

# New 3,3'[2,2'-Oxy-bis-(oxazaborolidine)]-ethylenes. Structural Studies by NMR, X-ray, and Quantum Chemistry Methods

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**ABSTRACT:** 3,3'-[2,2'-Oxy-bis-(4*S*-methyl, 5*R*-phenyl-1,3,2-oxazaborolidine)]ethylene (**4a**) and 3,3'-[2,2'-oxy-(4*S*-methyl-5*R*-phenyl-1,3,2-oxazaborolidine)-(1,3,2-benzoxazaborolidine)]ethylene (**4b**) were synthesized by the reaction of *N,N'*-bis-[(1*R*,2*S*)-norephedrine]oxalyl (**3a**) or *N,N'*-[((1*R*,2*S*)-norephedrine, *o*-hydroxyphenylamine]oxalyl (**3b**) with  $\text{BH}_3\text{-THF}$ . The molecular structure of these compounds was established by NMR and infrared spectroscopy. The molecular geometry for **4** was studied by means of theoretical methods, resulting in structures that were in total agreement with those obtained by spectroscopy data and X-ray diffraction. © 2005 Wiley Periodicals, Inc. *Heteroatom Chem* 16:513–519, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20151

## INTRODUCTION

The 2,2'-oxy-bis-(1,3,2-oxazaborolidines) **2** are compounds possessing a nitrogen–boron–oxygen heterocyclic system, in addition to an exocyclic boron–oxygen bond (Scheme 1). These substances are derivatives of oxazaborolidine **1** which is an excellent reagent for asymmetric reduction [1–4]. Although papers describing chemical studies of **1** are frequent, the synthesis of analogous **2** has not been reported [5–8]. Preparation of **2** is rather difficult because the 1,3,2-oxazaborolidines are easily hydrolyzed. Moreover, the formation of compound **2** implies decrease in the system's entropy that makes the process thermodynamically less viable.

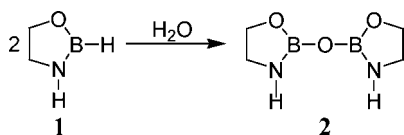
It is possible to obtain 2,2'-oxy-bis-(1,3,2-oxazaborolidines) if polyligands are used, and the addition of water is carefully controlled. The oxamides **3** have ideal molecular structures to obtain polycyclic compounds (Scheme 2). Compounds **3** have four coordinating centers that make possible to obtain bis-(1,3,2-oxazaborolidines) by addition of  $\text{BH}_3\text{-THF}$ . Thus, in this work, we report the synthesis of tricyclic 2,2'-oxy-bis-(1,3,2-oxazaborolidines) **4** by addition of water to bis-(1,3,2-oxazaborolidines) on

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**SCHEME 1** Synthesis of 2,2'-oxy-bis-(1,3,2-oxazaborolidines).

which an oxygen atom acts as a pivot to yield a seven-membered ring. The structures of **4** were studied by multinuclear NMR, X-ray crystallography, infrared spectroscopy, and theoretical methods.

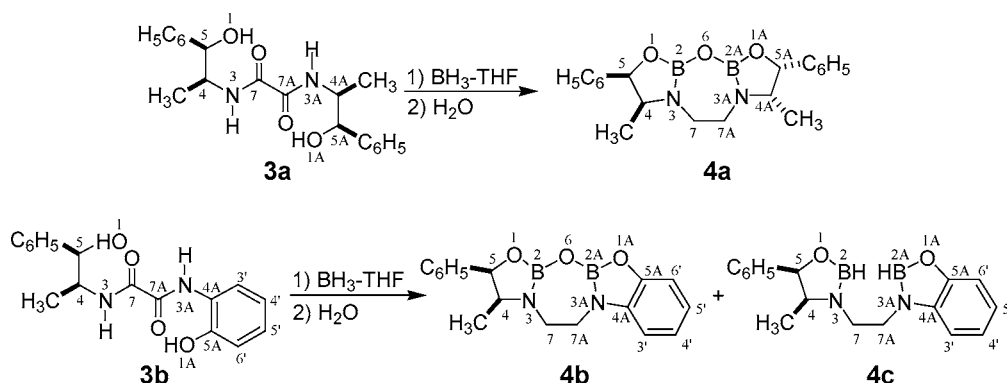
## RESULTS AND DISCUSSION

Compounds **3a,b** were synthesized by the procedure described previously [9,10]. The reduction of **3a** or **3b** with  $\text{BH}_3\text{-THF}$ , followed by the partial hydrolysis of the bis-(1,3,2-oxazaborolidine) containing the B-H bond, yielded the tricyclic 2,2'-oxy-bis-(1,3,2-oxazaborolidines) **4a** or **4b**, respectively (Scheme 2). Evidence of the formation of these compounds was obtained from multinuclear NMR spectroscopy and infrared spectra. Unequivocal  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignments for **4a** were made by DEPT experiments. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals of the *o*-aminophenol fragment in **4b** were assigned by 2D  $^1\text{H}$ - $^{13}\text{C}$  correlated experiments (HETCOR). Additionally, the structure of **4a** was corroborated by X-ray crystallography.

In the  $^{11}\text{B}$  NMR spectra of **4a** and **4b** were observed broad signals attributed to the oxazaborole group at  $\delta = 23.6$  ppm and  $\delta = 24.0$  ppm, respectively [11]. The compound **4a** in solution is a disymmetric molecule, and therefore the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra showed half of the total number of signals (Tables 1 and 2). The vicinal coupling constants of the methine protons in **4a** and **4b** ( $^3J_{\text{H-H}} = 7.7$  Hz)

suggest the double character for the  $\text{N}=\text{B}$  bond and the restriction of the pseudorotation of a five-membered heterocycle [12,13]. The chemical shifts of the methyl groups in  $^1\text{H}$  NMR ( $\delta = 0.66$  ppm for **4a** and 0.61 ppm for **4b**) and  $^{13}\text{C}$  NMR ( $\delta = 15.9$  ppm for **4a** and 16.0 for **4b**) are characteristic of heterocyclic derivatives of the ephedrine and show that these groups are under the diamagnetic protection of the phenyl group [13]. The  $^{13}\text{C}$  NMR signals of the methine carbon atoms neighboring the amino group are shifted to high frequencies, compared with equivalent fragments of the oxazaborolidine. This corroborates the double character of the  $\text{N}=\text{B}$  bond. Conversely, the  $^{13}\text{C}$  NMR signals of the methine carbon atoms next to oxygen are at lower frequencies than those in the oxazaborolidines. This shows that the five-membered heterocycles are strained.

The X-ray diffraction of **4a** (Table 3) corroborates the double character of B-N bonds (Fig. 1, Table 4). The bond lengths B-O in **4a** [1.360(3) Å for B2-O1, and 1.339(3) Å for B2-O6] are similar to B-O bond distances in boroxine (1.375 Å [14]), whereas the B-N bond lengths [1.407(4) Å] are shorter than the corresponding distances in borazine (1.429 Å [15]). The geometry of the B and N atoms is planar (the sum of the angles around the boron is  $360.0^\circ$  and  $357.8^\circ$  for nitrogen), and the systems N-B-O-B-N and O-B-O-B-O are almost on the same plane (the dihedral angle for B2-O6-B2A-O1A is  $174.1^\circ(3)$  and for B2-O6-B2A-N3A is  $-7.6^\circ(2)$ ). On the other hand, the seven-membered heterocycle showed a *cis-cis* conformation in which the nitrogen atoms have a *gauche* relation and the molecule adopts  $\text{C}_2$  symmetry [16]. Thus, with all these features, we can say that there is an electronic delocalization between B, O, and N atoms. The bond angles B2-O6-B2A [124.7(3)°], O6-B2-N3 [129.2(2)°], and B2-N3-C7 [130.7(2)°] show that the seven-membered heterocycle is perhaps strained.



**SCHEME 2** Synthesis of 2,2'-oxy-bis-(1,3,2-oxazaborolidines) **4a,b** from oxamides **3a,b**.

TABLE 1  $\delta^1\text{H}$  of **3** in DMSO- $d_6$  and **4** in  $\text{CDCl}_3$ 

	H1	H3	H4	H5	H1A	H3A	H4A	H5A	H7	H7A	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
<b>3a</b>	5.55	8.30	3.94	4.66	5.55	8.30	3.94	4.66			0.99	7.22–7.37
<b>3b<sup>a</sup></b>	5.60	8.71	4.02	4.70	10.24	9.69					1.09	7.18–7.37
<b>4a</b>			3.73	5.51			3.73	5.51	2.93	2.93	0.66	7.23–7.37
									3.25	3.25		
<b>4b<sup>b</sup></b>			3.80	5.55					3.30	3.70	0.61	7.31–7.41
									3.70			

<sup>a</sup>8.09 (H3'-Ph); 6.83 (H4'-Ph); 6.99 (H5'-Ph); 6.92 (H6'-Ph).

<sup>b</sup>7.18 (H3'-Ph); 7.08 (H4'-Ph); 6.96 (H5'-Ph); 6.89 (H6'-Ph)

### Calculations

Reported ab initio and DFT calculations describe very well the molecular parameters of oxazaborolidines [17,18]. In this work, we calculated the geometry and vibrational frequencies in the ground state of compounds **4** by using the HF and DFT (B3LYP) methods. These calculations were useful to assign the experimental infrared spectra and establish the presence of the tricyclic system.

All the calculations are performed by using the Molden molecular visualization program [19] and the GAUSSIAN 98 package [20]. Geometries were fully optimized at the HF-6-31G(d,p) level of ab initio and B3LYP-6-31G(d,p) level of the density functional theory. At the stationary points, second derivatives were calculated showing whether a minimum or a first-order saddle point was obtained. Two sets of vibrational frequencies of these species were calculated with these methods and then scaled by 0.8992 and 0.9614, respectively.

The ab initio and DFT calculations of **4a** and **4b** showed that these heterocycles have the C<sub>1</sub> point group (Figs. 2 and 3). The optimized geometry parameters (bond lengths and angles) of **4a** calculated by HF and B3LYP methods with 6-31G(d,p) as the basis set are listed in Table 4, and they are compared with the experimental crystal geometry. The optimized bond lengths for **4a** obtained by the two methods are approximately similar; the B3LYP ( $R^2 = 0.9517$ ) correlates well for the bond lengths

compared with HF ( $R^2 = 0.9372$ ). Furthermore, the HF and B3LYP methods give similar B–N and B–O bond distances, which are close to the experimental values and confirmed the double character of these bonds.

The bond angles calculated by B3LYP and HF are close to the experimental values (Table 4). The largest difference is about 2.54° for the first method ( $R^2 = 0.9792$ ) and 3.24° for the second one ( $R^2 = 0.9699$ ). In summary, the optimized bond lengths and dihedral angles (HF method) and obtained bond angles (DFT method) show the best agreement with the experimental values.

Table 5 presents the major calculated and experimental vibrational IR frequencies of **4a** and **4b**. The frequencies obtained have been scaled by 0.8992 and 0.9614, which are typical scaling factors for HF and B3LYP, respectively. Scaled fundamentals are in better agreement with the experimental fundamentals, and they are found to have a good correlation for B3LYP (0.9992 for **4a** and 0.9997 for **4b**) and HF (0.9992 for **4a** and 0.9997 for **4b**). The most intense IR peaks are calculated to be at 1319 (B3LYP)/1338 (HF)  $\text{cm}^{-1}$  for **4a** and 1338 (B3LYP)/1346 (HF)  $\text{cm}^{-1}$  for **4b**, and they correspond to the B–O–B tension. Moreover, other strong peaks are present at 1394 and 1381  $\text{cm}^{-1}$  (HF and B3LYP, respectively) for **4a** and 1352 and 1358  $\text{cm}^{-1}$  for **4b** due to the annular vibration of the N–B–O–B–N system. Thus, these signals could be used as a reference to detect the presence of 2,2'-oxy-bis-(1,3,2-oxazaborolidines).

TABLE 2  $\delta^{13}\text{C}$  of **3** in DMSO- $d_6$  and **4** in  $\text{CDCl}_3$ 

	C4	C5	C4A	C5A	C7	C7A	CH <sub>3</sub>	Ci	Co	Cm	Cp
<b>3a</b>	50.8	73.6	50.8	73.6	158.7	158.7	14.3	142.7	126.3	127.7	126.8
<b>3b<sup>a</sup></b>	51.3	73.7	124.8	146.8	158.6	156.9	14.6	142.8	126.1	127.7	126.8
<b>4a</b>	61.5	79.6	61.5	79.6	44.9	44.9	15.9	139.2	128.0	126.1	127.2
<b>4b<sup>b</sup></b>	61.3	80.0	138.4	146.8	43.7	43.1	16.0	138.7	128.1	126.0	127.4

<sup>a</sup>111.2 (C3'); 119.1 (C4'); 124.9 (C5'); 114.8 (C6').

<sup>b</sup>111.9 (C3'); 121.6 (C4'); 119.5 (C5'); 107.8 (C6').

TABLE 3 Crystal Data of **4a**

<b>4a</b>	
Formula	C <sub>20</sub> H <sub>24</sub> B <sub>2</sub> N <sub>2</sub> O <sub>3</sub>
F <sub>w</sub>	362.03
Space group	C <sub>2</sub>
a (Å)	20.474(4)
b (Å)	6.4589(13)
c (Å)	9.3063(19)
V (Å <sup>3</sup> )	1228.7(4)
Z	2
Absorption coefficient	0.064 mm <sup>-1</sup>
F(000)	384
θ range for data collection	1.99–28.44°
Reflections collected	4916
Independent reflections	2869 [ <i>R</i> (int) = 0.0276]
Completeness to θ = 28.44°	97.5%
Absorption correction	None
Data/restraints/parameters	2869/1/151
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.972
Final <i>R</i> indices [ <i>I</i> > 2σ ( <i>I</i> )]	<i>R</i> 1 = 0.0553, <i>wR</i> 2 = 0.1267
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1030, <i>wR</i> 2 = 0.1525
Largest difference in peak and hole	0.151 and -0.202 e.Å <sup>-3</sup>

### Summary and Conclusions

In conclusion, we have prepared 2,2'-oxy-bis-(1,3,2-oxazaborolidine) system by controlled hydrolysis of bis-(1,3,2-oxazaborolidines) with B–H bonds. NMR and crystallographic studies confirm the presence of this heterocyclic system. The theoretical studies are in agreement with experimental results, and we find evidence to support the presence of electronic delocalization in the N–B–O system.

### EXPERIMENTAL

The synthetic work and the handling of samples were carried out under an inert atmosphere of N<sub>2</sub>, using carefully dried glassware and dry solvents. The syn-

thesis of *N,N'*(hydroxyalkyl)oxamides was accomplished according to the reported procedures [9,10]. <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR spectra were recorded on a JEOL GX S 270 spectrometer. Chemical shifts are relative to TMS for <sup>1</sup>H and <sup>13</sup>C NMR and BF<sub>3</sub>OEt<sub>2</sub> for <sup>11</sup>B NMR. Infrared spectra were taken in CHCl<sub>3</sub> using a Perkin-Elmer System 200 FT-IR spectrophotometer. Mass spectra were obtained with an HP5989A equipment. Melting points were obtained on a Gallenkamp apparatus and are uncorrected. Elemental microanalyses were performed by Oneida Research Service, Whitesboro, NY 13492.

### X-Ray analysis

A selected monocrystal was set upon a Bruker Smart 6000 diffractometer. After optical alignment, the cell parameters were determined by using the reflections collected on four sets of 20 frames each [21]. Data collection was performed in the hemisphere mode, and corrections were made for Lorentz and polarization effects. Computations were performed by using SAINT-NT [22]. Atomic form factors for neutral C, N, O, and H were taken from the *International Tables for X-ray Crystallography* [23].

The structure was solved by direct methods using the SHELXTL-NT program [24]. Refinement method full-matrix least-squares on *F*<sup>2</sup> was used. Hydrogen atoms were calculated and refined with an overall isotropic temperature factor. Anisotropic temperature factors were introduced for all non-hydrogen atoms, and least-squares refinement was carried out by minimizing  $\Sigma w(|F_o| - |F_c|)^2$ , where *F*<sub>o</sub> and *F*<sub>c</sub> are the observed and calculated structure factors. Model reached convergence with *R* =  $\Sigma w(|F_o| - |F_c|) / \Sigma w|F_o|$  and *R*<sub>w</sub> =  $\Sigma [w(|F_o| - |F_c|)^2] / \Sigma w(F_o)^2$ <sup>1/2</sup>. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC

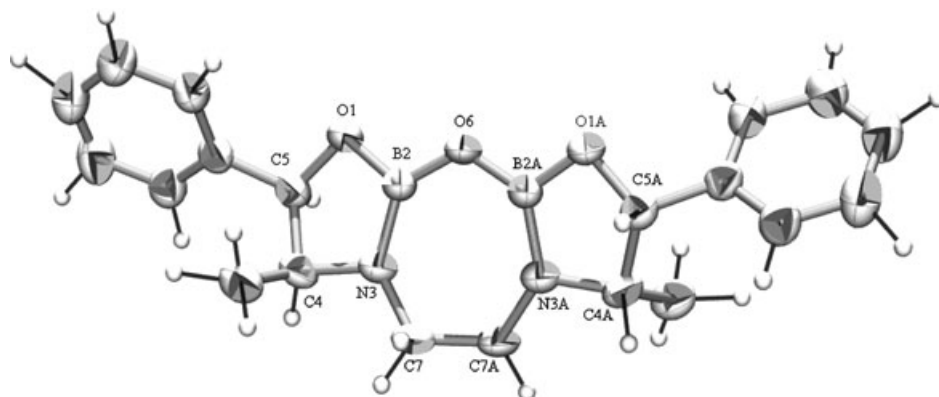


FIGURE 1 ORTEP representation of compound **4a**.

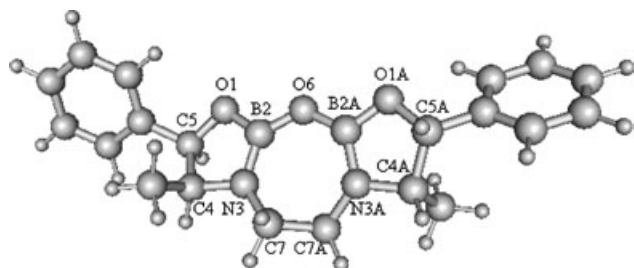
TABLE 4 Experimental Data for **4a** and Optimized Geometries for **4a** and **4b** in the Ground State

Parameters	<b>4a</b>			<b>4b</b>	
	X-ray	B3LYP 6-31G(d,p)	HF 6-31G(d,p)	B3LYP 6-31G(d,p)	HF 6-31G(d,p)
Bond lengths					
B2–N3	1.407(4)	1.423	1.416	1.423	1.416
B2–O1	1.360(3)	1.383	1.367	1.379	1.364
B2–O6	1.339(3)	1.368	1.354	1.371	1.357
O1–C5	1.434(3)	1.436	1.412	1.437	1.414
N3–C7	1.447(3)	1.453	1.445	1.453	1.445
C7–C7A	1.477(5)	1.533	1.525	1.533	1.525
B2A–N3A	1.407(4)	1.423	1.416	1.438	1.428
B2A–O1A	1.360(3)	1.383	1.367	1.394	1.376
B2A–O6	1.339(3)	1.368	1.354	1.360	1.348
O1A–C5A	1.434(3)	1.436	1.412	1.376	1.359
C5A–C4A	1.544(4)	1.568	1.555	1.407	1.395
N3A–C7A	1.447(3)	1.453	1.445	1.456	1.448
Bond angles					
B2–N3–C7	130.7(2)	129.406	129.297	129.407	129.014
B2–N3–C4	108.2(2)	107.814	107.611	107.614	107.407
B2–O1–C5	105.7(2)	107.574	108.247	107.525	108.148
B1–O6–B1A	124.7(3)	127.237	127.941	126.857	127.670
C7–N3–C4	118.9(2)	120.169	120.384	120.090	120.354
C5–C4–N3	99.8(2)	100.527	100.305	100.566	100.292
O1–B2–N3	111.8(2)	111.160	110.573	111.433	110.826
O1–C5–C4	105.8(2)	105.264	104.968	106.249	104.927
O6–B2–N3	129.2(2)	128.394	128.125	128.054	127.706
B2A–N3A–C7A	130.7(2)	129.406	129.297	130.207	130.467
B2A–N3A–C4A	108.2(2)	107.813	107.611	105.991	105.691
B2A–O1A–C5A	105.7(2)	107.573	108.247	106.516	107.064
C7A–N3A–C4A	118.9(2)	120.169	120.384	123.690	123.616
C5A–C4A–N3A	99.8(2)	100.527	100.305	107.303	107.260
O1A–B2A–N3A	111.8(2)	111.160	110.573	109.470	109.368
O1A–C5A–C4A	105.8(2)	105.264	104.968	110.701	110.580
O6–B2A–N3A	129.2(2)	128.394	128.126	128.867	128.523

273685. Copies of the data can be obtained free of charge on application to “The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

*3,3'*-[2,2'-Oxy-bis-(4*S*-methyl, 5*R*-phenyl-oxazaborolidine)]ethylene **4a**

28.2 mL (26.81 mmol) of BH<sub>3</sub>-THF 1.0 M was added to 2.4 g (2.7 mmol) of *N,N'*-(1*R*,2*S*)-norephedrine]-

FIGURE 2 HF 6-31G(d,p) structure of **4a**.

oxalyl **3a** at 0°C. The reaction mixture was warmed at room temperature for 3 h then heated to reflux for 4 h. The compound **4a** crystallized out of the reaction mixture (1.30 g, 54.8%). mp 227°C. MS (EI, 70 eV) *m/z*: M<sup>+</sup> = 362 (29), 361 (18), 348 (21), 347 (100), 346 (47), 117 (12), 105 (10), 91 (20). Anal. Calcd for C<sub>20</sub>H<sub>24</sub>B<sub>2</sub>N<sub>2</sub>O<sub>4</sub>·1.1H<sub>2</sub>O·0.5THF: C, 63.23; H, 7.28; N, 6.70. Found: C, 63.31; H, 7.05; N, 6.79.

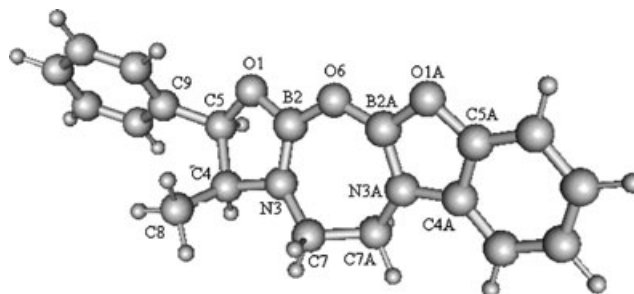
FIGURE 3 B3LYP 6-31G(d,p) structure of **4b**.

TABLE 5 Calculated and Observed (IR) Wave Numbers (in  $\text{cm}^{-1}$ ) of the Major Vibrational Modes of **4a** and **4b**

Assignment	<b>4a</b>			<b>4b</b>		
	Observed	B3LYP 6-31G(d,p)	HF 6-31G(d,p)	Observed	B3LYP 6-31G(d,p)	HF 6-31G(d,p)
$\nu(\text{B-O})$	1120	1137	1124	1120	1118	1122
$\nu(\text{B-O-B})$	1326	1319	1338	1326	1338	1346
$\nu(\text{N-B-O-B-N})$	1380	1381	1394	1378	1352	1358
$\nu(\text{B-O-N})$	1398	1424	1430	1394	1382	1384
$\nu(\text{B-N})$	1452	1483	1488	1452	1436	1445
$\delta(\text{CH}_2)$				1490	1482	1490
$\nu(\text{CH})$	2870	2902	2869	2870	2906	2893
$\nu(\text{CH}_3)$	2932	2932	2928	2936	2939	2928
$\nu(\text{CH}_3)$	2978	2934	2945	2978	3001	2989
$\nu(\text{CH})$				3036	3068	3036

### 3,3'-[2,2'-Oxy-(4*S*-methyl, 5*R*-phenyl-oxazaborolidine)-(benzoxazaborolidine)]ethylene **4b**

25.4 mL (24.1 mmol) of  $\text{BH}_3\text{-THF}$  0.95 M was added to 1.9 g (6.02 mmol) of *N,N'*-[(1*R*,2*S*)-norephedrine, *o*-hydroxyphenylamine]oxalyl **3b** at  $0^\circ\text{C}$ . The reaction mixture was warmed to room temperature for 3.5 h, then was heated under reflux for 6 h. Insoluble material was filtered off, and the THF was removed under vacuum to afford a mixture of the tricyclic compound **4b** and the bis-oxazaborolidine **4c** (89:11, respectively).

**4c**:  $^{11}\text{B}$  NMR( $\text{CDCl}_3$ ),  $\delta$  +29;  $^{13}\text{C}$ ( $\text{CDCl}_3$ ),  $\delta$  15.8 (Me), 42.7 (C7), 42.9 (C7A), 57.1 (C4), 83.3 (C5), 109.1 (C6'), 112.7 (C3'), 120.0 (C5'), 121.9 (C4'), 136.6 (C4A), 138.4 (Ci), 150.1 (C5A).

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