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New perspectives for boronic esters in macrocyclic chemistry

Norberto Farfán [a,*], Herbert Höpfl [b], Victor Barba [a], Ma. Eugenia Ochoa [a], Rosa Santillan [a], Elizabeth Gómez [a], Atilano Gutiérrez [c]

[a] *Depto. de Química, Centro de Investigación y de Estudios Avanzados del IPN, Apdo. postal 14-740, 07000, México D.F., Mexico*
[b] *Universidad Autónoma del Estado de Morelos, Centro de Investigaciones Químicas, Av. Universidad 1001, C. P. 62210, Cuernavaca, Morelos, Mexico*
[c] *Laboratorio de Resonancia Magnética Nuclear, Universidad Autónoma Metropolitana, Unidad Ixtapalapa, Av. Michoacán y la Purísima s/n, Col. Vicentina, 09340, Ixtapalapa, Mexico*

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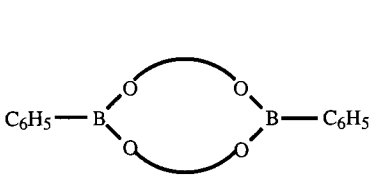
Abstract

In the present contribution a tetrameric macrocyclic compound derived from 2,6-pyridinedimethanol and 3-nitrophenyl boronic acid, as well as 10 new dimeric boronates prepared from 2-salicylideneaminoethanol and different aryl boronic acids such as a 2-methylphenyl-, 3-methylphenyl-, 4-methylphenyl-, 3-methoxyphenyl-, 4-methoxyphenyl-, 3-chlorophenyl-, 4-chlorophenyl-, 3-nitrophenyl-, 3-trifluoromethylphenyl- and 4-fluorophenylboronic acid are described. The tetrameric and three of the dimeric structures have been analyzed by X-ray crystallography, and a series of parameters such as bond length, bond angles, deviation of the boron atom from the boronate mean plane and intermolecular interactions are discussed.

Keywords: Boron; Boronic esters; Macrocyclic chemistry; X-ray crystallography; 2,6-Pyridinedimethanol, 2-salicylideneaminoethanol

1. Introduction

A review of the literature shows that a number of macrocyclic boron compounds are known. Among the simplest structure types are doubly bridged diboronate esters (**1**) [1,2] and triply bridged diborate esters (**2**) [3–7].



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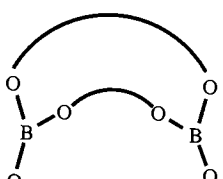

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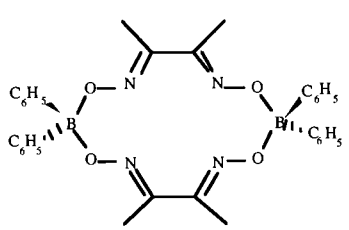
Other interesting macrocyclic boron compounds are the bis(dimethylglyoximato)diphenylboron chelate (**3**) [8–10], the very original boroncryptand (**4**), which has been designed for the complexation of alkali metal cations [11], the cyclotetrakis(triazolylborane) (**5**) [12–14], cyclotetrakis(aminoborazine) derivatives (**6**) [15–17] and the heterocycle B_8S_{16} (**7**), which is composed of four five-membered B_2S_3 rings that are linked through the boron atoms by sulfur atom bridges to form a planar inorganic porphine analog [18–20].



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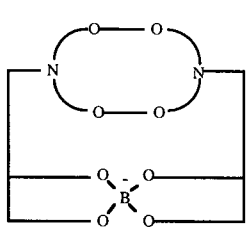

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* Corresponding author. Tel.: +52-5-7473800, ext. 4031; fax: +52-5-7477113.
E-mail address: jfarfan@mail.cinvestav.mx (N. Farfán)

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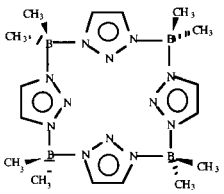

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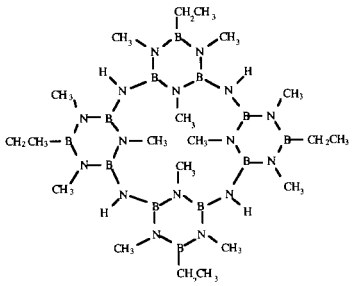

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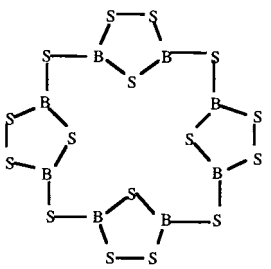

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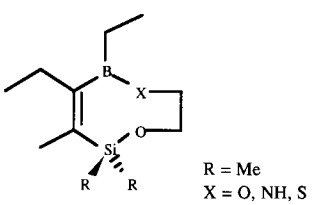
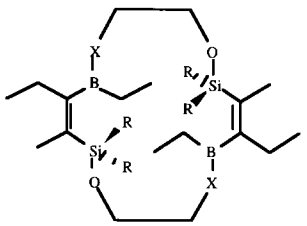
A somewhat uncommon macrocyclic dimer has been isolated during the synthesis and characterization of 1,6-dioxa-2-sila-5-bora-3-cycloalkenes (**8**), where it has been observed that actually the dimeric structure (**9**) is the correct one [21–23].



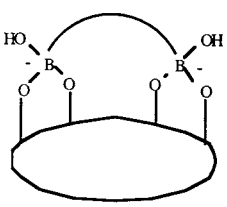
R = Me
X = O, NH, S

8



9

More recently, the synthesis of macrocyclic diboronate esters has received much attention. Compound types **10** and **11** represent the complexation of cyclic saccharides by diboronic acids, whereby the second option of boron stabilization is preferred [24]. Applying the same synthetic principle there have been also synthesized allosteric devices in order to study the saccharide transport through membranes [24].



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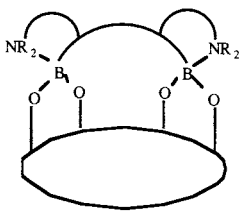
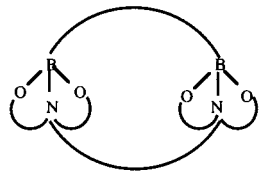


R = H, Me

11

The cyclic diboronate ester **12** represents a similar structure and has been designed as neutral receptor for paraquat. The host–guest complexation is due to the presence of a strong dipolarization directed along the N–B bond [25].



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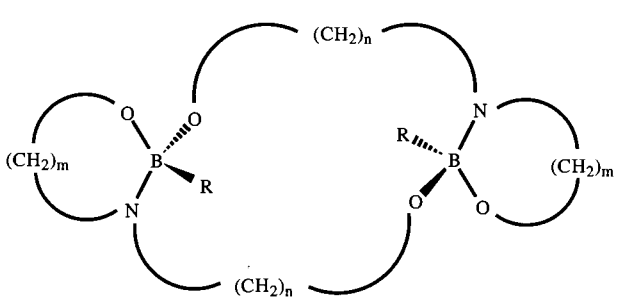
In previous studies of compounds containing nitrogen–boron co-ordination, we have described the preparation of borane complexes with 8-hydroxyquinoline, pyridinealcohols [26,27] and pyridine [28], as well as diphenyl borinates derived from aminoacids [29], ephedrine derivatives [30], pyridinealcohols [31] and piperidine alcohols [32]. These studies were performed to investigate by (dynamic) NMR and X-ray diffraction analyses electronic and steric aspects that influence the nitrogen–boron bond stability. The results obtained were completed by ab initio calculations of different substituted 2-aminoethylborinates at the HF/6-31G** level of theory [33].

In the last few years, we have been also interested in the reaction of phenylboronic acid with tridentate ligands such as phenolethanolamines [34], diethanolamines [35,36], diphenolamines [37], iminodiacetic acid [38] and *N*-alkyl-*N*-(2-hydroxyethyl)glycine [39]. We reported that, in all cases, [3.3.0] heterobicyclic compounds with an intra-molecular nitrogen–boron bond are obtained. Similarly, most salicylideneaminoalcohols were found to react with phenylboronic acid to produce [5.4.0], [4.4.0] and [4.3.0] heterobicyclic structures [40].

Since we have developed a new strategy of synthesis for the preparation of macrocyclic di- and tetrameric boronates [41,42] from iminodialcohols and boronic acids (**13**), we now direct our efforts to the preparation of new macrocyclic boronates. It is thereby important to note that the boronate units are connected by *covalent* B–O bonds and that the hydrolytic stability of these molecules is enhanced by co-ordinative N–B bonds.



R = aryl n= 2,3,4... m= 2, 3

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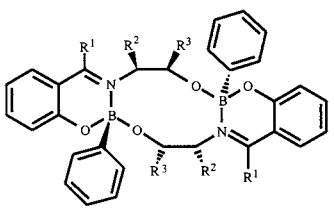
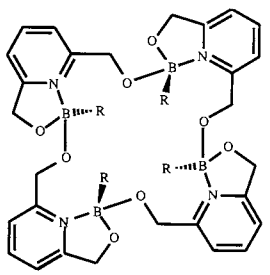
In this context, we recently reported the synthesis of macrocyclic compounds, that consist of a dimeric (**14a**–**e**) and tetrameric (**15**) boronate ring system of 10 and 20 members, respectively [41,42]. Both types of molecules are air-stable and are obtained in high yields by one step syntheses from the corresponding imino dialcohol and phenylboronic acid. The molecular structures of these compounds have been established by X-ray diffraction studies [41,42].



	R^1	R^2	R^3
14a	H	H	H
14b	H	H	Me
14c	H	H	Ph
14d	H	Me	Ph
14e	Me	H	H



R= C_6H_5

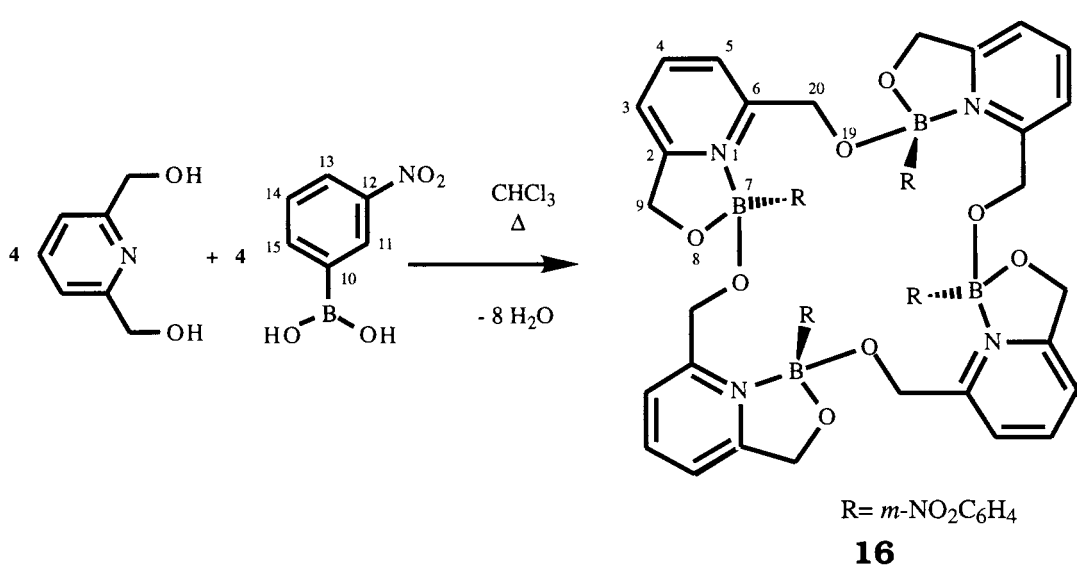
15

Based on the strategy developed to obtain these macrocyclic compounds, it can be expected that tetrameric and dimeric structures are also obtained, when different substituents are introduced in the phenyl ring of the boronic acid. Therefore, macrocycles with a nitro-, methyl-, methoxy,- chloro-, trifluoromethyl- or fluoro substituent in *ortho*, *meta* or *para* position of the phenylboryl group were prepared with the result that in all cases the reaction proceeded to give the expected dimeric or tetrameric structure.

2. Results and discussion

Compound **16** is obtained by condensation of 2,6-pyridinedimethanol with 3-nitrophenylboronic acid in chloroform (Scheme 1). The reaction is finished within 30 min to give a yield of 80%. Crystals suitable for X-ray crystallography have been obtained when the reaction was performed at room temperature without stirring. Experimental data, selected bond lengths and selected bond angles are resumed in Tables 1 and 2.

Normally, 2,6-pyridinedimethanol acts as a tridentate monochelating ligand as it has been shown for a series of complexes with metal ions and organometallic compounds [43–45]. In the case of the smaller boron atom, only one five-membered chelate ring is formed so that the second methyleneoxy group binds to another boron atom. As in the case of compound **15** [41], the formation of a cyclic structure instead of a polymeric one seems to be highly favored owing to the tetrahedral stereochemistry around the boron atom (Fig. 1). The tetrahedral environment of the boron atom and the planarity of the ligand with the collinearity of its primary bonds (the mean deviation of the aliphatic carbon atoms from the mean planes is 0.026 Å in compound **16**) dictate the tetrameric macrocyclic structure formation. The dihedral angles between the four boronate moieties are nearly perpendicular to each other (84.6 and 84.9°, respectively), but they are smaller than in compound **15** with a mean value of 90.7°. The configuration of the boron atoms is alternate so that S_4 symmetry could be expected for the macrocycles **15** and **16**. Actually, in both cases the point group is only



16

Scheme 1. Preparation of compound **16**.

Table 1
Experimental crystallographic data of compounds **16**, **17c**, **17i** and **17j**

	16	**17c**[a,b]	**17i**	**17j**
Crystal Data				
Chemical formula	$C_{52}H_{44}B_4N_8O_{16}$, 4 $CHCl_3$	$C_{32}H_{32}B_2N_2O_4$, 2 H_2O	$C_{32}H_{26}B_2F_6N_2O_4$	$C_{30}H_{26}B_2F_2N_2O_4$
Crystal size (mm)	$0.3\times0.5\times0.5$	$0.30\times0.18\times0.18$	$0.48\times0.48\times0.54$	$0.39\times0.36\times0.24$
MW (g mol^{-1})	1080.20	530.32	638.18	538.17
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Cell parameters				
a (Å)	16.617(1)	11.043(2)	11.210(1)	8.001(1)
b (Å)	18.395(1)	11.287(2)	6.420(1)	9.355(1)
c (Å)	22.766(2)	12.506(3)	20.952(1)	10.467(1)
α (°)	90	83.87(3)	90	113.084(8)
β (°)	93.336(9)	74.69(2)	100.76(1)	97.680(1)
γ (°)	90	80.89(3)	90	111.21(1)
V ($Å^3$)	6947.6(9)	1481.0(5)	1481.30(2)	604.65(2)
Z	4	2	2	1
μ (mm^{-1})	0.55	0.086	0.11	0.100
ρ (Calc.) (Mg m^{-3})	1.49	1.27	1.43	1.47
Data collection[c]				
Scan range (°)	0.50+0.51 tg θ	1.03+1.43 tg θ	0.98+0.84 tg θ	0.98+0.79 tg θ
θ limits (°)	$2<\theta<26$	$2<\theta<23$	$2<\theta<26$	$2<\theta<22$
No. of collected reflections	7228	4443	2331	1549
No. of independent reflections	6814	4102	2185	1445
No. of observed reflections[d]	2523	1744[e]	1276	1169
Refinement[f]				
R[g]	0.058	0.050	0.045	0.036
R_w[h]	0.050	0.130[i]	0.039	0.034
Goof	3.13	1.009	1.59	1.85
No. of variables	452	379	237	222
Maximum Δ/σ	0.001	0.002	0.08	0.02
$\Delta\rho_{min}$ (e $Å^{-3}$)	−0.35	−0.24	−0.17	−0.13
$\Delta\rho_{max}$ (e $Å^{-3}$)	0.46	0.26	0.17	0.13

[a] Program used Shelxs (Sheldrick 1993, version 1.8).
[b] $T=193$ K.
[c] ω–2θ scan; $T=293$ K, $\lambda_{Mo-K_\alpha}=0.71069$ Å.
[d] $(F_o)^2>3\sigma(F_o)^2$.
[e] $F>4\sigma(F)$.
[f] $w=1/\sigma^2$.
[g] $R=\Sigma(\|F_o|-|F_c\|)/\Sigma|F_o|)$.
[h] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w\,F_o^2]^{1/2}$.
[i] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2\}^{1/2}$.

pseudo S_4, whereby the molecular structure of **16** has higher symmetry (C_2-axis) than the one of **15** (no symmetry element). The average distance between two neighboring boron atoms is 5.36 Å for **16** and 5.42 Å for **15**. If all van der Waals interactions are considered, the void in the center of the molecule has a diameter of about 1.37 Å, but the B-aryl groups close the outside of the macrocycle, so that only a channel with a diameter of about 0.60 Å remains open for entrance. The cave should be therefore ideal for the lodging of small atoms or ions like Li^+ or Be^{2+}.

The mean N–B bond length in **16** is 1.650(9) Å and not significantly different from the one in **15** (1.667(9) Å), a fact that is also true for the rest of the bond lengths and bond angles.

The sum of bond angles in the five-membered boronate heterocycles with a mean value of 107.9 (7)° for the five bond angles in both molecules indicates a certain ring strain, that would still be higher in a monomeric species: the N–B–C_{aryl} bond angles with average values of 111.9 (5)° for **16** and 111.9 (5)° for **15** are significantly smaller than 120°.

The ring strain is also expressed by the mean deviation of the boron and oxygen atoms from the boronate mean planes. This average deviation is smaller in compound **16** (0.089 Å for the boron atoms and 0.040 Å for the oxygen atoms in the heterocyclic ring) when compared to compound **15** (0.065 Å for the boron atoms and 0.204 Å for the oxygen atoms), the boronate units are more planar.

Table 2
Selected bond lengths (Å) and bond angles (°) of compound **16**

	Ring B(7)	Ring B(27)
Bond lengths (Å)		
N–B	1.646(9)	1.653(8)
$B–O_{cycle}$	1.454(8)	1.466(7)
$B–O_{chain}$	1.444(8)	1.433(8)
$C–O_{cycle}$	1.391(8)	1.398(7)
$C–O_{chain}$	1.408(6)	1.415(7)
$C–C_{cycle}$	1.479(9)	1.508(8)
$C–N_{cycle}$	1.338(7)	1.343(7)
Bond angles (°)		
$N–B–O_{cycle}$	98.3(5)	98.8(5)
$N–B–O_{chain}$	109.3(5)	109.1(5)
$B–O–C_{cycle}$	114.3(5)	114.8(5)
$B–O–C_{chain}$	118.2(5)	114.9(5)
$O–C–C_{cycle}$	108.0(6)	107.0(5)
$N–C–C_{cycle}$	109.1(6)	109.7(6)
$B–N–C_{cycle}$	109.9(5)	109.7(5)
$N–B–C_{aryl}$	112.2(5)	111.6(5)
$C_{aryl}–B–O_{cycle}$	112.6(5)	111.1(5)
$C_{aryl}–B–O_{chain}$	109.3(6)	111.6(5)
$O_{chain}–B–O_{cycle}$	114.7(5)	114.0(5)

Compound **16** is nearly insoluble in all common solvents, and spectra could only be recorded from DMSO-d_6. However, the water present in the solvent decomposed part of the small amount of dissolved complex. The ^{1}H-NMR spectrum shows only one pattern of signals for the four boronate units of the tetrameric species so that the already proposed S_4 symmetry of the macrocycle in solution is most likely. The two $–OCH_2$ groups of each boronate unit appear at different chemical shifts in both the ^{1}H- and ^{13}C-NMR spectra (Fig. 2) and give rise to AB systems ($^2J = 18$ Hz, $\Delta\delta = 0.30$ ppm and $\Delta\delta = 0.67$ ppm, respectively). The high field shift of the bridging methyleneoxy group is due to a protection by the neighboring pyridine ring as can be seen from the molecular structure (Fig. 1). The most striking difference is the extreme low field shift of H-5 in the ^{1}H-NMR spectrum ($\delta =$ 7.99 ppm for H-5 and $\delta = 7.45$ ppm for H-3) that may be explained by an interaction with the O-19 atom (H-5···O-19 2.46 Å) [46].

The ^{1}H-NMR signals of the 3-nitrophenyl group are shielded due to the N–B coordination, since this bond diminishes the electron withdrawing effect of the tri-coordinated boron atom.

In accordance to the preparation of compounds **14a**–**e** [41,42], a series of arylboronic acids that include 2-methylphenyl-, 3-methylphenyl-, 4-methylphenyl-, 3-methoxyphenyl-, 4-methoxyphenyl-, 3-chlorophenyl-, 4-chlorophenyl-, 3-nitrophenyl-, 3-trifluoromethylphenyl- and 4-fluorophenylboronic acid were reacted with 2-(salicylideneamino)-1-hydroxyethane, whereupon the dimeric boronates **17a**–**j** were obtained (Scheme 2).

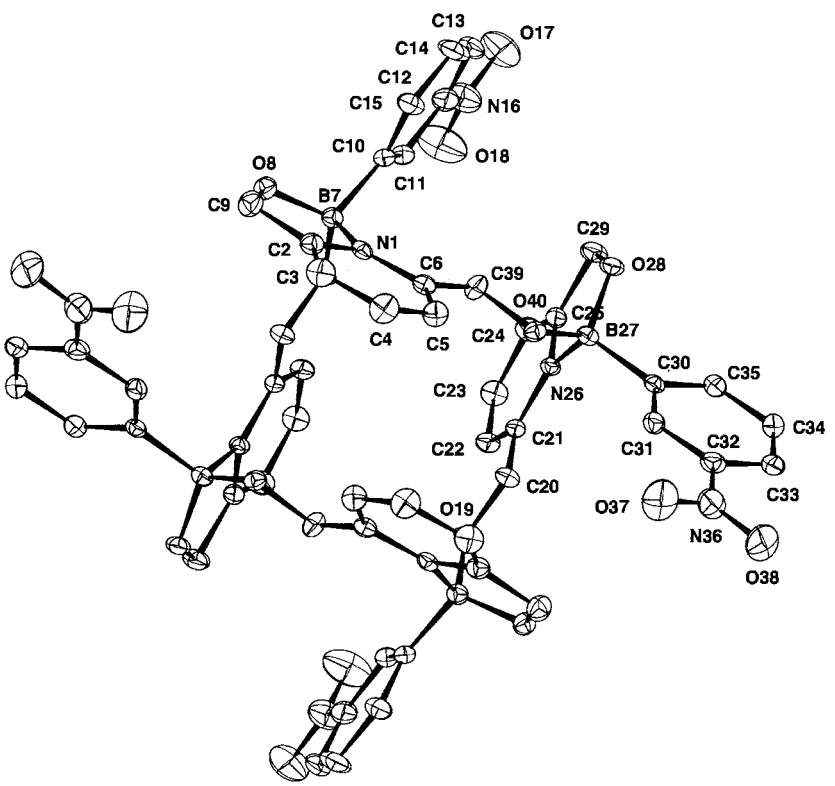


Fig. 1. Molecular structure of compound **16**.

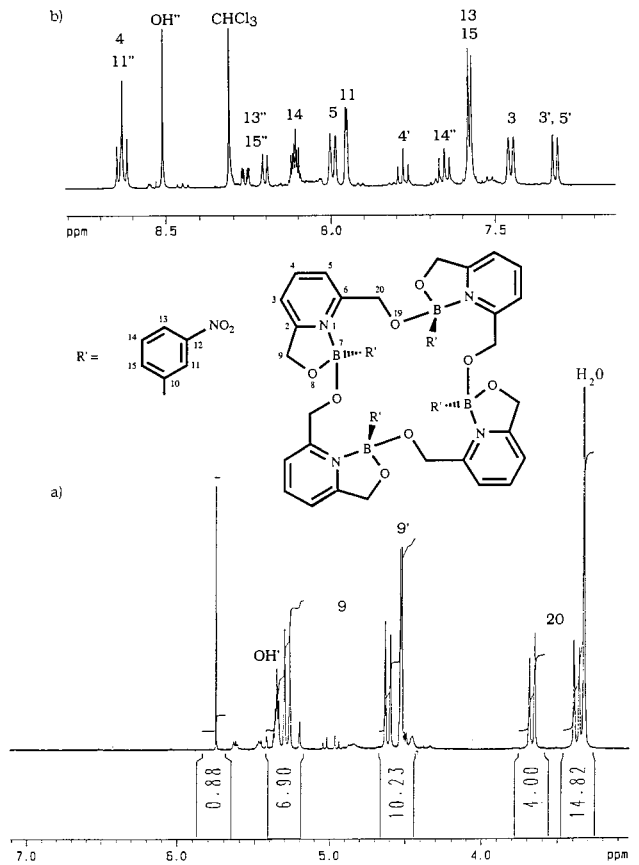
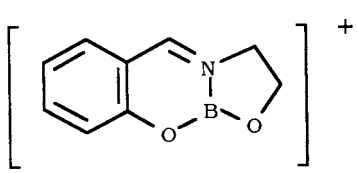


Fig. 2. ^{1}H-NMR spectrum of compound **16** in DMSO-d_6: (a) aliphatic region; (b) aromatic region. The signals of the starting materials are marked with ′ for the 2,6-pyridinedimethanol and ″ for the 3-nitrophenylboronic acid. The signal of H_2O results from an impurity in DMSO-d_6. $CHCl_3$ is forming part of the crystal lattice of compound **16**.

The reaction provides the highest yields (82–97%) in benzene or tetrahydrofuran, if a Dean–Stark trap is used to separate the water formed during the condensation.

The dimeric structures of compounds **17a–j** could be established by mass spectrometry, although in all cases only the $[M–Ar]^+$ ion was detected owing to the easy loss of the corresponding aryl radical [47–52]. At the same time the presence of different substituents at the B-phenyl group confirms the fragmentation pattern proposed for compounds **14a–e**. It is interesting to note that the highly dominating base peaks correspond to the cation **18**, where the ring strain is lowered due to the sp^2 hybridization of the boron atom.



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Thereby, the dimeric dication structure can be excluded on the basis of the isotopic abundance (^{10}B 19.6%, ^{11}B 80.4%) that would lead to a different relationship of the isotope peaks in a compound with two boron atoms [53].

The IR spectra show that the wavenumber of the C=N bond in the dimers with substituents in *para* position are shifted to higher energy by 2–6 cm^{-1}. In all cases the corresponding wavenumbers are between 1634 and 1640 cm^{-1}.

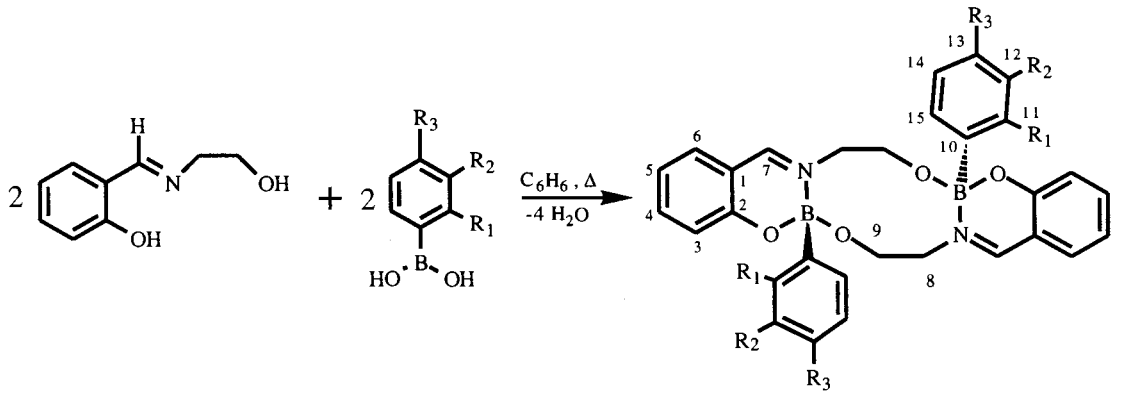
The dimeric compounds **17a–j** are nearly insoluble in all common solvents, and NMR spectra could only be recorded in the case of compounds **17b**, **17f** and **17g**. A comparison of the ^{1}H-NMR data between the ligand and the dimeric compounds **17b**, **17f** and **17g** shows that the signal of the azomethine hydrogen atom is shifted downfield ($\Delta\delta = 0.48$, 0.52 and 0.49 ppm, respectively) with formation of the co-ordinative N–B bond. The signals of the methylene hydrogens atoms are split in diastereotopic signals ($\Delta\delta = 0.08–0.14$ ppm for H-8 and $\Delta\delta = 0.28–0.35$ ppm for H-9). In comparison to the ligand the ^{13}C-NMR signals of the azomethine, the C-1, the C-2 and C-6 carbon atoms are shifted upfield, while the ones of C-3, C-4 and C-5 are shifted downfield. The $–OCH_2$ group its shifted upfield ($\Delta\delta = 1.6$, 1.4 and 1.7 ppm) and the $–NCH_2$ group is shifted downfield ($\Delta\delta = 0.4$, 0.7 and 0.3 ppm) in **17b**, **17f** and **17g**, respectively, with respect to the ligand.

The tetracoordination of the boron atom can be seen from the ^{11}B-NMR spectra of compounds **17b**, **17f** and **17g**, where values of $\delta = 3.0$ ppm ($h_{1/2} = 390$ Hz), 6.6 ppm ($h_{1/2} = 600$ Hz) and 2.1 ppm ($h_{1/2} = 1126$ Hz), respectively, have been measured. These shifts can be compared to those of diphenylboron chelates that have been synthesized from different amino-substituted salicylaldehyde azomethines [47,48].

One of the aims of the present investigation was to analyze, if the dimeric structures are also formed in the presence of substituents with different electronic and steric effects at the B-phenyl group. Owing to the insolubility of compounds **17a–j** (only **17b**, **17f** and **17g** dissolve slightly in chloroform) an X-ray crystallographic study had to be undertaken in order to obtain more detailed information. Crystals could be grown for the complexes **17c**, **17i** and **17j** and their molecular structures are presented in Figs. 3–5. The asymmetric unit of **17c** consists of a water molecule and two half dimers. Experimental data are summarized in Table 1 and selected bond lengths and bond angles are presented in Tables 2 and 3.

As in the case of compounds **14a–b** and **14d–e**, in all four crystal structures the dimeric molecules are located at an inversion center and belong therefore to the C_i point group.

A comparison of the bond lengths and bond angles in Table 3 with the data of compound **14a** [41,42]



	R_1	R_2	R_3
17a	CH_3	H	H
17b	H	CH_3	H
17c	H	H	CH_3
17d	H	OCH_3	H
17e	H	H	OCH_3
17f	H	Cl	H
17g	H	H	Cl
17h	H	NO_2	H
17i	H	CF_3	H
17j	H	H	F

Scheme 2. Preparation of compounds **17a**–**j**.

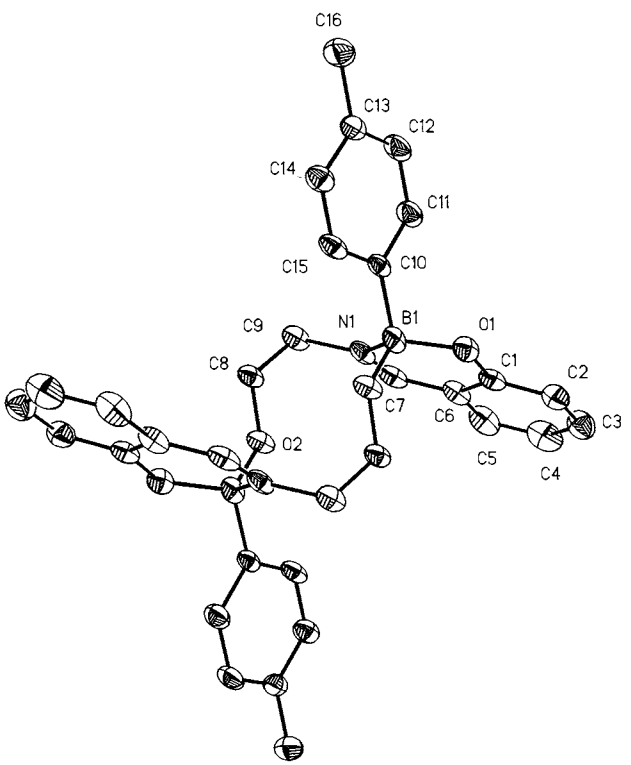


Fig. 3. Molecular structure of compound **17c**.

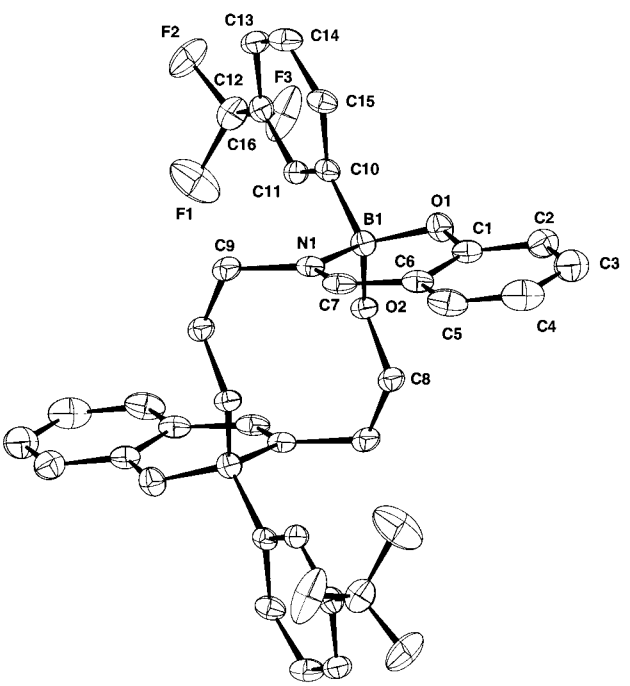


Fig. 4. Molecular structure of compound **17i**.

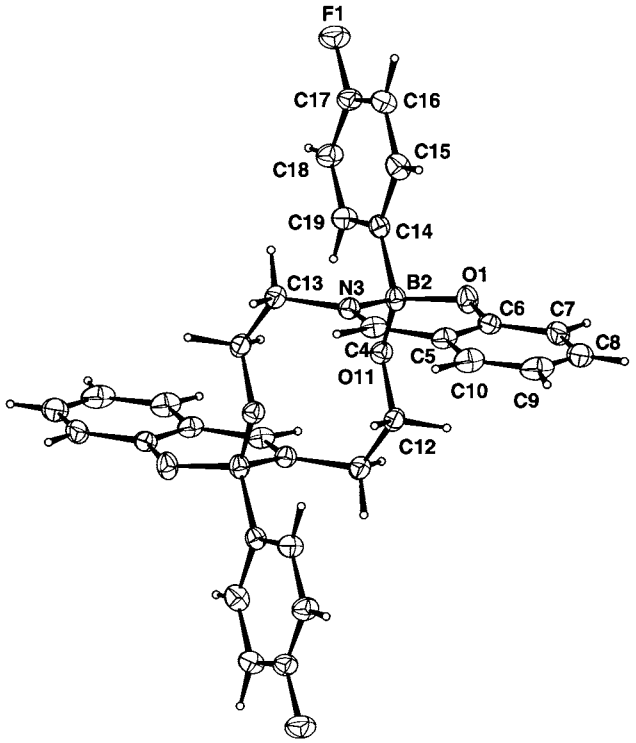


Fig. 5. Molecular structure of compound **17j**.

shows no significant differences, so that the electronic and/or steric effects of the substituents in *meta* or *para* positions of the B-phenyl moiety should be relatively small. In the case of electron withdrawing substituents, we would have expected a stronger effect on the N–B bond strength that could lead to its rupture by heating and enhancement of the ring size from 10 to 18 members. A variable temperature ^{1}H-NMR experiment of the slightly soluble compound **17b** has shown that this does not happen in the range of 25–110°C in DMSO-d_6. At higher temperatures the macrocycle starts to decompose.

3. Conclusions

The present contribution shows that dimeric compounds are the preferred reaction product of 2-salicylideneaminoethanol with arylboronic acids. Thereby, the presence of electron donating or withdrawing groups in *ortho*, *meta* or *para* positions does not alter the course of the reaction. The tetrameric compound with 3-nitrophenyl boronic acid presents the same behavior. We can conclude that the determining factor in the synthesis of these boron macrocycles is the ligand structure. The crystal structure analyses of **16**, **17c**, **17i** and **17j** show that the boron atom prefers an alternate configuration in the macrocyclic ring systems.

Together with the fact that condensation reactions are based on equilibria, a self assembly mechanism can be proposed [14,54]. Self assembly is the spontaneous association of different components to form a complex, highly ordered macromolecular or supramolecular building that is favored thermodynamically [55].

The substituents at the aryl group allow us to confirm that the fragmentation pattern in mass spectrometry involves the initial loss of the aryl substituent at the boron atom and that the base peak corresponds to a monomeric structure with a sigma boron–nitrogen bond.

4. Perspectives

Our interest in the synthesis of the macrocyclic boronates presented in this and other contributions [41,42] becomes clear, if one thinks of possible applications in host–guest chemistry. The advantage of these macrocycles lies in their easy, one step syntheses from readily available starting materials and there should be no doubt that it is possible to obtain other structures with 12, 14, 16, 18 etc. members forming the macrocyclic ring.

Once a series of compounds is known, one can start to introduce functional groups in the macrocycles that can enhance the complexing ability of these boronates or one can try to rupture the coordinative N–B bond in order to enhance the ring size of the macrocycle and to liberate the Lewis acid boron atom as co-ordination site for Lewis bases or anions.

We entered this field only recently and problems we have to deal with actually are related to low solubility, small cage radius and relatively strong N–B bonds in our complexes. In order to start the next millenium well prepared in boron chemistry, we hope to find solutions to some of these problems soon.

5. Experimental

^{1}H- and ^{13}C-NMR spectra were recorded on Jeol GSX 270, Jeol Eclipse + 400 and Bruker DMX-500 spectrometers. Special techniques (COSY, HETCOR, NOESY) were applied when necessary to assign the spectra adequately. Chemical shifts (ppm) are relative to $(CH_3)_4Si$ (^{1}H and ^{13}C) and $BF_3{\cdot}OEt_2$. Coupling constants are quoted in Hz. Infrared spectra were recorded on a Perkin–Elmer 16F-PC FT-IR spectrophotometer. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncorrected.

A selected monocrystal was set upon an automatic diffractometer, unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 24 well centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Corrections were made for Lorentz and polarization effects. Absorption corrections were not applied.

Table 3
Selected bond lengths (Å) and bond angles (°) of compounds **14a**, **17c**, **17i** and **17j**

	14a	**17c**	**17i**	**17j**
Bond lengths (Å)				
$B–O_{cycle}$	1.492(3)	1.500(7) / 1.493(6)	1.473(5)	1.492(4)
$B–O_{chain}$	1.433(3)	1.431(7) / 1 434(6)	1.469(5)	1.432(4)
B–N	1.624(3)	1.639(7) / 1.606(6)	1.619(6)	1.613(4)
$C_{ph}–O_{cycle}$	1.332(3)	1.335(6) / 1.347(5)	1.341(5)	1.333(3)
C=N	1.291(3)	1.275(7) / 1.294(5)	1.295(5)	1.292(4)
C–N	1.477(3)	1.467(6) / 1.460(5)	1.484(5)	1.482(4)
$C_{aliph}–O_{chain}$	1.412(3)	1.411(6) / 1.408(5)	1.419(4)	1.415(4)
$C_{aliph}–C_{aliph}$	1.512(3)	1.498(7) / 1.527(6)	1.517(6)	1.512(5)
$B–C_{aryl}$	1.601(3)	1.579(8) / 1.583(6)	1.593(6)	1.601(5)
Bond angles (°)				
$O_{cycle}–B–N$	106.5(3)	105.9(4) / 106.3(3)	107.6(4)	106.7(3)
$O_{cycle}–B–C$	109.4(2)	110.1 (4) / 110.2(4)	110.4(4)	109.2(3)
$O_{cycle}–B–O$	111.6(2)	110.6(4) / 111.4(4)	110.9(4)	111.9(3)
$N–B–C_{aryl}$	108.1(2)	108.3(4) / 110.7(4)	108.4(3)	108.8(3)
$N–B–O_{chain}$	109.0(2)	109.0(4) / 109.3(4)	107.6(4)	109.1(3)
$C–B–O_{chain}$	111.9(2)	112.8(5) / 108.8(4)	110.4(4)	111.1(3)
$B–N–C_{cycle}$	121.6(4)	122.8(5) / 122.3(4)	121.5(4)	122.7(3)
$B–O–C_{cycle}$	126.5(2)	126.3(4) / 123.1(4)	125.2(4)	125.7(3)
$B–O–C_{chain}$	118.7(2)	119.2(4) / 121.0(3)	119.0(3)	118.7(2)
$N–C_{cycle}–C_{cycle}$	122.8(2)	122.8(5) / 121.9(4)	122.6(4)	122.1(3)
$N–C_{chain}–C_{chain}$	113.0(2)	113.3(4) / 112.0(3)	112.3(3)	112.5(3)
$C_{cycle}–N–C_{chain}$	118.2(2)	118.1(4) / 118.5(5)	118.5(4)	120.7(3)
$O_{cycle}–C_{cycle}–C_{cycle}$	120.4(2)	120.1(6) / 120.4(4)	119.7(5)	120.7(3)
$C_{cycle}–C_{cycle}–C_{cycle}$	119.4(2)	119.7(6) / 119.4(4)	120.3(4)	119.6(3)
Deviation from the boronate mean plane (Å)				
B	−0.129	−0.233 /	−0.170	−0.169
O	0.070	0.047 / 0.072	0.055	0.070
C	0.037	−0.023 / 0.018	0.096	0.032
Intramolecular interactions (Å)				
C–H···O	2.43	2.46 / 2.52[a]	2.52[a]	2.43

[a] H atoms have been calculated.

Computations were performed by using CRYSTALS [56] adapted on a Micro Vax II. Atomic form factors for neutral B, C, N, O, and H were taken from lit. [57].

The structures were solved by direct methods using the SHELXS86 program [58]. 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 refinements were carried out by minimizing $\Sigma w(\|F_o| - |F_c\|)^2$, where F_o and F_c are the observed and calculated structure factors. Models reached convergence with $R = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$. Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation being less than 0.1 and no significant features in the final difference map. In all cases only reflections on the basis of Friedel's law have been collected and a reflections to parameter ratio > 5 has been considered sufficient for the kind of studies performed in here.

Supplementary material available: tables of atomic coordinates, thermal parameters, bond lengths and angles as well as observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Center.

Elemental microanalyses were performed by Oneida Research Services, Whitesboro, NY 13492.

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

*5.1. Preparation of 4,14,24,34-tetra(3-nitrophenyl) [3,5,13,15,23,25,33,35]octaoxa[41,42,43,44]tetraaza-[4,14,24,34]tetraborapentacyclo[31.3.1.1^{7,11}.1^{17,21}.1^{27,31}]-dotriaconta-1(41),7,9,11(42),17,19,21(43),27, 29,31(44),37,39-dodecaene (**16**)*

Compound **16** was prepared from 0.10 g (0.72 mmol) of 2,6-pyridinedimethanol and 0.12 g (0.72 mmol) of 3-nitrophenylboronic acid in chloroform. The product obtained is a colorless solid (0.16 g, 0.14 mmol), that is slightly soluble in DMSO. m.p. (dec.) 284–286°C, yield 80%.^{1}H-NMR (500 MHz, DMSO-d_6) δ (ppm): 3.37–3.67 (8H, AB, J 18 Hz, H-20), 4.61–5.28 (8H, AX, J 18 Hz, H-9), 7.45 (4H, d, H-3), 7.51 (8H, d, H-13, H-15), 7.95

(4H, d, H-11), 7.99 (4H, d, H-5), 8.11 (4H, m, H-14), 8.63 (4H, t, H-4); ^{13}C-NMR (125.8 MHz, DMSO-d_6) δ (ppm): 57.4 (C-20), 68.8 (C-9), 118.4 (C-5), 120.3 (C-3), 122.0 (C-14), 125.6 (C-11), 128.6 (C-13), 138.7 (C-15), 143.9 (C-4), 147.2 (C-12), 147.8 (C-10), 155.2, 158.2 (C-2, C-6); IR (KBr) ν (cm^{-1}): 3068 (C–$H_{arom.}$), 2928 (C–$H_{aliph.}$), 2850, 1654, 1648 (C=N), 1636, 1622 (C=N, C=C), 1252, 1198, 1092 (B–C, B–O, C–O), 808, 792, 732, 710 (C–$H_{arom.}$). Elemental analysis Anal. Calc.: C, 57.82, H, 4.11, N, 10.37%. Found: C, 57.94, H, 4.13, N, 9.86%.

5.2. Preparation of 2-(salicylideneamino)-1-hydroxyethane

2-(Salicylideneamino)-1-hydroxyethane (H_2SAE) was prepared from equimolar quantities of 2-aminoethanol and salicylaldehyde under reflux in benzene for 30 min. The solvent and the water formed during the reaction were removed by a Dean–Stark trap to obtain a yellow oil (2.98 g, 18.04 mmol), yield 95%.

5.3. Preparation of the boronates: general procedure for the preparation of compounds **17a–j**

The following procedure is representative for the preparation of all dimeric compounds described in this study.

Equimolar quantities of the corresponding arylboronic acid and H_2SAE were refluxed in 10 ml benzene for 30 min. The solvent and water formed during the reaction were removed by a Dean–Stark trap. The product was filtered, washed and dried.

5.3.1. 2,11-Di-(2′-methylphenyl)dibenzo[h,q]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (**17a**)

Compound **17a** was prepared from 0.50 g (3.00 mmol) of H_2SAE and 0.41 g (3.00 mmol) of 2-methylphenylboronic acid. The product obtained is a white solid (0.70 g 1.31 mmol), m.p. 293–294°C, yield 88%. MS (EI, 70 eV) m/z: 439 [M^+–C_7H_7, 7], 440 (2), 438 (3), 266 (1.5), 175 (10), 174 (100), 173 (26), 132 (2). IR (KBr) ν (cm^{-1}): 3058 (w), 3012 (w), 2970 (w), 2936 (w), 2858 (w), 1638 (C=N, s), 1560 (s), 1606 (s), 1464 (s), 1448 (s), 1310 (s), 1234 (s), 1202 (s), 1186 (s), 1150 (s), 1114 (s), 1016 (s), 966 (s), 746 (s), 740 (s). Elemental analysis Calc.: C, 72.48, H, 6.08, N, 5.29%. found: C, 72.16, H, 6.04, N, 5.21%.

5.3.2. 2,11-Di-(3′-methylphenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-7,16-diene (**17b**)

Compound **17b** was prepared from 0.50 g (3.00 mmol) of H_2SAE and 0.41 g (3.00 mmol) of 3-methylphenylboronic acid. The product obtained is a white solid (0.65 g, 1.22 mmol) that is slightly soluble in chloroform, m.p. 287–289°C, yield 82%. MS (EI, 70 eV) m/z: 439 [M^+–C_7H_7, 13], 440 (4), 438 (6), 266 (2), 264 (2), 175 (10) 174 (100), 173 (27) 132 (2), 91 (3). IR (KBr) ν (cm^{-1}): 3040 (w), 3022 (w), 2944 (w), 2914 (w), 2850 (w), 1638 (C=N, s), 1160 (s), 1482 (s), 1310 (s), 1170 (s), 1150 (s), 970 (s), 770 (s), 756 (s). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.49 (1H, s, H-7), 7.51 (1H, dt, J 7.7, 1.5 Hz, H-4), 7.47 (1H, dd, J 7.7, 1.5 Hz, H-6), 7.34 (1H, s, H-11), 7.32 (1H, d, J 7.3, Hz, H-15), 7.14 (1H, t, J 7.3 Hz, H-14), 7.03 (1H, d, J 7.7 Hz, H-3), 7.02 (1H, d, J 7.3, Hz, H-13), 6.94 (1H, dt, J 7.7, 1.46 Hz, H-5), 3.64 (1H, dt, J 10.1, 3.1 Hz, H-9), 3.50 (1H, dt, J 11.8, 3.6 Hz, H-8), 3.42 (1H, dd, J 11.8, 3.6 Hz, H-8′), 3.29 (1H, dd, J 10.1, 3.1 Hz, H-9′), 2.28 (3H, s, Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 164.4 (C-7), 160.8 (C-2), 137.5 (C-4), 136.3 (C-12) 132.9 (C-11), 131.0 (C-6), 129.1 (C-15), 127.8 (C-13), 127.3 (C-14), 119.0 (C-3), 118.7 (C-5), 115.9 (C-1), 60.6 (C-8), 59.8 (C-9), 21.7 (Me); ^{11}B-NMR (128 MHz, $CDCl_3$) δ (ppm): 3.5 ($h_{1/2}$ = 399 Hz); Elemental analysis Calc.: C, 72.48, H, 6.08, N, 5.29%. Found: C, 72.34, H, 5.98, N, 5.35%.

5.3.3. 2,11-Di-(4′-methylphenyl)dibenzo[h,q]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (**17c**)

Compound **17c** was prepared from 0.50 g (3.00 mmol) of H_2SAE and 0.41 g (3.00 mmol) of 4-methylphenylboronic acid. The product obtained is a white solid (0.72 g, 1.35 mmol) that is insoluble in all common solvents. Crystals suitable for X-ray diffraction were obtained, when the reaction was performed in THF at room temperature without stirring, m.p. 291–293°C, yield 91%. MS (EI, 70 eV) m/z: 439 [M^+–C_7H_7, 13], 440 (4), 438 (6), 266 (9), 175 (10) 174 (100), 173 (26), 132 (2), 91(2). IR (KBr) ν (cm^{-1}): 3060 (w), 2940 (w), 2916 (w), 2848 (w), 1640 (C=N, s), 1606 (s), 1560 (s), 1482 (s), 1450 (s), 1440 (s), 1388 (s), 1308 (s), 1234 (s) 1218 (s), 1194 (s), 1180 (s), 1150 (s), 1138 (s), 1128 (s), 1110 (s), 1026 (s), 1018 (s), 962 (s) 928 (s), 778 (s), 754 (s), 738 (s); Elemental analysis ($C_{32}H_{32}B_2N_2O_4 \cdot H_2O$) Calc.: C, 70.01, H, 6.20, N, 5.10%. Found: C, 69.58, H, 5.77, N, 4.96%.

5.3.4. 2,11-Di-(3′-methoxyphenyl)dibenzo[h,q]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (**17d**)

Compound **17d** was prepared from 0.50 g (3.00 mmol) of H_2SAE and 0.45 g (3.00 mmol) of 3-methoxyphenylboronic acid. The product obtained is a yellow solid (0.78 g, 1.42 mmol) that is insoluble in all common solvents, m.p. 278–280°C, yield 92%. MS (EI, 70 eV) m/z: 455 [M^+–C_7H_7O, 4], 456 (1), 454 (2), 281 (3), 175 (16), 174 (100), 173 (40), 148 (18), 132 (4), 77 (7). IR (KBr) ν (cm^{-1}) 3008 (w), 2956 (w), 2934 (w), 2910 (w), 2854 (w), 2832 (w), 1634 (C=N, s), 1606 (s), 1578 (s), 1560 (s), 1480 (s), 1408 (s), 1308 (s), 1254 (s), 1238 (s), 1174 (s), 1150 (s), 1138 (s), 1122 (s), 1026 (s), 1008 (s), 986 (s), 786 (s), 778 (s), 752 (s); Elemental analysis Anal. Calc.: C, 68.35, H, 5.73, N, 4.98%. Found: C, 67.48, H, 5.70, N, 4.87%.

*5.3.5. 2,11-Di-(4′-methoxyphenyl)dibenzo[h,q]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (**17e**)*

Compound **17e** was prepared from 0.50 g (3.00 mmol) of H_2SAE and 0.45 g (3.00 mmol) of 4-methoxyphenylboronic acid. The product obtained is a yellow solid (0.75 g, 1.33 mmol) that is insoluble in all common solvents, m.p. 283–285°C, yield 89%. MS (EI, 70 eV) *m/z*: 455 [M^+–C_7H_7O, 11], 456 (3), 454 (49), 281 (3), 280 (3), 175 (20), 174 (100), 173 (51), 148 (18). IR (KBr) ν (cm^{-1}) 3024 (w), 2962 (w), 2928 (w), 2870 (w), 2836 (w), 2748 (w), 1640 (C=N, s), 1600 (s), 1558 (s), 1504 (s), 1450 (s), 1440 (s), 1388 (s), 1308 (s), 1234 (s), 1218 (s), 1194 (s), 1234 (s), 1218 (s), 1200 (s), 1170 (s), 1148 (s), 1138 (s), 1124 (s), 1110 (s), 1024 (s), 1014 (s), 994 (s), 928 (s), 814 (s), 784 (s), 750 (s), 584 (s); Elemental analysis ($C_{32}H_{32}B_2N_2O_6 \cdot H_2O$) Calc.: C, 66.17, H, 5.89, N, 4.82%. Found: C, 66.66, H, 5.34, N, 4.89%.

*5.3.6. 2,11-Di-(3′-chlorophenyl)dibenzo[h,q]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (**17f**)*

Compound **17f** was prepared from 0.50 g (3.00 mmol) of H_2SAE and 0.47 g (3.00 mmol) of 3-chlorophenylboronic acid. The product obtained is a yellow solid (0.77 g, 1.35 mmol) that is slightly soluble in chloroform, m.p. 288–290°C, yield 90%. MS (EI, 70 eV) *m/z:* 459 [M^+–C_6H_4Cl, 10], 460 (4), 461 (3), 175 (13), 174 (100), 173 (34), 148 (10). IR (KBr) ν (cm^{-1}): 3046 (w), 2936 (w), 2864 (w), 1636 (C=N, s), 1608 (s), 1560 (s), 1480 (s), 1462 (s), 1448 (s), 1396 (s), 1304 (s), 1234 (s) 1194 (s), 1152 (s), 1140 (s), 1112 (s), 1090 (s) 1022 (s), 772 (s), 752 (s), 742 (s), 722 (s), 698 (s); ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 8.52 (1H, s, H-7), 7.59 (1H, dt, *J* 7.5, 1.5 Hz, H-4), 7.57 (1H, dd, *J* 7.7, 1.5 Hz, H-6), 7.54 (1H, d, *J* 1, Hz, H-11), 7.20 (1H, dd, *J* 8.4, 1.4 Hz, H-15), 7.19 (1H, dd, *J* 8.4, 1.4 Hz, H-13), 7.17 (1H, dt, *J* 8.4, 1.4 Hz, H-14), 7.05 (1H, d, *J* 8.1 Hz, H-3), 7.00 (1H, dt, *J* 7.7, 1.5 Hz, H-5), 3.60 (1H, dt, *J* 10.7, 2.9 Hz, H-9), 3.50 (1H, dt, *J* 10.5, 2.7 Hz, H-8), 3.40 (1H, dd, *J* 10.4, 2.3 Hz, H-8′), 3.32 (1H, dd, *J* 10.2, 2.3 Hz, H-9′); ^{13}C-NMR (75.47 MHz, $CDCl_3$) δ (ppm): 165.2 (C-7), 160.9 (C-2), 138.3 (C-4) 134.0 (C-12) 132.5 (C-11), 131.7 (C-6), 129.3 (C-15), 127.6 (C-13), 130.4 (C-14), 119.6 (C-3), 119.3 (C-5), 116.2 (C-1), 60.8 (C-8), 60.1 (C-9); ^{11}B-NMR (96.3 MHz, $CDCl_3$) δ (ppm): 6.6 ($h_{1/2} = 600$ Hz); Elemental analysis Calc.: C, 63.04, H, 4.59, N, 4.90%. Found: C, 63.58, H, 4.83, N, 5.35%.

*5.3.7. 2,11-Di-(4′-chlorophenyl)dibenzo[h,q]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (**17g**)*

Compound **17g** was prepared from 0.50 g (3.00 mmol) of H_2SAE and 0.47 g (3.00 mmol) of 4-chlorophenylboronic acid. The product obtained is a yellow solid (0.82 g 1.35 mmol) that is slightly soluble in chloroform, m.p. 292–294°C, yield 95%. MS (EI, 70 eV) *m/z:* 459 [M^+–C_6H_4Cl, 7], 460 (3), 461 (2), 255 (2), 254 (4), 175 (11), 174 (100), 173 (28), 148 (9); IR (KBr) ν (cm^{-1}): 2944 (w), 2856 (w), 1640 (C=N, s), 1636 (s),1560 (s), 1480 (s), 1308 (s), 1216 (s), 1198 (s), 1150 (s), 1138 (s), 1126 (s) 1150 (s), 1110 (s), 1086 (s), 1022 (s), 1014 (s), 966 (s), 754 (s); ^{1}H-NMR (270 MHz, $CDCl_3$) δ (ppm): 8.49 (1H, s, H-7), 7.53 (1H, dt, *J* 7.8, 1.7 Hz, H-4), 7.46 (1H, dd, *J* 8.1, 1.7 Hz, H-6), 7.43 (2H, d, *J* 8.4 Hz, H-11), 7.20 (2H, d, *J* 8.4 Hz, H-12), 7.01 (1H, d, *J* 7.8 Hz, H-3), 6.96 (1H, t, *J* 8.1, Hz, H-5), 3.58 (1H, dt, *J* 9.15, 1.98 Hz, H-9), 3.48 (1H, dt, *J* 11.6, 3.7 Hz, H-8), 3.34 (1H, dd, *J* 11.2, 3.7 Hz, H-8′), 3.28 (1H, dd, *J* 10.2, 2.96 Hz, H-9′); ^{13}C-NMR (68 MHz, $CDCl_3$) δ (ppm): 164.7 (C-7), 160.7 (C-2), 138.0 (C-4) 133.5 (C-12) 133.2 (C-11), 131.1 (C-6), 127.5 (C-13), 119.2 (C-3), 119.0 (C-5), 115.8 (C-1), 60.5 (C-8), 59.7 (C-9); ^{11}B-NMR (87 MHz, $CDCl_3$) δ (ppm): 2.14 ($h_{1/2} = 1126$ Hz); Elemental analysis Anal. Calc.: C, 63.04, H, 4.59, N, 4.90%. Found: C, 62.64, H, 4.54, N, 4.70%.

*5.3.8. 2,11-Di-(3-nitrophenyl)dibenzo[h,q]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (**17h**)*

Compound **17h** was prepared from 0.50 g (3.00 mmol) of H_2SAE and 0.501 g (3.00 mmol) of 3′-nitrophenylboronic acid. The product obtained is a white solid (0.83 g, 1.40 mmol) that is insoluble in all common solvents, m.p. 300–302°C, yield 93%; MS (EI, 70 eV) *m/z:* 470 [M^+–$C_6H_4NO_2$, 3], 471 (1), 469 (2), 351 (1), 297 (2), 296 (3), 175 (10), 174 (100), 173 (26), 148 (6); IR (KBr) ν (cm^{-1}): 3060 (w), 2972 (w), 2932 (w), 2918 (w), 2872 (w), 2856 (w), 1636 (C=N, s), 1616 (s), 1558 (s), 1516 (s), 1480 (s), 1462 (s), 1448 (s), 1344 (s), 1304 (s) 1234 (s), 1150 (s), 1140 (s), 1132 (s), 1010 (s) 1094 (s), 1028 (s), 984 (s), 968 (s), 762 (s), 732 (s), 708 (s); Elemental analysis Calc.: C, 60.84, H, 4.42, N, 9.45%. Found: C, 60.31, H, 4.24, N, 9.41%.

*5.3.9. 2,11-Di-(3′-trifluoromethylphenyl)dibenzo[h,q]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (**17i**)*

Compound **17i** was prepared from 0.50 g (3.00 mmol) of H_2SAE and 0.56 g (3.00 mmol) of 3′-trifluoromethylphenylboronic acid. The product obtained is a yellow solid (0.92 g, 1.44 mmol) that is insoluble in all common solvents. Crystals suitable for X-ray diffraction were obtained, when the reaction was performed in THF at r.t. without stirring, m.p. 290–292°C, yield 96%. MS (EI, 70 eV) *m/z:* 493 [M^+–$C_7H_4F_3$, 4], 494 (1), 492 (2), 288 (7), 175 (11), 174 (100), 173 (27), 148 (6); IR (KBr) ν (cm^{-1}): 3064 (w), 3034 (w), 2946 (w), 2876 (w), 1640 (C=N, s), 1608

(s), 1560 (s), 1482 (s), 1330 (s), 1308 (s), 1234 (s), 1190 (s), 1176 (s) 1162 (s), 1138 (s), 1118 (s), 1090 (s), 1018 (s) 980 (s), 970 (s), 786 (s), 762 (s), 708(s), 686 (s), 680 (s); Elemental analysis Anal. Calc.: C, 60.24, H, 4.10, N, 4.38%. Found: C, 60.01, H, 4.00, N, 4.35%.

*5.3.10. 2,11-Di-(4′-fluorophenyl)dibenzo[h,q]-7,16-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene (**17j**)*

Compound **17j** was prepared from 0.50 g (3.00 mmol) of H_2SAE and 0.42 g (3.00 mmol) of 4′-fluorophenylboronic acid. The product obtained is a yellow solid (0.78 g, 1.45 mmol) that is insoluble in all common solvents. Crystals suitable for X-ray diffraction were obtained, when the reaction was performed in dichloromethane at r.t. without stirring, m.p. 283–285°C, yield 97%; MS (EI, 70 eV) *m/z:* 443 [M^+–C_6H_4F, 6], 444 (1), 442 (3), 238 (7), 175 (10), 174 (100), 173 (26), 132 (2); IR (KBr) ν (cm^{-1}): 3040 (w), 2976 (w), 2932 (w), 2872 (w), 1640 (C=N, s), 1606 (s), 1588 (s), 1558 (s), 1310 (s), 1234 (s), 1208 (s), 1192 (s), 1152 (s), 1138 (s), 1124 (s), 1110 (s), 1038 (s), 1024 (s), 964 (s), 930 (s), 820 (s), 752 (s). Elemental analysis ($C_{30}H_{26}B_2F_2N_2O_4 \cdot H_2O$) Calc.: C, 64.49, H, 5.06, N, 5.03%. Found: C, 64.49, H, 4.74, N, 4.99%.

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