allow an interaction of the free electron-pair of the ketiminonitrogen atom and the p_z orbital of the boron atom in the five-membered heterocycle. With four π electrons the diazaborole **1a** should posses strong acceptor properties, however, its chemical reduction to the corresponding 6 π aromatic $[\mathbf{1a}]^{2-}$ has not been succesful. The cyclovoltammogram of **1a** exhibits an irreversible reduction at $E_{1/2} = -1.28$ eV. Because single crystals of **1a** could not be obtained, crystalline **1b** was synthesized by reacting 9,10-bis(trimethylsilylimino)-phenanthrene with Cl_2B-N*i*Pr_2. A dimerization of **1b** to a ten-membered ring does not take place, prevented by the syn-conformation of the fixed 1,4-diazadiene. In the ^1H-NMR spectrum the expected doublet and septet for the isopropyl group and four signals of the aromatic hydrogen atoms are observed in correspondence

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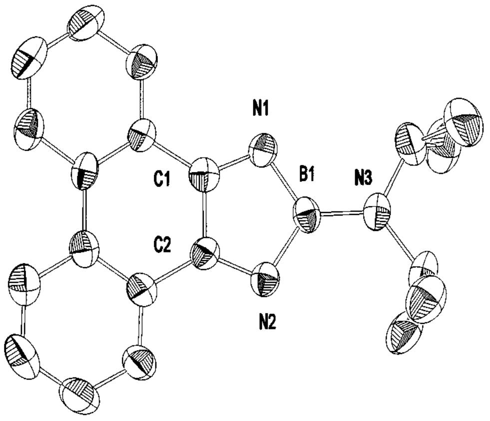

Figure 1. Molecular structure of **1b** in the crystal. Selected bond lengths [Å] and angles [°] for molecule A: B1−N3 1.383(7), B1−N1 1.505(7), B1−N2 1.506(7), C1−N1 1.296(6), C2−N2 1.295(6), C1−C2 1.513(7), N1−B1−N3 121.7(5), C1−N1−B1 101.5(4), N1−B1−N2 111.8(4), C15−N3−B1−N2 2.5.

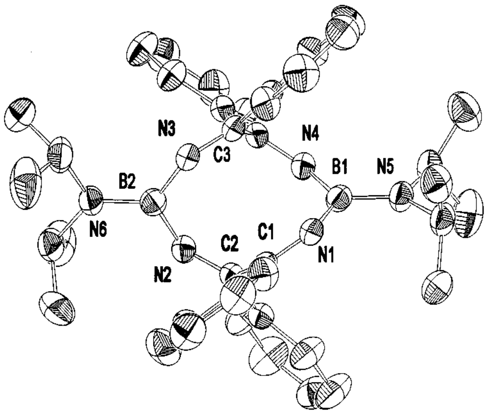

Figure 2. Molecular structure of **2a** in the crystal. Selected bond lengths [Å] and angles [°]: N5−B1 1.407(3), N6−B2 1.400(3), N1−B1 1.458(3), N4−B1 1.470(3), C1−N1 1.277(2), C2−N2 1.273(3), C3−N3 1.277(2), C4−N4 1.276(2), C1−C2 1.525(3), C3−C4 1.513(3), C1−N1−B1 128.6(2), C4−N4−B1 127.3(2), C3−N3−B2 127.9(2), C2−N2−B2 128.6(2), N1−B1−N4 121.5(2), N2−B2−N3 119.7(2), N1−B1−N5 119.9(2), N4−B1−N5 118.7(2), N2−B2−N6 120.6(2), N3−B2−N6 120.6(2), N1−C1−C2−N2 104.9, N3−C3−C4−N4 105.2.

with the symmetry of the molecule. The ^{11}B-NMR signal of **1b** is observed at the same shift ($\delta = 37$) as for **1a**.

In methylenchloride as solvent the silicon−boron exchange reaction leads to the ten-membered 2,7-bis(diisopropylamino)-4,5,9,10-tetraphenyl-1,3,6,8,2,7-tetraazadiborecin (**2a**) in 62% yield. Its ^{11}B-NMR signal at $\delta = 28$ appears at higher field than that of **1a**, **b**. Two signals for the methyl group of the isopropylamino substituents in the ^{1}H- and ^{13}C-NMR spectra point to a hindered rotation around the B−N(iPr)$_2$ bonds.

By slow diffusion of *n*-hexane into the CH_2Cl_2 solution of **1b** single crystals suitable for an X-ray structure analysis were obtained. The two independent molecules in the cell show no significant difference.

The molecule is almost planar. The five-membered diazaborole has two short C=N double bonds [1.295(6)−1.304(6) Å] and two longer B−N bonds [1.495(7)−1.515(7) Å]. The exocyclic B−N bond lengths [1.383(7), 1.386(7) Å] are in the region of B=N double bonds. The C−C bond length [1.508(7), 1.513(7) Å] is quite short. From this point of view **1a**, **b** may be described as triazaborafulvene derivatives.

2a crystallizes in cubes; its X-ray structure analysis shows that the heterocycle deviates considerably from planarity. The arrangement of the ring can be described as a figure-eight loop, being built from two 1,4-diazadiene units in anti conformation with a torsion angle of 105°, which are bridged by two B−NiPr$_2$ units. As indicated by the distances [N5−B1: 1.407(3) Å], the exocyclic B−N bonds have double-bond character. The bond lengths in the C=N−B units [C=N: 1.277(2) Å, =N−B: 1.458(3) Å] correspond to the values reported for a B(N=CH$_2$)$_3$[5]. One has to consider that the R$_2$C=N planes are turned out of the plane around the boron atoms. This geometry allows a partial interaction between the electron pair of the nitrogen atom and the p_z-orbital of the boron atom, as indicated by the high-field shift in the ^{11}B-NMR spectrum.

Experimental Section

General: Reactions were carried out under dry argon, using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. Glassware was dried with a heat-gun in high vaccum. − ^{1}H-, ^{13}C-, ^{11}B NMR: BRUKER AC 200 spectrometer, NMR references are $(CH_3)_4Si$ and $BF_3 \cdot Et_2O$. − Mass spectra were obtained with a Finnigan MAT 8200 plus spectrometer using EI technique. Cyclic voltammetry data (EG&G PARC 175 potentiostat): Pt disc (1mm) working electrode, CH_2Cl_2 solution, 0.1 M Bu_4NPF_6 as supporting electrolyte, Pt-wire as auxiliar electrode, SCE as reference electrode.

1a: 362 mg (2 mmol) of Cl$_2$BN(iPr)$_2$ dissolved in 10 mL of *n*-hexane was added dropwise within 50 min to a solution of 704 mg (2 mmol) **3** in 20 mL of *n*-hexane at room temp. After stirring for 14 h the yellow precipitate was filtered and washed with a small amount of cold *n*-pentane (0°C), yield: 447 mg (1.4 mmol, 71%) of **1a**. − ^{1}H NMR (δ in CDCl$_3$): 7.52−7.47 (m, 4 H, C$_6$H$_5$), 7.40−7.24 (m, 6 H, C$_6$H$_5$), 4.37 [sept, J = 6.8 *Hz*, 2 H, CH(CH$_3$)$_2$], 1.47 [d, J = 6.8 *Hz*, 12 H, CH(CH_3)$_2$]. − ^{13}C NMR (δ in CDCl$_3$): 178.5 (C=N), 136.3 (i-C, C$_6$H$_5$), 130.2, 129.1, 127.8 (CH, C$_6$H$_5$), 47.9 [CH(CH$_3$)$_2$], 24.5 [CH(CH$_3$)$_2$]. − ^{11}B NMR (δ in CDCl$_3$): 36.6. − MS (70 eV,EI): m/z (%): 317 (16) [M$^+$], 214 (27) [M − C$_6$H$_5$CN]$^+$, 171 (64) [M − C$_6$H$_5$CN, −iPr]$^+$, 103 (24) [C$_6$H$_5$CN$^+$], 44 (100) [iPrH$^+$]. − m.p. 185−187°C.

1b: 362 mg (2 mmol) of Cl$_2$BN(iPr)$_2$ dissolved in 10 mL of CH$_2$Cl$_2$ was added dropwise within 30 min to a solution of 700 mg (2 mmol) 9,10-bis(trimethylsilylimino)phenanthrene in 20 mL of CH$_2$Cl$_2$ at 0°C. After stirring for 14 h at room temp. the solvent and ClSiMe$_3$ were removed in vaccuo. The residue was dissolved in 2 mL of CH$_2$Cl$_2$ and *n*-hexane was allowed to diffuse into the solution at room temp. After 15 days crystalline **1b** was filtered, yield: 197 mg (0.6 mmol, 31%). − ^{1}H NMR (δ in CDCl$_3$): 8.37−8.33 (m, 2 H, C$_6$H$_5$), 7.95−7.92 (m, 2 H, C$_6$H$_5$), 7.53−7.44 (m, 2 H, C$_6$H$_5$), 7.36−7.28 (m, 2 H, C$_6$H$_5$), 4.38 [sept, J = 6.7 *Hz*, 2 H, CH(CH$_3$)$_2$], 1.48 [d, J = 6.7 *Hz*, 12 H, CH(CH_3)$_2$]. − ^{13}C NMR (δ in CDCl$_3$): 172.8 (C=N), 135.6 (i-C, C$_6$H$_5$), 132.7, 128.4, 124.1 (CH, C$_6$H$_5$), 48.4 [CH(CH$_3$)$_2$], 24.9 [CH(CH$_3$)$_2$]. − ^{11}B NMR (δ in CDCl$_3$): 37.1. − m.p. 202−206°C (decomp.).

2a: 905 mg (0.5 mmol) of $Cl_2BN(iPr)_2$ dissolved in 20 mL of CH_2Cl_2 was added within 1 h dropwise to a solution of 1.76 g (5 mmol) **3** in 50 mL of CH_2Cl_2 at room temp. After stirring for 14 h the solvent and $ClSiMe_3$ were removed in vaccuo. The residue was dissolved in 10 mL of CH_2Cl_2 and 5 mL of *n*-hexane was added. After 50 h at 6°C 1.91 g (3.0 mmol, 62%) **2a** was filtered. − ^1H NMR (δ in $CDCl_3$): 7.72−7.67 (m, 8 H, C_6H_5), 7.40−7.28 (m, 12 H, C_6H_5), 3.46 [sept, J = 6.7 *Hz*, 4 H, $CH(CH_3)_2$], 0.96 [d, J = 6.7 *Hz*, 6 H, $CH(CH_3)_2$], 0.91 [d, J = 6.7 *Hz*, 6 H, $CH(CH_3)_2$]. − ^{13}C NMR (δ in $CDCl_3$): 164.3 (C=N), 137.4 (*i*-C, C_6H_5), 130.4, 128.8, 127.8 (CH, C_6H_5), 45.3 [$CH(CH_3)_2$], 21.8 [$CH(CH_3)_2$]. − ^{11}B NMR (δ in $CDCl_3$): 28.2. − MS (70 eV, EI): *m/z* (%): 634 (1) $[M^+]$, 428 (56) $[M - (C_6H_5CN)_2]^+$, 328 (100) $[M - (C_6H_5CN)_2, - NiPr_2]^+$. − m.p. 150−152°C.

Crystal Structure Determination: Unique intensity data sets were collected at −70°C with a four-circle diffractometer (Mo-K_α radiation $\lambda = 0.71073$ Å, graphite monochromator, ω-scan). Empirical absorption corrections (ψ-scans) were applied. The structures were solved by direct methods [SHELXS86][13] and refined by least squares methods based on F^2 with all mesured reflections [SHELXL97][14]. All non-hydrogen atoms were refined anisotropically. − Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center **1b**: CCDC-102512, **2a**: CCDC-102512. Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: int. code +44 (0)1223/ 336-001; e-mail: deposit@ccdc.cam.ac.uk.

1b: Crystal Data: Orthorhombic, $P2_1cn$, a = 8.524(5), b = 16.080(9), c = 25.950(14) Å, Z = 8; 2084 reflections, $R1$ = 0.059.

2a: *Crystal Data:* Monoclinic, $P2_1/c$, a = 10.948(6), b = 10.433(5), c = 32.990(17) Å, β = 95.12(2), Z = 4; 4599 reflections, $R1$ = 0.047.

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