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Journal of Organometallic Chemistry 604 (2000) 273–282

Journal of Organometallic Chemistry

# Synthesis and molecular structures of dimeric boron compounds

Victor Barba, Rolando Luna, Dolores Castillo, Rosa Santillan, Norberto Farfán *

*Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, Apartado Postal 14-740, 07000 Mexico DF, Mexico*

Received 22 January 2000; received in revised form 4 May 2000

**Abstract**

A series of eleven new dimeric boron chelates: [B(SAE)(*m*-$NH_2$–$C_6H_4$)]$_2$ (**3a**), [B(SAE)(*p*-$CF_3$–$C_6H_4$)]$_2$ (**3b**), [B(SAE)(*p*-CHO–$C_6H_4$)]$_2$ (**3c**), [B(SAE)(*p*-Br–$C_6H_4$)]$_2$ (**3d**), [B(SAE)(*p*-EtO–$C_6H_4$)]$_2$ (**3e**), [B(SAE)(*m*-$CH_3CO$–$C_6H_4$)]$_2$ (**3f**), [B(SAE)(*p*-$CH_3CO$–$C_6H_4$)]$_2$ (**3g**), [B(SAE)(*o*-F, *p*-F–$C_6H_3$)]$_2$ (**3h**), [B(SAE)(*m*-F, *p*-F–$C_6H_3$)]$_2$ (**3i**), [B(SAE)(*m*-F, *m*-F–$C_6H_3$)]$_2$ (**3j**) and [B(SAE)(*o*-F, *o*-F–$C_6H_3$)]$_2$ (**3k**), prepared by condensation of 2-salicylideneamino hydroxyethane ($H_2$SAE) with arylboronic acids such as amino-, trifluoromethyl-, bromo-, formyl-, acetyl-, ethoxy- and difluoro-boronic acid allowed a study of the influence of different substituents in the B-phenyl moiety on coordination of the boron atom. In all cases, dimeric derivatives were formed and the molecular structures for [B(SAE)(*p*-$CH_3O$–$C_6H_4$)]$_2$ (**2e**), **3b**, **3d** and **3h** were established by X-ray diffraction analysis where the values of the intramolecular (N–B) bond lengths confirmed a donor–acceptor character. 

*Keywords:* Boron chelates; Boronic acids; Salicylideneaminoethanol; Macrocyclic chemistry

## 1. Introduction

The stabilization of boron compounds through the formation of complexes containing dative N–B bonds is well established, for instance, diphenylborinic ($Ph_2BOH$) or phenylboronic ($PhB(OH)_2$) acids readily condense with ethanolamine [1] or glycine [2,3] to form compounds stabilized by N–B dative bonds. Moreover, the hydrolytic stability of cyclic boronic esters derived from tridentate ligands has been increased owing to the presence of coordinative N–B and covalent B–O bonds [4–6]. In general, boronates containing intramolecular N–B bonds have been studied intensely [7–10].

We have reported previously [11] the synthesis of a dimeric macrocycle that is formed by the condensation of 2-salicylideneaminoethanol ($H_2$SAE) [12,13] with phenylboronic acid (**1a**) (Fig. 1). This molecule is very stable to air and is obtained in high yields. In addition, $H_2$SAE derivatives were allowed to react with phenylboronic acid (**1b**–**1e**) [14] (Fig. 1) to evaluate the effects of different substituents in the aminediol that lead to the formation of dimeric boronates and it was shown that the main requirements for the formation of dimeric complexes are the geometry of the ligand and the small atomic radius of the boron atom together with its tetrahedral geometry.

Following the method reported previously, a series of dimeric compounds derived from $H_2$SAE and arylboronic acids (**2a**–**2j**) (Fig. 1) were synthesized in order to evaluate the steric and electronic effects on the formation of the dimeric structure [15]. In this case, analysis of the X-ray crystallographic data of compounds **2c**, **2i** and **2f** showed no significant differences in the bond lengths and bond angles values.

Continuing our investigations on this area, the present contribution describes the preparation of 11 new dimeric compounds and a study of the effect of different substituents at the phenyl ring of the boronic acid. The influence of donor and acceptor groups attached to the B-phenyl moiety on the values of the bond angles and the length of the intramolecular N–B donor–acceptor bond will be evaluated. The results demonstrated a linear correlation between the N–B distances and the tetrahedral character (TCH) values.

* Corresponding author. Tel.: +52-5-7473800, ext. 3721; fax: +52-5-7477113.

*E-mail address:* jfarfan@mail.cinvestav.mx (N. Farfán).

0022-328X/00/$ - see front matter 
PII: S0022-328X(00)00285-0

## 2. Results and discussion

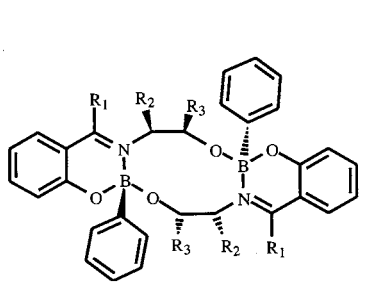
One of the principal aims of the synthesis of dimeric boron complexes with different substituents was to determine whether the dimeric structure is still obtained when the steric hindrance and the electronic effects around the phenyl group attached to the boron atom are increased. Dimeric compounds **3a**–**3k** were obtained from the reaction of $H_2SAE$ with a series of arylboronic acids (Scheme 1) that include amino-, trifluoromethyl-, bromo-, formyl-, acetyl- ethoxy- and difluoro- substituents in *ortho*, *meta* or *para* positions of the B-phenyl group (Fig. 2). The reaction provides yellow solids that are air stable, in moderate to good yields (52–95%).

The compounds were characterized by spectroscopic techniques. The identity of the dimeric boronates **3a**–**3k** was established by mass spectrometry based on detection of the dimeric-minus aryl ion $[M - Ar]^+$ since observation of the molecular ion is prevented by facile loss of the corresponding aryl radical, as has been shown previously [11,14–17].

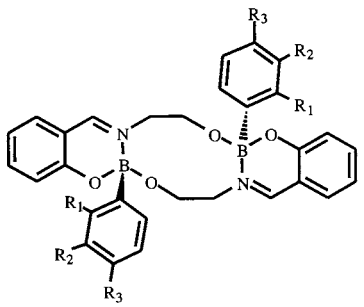
The boronates showed a strong IR absorption band for the C=N bond at 1638–1640 $cm^{-1}$ that is shifted to higher energy by 2 or 4 $cm^{-1}$ in comparison with the starting material ($H_2SAE$).

Although in general dimeric boron compounds are highly insoluble, for the compounds described herein, the presence of substituents at the B-phenyl increased their solubility allowing NMR measurements in solution.

The $^1$H-NMR data reveal a symmetric geometry in solution with singlets for the N=CH groups in the range of 8.39–9.14 ppm that are shifted to lower fields compared to the same group in $H_2SAE$ ($\delta = 8.1$ ppm) due to the formation of the dative N–B bond. The existence of a stereogenic center at the boron atom gives rise to diastereotopic signals for the methylene groups in the range of 3.00–3.82 ppm, in contrast with $H_2SAE$ where only two triplets are observed. In $^{13}$C-NMR spectra, the signals corresponding to the carbon atoms at positions 2 and 1 (Fig. 2) are shifted 2 to 3 ppm to higher fields compared to the shift shown by $H_2SAE$ owing to the

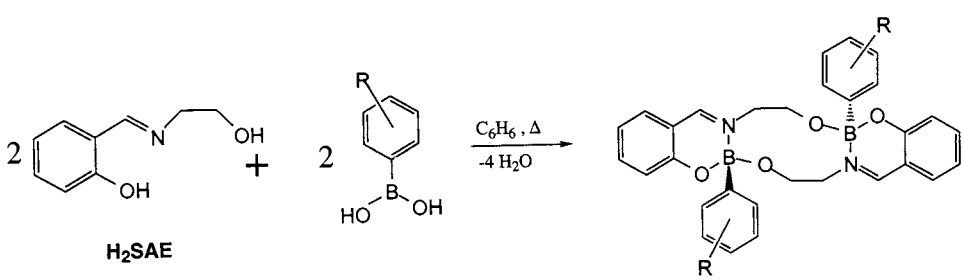


| | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| **1a** | H | H | H |
| **1b** | H | H | $CH_3$ |
| **1c** | H | H | Ph |
| **1d** | H | $CH_3$ | H |
| **1e** | $CH_3$ | H | H |



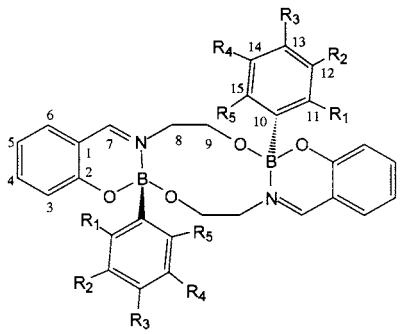
| | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| **2a** | $CH_3$ | H | H |
| **2b** | H | $CH_3$ | H |
| **2c** | H | H | $CH_3$ |
| **2d** | H | $OCH_3$ | H |
| **2e** | H | H | $OCH_3$ |
| **2f** | H | Cl | H |
| **2g** | H | H | Cl |
| **2h** | H | $NO_3$ | H |
| **2i** | H | $CF_3$ | H |
| **2j** | H | H | F |

Fig. 1. Structures of compounds **1a**–**1e** and **2a**–**2j**.




$H_2SAE$

Scheme 1. Synthesis of compounds **3a**–**3k**.



| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ |
|---|---|---|---|---|---|
| **3a** | H | $NH_2$ | H | H | H |
| **3b** | H | H | $CF_3$ | H | H |
| **3c** | H | H | CHO | H | H |
| **3d** | H | H | Br | H | H |
| **3e** | H | H | OEt | H | H |
| **3f** | H | $COCH_3$ | H | H | H |
| **3g** | H | H | $COCH_3$ | H | H |
| **3h** | F | H | F | H | H |
| **3i** | H | F | F | H | H |
| **3j** | H | F | H | F | H |
| **3k** | F | H | H | H | F |

Fig. 2. Structures of compounds **3a**–**3k**.

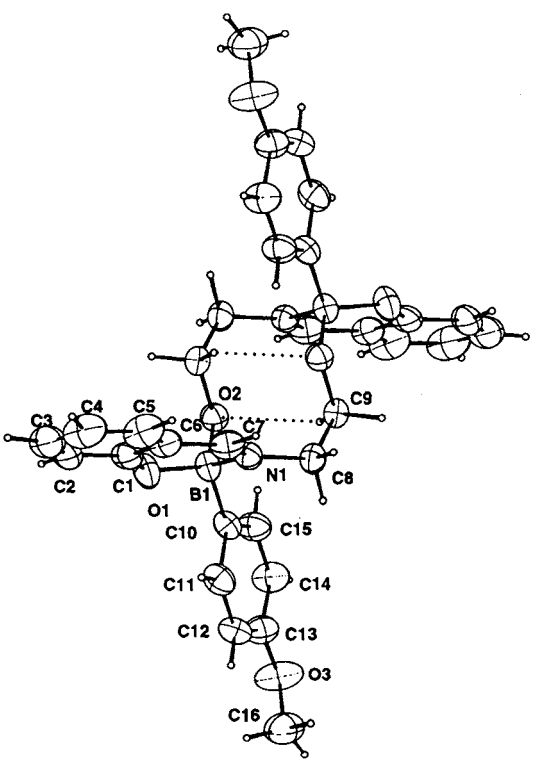



Fig. 3. An ORTEP diagram of the molecular structure of compound **2e**.

coordination of the boron atom with the nitrogen atom. The $^{11}$B-NMR spectra show broad signals for all compounds and the chemical shifts are indicative of a tetrahedral geometry for this atom [18]. In all cases the signals lie in the range from 1.5 to 6.9 ppm.

The X-ray analyses of compounds **2e**, **3b**, **3d** and **3h** established the dimeric structure of these compounds (Figs. 3–6, respectively). Details of the crystal data and a summary of data collection parameters for the com-

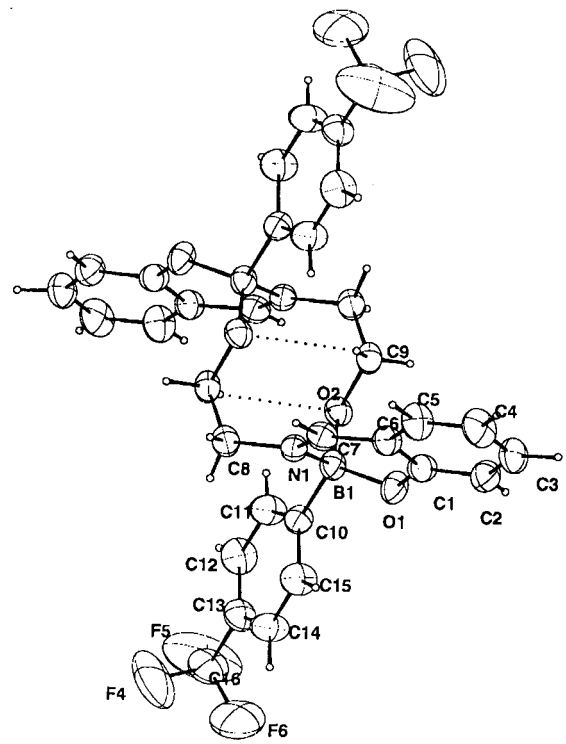



Fig. 4. An ORTEP diagram of the molecular structure of compound **3b**.

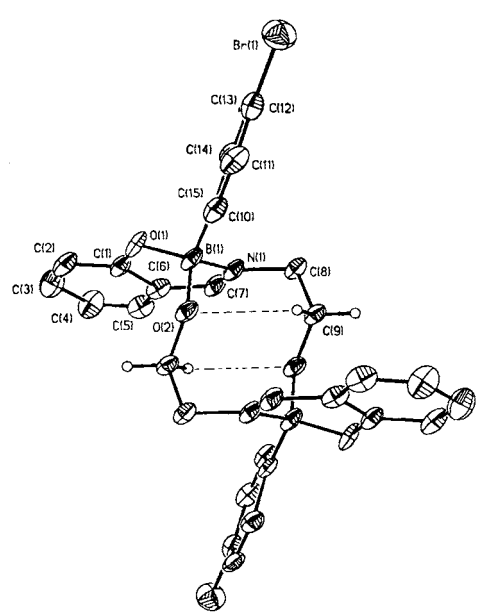



Fig. 5. An ORTEP diagram of the molecular structure of compound **3d**.

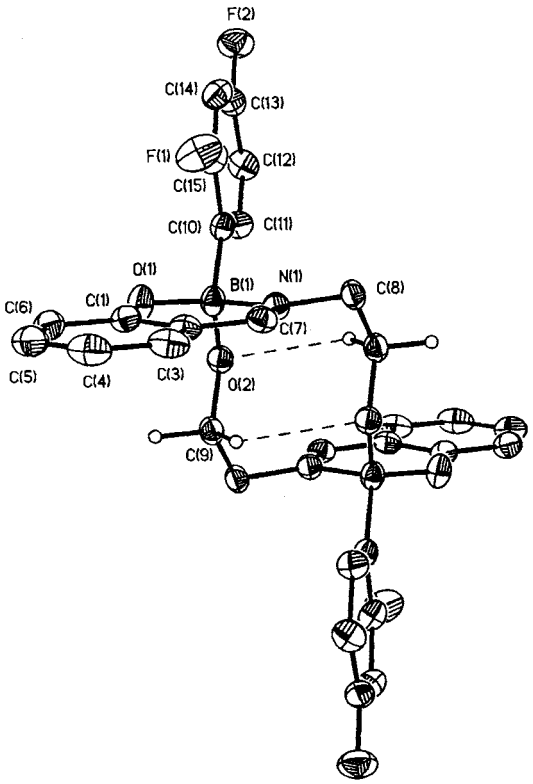



Fig. 6. An ORTEP diagram of the molecular structure of compound **3h**.

plexes are given in Table 1 and selected bond distances and angles are listed in Table 2. All four compounds crystallized in the space group $P\bar{1}$ and in the case of compound **3d**, the asymmetric unit contains two independent molecules. Often these structures contain a center of inversion and belong therefore to the $C_i$ point group [11,19], so that the boron atoms adopt a *trans* geometry in which the two B–Ar moieties are oriented away from one other. An important aim of this study was to investigate the effect of different substituents in the N–B bond length; however, the X-ray data show no significant differences (see Table 3). For example, the N–B bond lengths are in the range from 1.606(8) to 1.624(8) Å and there are no significant differences in comparison with similar structures described previously [11,14,15]. Nevertheless, there is a nearly linear correlation between the THC [20] values and the N–B bond distances as shown in Fig. 7, indicating that the boron atoms suffer greater distortion with increasing N–B lengths owing to the deformation of the six-membered ring. The six-membered CCCBNO ring heterocycles are approximately planar with a larger deviation (Δ, from −0.088 to 0.430 Å) from the mean plane corresponding to the boron atoms (Table 4). Comparison of the different O–B bond lengths shows that the shorter bonds correspond to those B–O lengths in the ten-membered heterocycles. Furthermore, the lowest value (1.414(7) Å) is obtained for compound **3b** due the electron withdrawing effect of the $CF_3$ group. This effect is transmitted to the C=N bond that also presents the lowest value (1.279(6) Å). The B–C (aryl) bond lengths lie in the range from 1.579(8)–1.628(9) Å and are longer than those described for tetrahedral boron complexes with B–OMe bonds (1.404(6)–1.417(2) Å) [21,22]. This difference in bond length values can be attributed to an increase in electron density of the OMe group compared with the aryl moieties.

The effect of the *para*-substituents in the B-phenyl moiety can be seen in Fig. 8, which shows a linear correlation between $\sigma$ Hammett values and B–C(aryl) distance. It is known that electron-donating substituents in the *para* position of an aromatic ring lead to important contribution of resonance structures showing double bond character between the donor and the aryl groups. For the dimeric compounds having OMe and Me groups at the *para* position (**2c**, **2e**), contribution from these resonance structures having partial double bond character between the boron and the $C_{ipso}$ atoms leads to a decrease in the B–C(aryl) bond length. For derivatives containing electron withdrawing substituents [F (**2j**) and Br (**3d**)] the inductive effects are more important and electron density is decreased at the aromatic ring leading to an increase in the B–C(aryl) bond length. In contrast, no apparent effect on the N–B bond lengths was observed.

The angles around the boron atoms are approximately tetrahedral, they are in the range from 105.5(4) to 111.2(3)°. The smallest values are for the O(1)–B(1)–N(1) angles that lie in the range from 105.5(4) to 108.0(2)° and are similar to the corresponding data of the salicylaldehyde azomethine boron chelates. The THC [20] values are from 89 to 93% and indicate the distorted tetrahedral geometry for the boron atoms. As shown in Figs. 3–6, these structures contain six- and ten-membered heterocycles, the ten-membered rings have a chair–boat–chair conformation and in all cases there are transannular interactions between one of the hydrogen atoms H(91) and the opposite oxygen atom O(2) where the distances are about 2.4–2.5 Å (see Table 3), which are below the sum of van der Waals radii (2.70 Å) [23].

## 3. Conclusions

Under the reaction conditions employed, only dimeric structures are formed from $H_2$SAE and arylboronic acids. The nature of the tridentate ligand determines the course of the reaction leading to the macrocyclic complex, so that electronic effects in the B-phenyl group have no influence on the reaction,

although the *p*-substituted derivatives that crystallized showed a linear correlation between the THC versus N–B bond lengths values, as well as $\sigma$ Hammett versus C–B lengths values. In contrast, the formation of compounds **3h** and **3k** that have fluorine substituents *ortho* to the boron atom showed that steric effects are not important. In previous work, we have mentioned that one of the interests for the synthesis of this type of compounds is their potential application in host–guest chemistry. Thus, the introduction of functional groups could allow one to control the strength of the coordinative N–B bond allowing an increase in the ring size of the macrocycle. However, in the case of the compounds described herein this was not observed, so further investigations using $H_2$SAE derivatives and different boronic acids that could weaken this bond are in progress.

## 4. Experimental

All starting materials were obtained commercially from Aldrich Chemical Company. Solvents were used without further purification, but single crystals were grown from spectrophotometric grade solvents. The reagent $H_2$SAE was prepared as described in the literature [12,13].

NMR spectra were recorded on JEOL GSX 270, JEOL Eclipse +400 and Bruker Avance DPX 300 spectrometers. Chemical shifts (ppm) are relative to $(CH_3)_4Si$ ($^1H$ and $^{13}C$) and $BF_3{\cdot}OEt_2$($^{11}B$). Coupling constants are quoted in Hz. Infrared spectra were recorded on a Perkin–Elmer 16F-PC FT-IR spectrophotometer. Mass spectra were obtained with a HP 5989 A spectrometer. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncor-

Table 1
Experimental crystallographic data for compounds **2e**, **3b**, **3d** and **3h**

| | **2e** [a] | **3b** [a] | **3d** [b] | **3h** [b] |
|---|---|---|---|---|
| *Crystal data* | | | | |
| Chemical formula | $C_{32}H_{32}B_2N_2O_6$ | $C_{32}H_{26}B_2F_6N_2O_4$, $2CHCl_3$ | $C_{30}H_{26}B_2Br_2N_2O_4$, 2THF | $C_{30}H_{24}B_2F_4N_2O_4$ |
| Crystal size (mm) | $0.18\times0.2\times0.6$ | $0.14\times0.14\times0.16$ | $0.45\times0.42\times0.18$ | $0.58\times0.50\times0.30$ |
| Molecular weight (g mol$^{-1}$) | 562.24 | 876.08 | 804.04 | 595.75 |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| *Cell parameters* | | | | |
| $a$ (Å) | 8.050(1) | 9.125(1) | 11.517(2) | 7.677(2) |
| $b$ (Å) | 10.177(1) | 9.930(1) | 12.756(3) | 9.613(2) |
| $c$ (Å) | 10.671(1) | 11.350(1) | 13.781(3) | 10.669(2) |
| $\alpha$ (°) | 60.85(1) | 104.16(1) | 99.79(3) | 115.04(3) |
| $\beta$ (°) | 69.34(1) | 94.23(1) | 92.02(3) | 95.41(3) |
| $\gamma$ (°) | 70.62(1) | 104.23(1) | 94.37(3) | 108.74(3) |
| $V$ (Å$^3$) | 700.58(1) | 956.74(1) | 1986.9(7) | 650.8(2) |
| $Z$ | 1 | 1 | 2 | 1 |
| $\mu$ (mm$^{-1}$) | 0.08 | 0.52 | 2.084 | 0.117 |
| $\rho_{calc}$ (kg m$^{-3}$) | 1.33 | 1.52 | 1.31 | 1.52 |
| *Data collection* [c] | | | | |
| $\theta$ limits (°) | $2<\theta<25$ | $2<\theta<26$ | $2<\theta<25$ | $2<\theta<25$ |
| Collected reflections | 4130 | 3498 | 6769 | 2683 |
| Independent reflections | 2300 | 3174 | 6769 | 2464 |
| Observed reflections | 1214 [d] | 1894 [d] | 2716 [e] | 1496 [e] |
| *Refinement* [f] | | | | |
| $R$ [g] | 0.035 | 0.061 | 0.074 | 0.046 |
| $R_w$ | 0.030 [h] | 0.062 [h] | 0.193 [i] | 0.135 [i] |
| Goodness-of-fit [j] | 1.12 | 2.3 | 0.884 | 0.986 |
| Variables | 240 | 288 | 402 | 190 |
| Maximum $\Delta/\sigma$ | 0.24 | 0.009 | 0.53 | 0.004 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | −0.13 | −0.41 | −0.79 | −0.21 |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0.27 | 0.46 | 0.50 | 0.21 |

[a] Program used, CRYSTALS 1996, version 10.
[b] Program used, SHELXS (Sheldrick 1993, version 1.8).
[c] $T=293$ K, $\lambda_{Mo-K_\alpha}=0.71073$ Å, $\omega$–$2\theta$ scan.
[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] $R_w=[\Sigma\, w(|F_o|-|F_c|)^2/\Sigma\, wF_o^2]^{1/2}$.
[i] $wR_2=\{\Sigma[w[F_o^2-F_c^2]^2]/\Sigma[w[F_o^2]^2]\}^{1/2}$.
[j] Goodness-of-fit $=[(\Sigma\, w(|F_o|-|F_c|)^2/m-n)]^{1/2}$.

Table 2
Selected bond lengths and bond angles of compounds **2e**, **3b**, **3d** and **3h**

| | 2e | 3b | 3d [a] | 3h |
|---|---|---|---|---|
| *Bond lengths* (Å) | | | | |
| O(1)–B(1) | 1.498(4) | 1.495(6) | 1.500(9)/1.525(9) | 1.478(3) |
| O(1)–C(1) | 1.330(4) | 1.336(5) | 1.335(8)/1.367(8) | 1.333(3) |
| B(1)–N(1) | 1.622(4) | 1.621(7) | 1.609(8)/1.624(8) | 1.624(3) |
| B(1)–O(2) | 1.441(4) | 1.414(7) | 1.465(9)/1.440(8) | 1.438(3) |
| B(1)–C(10) | 1.580(5) | 1.598(7) | 1.628(9)/1.625(9) | 1.617(4) |
| N(1)–C(7) | 1.294(4) | 1.279(6) | 1.296(8)/1.298(8) | 1.288(3) |
| N(1)–C(8) | 1.481(4) | 1.474(6) | 1.487(8)/1.521(8) | 1.472(3) |
| O(2)–C(9) | 1.409(4) | 1.401(6) | 1.472(8)/1.438(7) | 1.418(3) |
| C(8)–C(9) | 1.528(4) | 1.500(8) | 1.518(9)/1.509(9) | 1.508(4) |
| *Bond angles* (°) | | | | |
| O(1)–B(1)–N(1) | 106.7(3) | 105.5(4) | 106.0(5)/106.3(5) | 108.0(2) |
| O(1)–B(1)–O(2) | 110.6(3) | 112.0(4) | 110.7(6)/110.7(6) | 111.0(2) |
| O(1)–B(1)–C(10) | 110.2(3) | 109.2(4) | 109.7(5)/113.2(5) | 110.2(2) |
| O(2)–B(1)–N(1) | 108.6(2) | 109.4(4) | 108.6(5)/108.4(5) | 109.6(2) |
| O(2)–B(1)–C(10) | 111.2(3) | 110.6(4) | 110.9(5)/109.6(6) | 109.3(2) |
| N(1)–B(1)–C(10) | 109.4(3) | 109.9(4) | 110.8(6)/108.5(5) | 108.7(2) |
| B(1)–N(1)–C(7) | 123.0(3) | 120.7(4) | 120.0(6)/120.6(6) | 122.0(2) |
| B(1)–N(1)–C(8) | 118.8(3) | 119.6(4) | 119.0(5)/118.1(5) | 119.2(2) |
| B(1)–O(1)–C(1) | 125.9(3) | 124.1(4) | 123.6(5)/124.2(5) | 126.2(2) |
| B(1)–O(2)–C(9) | 119.3(2) | 121.5(4) | 123.5(5)/118.5(5) | 118.3(2) |
| N(1)–C(7)–C(6) | 122.0(3) | 124.1(5) | 123.7(6)/125.3(6) | 122.9(2) |
| N(1)–C(8)–C(9) | 112.6(3) | 111.4(4) | 110.8(5)/112.3(5) | 113.4(2) |
| C(7)–N(1)–C(8) | 118.2(3) | 119.4(4) | 120.4(5)/121.2(6) | 118.8(2) |
| O(2)–C(9)–C(8) | 108.5(3) | 109.3(4) | 108.9(5)/108.1(6) | 109.2(2) |

[a] There are two independent molecules into the asymmetric unit.

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

### 4.1. Preparation of boronates. General procedure for the preparation of compounds **3a**–**3k**

The following procedure is representative for the preparation of all boron compounds described in this study. Equimolar quantities of the corresponding arylboronic acid and $H_2SAE$ were refluxed in 20 ml benzene or THF 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.

#### 4.1.1. 2,11-Di-(4′-methoxyphenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (**2e**)

Crystals of compound **2e** suitable for X-ray diffraction were obtained when the reaction was performed in THF at 25°C without stirring. The synthesis and spectroscopic data have been published [15].

#### 4.1.2. 2,11-Di-(2′-aminophenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (**3a**)

Compound **3a** was prepared from 0.50 g (3.00 mmol) of $H_2SAE$ and 0.45 g (3.00 mmol) of 2-aminophenylboronic acid monohydrate. The product was a yellow solid (yield: 0.42 g, 0.80 mmol, 52%) m.p. 270–272°C. MS (EI, 70 eV) *m/z*: 440 ($[M-C_6H_4NH_2]^+$, 4), 267 (2), 175 (12), 174 (100), 173 (28), 148 (13), 132 (5) 107 (5) 77 (8); IR (KBr) $\bar{\nu}$ ($cm^{-1}$): 2920 (w), 2850 (m), 1640 (C=N, s), 1608 (s), 1558 (s), 1480 (m), 1316 (m), 1294 (s), 1174 (s), 1154 (s), 1140 (s), 1122 (w), 1112 (m), 1028 (s), 994 (m), 772 (s), 758 (s); $^1$H-NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm): 8.93 (1H, s, H-7), 7.75 (1H, d, $J=7.5$ Hz, H-6), 7.52 (1H, t, $J=7.5$ Hz, H-4), 6.92 (1H, t, $J=7.5$ Hz, H-5), 6.86 (1H, d, $J=7.5$ Hz, H-3), 6.81 (1H, t, $J=7.8$ Hz, H-14), 6.64 (1H, s, H-11), 6.62 (1H, d, $J=7.8$ Hz, H-15), 6.33 (1H, d, $J=7.8$ Hz, H-13), 4.61 (2H, s, $NH_2$), 3.45 (2H, t, $J=6.2$ Hz, H-9a, 8a), 3.16 (1H, d, $J=6.2$ Hz, H-8b), 3.01 (1H, d, $J=6.2$ Hz, H-9b); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm): 165.8 (C-7), 160.5 (C-2), 147.4 (C-12), 137.5 (C-4), 132.3 (C-6), 127.7 (C-14), 120.5 (C-11), 118.8 (C-3, 15), 118.2 (C-5), 116.5 (C-1), 113.0 (C-13), 59.7 (C-8), 59.6 (C-9); $^{11}$B-NMR (128 MHz, DMSO-$d_6$) $\delta$ (ppm): +2.8 ($h_{1/2}=2084$ Hz). Anal. Calc. for $C_{30}H_{30}B_2N_4O_4$: C, 67.68; H, 5.64; N, 10.53. Found: C, 67.59; H, 5.34; N, 10.33%.

#### 4.1.3. 2,11-Di-(4′-trifluoromethylphenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (**3b**)

Compound **3b** was prepared from 0.50 g (3.00 mmol) of $H_2SAE$ and 0.56 g (3.00 mmol) of 4-trifluoromethylphenylboronic acid. The product was obtained as yellow crystals that are slightly soluble in chloroform. Crystals suitable for X-ray diffraction were obtained when the reaction was performed in chloroform at 25°C without stirring (yield: 0.65 g, 1.02 mmol, 68%), m.p. 288–290°C. MS (EI, 70 eV) *m/z:* 493 ($[M-C_6H_4CF_3]^+$, 4), 288 (8), 175(11), 174 (100), 173 (29), 148 (7), 130 (2), 102 (2), 77 (2); IR (KBr) $\bar{\nu}$ ($cm^{-1}$): 3042 (w), 2942 (w), 2858 (w), 1640 (C=N, s), 1560 (s), 1482 (w), 1396 (m), 1328 (s), 1308 (s), 1236 (s), 1200 (w), 1158 (s), 1140 (s), 1022 (s), 1016 (w), 968 (m), 820 (s), 754 (s); $^1$H-NMR (270 MHz, DMSO-$d_6$) $\delta$ (ppm): 9.11 (1H, s, H-7), 7.78 (1H, dd, $J=7.7$, 1.5 Hz, H-6), 7.65 (1H, d, $J=7.8$ Hz, H-11, 15), 7.57 (1H, t, $J=7.7$ Hz, H-4), 7.52 (1H, d, $J=7.8$ Hz, H-12, 14), 6.99 (1H, t, $J=7.7$ Hz, H-5), 6.91 (1H, d, $J=7.7$ Hz, H-3), 3.01-3.60 (4H, m, H-8, 9); $^{13}$C-NMR (68 MHz, DMSO-$d_6$) $\delta$ (ppm): 167.1 (C-7), 160.0 (C-2), 138.1 (C-4), 133.0 (C-11, 15), 132.6 (C-6), 128.9 (C-12, 14), 128.0 (t, $J_{CF}=3.4$ Hz, $CF_3$), 124.0 (C-13), 119.5 (C-3), 118.3 (C-5), 116.5 (C-1), 59.6 (C-8), 59.5 (C-9); $^{11}$B-NMR (86 MHz, DMSO-$d_6$) $\delta$ (ppm): 2.0 ($h_{1/2}=964$ Hz). Anal. Calc. for $C_{32}H_{26}B_2F_6N_2O_4$: C, 60.24; H, 4.10; N, 4.38. Found: C, 59.98; H, 4.22; N, 4.38%.

Table 3
Some selected parameters of comparison for dimeric compounds: **1a**, **2c**, **2e**, **2i**, **2j**, **3b**, **3d** and **3h**

| Compound | Distance (Å) | | | Sum of bond angles in the six-membered ring heterocycles (°) | THC (%) |
|---|---|---|---|---|---|
| | B(1)–N(1) | B(1)–C(10) | O(2)–H(91) | | |
| **1a** [a] | 1.624(3) | 1.601(3) | 2.43 | 718.0 = 119.67 × 6 | 86.0 |
| **2c** [b,c] | 1.639(7) | 1.579(8) | 2.46 | 717.6 = 119.60 × 6 | 84.1 |
| | 1.606(6) | 1.583(6) | 2.52 | 713.4 = 118.90 × 6 | 94.0 |
| **2e** | 1.622(4) | 1.580(5) | 2.41 | 718.5 = 119.75 × 6 | 88.9 |
| **2i** [b] | 1.619(4) | 1.593(6) | 2.52 | 717.0 = 119.50 × 6 | 86.7 |
| **2j** [b] | 1.613(4) | 1.601(5) | 2.43 | 717.5 = 119.58 × 6 | 88.3 |
| **3b** | 1.621(4) | 1.598(6) | 2.59 | 713.0 = 118.83 × 6 | 89.5 |
| **3d** [c] | 1.609(8) | 1.628(9) | 2.53 | 711.8 = 118.63 × 6 | 91.1 |
| | 1.624(8) | 1.625(9) | 2.55 | 714.3 = 119.05 × 6 | 84.1 |
| **3h** | 1.624(3) | 1.617(4) | 2.48 | 717.7 = 119.62 × 6 | 93.7 |

[a] Ref. [11].
[b] Ref. [15].
[c] There are two independent molecules in the asymmetric unit.

#### 4.1.4. 2,11-Di-(4′-formylphenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (3c)

Compound **3c** was prepared from 0.50 g (3.00 mmol) of $H_2$SAE and 0.45 g (3.00 mmol) of 4-formylphenylboronic acid. The product was a yellow solid (yield: 0.72 g, 1.3 mmol, 85%), m.p. 281–283°C. MS (EI, 70 eV) *m/z:* 453 ($[M - C_6H_4COH]^+$, 12), 306 (2), 280 (2), 248 (2), 175 (12), 174 (100), 173 (28), 148 (2), 91(1), 77 (1); IR (KBr) $\bar{\nu}$ ($cm^{-1}$): 3338 (w), 2918 (w), 2864 (w), 2850 (w), 1684 (s), 1640 (C=N, s), 1604 (s), 1560 (s), 1210 (s), 1196 (s), 1142 (s), 1128 (s), 964 (s), 930 (m), 764(w), 726 (s); $^1$H-NMR (270 MHz, DMSO-$d_6$) $\delta$ (ppm): 9.94 (1H, s, H-16), 9.14 (1H, s, H-7), 7.81 (1H, d, $J = 8.0$, Hz, H-6), 7.74 (2H, d, $J = 7.7$ Hz, H-11, 15), 7.68 (2H, d, $J = 7.7$ Hz, H-12, 14), 7.57 (1H, t, $J = 8.0$ Hz, H-4), 7.03 (1H, t, $J = 8.0$ Hz, H-5), 6.92 (1H, d, $J = 8.0$ Hz, H-3), 3.59 (1H, t, $J = 10.4$ Hz, H-9a), 3.43 (1H, t, $J = 10.4$ Hz, H-8a) 3.10 (2H, d, $J = 10.4$ Hz, H-8b, 9b); $^{13}$C-NMR (68 MHz, DMSO-$d_6$) $\delta$ (ppm): 193.9 (CHO), 167.1 (C-7), 160.2 (C-2), 138.1 (C-4), 135.6 (C-13), 133.1 (C-11, 15), 132.6 (C-6), 128.7 (C-12, 14), 119.5 (C-3), 118.3 (C-5), 116.6 (C-1), 59.7 (C-8), 59.5 (C-9); $^{11}$B-NMR (86 MHz, DMSO-$d_6$) $\delta$ (ppm): 2.0 ($h_{1/2} = 1174$ Hz). Anal. Calc. for $C_{32}H_{28}B_2N_2O_6$: C, 68.86; H, 5.05; N, 5.01. Found: C, 69.28; H, 4.86; N, 4.47%.

#### 4.1.5. 2,11-Di-(4′-bromophenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (3d)

Compound **3d** was prepared from 0.50 g (3.00 mmol) of $H_2$SAE and 0.61 g (3.00 mmol) of 4-bromophenylboronic acid. The product was obtained as yellow crystals which were suitable for X-ray diffraction (yield: 0.78 g, 1.42 mmol 87%), m.p. 284–286°C. MS (EI, 70 eV) *m/z:* 505 ($[M + 2 - C_6H_4Br]^+$, (2)), 503 ($[M - C_6H_4Br]^+$, 2), 332 (1), 330 (1), 174 (100), 173 (30), 148 (1), 77 (2); IR (KBr) $\bar{\nu}$ ($cm^{-1}$) 3052 (w), 2918 (w), 2850 (w), 1640 (C=N, s), 1608 (m), 1560 (s), 1482 (s), 1462 (m), 1310 (s), 1238 (s), 1238 (s), 1212 (s), 1152 (s), 1124 (s), 1112 (s), 1008 (s), 994 (s), 758 (s); $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 8.47 (1H, s, H-7), 7.57 (1H, d,

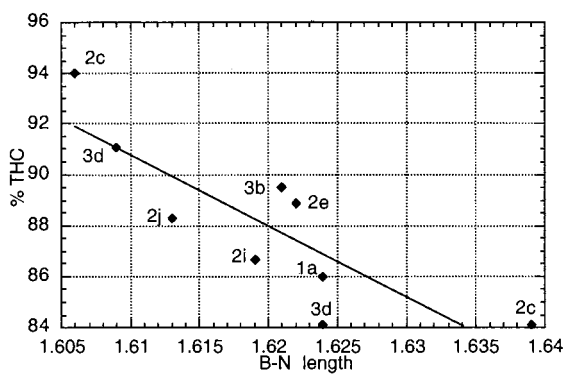



Fig. 7. Correlation between % THC versus N–B length values. Equation: % THC = 639.77 − 278.88 dist. N–B, $R = 0.837$. For compounds **2c** and **3d**, there are two molecules in the asymmetric unit.

Table 4
Deviations from the boronate mean plane [a] (Δ, Å) for compounds **2e**, **3b**, **3d** and **3h**.

| | 2e | 3b | 3d | 3h |
|---|---|---|---|---|
| O(1) | 0.093 | 0.004 | −0.017/−0.013 | −0.007 |
| B(1) | −0.088 | 0.430 | −0.413/−0.410 | 0.108 |
| N(1) | 0.000 | 0.074 | 0.031/0.034 | 0.009 |
| C(7) | 0.001 | −0.055 | −0.043/−0.045 | −0.008 |

[a] The mean plane is calculated for C(1) until C(6), equations of the planes: (**2e**) $6.92034x + 1.76926y + 7.24838z = 9.816$; (**3b**) $-1.49305x - 7.71826y - 2.84505z = -5.851$; (**3d**) $7.80926x + 0.68940y + 10.29431z = -1.495$; (**3h**) equation of the plane: $6.57105x - 4.23413y + 4.56307z = 3.910$; $x$, $y$, $z$ are orthogonal coordinates with respect to axes $a$, $b$, $c$.

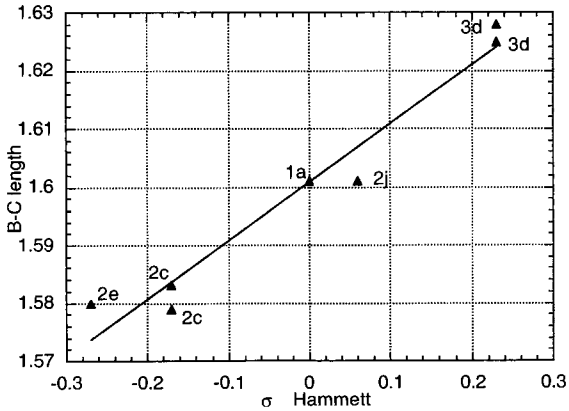



Fig. 8. Correlation between C–B length versus $\sigma$ Hammett for dimeric compounds with *para* substituents. Equation: dist. C–B = $1.6009 + 0.1007\sigma$ Hammett, $R = 0.9771$. For compounds **2c** and **3d**, there are two molecules in the asymmetric unit.

$J = 7.5$ Hz, H-6), 7.49 (1H, dd, $J = 7.5$, 1.6 Hz, H-4), 7.39 (2H, d, $J = 8.4$ Hz, H-11, 15), 7.28 (2H, d, $J = 8.4$ Hz, H-12, 14), 7.04 (1H, t, $J = 7.5$ Hz, H-5), 6.99 (1H, d, $J = 7.5$ Hz, H-3), 3.60 (1H, ddd, $J = 9.2$, 3.8, 2.6 Hz, H-9a), 3.50 (1H, ddd, $J = 9.2$, 2.6, 2.0 Hz, H-8a), 3.37 (1H, dd, $J = 3.8$, 2.6 Hz, H-8b), 3.3 (1H, dd, $J = 2.6$, 2.0 Hz, H-9b); $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$ (ppm): 165.1 (C-7), 160.9 (C-2), 138.3 (C-4), 131.5 (C-6), 134.2 (C-11, 15), 130.8 (C-12, 14), 122.0 (C-13), 119.6 (C-3), 119.4 (C-5), 116.1 (C-1), 60.9 (C-8), 60.1 (C-9); $^{11}$B-NMR (96 MHz, $CDCl_3$) $\delta$ (ppm): 2.4 ($h_{1/2} = 163$ Hz). Anal. Calc. for $C_{30}H_{26}B_2Br_2N_2O_4$: C, 54.55; H, 3.94: N, 4.24. Found: C, 54.71; H, 3.91; N, 4.41%.

### *4.1.6. 2,11-Di-(4′-ethoxyphenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (**3e**)*

Compound **3e** was prepared from 0.50 g (3.00 mmol) of $H_2$SAE and 0.5 g (3.00 mmol) of 4-ethoxyphenylboronic acid. The product was a yellow solid (yield: 0.80 g, 1.4 mmol, 90%), m.p. 266–268°C. MS (EI, 70 eV) *m/z*: 469 ($[M - C_6H_4OEt]^+$, 7), 468 (3), 296 (3), 295 (7), 294 (9), 175 (18), 174 (100), 173 (44), 148 (5), 122 (2); IR (KBr) $\bar{\nu}$ ($cm^{-1}$) 3024 (w), 2976 (w), 2936 (w), 2866 (w), 1640 (C=N, s), 1602 (s), 1560 (s), 1480 (s), 1310(m), 1234 (s), 1174 (s), 1138 (s), 1128 (s), 964 (s), 928(s), 784 (s), 756 (s); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 8.99 (1H, s, H-7), 7.71 (1H, d, $J = 7.5$, Hz, H-6), 7.53 (1H, t, $J = 7.5$ Hz, H-4), 7.30 (2H, d, $J = 8.4$ Hz, H-11, 15), 6.95 (1H, t, $J = 7.5$ Hz, H-5), 6.87 (1H, d, $J = 7.5$ Hz, H-3), 6.70 (2H, d, $J = 8.4$ Hz, H-12, 14), 3.92 (2H, q, $J = 6.9$, Hz, $OCH_2$), 3.30–3.50 (2H, m, H-9a, 8a), 3.03–3.11 (2H, m, H-9b, 8b), 1.27 (3H, t, $J = 6.9$ Hz, $CH_3$); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 166.2 (C-7), 160.5 (C-2), 157.6 (C-13), 137.6 (C-4), 132.3 (C-6), 133.5 (C-11, 15), 118.9 (C-3), 118.2 (C-5), 113.4 (C-12, 14), 116.5 (C-1), 62.9 ($OCH_2$), 59.7 (C-8), 59.5 (C-9), 15.3 ($CH_3$); $^{11}$B-NMR (128 MHz, $CDCl_3$) $\delta$ (ppm): 1.5 ($h_{1/2} = 1520$ Hz). Anal. Calc. for $C_{34}H_{36}B_2N_2O_6$: C, 69.15; H, 6.10; N, 4.75. Found: C, 70.81; H, 6.97; N, 4.39%.

### *4.1.7. 2,11-Di-(3′-acetylphenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (**3f**)*

Compound **3f** was prepared from 0.50 g (3.00 mmol) of $H_2$SAE and 0.50 g (3.00 mmol) of 3-acetylphenylboronic acid. The product was a yellow solid that is slightly soluble in chloroform (yield: 0.82 g, 1.4 mmol, 92%), m.p. 267–269°C. MS (EI, 70 eV) *m/z:* 467 ($[M - C_6H_4COCH_3]^+$, 23), 466 (10), 320 (3), 296 (5), 294 (5), 262 (3), 175 (25), 174 (100), 173 (55), 148 (2), 107 (2), 77 (2); IR (KBr) $\bar{\nu}$ ($cm^{-1}$): 3048 (w), 2972 (w), 2918 (w), 1668 (s), 1640 (C=N, s), 1608 (m), 1560 (s), 1482 (s), 1316 (s), 1306 (s), 1272 (s), 1186 (s), 1172 (s) 1140 (s), 1130 (s), 1024 (s), 1020 (s), 1090 (s) 998 (s), 982 (s), 786 (s); $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 8.59 (1H, s, H-7), 8.22 (1H, d, $J = 1.4$, H-11), 7.83 (1H, dd, $J = 7.5$, 1.4 Hz, H-15), 7.75 (1H, dt, $J = 7.5$, 1.4 Hz, H-13), 7.60 (1H, dd, $J = 7.9$, 1.6 Hz, H-6), 7.56 (1H, ddd, $J = 7.9$, 7.0, 1.6 Hz, H-4), 7.37 (1H, t, $J = 7.5$ Hz, H-14), 7.05 (1H, d, $J = 7.0$ Hz, H-3), 7.00 (1H, t, $J = 7.5$ Hz, H-5), 3.78 (1H, dd, $J = 10.6$, 2.6 Hz, H-9a), 3.51–3.68 (2H, m, H-8a-8b), 3.35 (1H, dt, $J = 10.6$, 2.6 Hz, H-9b), 2.59 (3H, s, $CH_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$ (ppm): 199.4 (CO), 165.3 (C-7), 161.0 (C-2), 138.3 (C-4) 137.5 (C-15) 136.5 (C-12), 132.3 (C-11), 131.8 (C-6), 128.0 (C-14), 127.9 (C-13), 119.6 (C-3), 119.4 (C-5), 116.3 (C-1), 60.9 (C-8), 60.2 (C-9), 27.13 ($CH_3$); $^{11}$B-NMR (96.3 MHz, $CDCl_3$) $\delta$ (ppm): 6.9 ($h_{1/2} = 242$ Hz). Anal. Calc. for $C_{34}H_{32}B_2N_2O_6$: C, 69.63; H, 5.46; N, 4.78. Found: C, 68.96; H, 5.71; N, 4.75%.

### *4.1.8. 2,11-Di-(4′-acetylphenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (**3g**)*

Compound **3g** was prepared from 0.50 g (3.00 mmol) of $H_2$SAE and 0.50 g (3.00 mmol) of 4-acetylphenylboronic acid. The product was a yellow solid that is slightly soluble in chloroform (yield: 0.76 g 1.3 mmol, 85%), m.p. = 278–280°C. MS (EI, 70 eV) *m/z:* 467 ($[M - C_6H_4COCH_3]^+$, 7), 320 (3), 294 (2), 262 (2), 175 (20), 174 (100), 173 (38), 148 (5), 134 (2), 107 (2), 105 (2), 77 (1); IR (KBr) $\bar{\nu}$ ($cm^{-1}$): 3012 (w), 2962 (w), 2926 (w), 2850 (w), 1674 (s), 1638 (C=N, s), 1314 (s), 1268 (s), 1239 (m), 1194 (s), 1150 (m), 1140 (s), 1126 (s), 1112 (m), 1028 (s) 1018 (s), 966 (s), 932 (m), 750 (s); $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 8.53 (1H, s, H-7), 7.86 (2H, d $J = 7.9$ Hz, H-11, 15), 7.68 (2H, d, $J = 7.9$ Hz, H-12, 14), 7.62 (1H, dd, $J = 7.8$, 1.6 Hz, H-6), 7.56 (1H, dt, $J = 7.8$, 1.6 Hz, H-4), 7.06 (1H, d, $J = 7.8$ Hz, H-3), 7.02 (1H, t, $J = 7.8$, Hz, H-5), 3.75 (1H, dt, $J = 9.2$, 2.0 Hz, H-9a), 3.50–3.70 (2H, m, H-8a, 8b),

3.34 (1H, dd, $J = 9.2$, 2.0 Hz, H-9b), 2.60 ($CH_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$ (ppm): 199.3 (CO), 165.2 (C-7), 161.0 (C-2), 138.4 (C-4) 136.5 (C-13) 132.6 (C-11, 15), 131.6 (C-6), 127.7 (C-12, 14), 119.7 (C-3), 119.4 (C-5), 116.1 (C-1), 60.9 (C-8), 60.1 (C-9), 27.0 ($CH_3$); $^{11}$B-NMR (87 MHz, $CDCl_3$) $\delta$ (ppm): 2.7 ($h_{1/2} = 1439$ Hz). Anal. Calc. for $C_{34}H_{32}B_2N_2O_6$: C, 69.63; H, 5.46; N, 4.11. Found: C, 69.87; H, 5.58: N, 4.38%.

### 4.1.9. 2,11-Di-(2′,4′-difluorophenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (3h)

Compound **3h** was prepared from 0.50 g (3.00 mmol) of $H_2$SAE and 0.48 g (3.00 mmol) of 2,4-difluorophenylboronic acid. The product was a yellow solid that is slightly soluble in chloroform. Crystals suitable for X-ray diffraction were obtained when the reaction was performed in THF at 25°C without stirring (yield: 0.79 g, 1.40 mmol, 90%), m.p. 283–285°C. MS (EI, 70 eV) *m/z:* 461 ($[M - C_6H_3F_2]^+$, 13), 460 (2), 288 (5), 256 (13), 238 (2), 175 (11), 174 (100), 173 (29), 148 (6), 132 (3), 77 (3); IR (KBr) $\bar{\nu}$ ($cm^{-1}$): 3062 (w), 2970 (w), 2926 (w), 1640 (C=N, s), 1602 (s), 1586 (m), 1560 (m), 1406 (s), 1230 (s), 1174 (s), 1150 (s) 1140 (s), 1124 (s), 1112 (s), 1092 (s), 1028 (s), 976 (s), 754 (s), $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 8.42 (1H, s, H-7), 7.61 (1H, t, $J = 7.8$ Hz, H-12), 7.49 (1H, ddd, $J = 8.6$, 7.5, 2.0 Hz, H-4), 7.43 (1H, dd, $J = 7.5$, 2.0 Hz, H-6), 6.96 (1H, d, $J = 8.6$ Hz, H-3), 6.91 (H, t, $J = 7.5$ Hz, H-5), 6.76 (1H, dd, $J = 8.2$, 2.3 Hz, H-15), 6.59 (1H, dd, $J = 8.2$, 2.3 Hz, H-14), 3.32-3.53 (4H, m, H-9, 8); $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$ (ppm): 164.5 (C-7), 160.0 (C-2), 138.0 (C-4), 131.4 (C-6), 129.8 (C-15), 128.4 (C-14), 127.6 (C-12), 119.0 (C-3), 118.9 (C-5), 116.3 (C-13, d, $J = 25.0$ Hz), 115.6 (C-1), 114.1 (C-11, d, $J = 25.0$ Hz), 61.9 (C-8), 60.7 (C-9); $^{11}$B-NMR (87 MHz, $CDCl_3$) $\delta$ (ppm): 2.9 ($h_{1/2} = 1647$ Hz). Anal. Calc. for $C_{30}H_{24}B_2F_4N_2O_4$: C, 62.72; H, 4.18; N, 4.88. Found: C, 62.35; H, 4.53; N, 4.64%.

### 4.1.10. 2,11-Di-(3′,4′-difluorophenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (3i)

Compound **3i** was prepared from 0.50 g (3.00 mmol) of $H_2$SAE and 0.48 g (3.00 mmol) of 3,4-difluorophenylboronic acid. The product was a yellow solid that is slightly soluble in chloroform (yield: 0.83 g, 1.40 mmol, 95%), m.p. 273–275°C. MS (EI, 70 eV) *m/z:* 461 ($[M - C_6H_3F_2]^+$, 21), 460 (1), 492 (10), 288 (5), 256 (5), 174 (100), 173 (45), 148 (2), 77 (4); IR (KBr) $\bar{\nu}$ ($cm^{-1}$): 3050 (w), 2948 (w), 2852 (w), 1638 (C=N, s), 1610 (s), 1560 (s), 1514 (s), 1482 (s), 1308 (s), 1274 (s), 1240 (s), 1144 (s), 1112 (s), 1026 (s), 988 (s), 978 (s), 808 (s), 766 (s), 752 (s); $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 8.46 (1H, s, H-7), 7.55 (1H, dt, $J = 7.5$, 1.5 Hz, H-4), 7.51 (1H, dd, $J = 7.5$, 1.5 Hz, H-6), 7.28 (1H, d, $J = 8.0$ Hz, H-11), 7.16 (1H, d, $J = 8.0$ Hz, H-15), 7.07 (1H, t, $J = 8.0$ Hz, H-14), 7.02 (1H, d, $J = 7.5$ Hz, H-3), 6.98 (1H, t, $J = 7.5$ Hz, H-5), 3.56 (1H, d, $J = 2.9$ Hz, H-9a), 3.49 (1H, d, $J = 4.2$ Hz, H-8a), 3.33 (1H, d, $J = 2.9$ Hz, H-8b), 3.29 (1H, d, $J = 4.2$ Hz, H-9b); $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$ (ppm): 164.9 (C-7), 160.5 (C-2), 138.1 (C-4), 131.2 (C-6), 128.0 (C-11), 127.8 (C-15), 127.6 (C14), 120.3 (C-12, d, $J = 21.7$ Hz), 119.4 (C-3), 119.0 (C-5), 116.3 (C-13, d, $J = 21.7$ Hz), 115.7 (C-1), 60.5 (C-8), 59.8 (C-9); $^{11}$B-NMR (87 MHz, $CDCl_3$) $\delta$ (ppm): 2.2 ($h_{1/2} = 857$ Hz). Anal. Calc. for $C_{30}H_{24}B_2F_4N_2O_4$: C, 62.72; H, 4.18; N, 4.88. Found: C, 62.83; H, 4.00; N, 4.40%.

### 4.1.11. 2,11-Di-(3′,5′-difluorophenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (3j)

Compound **3j** was prepared from 0.50 g (3.00 mmol) of $H_2$SAE and 0.48 g (3.00 mmol) of 3,5-difluorophenylboronic acid. The product was a yellow solid that is slightly soluble in chloroform (yield: 0.73 g, 1.30 mmol, 84%), m.p. 276–278°C. MS (EI, 70 eV) *m/z:* 461 ($[M - C_6H_3F_2]^+$, 13), 460 (6), 288 (4), 256 (5), 175 (18), 174 (100), 173 (39), 129 (3), 98 (3); IR (KBr) $\bar{\nu}$ ($cm^{-1}$): 3064 (w), 2968 (w), 2936 (w), 1638 (C=N, s), 1618 (s), 1584 (s), 1560 (s), 1482 (s), 1416 (s), 1314 (s), 1296 (s), 1154 (s), 1140 (s), 1112 (s), 970 (s), 756 (s); $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 8.51 (1H, s, H-7), 7.59 (1H, ddd, $J = 8.1$, 7.0, 1.4 Hz, H-4), 7.55 (1H, dd, $J = 7.0$, 1.4 Hz, H-6), 7.06 (1H, d, $J = 8.1$ Hz, H-3), 7.02 (1H, t, $J = 7.0$ Hz, H-5), 7.00 (2H, dd, $J = 8.2$, 2.4 Hz, H-11, 15), 6.65 (1H, tt, $J = 8.2$, 1.4 Hz, H-13), 3.53-3.59 (2H, m, H-9a, 8a), 3.32-3.40 (2H, m, H-9b, 8b); $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$ (ppm): 165.4 (C-7), 160.7 (C-2), 138.6 (C-4), 131.7 (C-6), 119.9 (C-3), 119.3 (C-5), 116.0 (C-1), 114.4 (C-11, 15), 114.2 (C-12, 14 d, $J = 22.5$ Hz), 102.7 (C-13), 60.8 (C-8), 60.1 (C-9); $^{11}$B-NMR (87 MHz, $CDCl_3$) $\delta$ (ppm): 2.7 ($h_{1/2} = 1218$ Hz). Anal. Calc. for $C_{30}H_{24}B_2F_4N_2O_4$: C, 62.72; H, 4.18; N, 4.88. Found: C, 61.96; H, 4.43; N, 4.61%.

### 4.1.12. 2,11-Di-(2′,6′-difluorophenyl)dibenzo[h,q]-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclo-octadeca-6,15-diene (3k)

Compound **3k** was prepared from 0.50 g (3.00 mmol) of $H_2$SAE and 0.48 g (3.00 mmol) of 2,4-difluorophenylboronic acid. The product was a yellow solid that is slightly soluble in chloroform (yield: 0.69 g, 1.20 mmol, 79%), m.p. 278–280°C. MS (EI, 70 eV) *m/z:* 461 ($[M - C_6H_3F_2]^+$, 9), 460 (4), 288 (15), 256 (17), 238 (4), 175 (11), 174 (100), 173 (27), 148 (6), 132 (3), 114 (3), 77 (3); IR (KBr) $\bar{\nu}$ ($cm^{-1}$): 3058 (w), 2970 (w), 2960 (w), 2926 (w), 2874 (w), 1640 (C=N, s), 1612 (s), 1560 (s), 1444 (s), 1314 (s), 1256 (s), 1220 (s), 1168 (s), 1152 (m), 1140 (s), 1126 (s), 1112 (m), 1030 (m), 982

(s), 974 (s), 964 (s), 760 (s); $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 8.39 (1H, s, H-7), 7.49 (1H, dt, $J = 7.5$, 1.5 Hz, H-4), 7.44 (1H, dd, $J = 7.5$, 1.5 Hz, H-6), 7.12 (1H, dt, $J = 8.3$, 1.5 Hz, H-13), 6.95 (1H, t, $J = 7.5$ Hz, H-5), 6.89 (H, d, $J = 7.5$ Hz, H-3), 6.68 (2H, dt, $J = 8.3$, 1.5 Hz, H-12, 14), 3.82 (1H, dt, $J = 11.6$, 3.7 Hz, H-9a), 3.73 (1H, dt, $J = 9.9$, 3.7 Hz, H-8a), 3.36 (1H, dd, $J = 9.9$, 3.2 Hz, H-8b), 3.20 (1H, dd, $J = 11.6$, 3.2 Hz, H-9b); $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$ (ppm): 164.8 (C-7), 160.1 (C-2), 137.5 (C-4), 131.6 (C-6), 129.5 (C-13), 129.6 (C-12, 14), 118.7 (C-3), 118.6 (C-5), 111.1 (C-11, 15, d, $J = 26.1$ Hz), 115.7 (C-1), 60.7 (C-8), 59.5 (C-9); $^{11}$B-NMR (87 MHz, $CDCl_3$) $\delta$ (ppm): 2.2 ($h_{1/2} = 1131$ Hz). Anal. Calc. for $C_{30}H_{24}B_2F_4N_2O_4$: C, 62.72; H, 4.18; N, 4.88. Found: C, 62.57; H, 4.30; N, 4.89%.

### 4.2. X-ray analyses

X-ray diffraction studies of single crystals of compounds **2e**, **3b**, **3d** and **3h** were performed on an Enraf-Nonius CAD4 diffractometer ($\lambda_{Mo-K_\alpha} = 0.71073$ Å, monochromator: graphite, $T = 293$, $\omega$–$2\theta$ scan). Crystals were mounted generally in Lindeman capillaries. Cell parameters were determined by least-squares refinement on diffractometer angles for 24 automatically centered reflections in the $\theta$-range of 10–12°. Absorption corrections were not performed. Corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-86) for structure solution and Crystals (version 10) [24] and SHELXS (version 1.8) [25] software packages for refinement and data output. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in difference Fourier maps and their positions as well as one overall isotropic thermal parameter were refined.

## 5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 138889, 138888, 138887 and 38886 for compounds **2e**, **3b**, **3d** and **3h**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

The authors thank CONACYT for financial support.

## References

[1] E. Hohaus, Z. Anorg. Allg. Chem. 506 (1983) 185.
[2] J.H. Skoog, J. Org. Chem. 29 (1964) 492.
[3] L.K. Mohler, A.W. Czarnik, J. Am. Chem. Soc. 115 (1993) 7037.
[4] R. Contreras, C. García, T. Mancilla, B. Wrackmeyer, J. Organomet. Chem. 246 (1983) 213.
[5] N. Farfán, T. Mancilla, D. Castillo, G. Uribe, L. Carrillo, P. Joseph-Nathan, R. Contreras, J. Organomet. Chem. 381 (1990) 1.
[6] T. Mancilla, R. Contreras, B. Wrackmeyer, J. Organomet. Chem. 307 (1986) 1.
[7] S.J. Rettig, J. Trotter, Can. J. Chem. 53 (1975) 1393.
[8] N. Farfán, P. Joseph-Nathan, L.M. Chiquete, R. Contreras, J. Organomet. Chem. 348 (1988) 149.
[9] H. Höpfl, N. Farfán, V. Barba, M. Sanchez, Can. J. Chem. 76 (1998) 1352.
[10] V. Barba, D. Cuahutle, R. Santillan, M.E. Ochoa, N. Farfán, Inorg. Chim. Acta 303 (2000) 7.
[11] H. Höpfl, N. Farfán, J. Organomet. Chem. 547 (1997) 71.
[12] E.C. Alyea, A. Malek, Can. J. Chem. 76 (1998) 1352.
[13] J. Carrano, C.M. Nunn, R. Quan, J.A. Boandies, V.L. Pecoraro, Inorg. Chem. 29 (1990) 945.
[14] H. Höpfl, M. Sanchez, V. Barba, N. Farfán, S. Rojas, R. Santillan, Inorg. Chem. 37 (1998) 1679.
[15] N. Farfán, H. Höpfl, V. Barba, M.E. Ochoa, R. Santillan, E. Gómez, A. Gutiérrez, J. Organomet. Chem. 581 (1999) 71.
[16] E. Hohaus, W. Riepe, Org. Mass Spectrom. 18 (1983) 359.
[17] E. Hohaus, W. Riepe, Z. Naturforsch. 29b (1974) 663.
[18] B. Wrackmeyer, Prog. NMR Spectrosc. 12 (1979) 227.
[19] S.J. Rettig, J. Trotter, Can. J. Chem. 61 (1983) 206.
[20] S. Toyota, M. Oki, Bull. Chem. Soc. Jpn. 65 (1992) 1832.
[21] P. Wei, D.A. Atwood, Inorg. Chem. 37 (1998) 4934.
[22] P. Wei, T. Keizer, D.A. Atwood, Inorg. Chem. 38 (1999) 3914.
[23] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[24] J. Watkin, J.R. Carruthers, P.V. Betteridge, CRYSTALS, An Advanced Crystallographic Program System, Version 10, Chemical Crystallography Laboratory, University of Oxford, UK, 1996.
[25] G.M. Sheldrick, SHELXS86, Program for Crystal Structure Solution, University of Göttingen, Germany, 1986.