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X-RAY CRYSTALLOGRAPHIC STUDY OF THREE (N⟶B)-BORINATES PREPARED FROM 8-HYDROXYQUINOLINE AND 2-HYDROXYPYRIDINE

8-Hydroxyquinoline and 2-hydroxypyridine have been reacted with diphenylborinic acid or 9-BBN; the molecular structure of the resulting heterocycles has been studied by X-ray crystallography. A structural comparison of the so formed five- and six-membered heterocycles with similar complexes obtained from aliphatic amino alcohol and α-amino acid derivatives shows significant differences for the N →B, B—O and B—C bond lengths and some of the inner cycle bond angles. Other structural parameters discussed in this respect are the sum of bond lengths at the boron atom, the sum of bond angles in the heterocycle and the tetrahedral character of the boron atom. On the basis of these parameters a qualitative comparison of heterocycle stability is possible.

INTRODUCTION

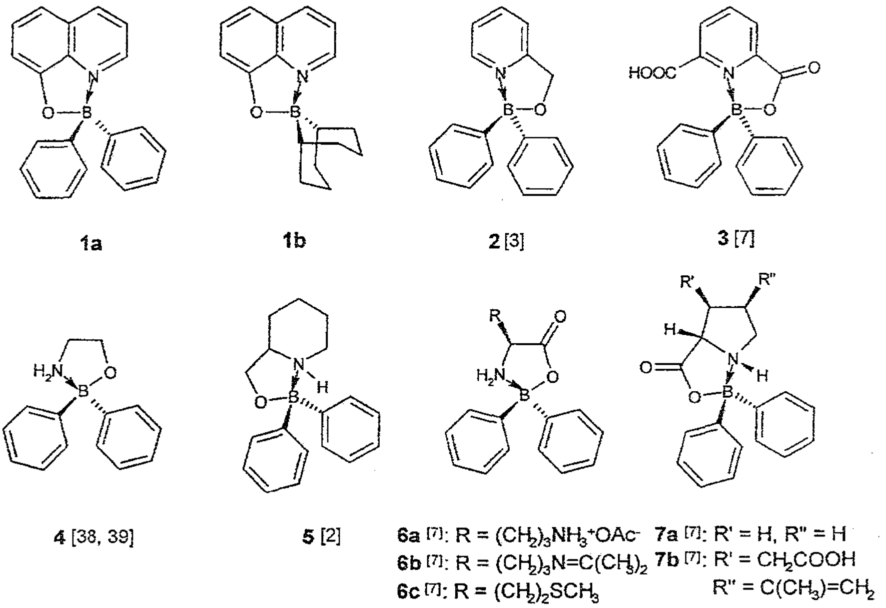
In the last few years we have investigated systematically neutral boron chelates with a dative N →B or O →B bond in order to establish, how electronic and steric effects influence the structure and stability of these heterocycles. Such neutral chelates containing five- or six-membered rings have been prepared from boranes, boric esters or borinic esters in their reaction with α-amino alcohol derivatives like ephedrines and pseudoephedrines [1], piperidine and piperazine alcohols [2], 2-pyridinealcohols [3, 4], 2′-hydroxyacetophenone azine [5], as well as amino acids [6, 7], 2-pyridinecarboxylic acids [7], tropolone and 1,3-diketones [8, 9].

The N →B or O →B bond is the weakest bond in the complex and a strong coordinative bond is therefore indispensable to guarantee hydrolytic stability. Boron complexes possesing a strong N →B bond (for theoretical studies of the N →B bond see references 10 and 11) are used in asymmetric hydroborations [12], in the purification of a-amino acids [13, 14] and for the enhancement of the transport rate through lipophilic solvents [15]. A further application is the separation of primary alkylamines. This method is based on the reaction of salicylaldehyde or 2′-hydroxyacetophenone with primary alkylamines and diphenylborinic acid to form the corresponding azomethine chelates that can be separated by high-performance liquid chromatography [16]. Complexes with an extended π-electron system in the coordinated ligand are often colored and permit the quantitative determination of the chelate components [17—20]. They have interesting physical properties such as fluorescence [21, 22], barrier crossing [23, 24], photoconductive charge transfer [25—27], electron acceptance in the photoexcited state [21, 22] and second harmonic generation [28].

So far little is known about structure and stability of borinic esters obtained with azaarene alcohol derivatives. It may be expected that the hydrolytic stability of such chelate compounds is lower in comparison to the corresponding aliphatic amino alcohol complexes, because the ligands are more rigid and the Lewis basicity of the nitrogen atom is reduced. In order to extend the series of structures analyzed in this area so far, we prepared compounds 1a—1b and 8 (Schemes 1 and 2) and report herein their molecular structures.

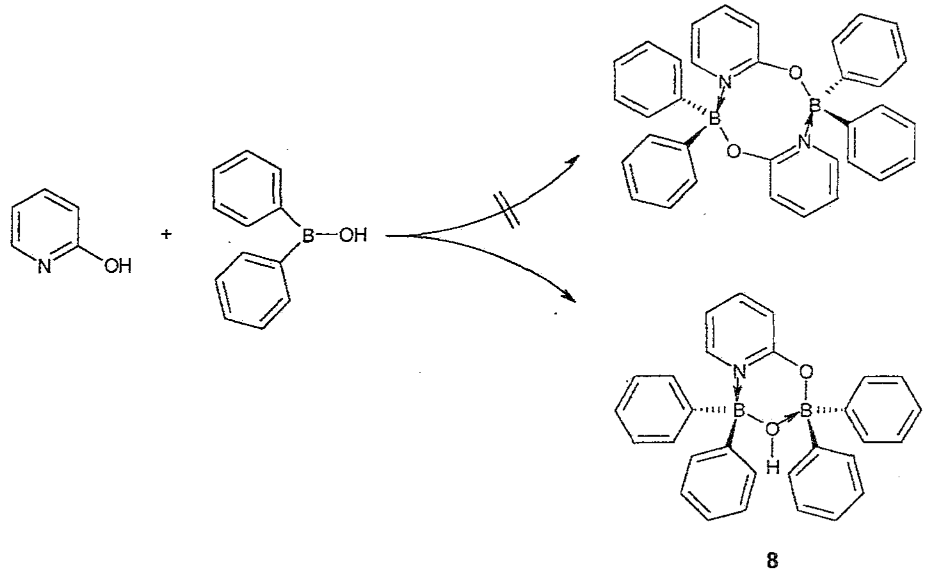
Scheme 1

Five-membered (N → B)-borinates obtained from different 2-aminoalcohol derivatives



Scheme 2

Possible products from the reaction between 2-hydoxypyridine and diphenylborinic acid



RESULTS AND DISCUSSION

Compounds **1a**—**1b** have been already reported in the literature [29—34] and received some attention as boron-containing antibacterial and fungicidal agents [35, 36]. Crystals suitable for X-ray crystallography of **1a**—**1b** could be grown from THF/hexane, and their molecular structures are depicted in Figures 1 and 2. The crystallographic data, fractional atomic coordinates as well as selected bond lengths, bond angles and torsion angles are resumed in Tables 1—3. Crystals of **1a** reflected poorly, so that the B-phenyl carbon atoms could be

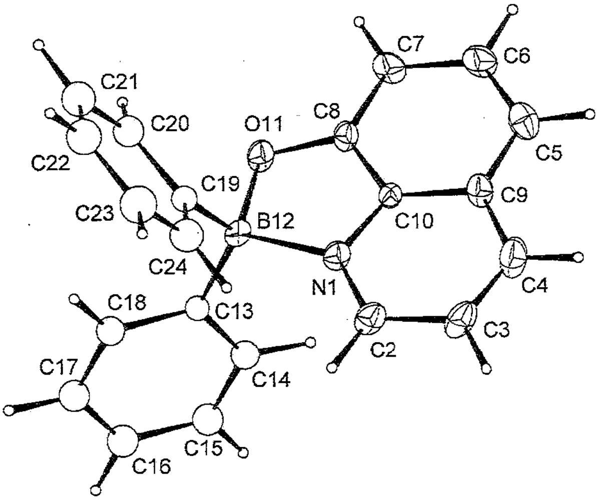


Fig. 1. Molecular structure of (N —B)-diphenylboryl-8-quinolinate **1a**

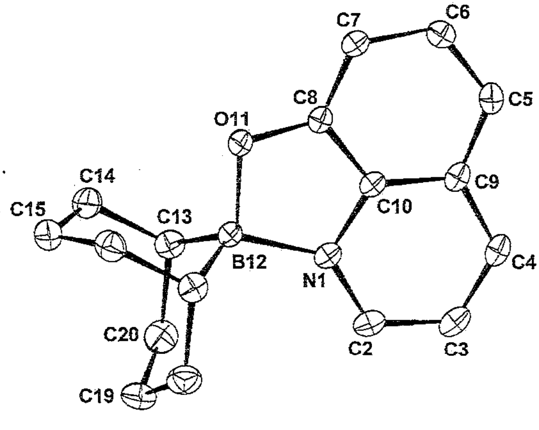


Fig. 2. Molecular structure of (N —B)-9-borabicyclo[3.3.1]non-9-yl-8-quinolinate **1b**

refined only isotropically to keep a reasonable reflections/variables proportion (6 : 1). Compound **1b** crystallized in the monoclinic space group $P2_1/m$ with $Z = 2$, whereby the molecules are imposed on the mirror planes parallel to the *ac*-plane of the crystal lattice. This means that 14 atoms ($N_{(1)}$—$C_{(12)}$, $C_{(14)}$ and $C_{(19)}$, respectively) are located on special positions. Due to the fact that this location is a very rare case in X-ray crystallography and to exclude the possibility that there might exist a slight disorder of the boron atom, the U_{11}, U_{22} and U_{33} anisotropical parameters had to be carefully examined. Their root values are equal to the rms displacements along x, y and z. For $B_{(12)}$ values of 0.17, 0.23 and 0.20 Å are calculated that are within the normal range of 0.2...0.3 Å at $T = 300$ K [37], so that a significant disorder can be excluded.

Table 1

Crystallographic data for compounds **1a**, **1b** and **8**

	Compound 1a[a]	**Compound 1b**	**Compound 8**
Crystal data			
Formula	$C_{21}H_{16}BNO$	$C_{17}H_{20}BNO$	$C_{29}H_{25}B_2NO_2$, 1.5 THF[b]
Crystal size (mm)	0.2×0.3×0.4	0.2×0.3×0.3	0.30×0.3×0.6
MW (g mol^{-1})	309.17	265.16	441.14
Space group	$P\ 2_1/c$	$P\ 2_1/m$	$P\ 2_1/n$
Cell parameters			
a (Å)	12.280(1)	8.188(1)	9.505(1)
b (Å)	17.523(3)	7.005(1)	14.535(1)
c (Å)	15.158(3)	12.059(1)	22.269(1)
β (deg)	94.28(2)	91.05(1)	92.03(1)
V (Å^3)	3252.7(10)	691.6(1)	3073.79(2)
Z	8	2	4
μ (mm^{-1})	0.071	0.072	0.071
ρ_{calcd} (g cm^{-3})	1.26	1.27	1.20
Data collection[c]			
Scan range (deg)	$0.77 + 0.68\ \mathrm{tg}\,\theta$	$0.37 + 0.53\ \mathrm{tg}\,\theta$	$0.74 + 0.92\ \mathrm{tg}\,\theta$
θ limits (deg)	$2 < \theta < 26$	$2 < \theta < 28$	$2 < \theta < 25$
hkl limits	0, 15; −21, 0; —18, 18	−10, 10; 0, 9; −15, 15	0, 11; 0, 17; −26, 26
No. collected reflections	6913	1924	4536
No. independent reflections (R_{int})	6370 (0.03)	1800 (0.03)	4192 (0.02)
No. observed reflections	1866	1008	1958
Refinement			
R[d]	0.072	0.036	0.057
R_w[e]	0.074	0.031	0.055
w	$1/\sigma^2$	$1/\sigma^2$	1.0
No. of variables	315	149	383
GooF	3.23	2.13	0.82
$\Delta\rho_{min}$ (e Å^{-3})	−0.21	−0.13	−0.23
$\Delta\rho_{max}$ (e Å^{-3})	0.19	0.13	0.28

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a Two independent molecules in the asymmetric unit;

b The second solvent molecule is disordered;

c $T = 293$ K, $\lambda_{MoK\alpha} = 0.71069$ Å;

d $R = \Sigma(||F_o| - |F_c||)/\Sigma |F_o|$;

e $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$.

Table 2

Fractional atomic coordinates for compounds 1a and 1b

Atom	x/a	y/b	z/c	$U_{\text{equiv/iso}}$
1	2	3	4	5
		Compound 1a		
$N_{(1)}$	0.0971(6)	0.0513(5)	0.8377(5)	0.0416
$O_{(11)}$	0.2762(5)	0.0364(4)	0.7913(4)	0.0424
$B_{(12)}$	0.1576(8)	0.0131(7)	0.7576(8)	0.0200
$C_{(2)}$	−0.0071(8)	0.0521(7)	0.8574(6)	0.0495
$C_{(3)}$	−0.0393(8)	0.0962(7)	0.9295(7)	0.0533
$C_{(4)}$	0.034(1)	0.1383(8)	0.9797(7)	0.0658
$C_{(5)}$	0.234(1)	0.1759(7)	1.0053(7)	0.0585
$C_{(6)}$	0.3373(8)	0.1684(7)	0.9769(7)	0.0572
$C_{(7)}$	0.3593(8)	0.1221(6)	0.9048(7)	0.0456
$C_{(8)}$	0.2747(8)	0.0836(6)	0.8612(6)	0.0409
$C_{(9)}$	0.1458(8)	0.1377(6)	0.9607(6)	0.0461
$C_{(10)}$	0.1691(7)	0.0923(5)	0.8895(6)	0.0350
$C_{(13)}$	0.1472(7)	−0.0775(5)	0.7592(6)	0.036(2)
$C_{(14)}$	0.1519(8)	−0.1186(6)	0.8372(6)	0.049(3)
$C_{(15)}$	0.1459(9)	−0.1977(6)	0.8375(7)	0.056(3)
$C_{(16)}$	0.1325(9)	−0.2376(6)	0.7600(7)	0.059(3)
$C_{(17)}$	0.1278(9)	−0.1991(6)	0.6820(7)	0.056(3)
$C_{(18)}$	0.1337(8)	−0.1194(6)	0.6807(6)	0.048(3)
$C_{(19)}$	0.1259(7)	0.0552(5)	0.6675(6)	0.040(2)
$C_{(20)}$	0.2011(8)	0.0705(6)	0.6082(7)	0.056(3)
$C_{(21)}$	0.177(1)	0.1063(7)	0.5267(8)	0.070(4)
$C_{(22)}$	0.072(1)	0.1282(7)	0.5026(8)	0.075(4)
$C_{(23)}$	−0.007(1)	0.1148(7)	0.5589(8)	0.083(4)
$C_{(24)}$	0.0191(9)	0.0782(7)	0.6389(7)	0.066(3)
$N_{(51)}$	0.4083(6)	−0.5629(5)	0.7452(5)	0.0406
$O_{(61)}$	0.2271(5)	−0.5212(4)	0.7564(5)	0.0470
$B_{(62)}$	0.3409(8)	−0.4844(7)	0.7532(9)	0.0364
$C_{(52)}$	0.5163(8)	−0.5762(6)	0.7404(7)	0.0448
$C_{(53)}$	0.5529(8)	−0.6516(7)	0.7319(7)	0.0512
$C_{(54)}$	0.4835(9)	−0.7130(6)	0.7296(7)	0.0520
$C_{(55)}$	0.2860(9)	−0.7529(6)	0.7327(7)	0.0525
$C_{(56)}$	0.1787(9)	−0.7295(6)	0.7390(7)	0.0541
$C_{(57)}$	0.1513(8)	−0.6522(7)	0.7488(7)	0.0485
$C_{(58)}$	0.2329(8)	−0.5980(6)	0.7497(6)	0.0422
$C_{(59)}$	0.3687(8)	−0.6987(6)	0.7353(6)	0.0417
$C_{(60)}$	0.3417(7)	−0.6237(5)	0.7440(6)	0.0337
$C_{(63)}$	0.3465(7)	−0.4360(6)	0.6651(6)	0.039(2)
$C_{(64)}$	0.3607(8)	−0.4685(6)	0.5831(7)	0.055(3)
$C_{(65)}$	0.3661(9)	−0.4247(6)	0.5086(7)	0.059(3)
$C_{(66)}$	0.3576(8)	−0.3458(6)	0.5129(7)	0.055(3)
$C_{(67)}$	0.3396(8)	−0.3127(6)	0.5920(7)	0.054(3)
$C_{(68)}$	0.3353(7)	−0.3574(6)	0.6669(6)	0.043(3)
$C_{(69)}$	0.3770(7)	−0.4441(6)	0.8440(6)	0.042(3)
$C_{(70)}$	0.4781(9)	−0.4076(6)	0.8556(7)	0.057(3)
$C_{(71)}$	0.5158(9)	−0.3723(7)	0.9343(7)	0.065(3)
$C_{(72)}$	0.452(1)	−0.3732(8)	1.0052(8)	0.082(4)
$C_{(73)}$	0.353(1)	−0.4077(8)	0.9960(9)	0.091(4)
$C_{(74)}$	0.316(1)	−0.4436(7)	0.9170(8)	0.076(4)

Table 2 (Continued)

1	2	3	4	5
		Compound 1b		
$N_{(1)}$	0.0910(2)	0.2500	0.6469(2)	0.0409
$O_{(11)}$	0.3797(2)	0.2500	0.6156(1)	0.0462
$B_{(12)}$	0.2655(3)	0.2500	0.7153(2)	0.0400
$C_{(2)}$	-0.0651(3)	0.2500	0.6757(3)	0.0492
$C_{(3)}$	-0.1911(3)	0.2500	0.5955(3)	0.0490
$C_{(4)}$	-0.1562(3)	0.2500	0.4855(2)	0.0451
$C_{(5)}$	0.0679(3)	0.2500	0.3424(2)	0.0447
$C_{(6)}$	0.2333(3)	0.2500	0.3258(2)	0.0472
$C_{(7)}$	0.3492(3)	0.2500	0.4137(2)	0.0445
$C_{(8)}$	0.2942(3)	0.2500	0.5203(2)	0.0387
$C_{(9)}$	0.0079(3)	0.2500	0.4514(2)	0.0378
$C_{(10)}$	0.1250(3)	0.2500	0.5367(2)	0.0355
$C_{(13)}$	0.2939(2)	0.4334(3)	0.7912(2)	0.0478
$C_{(14)}$	0.4767(3)	0.4332(3)	0.8264(2)	0.0541
$C_{(15)}$	0.5366(4)	0.2500	0.8820(3)	0.0581
$C_{(19)}$	0.1762(4)	0.2500	0.9581(3)	0.0620
$C_{(20)}$	0.1776(3)	0.4339(3)	0.8898(2)	0.0583

Table 4 represents a summary of the most important structural data for compounds **1**—**7** (Scheme 1) whereby the structures of **2**—**7** have been included for comparison with **1a**—**1b**, and will be the basis for the following discussion.

If it is considered that $N_{sp2}\rightarrow B$ bond lengths should be corrected by 0.023 Å in order to be comparable to $N_{sp3}\rightarrow B$ bond lengths [11], the bonds between the borinic esters of the pyridine derivatives **1**—**3** are significantly longer than the ones in the 2-aminoalcohol (**4**, **5**) and amino acid derivatives (**6**, **7**). The average values are 1.660, 1.651 and 1.623 Å, respectively, if the above mentioned correction is included. As an effect of the heterocycle formation the $N\rightarrow B$ bonds in compounds **1**—**3** are shorter (the average value is 1.637 Å) than that in the pyridine monoadduct of bis(1,5-cyclooctanediyl)diboroxane, for which a value of 1.661(4) Å has been reported [40].

In a former study it has been outlined that B—O bonds are significantly shorter for aliphatic alkoxy groups (the average value for **2**, **4** and **5** is 1.479 Å) than for carboxy groups (the average value for **3** and **6**—**7** is 1.536 Å) [7]. The B—O bond lengths of compounds **1a** (1.55(1) Å) and **1b** (1.537(3) Å) permit therefore to conclude that in the presence of phenoxy groups this bond is also lengthened. In complexes with long B—O bonds the B—C bonds are shorter in order to compensate for the electron deficiency of the boron atom and vice versa, so that in compounds **2**, **4** and **5** with the shortest B—O bonds the B—C bonds are the longest (1.621(3) Å, 1.612(2) Å and 1.622(3) Å, respectively).

The complexation of the diphenylboryl group by a planar ligand like 8-hydroxyquinoline influences the conformation of the boroxazolidine or boroxazolidone rings that normally is twisted. Due to the planar arrangement of the OCCN moiety in chelates **1**—**3** the heterocycles are nearly planar in **1a**, **2** and **3** with B-deviations of 0.136, -0.058 and -0.022 Å and O-deviations of -0.023, 0.460 and -0.110 Å from the pyridine mean plane, respectively, so that the puckering is largest in structure 2. Moreover, the BOCCN ring in **1b** is completely planar.

The sum of bond angles in a planar cyclic arrangement of five atoms is 5×108° = 540°, while the theoretical bond angles in cyclopentane range from 102.6 to 106.7° [41—45]. Nevertheless, the OBN bond angles are similar for all 11 complexes in Table 4 and range from 95.9(3) to 99.1(1)°. This means that the

Table 3

Selected bond lengths (Å), bond angles (deg) and torsion angles (deg) for compounds 1a and 1b

Bond lengths (Å)

Compound **1a**				Compound **1b**	
Molecule 1		Molecule 2			
$N_{(1)}$—$C_{(2)}$	1.34(1)	$N_{(51)}$—$C_{(52)}$	1.35(1)	$N_{(1)}$—$C_{(2)}$	1.331(3)
$N_{(1)}$—$C_{(10)}$	1.34(1)	$N_{(51)}$—$C_{(60)}$	1.34(1)	$N_{(1)}$—$C_{(10)}$	1.363(3)
$N_{(1)}$—$B_{(12)}$	1.61(1)	$N_{(51)}$—$B_{(62)}$	1.61(1)	$N_{(1)}$—$B_{(12)}$	1.637(3)
$C_{(8)}$—$C_{(10)}$	1.40(1)	$C_{(58)}$—$C_{(60)}$	1.42(1)	$C_{(8)}$—$C_{(10)}$	1.403(3)
$C_{(7)}$—$C_{(8)}$	1.37(1)	$C_{(57)}$—$C_{(58)}$	1.38(1)	$C_{(7)}$—$C_{(8)}$	1.370(3)
$O_{(11)}$—$B_{(12)}$	1.56(1)	$O_{(61)}$—$B_{(62)}$	1.54(1)	$O_{(11)}$—$B_{(12)}$	1.537(3)
$O_{(11)}$—$C_{(8)}$	1.34(1)	$O_{(61)}$—$C_{(58)}$	1.35(1)	$O_{(11)}$—$C_{(8)}$	1.335(3)
$B_{(12)}$—$C_{(13)}$	1.59(1)	$B_{(62)}$—$C_{(63)}$	1.59(1)	$B_{(12)}$—$C_{(13)}$	1.592(2)
$B_{(12)}$—$C_{(19)}$	1.58(1)	$B_{(62)}$—$C_{(69)}$	1.58(1)		

Bond angles (deg)

$N_{(1)}$—$C_{(10)}$—$C_{(8)}$	110.2(8)	$N_{(51)}$—$C_{(60)}$—$C_{(58)}$	108.8(9)	$N_{(1)}$—$C_{(10)}$—$C_{(8)}$	111.0(2)
$N_{(1)}$—$C_{(10)}$—$C_{(9)}$	126.5(9)	$N_{(51)}$—$C_{(60)}$—$C_{(59)}$	127.9(9)	$N_{(1)}$—$C_{(10)}$—$C_{(9)}$	124.7(2)
$N_{(1)}$—$B_{(12)}$—$O_{(11)}$	96.6(7)	$N_{(51)}$—$B_{(62)}$—$O_{(61)}$	96.7(8)	$N_{(1)}$—$B_{(12)}$—$O_{(11)}$	98.3(2)
$N_{(1)}$—$B_{(12)}$—$C_{(13)}$	111.1(8)	$N_{(51)}$—$B_{(62)}$—$C_{(63)}$	109.7(8)	$N_{(1)}$—$B_{(12)}$—$C_{(13)}$	114.0(1)
$N_{(1)}$—$B_{(12)}$—$C_{(19)}$	111.1(8)	$N_{(51)}$—$B_{(62)}$—$C_{(69)}$	109.5(9)	—	—
$C_{(2)}$—$N_{(1)}$—$B_{(12)}$	132.4(8)	$C_{(52)}$—$N_{(51)}$—$B_{(62)}$	131.3(8)	$C_{(2)}$—$N_{(1)}$—$B_{(12)}$	134.6(2)
$C_{(2)}$—$N_{(1)}$—$C_{(10)}$	117.6(8)	$C_{(52)}$—$N_{(51)}$—$C_{(60)}$	117.4(9)	$C_{(2)}$—$N_{(1)}$—$C_{(10)}$	118.0(2)
$C_{(7)}$—$C_{(8)}$—$C_{(10)}$	118.9(9)	$C_{(57)}$—$C_{(58)}$—$C_{(60)}$	117.8(10)	$C_{(7)}$—$C_{(8)}$—$C_{(10)}$	118.4(2)
$C_{(7)}$—$C_{(8)}$—$O_{(11)}$	129.1(9)	$C_{(57)}$—$C_{(58)}$—$O_{(61)}$	130.1(10)	$C_{(7)}$—$C_{(8)}$—$O_{(11)}$	129.1(2)
$C_{(8)}$—$O_{(11)}$—$B_{(12)}$	110.6(7)	$C_{(58)}$—$O_{(61)}$—$B_{(62)}$	111.2(8)	$C_{(8)}$—$O_{(11)}$—$B_{(12)}$	110.9(2)
$C_{(8)}$—$C_{(10)}$—$C_{(9)}$	123.3(9)	$C_{(58)}$—$C_{(60)}$—$C_{(59)}$	123.3(9)	$C_{(8)}$—$C_{(10)}$—$C_{(9)}$	124.3(2)
$C_{(10)}$—$N_{(1)}$—$B_{(12)}$	109.9(7)	$C_{(60)}$—$N_{(51)}$—$B_{(62)}$	111.3(7)	$C_{(10)}$—$N_{(1)}$—$B_{(12)}$	107.4(2)
$C_{(10)}$—$C_{(8)}$—$O_{(11)}$	111.9(8)	$C_{(60)}$—$C_{(58)}$—$O_{(61)}$	112.0(8)	$C_{(10)}$—$C_{(8)}$—$O_{(11)}$	112.5(2)
$O_{(11)}$—$B_{(12)}$—$C_{(13)}$	109.2(8)	$O_{(61)}$—$B_{(62)}$—$C_{(63)}$	110.2(9)	$O_{(11)}$—$B_{(12)}$—$C_{(13)}$	111.4(1)
$O_{(11)}$—$B_{(12)}$—$C_{(19)}$	109.0(8)	$O_{(61)}$—$B_{(62)}$—$C_{(69)}$	110.8(8)	—	—
$B_{(12)}$—$C_{(13)}$—$C_{(14)}$	122.3(9)	$B_{(62)}$—$C_{(63)}$—$C_{(64)}$	123.4(10)	$B_{(12)}$—$C_{(13)}$—$C_{(14)}$	106.7(2)
$B_{(12)}$—$C_{(13)}$—$C_{(18)}$	121.0(9)	$B_{(62)}$—$C_{(63)}$—$C_{(68)}$	120.3(9)	$B_{(12)}$—$C_{(13)}$—$C_{(20)}$	111.1(2)
$B_{(12)}$—$C_{(19)}$—$C_{(20)}$	121.9(9)	$B_{(62)}$—$C_{(69)}$—$C_{(70)}$	120.2(9)	—	—
$B_{(12)}$—$C_{(19)}$—$C_{(24)}$	124.4(9)	$B_{(62)}$—$C_{(69)}$—$C_{(74)}$	124.4(9)	—	—
$C_{(13)}$—$B_{(12)}$—$C_{(19)}$	117.7(9)	$C_{(63)}$—$B_{(62)}$—$C_{(69)}$	117.9(9)	$C_{(13)}$—$B_{(12)}$—$C_{(13)}$	107.6(2)
$C_{(14)}$—$C_{(13)}$—$C_{(18)}$	116.7(9)	$C_{(64)}$—$C_{(63)}$—$C_{(68)}$	116.3(9)	$C_{(14)}$—$C_{(13)}$—$C_{(20)}$	113.4(2)
$C_{(20)}$—$C_{(19)}$—$C_{(24)}$	113.7(9)	$C_{(70)}$—$C_{(69)}$—$C_{(74)}$	115.3(10)	—	—

Torsion angles (deg)[a]

$N_{(1)}$—$C_{(10)}$—$C_{(8)}$—$O_{(11)}$	-0.7	$N_{(51)}$—$C_{(60)}$—$C_{(58)}$—$O_{(61)}$	-1.3	$N_{(1)}$—$C_{(10)}$—$C_{(8)}$—$O_{(11)}$	0
$C_{(10)}$—$C_{(8)}$—$O_{(11)}$)—$B_{(12)}$	+6.0	$C_{(60)}$—$C_{(58)}$—$O_{(61)}$—$B_{(62)}$	+1.6	$C_{(10)}$—$C_{(8)}$—$O_{(11)}$—$B_{(12)}$	0
$N_{(1)}$—$B_{(12)}$—$O_{(11)}$—$C_{(8)}$	-7.7	$N_{(51)}$—$B_{(62)}$—$O_{(61)}$—$C_{(58)}$	-1.2	$N_{(1)}$—$B_{(12)}$—$O_{(11)}$—$C_{(8)}$	0
$C_{(10)}$-$N_{(1)}$—$B_{(12)}$—$O_{(11)}$	+7.3	$C_{(60)}$—$N_{(51)}$—$B_{(62)}$—$O_{(61)}$	+0.4	$C_{(10)}$—$N_{(1)}$—$B_{(12)}$—$O_{(11)}$	0
$C_{(8)}$—$C_{(10)}$—$N_{(1)}$—$B_{(12)}$	-4.7	$C_{(58)}$—$C_{(60)}$—$N_{(51)}$—$B_{(62)}$	+0.4	$C_{(8)}$—$C_{(10)}$—$N_{(1)}$—$B_{(12)}$	0

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[a] A positive rotation is counter-clockwise from atom 1, when viewed from atom 3 to atom 2.

Table 4

Comparison of structural data for compounds 1—7

Compound	Bond lengths, Å				Bond angles, deg.							THC[d] [%]
	N ⟶ B	B—O	B—C[a]	Σ_B[b]	OBN	BNC	NCC	CCO	COB	CBC	Σ_{cycle}[c]	
1a[e]	1.61(1)	1.55(1)	1.59(1)	6.33	96.7(8)	110.6(7)	109.5(9)	112.0(8)	110.9(8)	117.8(9)	539.6	73.1
1b	1.637(3)	1.537(3)	1.592(2)	6.358	98.3(2)	107.4(2)	107.4(2)	112.5(2)	110.9(2)	107.6(2)	540.1	71.2
2	1.642(3)	1.477(3)	1.621(3)	6.370	97.4(2)	108.4(2)	108.5(2)	105.6(2)	109.0(2)	115.6(2)	528.9	72.0
3	1.658(6)	1.543(6)	1.595(8)	6.390	96.2(4)	109.0(4)	110.4(5)	109.6(5)	114.8(4)	120.6(5)	540.0	64.4
4[f]	1.654(3)	1.480(3)	1.612(2)	6.358	99.1(1)	105.8(2)	104.1(2)	105.6(2)	108.9(2)	113.8(2)	523.4	74.4
5	1.648(3)	1.481(3)	1.622(3)	6.373	98.4(2)	99.7(2)	103.1(2)	107.8(2)	110.1(2)	113.1(2)	519.1	74.1
6[a]	1.624(6)	1.528(6)	1.595(8)	6.341	98.1(4)	106.2(3)	102.7(4)	113.0(3)	113.0(4)	116.4(4)	533.0	75.9
6b	1.606(5)	1.540(4)	1.602(5)	6.349	97.4(3)	104.7(3)	102.7(3)	111.7(3)	111.9(3)	116.2(3)	528.4	74.3
6c	1.613(6)	1.535(5)	1.597(7)	6.341	97.7(3)	105.6(3)	102.8(3)	111.9(4)	113.0(3)	114.1(4)	531.0	75.2
7a	1.626(3)	1.524(3)	1.609(3)	6.367	98.5(2)	103.4(2)	103.6(2)	112.4(2)	112.6(2)	114.8(2)	530.5	76.6
7b	1.646(6)	1.545(6)	1.586(7)	6.363	95.9(3)	103.9(3)	102.7(4)	111.9(4)	111.3(4)	117.5(4)	525.7	66.9

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[a] Average value for both B—C bonds.

[b] Sum of bond lengths at the boron atom.

[c] Sum of bond angles in the five-membered heterocyclic ring.

[d] THC = tetrahedral character at the boron atom being calculated as lined out in ref. [11].

[e] Average values for the two crystallographically independent molecules in the asymmetric unit.

[f] Average values for the monoclinic and orthorhombic form of the compound.

ring strain in the planar heterocycles **1**—**3** is enhanced and this is mostly expressed by the BNC, NCC and CCO bond angles with values between 105.6(2) and 112.5(2)°. On the other hand, they deviate significantly from the geometrically required bond angle of 120° in the pyridine moiety. It should be also mentioned that the external BNC and OCC bond angles range from 126.0(5) to 134.6(2)°. All in all the sum of bond angles in the five-membered heterocyclic rings is smallest for **4** and **5** (519.1 and 523.4°, respectively) and largest for **1**, **2** and **3** (539.6, 540.1 and 540.0°, respectively).

From the above mentioned it can be resumed that the stability of BOCCN heterocyclic rings can be evaluated by several structural parameters, the N → B, B—O and B—C bond lengths as well as the inner bond angles of the heterocycles. These values can be resumed by the sum of bond lengths at the boron atom Σ_B [46], the sum of bond angles in the heterocyclic rings Σ_{cycle} [47] and the tetrahedral character THC of the boron atom [11]. Although a quantitative evaluation by the three parameters should be difficult, a careful analysis permits at least some qualitative predictions, e. g. compound **3** should be of lower hydrolytic stability due to a long N → B bond (1.658(6) Å), a large sum of bond lengths around the boron atom Σ_B (6.390 Å), a large sum of bond angles Σ_{cycle} (540.0 Å) and a small THC-value (64.4%). Furthermore the CBC bond angle is extremely large (120.6(5)°). On the other hand, compounds **6a**—**6c** should be hydrolytically more stable due to short N → B bonds (1.624(6), 1.606(5) and 1.613(6) Å, respectively), small sums of bond lengths Σ_B (6.341, 6.349 and 6.341 Å, respectively), relatively small sums of bond angles Σ_{cycle} (533.0, 528.4 and 531.0°, respectively) and relatively large THC values (75.9, 74.3 and 75.2%, respectively).

As it has been outlined in Scheme 2 the reaction between 2-hydroxypyridine and diphenylborinic acid can result either in a monomeric or dimeric complex. Although it may be assumed that a stoichiometric control of the reaction (1 : 1 or 1 : 2) could permit the selective formation of both chelates, only the tetraphenyl-μ_2-hydroxodiborane complex **8** could be isolated. Crystals suitable for X-ray crystallography were grown from THF/hexane and the molecular structure is shown in Figure 3. The crystallographic data of **8** are resumed in Table 1, the fractional atomic coordinates — Table 5 and selected bond lengths, bond angles as well as torsion angles — Table 6. Table 7 represents a structural comparison of compounds **8**—**14** (Scheme 3) and will be the basis for the following discussion.

The N → B bond lengths in the six-membered BOBOCN heterocycle of **8** (1.612(8) Å) and the BNCNCN heterocycle **11** (1.599(9) Å) are comparable, while the bonds are significantly longer in **9** (1.685(6) Å) and **10** (1.642(3) Å). A similar divergence has been determined for the primary and secondary 1,3-amino alcohol derivatives **12**—**14**, whose N → B bond lengths range from 1.638(3) to 1.674(5) Å. Due to the coordinative bonding of the μ_2-hydroxo group to a second boron atom, the covalent $B_{(1)}$—$O_{(1)}$ bond of **8** (1.553(7) Å) is significantly longer than the one of compounds **9**, **10** and **12**—**14** with values between 1.437(5) and 1.478(2) Å. The covalent bond between the 2-pyridyloxy group and the second boron atom is shorter (1.532(7) Å) than the corresponding bond with the bridging hydroxyl group (1.558(8) Å), thus confirming its coordinative character. In other boron complexes with Ph_2BO_2 moiety the O → B bond has been found to be even longer, e. g., 1.595(3) Å in (maltolato)-diphenylboron [51]. The O → B bond in (salicylaldehydato)diphenylboron is 1.569(4) Å long [52].

Up to now only few X-ray structures of the μ_2-hydroxodiborane(4) type have been reported and as far as we know none with a BO(H)BOCN heterocycle. The B—O bond lengths in the μ_2-hydroxo compounds **15**—**17** [53—55] are indicated in Scheme 4 and it should be noticed that the B—O bond is extremely long in the 1,1′-bis(diisopropylboryl)cobaltocenium cation **17** (1.605(6) Å) [55]. In contrast, the B—O bonds in the μ_3-oxo complexes **18**—**19** are shorter (1.441...1.524(6) Å) [56—57].

Table 5

Fractional atomic coordinates for compound 8

Atom	*x/a*	*y/b*	*z/c*	U_{equiv}	Occ
B$_{(1)}$	0.4895(7)	0.4228(5)	0.2066(3)	0.0496	
B$_{(2)}$	0.6496(7)	0.4711(5)	0.1121(3)	0.0506	
N$_{(1)}$	0.3874(5)	0.4948(3)	0.1714(2)	0.0511	
O$_{(1)}$	0.6333(4)	0.4479(3)	0.1799(2)	0.0483	
O$_{(2)}$	0.5002(4)	0.4592(3)	0.0853(2)	0.0551	
C$_{(1)}$	0.3963(6)	0.5025(4)	0.1116(3)	0.0536	
C$_{(2)}$	0.2964(7)	0.5523(5)	0.0770(3)	0.0642	
C$_{(3)}$	0.1895(7)	0.5960(5)	0.1062(4)	0.0754	
C$_{(4)}$	0.1831(7)	0.5902(5)	0.1681(3)	0.0722	
C$_{(5)}$	0.2818(7)	0.5395(5)	0.1997(3)	0.0641	
C$_{(6)}$	0.6969(6)	0.5754(4)	0.1048(3)	0.0475	
C$_{(7)}$	0.6576(6)	0.6240(4)	0.0533(3)	0.0590	
C$_{(8)}$	0.7039(7)	0.7123(5)	0.0426(3)	0.0736	
C$_{(9)}$	0.7942(8)	0.7547(5)	0.0848(4)	0.0738	
C$_{(10)}$	0.8356(7)	0.7082(5)	0.1360(3)	0.0715	
C$_{(11)}$	0.7875(6)	0.6199(5)	0.1461(3)	0.0646	
C$_{(12)}$	0.7479(6)	0.3962(4)	0.0821(3)	0.0546	
C$_{(13)}$	0.7014(7)	0.3091(5)	0.0660(3)	0.0675	
C$_{(14)}$	0.7885(9)	0.2444(5)	0.0398(3)	0.0817	
C$_{(15)}$	0.9280(9)	0.2670(6)	0.0300(3)	0.0812	
C$_{(16)}$	0.9774(7)	0.3520(6)	0.0453(3)	0.0816	
C$_{(17)}$	0.8895(7)	0.4166(5)	0.0709(3)	0.0671	
C$_{(18)}$	0.4438(6)	0.3214(4)	0.1884(3)	0.0549	
C$_{(19)}$	0.3169(7)	0.2977(5)	0.1581(3)	0.0721	
C$_{(20)}$	0.2823(8)	0.2070(7)	0.1442(4)	0.0893	
C$_{(21)}$	0.373(1)	0.1374(6)	0.1602(4)	0.0925	
C$_{(22)}$	0.499(1)	0.1579(6)	0.1888(4)	0.0931	
C$_{(23)}$	0.5318(7)	0.2478(5)	0.2025(3)	0.0713	
C$_{(24)}$	0.4950(6)	0.4460(4)	0.2762(3)	0.0494	
C$_{(25)}$	0.4178(6)	0.3955(5)	0.3171(3)	0.0652	
C$_{(26)}$	0.4148(8)	0.4203(7)	0.3771(4)	0.0826	
C$_{(27)}$	0.490(1)	0.4952(8)	0.3980(4)	0.0901	
C$_{(28)}$	0.5675(8)	0.5450(6)	0.3589(4)	0.0879	
C$_{(29)}$	0.5709(7)	0.5210(5)	0.2989(3)	0.0690	
O$_{(30)}$	0.8514(5)	0.3709(4)	0.2373(2)	0.0891	
C$_{(30)}$	0.937(1)	0.3007(9)	0.2156(4)	0.1226	
C$_{(31)}$	1.018(1)	0.2633(7)	0.2648(5)	0.1253	
C$_{(32)}$	1.0083(9)	0.3272(9)	0.3123(5)	0.1191	
C$_{(33)}$	0.8974(9)	0.3947(6)	0.2935(4)	0.1073	
O$_{(40)}$	0.624(1)	1.003(2)	-0.012(1)	0.2936	
C$_{(40)}$	0.519(4)	1.073(2)	-0.020(2)	0.2016	0.7500
C$_{(41)}$	0.565(4)	0.982(3)	0.041(1)	0.2104	0.7500

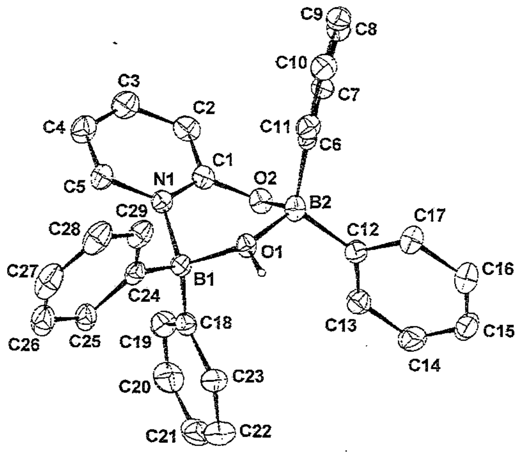


Fig. 3. Molecular structure of (N $\rightarrow$B) (diphenylborylhydroxy)-2-[(O $\rightarrow$B((diphenylboryloxy)]pyridine 8

As already mentioned before, long N $\rightarrow$ B and B—O bonds are normally compensated by short B—C bonds and this observation is confirmed also for compounds 8—14. The mean B—C bond lengths are 1.590(9) and 1.599(9) Å for 8 and 11 with long B—O bonds and 1.615(3) to 1.63(1) Å for 9, 10 and 12—14 with shorter B—O bonds.

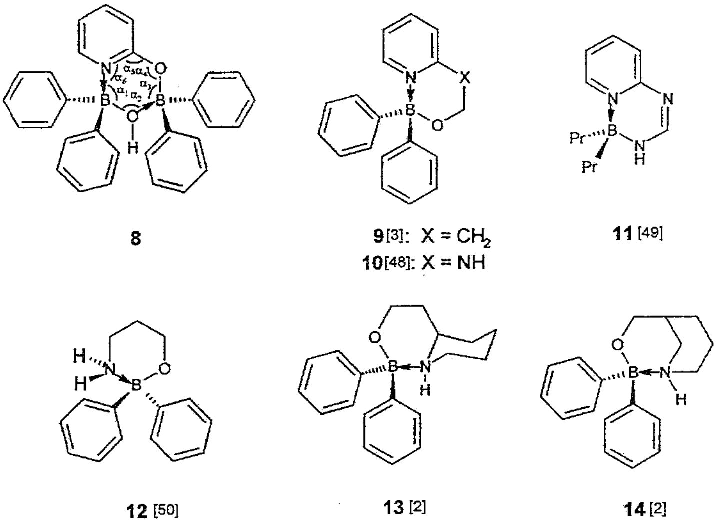
Although the ring conformations in compounds 8—14 are quite different, the OBN bond angles α_1 are with the exception of 8 (100.6(5)°) very similar (the average value is 105.3° for 9—14), so that the coordinative character of the N $\rightarrow$B bond is still reflected by this bond angle. Due to this significant deviation from the optimum bond angle of 109.5° for a chair or 120° for a planar ring conformation, the rest of the inner cycle bond angles α_2—α_6 are strained, e. g., in the nearly planar heterocycle 11 with a sum of bond angles of 719.0° the α_2—α_6 bond angles are significantly different from 120° (Δ = 2.1...10.2°). In contrast, the α_2—α_6 bond angles of the chair-like heterocycle 12 deviate only 0.8...7.5° from the ideal tetrahedral angle. The BOB bond angle of the μ_2-hydroxodiborane(4) moiety in 8 is 122.7(4)°, whereas the OBO bond angle is significantly smaller (103.4(5)°). In compound 15 (Scheme 4) with six-membered rings these angles have very similar values (122.5(1) and 103.6(1)°, respectively), while the BOB bond angles in the less related structures 16 and 17 are quite different (116.3(1) and 144.8(5)°, respectively). In comparison the BOB bond angle of the μ_3-oxo derivative 19 is 127.45°. The sum of bond angles at the bridging oxygen atom $O_{(1)}$ in 8 is 354.3°, so that it possesses a nearly planar geometry. Additionally, the μ_2-hydroxy group is incorporated in hydrogen bond with one of THF molecules in crystal red (1.722 Å, 176.7°).

The conformation of the BOBOCN heterocyclic ring of 8 is a twisted boat with the $B_{(1)}$ and $O_{(2)}$ atoms forming the bows. The deviations of $B_{(1)}$, $B_{(2)}$, $O_{(1)}$ and $O_{(2)}$ from the pyridine mean plane are −0.246, 0.777, 1.011 and 0.011 Å, respectively. The $B_{(1)}$- and $B_{(2)}$-phenyl groups are orientated *anti* between each other.

For the six-membered boron heterocycles 8—14 evaluation of the ring stability would be as interesting as in the case of the five-membered complexes 1—7, but their molecular structures are too different to permit a reliable qualitative prediction. Further structural studies will be necessary in order to obtain more insight into the interatomic organization of these molecules.

Scheme 3

Six-membered (N → B)-borinates obtained from different 3-aminoalcohol and 1,3-diamine derivatives



8

9[3]: X = CH$_2$
10[48]: X = NH

11 [49]

12 [50]

13 [2]

14 [2]

Table 6

Selected bond lengths (Å), bond angles (deg) and torsion angles (deg) for compound 8

	Bond lengths (Å)		
N(1)—C(1)	1.342(7)	B(2)—O(1)	1.558(8)
N(1)—B(1)	1.612(8)	B(2)—O(2)	1.532(7)
B(1)—O(1)	1.553(7)	B(2)—C(6)	1.591(9)
B(1)—C(18)	1.585(9)	B(2)—C(12)	1.597(9)
B(1)—C(24)	1.585(9)	C(1)—O(2)	1.325(6)
	Bond angles (deg)		
N(1)—C(1)—O(2)	118.3(5)	O(1)—B(2)—O(2)	103.4(5)
N(1)—B(1)—O(1)	100.6(5)	O(1)—B(2)—C(6)	110.1(5)
N(1)—B(1)—C(18)	109.0(5)	O(1)—B(2)—C(12)	109.8(5)
N(1)—B(1)—C(24)	109.6(5)	O(2)—B(2)—C(6)	109.2(5)
C(18)—B(1)—C(24)	116.5(5)	O(2)—B(2)—C(12)	107.9(5)
B(1)—O(1)—B(2)	122.7(4)	C(6)—B(2)—C(12)	115.8(5)
B(1)—N(1)—C(1)	118.6(5)	B(2)—O(2)—C(1)	117.9(5)
B(1)—N(1)—C(5)	121.6(5)	B(2)—C(12)—C(13)	123.1(6)
B(1)—C(18)—C(19)	125.1(6)	B(2)—C(12)—C(17)	120.5(6)
B(1)—C(18)—C(23)	120.1(6)	B(2)—C(6)—C(7)	120.1(5)
B(1)—C(24)—C(25)	121.7(6)	B(2)—C(6)—C(11)	122.9(6)
B(1)—C(24)—C(29)	121.3(6)	C(1)—N(1)—C(5)	119.4(5)
O(1)—B(1)—C(18)	111.0(5)	O(2)—C(1)—N(1)	118.3(5)
O(1)—B(1)—C(24)	109.0(5)	O(2)—C(1)—C(2)	120.1(6)
	Torsion angles (deg)[a]		
N(1)—C(1)—O(2)—B(2)	−49.0	B(1)—O(1)—B(2)—O(2)	−1.6
N(1)—B(1)—O(1)—B(2)	−40.2	O(1)—B(2)—O(2)—C(1)	+51.5
B(1)—N(1)—C(1)—O(2)	−8.3	C(1)—N(1)—B(1)—O(1)	+48.2

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[a] A positive rotation is counter-clockwise from atom 1, when viewed from atom 3 to atom 2.

Scheme 4

μ_2-Hydroxodiborane (15—17), μ_3-oxotriborane (18) and μ_3-oxodiborane (19) derivatives reported in the literature

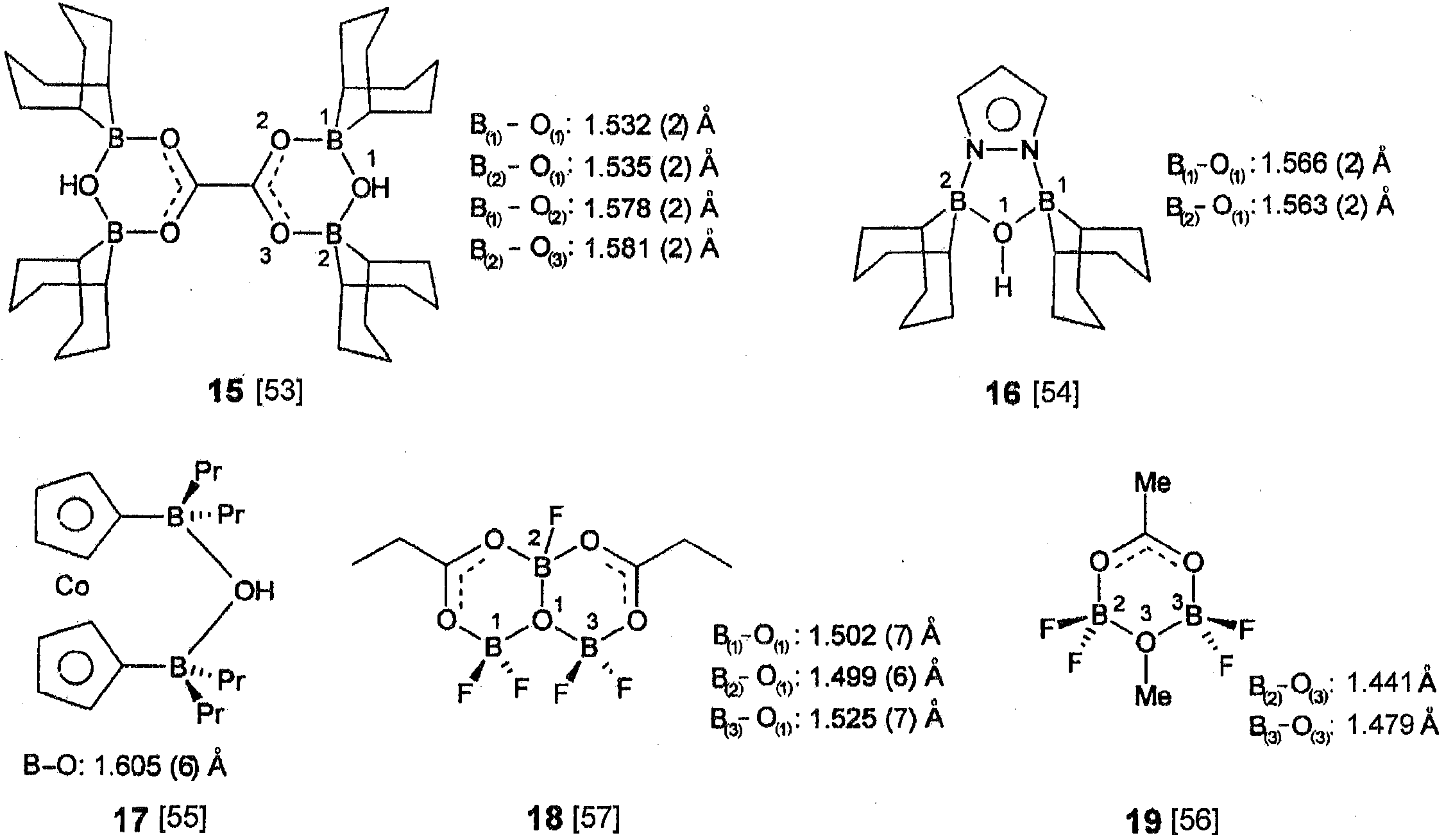

Table 7

Comparison of structural data for compounds 8—14

Compound	Bond lengths, Å				Bond angles, deg.							THC[d], %
	N → B	B—O	B—C[a]	Σ_B[b]	α_1	α_2	α_3	α_4	α_5	α_6	Σ_{cycle}[c]	
8	1.612(8)	1.553(7)[e] 1.558(8)[f] 1.532(7)[g]	1.585(9)[h] 1.594(9)[i]	6.335[j] 6.278[k]	100.6(5)	122.7(4)	103.4(5)	117.9(5)	118.3(5)	118.6(5)	681.5	79.4
9	1.685(6)	1.452(6)	1.625(6)	6.387	105.9(3)	114.1(3)	110.2(3)	113.5(3)	118.8(3)	122.3(3)	684.8	78.4
10	1.642(3)	1.477(3)	1.615(3)	6.348	104.7(2)	112.6(2)	110.0(2)	121.9(2)	118.9(2)	121.5(2)	689.6	78.3
11[l]	1.599(9)	—	1.599(9)	6.368	104.4(5)	122.1(5)	130.2(6)	116.3(5)	123.2(5)	122.9(5)	719.0	86.1
12	1.638(3)	1.478(2)	1.619(3)	6.345	104.9(1)	117.0(2)	110.5(2)	110.8(2)	108.7(2)	113.3(2)	665.2	82.4
13	1.673(2)	1.449(2)	1.620(3)	6.362	105.8(2)	115.7(1)	110.5(1)	111.8(2)	109.6(1)	110.5(1)	664.0	84.8
14	1.674(5)	1.437(5)	1.621(6)	6.352	106.3(3)	117.8(3)	111.6(4)	109.1(4)	108.1(4)	108.9(3)	661.8	85.1

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[a] Average value for both B—C bonds;
[b] Sum of bond lengths at the boron atom;
[c] Sum of bond angles in the six-membered heterocyclic ring,
[d] THC = tetrahedral character at the boron atom being calculated as lined out in ref. 11;
[e] $B_{(1)}$—$O_{(1)}$;
[f] $B_{(2)}$—$O_{(1)}$;
[g] $B_{(2)}$—$O_{(2)}$;
[h] $B_{(1)}$—C;
[i] $B_{(2)}$—C;
[j] $B_{(1)}$;
[k] $B_{(2)}$;
[j] Average values for the two crystallographically independent molecules in the asymmetric unit.

CONCLUSIONS

In the present contribution the molecular structure of three (N →B) borinates that have been prepared from 8-hydroxyquinoline and 2-hydroxypyridine have been described in a comparative manner with other five- and six-membered boron chelates. Thereby, significant structural differences could be detected that allow in some cases at least a qualitative comparison of complex stability.

The reaction between diphenylborinic acid and 2-hydroxypyridine led to the formation of a new μ_2-hydroxodiborane complex with two coordinative bonds at a time, an N →B and an O →B bond.

EXPERIMENTAL

1. Instrumentation

IR spectra have been recorded with a Perkin Elmer 16F-PC FT-IR spectrophotometer. Mass spectra were obtained with an HP 5989 A equipment. Melting points were determined with a Gallenkamp MFB-595 apparatus and have not been corrected.

X-ray diffraction studies of single crystals were realized on an Enraf-Nonius CAD4 diffractometer ($\lambda_{MoK\alpha} = 0.71069$ Å, monochromator: graphite, $T = 293$ K, ω-2θ scan). Crystals were generally mounted in LINDEMAN tubes. Cell parameters were determined by least-squares refinement on diffractometer angles for 24 automatically centered reflections. Absorption correction was not necessary, corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-86) for structure solution and the CRYSTALS (version 9, 1994) software package for refinement and data output. Non hydrogen atoms were refined anisotropically. Hydrogen atoms were determined by difference Fourier maps (in the case of **1b**) or calculated (in the case of **1a** and **8**). In the first case their positions and one overall isotropic thermal parameter were refined, while in the second case only one overall isotropic thermal parameter was refined.

$I > 3\sigma(I)$. ($R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$)

In all cases only independent reflections on the basis of Friedels law have been collected and a reflection — parameter ratio 5 has been considered sufficient for the type of structural studies performed in here.

2. Reagents

Commercial starting materials were used when available (Aldrich). Diphenylborinic acid was prepared from 2-aminoethyldiphenylborinate (5% of molar excess) as described in the literature [58].

3. Preparation of the boron complexes 1a, 1b and 8

(N →B)-Diphenylboryl-8-quinolinate (1a). Compound **1a** was prepared as described in the literature [30, 31, 33]. Crystals suitable for X-ray crystallography were obtained from THF/hexane.

(N →B)-9-Borabicyclo[3.3.1]non-9-yl-8-quinolinate (1b). Compound **1b** was prepared as described in the literature [33]. Crystals suitable for X-ray crystallography were obtained from THF/hexane.

(N →B)(Diphenylborylhydroxy)-2-[(O →B)-(diphenylboryloxy)]pyridine (8). 0.76 g (4.20 mmol) of diphenylborinic acid and 0.20 g (2.10 mmol) of 2-hydroxypyridine were heated for 30 min in 20 ml of THF. Then the solution was concentrated by evaporation of solvent with Dean—Stark trap and after 24 h transparent crystals of **8** had formed that were separated by vacuum filtration. Crystals suitable for X-ray crystallography were obtained from THF/hexane. Yield: 90%, m. p. 128...130 °C. IR ν (KBr): 3092 (m), 3068 (m), 3044 (m), 3022 (m), 3002 (m), 2974 (m), 2878 (m), 2642 (br, m), 1630 (s), 1558 (m), 1488 (s), 1452 (m), 1430 (s), 1348 (s), 1264 (m), 1196 (s), 1144 (m), 1126 (m), 1082 (m), 1072 (m), 1046 (m), 1040 (m), 956 (s), 920 (m), 750 (s), 740 (s), 704 (s) cm^{-1}; MS, m/z (I, %) 364 (M-C_6H_5, 0.4), 363 (2), 346 ($(Ph_2B)_2O$, 67), 286 ($C_{17}H_{14}B_2NO_2$, 100), 268 (22), 242 (53), 182 (Ph_2BOH, 41), 165 (Ph_2B, 76), 78 (33).

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