Synthesis and Study of Monomeric and Dimeric Boronates by Spectroscopic Methods and X-ray Crystallography

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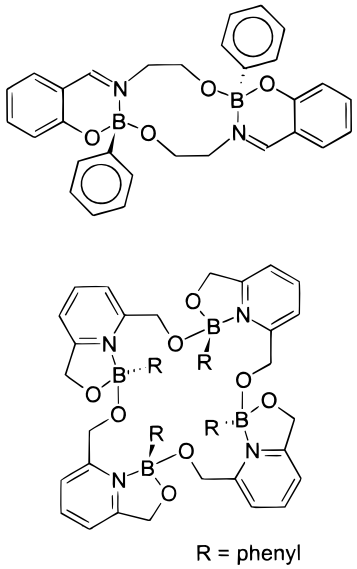
A series of 2-salicylideneamino ethanol derivatives with substituents in different positions have been brought to reaction with phenylboronic acid. Depending on the number and position of the substituents in the ligand, three boronate structure types have been obtained. Thereby, it could be shown that the formation of a macrocyclic dimeric boronate is preferred over the monomeric compound and a [5.4.0]heterobicyclic system with a B(4)−O−B(3) structural unit. The three structure types have been analyzed by X-ray crystallography, where a series of parameters such as N→B bond length, torsion angles, tetrahedral character at the boron atom, deviation of the boron atom from the mean plane and sum of bond angles in the heterocyclic rings have been evaluated in order to determine the factors for the preferred formation of each compound. Finally a new synthetic strategy is presented that permits the synthesis of other macrocyclic boronates in the future.

Introduction

During our studies of boron complexes with a coordinative N→B bond,[1] we recently reported the synthesis of two new macrocyclic structures that consist of a dimeric and a tetrameric boronate ring system of 10 and 20 members, respectively[2] (Chart 1).

Both molecules are stable in the air and are obtained in high yields in one step syntheses from the corresponding amino dialcohol and phenylboronic acid. The molecular structures of both macrocycles have been studied by X-ray crystallography,[2] and it could be shown that the monomeric system would be too strained due to the tetrahedral geometry at the boron atom and its small atomic radius. This is in contrast to other metal complexes, where only monomeric species have been obtained with the same ligand.[3]

Chart 1



In the present contribution the effects of different substituents in the amino dialcohol that lead to the dimeric boronates are studied by spectroscopic methods and X-ray crystallography. It will be shown that the presence of certain substituents inhibits the formation of the dimeric structure and leads to the monomeric boronate.

Results and Discussion

Synthesis and Characterization of Dimeric Boronates. In accordance with the preparation of **2a**,[2] a series of amino dialcohols **1b**−**e** with different substituents have been synthesized from salicylaldehyde or 2′-hydroxyacetophenone and the corresponding amino alcohol and reacted with phenylboronic acid, whereupon the dimeric boronates **2b**−**e** were obtained (Scheme 1).

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(1) See for example: (a) Höpfl, H.; Farfán, N.; Castillo, D.; Santillan, R.; Contreras, R.; Martínez-Martínez, F.; Galván, M.; Alvarez, R.; Fernández, L.; Halut, S.; Daran, J.-C. *J. Organomet. Chem.* **1997**, *544*, 175. (b) Höpfl, H.; Galván, M.; Farfán, N.; Santillan, R. *J. Mol. Struct. THEOCHEM* **1998**, *427*, 1. (c) Farfán, N.; Castillo, D.; Joseph-Nathan, P.; Contreras, R.; Szentpály, L.v. *J. Chem. Soc., Perkin Trans. 2* **1992**, 527. (d) Farfán, N.; Contreras, R. *Nouveau J. Chim.* **1982**, *6*, 269. (e) Farfán, N.; Contreras, R. *J. Chem. Soc., Perkin Trans 2*, **1988**, 1787. (f) Mancilla, T.; Höpfl, H.; Bravo, G.; Carrillo, L.; *Main Group Met. Chem.* **1997**, *20*, 31. (g) Farfán, N.; Contreras, R. *Heterocycles* **1985**, *23*, 2989. (h) Farfán, N.; Mancilla, T.; Castillo, D.; Uribe, G.; Carillo, L.; Joseph-Nathan, P.; Contreras, R. *J. Organomet. Chem.* **1990**, *381*, 1. (i) Farfán, N.; Joseph-Nathan, P.; Chiquete, L. M.; Contreras, R. *J. Organomet. Chem.* **1988**, *348*, 149. (j) Farfán, N.; Silva, D.; Santillan, R. *Heteroatom Chem.* **1993**, *4*, 533.

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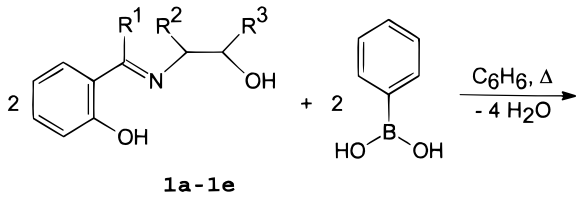
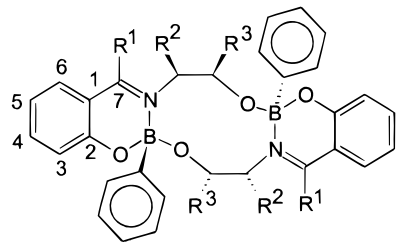
Scheme 1



1a-1e



	R^1	R^2	R^3
2a[2]	H	H	H
2b	H	H	Me
2c	H	H	Ph
2d	H	Me	Ph
2e	Me	H	H

The reaction provides the highest yields (56−77%) in benzene, if a Dean−Stark trap is used to separate the water formed during the condensation.

The 10-membered heterocyclic compounds **2a**−**e** are practically insoluble in all common solvents, and NMR spectra could only be recorded in the case of compound **2e**. The ^{1}H and ^{13}C NMR data for the ligand **1e** and the corresponding product **2e** are presented in Table 1. A comparison of the ^{1}H NMR data between the ligand and the corresponding boron chelate shows that the signal of the methyl group is shifted downfield ($\Delta\delta$ = 0.56 ppm) with the formation of the coordinative N→B bond. The same can be observed for the resonance signals of the phenoxy group ($\Delta\delta$ = 0.16−0.30 ppm for H-3, H-4, H-5, and H-6) and is in agreement with observations on similar structures.[4,5] The signals of the methylene hydrogen atoms are split in diastereotopic signals ($\Delta\delta$ = 0.26 ppm for NCH_2 and $\Delta\delta$ = 0.35 ppm for OCH_2), whereby those adjacent to nitrogen are shifted upfield ($\Delta\delta$ = 0.37 ppm) and those adjacent to oxygen are shifted downfield ($\Delta\delta$ = 0.35 ppm) with respect to the corresponding signals of the tridentate ligand **1e**.

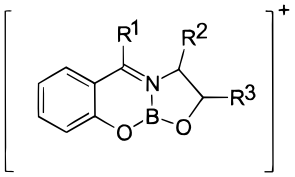
From the ^{13}C NMR data it can be seen that the azomethine signal is shielded ($\Delta\delta$ = 0.7 ppm), while the methyl group is shifted to lower field ($\Delta\delta$ = 2.4 ppm) due to the N→B coordination.

The tetracoordination of the boron atom can be seen from the ^{11}B NMR spectrum, where a value of δ = +4 ppm has been measured. This shift can be compared to those of diphenylboron chelates that have been synthesized from different amino-substituted salicylaldehyde azomethines.[4,5b]

The dimeric structures of compounds **2b**−**e** could be established by mass spectrometry. In all four cases only the $[M - C_6H_5]^+$ ion is detected due to the easy loss of a phenyl radical.[6] It is interesting to notice that the highly dominating base peaks correspond to the cations shown in Chart 2, where the ring strain is lowered by the sp^2 hybridization of the boron atom.

Thereby, the dimeric dicationic structure can be excluded on the basis of the isotopic abundance that would be expected for two boron atoms. The intensity of the peak that corresponds to the molecules with the ^{10}B isotope is only about one-fourth of the base peak.[7] For two boron atoms in one molecule a relation of about 2:1 (^{11}B/^{11}B:^{11}B/^{10}B) should be expected.

Chart 2



The discussion so far has shown that the spectroscopic characterization of compounds **2a**−**e** is rather difficult. Therefore a big effort was undertaken to obtain single crystals of the new structures in order to perform an X-ray crystallographic study. Besides **2a**[2], the macrocycles **2b**,**d**, and **e** could be crystallized. Figures 1−3 show their crystal structures (Tables 2−4). For comparison selected crystallographic data for compound **2a**[2] have been also included in Tables 3 and 4.

The macrocycles consist of two rigid boronate units. This rigidity and the required tetrahedral boron environment are responsible for the preferred dimerization of the compounds with a tridentate chelation around the boron atom being too strained. The structures consist of 10-membered heterocyclic rings in a boat−chair−boat conformation. As in the case of **2a**,[2] all molecules are symmetric having a crystallographic inversion center and thus belong to the C_i point group. The inversion center of all four molecules is located at this special position in the crystal lattice (Table 2). Interestingly, the distance between one of the hydrogen atoms of the OCH_2 group (H-121) and the opposite oxygen atom (O-11) is below the sum of the van der Waals radii[8] in compounds **2a** (2.43 Å),[2] **2d** (2.57 Å), and **2e** (2.46 Å), indicating a transannular interaction (Table 4).

A comparison of the bond lengths (Table 3) shows no significant differences between the four compounds **2a**−**b** and **2d**−**e**. The phenolic O(1)−B(2) bond is about 0.05 Å longer than the O(11)−B(2) bond in all four structures. The mean value of the O(11)−B(2) bond lengths for the four compounds of 1.438(5) Å is significantly shorter than the mean O−B bond length of 1.477(5) Å observed in different ethanolamine esters of diarylborinic acids.[9] The N→B bond lengths with values of 1.624(3) − 1.634(7) Å are in the upper range of bond lengths found for diphenylboron chelates with salicylaldehyde azomethines (1.572(2)−1.634(5) Å).[10] The N→B bond strength can also be evaluated by the *t*etra*h*edral *c*haracter around the boron atom,[11] the corresponding THC values being in the range of 86−91% (Table 4). Thereby, a linear correlation between the N→B bond length and the magnitude of the THC character is not observed probably due to the chelative bonding of the ligand.

In contrast to the bond lengths, the bond angles are more sensitive to the variation of substituents around the macrocyclic structure (Table 3). In comparison to the unsubstituted deriva-

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(7) The natural abundances of ^{11}B and ^{10}B are 80.4 and 19.6%, respectively: Hesse, M.; Meier, G.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie;* Georg Thieme Verlag: Stuttgart, Germany, 1987.
(8) The sum of the van der Waals radii of oxygen and hydrogen is 2.70 Å: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
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(11) Toyota, S.; Oki, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1832.

Table 1. ^{1}H, ^{13}C, and ^{11}B NMR Data (270.1, 67.8, and 86.6 MHz) for Compounds **1e** (in $CDCl_3$) and **2e** (in DMSO-d_6) (ppm)

								BC_6H_5			
compd	H-3	H-4	H-5	H-6	CH_3	NCH_2	OCH_2	*o*	*m*	*p*	^{11}B ($h_{1/2}$ (Hz))
1e[a]	6.75	7.26	6.71	7.62	2.37	3.67	3.67				
2e	7.05	7.47	6.94	7.78	2.93	3.17	3.85	7.49	7.21	7.24	4 (490)
						3.43	4.19				

											BC_6H_5		
compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	CH_3	NCH_2	OCH_2	*o*	*m*	*p*
1e[b]	117.7	164.9	116.3[c]	132.6	118.7[c]	128.9	173.1	14.5	51.0	60.8			
2e	117.7	160.0	120.0[c]	136.2	118.5[c]	128.5	172.4	16.9	51.3	60.9	132.0	127.3	126.8

[a] ^{1}H NMR, 90 MHz. [b] 22.6 MHz. [c] Signals may be interchanged.

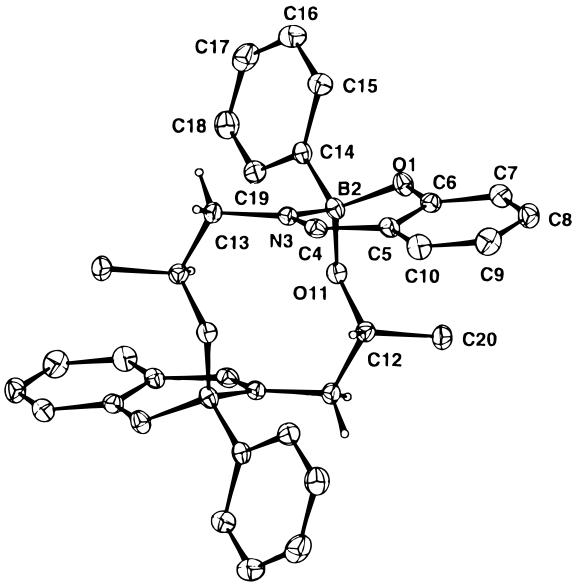


Figure 1. Molecular structure of compound **2b**.

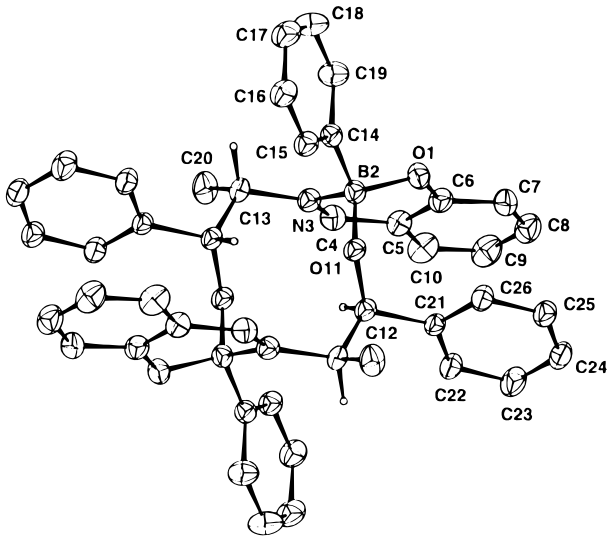


Figure 2. Molecular structure of compound **2d**.

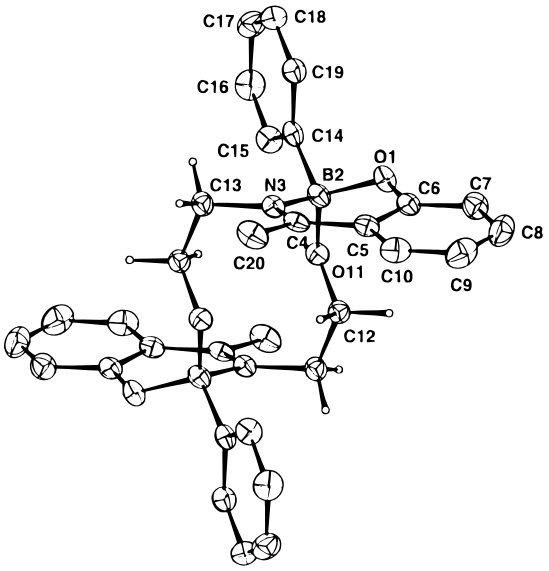


Figure 3. Molecular structure of compound **2e**.

tive **2a** the most striking changes are the decrease of the B(2)−N(3)−C(13) bond angle by 4.3°, when a substituent on C(4) is introduced (**2e**), the decrease of the B(2)−O(1)−C(6) bond angle by 3.3−4.5°, when any substituent is introduced, the increase of the B(2)−O(11)−C(12) bond angle by 4.3−5.3°, when a substituent on C(12) is introduced, and the decrease of the N(3)−C(13)−C(12) bond angle by 3.1°, when the substituent at C(12) is a phenyl group.

To examine the effects of the substituents in the 10-membered heterocyclic ring, a series of torsion angles have been selected and summarized in Table 4. The ideal values for the torsion angles are 60° for the first four values and 180° for the fifth, while the last two values should not vary too much from 0° due to the planarity of the six-membered heterocycle. An evaluation of the data shows that already the unsubstituted derivative **2a** is somewhat strained. A comparison of the torsion angles between the four molecular structures demonstrates that the rest of the compounds deviate still more from the ideal values, particularly **2b**. When all the deviations from the seven ideal values in Table 4 are summed up for each structure and divided by seven and a qualitative evaluation of the torsion angles is not considered necessary, a factor is obtained that may be used to express the relative strain of each molecule. The factors calculated are 6.4, 13.5, 11.5, and 12.4° for **2a**,**b**,**d**,**e**, respectively, confirming the above stated observations. The elevated ring strain of the substituted dimers can also be seen from the deviation of the boron atoms from the molecular mean plane. While the deviation in **2a** is only 0.129 Å, this value varies from 0.459 to 0.504 Å for the rest of the molecules. The maximum ring strain in **2b** can only be in part confirmed by the sum of bond angles in the heterocycles (Table 4) that indeed provides the highest average value for **2b** with 115.2(4)° in comparison to 113.9(2)° for **2a** and 114.1(3)° for **2d**, but **2e** surprisingly presents the lowest value with 112.8 (4)°.

A further interesting observation goes along with the introduction of substituents around the macrocyclic ring. Compounds **2b**,**d**,**e** include one or two solvent molecules per macrocycle in the crystal lattice (solvent channels), while the unsubstituted compound **2a** crystallizes without them.

Table 2. Crystallographic Data for Compounds **2b,d,e**

	2b[a]	**2d**	**2e**
	Crystal Data		
formula	$C_{32}H_{32}B_2N_2O_4 \cdot 2CHCl_3$	$C_{44}H_{40}B_2N_2O_4 \cdot 2C_6H_6$	$C_{32}H_{32}B_2N_2O_4 \cdot CH_2Cl_2$[b]
cryst size	0.3 × 0.4 × 0.5	0.3 × 0.4 × 0.5	0.3 × 0.4 × 0.4
MW	530.24	682.43	530.24
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
	Cell Parameters		
a (Å)	13.373(2)	10.465(2)	10.7924(4)
b (Å)	9.752(1)	19.631(2)	11.9838(5)
c (Å)	14.299(1)	11.553(2)	11.8659(11)
β (deg)	101.760(8)	100.10(1)	97.162(4)
V (Å^3)	1825.7(5)	2336.6(7)	1522.9(2)
Z	2	2	2
μ (cm^{-1})	5.1	0.69	2.5
ρ_{calcd} (g cm^{-3})	1.40	1.19	1.34
	Data Collection[c]		
scan range (deg)	0.89 + 0.83 tan θ	0.42 + 0.54 tan θ	0.41 + 0.52 tan θ
scan speed (deg min^{-1})	1.8 < sp. < 20.1	1.0 < sp. < 20.1	0.8 < sp. < 20.1
θ limits (deg)	$2 < \theta < 26$	$2 < \theta < 21$	$2 < \theta < 26$
hkl limits	−16, 16; 0, 12; −17, 0	−10, 0; 0, 19; −11, 11	−13, 13; −14, 0; −14, 0
no. collcd reflcns	3955	2781	3297
no. ind reflcns (R_{int})	3574 (0.02)	2502 (0.01)	2990 (0.02)
no. obsd reflcns	1535	1732	1318
	Refinement		
R[d]	0.047	0.042	0.061
R_w[e]	0.037	0.038	0.052
w	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$
no. of variables	260	316	248
GOOF	3.34	3.17	3.17
max, Δ/σ	0.03	0.3	0.05
$\Delta\rho_{min}$ (e Å^{-3})	−0.27	−0.15	−0.53
$\Delta\rho_{max}$ (e Å^{-3})	0.22	0.18	0.69

[a] Crystal with intensity loss of 42% during data collection that had to be corrected. [b] The solvent is disordered, therefore the high values of $\Delta\rho_{min}$ and $\Delta\rho_{max}$. [c] $T = 293$ K, $\lambda_{MoK\alpha} = 0.710\,69$ Å. [d] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [e] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 3. Selected Bond Lengths and Bond Angles of Compounds **2a,b,d,e**

	2a[2] (R^1 = H, R^2 = H, R^3 = H)	**2b** (R^1 = H, R^2 = H, R^3 = Me)	**2d** (R^1 = H, R^2 = Me, R^3 = Ph)	**2e** (R^1 = Me, R^2 = H, R^3 = H)
		Bond Lengths (Å)		
O(1)−B(2)	1.492(3)	1.480(6)	1.494(5)	1.481(7)
O(1)−C(6)	1.332(3)	1.332(5)	1.339(4)	1.337(5)
B(2)−N(3)	1.624(3)	1.632(6)	1.626(5)	1.634(7)
B(2)−O(11)	1.433(3)	1.441(6)	1.448(5)	1.431(6)
N(3)−C(4)	1.291(3)	1.293(5)	1.297(4)	1.303(6)
N(3)−C(13)	1.477(3)	1.462(6)	1.496(4)	1.481(6)
O(11)−C(12)	1.412(3)	1.415(5)	1.419(4)	1.412(6)
C(12)−C(13)	1.512(3)	1.524(7)	1.528(5)	1.524(7)
		Bond Angles (deg)		
O(1)−B(2)−N(3)	106.5(2)	105.4(4)	105.6(3)	105.7(4)
O(1)−B(2)−O(11)	111.6(2)	114.1(4)	112.7(3)	113.4(5)
B(2)−N(3)−C(4)	122.4(2)	120.4(4)	119.9(3)	123.5(4)
B(2)−N(3)−C(13)	119.4(2)	122.6(4)	119.7(3)	115.1(4)
B(2)−O(1)−C(6)	126.5(1)	123.2(4)	122.7(3)	122.0(4)
B(2)−O(11)−C(12)	118.7(2)	123.0(4)	124.0(3)	119.1(4)
N(3)−B(2)−O(11)	109.0(2)	108.6(4)	109.2(3)	108.6(4)
N(3)−C(4)−C(5)	122.8(2)	122.3(4)	122.9(4)	119.2(5)
N(3)−C(13)−C(12)	113.0(2)	114.0(4)	109.9(3)	111.4(4)
C(4)−N(3)−C(13)	118.2(2)	116.9(4)	120.3(3)	121.3(5)
O(11)−C(12)−C(13)	109.6(2)	107.9(4)	107.6(3)	110.0(4)

Synthesis and Characterization of Monomeric Boronates. The aim of the synthesis of tridentate ligands with different substituents was also to investigate, if the dimeric structure is still obtained, when the steric hindrance around the heterocycles is enhanced (Scheme 2).

It can be seen that this is not the case, especially when the amino dialcohol is substituted by two methyl groups at the carbon atom adjacent to the nitrogen (**4a**,**4b**). A monomeric compound is also formed, when the tridentate ligand permits the formation of a [4.4.0]heterobicyclic system (**4c**).

The monomeric composition of compounds **4a**−**c** can be concluded from mass spectrometry, where the molecular ion is detected in all three cases. In contrast to the dimeric boronates **2b**−**e** the base peak corresponds now to the $[M - C_6H_5]^+$ fragment ion.

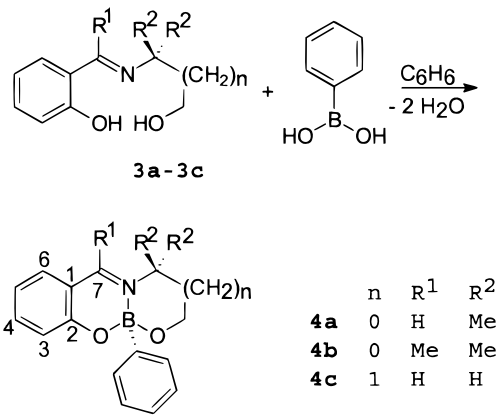
The ^{1}H, ^{13}C, and ^{11}B NMR data for the tridentate ligands **3a**−**c** and the corresponding boronates **4a**−**c** are presented in Tables 5 and 6. All three compounds **4a**−**c** have diastereotopic ^{1}H NMR signals for the OCH_2 group ($\Delta\delta$ = 0.13, 0.07, and 0.30 ppm). In the ^{13}C NMR spectra two signals for the R^2

Table 4. Selected Torsion Angles, Sum of Bond Angles in the Heterocycles, THC, and O(11)···H(121) Hydrogen Bond Length of Compounds **2a,b,d,e**

	2a[2] (R^1 = H, R^2 = H, R^3 = H)	**2b** (R^1 = H, R^2 = H, R^3 = Me)	**2d** (R^1 = H, R^2 = Me, R^3 = Ph)	**2e** (R^1 = Me, R^2 = H, R^3 = H)
		Torsion Angles (deg)[a]		
O(11)−C(12)−C(13)−N(3)	58.1	−49.7	61.1	89.8
C_{ph}−B(2)−N(3)−C(13)	−51.6	37.3	−37.1	−46.1
R^2−C(13)−C(12)−R^3	−53.8	48.4	58.0	−53.2
B(2)−O(11)−C(12)−R^3	77.2	−88.0	80.0	74.5
N(3)−C(13)−C(12)−R^3	−176.8	170.0	−174.6	−175.1
C(4)−N(3)−C(13)−R^2	−3.2	14.6	12.8	−14.7
R^1−C(4)−N(3)−C(13)	−4.6	3.2	6.0	2.1
		Sum of Bond Angles in the Heterocycles (deg)		
six-membered ring	718.0 = 6 × 119.7(2)	710.7 = 6 × 118.5(4)	710.3 = 6 × 118.4(4)	711.4 = 6 × 118.6(5)
ten-membered ring	1139.4 = 10 × 113.9(2)	1152.2 = 10 × 115.2(4)	1140.8 = 10 × 114.1(3)	1128.4 = 10 × 112.8(4)
		THC (%)		
	86	88	91	87
		Hydrogen Bond H(121)···O(11) (Å)		
	2.43	2.87	2.57	2.46

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

Scheme 2



methyl groups are detected for both compounds **4a**,**b**, although in the ^{1}H NMR spectrum they appear only for **4a**. The displacements in the ^{11}B NMR spectra indicate tetracoordinated species in all three cases (δ = +7, +7, and +5 ppm for **4a**−**c**).[12]

Since it was desirable to get some information about the stereochemistry in the monomeric structures **4a**−**c** in order to compare them with the dimeric boronates, an X-ray crystallographic study was performed for compounds **4b**,**c**. Adequate crystals of compound **4a** could not be obtained. The crystallographic data are displayed in Tables 7−9. The data of structure **4c** are of lower quality (Table 7), because the rotational disorder of the dichloromethane incorporated in the crystal lattice could only be partially resolved. The molecular structures of compounds **4b**,**c** are presented in Figures 4 and 5.

Molecular modeling shows that the heterobicyclic structure **4b** with a five-membered ring is more strained than the one of **4c** with a six-membered ring instead. The different ring strain can be studied in more detail based on the bond lengths and bond angles of the molecular structures that are displayed in Table 8.

Significantly different in the two heterocycles are the N(3)−C(13,14) bond length (1.508(3) vs 1.459(9) Å), the B(2)−N(3)−C(13,14) bond angle (108.8(2) vs 116.2(6)°), the B(2)−O(1)−C(6) bond angle (114.8(2) vs 124.1(6)°), the B(2)−O(11)−C(12) bond angle (105.7(2) vs 115.4(6)°), the N(3)−B(2)−O(11) bond angle (100.7(2) vs 107.6(6)°), the N(3)−C(13)−C(12)/N(3)−C(14)−C(13) bond angle (99.5(3) vs 109.0(6)°) and the C(4)−N(3)−C(13,14) bond angle (129.2(3) vs 120.7(6)°) for compounds **4b**,**c**, respectively.

Interestingly, the ring strain in the five-membered ring of **4b**, which is expressed by an average value of 104.5(3)° for the five bond angles (Table 9), is transmitted also to the six-membered ring, where an average value of only 116.7(3)° can be determined. The corresponding bond angles for **4c** are 111.7-(7)/119.3(7)°, and the mean values for the dimeric compounds **2a,b** and **2d,e** are 114.0(3)/118.8(4)° (Table 4). The high strain can also be evaluated by the deviation of the boron atom from the molecular mean plane, that is 0.629 Å for **4b**, 0.264 Å for **4c**, and 0.394 Å (mean value) for the dimeric structures. It should be noted that the deviation of the C(4) atom is very characteristic, too (0.280 Å vs 0.073 Å).

Although unexpectedly the N→B bond lengths of the two compounds **4b,c** are practically identical (1.601 Å), the THC characters are different (Table 9). The lower THC value is obtained for the [4.3.0]heterobicyclic molecule **4b** (71% vs 86%). The N→B bond lengths are 0.28 Å shorter than the mean value for the dimeric structures (1.601(4), 1.601(9) Å vs 1.629-(5) Å), where the THC values are 86−91% (Table 4).

When the bond angles of the monomer **4b** and the unsubstituted dimer **2a** are compared, some very striking differences can be found that may vary up to 13.5°, while a comparison between **4c** and **2a** shows a maximum difference of 5.5° (Tables 3 and 8).

If all the observations mentioned so far are summarized, it can be concluded that there must exist at least one decisive factor that inhibits the formation of the much more favorable dimeric structure in the case of **4a**,**b**; for **4c** the formation of the monomer is sufficiently reasonable. This factor should be the necessary inward orientation of the additional R^2 methyl group, if the dimeric species were formed, that would cause a repulsive interaction with the B-phenyl group (compare the molecular structures of **4b**, Figure 4, and **2d**, Figure 2). In structure **4b** a repulsive interaction between the R^1 and the R^2 (cis to R^1) methyl groups could also be relevant.

It is important to note that compound **4a** cannot be obtained in a one-step synthesis between **3a** and phenylboronic acid, because **5a** with a seven-membered NBOBOCC ring precipitates first (Scheme 3).

(12) Nöth, H.; Wrackmeyer, B. In *NMR Spectroscopy of Boron Compounds*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; NMR-Basic Principles and Progress, Vol. 14; Springer-Verlag: Berlin, 1978.

Table 5. ^{1}H and ^{11}B NMR Data (270 and 86.6 MHz) for Compounds **3a−c** and **4a−c** in $CDCl_3$ (ppm)

									BC_6H_5			
compd	H-3	H-4	H-5	H-6	R^1	R^2	NCH_2	OCH_2	*o*	*m*	*p*	^{11}B ($h_{1/2}$ (Hz))
3a[a,b]	6.81	7.41	6.93	7.26	8.69	1.25		3.40				
3b[a]	6.84	7.41	6.84	7.75	2.63	1.07		3.27				
3c[c]	6.92	7.30	6.83	7.20	8.30		3.67	3.67				
4a[b]	6.81	7.43	6.89	7.60	8.81	1.28		3.60	7.21	7.07	7.07	7 (250)[d]
						1.43		3.73				
4b	6.96	7.33	6.78	7.45	2.68	1.60		3.82	7.30	7.11	7.15	7 (130)
								3.89				
4c[e]	7.27	7.27	6.76	7.27	8.14		3.64−4.11		7.38	7.27	7.27	5 (160)

[a] ^{1}H NMR, 90 MHz. [b] In DMSO-d_6. [c] OCH_2CH_2: $\delta = 1.91$ ppm. [d] In $CDCl_3$. [e] OCH_2CH_2: $\delta = 1.97$ ppm.

Table 6. ^{13}C NMR Data (67.8 MHz) for Compounds **3a,c** and **4a−c** in $CDCl_3$ (ppm]

											BC_6H_5		
compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	R^2	NCR_2	OCH_2	*o*	*m*	*p*
3a[a,b]	118.7	162.1[c]	116.9[d]	132.2[e]	117.5[d]	132.0[e]	162.4[c]	23.8	60.6	69.2			
3c[f]	118.3	161.8	117.0[c]	132.2[d]	118.1[c]	131.2[d]	165.1		55.2	59.5			
4a[b]	119.2	159.0	119.0[c]	136.6	118.6[c]	131.6	157.9	23.6	63.8	75.5	130.3	126.8	126.2
								24.9					
4b[g]	121.7	159.8	120.9[c]	136.2	118.8[c]	127.5[d]	167.2	24.8	64.2	76.6	131.3	127.1	126.6[d]
								26.4					
4c[h]	115.5	159.6	119.8[c]	137.8	118.7[c]	131.1	160.3		55.5	61.5	131.1	127.8	127.2

[a] 22.6 MHz. [b] In DMSO-d_6. [c−e] Signals may be interchanged. [f] OCH_2CH_2: $\delta = 33.2$ ppm. [g] R^1: $\delta = 18.0$ ppm. [h] OCH_2CH_2: $\delta = 30.9$ ppm.

Table 7. Crystallographic Data of Compounds **4b,c**

	4b	**4c**
	Crystal Data	
formula	$C_{18}H_{22}BNO_2$	$C_{16}H_{16}BNO_2 \cdot 1/2CH_2Cl_2$[a]
cryst size (mm)	0.3 × 0.5 × 0.5	0.20 × 0.25 × 0.48
MW	293.17	265.12
space group	$P2_12_12_1$	$P2_1/c$
	Cell Parameters	
a (Å)	8.1170(3)	6.4556(6)
b (Å)	13.2085(6)	12.6603(7)
c (Å)	14.4774(8)	18.753(1)
β (deg)	90	92.479(7)
V (Å^3)	1552.2(1)	1531.3(2)
Z	4	4
μ (cm^{-1})	0.75	2.5
ρ_{calcd} (g cm^{-3})	1.25	1.36
	Data Collection[b]	
scan range (deg)	0.34 + 0.55 tan θ	0.72 + 1.03 tan θ
scan speed (deg min^{-1})	0.9 < sp. < 20.1	1.4 < sp. < 20.1
θ limits (deg)	2 < θ < 28	2 < θ < 26
hkl limits	−10, 0; 0, 17; 0, 19	−7, 0; 0, 15; −23, 23
no. collcd reflcns	2160	3424
no. ind reflcns (R_{int})	2138	2992 (0.04)
no. obsd reflcns	1427	1166
	Refinement	
R[c]	0.035	0.080
R_w[d]	0.030	0.067
w	$1/\sigma^2$	$1/\sigma^2$
no. of variables	261	200
GOOF	2.49	4.91
max. Δ/σ	0.03	0.26
$\Delta\rho_{min}$ (e Å^{-3})	−0.13	−0.88
$\Delta\rho_{max}$ (e Å^{-3})	0.14	0.71

[a] The solvent is disordered, therefore the high values of max Δ/σ, $\Delta\rho_{min}$ and $\Delta\rho_{max}$. [b] $T = 293$ K, $\lambda_{MoK\alpha} = 0.710\,69$ Å. [c] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

Table 8. Selected Bond Lengths and Bond Angles of Compounds **4b,c**

	4b (*n* = 0, $R^1 = R^2 =$ Me)	**4c** (*n* = 1, $R^1 = R^2 =$ H)
	Bond Lengths (Å)	
O(1)−B(2)	1.463(4)	1.48(1)
O(1)−C(6)	1.337(4)	1.337(8)
B(2)−N(3)	1.601(4)	1.601(9)
B(2)−O(11)	1.450(4)	1.45(1)
N(3)−C(4)	1.284(3)	1.292(9)
N(3)−C(13,14)	1.508(3)	1.459(9)
O(11)−C(12)	1.416(4)	1.412(9)
C(12)−C(13)	1.548(4)	1.53(1)
C(13)−C(14)	−	1.52(1)
	Bond Angles (deg)	
O(1)−B(2)−N(3)	106.7(3)	107.6(6)
O(1)−B(2)−O(11)	110.7(3)	106.1(6)
B(2)−N(3)−C(4)	121.4(3)	123.1(7)
B(2)−N(3)−C(13,14)	108.8(2)	116.2(6)
B(2)−O(1)−C(6)	114.8(2)	124.1(6)
B(2)−O(11)−C(12)	105.7(2)	115.4(6)
N(3)−B(2)−O(11)	100.7(2)	107.6(6)
N(3)−C(4)−C(5)	116.5(3)	120.7(7)
N(3)−C(13)−C(12)[a]	99.5(3)	109.0(6)
C(4)−N(3)−C(13,14)	129.2(3)	120.7(6)
C(4)−C(5)−C(6)	118.2(3)	119.7(7)
O(11)−C(12)−C(13)	107.9(3)	110.9(7)
C(12)−C(13)−C(14)	−	111.0(7)

[a] N(3)−C(14)−C(13) in the case of **4c**.

The desired product **4a** can only be synthesized in a further step, when an additional 1 equiv of the corresponding ligand **3a** is added to a solution of **5a** in benzene (Scheme 4).

The [5.4.0]heterobicyclic compound type **5** is also favored, when ligand **1d** is brought to reaction *enantiomerically* pure with phenylboronic acid (**5d**),[13] whereby the formation of a dimeric structure could be inhibited due to the impossibility to obtain a centrosymmetric molecule that seems to be a necessary requisite. The same is observed with ligand **1f**, a derivative of **1d** with an additional methyl group at the C-7 atom, either with the *racemic* mixture or the *enantiomerically* pure form. In both cases only *one* diastereomer is obtained. Compound **5f** cannot be transformed into a dimeric or [4.3.0]heterobicyclic monomeric system, as it has been achieved with compound **5a**, even when toluene is used as a solvent. Herewith it is demonstrated that the substituents in this molecule inhibit both the formation of the monomeric and dimeric structure in favor of a third

(13) Note that the *racemic* mixture provides the dimeric structure **2d**.

Table 9. Selected Torsion Angles, Sum of Bond Angles in the Heterocycles, and THC of Compounds **4b,c**

	4b ($n = 0$, $R^1 = R^2 = Me$)	**4c** ($n = 1$, $R^1 = R^2 = H$)
Torsion Angles (deg)[a]		
O(11)−B(2)−N(3)−C(13,14)	17.8	−49.1
C_{ph}−B(2)−N(3)−C(13,14)	−104.5	76.1
C(4)−N(3)−C(13)−R^2 [b,c]	62.4	−7.6
R^1−C(4)−N(3)−C(13,14)	11.3	−2.5
Sum of Bond Angles in the Heterocycles (deg)		
six-membered ring	700.0 = 6 × 116.7(3)	715.9 = 6 × 119.3(7)
five- and six-membered rings	522.6 = 5 × 104.5(3)	670.1 = 6 × 111.7(7)
THC (%)	71	86

[a] A positive rotation is counterclockwise from atom 1, when viewed from atom 3 to atom 2. [b] C(4)−N(3)−C(14)−R^2 in the case of **4c**. [c] Only the R^2 methyl group (*cis* to R^1) is considered.

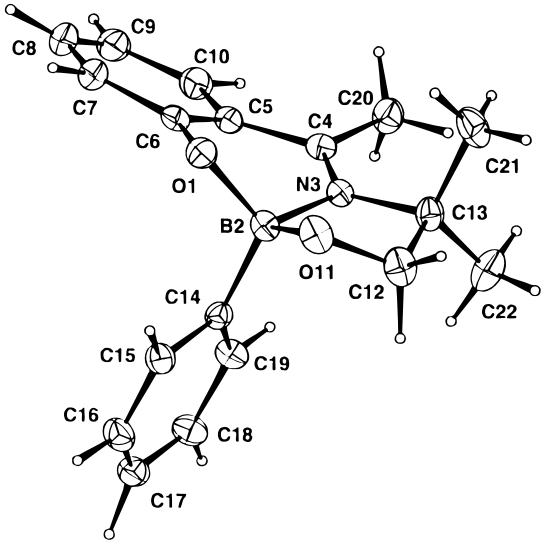


Figure 4. Molecular structure of compound **4b**.

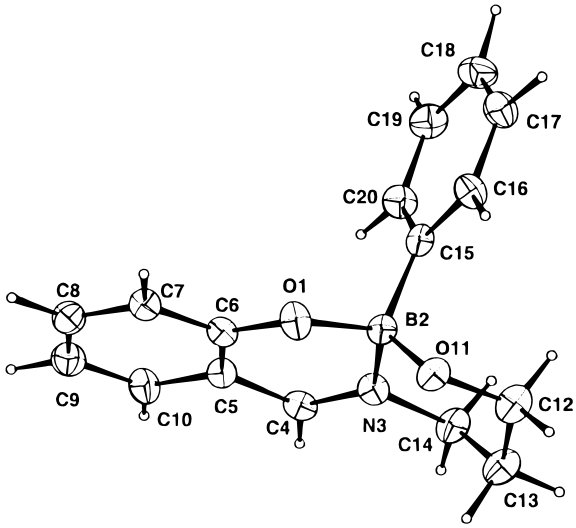
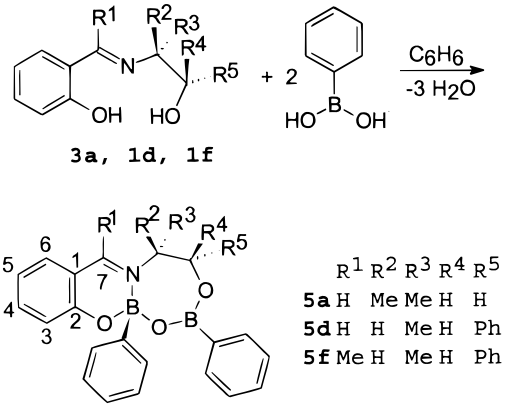


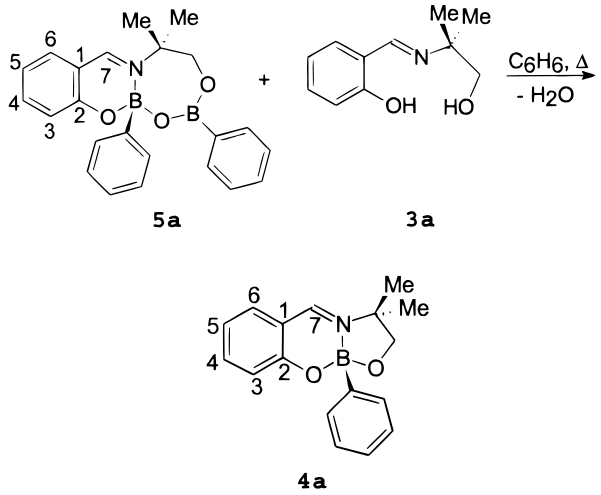
Figure 5. Molecular structure of compound **4c**.

structure type (**5**). The dimer should be placed at a disadvantage by the 1,3-repulsive interaction between the R^1 and R^3 methyl groups and the gauche interaction between the R^3 methyl and R^5 phenyl group. The monomer is disfavored, because the already high ring strain is still enhanced by the repulsive

Scheme 3



Scheme 4



interaction between the R^3 and R^5 substituents in a *cis*-orientation that must be eclipsed, when it is assumed that the boron atom prefers to leave the molecular plane of the five-membered ring.[1b]

The formulation of molecules **5a**,**d**,**f** has been determined by mass spectrometry. The molecular peak is only observed for **5d**, while for the other two compounds the $[M - C_6H_5]^+$ ion could be detected. The base peak is the *monomeric* cation with one boron atom as it has been observed already for the dimeric boronates.

Compounds **5a**,**f** have been further studied by NMR spectroscopy. The ^1H, ^{13}C, and ^{11}B NMR data are given in Tables 10 and 11, whereby compound **4a** has been included for comparison. The ^1H NMR data show that the R^1 hydrogen atom in the seven-membered compound **5a** is shifted to higher field when compared to the ligand **3a** ($\Delta\delta = 0.29$ ppm), while it has been shifted downfield in the five-membered compound **4a** ($\Delta\delta = 0.12$ ppm). The R^2 and R^3 methyl groups in **5a** and **4a** are diastereotopic, whereby the shift difference in the seven-membered heterocycle is higher ($\Delta\delta = 0.15$ and 0.38 ppm, respectively). The AX system of the OCH_2 group in **5a** ($\Delta\delta = 1.39$ ppm) could be due to the proximity of the hydrogen atom R^4 to the B−C_6H_5 phenyl group of the tetracoordinated boron atom (compare **5f**, Figure 6).

The inclusion of two different coordinated boron atoms in the structure type **5** can be confirmed by the ^{11}B NMR spectra, where the signals at $\delta = +5$ (**5a**) and +6 (**5f**) ppm indicate the tetracoordination and the ones at $\delta = +28$ (**5a**) and +25 (**5f**) ppm indicate the tricoordination of the boron atoms.[12]

Table 10. ^{1}H and ^{11}B NMR Data (270 and 86.6 MHz) for Compounds **3a**, **1f**, **4a**, and **5a**,**f** in $CDCl_3$ (ppm)

										BC_6H_5[a]			
compd	H-3	H-4	H-5	H-6	R^1	R^2	R^3	R^4	R^5	*o*	*m*	*p*	^{11}B ($h_{1/2}$ (Hz))
3a[b,c]	6.81	7.41	6.93	7.26	8.69	1.25	1.25	3.40					
1f[c]	7.12	7.60	7.04	7.84	2.50	4.43	1.58	5.00	*d*				
4a[c]	6.81	7.43	6.89	7.60	8.81	1.43	1.28	3.59	3.76	7.21	7.07	7.07	+7 (250)
5a	6.94	7.28	6.84	7.28	8.40	1.61	1.23	4.75	3.36	7.47	7.28	7.28	+5 (580)
										7.99	7.28	7.28	+28 (190)
5f[e,f]	6.97	7.38	6.85	7.57	2.65	4.42	1.42	5.78	*g*	7.42	7.17	7.17	+6 (320)
										8.26	7.49	7.49	+25 (1280)

[a] The first row corresponds to the phenyl group of the tetracoordinated boron atom, and the second one, to the tricoordinated boron atom. [b] ^{1}H NMR, 90 MHz. [c] In DMSO-d_6. [d] $\delta = 7.54-7.74$ (*o*-H, *m*-H, *p*-H) ppm. [e] ^{1}H NMR, 400 MHz. [f] ^{11}B NMR, 128.3 Hz. [g] $\delta = 7.35-7.49$ (*o*-H, *m*-H, *p*-H) ppm.

Table 11. ^{13}C NMR Data (67.8 MHz) for Compounds **3a**, **1f**, **4a**, and **5a**,**f** in $CDCl_3$ (ppm)

											BC_6H_5[a]		
compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	R^2/R^3	NCR^2R^3	OCR^4R^5	*o*	*m*	*p*
3a[b,c]	118.7	162.1[d]	116.9[e]	132.2[f]	117.5[e]	132.0[f]	162.4[d]	23.8	60.6	69.2			
1f[c,g,h]	118.9	164.1	116.4[d]	132.2	118.3[d]	128.7	170.6	17.5	59.8	76.3			
4a[c]	119.2	159.0	119.0[d]	136.6	118.6[d]	131.6	157.9	23.6	63.8	75.5	130.3	126.8	126.2
								24.9					
5a[b]	115.3	159.9	119.5	138.5	118.6	130.4[d]	162.2	26.6	65.8	69.7	130.6	127.4[e]	127.3
								27.3			134.9	127.6[e]	131.7[d]
5f[i-k]	121.2	160.7	122.0	138.0	120.2	129.3	171.7	14.6	66.8	74.6	131.3	129.1	128.4
											136.3	128.7	131.7

[a] The first row corresponds to the phenyl group of the tetracoordinated boron atom, and the second one, to the tricoordinated one. [b] 22.6 MHz. [c] In DMSO-d_6. [d-f] Signals may be interchanged. [g] R^5: $\delta = 126.9$, 127.7 (*o*, *m*), 127.0 (*p*), 143.1 (*i*) ppm. [h] R^1: $\delta = 14.0$ ppm. [i] ^{13}C NMR, 100.5 MHz. [j] R^5: $\delta = 127.2$ (*m*), 128.9 (*p*), 129.8 (*o*), 142.8 (*i*) ppm. [k] R^1: $\delta = 17.6$ ppm.

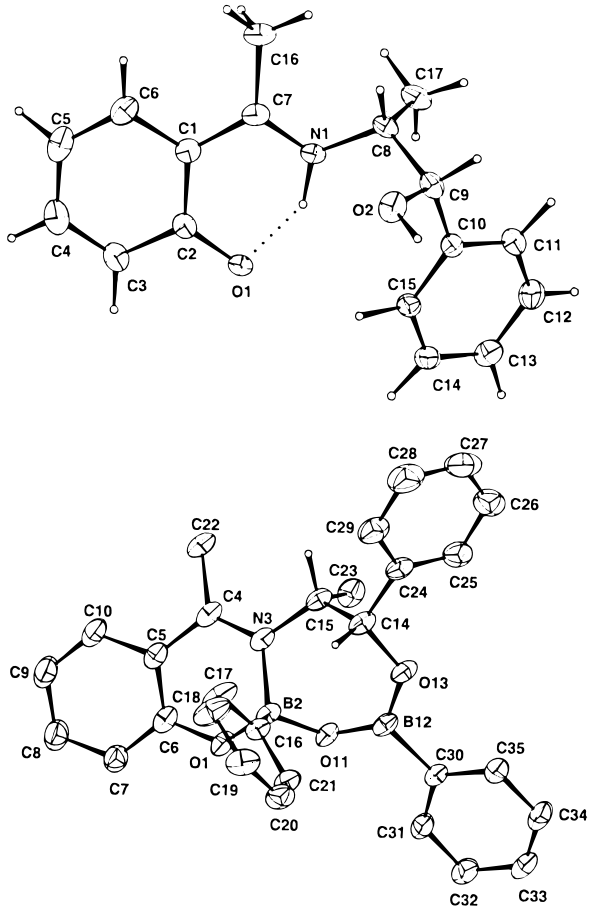


Figure 6. Molecular structures of compounds **1f** and **5f**.

For compound **5f** and the corresponding ligand **1f** a crystallographic study could be carried out (Tables 12 and 13). The molecular structures of the two molecules are represented in Figure 6.

It is interesting to note that the tridentate amino dialcohol **1f** is a zwitterion in the solid state. The hydrogen atom of the phenolic hydroxyl group is associated with the nitrogen atom, and an iminium cation is formed.[14]

The structure analysis of **5f** confirms the [5.4.0]heterobicyclic formulation with a seven-membered NBOBOCC ring.

The N→B bond length of compound **5f** (Table 13) is comparable to the mean value that has been found for the dimers **2a,b** and **2d,e** (1.629(5) vs 1.629(6) Å). Comparing the different O−B bond lengths in the heterobicycle, there is evidence of O−B pp (π) back-donation in the O−(sp^2)B−O fragment of the seven-membered ring, the partial π-bond character causing short O−B bonds, especially at the O(11)−B(12) bond. The bond lengths of 1.431(5), 1.346(5), and 1.375(5) Å in the (sp^3)B−O−(sp^2)B−O portion are similar to corresponding bond lengths in five-membered heterocycles, where mean values of 1.471, 1.333, and 1.410 Å have been found,[15-17] although the (sp^3)B−O and (sp^2)B−O bond lengths are somewhat smaller. As compensation, the B(12)−C(30) bond length with 1.569(6) Å is slightly longer than the mean value for the above-mentioned compounds (1.554 Å).[15,16] Nevertheless, the B(12)−C(30) bond length is still indicative of some π-interaction between the phenyl group and the sp^2-boron atom. The mean value of the (sp^3)B−C_{phenyl} bond length is 1.601 Å.[15b] The planarity of the fragment can be also confirmed by the deviation of the B(12) atom from the O(11)−O(13)−C(30) mean plane that is only 0.013 Å.

(14) The hydrogen atoms have been determined by difference Fourier maps.

(15) (a) Kliegel, W.; Nanninga, D.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1984**, *62*, 845. (b) Amt, H.; Kliegel, W.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1990**, *68*, 1791.
(16) (a) Rettig, S. J.; Trotter, J.; Kliegel, W.; Becker, H. *Can. J. Chem.* **1976**, *54*, 3142. (b) Kliegel, W.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1984**, *62*, 515.
(17) (a) Kliegel, W.; Nanninga, D.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1983**, *61*, 2329. (b) Kliegel, W.; Motzkus, H.-W.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1984**, *62*, 838.

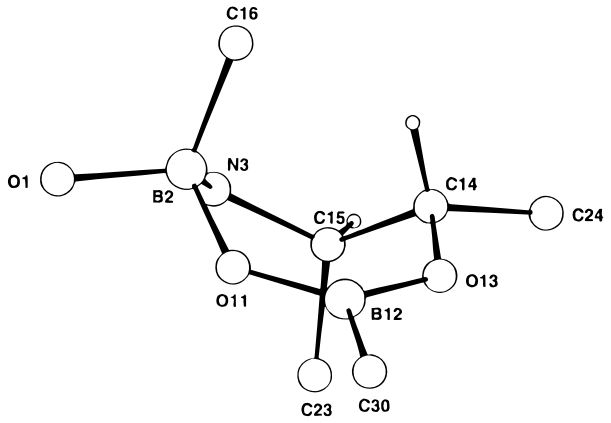
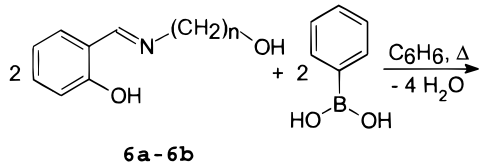
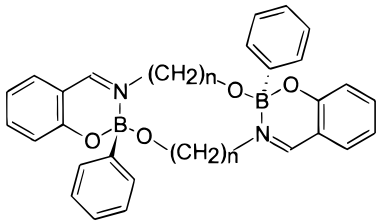


Figure 7. Twisted boat conformation of compound **5f**.

Scheme 5



6a-6b



7a n=5
7b n=6

The average value for the bond angles of the seven-membered ring is 118.8(3)° and is similar to the value observed for the six-membered heterocycle (117.3(4)°). But the variety between the bond angles can be remarkable, e.g. the smallest bond angle is N(3)−B(2)−O(11) with 108.5 (4)° and the largest one is B(2)−O(11)−B(12) with 131.4(3)°.

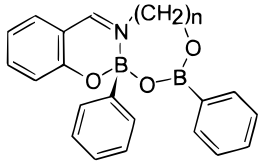
The ring presents a twisted boat conformation with the B(2) atom at the top (Figure 7).[18] The deviation of the boron atom from the mean plane is 0.714 Å, the highest value observed so far, so that a certain ring strain in this [5.4.0]heterobicycle is indicated. Up to now only few seven-membered boronate complexes have been prepared, and none has been characterized by X-ray crystallography,[19] so that a further comparison is not possible.

The reaction of 3-(salicylideneamino)-1-hydroxypropane (**3c**) with phenylboronic acid has shown that a monomeric species is obtained, because the formation of an unstrained [4.4.0]-heterobicyclic compound is possible (**4c**). A further study with amino dialcohols, where the number of methylene groups between the imino and hydroxyl functional groups is increased, shows that the dimeric structure can again be favored, e.g. ligands **6a,b** provide compounds **7a,b** (Scheme 5).

Compound **7a** is a yellow oil, while compound **7b** is a solid. During the preparation of compound **7b**, **8b** precipitates first. This intermediate can be transformed to **7b** by reaction with another 1 equiv of the ligand **6b** as it has been shown for compound **4a** (Chart 3).

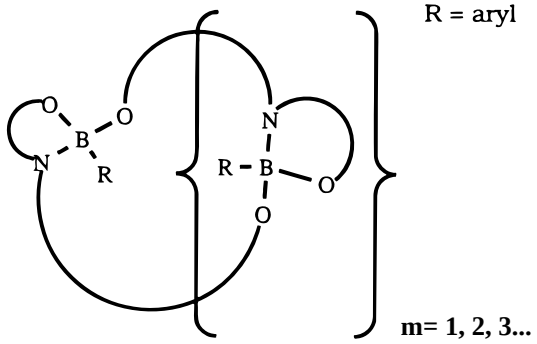
(18) Bocian, D. F.; Pickett, H. M.; Rounds, T. C.; Strauss, H. L. *J. Am. Chem. Soc.* **1974**, *97*, 687.

Chart 3



n=6
8b

Chart 4



The formulation of the three structures is confirmed by mass spectrometry, where in all cases the $[M - C_6H_5]^+$ ion is detected. The base peak represents the *monomeric* structure minus the phenyl group at the boron atom with a relation of about 4:1 for the corresponding isotope peaks.[7]

Conclusions and Perspectives

The above discussion has shown that macrocyclic boronates can easily be formed, when ligands of appropriate geometry are present. A key point is the formation of a dative N→B bond providing rigidity to the structure. On the basis of the dimeric boronates, it has been shown, in detail, that the formation of the macrocyclic structure may be favored by only small energetic advantages which can be easily lost by the introduction of two methyl substituents at the carbon atom adjacent to the nitrogen.

No doubt further tridentate ligands that conduce to macrocyclic boronates exist and may be designed using the model in Chart 4. It can be expected that macrocyclic structures are obtained when ligands with one amino and two hydroxyl groups are designed in such a way that a cyclic structure with a N→B bond is only formed between one hydroxyl group and the amino function, while the second hydroxyl group has to form an ester with the boron atom from another molecule.

The present macrocylic compounds could serve as receptors for Lewis bases and even anionic molecules, if the dative N→B bond is broken, so that the Lewis acidity of the boron atom can be exploited. In the case of an application as anionic host the nitrogen atom could be transformed to an ammonium ion, so that the overall host−guest molecule would be neutral.[2]

Up to now the host−guest chemistry of the tetrameric and dimeric boronates obtained has not been carried out due to their insolubility. Therefore the introduction of hydrophilic or lipophilic functional groups into the ligands would be a perspective to undertake further studies.

Experimental Section

1. Instrumentation. NMR studies were performed with the following spectrometers: JEOL FX 90 Q, JEOL GSX 270, and JEOL ECLIPSE+400. Special techniques (COSY, HETCOR) were applied when necessary to assign the spectra adequately. Standards were TMS

Table 12. Crystallograpic Data for Compounds **1f** and **5f**

	1f	**5f**
	Crystal Data	
formula	$C_{17}H_{19}NO_2$	$C_{29}H_{27}B_2NO_3$
cryst size (mm)	0.21 × 0.39 × 0.48	0.21 × 0.48 × 0.60
MW	269.34	459.16
space group	$P2_1$	$P2_12_12_1$
	Cell Parameters	
a (Å)	7.6083(2)	11.880(2)
b (Å)	8.5934(7)	13.924(1)
c (Å)	11.004(1)	15.521(3)
β (deg)	99.003(8)	90
V (Å^3)	710.6(2)	2567.4(8)
Z	2	4
μ (cm^{-1})	0.77	0.70
ρ_{calcd} (g cm^{-3})	1.26	1.19
	Data Collection[a]	
scan range (deg)	0.56 + 0.56 tan θ	0.65 + 0.76 tan θ
scan speed (deg min^{-1})	1.3 < sp. < 20.1	0.9 < sp. < 20.1
θ limits (deg)	2 < θ < 28	2 < θ < 30
hkl limits	−10, 0; 0, 11; −14, 14	0, 16; −19, 0; 0, 22
no. collcd reflcns	1952	4347
no. ind reflcns (R_{int})	1817 (0.04)	4309
no. obsd reflcns	1357	1897
	Refinement	
R^b	0.038	0.042
R_w[c]	0.033	0.037
w	$1/\sigma^2$	$1/\sigma^2$
no. of variables	240	318
GOOF	3.12	2.51
max Δ/σ	0.06	0.001
$\Delta\rho_{min}$ (e Å^{-3})	−0.16	−0.16
$\Delta\rho_{max}$ (e Å^{-3})	0.14	0.14

[a] T = 293 K, $\lambda_{MoK\alpha}$ = 0.710 69 Å. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(^{1}H, ^{13}C) and $BF_3{\cdot}OEt_2$ (^{11}B). Chemical shifts are stated in ppm; they are positive, when the signal is shifted to higher frequencies than the standard.

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.

Elemental microanalyses were performed by Oneida Research Services, Whitesboro, NY 13492, and by the Institut für Anorganische Chemie, Ludwig-Maximilians-Universität München, Germany.[20]

X-ray diffraction studies of single crystals were determined on an Enraf-Nonius CAD4 diffractometer ($\lambda_{MoK\alpha}$ = 0.710 69 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 **2b**,**e**, **4b**, and **1f**) or calculated (in the case of **2d**, **4c**, and **5f**). 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 [$I > 3\sigma(I)$; $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. In all cases only independent reflections on the basis of Friedel's law have been collected and a reflection−parameter ratio > 5 has been considered sufficient for the type of structural studies performed in here. This ratio could have been improved in those cases if the hydrogen coordinates had been refined, but we would have lost important information on intra- and intermolecular hydrogen interactions.

2. Reagents. All starting materials were commercial. Solvents were used without further purification, but single crystals were grown from spectrophotometric grade solvents.

3. Preparation of the Tridentate Ligands. General Method for the Preparation of the Ligands 1a−f, 3a−c, and 6a,b. To prepare the tridentate ligands **1a**−**f**, **3a**−**c**, and **6a,b**, equimolar quantities of the corresponding amino alcohol and salicylaldehyde or 2′-hydroxyacetophenone were refluxed in benzene for 30 min. The solvent and the water formed during the reaction were then removed by a Dean−Stark trap to yield an oil or a solid that was washed with chloroform and used without further purification.

Part of the spectroscopic data for some of the ligands has already been published. This is the case for **1b**[5a] (elemental analysis), **1d**[21] (^{1}H NMR), **1e**[22] (elemental analysis, IR), **3a**[23] (^{1}H and ^{13}C NMR in $CDCl_3$, IR), and **3c**[5a] (elemental analysis, ^{1}H NMR). Therefore our spectroscopic data are only included when they could be obtained in more detail.

Preparation of 2-[[(2-Hydroxypropyl)imino]methyl]phenol (1b). Compound **1b** was prepared from 1.00 g (13.36 mmol) of DL-1-amino-2-propanol and 1.62 g (13.36 mmol) of salicylaldehyde. The product obtained is a yellow oil (2.20 g, 12.30 mmol). Yield: 92%.

^{1}H NMR (270 MHz, $CDCl_3$) [δ (ppm)]: 1.24 (3H, d, J = 5.9 Hz, CH_3), 3.45 and 3.65 (2H, dd, J = 12.8 and 7.5 Hz, ddd, J = 12.8, 3.4 and 1.3 Hz, NCH_2), 4.05 (1H, m, OC*H*CH_3), 6.83 (1H, t, J = 5.6 Hz, H-5), 6.91 (1H, d, J = 6.6 Hz, H-3), 7.20 (1H, d, J = 5.9 Hz, H-6), 7.28 (1H, t, J = 6.6 Hz, H-4), 8.28 (1H, s, H-7). ^{13}C NMR (67.8 MHz, $CDCl_3$) [δ (ppm)]: 20.8 (CH_3), 66.6, 67.1 (NCH_2, O*C*HCH_3), 117.2, 118.5 (C-1, C-3, C-5), 131.5, 132.5 (C-4, C-6), 161.6 (C-2), 166.7 (C-7).

IR (NaCl) [$\tilde{\nu}$ (cm^{-1})]: 3384 (br, m), 3060 (w), 2970 (m), 2926 (m), 1632 (s), 1614 (m), 1580 (w), 1520 (w), 1496 (m), 1456 (w), 1418 (w), 1374 (w), 1278 (m), 1220 (w), 1150 (m), 1136 (m), 1086 (w), 1044 (m), 1024 (w).

Preparation of α-[[[(2-Hydroxyphenyl)methylene]amino]methyl]-benzenemethanol (1c). Compound **1c** was prepared from 1.00 g (7.29 mmol) of DL-2-amino-1-phenylethanol and 0.89 g (7.29 mmol) of salicylaldehyde. The product obtained is a yellow solid (1.44 g, 5.98 mmol). Mp: 97−99 °C. Yield: 82%.

^{1}H NMR (270 MHz, $CDCl_3$) [δ (ppm)]: 3.80 (2H, m, NCH_2), 5.00 (1H, dd, OC*H*Ph), 6.86 (1H, t, J = 7.2 Hz, H-5), 6.94 (1H, d, J = 6.6 Hz, H-3), 7.21−7.43 (7H, m, H-3, H-5, Ph), 8.33 (1H, s, H-7). ^{13}C NMR (67.8 MHz, $CDCl_3$) [δ (ppm)]: 67.1 (NCH_2), 73.5 (O*C*HPh), 117.1, 118.7 (C-1, C-3, C-5), 126.0, 128.0, 128.6 (*o*-Ph, *m*-Ph, *p*-Ph), 131.5, 132.5 (C-4, C-6), 141.7 (*i*-Ph), 161.2 (C-2), 167.1 (C-7).

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3346 (br, m), 3162 (m), 3060 (m), 3028 (m), 2920 (m), 2850 (m), 1648 (s), 1610 (s), 1578 (w), 1560 (w), 1540 (w), 1522 (s), 1496 (s), 1464 (m), 1452 (m), 1432 (m), 1340 (w), 1316 (w), 1282 (m), 1254 (w), 1222 (m), 1194 (s), 1152 (s), 1146 (s), 1120 (m), 1090 (w), 1058 (s), 1026 (m), 918 (m).

Preparation of α-[1-[[(2-Hydroxyphenyl)methylene]amino]ethyl]-benzenemethanol (1d). Compound **1d** was prepared from 1.23 g (8.18 mmol) of racemic norephedrine and 1.00 g (8.19 mmol) of salicylaldehyde. The product obtained is a yellow oil (1.81 g, 7.10 mmol). Yield: 86%.

^{1}H NMR (270 MHz, DMSO-d_6) [δ (ppm)]: 1.20 (3H, d, J = 6.6 Hz, CH_3), 3.61 (1H, m, NC*H*CH_3), 4.62 (1H, t, J = 4.3 Hz, OC*H*Ph), 5.57 (1H, d, J = 3.6 Hz, $OH_{aliph.}$), 6.82 (1H, d, J = 7.9 Hz, H-3), 6.84 (1H, t, J = 6.7 Hz, H-5), 7.19−7.37 (7H, m, H-4, H-6, Ph), 8.37 (1H, s, H-7), 13.50 (1H, br, s, $OH_{aromat.}$). ^{13}C NMR (67.8 MHz, DMSO-d_6) [δ (ppm)]: 18.1 (CH_3), 69.0 (N*C*HCH$_3$), 75.9 (O*C*HPh), 116.4, 118.1 (C-3, C-5), 118.5 (C-1), 126.9 (*p*-Ph), 127.0, 127.5 (*o*-Ph, *m*-Ph), 131.5, 132.0 (C-4, C-6), 142.5 (*i*-Ph), 160.7 (C-2), 164.6 (C-7).

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Table 13. Selected Bond Lengths, Bond Angles, and Torsion Angles of Compound **5f**

		Bond Lengths (Å)	
O(1)−B(2)	1.470(6)	O(11)−B(12)	1.346(5)
O(1)−C(6)	1.340(5)	B(12)−O(13)	1.375(5)
B(2)−N(3)	1.629(5)	O(13)−C(14)	1.430(4)
B(2)−O(11)	1.431(5)	C(14)−C(15)	1.560(5)
N(3)−C(4)	1.307(5)	B(2)−C(16)	1.600(6)
N(3)−C(15)	1.491(5)	B(12)−C(30)	1.569(6)
		Bond Angles (deg)	
O(1)−B(2)−N(3)	105.6(3)	N(3)−C(15)−C(23)	111.0(4)
O(1)−B(2)−O(11)	105.1(3)	C(4)−N(3)−C(15)	121.0(4)
O(1)−C(6)−C(5)	120.4(4)	C(4)−C(5)−C(6)	119.4(4)
B(2)−N(3)−C(4)	120.7(4)	C(5)−C(4)−C(22)	119.2(4)
B(2)−N(3)−C(15)	118.3(3)	O(11)−B(12)−O(13)	124.2(4)
B(2)−O(1)−C(6)	119.3(3)	O(11)−B(12)−C(30)	118.5(4)
B(2)−O(11)−B(12)	131.4(3)	B(12)−C(30)−C(31)	120.3(4)
B(2)−C(16)−C(17)	125.6(3)	B(12)−C(30)−C(35)	123.0(4)
B(2)−C(16)−C(21)	119.0(4)	O(13)−B(12)−C(30)	117.3(4)
N(3)−B(2)−O(11)	108.5(4)	O(13)−C(14)−C(15)	114.1(3)
N(3)−C(4)−C(5)	118.6(4)	O(13)−C(14)−C(24)	108.7(4)
N(3)−C(15)−C(14)	111.8(3)	C(14)−C(15)−C(23)	113.7(4)
N(3)−C(4)−C(22)	122.2(4)	C(15)−C(14)−C(24)	109.1(3)
		Torsion Angles (deg)[a]	
O(1)−B(2)−N(3)−C(4)	31.5	B(2)−O(11)−B(12)−O(13)	−29.3
B(2)−N(3)−C(4)−C(5)	−2.3	N(3)−B(2)−O(11)−B(12)	70.6
N(3)−C(4)−C(5)−C(6)	−18.4	N(3)−C(15)−C(14)−O(13)	85.2
C(4)−C(5)−C(6)−O(1)	5.5	O(11)−B(2)−N(3)−C(15)	−36.8
C(5)−C(6)−O(1)−B(2)	29.9	O(11)−B(12)−O(13)−C(14)	4.3
C(6)−O(1)−B(2)−N(3)	−44.9	B(12)−O(13)−C(14)−C(15)	−49.8
B(2)−N(3)−C(15)−C(14)	−35.4		

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

IR (NaCl) [$\tilde{\nu}$ (cm^{-1})]: 3420 (br, m), 3062 (w), 2974 (w), 2876 (w), 1652 (m), 1644 (m), 1634 (m), 1622 (m), 1614 (m), 1574 (m), 1558 (m), 1538 (m), 1532 (m), 1520 (m), 1504 (m), 1488 (m), 1454 (m), 1418 (m), 1276 (m), 1196 (m), 1134 (m), 1076 (m), 1046 (m), 1002 (m).

MS (EI, 70 eV, DIP): *m*/*z* 255 (M, 15), 148 (100), 131 (66), 107 (22), 77 (79), 51 (31), 28 (21).

Preparation of 2-[1-[(2-Hydroxyethyl)imino]ethyl]phenol (1e). Compound **1e** was prepared from 0.44 g (7.34 mmol) of 2-aminoethanol and 1.00 g (7.34 mmol) of 2′-hydroxyacetophenone. The product obtained is a yellow solid (0.82 g, 4.58 mmol). Mp: 89−90 °C. Yield: 62%.

^{1}H NMR (90 MHz, DMSO-d_6) [δ (ppm)]: 2.37 (3H, s, CH_3), 3.67 (4H, s, NCH_2, OCH_2), 6.71 (1H, t, J = 7.7 Hz, H-5), 6.75 (1H, d, J = 7.8 Hz, H-3), 7.26 (1H, t, J = 8.5 Hz, H-4), 7.62 (1H, d, J = 8.1 Hz, H-6). ^{13}C NMR (22.5 MHz, DMSO-d_6) [δ (ppm)]: 14.5 (CH_3), 51.0 (NCH_2), 60.8 (OCH_2), 116.3, 118.7 (C-3, C-5), 117.7 (C-1), 128.9 (C-6), 132.6 (C-4), 164.9 (C-2), 173.1 (C-7).

Preparation of α-[1-[1-[(2-Hydroxyphenyl)ethylene]amino]ethyl]-benzenemethanol (1f). Compound **1f** was prepared from 1.00 g (6.61 mmol) of (+)-norephedrine and 0.90 g (6.61 mmol) of 2′-hydroxyacetophenone. The crystals (1.57 g, 5.84 mmol) obtained after recrystallization from methanol are green and fluorescent. Mp: 139−141 °C. Yield: 88%.

^{1}H NMR (270 MHz, DMSO-d_6) [δ (ppm)]: 1.58 (3H, d, J = 6.2 Hz, CH_3), 2.50 (3H, s, CH_3), 4.43 (1H, m, NC*H*CH_3), 5.00 (1H, t, J = 5.6 Hz, OC*H*Ph), 6.10 (1H, d, $OH_{aliph.}$), 7.04 (1H, t, J = 7.6 Hz, H-5), 7.12 (1H, d, H-3), 7.54−7.74 (6H, m, H-4, Ph), 7.84 (1H, d, J = 5.6 Hz, H-6), 16.83 (1H, br, s, $OH_{aromat.}$). ^{13}C NMR (67.8 MHz, DMSO-d_6) [δ (ppm)]: 14.0 (CH_3), 17.5 (CH_3), 59.8 (N*C*HCH$_3$), 76.3 (O*C*HPh), 116.4, 118.3 (C-3, C-5), 118.9 (C-1), 127.0 (*p*-Ph), 126.9, 127.7 (*o*-Ph, *m*-Ph), 128.7 (C-6), 132.2 (C-4), 143.1 (*i*-Ph), 164.1 (C-2), 170.6 (C-7).

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3134 (br, w), 2982 (w), 2934 (w), 2866 (w), 1608 (s), 1560 (m), 1540 (m), 1376 (m), 1154 (m), 1058 (m).

MS (EI, 70 eV): *m*/*z* 193 (M + H − C_6H_5, 49), 192 (M − C_6H_5, 6), 162 (78), 136 (75), 121 (36), 91 (63), 65 (28), 42 (39), 31 (100).

Preparation of 2-[[(2-Hydroxy-1,1-dimethylethyl)imino]methyl]-phenol (3a). Compound **3a** was prepared from 0.73 g (8.19 mmol) of 2-amino-2-methyl-1-propanol and 1.00 g (8.19 mmol) of salicylaldehyde. The product obtained is a yellow oil (1.22 g, 6.32 mmol). Yield: 77%.

^{1}H NMR (90 MHz, DMSO-d_6) [δ (ppm)]: 1.25 (6H, s, CH_3), 3.40 (2H, s, OCH_2), 4.90 (1H, br, s, $OH_{aliph.}$), 6.81 (1H, t, J = 7.9 Hz, H-3), 6.93 (1H, d, J = 7.9 Hz, H-5), 7.26 (1H, d, J = 8.1 Hz, H-6), 7.41 (1H, t, J = 8.2 Hz, H-4), 8.69 (1H, s, H-7), 14.30 (1H, br, s, $OH_{aromat.}$). ^{13}C NMR (22.5 MHz, DMSO-d_6) [δ (ppm)]: 23.8 (CH_3), 60.6 (N*C*Me$_2$), 69.2 (OCH_2), 116.9, 117.5 (C-3, C-5), 118.7 (C-1), 132.0, 132.2 (C-4, C-6), 162.1, 162.4 (C-2, C-7).

Preparation of 2-[1-[(2-Hydroxy-1,1-dimethylethyl)imino]ethyl]-phenol (3b). Compound **3b** was prepared from 0.65 g (7.36 mmol) of 2-amino-2-methyl-1-propanol and 1.00 g (7.36 mmol) of 2′-hydroxyacetophenone. The product obtained is a yellow oil (1.48 g, 7.10 mmol). Yield: 96%.

^{1}H NMR (90 MHz, $CDCl_3$) [δ (ppm)]: 1.07 (6H, s, CH_3), 2.63 (3H, s, CH_3), 3.27 (2H, s, OCH_2), 6.84 (2H, m, H-3, H-5), 7.46 (1H, t, J = 7.9 Hz, H-4), 7.75 (1H, d, J = 7.8 Hz, H-6).

IR (NaCl) [$\tilde{\nu}$ (cm^{-1})]: 3283 (br, w), 3160 (br, w), 3050 (w), 2968 (w), 2930 (w), 2872 (w), 1644 (s), 1614 (m), 1584 (w), 1558 (w), 1540 (w), 1488 (w), 1470 (w), 1448 (w), 1418 (w), 1370 (w), 1302 (w), 1244 (w), 1222 (w), 1186 (w), 1158 (w), 1044 (w).

Preparation of 2-[[3-Hydroxypropyl)imino]methyl]phenol (3c). Compound **3c** was prepared from 0.61 g (8.19 mmol) of 3-amino-1-propanol and 1.00 g (8.19 mmol) of salicylaldehyde. The product obtained is a yellow oil (1.41 g, 7.87 mmol). Yield: 96%.

^{1}H NMR (270 MHz, $CDCl_3$) [δ (ppm)]: 1.91 (2H, q, J = 6.6 Hz, OCH_2CH_2), 3.67 (4H, m, NCH_2, OCH_2), 6.83 (1H, t, J = 6.9 Hz, H-5), 6.92 (1H, d, J = 8.1 Hz, H-3), 7.20 (1H, d, J = 7.6 Hz, H-6), 7.30 (1H, t, J = 7.5 Hz, H-4), 8.30 (1H, s, H-7). ^{13}C NMR (67.8 MHz, $CDCl_3$) [δ (ppm)]: 33.2 (OCH_2CH_2), 55.2 (NCH_2), 59.5 (OCH_2), 117.0, 118.1 (C-3, C-5), 118.3 (C-1), 131.2, 132.2 (C-4, C-6), 161.8 (C-2), 165.1 (C-7).

IR (NaCl) [$\tilde{\nu}$ (cm^{-1})]: 3358 (br, m), 2942 (m), 2876 (m), 1634 (s), 1582 (m), 1558 (m), 1540 (m), 1522 (m), 1496 (m), 1456 (m), 1436 (w), 1418 (w), 1338 (w), 1278 (m), 1212 (w), 1150 (w), 1118 (w), 1064 (w).

MS (EI, 70 eV, DIP): *m*/*z* 179 (M, 70), 148 (69), 134 (100), 107 (86), 77 (49), 65 (37), 51 (37), 39 (47), 31 (77).

Preparation of 2-[[(5-Hydroxypentyl)imino]methyl]phenol (6a). Compound **6a** was prepared from 1.50 g (14.56 mmol) of 5-aminopentanol and 1.78 g (14.56 mmol) of salicylaldehyde. The product obtained is an orange oil (2.78 g, 13.43 mmol). Yield: 92%.

^{1}H NMR (270 MHz, $CDCl_3$) [δ (ppm)]: 1.38−1.73 (6H, m, H-9, H-10, H-11), 3.56 (4H, m, NCH_2, OCH_2), 6.83 (1H, t, J = 7.3 Hz, H-5), 6.92 (1H, d, J = 7.9 Hz, H-3), 7.19 (1H, d, J = 7.3 Hz, H-6), 7.27 (1H, t, J = 7.3 Hz, H-4), 8.26 (1H, s, H-7). ^{13}C NMR (67.8 MHz, $CDCl_3$) [δ (ppm)]: 23.8 (C-10), 30.6, 32.3 (C-9, C-11), 59.0 (NCH_2), 62.3 (OCH_2), 117.1, 118.3 (C-3, C-5), 118.6 (C-1), 131.1, 132.2 (C-4, C-6), 161.7 (C-2), 164.7 (C-7).

IR (NaCl) [$\tilde{\nu}$ (cm^{-1})]: 3360 (br, m), 2934 (w), 1634 (s), 1616 (w), 1576 (w), 1558 (w), 1506 (w), 1496 (w), 1456 (m), 1436 (w), 1418 (w), 1280 (m), 1150 (w), 1056 (w).

Preparation of 2-[[(6-Hydroxyhexyl)imino]methyl]phenol (6b). Compound **6b** was prepared from 1.50 g (12.84 mmol) of 6-aminohexanol and 1.56 g (12.84 mmol) of salicylaldehyde. The product obtained is an orange oil (2.67 g, 12.06 mmol). Yield: 94%.

^{1}H NMR (270 MHz, $CDCl_3$) [δ (ppm)]: 1.36 (4H, m, H-10, H-11), 1.58 (4H, m, H-9, H-12), 3.50 (2H, t, J = 6.6 Hz, NCH_2), 3.58 (2H, t, J = 6.6 Hz, OCH_2), 6.81 (1H, t, J = 7.9 Hz, H-5), 6.92 (1H, d, J = 7.9 Hz, H-3), 7.19 (1H, d, J = 7.3 Hz, H-6), 7.26 (1H, t, J = 7.3 Hz, H-4), 8.23 (1H, s, H-7). ^{13}C NMR (67.8 MHz, $CDCl_3$) [δ (ppm)]: 25.5, 26.9 (C-10, C-11), 30.7, 32.5 (C-9, C-12), 58.8 (NCH_2), 62.2 (OCH_2), 117.1, 118.2 (C-3, C-5), 118.6 (C-1), 131.2, 132.2 (C-4, C-6), 161.9 (C-2), 164.6 (C-7).

IR (NaCl) [$\tilde{\nu}$ (cm^{-1})]: 3360 (br, m), 3080 (w), 3020 (w), 2932 (w), 2856 (m), 1634 (s), 1582 (w), 1558 (w), 1540 (w), 1496 (w), 1456 (m), 1418 (w), 1340 (w), 1280 (m), 1210 (w), 1150 (w), 1118 (w), 1056 (w).

4. Preparation of the Boronates. General Method for the Preparation of Compounds 2b−e, 4a−c, 5a,d,f, 7a,7b, and 8b. An equimolar amount of phenylboronic acid was added to a solution of the tridentate ligand in benzene (usually about 10 mL for 2−3 mmol). The mixture was refluxed for 30 min and quantified by water and solvent separation with a Dean−Stark trap. The solid obtained was collected by filtration under vacuum and washed with small amounts of benzene and hexane.

Preparation of 4,13-Dimethyl-2,11-diphenyldibenzo[*h*,*q*]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (2b). Compound **2b** was prepared from 0.50 g (2.82 mmol) of **1b** and 0.34 g (2.82 mmol) of phenylboronic acid. The product obtained is a yellow solid (0.42 g, 0.79 mmol) that is slightly soluble in chloroform. Crystals suitable for X-ray diffraction were obtained when the reaction was performed in a small amount of chloroform at room temperature without stirring. Mp: 265 °C. Yield: 56%.

In the NMR spectra a series of decomposition products are observed. The data reported here correspond to the major product that may be the dimeric structure. ^{1}H NMR (270 MHz, $CDCl_3$) [δ (ppm)]: 0.64 (6H, d, J = 6.2 Hz, CH_3), 3.07−4.12 (6H, m, NCH_2, $OCHCH_3$), 6.85−7.58 (18H, m, $H_{arom.}$), 8.49 (2H, s, H-7). ^{13}C NMR (67.8 MHz, $CDCl_3$) [δ (ppm)]: 21.2 (CH_3), 64.5, 67.5 (NCH_2, $OCHCH_3$), 118.8, 119.6 (C-3, C-5), 126.9 (*p*-BC_6H_5), 127.3 (*m*-BC_6H_5), 131.1 (C-6), 132.2 (*o*-BC_6H_5), 137.4 (C-4), 164.3 (C-7). ^{11}B NMR (86.6 MHz, $CDCl_3$) [δ (ppm)]: 4 ($h_{1/2}$ = 360 Hz).

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3068 (w), 3042 (w), 3006 (w), 2968 (w), 2932 (w),1636 (s), 1608 (w), 1560 (m), 1480 (m), 1464 (w), 1448 (w), 1434 (w), 1400 (w), 1314 (m), 1260 (w), 1238 (w), 1198 (s), 1156 (s), 1140 (m), 1090 (m), 1072 (w), 1042 (m), 1030 (m), 952 (s).

MS (EI, 70 eV, DIP): *m*/*z* 453 (M − C_6H_5, 7), 264 (1), 220 (26), 187 (26), 188 ($C_{10}H_{11}BNO_2^+$, 100), 148 (8), 77 ($C_6H_5^+$, 5), 41 (14).

Anal. Calcd: C, 72.49, H, 6.08, N, 5.28. Found: C, 71.73, H, 5.86, N, 5.11.

Preparation of 2,4,11,13-Tetraphenyldibenzo[*h*,*q*]-7,16-diaza-1,3,-10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (2c). Compound **2c** was prepared from 0.50 g (2.07 mmol) of **1c** and 0.25 g (2.07 mmol) of phenylboronic acid. The product obtained is a yellow solid (0.51 g, 0.78 mmol) that is insoluble in all common solvents. Mp: 304 °C (dec). Yield: 76%.

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3046 (m), 3020 (m), 3004 (m), 2908 (m), 1638 (s), 1610 (m), 1558 (s), 1480 (m), 1462 (m), 1452 (m), 1442 (m), 1398 (w), 1370 (w), 1352 (m), 1306 (s), 1270 (m), 1236 (s), 1198 (s), 1148 (m), 1130 (m), 1110 (s), 1094 (m), 1070 (m), 1058 (w), 1016 (s), 956 (s).

MS (EI, 70 eV, DIP): *m*/*z* 577 (M − C_6H_5, 10), 298 (6), 249 (26), 250 ($C_{15}H_{13}BNO_2^+$, 100), 220 (37), 148 (5), 103 (5), 91 (4), 77 ($C_6H_5^+$, 9), 58 (8), 51 (4).

Anal. Calcd: C, 77.09, H, 5.54, N, 4.28. Found: C, 75.89, H, 5.14, N, 4.24.

Preparation of 5,14-Dimethyl-2,4,11,13-tetraphenyldibenzo[*h*,*q*]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (2d). Compound **2d** was prepared from 0.50 g (1.96 mmol) of **1d** and 0.24 g (1.96 mmol) of phenylboronic acid. The product obtained is a yellow solid (0.51 g, 0.75 mmol) that is insoluble in all common solvents. Crystals suitable for X-ray diffraction were obtained when the reaction was performed in benzene at room temperature without stirring. Mp: 254−256 °C. Yield: 77%.

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3068 (w), 3028 (w), 3010 (w), 2920 (w), 1634 (s), 1608 (m), 1560 (m), 1492 (w), 1480 (m), 1462 (m), 1434 (m), 1402 (w), 1336 (m), 1316 (m), 1240 (m), 1220 (w), 1202 (s), 1152 (m), 1140 (w), 1128 (m), 1106 (m), 1094 (m), 1074 (m), 1048 (m), 1028 (m), 956 (m).

MS (EI, 70 eV, DIP): *m*/*z* 605 (M − C_6H_5, 6), 342 (6), 312 (6), 263 (27), 264 ($C_{16}H_{15}BNO_2^+$, 100), 234 (96), 148 (24), 117 (12), 105 (9), 91 (11), 77 ($C_6H_5^+$, 15), 51 (8).

Anal. Calcd: C, 77.44, H, 5.91, N, 4.10. Found: C, 77.71, H, 5.57, N, 4.11.

Preparation of 7,16-Dimethyl-2,11-diphenyldibenzo[*h*,*q*]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (2e). Compound **2e** was prepared from 0.50 g (2.73 mmol) of **1e** and 0.34 g (2.73 mmol) of phenylboronic acid. The product obtained is a yellow solid (0.52 g, 0.98 mmol) that is slightly soluble in chloroform, dichloromethane, methanol, and DMSO. Crystals suitable for X-ray diffraction were obtained when the reaction was performed in dichloromethane at room temperature without stirring. Mp: 232−234 °C. Yield: 70%.

^{1}H NMR (270 MHz, $CDCl_3$) [δ (ppm)]: 2.93 (6H, s, CH_3), 3.30 (4H, m, NCH_2), 4.02 (4H, m, OCH_2), 6.94 (2H, t, J = 7.9 Hz, H-5), 7.05 (2H, d, J = 8.5 Hz, H-3), 7.21 (4H, m, *m*-BC_6H_5), 7.24 (2H, m, *p*-BC_6H_5), 7.47 (2H, t, J = 6.9 Hz, H-4), 7.49 (4H, m, *o*-BC_6H_5), 7.78 (2H, d, J = 7.8 Hz, H-6). ^{13}C NMR (67.8 MHz, $CDCl_3$) [δ (ppm)]: 16.9 (CH_3), 51.3 (NCH_2), 60.9 (OCH_2), 117.7 (C-1), 118.5, 120.0 (C-3, C-5), 126.8 (*p*-BC_6H_5), 127.3 (*m*-BC_6H_5), 128.5 (C-6), 132.0 (*o*-BC_6H_5), 136.2 (C-4), 160.0 (C-2), 172.4 (C-7). ^{11}B NMR (86.6 MHz, $CDCl_3$) [δ (ppm)]: 4 ($h_{1/2}$ = 490 Hz).

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3066 (m), 3038 (m), 3004 (m), 2942 (m), 2864 (m), 2758 (m), 1614 (s), 1554 (s), 1456 (s), 1432 (m), 1370 (m), 1332 (m), 1276 (s), 1198 (s), 1166 (m), 1142 (m), 1132 (m), 1114 (s), 1076 (m), 1010 (s), 1002 (s), 994 (s).

MS (EI, 70 eV, DIP): *m*/*z* 453 (M − C_6H_5, 2), 296 (1), 268 (26), 234 (3), 187 (14), 188 ($C_{10}H_{11}BNO_2^+$, 100), 162 (10), 146 (5), 77 ($C_6H_5^+$, 13), 51 (12).

Anal. Calcd: C, 72.49, H, 6.08, N, 5.28. Found: C, 74.02, H, 5.85, N, 4.62.

Preparation of 5,5-Dimethyl-2-phenylbenzo[*h*]-6-aza-1,3,2-dioxaboracyclonon-6-ene (4a). Compound **4a** has been synthesized in two steps. First, 0.50 g (2.60 mmol) of **3a** and 0.32 g (2.60 mmol) of phenylboronic acid have been brought to reaction. After 15 min 7,7-dimethyl-2,4-diphenylbenzo[*j*]-8-aza-1,3,5,2,4-trioxadiboracycloundeca-8-ene (**5a**) precipitated (0.72 g, 1.87 mmol) as a yellow solid that is slightly soluble in benzene, THF, chloroform, dichloromethane, and diethyl ether. Mp: 238−240 °C. Yield: 72%.

^{1}H NMR (270 MHz, $CDCl_3$) [δ (ppm)]: 1.23, 1.61 (6H, s, CH_3), 3.36−4.75 (2H, m, OCH_2), 6.84 (1H, m, H-5), 6.94 (1H, d, J = 8.5 Hz, H-3), 7.22−7.33 (8H, m, H-4, H-6, *m*-B(3,4)C_6H_5, *p*-B(3,4)C_6H_5), 7.47 (2H, d, J = 7.2 Hz, *o*-B(4)C_6H_5), 7.99 (2H, d, J = 8.5 Hz, *o*-B(3)-C_6H_5), 8.40 (1H, s, H-7). ^{13}C NMR (67.8 MHz, $CDCl_3$) [δ (ppm)]: 26.6, 27.3 (CH_3), 65.8 (NCH_2), 69.7 (OCH_2), 115.3 (C-1), 118.6 (C-5), 119.5 (C-3), 127.3 (*p*-B(4)C_6H_5), 127.4, 127.6 (*m*-B(3,4)C_6H_5), 130.6 (*o*-B(4)C_6H_5), 130.4, 131.7 (C-6, *p*-B(3)C_6H_5), 134.9 (*o*-B(3)C_6H_5), 138.5 (C-4), 159.9 (C-2), 162.2 (C-7). ^{11}B NMR (86.6 MHz, $CDCl_3$) [δ (ppm)]: 5 ($h_{1/2}$ = 190 Hz), 28 ($h_{1/2}$ = 580 Hz).

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3070 (w), 3050 (w), 3008 (w), 2978 (w), 2936 (w), 1628 (s), 1606 (w), 1576 (w), 1558 (s), 1534 (w), 1526 (w), 1522 (w), 1508 (w), 1482 (s), 1460 (m), 1438 (m), 1432 (w), 1418 (w), 1394 (m), 1386 (m), 1364 (m), 1342 (w), 1312 (s), 1278 (s), 1250 (m), 1230 (w), 1190 (m), 1178 (m), 1150 (w), 1138 (m), 1074 (w), 1030 (w), 1010 (w).

MS (EI, 70 eV, DIP): *m*/*z* 306 (M − C_6H_5, 34), 305 (16), 202 (M − C_6H_5 − C_6H_5BO, 100), 148 (31), 130 (7), 103 (7), 77 ($C_6H_5^+$, 23), 51 (18), 41 (10).

Anal. Calcd: C, 72.12, H, 6.05, N, 3.66. Found: C, 72.41, H, 6.08, N, 3.59.

To obtain compound **4a**, 0.50 g of **5a** (1.30 mmol) was dissolved in benzene and a further 1 equiv of **3a** (0.25 g, 1.30 mmol) was added. The product then obtained (**4a**) is a yellow solid (0.22 g, 0.78 mmol) that is slightly soluble in chloroform. Mp: 188−190 °C. Yield: 30%.

^{1}H NMR (270 MHz, DMSO-d_6) [δ (ppm)]: 1.28, 1.43 (6H, s, CH_3), 3.67 (2H, m, OCH_2), 6.81 (1H, d, J = 7.3 Hz, H-3), 6.89 (1H, t, J = 8.5 Hz, H-5), 7.07 (3H, m, *m*-BC_6H_5, *p*-BC_6H_5), 7.21 (2H, d, *o*-BC_6H_5), 7.43 (1H, t, J = 8.5 Hz, H-4), 7.60 (1H, d, J = 7.9 Hz, H-6), 8.81 (1H, s, H-7). ^{13}C NMR (67.8 MHz, DMSO-d_6) [δ (ppm)]: 23.6, 24.9 (CH_3), 63.8 (N*C*Me$_2$), 75.5 (OCH_2), 118.6, 119.0 (C-3, C-5), 119.2 (C-1), 126.2 (*p*-BC_6H_5), 126.8 (*m*-BC_6H_5), 130.3 (*o*-BC_6H_5), 131.6 (C-6), 136.6 (C-4), 157.9 (C-7), 159.0 (C-2). ^{11}B NMR (86.6 MHz, $CDCl_3$) [δ (ppm)]: 7 ($h_{1/2}$ = 250 Hz).

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3064 (w), 3044 (w), 2998 (w), 2966 (w), 2922 (w), 2852 (w), 1644 (s), 1608 (m), 1554 (m), 1476 (m), 1456 (m), 1430 (m), 1396 (m), 1352 (w), 1294 (m), 1226 (m), 1202 (m), 1178 (m), 1152 (w), 1128 (w), 1066 (s), 1032 (m), 1012 (m), 984 (m), 924 (m).

MS (EI, 70 eV, DIP): *m*/*z* 279 (M, 1), 278 (1), 248 (4), 202 (M − C_6H_5, 100), 148 (53), 77 ($C_6H_5^+$, 8), 51 (7), 39 (3).

Anal. Calcd: C, 73.15, H, 6.50, N, 5.02. Found: C, 72.77, H, 6.45, N, 4.42.

Preparation of 5,5,7-Trimethyl-2-phenylbenzo[*h*]-6-aza-1,3,2-dioxaboracyclonon-6-ene (4b). Compound **4b** was prepared from 0.50 g (2.42 mmol) of **3b** and 0.29 g (2.38 mmol) of phenylboronic acid. The product obtained is a yellow solid (0.64 g, 2.18 mmol) that is soluble in most of the common solvents. Crystals suitable for X-ray diffraction were obtained from ethyl acetate/hexane. Mp: 281−283 °C. Yield: 91%.

^{1}H NMR (270 MHz, $CDCl_3$) [δ (ppm)]: 1.60 (6H, s, CH_3), 2.68 (3H, s, CH_3), 3.85 (2H, m, OCH_2), 6.78 (1H, t, J = 7.3 Hz, H-5), 6.96 (1H, d, J = 8.5 Hz, H-3), 7.13 (3H, m, *m*-BC_6H_5, *p*-BC_6H_5), 7.30 (2H, d, J = 8.5 Hz, *o*-BC_6H_5), 7.33 (1H, t, J = 7.3 Hz, H-4), 7.45 (1H, d, J = 7.8 Hz, H-6). ^{13}C NMR (67.8 MHz, $CDCl_3$) [δ (ppm)]: 18.0 (CH_3), 24.8, 26.4 (CH_3), 64.2 (N*C*Me$_2$), 76.6 (OCH_2), 118.8, 120.9 (C-3, C-5), 121.7 (C-1), 126.6, 127.5 (C-6, *p*-BC_6H_5), 127.1 (*m*-BC_6H_5), 131.3 (*o*-BC_6H_5), 136.2 (C-4), 159.8 (C-2), 167.2 (C-7). ^{11}B NMR (86.6 MHz, $CDCl_3$) [δ (ppm)]: 7 ($h_{1/2}$ = 130 Hz).

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3068 (m), 2970 (m), 2934 (m), 2870 (m), 1652 (s), 1640 (s), 1616 (s), 1608 (s), 1570 (w), 1558 (w), 1540 (w), 1534 (w), 1526 (w), 1522 (w), 1506 (w), 1486 (s), 1472 (m), 1456 (s), 1448 (s), 1374 (m), 1304 (s), 1244 (m), 1222 (m), 1188 (w), 1112 (w), 1076 (m), 1050 (m).

MS (EI, 70 eV, DIP): *m*/*z* 293 (M, 1), 292 (1), 216 (M − C_6H_5, 100), 215 (27), 162 (36), 77 ($C_6H_5^+$, 16), 51 (11), 42 (5).

Anal. Calcd: C, 73.74, H, 6.88, N, 4.78. Found: C, 73.58, H, 6.94, N, 4.69.

Preparation of 2-Phenylbenzo[*i*]-7-aza-1,3,2-dioxaboracyclodec-7-ene (4c). Compound **4c** was prepared from 0.50 g (2.79 mmol) of **3c** and 0.34 g (2.79 mmol) of phenylboronic acid. The product obtained is a yellow solid (0.69 g, 2.60 mmol) that is slightly soluble in chloroform, dichloromethane, methanol, and DMSO. Crystals suitable for X-ray diffraction were obtained when the reaction was performed in a small amount of dichloromethane at room temperature without stirring. Mp: 229−231 °C. Yield: 93%.

^{1}H NMR (270 MHz, $CDCl_3$) [δ (ppm)]: 1.72−2.22 (2H, m, OCH_2CH_2), 3.64−4.11 (4H, m, NCH_2, OCH_2), 6.76 (1H, t, J = 8.5 Hz, H-5), 7.27 (6H, m, H-3, H-4, H-6, *m*-BC_6H_5, *p*-BC_6H_5), 7.38 (2H, m, *o*-BC_6H_5), 8.14 (1H, s, H-7). ^{13}C NMR (67.8 MHz, $CDCl_3$) [δ (ppm)]: 30.9 (OCH_2CH_2), 55.5 (NCH_2), 61.5 (OCH_2), 115.5 (C-1), 118.7, 119.8 (C-3, C-5), 127.2 (*p*-BC_6H_5), 127.8 (*m*-BC_6H_5), 131.1 (C-6, *o*-BC_6H_5), 137.8 (C-4), 159.6 (C-2), 160.3 (C-7). ^{11}B NMR (86.6 MHz, $CDCl_3$) [δ (ppm)]: 5 ($h_{1/2}$ = 160 Hz).

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3060 (w), 3014 (w), 2998 (w), 2960 (w), 2942 (w), 2918 (w), 2858 (w), 1644 (s), 1610 (m), 1558 (s), 1540 (w), 1478 (w), 1464 (w), 1442 (w), 1412 (w), 1380 (w), 1368 (w), 1348 (w), 1338 (m), 1302 (m), 1232 (w), 1168 (m), 1154 (m), 1146 (m), 1098 (s), 1032 (m), 1022 (s), 1012 (m), 950 (m).

MS (EI, 70 eV, DIP): *m*/*z* 265 (M, 1), 206 (1), 188 (M − C_6H_5, 100), 148 (9), 132 (16), 77 ($C_6H_5^+$, 15), 51 (17), 41 (5).

Anal. Calcd: C, 72.49, H, 6.08, N, 5.28. Found: C, 72.42, H, 6.14, N, 5.17.

Preparation of 7-Methyl-2,4,6-triphenylbenzo[*j*]-8-aza-1,3,5,2,4-trioxadiboracycloundec-8-ene (5d). Compound **5d** was prepared from 0.50 g (1.96 mmol) of enantiomerically pure **1d** and 0.24 g (1.96 mmol) of phenylboronic acid. The product obtained is a yellow solid (0.46 g, 0.13 mmol) that is slightly soluble in THF and dichloromethane. Mp: 141−143 °C. Yield: 7%.

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3014 (w), 2972 (w), 2884 (w), 1633 (s), 1616 (m), 1580 (w), 1574 (w), 1538 (w), 1532 (w), 1520 (w), 1514 (w), 1488 (m), 1472 (m), 1456 (s), 1446 (s), 1434 (m), 1428 (m), 1402 (m), 1392 (s), 1354 (m), 1326 (s), 1284 (m), 1246 (w), 1224 (w), 1164 (w), 1142 (w), 1116 (w), 1100 (w), 1060 (w), 1036 (m), 1012 (w).

MS (EI, 70 eV, DIP): *m*/*z* 445 (M, 1), 368 (M − C_6H_5, 45), 367 (25), 264 (M − C_6H_5 − C_6H_5BO, 100), 234 (18), 165 (4), 148 (52), 77 ($C_6H_5^+$, 29), 51 (15).

Anal. Calcd: C, 75.55, H, 5.66, N, 3.15. Found: C, 73.75, H, 5.83, N, 3.68.

Preparation of (2*R*,6*S*,7*R*)-7,9-Dimethyl-2,4,6-triphenylbenzo[*j*]-8-aza-1,3,5,2,4-trioxadiboracycloundec-8-ene (5f). Compound **5f** was prepared from 0.50 g (1.86 mmol) of enantiomerically pure **1f** and 0.22 g (1.86 mmol) of phenylboronic acid. The product obtained is a yellow solid (0.40 g, 0.87 mmol) that is slightly soluble in chloroform. Crystals suitable for X-ray diffraction were obtained when the reaction was performed in dichloromethane at room temperature without stirring. Mp: 243−245 °C (dec). Yield: 47%.

^{1}H NMR (400 MHz, $CDCl_3$) [δ (ppm)]: 1.42 (3H, d, J = 6.9 Hz, CH_3), 2.65 (3H, s, CH_3), 4.42 (1H, m, NC*H*CH_3), 5.78 (1H, d, J = 4.6 Hz, OC*H*Ph), 6.85 (1H, t, J = 7.7 Hz, H-5), 6.97 (1H, d, J = 8.4 Hz, H-3), 7.17 (3H, m, *m*-B(4)C_6H_5, *p*-B(4)C_6H_5), 7.38 (1H, t, J = 8.6 Hz, H-4), 7.42 (7H, m, *o*-B(4)C_6H_5, Ph), 7.49 (3H, m, m−B(3)C_6H_5, *p*-B(3)-C_6H_5), 7.57 (1H, d, J = 7.6 Hz, H-6), 8.26 (2H, d, J = 6.1 Hz, *o*-B(3)-C_6H_5). ^{13}C NMR (100.5 MHz, $CDCl_3$) [δ (ppm)]: 14.6 (CH_3), 17.6 (CH_3), 66.8 (N*C*HCH$_3$), 74.6 (O*C*HPh), 120.2 (C-5), 121.1 (C-1), 122.0 (C-3), 127.2 (*m*-Ph), 128.4 (*p*-B(4)C_6H_5), 128.7 (*m*-B(3)C_6H_5), 128.9 (*p*-Ph), 129.1 (*m*-B(4)C_6H_5), 129.3 (C-6), 129.8 (*o*-Ph), 131.3 (*o*-B(4)-C_6H_5), 131.7 (*p*-B(3)C_6H_5), 136.3 (*o*-B(3)C_6H_5), 138.0 (C-4), 142.8 (*i*-Ph), 160.7 (C-2), 171.7 (C-7). ^{11}B NMR (128.3 MHz, $CDCl_3$) [δ (ppm)]: 6 ($h_{1/2}$ = 170 Hz).

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3056 (w), 3026 (w), 3008 (w), 2952 (w), 1604 (s), 1574 (w), 1524 (w), 1514 (w), 1504 (w), 1486 (m), 1470 (m), 1444 (s), 1434 (m), 1428 (m), 1392 (s), 1362 (m), 1336 (s), 1318 (s), 1310 (s), 1286 (s), 1216 (w), 1200 (w), 1162 (m), 1134 (m), 1120 (m), 1098 (m), 1080 (m), 1058 (m), 1022 (m), 1008 (w).

MS (EI, 70 eV, DIP): *m*/*z* 459 (M, 0.1), 382 (M − C_6H_5, 67), 381 (33), 278 (M − C_6H_5 − C_6H_5BO, 100), 162 (24), 117 (4), 77 ($C_6H_5^+$, 22), 51 (11).

Anal. Calcd: C, 75.86, H, 5.93, N, 3.05. Found: C, 73.21, H, 5.81, N, 3.06.

Preparation of 2,14-Diphenyldibenzo[*k*,*v*]-9,21-diaza-1,3,13,15-tetraoxa-2,14-diboracyclotetracosa-9,21-diene (7a). Compound **7a** was prepared from 0.50 g (2.40 mmol) of **6a** and 0.29 g (2.26 mmol) of phenylboronic acid. The product obtained is a yellow oil (0.55 g, 0.94 mmol) that is insoluble in all common solvents. Yield: 79%.

IR (NaCl) [$\tilde{\nu}$ (cm^{-1})]: 3344 (br, w), 3048 (w), 3006 (w), 2932 (w), 2864 (w), 1652 (m), 1646 (m), 1608 (m), 1558 (m), 1480 (m), 1456 (m), 1436 (m), 1316 (m), 1236 (m), 1196 (m), 1152 (m), 1028 (m), 950 (m).

MS (EI, 70 eV, DIP): *m*/*z* 509 (M − C_6H_5, 1), 424 (2), 397 (1), 362 (2), 320 (12), 292 (3), 215 (27), 216 ($C_{12}H_{15}BNO_2^+$, 100), 148 (17), 77 ($C_6H_5^+$, 8), 51 (4), 41 (7).

Preparation of 2,15-Diphenyldibenzo[*l*,*x*]-10,23-diaza-1,3,14,16-tetraoxa-2,15-diboracyclohexacosa-10,23-diene (7b). Compound **7b** was prepared from 0.50 g (2.26 mmol) of **6b** and 0.27 g (2.26 mmol) of phenylboronic acid. The first product obtained is 2,4-diphenylbenzo-[*n*]-12-aza-1,3,5,2,4-trioxadiboracyclopentadec-12-ene (**8b**), a yellow solid (0.45 g, 1.12 mmol) that is slightly soluble in chloroform. Mp: 210−212 °C. Yield: 48%.

^{11}B NMR (86.6 MHz, $CDCl_3$) [δ (ppm)]: 4 ($h_{1/2}$ = 390 Hz), 29 ($h_{1/2}$ = 200 Hz).

MS (EI, 70 eV, DIP): *m*/z 334 (M − C_6H_5, 3), 296 (7), 268 (4), 229 (26), 230 ($C_{13}H_{17}BNO_2^+$, 100), 208 (6), 162 (5), 148 (36), 91 (6), 77 (7), 58 (9), 44(4).

To obtain compound **7b**, 0.30 g (0.73 mmol) of **8b** was dissolved in methanol and a further 1 equiv of **6b** (0.16 g, 0.73 mmol) was added. After 2 h of reflux, the solvent was evaporated and a yellow solid was obtained (0.58 g, 0.94 mmol) that is insoluble in all common solvents. Mp: 239−240 °C. Yield: 64%.

IR (KBr) [$\tilde{\nu}$ (cm^{-1})]: 3066 (w), 3006 (w), 2932 (m), 2858 (m), 2838 (m), 1644 (s), 1610 (w), 1560 (m), 1480 (m), 1464 (m), 1432 (w), 1404 (w), 1310 (m), 1264 (w), 1236 (m), 1194 (m), 1152 (m), 1126 (m), 1112 (m), 1090 (m), 1056 (w), 1040 (w), 1032 (w), 1006 (w), 948 (m).

MS (EI, 70 eV, DIP): *m*/z 537 (M − C_6H_5, 1), 438 (1), 334 (6), 308 (4), 229 (26), 230 ($C_{13}H_{17}BNO_2^+$, 100), 222 (19), 208 (10), 148 (25), 77 ($C_6H_5^+$, 13), 41 (14).

Anal. Calcd: C, 74.29, H, 7.22, N, 4.56. Found: C, 74.25, H, 7.63, N, 4.47.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal parameters, and bond lengths and angles (49 pages). Ordering information is given on any current masthead page.

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