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Two new complexes of phenylboronic acid with *N*-salicylidene-4-aminobutanol

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Abstract

The tridentate ligand *N*-salicylidene-4-aminobutanol (**6**) was obtained by condensation of salicylaldehyde with 4-aminobutanol and reacted with phenylboronic acid to afford either the dimeric structure, bis[μ-[2-[[(4-hydroxy-κO)butyl]imino-κN]methyl-phenolato(2 −)-κO]]diphenyldiboro (**7**) or the monomeric derivative, 2-phenylbenzo[j]-8-aza-1,3-dioxa-2-boracycloundeca-8-ene (**8**), depending on the reaction conditions. The monomeric structure is a [5.4.0] heterobicycle boronate and has been analyzed by X-ray crystallography.

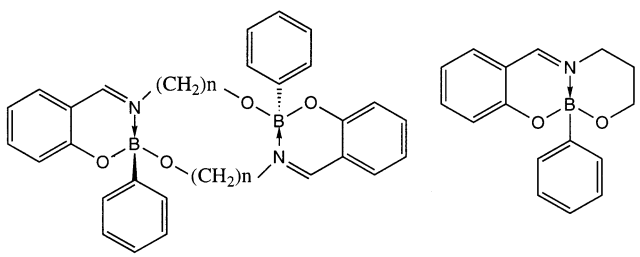
Keywords: Crystal structures; Boronate complexes; Tridentate ligand complexes

1. Introduction

In previous studies it has been shown that the addition of phenylboronic acid to salicylidenimino alcohols produces the corresponding dimeric (**1**–**4**) or monomeric (**5**) boronates [1–3] which are stable in air and are obtained in high yields in a one step synthesis (Scheme 1). These boronate units are connected by covalent B–O and coordinative N→B bonds which are responsible for the hydrolytic stability of these molecules [4–6].

Dimeric complexes have been obtained when the ligands have zero (**1**), two (**2**) five (**3**) or six (**4**) methylene units between the imino and hydroxyl groups, and the molecular structures of compounds **1** and **2** were established by X-ray crystallography [1,2]. The studies indicate that formation of the dimeric compounds is favored by the fact that the monomeric systems would be too strained owing to the tetrahedral geometry at the boron atom as well as its small atomic radius. However, when the imino alcohol is substituted with three methylene groups, a monomeric species is formed because the tridentate ligand permits the formation of a stable [4.4.0] heterobicyclic system (**5**) [3].

In the present work, we describe the synthesis of an imino alcohol containing four methylene units between the hydroxyl and imino groups (**6**) and its reaction with phenylboronic acid which leads to both the dimeric (**7**) and monomeric (**8**) boronates.



1 : n = 0
2 : n = 2
3 : n = 5
4 : n = 6

5

Scheme 1. Monomeric and dimeric boronates obtained with different methylene units in the iminodialcohols.

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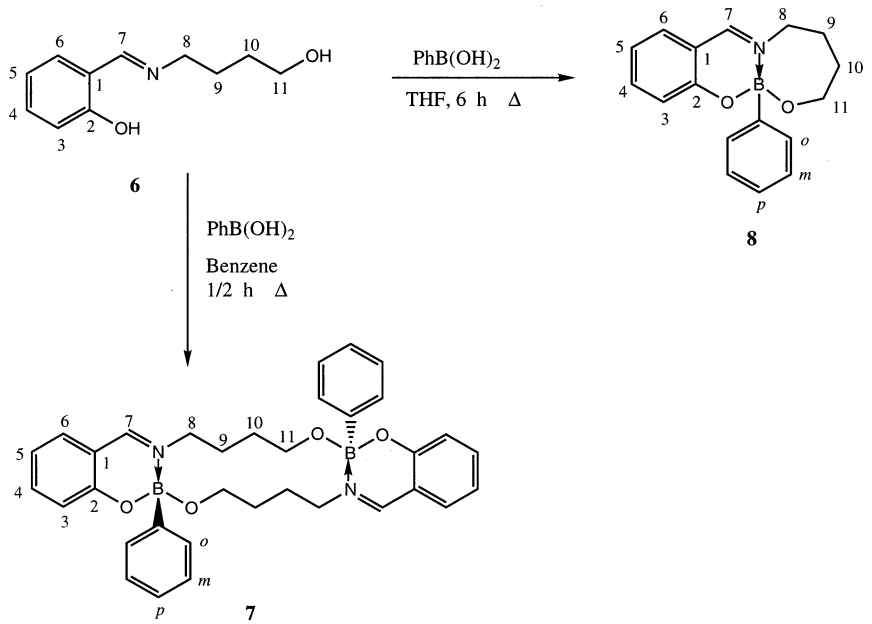


Scheme 2. Synthesis of compounds **7** and **8**.

2. Experimental

2.1. Instrumentation

NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 solutions on Bruker Advance DPX 300 and Jeol Eclipse + 400 spectrometers. Chemical shifts (ppm) are relative to $(CH_3)_4Si$ for ^1H and ^{13}C and $BF_3{\cdot}OEt_2$ for ^{11}B. Coupling constants are quoted in Hz. IR spectra were recorded on a Perkin–Elmer 16F-PC FT-IR spectrophotometer. Mass spectra were recorded on a Hewlett–Packard 5989A spectrometer. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncorrected.

The X-ray diffraction study was determined on an Enraf-Nonius CAD4 diffractometer ($\lambda_{Mo\ K\alpha} = 0.71073$ Å, monochromator: graphite, $T = 293$ K, ω–2θ scan) and the crystal was mounted in a LINDEMAN tube. 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 SHELXS (version 1.8, 1993) software package for refinement and data output. Hydrogen atoms were determined by difference Fourier maps and their positions as well as one overall isotropic thermal parameter were refined. $I > 4\sigma(I)$, $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$. Elemental microanalyses were performed by Oneida Research Services, Whitesboro, NY 13492.

2.2. Reagents

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

2.3. Preparation of *N*-salicylidene-4-aminobutanol (*6*)

Compound **6** was prepared from 0.33 g (3.73 mmol) of 4-aminobutanol and 0.46 g (3.73 mmol) of salicylaldehyde; the mixture was refluxed in 40 ml of ethyl

Table 1
Crystallographic data for compound **8**

Chemical formula	$C_{17}H_{18}BNO_2$
Formula weight	279.13
Space group	$P2_1/c$
Crystal size (mm)	$0.3 \times 0.4 \times 0.5$
a (Å)	12.021(2)
b (Å)	6.425(1)
c (Å)	19.134(4)
β (°)	99.97(3)
V (Å^3)	1455.5(5)
Formula units per cell Z	4
ρ_{calc} (g cm^{-3})	1.274
$F(000)$	592
Temperature of measurement (K)	293
θ Limits (°)	0–25
No. of reflections collected	2689
No. of independent reflections	2559
No. of observed reflections, $(F_o)^2 > 4\sigma\ (F_o)^2$	1477
$R = \Sigma||F_o| - |F_c||)/\Sigma|F_o|$	0.044
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/\sigma^2$	0.124
Goodness-of-fit σ	1.011
No. of parameters	191
Maximum Δ/σ	−0.001
$\Delta\rho_{min}$ (e Å^{-3})	−0.214
$\Delta\rho_{max}$ (e Å^{-3})	0.181

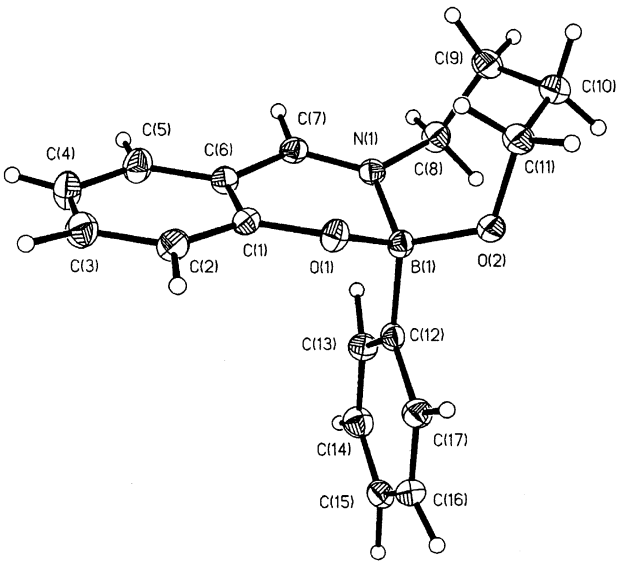
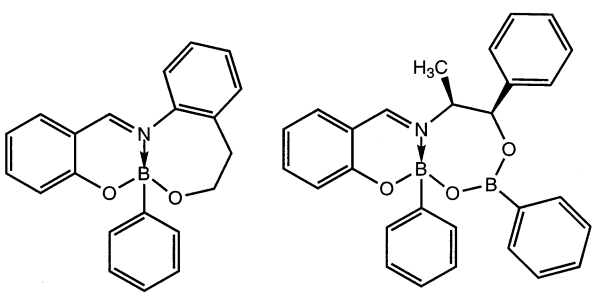


Fig. 1. Molecular structure for compound **8**.

Table 2
Selected bond distances (Å) and bond angles (°) for compound **8**

Bond distances			
O(1)–B(1)	1.505(3)	O(1)–C(1)	1.336(3)
O(2)–B(1)	1.425(3)	O(2)–C(11)	1.429(3)
N(1)–B(1)	1.610(3)	N(1)–C(7)	1.282(3)
N(1)–C(8)	1.476(3)	B(1)–C(12)	1.611(4)
Bond angles			
B(1)–O(1)–C(1)	119.8(2)	B(1)–O(2)–C(11)	119.6(2)
B(1)–N(1)–C(7)	120.7(2)	B(1)–N(1)–C(8)	119.6(2)
C(7)–N(1)–C(8)	119.6(2)	O(1)–B(1)–O(2)	109.3(2)
O(1)–B(1)–N(1)	105.3(2)	O(2)–B(1)–N(1)	110.9(2)
O(1)–B(1)–C(12)	111.4(2)	O(2)–B(1)–C(12)	110.7(2)
N(1)–B(1)–C(12)	109.5(2)	O(1)–C(1)–C(6)	120.7(2)
C(1)–C(6)–C(7)	118.9(3)	N(1)–C(7)–C(6)	121.7(2)



9 **10**

Scheme 3. Structures of compounds **9** and **10**.

acetate for 30 min. The solvent and the water formed during the reaction were removed by a Dean Stark trap to yield a yellow oil (0.69 g, 3.6 mmol, 97.4%). IR (NaCl): 3356 (s), 2934 (s), 2864 (m), 1632 (C=N, s), 1498 (m), 1462 (m), 1280 (m), 1050 (m) cm^{-1}; MS (*m*/*z*, 70 eV, %): 193 (M^+, 51), 175 (19), 148 (48), 134 (46), 120 (44), 107 (100), 77 (41), 39 (28), 31 (43); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.24 (1H, s, H-7), 7.23 (1H, td, $J = 7.8$, 1.5 Hz, H-4), 7.17 (1H, dd, $J = 7.7$, 1.5 Hz, H-6), 6.91 (1H, d, $J = 7.8$ Hz, H-3), 6.80 (1H, t, $J = 7.7$ Hz, H-5), 3.59 (2H, t, $J = 6.6$ Hz, H-11), 3.53 (2H, t, $J = 6.6$ Hz, H-8), 1.68 (2H, q, $J = 6.6$ Hz, H-10), 1.58 (2H, q, $J = 6.2$ Hz, H-9) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.8 (C-7), 161.8 (C-2), 132.3 (C-4), 131.3 (C-6), 118.6 (C-1), 118.4 (C-5), 117.2 (C-3), 62.0 (C-11), 58.8 (C-8), 30.2 (C-10), 27.2 (C-9) ppm.

*2.4. Preparation of bis[μ-[2-[[(4-hydroxy-κO)butyl]-imino-κN]methyl-phenolato(2−)-κO]]diphenyldi-boro (**7**)*

A solution of phenylboronic acid (0.32 g, 2.58 mmol) in 20 ml of benzene was added to a solution of *N*-salicylidene-4-aminobutanol (0.5 g, 2.58 mmol) in 20 ml of benzene. The mixture was refluxed for 30 min using a Dean Stark trap until a yellow precipitate was formed. The solid was collected by filtration and dried to give a product insoluble in all common solvents. Yield: 0.54 g, 3.85 mmol, 75%. 180°C (decomp.). IR (KBr): 2924 (m), 2914 (m), 2840 (m), 1644 (C=N, s), 1608 (m), 1560 (s), 1478 (s), 1312 (s), 1234 (s), 1188 (s), 1152 (s), 1130 (s), 1116 (s), 1108 (s), 940 (s), 754 (s) cm^{-1}; MS (*m*/*z*, 70 eV, %): 481 ($M^+ - C_6H_6$, 3), 296 (6), 268 (2), 220 (3) 202 (100), 148 (13), 132 (7), 77 (8), 55 (10), 44 (10). *Anal.* Calc. for $C_{34}H_{36}B_2N_2O_4$: C, 73.14; H, 6.51; N, 5.02. Found: C, 72.96; H, 6.39; N, 4.89%.

*2.5. Preparation of 2-phenylbenzo[j]-8-aza-1,3-dioxa-2-boracycloundeca-8-ene (**8**)*

A solution of phenylboronic acid (0.32 g, 2.58 mmol) in 20 ml of THF was added to a solution of *N*-salicylidene-4-aminobutanol (0.5 g, 2.58 mmol) in 20 ml of THF. The mixture was refluxed for 6 h using a Dean Stark trap, cooled to room temperature (r.t.) and 10 ml of hexane were added until a precipitate was formed. The solid was collected by filtration, and dried. The product obtained is a yellow solid that is slightly soluble in chloroform, methanol and DMSO. Crystals suitable for X-ray diffraction were obtained when the reaction was performed in a CH_2Cl_2/hexane mixture at r.t. without stirring. Yield: 0.56 g, 2.0 mmol, 78%. M.p. 197–198°C. IR (KBr): 2942 (m), 2922 (m), 2888 (s), 2852 (s), 1636 (C=N, s), 1608 (m), 1558 (m), 1478 (m), 1234 (m), 1204 (m), 1182 (m), 1136 (s), 1104 (s), 994 (s), 946 (s), 904 (s), 746 (s), 700 (s) cm^{-1}; MS (*m*/*z*, 70 eV, %): 279 (M^+, 6), 220 (4), 202 (100), 172 (2), 148 (18), 103 (3), 77 (10), 51 (8), 39 (4); ^1H NMR (300 MHz, DMSO-d_6) δ: 8.76 (1H, s, H-7), 7.47 (1H, t, $J = 7.8$ Hz, H-4), 7.45 (1H, d, $J = 7.7$ Hz, H-6), 7.28 (2H, d, $J = 6.7$ Hz, H-*o*), 7.09 (3H, d, $J = 6.7$ Hz, H-*m*, *p*), 6.86 (1H, d, $J = 7.8$ Hz, H-3), 6.85 (1H, t, $J = 7.7$ Hz, H-5), 3.66 (4H, m, H-8, 11), 1.48–1.57 (4H, m, H-9, 10) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 165.5 (C-7), 161.8 (C-2),

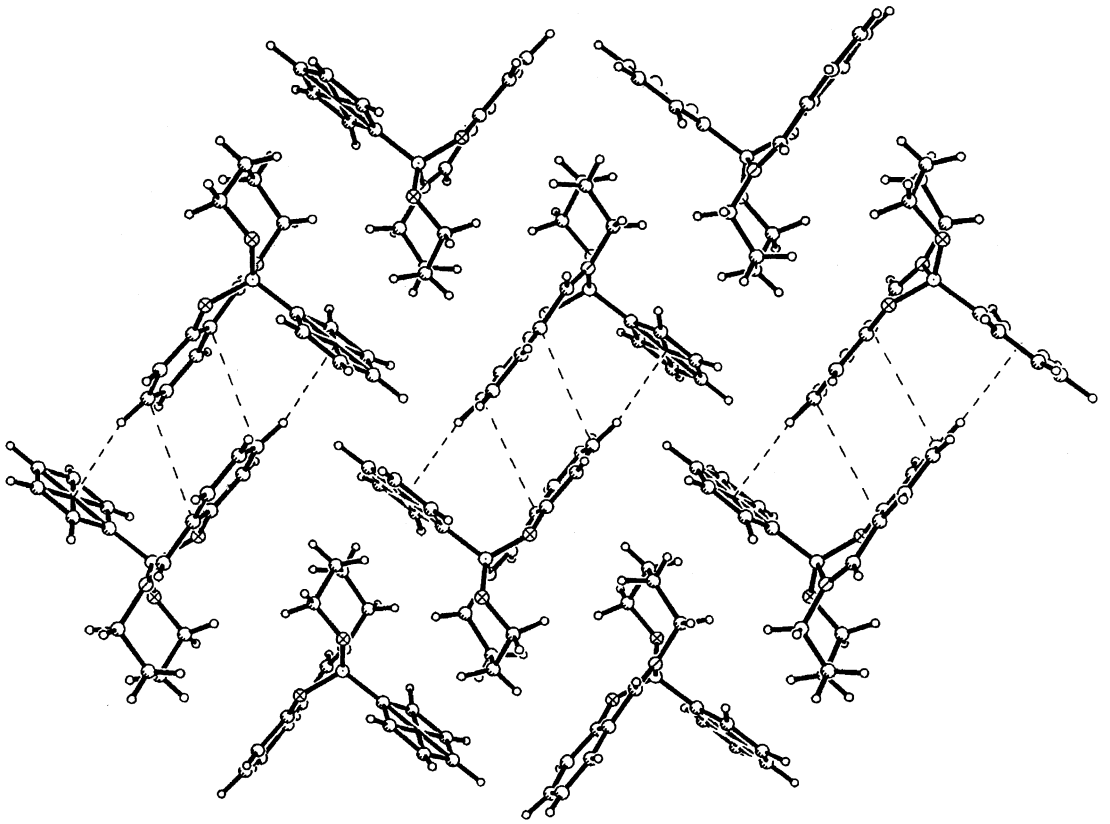


Fig. 2. Molecular packing for compound **8**.

138.0 (C-4), 132.9 (C-6), 131.4 (C-*o*), 127.7 (C-*m*), 127.4 (C-*p*), 119.1 (C-3), 119.0 (C-5), 117.7 (C-1), 62.7 (C-8), 55.5 (C-11), 31.8 (C-9), 31.7 (C-10) ppm; ^{11}B NMR (96 MHz, DMSO-d_6) δ: +7.0 ($h_{1/2}$ = 221 Hz) ppm. *Anal.* Calc. for $C_{17}H_{18}BNO_2$: C, 73.14; H, 6.51; N, 5.02. Found: C, 73.07; H, 6.65; N, 5.02%.

3. Results and discussion

Reacting 4-aminobutanol with salicylaldehyde in ethanol gives *N*-salicylidene-4-aminobutanol (**6**) in high yields. The reaction of **6** with phenylboronic acid was carried out in benzene under reflux yielding, after 30 min, bis[μ-[2-[[(4-hydroxy-κO)butyl]imino-κN]methylphenolato(2−)-κO]]diphenyldiboro (**7**), which was a solid insoluble in all common solvents (Scheme 2). The dimeric structure of this compound was proved by mass spectrometry which showed the fragment ion characteristic for the dimeric compounds [3,7]. Thus, the molecular ion is not observed and instead the $[M^+-C_6H_5]$ ion is detected owing to the easy loss to a phenyl radical. Also the C=N stretching band in the IR spectrum is shifted to higher wavenumbers after complex formation (1632 cm^{-1} for **6** and 1644 cm^{-1} for **7**).

When the same reaction was performed in THF using 6 h of reaction, the monomeric compound 2-phenylbenzo[j]-8-aza-1,3-dioxa-2-boracycloundeca-8-ene (**8**) was obtained in good yield (Scheme 2). The monomeric composition of compound **8** can also be concluded from mass spectrometry, where the molecular ion is detected and the base peak corresponds to the $[M^+-C_6H_5]$ fragment ion. In this case longer reaction times produced contraction of the ring size from 14- to seven-members, indicating that the monomeric compound is the thermodynamic product.

In the ^{1}H NMR spectrum the azomethine hydrogen atom is shifted to lower fields for **8** than the corresponding hydrogen in **6** ($\Delta\delta$: 0.52 ppm) owing to the coordination of the nitrogen to the boron atom. The same result is found in the ^{13}C NMR spectrum where the azomethine carbon atom (C-7) is slightly shifted to lower fields for compound **8** than in **6** ($\Delta\delta$: 0.70 ppm). The ^{11}B NMR spectrum of **8** showed a signal at +7.0 ppm, which confirms the N→B bond coordination.

The X-ray analysis establishes the molecular structure of **8** (Table 1), where a [5.4.0] heterobicycle is formed (Fig. 1). The selected bond lengths and angles are summarized in Table 2. The N→B bond distance for **8** is 1.610(3) Å, similar to that observed in the

boron complex **5** (1.601(9) Å) [3] and shorter than in [5.4.0] heterobicycles **9** (1.635(4) Å) [8] and **10** (1.629(5) Å) [3] (Scheme 3).

Moreover, significant differences are found in the B(1)–O(1) bond distance, where compound **8** shows the longest value of 1.505(3) Å, while the distances for the same bond in **5**, **9** and **10** are significantly shorter (1.480(4), 1.480(10) and 1.470(6) Å, respectively). A comparison of the B(1)–C(12) bond lengths for compounds **8**, **9** and **10** (1.611(4), 1.609(4) and 1.600(6) Å, respectively) shows that they are very similar.

The bond angles around the boron atom for **8** are in the range of 105.3–111.1°, and are very similar to the value observed for compound **9**. The average value for the bond angles of the seven-membered ring is 114.6(2)° which is shorter than the value observed for similar heterocycles such as **9** (117.1(3) and **10** (118.8(3)°) and indicates a lower ring strain for compound **8**. The seven-membered ring in the boronate compound **8** presents a chair conformation, while the same ring in **9** and **10** presents a twisted boat conformation. This observation gives additional evidence for the lower ring strain in the seven-membered heterocycle in **8**, and is in accordance with the tetrahedral character value (THC, 91% for **8**) which is higher than for **9** (81%) and very similar to that of **10** (90%) [9]. The deviation of the boron atom from the boronate mean plane in **8** (0.550 Å) is similar to that in the boronate **9** (0.585 Å) and lower than that in **10** (0.714 Å).

Fig. 2 depicts the molecular packing in the unit cell, indicating that the two adjacent molecules present the two most common arrangements for single aromatic hydrocarbons: the parallel displacement which shows π–π electron interactions with a distance of 4.330 Å and the T-shaped arrangement with an intermolecular C–H···π distance of 2.794 Å [10].

4. Conclusions

The present contribution shows that the reaction between the tridentate ligand **6** and phenylboronic acid can lead to the monomeric (**8**) or dimeric boronate (**7**) depending on the reaction conditions. The dimeric complex is the kinetic product while the monomeric complex is the thermodynamic product and was obtained because the formation of a slightly strained [5.4.0] heterobicyclic boronate is favored.

5. Supplementary material

Tables of crystallographic parameters, atomic coordinates, anisotropic thermal parameters, bond distances, bond angles as well as a listing of structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 138687 for **8**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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